

Fabrication and spectroscopic properties of Yb³⁺-doped silica glasses using the sol-gel method

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Received November 28, 2011; accepted February 24, 2012; posted online April 20, 2012

Two series of Yb³⁺-doped silica glasses (YA and YAP) are fabricated using the sol-gel method, and their spectroscopic properties are investigated. The longest fluorescence lifetime of 0.96 ms is obtained in YAP2 and YAP3 glasses. The emission cross-section (σ_{emi}) and $\sigma_{\text{emi}} \times \tau$ of Yb³⁺ in the YAP1 glass are 1.00 pm² and 0.94 pm²·ms, respectively. Co-doping with Al and P decreases the hydroxyl group content in the glasses because of the reduction in non-bridging oxygen content. The lowest OH content in the YAP3 glass is 9.6 ppm.

OCIS codes: 160.5690, 160.6060, 160.6030, 160.4760.

doi: 10.3788/COL201210.081601.

Over the last few years, Yb-doped silica glass has attracted increasing interest for high power and short pulse laser applications^[1–3]. Yb ions have advantages, such as high efficiency as well as broad absorption and emission bands. The high quantum efficiency of Yb³⁺ leads to low thermal loading in laser materials^[4]. Theoretically, Yb³⁺ avoids excited state absorption and upconversion energy transfer because of its simple energy level structure with only two electronic multiplets (²F_{5/2} and ²F_{7/2}). Moreover, Yb ions have long fluorescence lifetimes, which provide the benefit of energy storage. Compared with multi-component glasses, such as phosphate, borate, and gallium glasses that have high emission cross sections^[5], silica glasses have their own advantages, including low thermal expansion coefficient, good high-temperature and thermal shock resistance, high mechanical strength, and stable chemical properties. However, systematic investigations on the optical properties of Yb³⁺-doped silica glasses are few^[6,7]. In this letter, silica glass is selected as the matrix for Yb³⁺ doping.

Most rare-earth-doped silica fiber preforms are well known to be fabricated using the traditional modified chemical vapor deposition (MCVD) method combined with solution doping^[8,9]. However, the MCVD method has its geometrical and rare earth ion doping level limitations^[10], and achieving high Yb-doped silica is difficult^[11–13]. The sol-gel process is available for the fabrication of silica glass at low cost and using simple equipment. Different species can be mixed at the molecular scale through the sol-gel process^[14], so that high Yb ion doping in silica and good homogeneity can be achieved. However, high Yb³⁺ ion doping produces clusters and defects, which are extremely harmful to emission and laser properties. Co-doping with Al and P can effectively suppress the cluster formations of Yb ions^[15]. In this letter, the sol-gel method was used to prepare Yb³⁺-doped silica glasses. The physical and spectroscopic characteristics of the Yb³⁺-doped silica glasses through the sol-gel method were investigated in detail.

Reagent grade chemical reagents were used as starting

materials. Tetraethoxysilane was used as the precursor of SiO₂. AlCl₃·6H₂O, YbCl₃·6H₂O, and H₃PO₄ were used for the realization of Al₂O₃, Yb₂O₃, and P₂O₅ doping, respectively. Ethanol was used as the solvent. Deionized water was added to sustain the hydrolysis reaction. To achieve a homogeneous sol, the mixed solution was kept stirred at room temperature for approximately 2 h, during which the hydrolysis reaction and the condensation polymerization of the mixture occurred^[16]. The homogeneous sol quickly gelled at 90 °C and desiccated within 3 h at 600 °C. The gel was sintered at 1650 °C and transformed into vitreous chippings, which were then molded on an oxy-hydrogen flame. The obtained Yb³⁺-doped silica glasses are shown in Table 1.

Glass density was tested through the Archimedes method using distilled water as immersion liquid. The refractive index of the glass was measured through the wave guide prism coupling method with thickness of 0.5 mm. Glass samples were polished to 1-mm thickness for spectroscopic measurements. The absorption spectrum was recorded using a spectrophotometer (Lambda 900 UV-VIS-NIR, Perkin-Elmer, USA) in the range of 200–1100 nm. Fluorescence spectrum was measured using the combined fluorescence lifetime and steady state spectrometer (FLSP 920, Edingburg Co., UK) upon excitation at 896 nm. The fluorescence lifetime was measured

Table 1. Glass Compositions

Glass Sample	Glass Composition (mol%)
YA	0.3Yb ₂ O ₃ -0.3xAl ₂ O ₃ -(100-0.3-0.3x) SiO ₂ (x = 4, 8, 12; corresponding to YA1, YA2, YA3, respectively)
YAP	0.3Yb ₂ O ₃ -0.3xAl ₂ O ₃ -0.3xP ₂ O ₅ -(100-0.3-0.3x-0.3x) SiO ₂ (x = 8, 10, 12; corresponding to YAP1, YAP2, YAP3, respectively)

via pulsed 980-nm LD excitation using the instrument FLSP920. Fourier transform infrared spectroscopy (FTIR) spectrum was measured using a spectrophotometer (Nexus FT-IR Spectrometer, Thermo Nicolet). X-ray photoelectron spectroscopy (XPS) spectra were recorded on K-Alpha (Thermo Fisher Scientific, USA) using a monochromatic Al source ($K\alpha$, 1486.6 eV), operated at a constant pass energy of 200.0 eV. All measurements were performed at room temperature.

