



Effect of P^{5+} on spectroscopy and structure of $Yb^{3+}/Al^{3+}/P^{5+}$ co-doped silica glass

Wenbin Xu ^{a,b}, Jinjun Ren ^a, Chongyun Shao ^{a,c}, Xue Wang ^{a,b}, Meng Wang ^{a,b}, Liyan Zhang ^a, Danping Chen ^a, Shikai Wang ^{a,*}, Chunlei Yu ^{a,**}, Lili Hu ^{a,***}

^a Key Laboratory of Materials for High Power Laser, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, PR China

^b University of Chinese Academy of Sciences, Beijing 100049, PR China

^c Shanghai University, Shanghai 200436, PR China

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ABSTRACT

Two series of silica glasses $[(95.9-x)SiO_2-4Al_2O_3-xP_2O_5-0.1Yb_2O_3]$ (in mol%, $x=0-10$) and $(92-y)SiO_2-4Al_2O_3-4P_2O_5-yYb_2O_3]$ (in mol%, $y=0-0.2$) were prepared by sol-gel method combined with high-temperature sintering. The relationship between the glass structure and spectroscopic properties is investigated. Significant alterations in density, refractive index, absorption and emission cross sections, fluorescence lifetime, and scalar crystal field N_j are observed at a molar ratio of $P^{5+}/Al^{3+}=1$ due to the transformation of P^{5+} structure type from $AlPO_4$ -like to PO_4 units. This structural change is clearly observed in Raman spectra. In addition, NMR experimental results suggest that Yb^{3+} is mainly located in $AlPO_4$ -like but not SiO_4 units at a molar ratio of $P^{5+}/Al^{3+}=1$, and also Raman spectra reveals the presence of $P=O$ linkage in samples with molar ratio of $P^{5+}/Al^{3+}>1$. This further demonstrates that it is due to the formation of $P=O$ site but not the simple addition of P_2O_5 in $Yb^{3+}/Al^{3+}/P^{5+}$ co-doped silica glass to significantly decrease the absorption and emission cross sections of Yb^{3+} . It reflects in the change of Yb^{3+} Stark splitting, and is revealed by the decline of Yb^{3+} asymmetry degree.

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1. Introduction

Yb^{3+} -doped silica glass has attracted much interest [1–4] because of its excellent properties for practical application in high-power laser [5–9]. This material has been greatly developed in recent years. The output power of Yb^{3+} -doped silica fiber laser has achieved several kilowatts [6,7,10]. High-power laser generally requires high Yb^{3+} doping concentration to obtain sufficient pump absorption, which can effectively reduce fiber length and decrease the nonlinear effect in the fiber [11]. However, rare earth ions have very low solubility in pure silica glass [12,13]. A doping level above the solubility threshold, which is approximately 1000 ppm by weight, will lead to Yb^{3+} clustering or even phase separation [14,15]. Hence, Al^{3+} is widely adopted in silica glass to increase Yb^{3+} solubility [1,16,17] on account of its dispersion effect on rare earth ions [15,18].

* Corresponding author. Tel.: +86 21 59913348; fax: +86 21 59914516.

** Corresponding author. Tel.: +86 21 59910854; fax: +86 21 59914516.

*** Corresponding author. Tel./fax: +86 21 59910995.

E-mail addresses: woshiwsk@163.com (S. Wang), sdyclcy@163.com (C. Yu), hulili@siom.ac.cn (L. Hu).

Recent studies have shown that P^{5+} doping improves Yb^{3+} solubility [14,15] and suppresses the photodarkening effect in Yb^{3+} -doped or Yb^{3+}/Al^{3+} co-doped silica glass fiber [11,19,20]. Thus, the great potential of P^{5+} doping in high-power fiber laser has been demonstrated [11,21]. Furthermore, incorporation of P^{5+} into Yb^{3+}/Al^{3+} co-doped silica glass is advantageous for the stabilization of the Yb^{3+} valence state [1] and also results in a refractive index lower than that of Yb^{3+}/Al^{3+} or Yb^{3+}/P^{5+} co-doped silica glass [19,22]. This characteristic provides an available solution to achieve low core numerical aperture for large mode area fiber [11].

