



# Calculation on the energy transition coefficient by up-conversion emission intensity ratio

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## ABSTRACT

The Er<sup>3+</sup>/Yb<sup>3+</sup> co-doped phosphate glass was prepared by high temperature fusing method. The up-conversion (UC) emission of the sample was measured at 975 nm laser diode (LD) excitation. Using the ratio of the integral intensity of the UC green emission to that of the UC red emission at different pump powers, we calculated the energy transition (ET) coefficient of Yb<sup>3+</sup> to Er<sup>3+</sup>.

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## 1. Introduction

The materials doped with rare earth ions have widely been studied for the photo-electricity and biomedicine devices. Especially, the UC emission of the Er<sup>3+</sup> ions doped materials has been applied to the short wavelength laser, temperature sensor, color display [1–3], and so on. Considering the larger absorption cross-section of Yb<sup>3+</sup> ion for 975 nm light, the Yb<sup>3+</sup> ion is usually introduced as sensitizer. The ET of Yb<sup>3+</sup> to Er<sup>3+</sup> is very complicated and strong in the Er<sup>3+</sup>/Yb<sup>3+</sup> co-doped materials, such as ET1:  ${}^2F_{2/5}(Yb^{3+}) + {}^4I_{15/2}(Er^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^4I_{11/2}(Er^{3+})$ , ET2:  ${}^2F_{2/5}(Yb^{3+}) + {}^4I_{11/2}(Er^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^4F_{7/2}(Er^{3+})$ , ET3:  ${}^2F_{2/5}(Yb^{3+}) + {}^4I_{13/2}(Er^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^4F_{9/2}(Er^{3+})$ , ET4:  ${}^2F_{2/5}(Yb^{3+}) + {}^4F_{9/2}(Er^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^4G_{11/2}(Er^{3+})$ . It is necessary to make clear the micro-mechanism of the ET. Dexter [4–6] and Inokuti–Hirayama models [7–9] are usually used to calculate the ET coefficient between rare earth ions. For the Dexter model, the overlap integral of the emission spectrum (donor ions) and the absorption spectrum (acceptor ions) is very important. But sometimes the spectra are obtained very difficult. For example, if we want to calculate the energy transition coefficient of ET2, ET3 and ET4, the absorption spectra of Er<sup>3+</sup> corresponding to the transitions:  ${}^4I_{11/2} \rightarrow {}^4F_{7/2}$ ,  ${}^4I_{13/2} \rightarrow {}^4F_{9/2}$  and  ${}^4F_{9/2} \rightarrow {}^4G_{11/2}$  must be obtained. But their absorption spectra can hardly be measured (needing very low temperature). Using Inokuti–Hirayama model,

we can calculate the total energy transition coefficient of Yb<sup>3+</sup> to Er<sup>3+</sup>. But the ET coefficients of ET2, ET3 and ET4 cannot be obtained. In this letter, using the ratio of the integral intensity of the UC emissions at different pump powers, we calculated the energy transition coefficients of ET2, ET3 and ET4.

## 2. Experimental procedures

The phosphate glass with the composition of (80P<sub>2</sub>O<sub>5</sub> – 20Li<sub>2</sub>O) – 0.05Er<sub>2</sub>O<sub>3</sub> – 0.5Yb<sub>2</sub>O<sub>3</sub> (mol%) was prepared by high temperature fusing method. The start raw materials, consisting of reagent grade NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, Li<sub>2</sub>CO<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub>, were mixed thoroughly. Initially, the furnace was heated to 600 K at the rate of 1 K min<sup>–1</sup>, and held at the temperature for 2 h to release the volatile components. Finally, the furnace temperature was raised to 1620 K at the rate of 2 K min<sup>–1</sup>, and controlled at the temperature for 3 h to melt the raw materials completely. A clear, viscous melt was poured onto a preheated stainless-steel plate in air. The glass sample was heated at 720 K for 6 h to release the thermal stress. Finally, the sample was incised and surface-polished for optical measurements.

The photoluminescence spectrum was measured with a model F111AI fluorescence spectrophotometer at 975 nm LD excitation. The visible light and near infrared luminescence were detected by photomultiplier tube detector and Ge detector, respectively.

## 3. Results and discussion

Fig. 1 shows the UC emission spectrum of the Er<sup>3+</sup>/Yb<sup>3+</sup> co-doped phosphate glass in the 500–700 nm wavelength range at 975 nm LD excitation. The UC red emission at 659 nm, the UC green emissions at 523 and 546 nm are observed. They come from the transition of Er<sup>3+</sup> ions:  ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ ,  ${}^2H_{11/2} \rightarrow {}^4I_{15/2}$  and  ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ , respectively.

