

Effect of aluminum co-doping on the formation of Yb^{2+} in Ytterbium-doped high silica glass

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Yb^{3+} singly doped and $\text{Yb}^{3+}/\text{Al}^{3+}$ co-doped high silica glass samples are prepared, and their luminescent properties are investigated. Al^{3+} is considered as a beneficial activator for Yb^{3+} -doped glass. However, the experimental result shows that the addition of Al^{3+} results in the transformation from Yb^{3+} to Yb^{2+} and the improvement in the photon luminescence of Yb^{2+} . These characteristics indicate the role of Al^{3+} in Yb^{3+} -doped glass.

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Ytterbium-doped fiber lasers have achieved multi-kilowatt continuous wave power and has become the currently preferred gain medium for high power fiber lasers because of its high efficiency and broad gain bandwidth of the ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ transition of Yb^{3+} [1]. However, the simple transformation of Yb^{3+} to Yb^{2+} during the preparation process is unavoidable, and may lead to several unfavorable factors, such as the increase in optical loss at laser wavelengths and the reduction of the equilibrium value of photodarkening^[2,3] that severely limits the further development of Yb^{3+} -doped high power fiber lasers.

A clear understanding of the forming mechanism of Yb^{2+} is important to eliminate it in the fibers. High silica glass (HSG) prepared by sintering porous glass has a very similar composition (contained $\text{SiO}_2 > 95$ wt.-%) with quartz glass fibers. Rare-earth ions can be easily doped into HSG because the porous structure provided a strong desorption capability, and the preparation process is not performed at a very high temperature, which may result in the agglomeration of ions^[4]. Identifying the variation between Yb^{2+} and Yb^{3+} and its influence in the photon luminescence (PL) properties in bulk HSG can promote and simplify the study on fibers.

Several studies have found that Al^{3+} can enhance the fluorescence intensity of rare-earth ion-doped glass. Some studies have suggested that the enhancement is attributed to the restrained concentration quenching through the physical cluster dispersion caused by Al^{3+} ^[5]. Other studies have considered the modification of structures around rare-earth ions, which is attributed to the addition of Al^{3+} ^[6]. In any case, co-doping Al^{3+} is evidently a benefit and also a popular method in improving the PL properties of Yb^{3+} -doped glass^[7,8]. However, the possible effect of Al^{3+} on the formation of Yb^{2+} is still unclear. In this letter, HSGs simply doped with Al^{3+} and Yb^{3+} in different concentrations are prepared. The absorption, excitation, and emission spectra are measured, and the result showing the existence of Al^{3+} as the main reason for the reduction of Yb^{3+} is presented.

Porous glass containing more than 95% silica with a porosity of 34% is prepared using a phase-separation method^[4]. The obtained porous glasses are soaked in different solutions prepared with $\text{Al}(\text{NO}_3)_3$, Yb_2O_3 , and HNO_3 for 1 h, and then sintered into the dense, colorless, and transparent HSGs at 1100 °C in a CO-reducing atmosphere. Afterward, the glasses are cut and polished into the size of $7 \times 7 \times 1$ (mm).

The doping-concentrations in glass c_g can be calculated from the porosity of porous glass p , the density of sintered glass d , the concerning atomic mass M , and the doping-concentrations in solutions c_s :

$$c_g = \frac{p \cdot c_s \cdot M}{d \cdot (1 - p)}, \quad (1)$$

where $p = 34\%$ and $d = 2.2 \text{ g}\cdot\text{cm}^{-3}$. Table 1 shows the concentration of each ion in the solutions and glass samples.

The ultraviolet-visible (UV-vis) excitation and emission spectra are obtained using a spectrophotometer (FP-6500, JASCO, Japan). The near infrared (NIR) emission spectra are recorded using a Zolixsbp300 spectrophotometer (SBP300, ZOLZX, China) and a 980-nm laser diode (LD). The absorption spectra are obtained using a spectrophotometer (V-570, JASCOV, Japan).

Figure 1(a) shows the absorption spectra of A_0 , A_1 ,

Table 1. Concentration of Each Ion in the Solutions and Glass Samples

Sample	Yb^{3+} in Marked Solutions (mol/L)	Al^{3+} in Solutions (mol/L)	Yb^{3+} in HSGs (ppm)	Al^{3+} in HSGs (ppm)
A_0	0.15	0	6 078	0
A_1	0.15	0.3	6 078	1 897
A_2	0.15	3.0	6 078	18 967
B_1	0.03	0.3	1 216	1 897

and A_2 in the comparatively long wavelength range. Both absorption bands at 980 and 903 nm are due to the ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transitions of Yb^{3+} [9]. The peaks are significantly enhanced by the increase in Al^{3+} concentration. This phoneme proves that the existence of Al^{3+} is beneficial to the PL properties of Yb^{3+} -doped glass, regardless of the two reasons previously discussed. However, the absorption edge evidently exhibits a redshift with the addition of Al^{3+} , which is caused by the increasing absorption of Yb-associated oxygen deficiency centers (ODC) in the 220-nm band, as shown in Fig. 1 (b)[10]. This phoneme indicates that the increasing Al^{3+} concentration can also substantially boost the ODC, which is an important factor of the appearance of Yb^{2+} and the photodarkening effect.

Figure 2(a) shows the emission spectra of A_0 , A_1 , and A_2 excited below 980 nm. Similar with the absorption spectra shown in Fig. 1(a), the emission peaks located in the 1020-nm range caused by the ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transitions of Yb^{3+} is also enhanced when the doping concentration of Al^{3+} is raised. The corresponding peak of the spectrum of A_0 , the sample without Al^{3+} doping, is almost unobservable.