Table 2 shows the densities and refractive indices of the glass samples. By penetrating into the $[\text{SiO}_4]$ network, Al and P ions slightly change the network size. In the YA and YAP series, the densities of the samples are proportional to the Al_2O_3 and P_2O_5 concentrations. Table 2 shows that the introduction of Al_2O_3 increases the refractive index of the YA glass. With the addition of near equimolar P_2O_5 , almost all available Al and P cations are paired with the formation of an AlPO_4 joint^[17]. The AlPO_4 joint has the same type of network as pure silica and is much like silica in terms of refractive index. As a result, the refractive indices of the YAP glasses co-doped with Al and P ions are lower than those of the YA glasses doped with single Al ions.

Figure 1 shows the absorption spectrum of the glass with 0.3 mol% Yb_2O_3 . The Yb^{3+} ion has two manifolds, namely, ${}^2\text{F}_{5/2}$ and ${}^2\text{F}_{7/2}$. Transitions occur between the four Stark levels of ${}^2\text{F}_{7/2}$ and the three Stark levels of ${}^2\text{F}_{5/2}$. As shown in Fig. 1, the glass has major absorption peak at 977 nm and the second peak at approximately 920 nm.

Yb^{3+} ions are responsible for the laser activity of doped silica. As shown in Fig. 2, the Yb^{3+} -doped silica glasses have broad emissions in the range of 975–1080 nm, corresponding to the ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transitions. The primary peak of the emission band is at 977 nm, and the second peak is at approximately 1020 nm. As shown in Table 3, the fluorescence lifetimes (τ) of the YA batch are 0.86, 0.89, and 0.89 ms, whereas those of the YAP batch are 0.94, 0.96, and 0.96 ms, which are comparable with those usually reported for Yb^{3+} -doped silica glasses^[18]. In addition, the fluorescent lifetime of Yb^{3+} in the YAP glasses is longer than that in the YA glasses.

Table 2. Density and Refractive Index of Glass Samples

Sample	YA1	YA2	YA3	YAP1	YAP2	YAP3
ρ ($\text{g}\cdot\text{cm}^{-3}$)	2.20	2.24	2.27	2.262	2.267	2.271
n_d	1.467	1.470	1.471	1.466	1.468	1.468

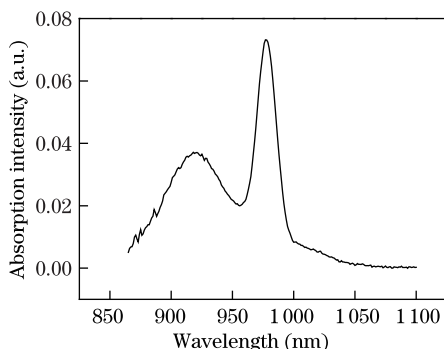


Fig. 1. Absorption spectrum of Yb^{3+} in silica glass.

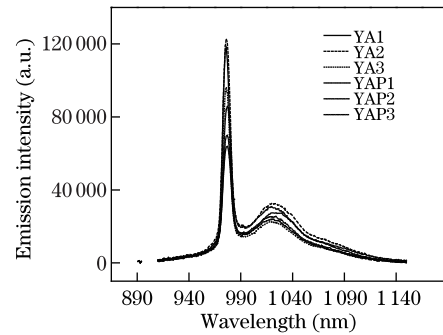


Fig. 2. Fluorescence spectra of Yb^{3+} in the glass samples.

Table 3. Spectroscopic Properties of Yb^{3+} Ions in YA and YAP Glasses

Sample	λ_p (nm)	σ_{abs} (pm^2)	$\Sigma\sigma_{\text{abs}}$ (pm^3)	λ_{emi} (nm)	σ_{emi} (pm^2)	τ (ms)	$\sigma_{\text{emi}} \cdot \tau$ ($\text{pm}^2 \times \text{ms}$)
YA1	977	1.26	65.1	1022	0.83	0.86	0.71
YA2	977	1.21	62.3	1023	0.81	0.89	0.72
YA3	977	1.09	55.7	1022	0.70	0.89	0.62
YAP1	977	1.03	69.1	1022	1.00	0.94	0.94
YAP2	977	1.04	65.6	1024	0.96	0.96	0.92
YAP3	977	1.12	61.2	1019	0.90	0.96	0.86

Based on the measured absorption spectrum in Fig. 1, the absorption cross section (σ_{abs}) can be calculated using the Beer-Lambert equation^[19]:

$$\sigma_{\text{abs}}(\lambda) = \frac{2.303 \lg \left[\frac{I_0(\lambda)}{I(\lambda)} \right]}{Nl}, \quad (1)$$

where $I_0(\lambda)$ is the incident optical intensity, $I(\lambda)$ is the optical intensity throughout the sample, N is the rare earth ion concentration ($\text{ions}\cdot\text{cm}^{-3}$), and l is the sample thickness.

