Spectra and lasing properties of Er^{3+}, Yb^{3+}:phosphate glasses

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Received July 12, 2002

The effects of Al_2O_3, Yb_2O_3, Er_2O_3 and OH^- on spectral properties of $P_2O_5.Na_2O.SrO.Al_2O_3.Yb_2O_3.Er_2O_3$ erbium phosphate glass were studied. 5, 8, and 13 mol% Al_2O_3, 4, 5, 6, 7 and 8 mol% Yb_2O_3 and 0.05, 0.2, and 0.4 mol% Er_2O_3 were used. It was found that Al_2O_3 can improve fluorescent lifetime of Er^{3+} ions, but the integrated absorption cross section of Er^{3+} ions decreases with the increase of Al_2O_3 concentration. Evaluating from energy transfer efficiency of Yb^{3+} to Er^{3+} and spectral parameters of Yb^{3+} and Er^{3+}, we conclude that 6 mol% Yb_2O_3 and 0.4 mol% Er_2O_3 are needed for LD pumped microchip laser applications. OH^- groups in glass affect greatly fluorescent intensity and lifetime of Er^{3+}, Yb^{3+}:phosphate glass. The OH^- absorption coefficient at 3000 cm^{-1} should be less than 1 cm^{-1} for laser applications. Pumped with a 2-W, 974-nm InGaAs laser diode, CW laser centered at 1530 nm with slope efficiency of 10.6 % and maximum output of 43 mW was achieved in our 2-mm-thick Er^{3+}, Yb^{3+}:phosphate glass at room temperature.

OCIS codes: 160.5690, 300.6170, 140.3500.

Erbium laser glasses have attracted much attention due to their capability for emission at the eye-safe wavelengths and optical communication windows of 1.54 μm [1]. With the development of laser diodes, study on microchip erbium glass laser has made a great progress in recent years[2−4].

As well known, the spectroscopic properties of laser glasses depend on glass compositions and fabrication process. There were a few reports on the effect of glass compositions on spectroscopic properties in erbium glass[5]. Phosphate glass is considered to be the best matrix for ytterbium sensitized erbium glass laser because of its high stimulated emission cross section, weak up-conversion luminescence and low probability of energy back transfer from Er^{3+} to Yb^{3+}. In present work, the effect of glass compositions (Al_2O_3, Yb_2O_3, Er_2O_3) and OH^- content on spectroscopic properties and the energy transfer efficiency from Yb^{3+} to Er^{3+} of an Er^{3+}, Yb^{3+} co-doped $P_2O_5.Na_2O.SrO.Al_2O_3.Yb_2O_3.Er_2O_3$ phosphate glass has been investigated. The glass compositions can be optimized according to the spectroscopic measurement results. With a 2-W, 974-nm InGaAs LD pump, laser experiments were carried out on our Er^{3+}, Yb^{3+} co-doped phosphate glass.

Glasses for spectroscopic measurements and laser experiments were melted at 1200−1300 °C. All glasses were oxygen-bubbled to reduce their OH^- content and annealed at glass transition temperature after casting. Then it was cut and polished into 5×10×20 mm^3 size for spectroscopic measurements. The absorption spectra were measured using PERKIN-ELMER UV/VIS/NIR LAMDA 9 spectrophotometer. The fluorescence lifetime and emission spectra were detected by exciting the glass samples from a front surface with a 974-nm, 0.5-W InGaAs laser diode. An oscilloscope was used to measure the fluorescent lifetime. The laser consists of an LD pump source, two reshape lens, glass sample, output coupling mirror and two filters[6]. The glass with flat-flat surface sized 10×20×2 mm^3 was longitudinally pumped. One side of glass was coated antireflection at 974 nm (92% transmission) and high reflectivity at 1530 nm ($R > 99.9\%$). The other side was antireflection coated at 1530 nm and 70% transmission at 970 nm. Output coupling mirror with 0.4% transmission at 1530 nm and 55% transmission at 970 nm was used. Two filters were used to isolate the pump light because there was about 30% pump power leaked out from output coupling mirror. The output power was measured by a power meter. An InGaAs detector following a monochrometer was used for laser spectrum measurement. The slit width of momochrometer was 0.2 mm.