Fig. 2 shows the ratios of the integral intensity of the UC green emissions to that of the red emission dependence on the pump

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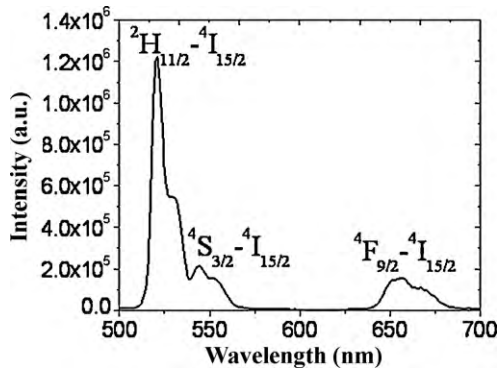


Fig. 1. UC emission spectrum of the sample at 975 nm LD excitation.

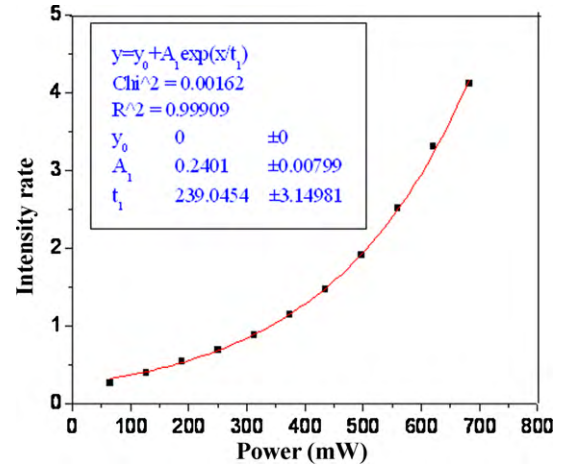


Fig. 2. Ratios of the integral intensity of the UC green emissions to that of the red emission VS the pump power.

power. It is very obvious that the ratios continuously increase with the increasing of the pump power. By exponential fitting, the fitting curve is in good agreement with the experimental curve. The fitting results are indicated in Fig. 2. Finally, we obtain the function:

$$I_{\text{green}}/I_{\text{red}} = 0.2401 \exp(P/239.0454). \quad (1)$$

Fig. 3 shows the energy level diagram of Yb<sup>3+</sup> and Er<sup>3+</sup>, as well as the proposed UC processes at the excitation of 975 nm LD. The population processes of the UC green emissions can be described as follows: by ET1 and ET2, the Er<sup>3+</sup> ions in the ground state are excited to <sup>4</sup>F<sub>7/2</sub> state. Then the ions rapidly relax to <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> states by non-radiative transition, from which the green emissions arise. For the red emission, the ions in the ground state transfer to <sup>4</sup>I<sub>13/2</sub> state by ET1. Then the ions relax to <sup>4</sup>I<sub>15/2</sub> non-radiatively. By ET3, the ions in <sup>4</sup>I<sub>13/2</sub> state are pumped to <sup>4</sup>F<sub>9/2</sub> state. At the same time, the ions in <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> states also relax to <sup>4</sup>F<sub>9/2</sub> state by non-radiative transition. At higher pump power, the ions in the <sup>4</sup>F<sub>9/2</sub> state can also be excited to <sup>4</sup>G<sub>11/2</sub> by ET4. Subsequently, the ions relax to <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> states by non-radiative transition.

To verify and make a theoretical interpretation of the dependence relation between emission intensity and pump power, we

utilize the following rate equations:

$$dN_2/dt = -A_2N_2 + \sigma_{\text{Yb}}N_1P/Sh\nu_p - k_{23}N_2N_3 - k_{24}N_2N_4 - k_{25}N_2N_5 - k_{26}N_2N_6 \quad (2)$$

$$N_1 = N_{\text{Yb}} - N_2 \quad (3)$$

$$dN_4/dt = -(A_4 + w_{43})N_4 - k_{24}N_2N_4 + w_{54}N_5 \quad (4)$$

$$dN_5/dt = -(A_5 + w_{54})N_5 + k_{23}N_2N_3 - k_{25}N_2N_5 + w_{65}N_6 \quad (5)$$

$$dN_6/dt = -(A_6 + w_{65})N_6 + k_{24}N_2N_4 - k_{26}N_2N_6 + w_{76}N_7 \quad (6)$$

$$dN_7/dt = -(A_7 + w_{76})N_7 + k_{25}N_2N_5 + k_{26}N_2N_6 \quad (7)$$

$$N_3 = N_{\text{Er}} - N_4 - N_5 - N_6 - N_7 \quad (8)$$

where N<sub>Yb</sub> and N<sub>Er</sub> are the total ytterbium and erbium concentrations, N<sub>i</sub> represents the population density of the corresponding