Stimulated emission cross sections of the fluorescence band were calculated from the corresponding absorption spectrum using the Weber method through^[20]

$$\sigma_p = \frac{4 \Sigma_{\text{abs}}}{3 \Delta \lambda_{\text{eff}}}, \quad (2)$$

where σ_p is the main peak cross section of the fluorescence spectrum, Σ_{abs} is the integrated absorption cross section of the ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ transition, and $\Delta \lambda_{\text{eff}}$ is the effective emission line width obtained by integrating over the ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ fluorescence band and normalizing the peak intensity to unity. The cross section σ_s of the broad

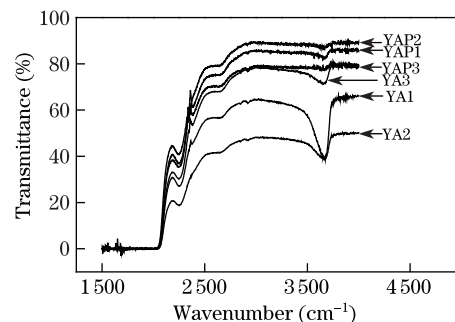


Fig. 3. FTIR spectra of YAP and YA glasses.

Table 4. Comparison of $\sigma_{\text{emi}} \times \tau$ between the Samples and Other Yb³⁺-doped Glasses

Sample	YA1	YA2	YA3	YAP1	YAP2	YAP3	FP ^[21]	LY ^[22]	QX ^[23]
$\sigma_{\text{emi}} \times \tau$ ($\text{pm}^2 \cdot \text{ms}$)	0.71	0.72	0.62	0.94	0.92	0.86	0.60	1.35	1.40

secondary peak in Fig. 3 at 990–1050 nm can be calculated as^[20]

$$\frac{\sigma_s}{\sigma_p} = \left(\frac{n_p}{n_s}\right)^2 \left(\frac{\lambda_s}{\lambda_p}\right)^2 \left[\frac{(dI/d\lambda)_s}{(dI/d\lambda)_p}\right], \quad (3)$$

where $\lambda_{s,p}$ and $n_{s,p}$ are the wavelengths and refractive indices at the main and secondary peaks in the fluorescence spectra.

Table 3 shows the spectroscopic properties of Yb³⁺ in the silica glass samples. σ_{emi} is the emission cross section at the secondary peak position. The YAP glasses have higher emission cross sections and longer fluorescent lifetimes than the YA glasses. In both YA and YAP glasses, emission cross section decreases with increasing Al₂O₃ or (Al₂O₃+P₂O₅) content. This result can be mainly attributed to the decrease in absorption cross section, as shown in Table 3. As a network modifier, Yb³⁺ is surrounded by six oxygen ions, forming a [YbO₆] octahedron. Stimulated emission cross-section is strongly related to the local environment of Yb³⁺ ions. The asymmetry of the [YbO₆] octahedron contributes to the stimulated emission cross-section of Yb³⁺. The co-doping of Al and P ions increases the asymmetry of the [YbO₆] octahedron because of the presence of both AlPO₄ and SiO₄ around it. As a result, the emission cross section of Yb³⁺ in the YAP glass increases. Table 3 shows that YAP1 exhibits the highest emission cross-section (1.00 pm^2) at 1022 nm. For laser glasses, $\sigma_{\text{emi}} \times \tau$ is a significant parameter that characterizes the laser gain, and it is generally desirable to be as large as possible. As shown in Table 4, all $\sigma_{\text{emi}} \times \tau$ values of the YA and YAP glasses are higher than that of FP glass (0.60 $\text{pm}^2 \cdot \text{ms}$)^[21]. The YAP glasses have higher $\sigma_{\text{emi}} \times \tau$ values than the YA glasses, and the YAP1 sample has the highest $\sigma_{\text{emi}} \times \tau$ value among the samples. These results suggest that co-doping with Al and P can improve the spectroscopic properties of Yb-doped silica glass compared with single Al-doping.