The absorption cross section of Er^{3+} and Yb^{3+} $\sigma_{\rm abs}(\lambda)$ was calculated according to the expression[7]

$$\sigma_{\rm abs}(\lambda) = \frac{2.303\log(I_0/I)}{Nl}, \tag{1}$$

where $\log(I_0/I)$ is optic density, N is the ion concentration of Er^{3+} or Yb^{3+}, l is sample thickness. The integrated absorption cross section $\sum_{\rm abs}$ and spontaneous radiation probability $A_{\rm rad}$ can be expressed by

$$\Sigma_{\rm abs} = \int \sigma_{\rm abs}(\lambda){\rm d}\lambda, \tag{2a}$$

$$A_{\rm rad} = 32\pi cn^2/(3\lambda_1^4)\Sigma_{\rm abs}, \tag{2b}$$

where λ_1 is the mean wavelength of absorption band. The stimulated emission cross section of Er^{3+}, $\sigma_{\rm emi}(\lambda)$ can be calculated according to the McCumber theory[8] from the absorption cross section $\sigma_{\rm abs}(\lambda)$,

$$\sigma_{\rm emi}\lambda = \sigma_{\rm abs}(\lambda)\exp(\frac{\varepsilon - hc\lambda^{-1}}{kT}), \tag{3}$$

ε can be calculated by

$$\frac{N_1}{N_2} = \exp(\frac{\varepsilon}{kT}), \tag{4}$$

where N_1 and N_2 are the equilibrium populations of $^4I_{15/2}$ and $^4I_{13/2}$ levels at temperature T without optical pumping, respectively. According to the approximate calculation[7]

$$\exp(\frac{\varepsilon}{kT}) \approx 1.1 \exp(\frac{E_0}{kT}), \tag{5}$$

where E_0 is the energy interval between the lowest manifolds of $^4I_{13/2}$ and $^4I_{15/2}$ levels.

The gain coefficient $\alpha(\nu)$ at frequency ν is expressed as

$$\alpha(\nu) = N_2\sigma_{\rm emi}(\nu) - N_1\sigma_{\rm abs}(\nu). \tag{6}$$

Laser oscillation will occur when gain is larger than losses. It was found that a high gain efficiency is generally associated with a large integrated absorption cross section in erbium glass[5]. Large integrated absorption cross section of erbium can be used as one of criteria to optimize the glass composition. In addition in an LD pumped Er^{3+}, Yb^{3+} co-doped glass, pump energy was transferred from Yb^{3+} ions ($^2F_{5/2}$ level) to Er^{3+} ion ($^4I_{11/2}$ level). For efficient pump, the high absorption cross section of ytterbium and efficient energy transfer from Yb^{3+} to Er^{3+} are required. Laser efficiency and laser threshold are influenced greatly by the fluorescence lifetime of erbium ion[9]. Fluorescent lifetime is directly related to OH^- in glass[8]. Reactive atmosphere processing (RAP) method is used to remove OH^- in glass during melting process. To optimize the composition of an ytterbium sensitized erbium laser glass, the absorption cross section of ytterbium ion at pump wavelength, energy transfer efficiency of $Yb^{3+} \rightarrow Er^{3+}$, fluorescent lifetime of erbium, the integrated absorption cross section of erbium must be considered.

In phosphate glass, Al_2O_3 is often used as a component to modify the glass structure and improve chemical stability. In present work, 5, 8 and 13 mol% Al_2O_3 were used to study the effect of Al_2O_3 content on the spectroscopic properties. Figure 1 shows the absorption spectra of Yb^{3+} ions at three Al_2O_3 concentrations and the absorption and emission spectra of Er^{3+} ions in an Er^{3+}, Yb^{3+} co-doped phosphate glass. According to the absorption spectrum of the erbium and the expressions (1) and (3), absorption and stimulated-emission cross sections of erbium as the function of the wavelength were calculated as shown in Fig. 2. It is shown that the peak of absorption and stimulated-emission cross sections of erbium is around 1532 nm ($\lambda_{\rm p}$). At wavelength longer than $\lambda_{\rm p}$, $\sigma_{\rm emi}$ is larger than $\sigma_{\rm abs}$. At wavelength shorter than $\lambda_{\rm p}$, $\sigma_{\rm emi}$ is smaller than $\sigma_{\rm abs}$.

The spectroscopic properties of three glasses with different Al_2O_3 concentrations are shown in Table 1. The main peaks of absorption spectra of Yb^{3+} and Er^{3+} ions are at 974 nm and 1531−1532 nm, respectively. The main peak of erbium fluorescent spectrum is near 1531−1533 nm, and is usually separated from absorption peak within 1 nm in the same glass. It indicates that the absorption and fluorescence of erbium are determined by the same pair of Stark manifolds. There is a sub-peak around 915−930 nm in Yb^{3+} absorption spectrum. A sub-peak at 1490 and 1500 nm for erbium absorption and fluorescence spectra indicates that a part of erbium ions occupy the high Stark manifolds of $^4I_{13/2}$ and $^4I_{15/2}$ levels at room temperature.