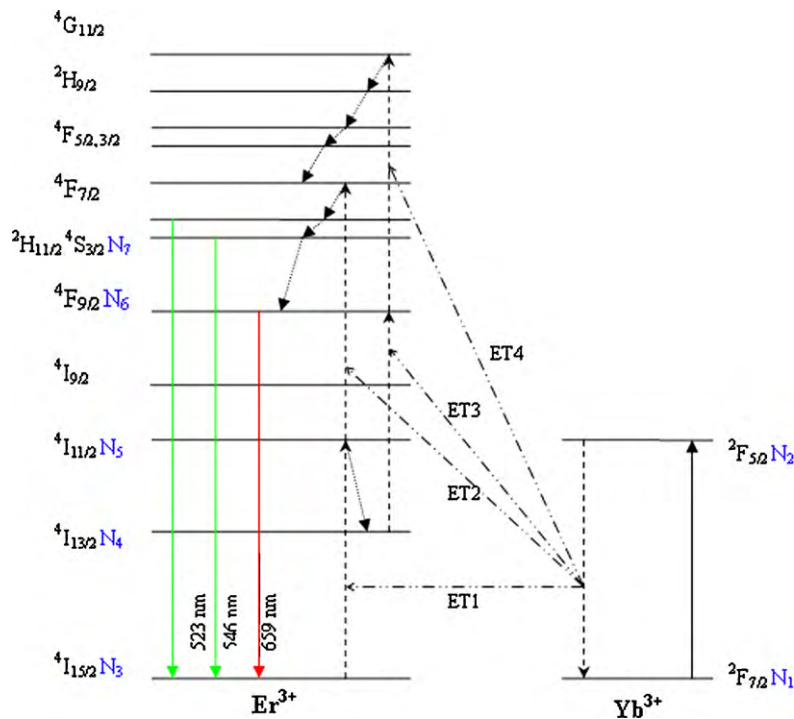


Fig. 3. Energy level diagram of Yb<sup>3+</sup> and Er<sup>3+</sup>, as well as the proposed UC processes at the excitation of 975 nm LD.

levels shown in Fig. 3,  $k_{ij}$  and  $w_{ij}$  are the coefficients of energy transfer and non-radiative transition probabilities between the  $i$  and  $j$  level,  $A_i$  corresponds to the spontaneous radiative probabilities of level  $i$ , the  $P$  and  $\nu_p$  symbolize the laser power and frequency,  $S$  and  $\sigma_{Yb}$  are the area of the laser spot and the absorption cross-section of  $Yb^{3+}$ .

Under steady-state excitation, considering  $A_2N_2 \gg (k_{23}N_2N_3 + k_{24}N_2N_4 + k_{25}N_2N_5 + k_{26}N_2N_6)$ , the equation can be obtained from Eq. (2):

$$N_2 = \sigma_{Yb}N_{Yb}P/SA_2h\nu_p. \quad (9)$$

From Eqs. (4)–(7), we get the following expression:

$$N_7/N_6 = (k_{25}k_{26}/w_{54}A_7)N_2^2 + [k_{25}A_6/w_{54}A_7 + k_{25}k_{26}A_4/k_{24}w_{54}A_7 + k_{26}/A_7]N_2 + k_{25}A_4A_6/k_{24}w_{54}A_7. \quad (10)$$

The emission intensity  $I$  and the population density  $N_i$  have the following relation:

$$I = \sum h\nu_i A_i N_i. \quad (11)$$

From Eqs. (9)–(11), we obtain the following equation:

$$I_7/I_6 = (k_{25}k_{26}\nu_7/w_{54}\nu_6A_6)(\sigma_{Yb}N_{Yb}/SA_2h\nu_p)^2 p^2 + [k_{25}\nu_7/\nu_6w_{54} + k_{25}k_{26}A_4\nu_7/k_{24}w_{54}A_6\nu_6 + k_{26}\nu_7/A_6\nu_6] \times \sigma_{Yb}N_{Yb}P/SA_2h\nu_p + k_{25}A_4\nu_7/k_{24}w_{54}\nu_6. \quad (12)$$

Form Eq. (1), by Taylor expansion, we obtain (the first three items retained):

$$I_{\text{green}}/I_{\text{red}} = 0.240 + 0.001P + 2.083 \times 10^{-6}P^2. \quad (13)$$

Comparing Eq. (12) with (13), we obtain  $K_{24} = 2.42 \times 10^{-17}$  (ET3),  $K_{25} = 1.53 \times 10^{-15}$  (ET2) and  $K_{26} = 8.16 \times 10^{-17}$  (ET4). The radiative transition probabilities  $A_i$  are calculated by Judd–Ofelt theory [10,11]. The non-radiative transition probabilities  $w_{ij}$  are calculated by the following equation [12]:

$$w = w_0 \exp(\alpha\Delta E), \quad (14)$$

where  $w_0$  and  $\alpha$  are positive constant depending on the properties of host material and generally independent of the kind of rare earth

ions or the electronic state involved.  $\Delta E$  is the energy gap between the two energy levels of interest.

#### 4. Conclusions

In a word, by high temperature fusing method, the  $Er^{3+}/Yb^{3+}$  co-doped phosphate glass was prepared. At 975 nm LD excitation, the UC red and green emissions were observed. Using the ratio of the integral intensity of the green emission to that of the red emission, we calculated the ET coefficients of ET2, ET3 and ET4. The result shows that this way is feasible to calculate the ET of  $Yb^{3+}$  to  $Er^{3+}$ . The work will be helpful to analyze the ET between rare earth ions.

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