Jetschke et al. reported the influence of P^{5+} on the absorption cross section of Yb^{3+} in $Yb^{3+}/Al^{3+}/P^{5+}$ co-doped silica glass fiber [22]. No obvious change in the absorption cross section was found in the low P^{5+}/Al^{3+} molar ratio region, while a rapid decline occurred at the high P^{5+}/Al^{3+} molar ratio region. Wang et al. examined the influence of P^{5+} on the valence state of Yb^{3+} in silica glass [1]. Reduction in the emission intensity of Yb^{3+} was observed, especially at the high P^{5+}/Al^{3+} molar ratio region. However, the mechanism for the decrease in Yb^{3+} absorption and emission intensity caused by P^{5+} doping has not been reported. Because of this disadvantage of P^{5+} for Yb^{3+} spectroscopy, the optimal content of P_2O_5 in silica fiber is difficult to be determined.

Introducing P^{5+} into silica glass can effectively modulate the glass structure, and thus lead to a change in the Yb^{3+} local field [14,15,23]. The local environment of Yb^{3+} in $Yb^{3+}/Al^{3+}/P^{5+}$ co-doped silica glass has been examined using pulse electron paramagnetic resonance (EPR) spectroscopy [14,24]. Results show that large P^{5+} ions are located in the vicinity of Yb^{3+} ions when the molar ratio of $P^{5+}/Al^{3+} > 1$. However, no local structural information on Yb^{3+} in glass with molar ratio of $P^{5+}/Al^{3+} = 1$ is available. Additionally, no relationship between the glass structure and Yb^{3+} spectroscopic properties has been revealed in previous studies.

In this study, starting from well-mixed $Yb^{3+}/Al^{3+}/P^{5+}$ co-doped silica precursor via sol–gel method and combined with high-temperature sintering, silica glasses doped with Al^{3+} , Yb^{3+} , and P^{5+} ions were prepared. Experimental results from the nuclear magnetic resonance (NMR) and Raman analysis show that the Yb^{3+} ion coordinates to the P–O site in glass with a molar ratio of $P^{5+}/Al^{3+} \leq 1$, and it coordinates to the P=O site with a molar ratio of $P^{5+}/Al^{3+} > 1$. Furthermore, a relationship between the glass structure and properties of $Yb^{3+}/Al^{3+}/P^{5+}$ co-doped silica glass is revealed through the evaluation of the scalar crystal field N_j and Yb^{3+} asymmetry degree. The decline of Yb^{3+} absorption and emission cross sections primarily resulted from the decrease in the asymmetry degree of Yb^{3+} ligands caused by P^{5+} doping, especially in the glass with Yb^{3+} coordinating to the P=O site. To the best of our knowledge, by discussing the glass structure, this study is the first one to report the mechanism of the decrease in Yb^{3+} absorption and emission cross sections in $Yb^{3+}/Al^{3+}/P^{5+}$ co-doped silica glass caused by P^{5+} doping.

2. Experimental procedure

Tetraethoxysilane (TEOS), C_2H_5OH , $AlCl_3 \cdot 6H_2O$, H_3PO_4 , and $YbCl_3 \cdot 6H_2O$ were used as precursors. Deionized water was added to sustain the hydrolysis reaction. The pure analytical-grade chemical reagents were weighed according to the molar composition of samples listed in Table 1. Fixed contents of Al_2O_3 (4 mol%) and Yb_2O_3 (0.1 mol%), as well as varied P_2O_5 content from 0 mol% to 10 mol%, were adopted in the series of AP glasses. The resultant samples were named AP1, AP2, AP3, AP4, AP5, and AP6 from the lowest to the highest P^{5+}/Al^{3+} molar ratio. Fixed contents of Al_2O_3 (4 mol%) and P_2O_5 (4 mol%), as well as varied Yb_2O_3 content from 0 mol% to 0.2 mol%, were adopted in the series of AY glasses, and the resultant samples were named AY1, AY2, AY3, and AY4 from the lowest to the highest Yb_2O_3 content. The series of AY glasses were only used for magic angle spinning (MAS) NMR tests. All precursors were thoroughly stirred at 30 °C to form homogeneous doping sols. The above sols were heated from 70 °C to 1100 °C to produce dried powders, in which organics were almost decomposed. The powders were melted in alumina crucibles at 1750 °C

for 2.5 h to obtain vitreous chippings and then molded using an oxy-hydrogen flame to obtain bulk glasses. For reference, a pure silica glass was prepared using the same method. Glass slices were polished into 0.5 and 1.5 mm for the refractive index and spectroscopic property tests, respectively. The results from the inductively coupled plasma (ICP) analysis show that Yb_2O_3 , Al_2O_3 , and P_2O_5 contents in silica glasses are close to theoretical values.

