Effect of Erbium Concentration on Upconversion Luminescence of Er:Yb:phosphate Glass Exited by InGaAs Laser Diode

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ABSTRACT

The effect of concentration of Er^{3+} on the upconversion luminescence of the Er:Yb:glass excited by InGaAs laser diode is reported. With different concentration of Er3+, the upconversion luminescence intensity, the intensity ration of green and red lights, and the near infrared lights are different. The detailed mechanism of upconversion luminescence are analyzed.
Keywords: Er:Yb: phosphate glass, upconversion, concentration

1. INTRODUCTION

Upconversion luminescence of materials doped with rare-earth-ions is receiving great interests. As a laser media which can emit eye-safe wavelength laser, 1.54μm Er:Yb:phosphate glass laser is widely studied[1], but the upconversion luminescence of the media has received little attention. Chen etc.[2][3] has studied the upconversion luminescence of Er3+ doped phosphate glass excited by dye laser. Lu etc.[4][5] reported the upconversion luminescence of Erbium doped phosphate glass and fibre excited by Nd:YAG laser. Research of upconversion of Er:Yb:glass is not only important in upconversion itself, but in understanding of the relationship between the normal 1.5mm range fluorescence and upconversion luminescence and the whole luminescence mechanics of the glass. Hutchinson[6] observed the obvious upconversion phenominon when he used 980nm LD laser to pump Er:Yb:phosphate glass to get 1.54mm laser. We have also found the upconversion luminescence when realizing the 1.54mm laser.

Concentration of doped ions in glass is very important to the characteristics of the material. In erbium, ytterbium codoped phosphate glass, what is the effect of the erbium ions concentration on the upconversion luminescence? In this paper we report the effect of concentration of Er^{3+} on the upconversion luminescence of the Er:Yb:glass excited by InGaAs laser diode.

2. EXPERIMENTAL ARRANGEMENT

2.1. Samples

All Er:Yb:phosphate glass samples we used are manufactured and provide by Kigre Incorpoartion. The concentration of Er2O3 varied from 0.13% to 4% (A sample:0.13%wt; B sample: 0.206%wt; C sample: 1.08%wt; D sample: 2.1%wt; E sample: 4.0%wt), and the concentration of Yb2O3 is about 15-20%. Because the concentration of Yb3+ is much higher than that of Er3+, so 5% difference between Yb3+ can be omitted in samples. The both sides of samples are well polished and the thickness is 1.5mm.

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3.2. Experimental setup

The excited spectra and emission spectra of the samples are measured by Model F11AI Fluoremeter. When upconversion luminescence spectra are measured, the InGaAs laser diode is used as the excited source. The laser are focused on the samples after two lenses. The central wavelength of laser in the room temperature is 966nm and the power can be adjusted from 0 to 300mW. Figure 1 shows the experimental setup diagram.

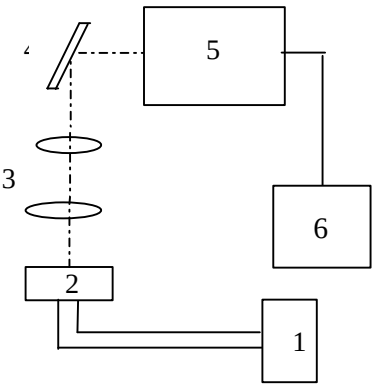


Fig.1 Optical Setup for luminescence experiments

1 LD driver 2 LD
3 collimate lens 4 sample
5 fluometer 6 computer

3. EXPERIMENTAL RESULTS

3.1 Upconversion spectra of samples.

Fig.2 shows the upconversion luminescence spectra of five samples with different Er^{3+} concentration . Green lights(central wavelength of 520nm and 543nm, corresponding to 2H11/2--$^4I_{15/2}$ and $^4S_{3/2}$ –$^4I_{15/2}$ respectively), red light(central wavelength of 650nm, corresponding to $^4F_{9/2}$ to $^4I_{15/2}$) and near infrared lights(from 780nm to 850nm) are measured. Fig.3 shows the typical variation of fluorescence intensities of the green and red bands as the pumping power in a logarithmic coordinate. No matter which concentration of Er^{3+}, we find that the slope of the red light is near 2 which means it is two phonon process. As to the green upconversion luminescence, when the pumping power is low (less than 100mW), the slope is near 2, when pumping power is high (more than 100mW), the slope is between 2 and 3, which means the three phonon process.