The emission spectra of the samples excited below 330 nm are shown in Fig. 2(b). Peaks are centered in the 400-nm range due to the emission of ODC in the spectra of all samples. Moreover,

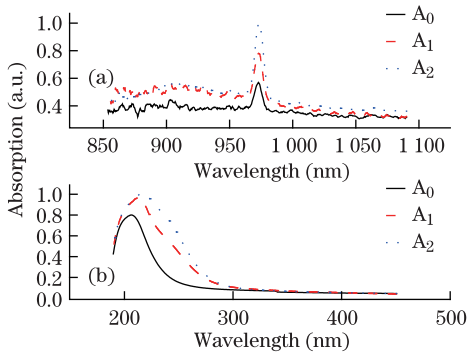


Fig. 1. Absorption spectra of samples A_0 , A_1 , and A_2 in the (a) NIR range and (b) UV-vis range, respectively.

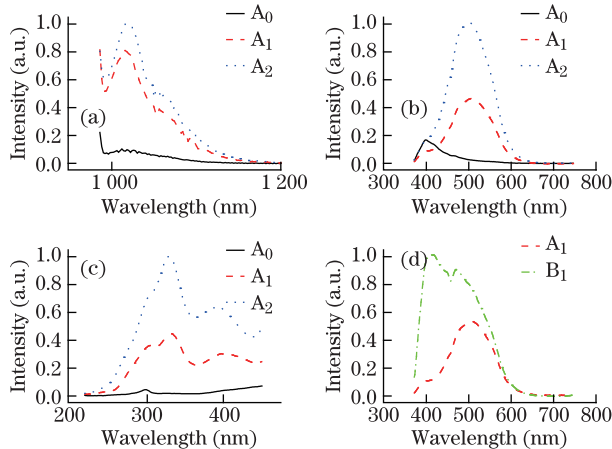


Fig. 2. Emission spectra of samples A_0 , A_1 , and A_2 excited below (a) 980 nm and (b) 330 nm respectively; (c) excitation spectra of samples A_0 , A_1 , and A_2 monitored at 505 nm; (d) emission spectra of samples A_1 and B_1 excited below 330 nm.

lines A_0 , A_1 , and A_2 exhibit apparent emission peaks in 505 nm, instead of the typical straight line. This result is attributed to the $4f^{14} \rightarrow 4f^{13}5d$ transitions of Yb^{2+} , which is much stronger than that of ODC in the 400-nm range[11]. This result also indicates that Yb^{2+} does not exist in A_0 , although A_0 is also sintered in a CO-reducing atmosphere. However, Al^{3+} doping can result in the transformation from Yb^{3+} to Yb^{2+} and improve the PL of Yb^{2+} in A_1 and A_2 . These phonemes have two reasons. Firstly, Al^{3+} provides a spontaneous reduction effect when sintering porous glass, boosts the reduction of Yb^{2+} during the sintering of porous glass, and encourages the transformation[12]. Secondly, similar with that of Yb^{3+} , the fluorescence intensity of Yb^{2+} can also be enhanced by Al^{3+} in glass. The excitation spectra shown in Fig. 2 (c) also indicate similar phonemes, that is, more doped Al^{3+} results in a stronger PL of Yb^{2+} in 505 nm. A shoulder peak and two strong peaks are observed in the excitation spectra of A_1 and A_2 . The shoulder peak is due to ODC, which indicates an energy transformation from ODC to Yb^{2+} . The two strong peaks originate from the $4f^{14} \leftarrow 4f^{13}5d$ transitions of Yb^{2+} . Thus, improving the PL properties of Yb^{3+} in HSG by adding Al^{3+} only is not an ideal method. Based on some studies, co-doping both P^{5+} and Al^{3+} in Yb^{3+} -doped glass can release the spontaneous reduction effect of Al^{3+} by forming AlPO_4 [7].

However, the yellow emission of Yb^{2+} also has extensive potential applications, such as the preparation of the white light source[13]. Figure 2(d) shows the emission spectra of A_1 and B_1 . B_1 is the sample doped by the same Al^{3+} and comparatively lesser Yb^{3+} than A_1 . It exhibits a stronger broad PL in both 400 and 505-nm range than that of A_1 , which is attributed to concentration quenching. In the comparison of A_1 in Figs. 2(b) and (d), raising Al^{3+} concentration and decreasing Yb^{3+} concentration can both evidently enhance the intensity of Yb^{2+} . However, the latter also results in an extra increase in ODC. Thus, the aforementioned phenomenon can be maximized in obtaining strong yellow Yb^{2+} PL. Similar with the PL of Ce^{3+} or Eu^{2+} , the PL of Yb^{2+} was also caused by the $f \rightarrow d$ transformation, which is sensitive to its surroundings and exhibit different PL properties in different host materials. Notably, the PL values of Ce^{3+} , Eu^{2+} , and Yb^{2+} have an evident redshift with the increase in atomic number. This observation is attributed to the high electric density of elements with big atomic number, resulting in a low excited state level. Therefore, Yb^{2+} could be a new active ion in fiber laser technology with the advantage of a long excitation wavelength by blue LD.

In conclusion, series samples of Yb^{3+} -doped and $\text{Al}^{3+}/\text{Yb}^{3+}$ co-doped HSG are prepared in this letter. The role of Al^{3+} in these samples is analyzed. Although the addition of Al^{3+} is popular in improving the PL properties of Yb^{3+} in silica glass, it also leads to a disadvantage, that is, the formation of Yb^{2+} . Thus, an optimal ratio of $\text{Yb}^{3+}/\text{Al}^{3+}$ exists for the balance of PL and photodarkening capabilities of Yb^{3+} -doped HSG. However, adding Al^{3+} is also an effective way to enhance the PL of Yb^{2+} , if needed.

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