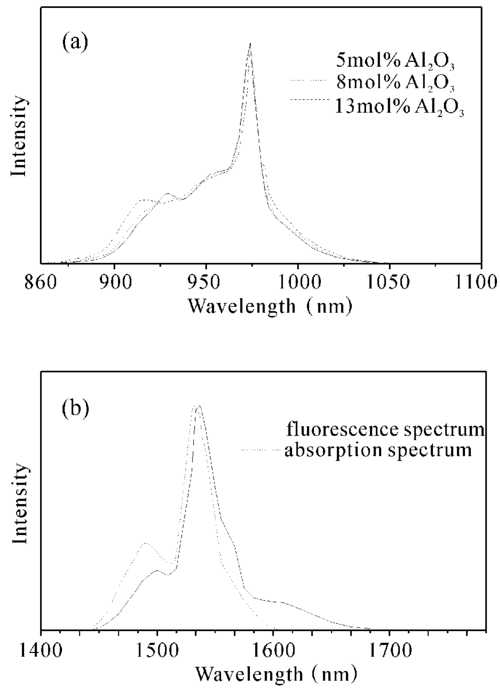

Fig. 1. The absorption spectra of ytterbium with 5, 8 and 13 mol% Al_2O_3 (a) and absorption and emission spectra of erbium (b) in an Er^{3+}, Yb^{3+} co-doped phosphate glass.

Table 1. The Compositions and Spectroscopic Properties of Er^{3+}, Yb^{3+}:Phosphate Glasses with Different Contents of Al_2O_3

Spectroscopic Properties	$60P_2O_515Na_2O13SrO$ $5Al_2O_36Yb_2O_3$ $0.6La_2O_30.4Er_2O_3$	$60P_2O_512Na_2O13SrO$ $8Al_2O_36Yb_2O_3$ $0.6La_2O_30.4Er_2O_3$	$60P_2O_57Na_2O13SrO$ $13Al_2O_36Yb_2O_3$ $0.6La_2O_3\ 0.4Er_2O_3$
$\sum_{\rm abs}(Yb^{3+})$ (10^4 pm^3)	2.88	2.84	2.85
$\sum_{\rm abs}(Er^{3+})$ (10^4 pm^3)	2.74	2.19	2.43
$A_{\rm rad}(Er^{3+})$ (s^{-1})	117	94	104
$\tau_{\rm rad}(Er^{3+})$ (ms)	8.5	10.7	9.6
$\tau_{\rm m}(Er^{3+})$ (ms)	7.0	7.8	8.0
$\sigma_{\rm abs}(Yb^{3+})$ at 974 nm (10^{-20} cm^2)	0.83	0.76	0.69
$\tau_{\rm abs}(Er^{3+})$ at 1530 nm (10^{-20} cm^2)	0.54	0.48	0.50

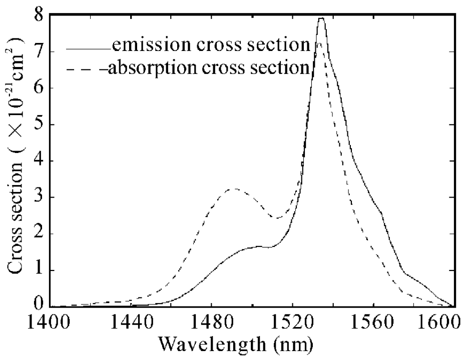

Fig. 2. The absorption and emission cross section of an Er^{3+}, Yb^{3+} co-doped phosphate glass.

In Table 1 and Fig. 1(a), it is found that the sub-peak of ytterbium absorption spectrum is blue-shifted from 930 to 915 nm with the increase of Al_2O_3 content. This is due to the local environmental change of Yb^{3+} ions. The glass network is reinforced for the phosphate glass with 13 mol% Al_2O_3. This leads to the large population at high Stark manifolds of Yb^{3+} ions. There is also a blue shift of sub-peak in the erbium fluorescent spectrum when Al_2O_3 content is 13 mol%.