When exciting power is high enough (over 1000mW) and the concentration of Er^{3+} is low, some upconversion luminescence whose central wavelength are 361nm, 405nm and 450nm are measured. But the intensities are very weak, which can be omitted compared with green and red luminescence intensities.

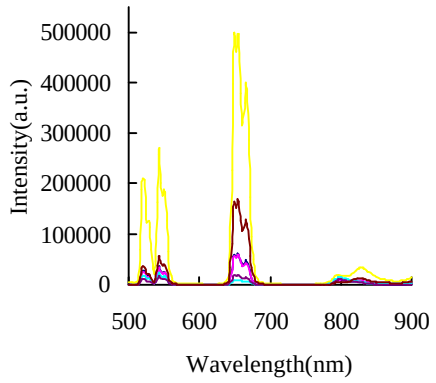


Fig.2Upconversion luminescence spectra of five samples

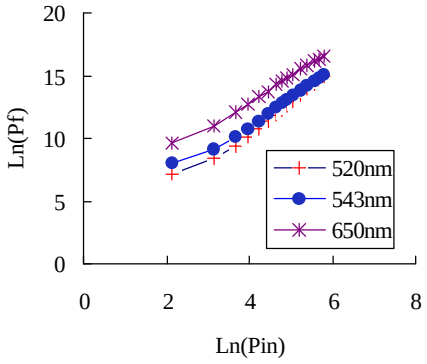


Fig.3 the relationship between the intensities of upconversion lights(520nm,543nm,650nm bands with pumping power

3.2 Effect of Er^{3+} concentration on the upconversion luminescence.

3.2.1. Effect of Er^{3+} concentration on the intensities of upconversion luminescnec

The concentration of Er^{3+} will effect the intensity of upconversion luminescence. Usually, when the concentration is high, the non-radiative decay process will increase, while radiation relax decrease. So

the intensity of luminescence decrease. From Fig.1, we can find that the intensities of three upconversion luminescence bands degrease with the concentration of ER^{3+} concentration.

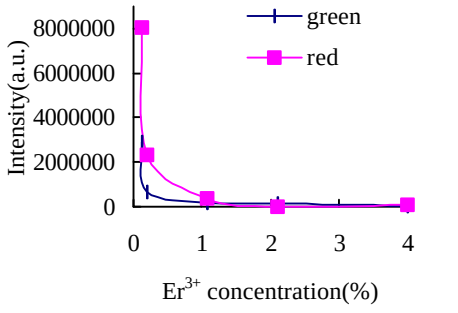
3.2.2 Effect of Er^{3+} concentration on the relative intensities of green and red lights.

When the exciting power is low(less than 100mW), the intensity of green lights is always weaker than that of red lights. But when the power is high enough, the case becomes complicated

As to the samples with lower Er^{3+} concentraion, the intensity of green lights(520nm and 543nm luminescence bands) is weaker than that of red light. For instance, for A sample whose Er^{3+} concentraion of Er^{3+} is 0.13%wt, , the intensity of green lights of is less than a half of that of red light. When Er^{3+} concentration increase, the intensity of green lights increase much faster than that of red lights, when Er^{3+} concentration is high enough, the intensity of green lights is stronger than that of red lights. For example, for C sample whose Er^{3+} concentration is 4.0%wt, the intensity of green light is 1.6 times stronger than that of red lights. Table 1 shows the detailed intensities for five samples, where Ig/Ir means the ratio of the intensities of green lights and red lights.

Table1 The intensities variation for five samples with different Er^{3+} concentrations

SAMPLE	A	B	C	D	E
I(520nm)	1.130E6	2.336E5	65944	45642	11670
I(543nm)	1.782E6	4.396E5	1.047E5	81298	41224
I(650nm)	8.060E6	2.343E6	3.713E5	79138	96846
Ig/Ir	0.36	0.29	0.46	1.60	0.55



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ig.4 concentration -intensity

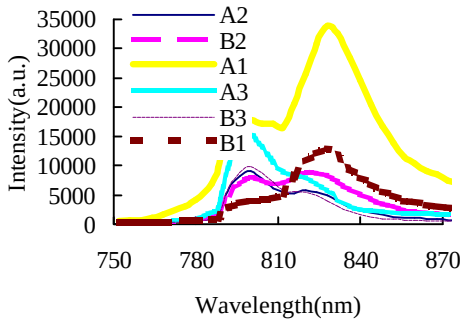

Fig.5 the infrared luminescence bands of samples with different Er^{3+} concentration

3.3.3 Effect of Er^{3+} concentration on the 800nm luminescnce bands.

There are two peaks in the near infrared region, one is at 800nm and another is at 830nm. When the Er^{3+} concentration is low, the peak at 830nm is obvious, while the Er^{3+} concentration is high, the peak

at 830nm disappear and the peak at 800nm is obvious. Fig.3 shows the phenomenon.