The glass densities were obtained through the Archimedes method using distilled water as immersion liquid. The refractive indices at 1064 nm of samples were measured using the waveguide prism coupling method. Raman spectroscopy was conducted using a Renishawinvia Raman microscope in the range of 200–1400 cm^{-1} with the 488 nm laser line as the excitation wavelength. Yb^{3+} , P^{5+} , and Al^{3+} contents were determined by a Thermo iCAP 6300 radial view Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) after complete dissolution of the samples in HF solution. The absorption spectra were recorded using a Lambda 950 UV–vis–NIR spectrophotometer in the range of 800–1200 nm. The emission spectra excited at 896 nm for Yb^{3+} and at 335 nm for Yb^{2+} ions using a Xe lamp, and the fluorescence lifetimes excited at 896 nm using a microsecond-pulsed Xe flash lamp were measured by a high resolution spectrofluorometer, Edinburgh Instruments FLS 920. The scanning step of 1 nm was used to measure both absorption and emission spectra.

NMR experiments were carried out at the magnetic field strength of 11.7 and 7.4 T, using a 4 mm rotor. ^{31}P experiments were carried out on Bruker Avance-300 spectrometer, operating at the spinning rate of 10 kHz. Typical acquisition parameters are pulse length 3 μs (90°) and recycle delay 90 s. ^{27}Al experiments were carried out on Bruker Avance-500 spectrometer, operating at the spinning rate of 14 kHz, using pulse length 1.0 μs (30° solid pulse length) and relaxation time of 1 s. ^{29}Si experiments were carried out on Bruker Avance-500 spectrometer, operating at the spinning rate of 8 kHz, using pulse length 6.0 μs (90°) and relaxation time of 250 s. Reported chemical shift of ^{31}P , ^{27}Al and ^{29}Si were referenced to 85% H_3PO_4 , an aqueous solution of $Al(NO_3)_3$ (1 M) and liquid tetramethylsilane (TMS), respectively. All tests in this work were performed at room temperature.

3. Results and discussion

3.1. Effect of P^{5+} on density and refractive index of Yb^{3+}/Al^{3+} co-doped silica glass

The densities and refractive indices (n) of series AP samples are depicted in Fig. 1. An obvious turning point occurs in sample AP3 as shown in the variation trends of density and refractive index. This behavior indicates a structural difference between the samples with the molar ratio of $P^{5+}/Al^{3+} > 1$ and those with $P^{5+}/Al^{3+} \leq 1$. The smallest density of 2.221 g/cm^3 and the smallest

Table 1
Mean compositions of sample glasses (mol%).

Samples		Yb ₂ O ₃	Al ₂ O ₃	P ₂ O ₅	SiO ₂	P ⁵⁺ /Al ³⁺
#AP	AP1	0.1	4	0	95.9	0
	AP2	0.1	4	1	94.9	0.25
	AP3	0.1	4	4	91.9	1
	AP4	0.1	4	6	89.9	1.5
	AP5	0.1	4	8	87.9	2
	AP6	0.1	4	10	85.9	2.5
#AY	AY1	0	4	4	92	1
	AY2	0.05	4	4	91.95	1
	AY3=AP3	0.1	4	4	91.9	1
	AY4	0.2	4	4	91.8	1

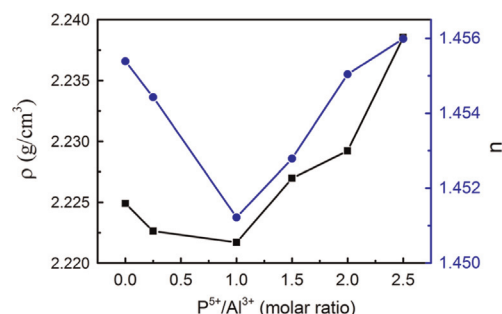


Fig. 1. Densities and refractive indices of series AP samples versus the mean P^{5+}/Al^{3+} molar ratio.

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