In Table 1, it is known that glass with 5 mol% Al_2O_3 has the largest integrated absorption cross section (Σ_{abs}) of erbium. It infers that this glass has the highest oscillator strength. Glass with 8 mol% Al_2O_3 has the smallest Σ_{abs} of erbium. The integrated absorption cross section of ytterbium seems not dependent on Al_2O_3 content. The spontaneous emission probability A_{rad} of erbium is the largest for the glass with 5 mol% Al_2O_3. Consequently this glass has the shortest radiation lifetime τ_{rad}. The peak absorption cross section of both Er^{3+} and Yb^{3+} shows the largest in 5 mol% Al_2O_3 content. The variation of Σ_{abs} of erbium with Al_2O_3 concentration is in good agreement with that of peak σ_{abs} of erbium. The measured fluorescent lifetime τ_m of erbium in Table 1 is generally in accordance with radiation lifetime. The measured fluorescent lifetime is affected by both radiation lifetime and the residual OH^- contents in glass. For the same glass, the measured fluorescent lifetime can be greatly degraded when there is large amount of OH^- in glass. It is known from measured emission spectrum that glass with 5 mol% Al_2O_3 content has the strongest fluorescent intensity. Evaluating from Σ_{abs}, A_{rad} of Er^{3+} and peak σ_{abs} of Er^{3+} and Yb^{3+}, it is found that glass with 5 mol% Al_2O_3 content is the most promising erbium laser material.

4, 5, 6, 7 and 8 mol% Yb_2O_3 were used to investigate the effect of Yb_2O_3 concentration on the spectroscopic properties of Er^{3+},Yb^{3+} co-doped phosphate glasses. All glasses contain 0.4 mol% Er_2O_3 and low Al_2O_3 contents. Table 2 shows the dependence of integrated absorption cross section Σ_{abs} of erbium, peak σ_{abs} of erbium and ytterbium and fluorescent lifetime of erbium on Yb_2O_3 contents. The integrated absorption cross section, fluorescent lifetime and peak absorption cross section of erbium first increase with Yb_2O_3 content, and then decrease with Yb_2O_3 content. 4 mol% Yb_2O_3 is not sufficient to activate full Er^{3+} ions. High Yb_2O_3 concentration leads to the concentration quenching due to Yb^{3+} clusters formation and energy cross relaxation between Yb^{3+} and OH^- or other impurities. It is shown that glass with 5−6 mol% Yb_2O_3 has the best spectroscopic parameters. Peak absorption cross section of ytterbium decreases with Yb_2O_3 content. This indicates that with the increase of ytterbium, the distance between Yb^{3+} ions shortens. The interaction between Yb^{3+} becomes strong and this may influence the spectroscopic property.

Table 3 shows the effect of Er_2O_3 content on some spectroscopic parameters and the energy transfer efficiency η of Yb^{3+}→Er^{3+}. η is calculated by

$$\eta_{Er} = 1 - \tau_{Yb}/\tau_0, \tag{7}$$

where τ_0 is ytterbium fluorescent lifetime without Er_2O_3 doping and τ_{Yb} is the ytterbium fluorescent lifetime with

Table 2. Effect of Yb_2O_3 Concentrations on the Spectroscopic Properties (0.4 mol% Er_2O_3)

Yb_2O_3 Content (mol%)	$\sigma_{abs(Yb)}$ (10^{-20} cm^2)	$\sigma_{abs(Er)}$ (10^{-20} cm^2)	$\tau_{m(Er)}$ (ms)	$\Sigma_{abs(Er)}$ (10^4pm^3)
4	0.95	0.54	6.8	2.60
5	0.92	0.58	7.5	2.85
6	0.90	0.58	7.5	2.80
7	0.87	0.54	7.2	2.70
8	0.80	0.50	6.8	2.40

Table 3. The Effect of Er_2O_3 Content on Spectroscopic Properties and Energy Transfer Efficiency of Yb^{3+} to Er^{3+} (6 mol% Yb_2O_3)

Er_2O_3 Content (mol%)	$\sigma_{abs(Yb)}$ (10^{-20} cm^2)	$\sigma_{abs(Er)}$ (10^{-20} cm^2)	$\Sigma_{abs(Er)}$ (10^4 pm^3)	$\tau_{m(Er)}$ (ms)	$\tau_{m(Yb)}$ (μs)	η_{Er} (%)
0.05	0.86	0.65	3.50	7.5	210	81
0.2	0.87	0.60	3.10	7.5	65	94
0.4	0.9	0.58	2.80	7.5	40	96

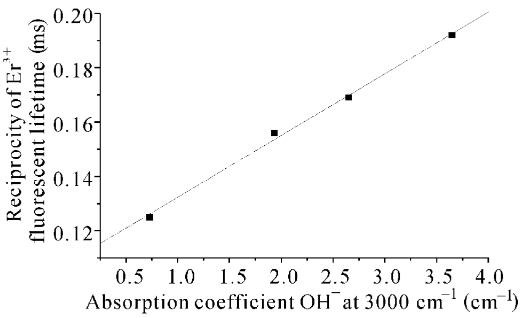

Fig. 3. The rlationship between $1/\tau$ and the absorption conefficient of OH^- at 3000 cm^{-1}.

