# Up-conversion photoluminescence characteristics of $Yb^{3+}$:$Er^{3+}$:$Tm^{3+}$ co-doped borosilicate glasses*

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$Yb^{3+}$:$Er^{3+}$:$Tm^{3+}$co-doped borosilicate glasses are prepared. Their strong up-conversion photoluminescence spectra in a range from ultra-violet to near-infrared, which are excited by a 978-nm laser diode, are measured, and the mechanisms of energy transfer among $Yb^{3+}$, $Er^{3+}$ and $Tm^{3+}$ ions are discussed. The results show that there is an unexpected wavelength at 900-nm emission from $Yb^{3+}$ Stark splitting levels to pump $Tm^{3+}$ ions and there exists an optimum pump power. The concentration of the $Tm^{3+}$ dopant gives rise to a prominent effect on the intensity of visible and near-infrared emissions for the $Yb^{3+}$:$Er^{3+}$:$Tm^{3+}$ co-doped borosilicate glasses.

**Keywords:** $Er^{3+}$:$Yb^{3+}$:$Tm^{3+}$ co-doped borosilicate glasses, up-conversion emission, two pump wavelengths, optimum pump power

**PACC:** 7840, 3380K

## 1. Introduction

In recent decades, rare earth ions with abundant energy levels have been studied effectively for lasers and optical amplifiers.[1−4] Most recently, their up-conversion photoluminescence exhibits extensive applications in colour displays, high density optical data storage and reading, biomedical diagnostics, optical temperature sensors, and so on.[5−8] Chen *et al.* investigated efficient blue up-conversion emission from $Yb^{3+}$:$Tm^{3+}$ co-doped fluoride glasses.[9] The strong red and green up-conversion luminescence emitted from $Yb^{3+}$:$Er^{3+}$ co-doped silicate glasses or $Al_2O_3$ substrate was discussed in detail in our previous studies.[10,11] Up-conversion properties of $Er^{3+}$, $Yb^{3+}$, and $Tm^{3+}$ co-doped fluorophosphate glasses were reported by Liao *et al.*[12] In their work, up-conversion emissions at 476, 522, 543, 653 and 794 nm were obtained, respectively, for different dopant samples. In the present paper, samples of $Yb^{3+}$:$Er^{3+}$:$Tm^{3+}$ co-doped borosilicate glasses are prepared. The up-conversion spectra from ultra-violet to near-infrared, which are excited by a 978-nm semiconductor laser diode (LD), are measured at 376, 399, 474, 519, 537, 659, 788, 800, 900 nm, etc. separately, and dominant mechanisms of energy transfer among $Yb^{3+}$, $Er^{3+}$ and $Tm^{3+}$ ions are discussed. In particular, it is found that the 900-nm emission due to $Yb^{3+}$ Stark splitting levels also contributes to the pumping for $Tm^{3+}$ ions and there exists an optimum pump power.

## 2. Experiment

The $Yb^{3+}$:$Er^{3+}$:$Tm^{3+}$ co-doped borosilicate glasses have been prepared by the technique of high-temperature melting as described in the literature.[10,13] The original compositions of the borosilicate glass substrate are $65.6SiO_2$-$14.5B(OH)_3$-$16.8Na_2CO_3$-$3.1Ba_2CO_3$, and the dopant concentrations of two samples, which are marked with $Z_1$ and $Z_2$, are 0.5at.%$Yb^{3+}$-0.1at.%$Er^{3+}$-0.1at.%$Tm^{3+}$ and 0.5at.%$Yb^{3+}$-0.1at.%$Er^{3+}$-0.5at.%$Tm^{3+}$, respectively. They were cut into the pieces each with a dimension of 20 mm×10 mm×2 mm and then polished. The up-conversion emissions from ultra-violet to infrared are measured with a universal system composed of detectors at different wavebands, a monochromator, a lock-in amplifier, and so on. The pump source is a 978-nm semiconductor laser diode with a maximal output power of 578 mW.