4. ANALYZE AND DISCUSSION

According to the experimental results and the energy level diagram of Er,Yb codoped glass, we can analyze the luminescence process.

First, the ions in ground state will excited to $^2F_{7/2}$ state(Yb^{3+}) and $^4I_{11/2}$(Er3+) state, because of that the concentration of Yb^{3+} is much high than that of Er^{3+}, those ions in $^2I_{11/2}$ state can be omitted. Secondly, energy transfer (ET) will occur between the Yb^{3+} ions and Er^{3+} ions, which will cause to the ESA of Er^{3+} ions. We will explain the several upconversion luminescence process respectively.

4.1 Red upconversion luminescence.

According to the experimental results, the red upconversion luminescence is caused by two photon process. First, Er^{3+} in ground state will excited to ^{4}I11/2 by ET, because of the short lifetime of $^4I_{11/2}$ state, most of ions will non-radiatively decay to $^4I_{13/2}$ state. Secondly, Er^{3+} at $^4I_{13/2}$ state will excited to $^4F_{9/2}$ state by ET. The process can be described by the following expressions:

$$^2F_{5/2}(Yb^{3+})+{}^4I_{15/2}(Er^{3+}) \quad {}^2F_{7/2}(Yb^{3+})+{}^4I_{11/2}(Er^{3+})$$

$$^4I_{11/2}(Er^{3+}) \sim {}^4I_{13/2}(Er^{3+})$$

$$^2F_{5/2}(Yb^{3+})+{}^4I_{13/2}(Er^{3+}) \quad {}^2F_{7/2}(Yb^{3+})+{}^4F_{9/2}(Er^{3+})$$

4.2 Green upconversion luminescence

After the first step ET between the Yb^{3+} and Er^{3+}, a part of ions at $^4I_{11/2}$ state will excite to $^2H_{11/2}$ level by ET between Er3+ and Yb3+:

$$F_{5/2}(Yb^{3+})+{}^4I_{15/2}(Er^{3+}) \quad {}^2F_{7/2}(Yb^{3+})+{}^4I_{11/2}(Er^{3+})$$

$$^2F_{5/2}(Yb^{3+})+{}^4I_{11/2}(Er^{3+}) \quad {}^2F_{7/2}(Yb^{3+})+{}^2H_{11/2}(Er^{3+})$$

some ions at 2H11/2 will non-radiatively decay to the $^4S_{3/2}$ state. Radiative trasistion from $^2H_{11/2}$ and $^4S_{3/2}$ states to the ground will emit green lights. It is two-photon process.

When pumping power increase and is high enough, the ions at ^{4}F9/2 and ^{4}I9/2 will excited to $^2H_{9/2}$ $^4F_{5/2}$ statesby ET between Yb^{3+} and Er^{3+},then the ions transist to $^2H_{11/2}$ states via cross-relaxing, non-radiatively decay it is three pnoton process, which can be describes as follows:

$$^2H_{9/2}(Er^{3+})+{}^4I_{15/2}(Er^{3+}) \quad {}^2H_{11/2}(Er^{3+})+{}^4I_{13/2}(Er^{3+})$$

$$^2H_{9/2}(Er^{3+}), {}^4F_{5/2} \quad Er^{3+} \qquad {}^2H_{11/2}(Er^{3+}) \text{ or } {}^4S_{3/2} \quad Er^{3+}$$

When Er^{3+} concentration is high, ET, cross-relaxing, and nonradiative decay becomes more strong, so that more ions at $^4F_{9/2}$ $^4I_{9/2}$ states excited to $^2H_{9/2}$ and $^4F_{5/2}$ state Finally radiative transition from $^2H_{11/2}$ $^4S_{3/2}$ states to ground state will emit green lights; Meanwhile, ions directively transited from $^4F_{9/2}$ to ground state becomes less so the intensity of red light becomes weak. That is the reason why the intensity of green light is stronger than that of red light when the concentration of Er^{3+} is high.

When pumping power is high,405nm(correspong to 2H9/2 to $^4I_{15/2}$) 450nm(corresponding to ^{4}F5/2 to $^4I_{15/2}$) lights are measured, which shows that some ions are excited to the higher $^2H_{9/2}$ $^4F_{5/2}$ states when pumping power is high.