OH groups are well known to affect the fluorescence properties of Yb³⁺ ions in silica glass. During the sol-gel process, a large number of H₂O is present in the precursor materials. Although most of them are volatilized during the fabrication process, a fraction still remains in the glass in the form of -OH. Molecular water penetrates into the glass and reacts to form immobile silanol groups, which are frequently called hydroxyl groups. The process can be formulated as

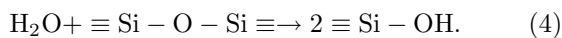


Figure 3 shows the FTIR spectra of the YAP and YA glasses. The absorption peak of -OH in SiO₂ glass is approximately 3670 cm^{-1} . The OH absorption band in the YA glass is more obvious than that in the YAP glass.

The absorption coefficient (α) of the OH groups in the

glass can be calculated as^[24]

$$\alpha = \frac{1}{l} \ln \frac{T_0}{T}, \quad (5)$$

where T_0 is the baseline transmission of the infrared spectrum, and T is the transmission near the 3670 cm^{-1} absorption peak. The OH content can be expressed as^[25]

$$C_{\text{OH}} = \frac{M_{\text{OH}}}{\varepsilon \times \rho} \times \frac{1}{l} \times \lg \frac{T_0}{T}, \quad (6)$$

where M_{OH} is the molar weight of the OH group, ρ ($\text{g} \cdot \text{cm}^{-3}$) is the density of the glass sample, and ε is the extinction coefficient. The value of ε used in this letter is 77.51 $\text{mol}^{-1} \cdot \text{cm}^{-1}$, according to Ref. [26]. The calculated absorption coefficients of the OH groups in both YA and YAP glasses are given in Table 5. Table 5 shows that the absorption coefficient of OH groups in the YA glasses decreases with increasing Al₂O₃ concentration, whereas that in the YAP glasses also decreases with increasing Al₂O₃ and P₂O₅. Co-doping with P and Al obviously reduces the OH group content. The lowest value of OH group (9.6 ppm) content is obtained. For comparison, a rare-earth-doped silica glass fiber fabricated through the typical MCVD method has an OH content of 0.5 ppm^[27].

Figure 4 shows the O 1s XPS spectra of the YA3 and YAP3 samples having similar concentrations of Al₂O₃. After co-doping with P₂O₅, the YAP3 glass has a higher binding energy of 531.68 eV than the YA3 glass, the peak of which is at 531.58 eV. According to Ref. [28], high binding energy O 1s peaks indicate a stronger band of bridging oxygen in the YAP glass than that in the YA glass. Thus, the probability of -OH bonding with non-bridging oxygen decreases, and the concentration of -OH reduces in P and Al co-doped YAP glass. Therefore, the fluorescence lifetimes of the YAP glasses are longer than

Table 5. Absorption Coefficients and OH Group Content

Sample	YA1	YA2	YA3	YAP1	YAP2	YAP3
α (cm^{-1})	5.20	2.54	1.13	0.48	0.33	0.23
C_{OH} (ppm)	225	108	47	20.2	13.9	9.6

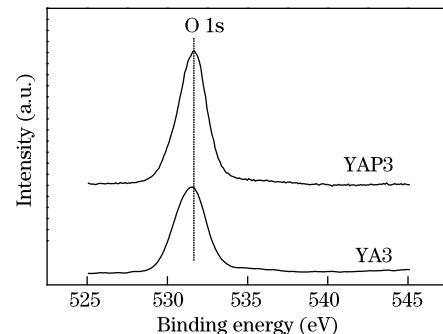


Fig. 4. XPS spectra of O 1s for YA3 and YAP3 glasses.

those of the YA glasses (see Table 3).

In conclusion, starting from the sol-gel method combined with a melting process, two series of high Yb^{3+} ion-doped YA($\text{Al}_2\text{O}_3\text{-SiO}_2$) and YAP($\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-SiO}_2$) silica glasses are prepared. The spectroscopic properties of these glasses are studied. Yb^{3+} -doped silica glasses have broad emissions ranging from 975 to 1080 nm. The longest fluorescence lifetime (0.96 ms) is achieved in the YAP2 and YAP3 glasses. Relatively short fluorescent lifetimes of 0.86, 0.89, and 0.89 ms are obtained in the YA glasses. The FTIR spectra demonstrate that the lowest absorption coefficient of the OH groups in the YAP glass is 0.23 cm^{-1} . The stimulated emission cross-section (σ_{emi}) of the Yb^{3+} ions at approximately 1020 nm is calculated to be as large as $1 \times 10^{-20}\text{ cm}^2$. In the glass, the value of $\sigma_{\text{emi}} \times \tau$ can reach as high as $0.94\text{ pm}^2 \cdot \text{ms}$. These results suggest that Yb^{3+} -doped silica glass with proper Al_2O_3 and P_2O_5 contents have better spectroscopic characteristics than ytterbium silica glasses doped singly with Al_2O_3 .

The author would like to thank Dr. Shengming Zhou, Dr. Hui Lin, Dr. Hao Teng, and Mr. Yirong Mao for their assistance in the sintering process.

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