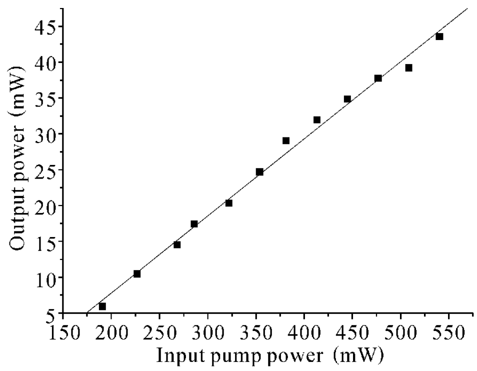

Fig. 4. Output power versus absorbed input pump power of an LD pumped Er^{3+}, Yb^{3+} co-doped phosphate glass laser.

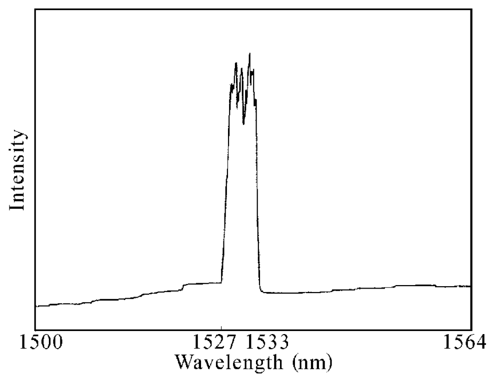

Fig. 5. Laser spectrum of an LD pumped Er^{3+}, Yb^{3+} co-doped phosphate glass laser.

Er_2O_3 doping. The ytterbium fluorescent lifetime is 1.1 ms in the present glass. All glasses have 6 mol% Yb_2O_3 and low Al_2O_3 content. It is known from Table 3 that energy transfer efficiency of $Yb^{3+}\rightarrow Er^{3+}$ is greatly dependent on Er_2O_3 concentration. From above results, it is found that the higher the Er_2O_3 content, the more efficient the energy transfers from Yb^{3+} ions to Er^{3+} ions. 96% energy transfer efficiency can be achieved in the glass with 0.4 mol% Er_2O_3. Glass with 0.05 mol% Er_2O_3 has the highest peak absorption cross section of erbium. Fluorescent lifetime of erbium has no change with Er_2O_3 content. For microchip laser application, large amount of Er_2O_3 is needed to get efficient energy transfer from Yb^{3+} to Er^{3+}.

It is well known that fluorescent lifetime and laser performance of erbium glass are strongly influenced by OH^- in glass[8]. Er^{3+}, Yb^{3+} :phosphate glass was sampled after different oxygen bubbling time from the same glass. Fluorescent lifetime of erbium and absorption coefficient of OH^- at 3000 cm^{-1} were measured. Figure 3 is the relationship between $1/\tau$ and α_{OH^-} of the glass, in which content of Al_2O_3 is 5 mol%. It shows that there is a nearly linear relationship between $1/\tau$ and α_{OH^-}, absorption coefficient of OH^- at 3000 cm^{-1}. To improve stimulated emission and increase fluorescent lifetime of erbium, α_{OH^-} should be less than 1 cm^{-1}. It is known from our work that fluorescent lifetime is more sensitive to the existence of OH^- in glass with high rare earth oxide concentration and alkali oxide components.

Figures 4 and 5 depict the output power versus the absorbed input pump power and the laser spectrum of a 2-W, 974-nm LD pumped microchip Er^{3+}, Yb^{3+} :phosphate glass laser. The thickness of glass sample is 2 mm. The concentrations of Yb_2O_3 and Er_2O_3 are 6 and 0.2 mol%, respectively. CW laser operation achieved for this microchip laser at room temperature without cooling. The slope efficiency is 10.6%. Laser threshold is about 118 mW and the maximum output is 43 mW. Because pump spot size on glass sample is large (about 200 μm), laser threshold is high and high output is achieved without damage in coating and glass. Further work needed is to improve pump light quality and to optimize coating parameters. Several longitudinal modes were detected as shown in Fig. 5. The center laser wavelength is about 1530 nm with FWHM of 4.4 nm.

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