4.3. 750-850nm upconversion luminescence

It is a complex luminescence band, it is due to several radiative transition including $^4S_{3/2}$ $^4I_{13/2}$ central wavelength 842nm $^2H_{11/2}$ $^4I_{13/2}$ central wavelength 820nm and $^4I_{9/2}$ $^4I_{15/2}$ central wavelength 800nm

$$^2F_{5/2}(Yb^{3+}) + \begin{cases} ^2H_{11/2}(Er^{3+}) \\ ^4S_{3/2}(Er^{3+}) \end{cases} \rightarrow {}^2F_{7/2}(Yb^{3+}) + \begin{cases} ^2G_{7/2}(Er^{3+}) \\ ^2G_{9/2}(Er^{3+}) \end{cases}$$

When Er^{3+} concentration increases, possibility of non-radiative decay from higher states to $^4I_{9/2}$ increase the possibility of ET between Er^{3+} ions at $^2H_{11/2}$ $^4S_{3/2}$ to $^4I_{9/2}$ increase $^2H_{11/2}$ $^4S_{3/2}+{}^4I_{15/2}$ $^4I_{9/2}+{}^4I_{13/2}$, which causes to the increase of ions at $^4I_{9/2}$ state, and decrease of ions at $^2H_{11/2}$ $^4S_{3/2}$ states so that the transition from $^4I_{9/2}$ to ground state(800nm) increase surpassing the transition from $^2H_{11/2}$ and $^4S_{3/2}$ to $^4I_{13/2}$ so in the spectra figure, the peak at 830nm disappears while peak at 800nm appears.

Fig.6 shows the Er3+,Yb3+ energy levels diagram and the possible transist processes which are anylyaed as before.

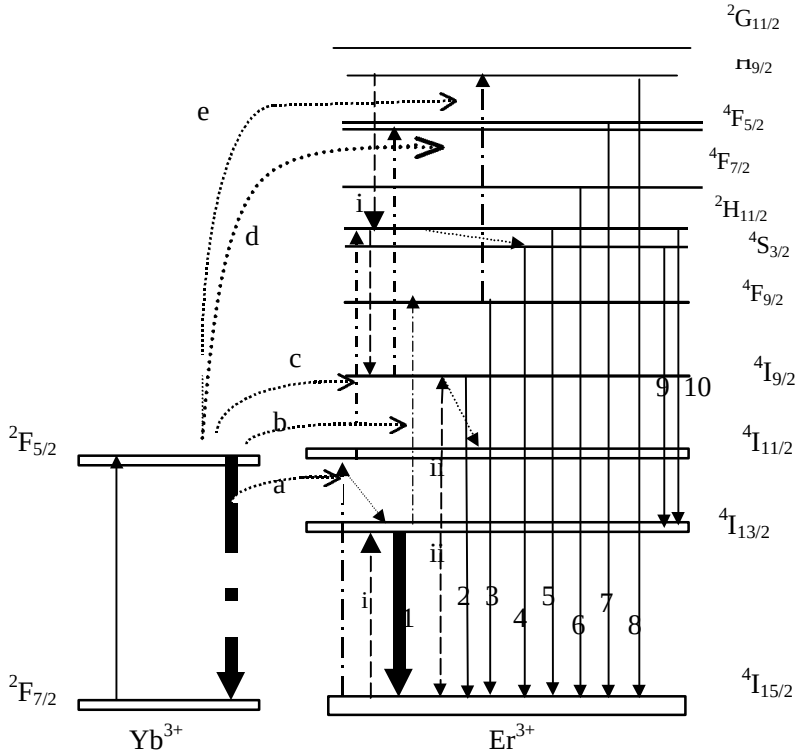

Fig.6 Energy level diagram of Er:Yb:phosphate glass

5. CONCLUSIONS

From the experimental results and analyze, the following conclusions can be drawn.

1. The concentration of Er^{3+} higher, the upconversion luminescence intensity lower. We believe that the concentration quench is important in the luminescence mechanics.
2. When excitation power is high enough, as to the samples with lower concentration of Er^{3+}, the intensity of green light is weaker than that of red light. The reason is that more ions will non-radiatively decay from higher levels to $^2H_{11/2}$ and $^4S_{3/2}$ levels.
3. As to the upconversion light at infrared wavelength, there are two peaks, one is at 800nm, another at 830nm. When the concentration of Er^{3+} is lower, the peak at 830nm is more apparent than that at 800nm, but with the increase of the increase of concentration of Er^{3+}, the peak at 800nm disappear while peak at 800nm becomes clearer. Several processes are contributed to the luminescence band.

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