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# 3. Results and discussion

## 3.1. Spectrum analysis

Figure 1 presents the photoluminescence spectra of samples $Z_1$ and $Z_2$ in a wavelength range of 350–950 nm under 978-nm laser diode excitation. The initial states of the transitions are marked in the figures and all final states are the ground states of the relevant ions. It should be noted that the intensities of spectra centred at about 788 and 900 nm in Fig. 1(a) are reduced to the one-third of their real intensities for the clear shapes of other spectra. It can be seen from the figures that the peak intensities of sample $Z_2$ at 399, 537 and 659 nm increase evidently, compared with the peak intensities of corresponding wavelengths for sample $Z_1$. The spectra at 474, 788 and 900 nm, however, become weaker or even disappear, which means that the $Tm^{3+}$ concentration has an important influence on the photoluminescence characteristics for $Yb^{3+}$:$Er^{3+}$:$Tm^{3+}$ co-doped borosilicate glasses. It is worthwhile to point out that the spectrum at about 484 nm belongs to the laser source, because its peak position shifts towards the long-wavelength region with increasing laser working current.[14]

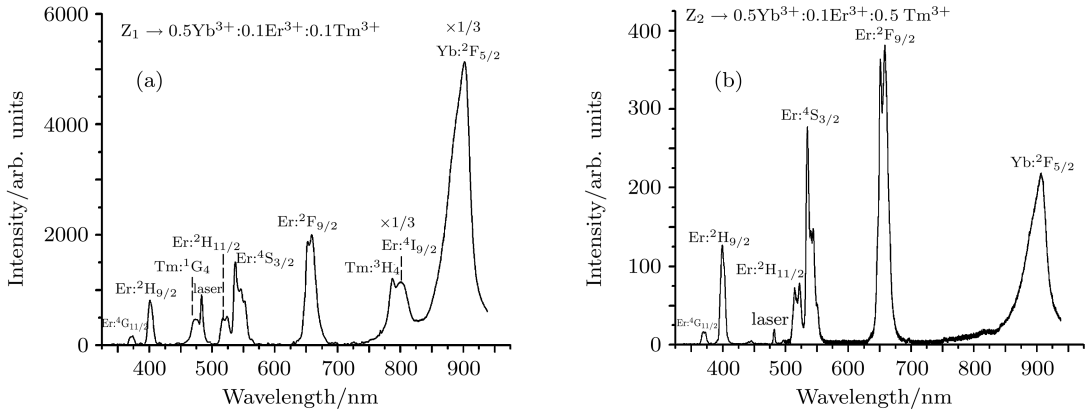



**Fig. 1.** Photoluminescence spectra of $Z_1$:0.5at.%$Yb^{3+}$-0.1at.%$Er^{3+}$-0.1at.%$Tm^{3+}$ (a), and $Z_2$:0.5at.%$Yb^{3+}$-0.1at.%$Er^{3+}$-0.5at.%$Tm^{3+}$ (b) co-doped borosilicate glasses under 978-nm laser diode excitation.

The logarithmic dependences of peak intensities of up-conversion emissions for sample $Z_1$ as a function of pump power are given in Fig. 2 for ultra-violet up-conversion emissions, in Fig. 3 for green and red up-conversion emissions, and in Fig. 4 for 474-, 788- and 900-nm up-conversion emissions. The slope of the curve represents the number of photons required to populate one ion into up-conversion emission states.[15] From Fig. 2 we can know that the slopes are both approximately 3.28 for the ultra-violet up-conversion emissions centred at about 399 and 376 nm, indicating that a three-photon process is involved in the up-conversion emission mechanism for the $Yb^{3+}:Er^{3+}:Tm^{3+}$ co-doped borosilicate glass. Analogously, the slopes are 2.00 and 1.95 for the green and the red up-conversion emissions centred at about 537 and 659 nm, shown in Fig. 3, meaning that a two-photon process is involved.

Figure 4 shows logarithmic curves for power spectra of up-conversion emissions at 900, 788 and 474 nm. Their slopes are 1.19, 1.90 and 2.54, corresponding to one-, two- and two-/three-photon processes respectively. It can also be seen that there is a best pump power for the three curves, in other words, photoluminescence intensities decrease with the increase of pump power when the power exceeds 324 mW. The reason for the "power quenching" will be discussed in the following part.

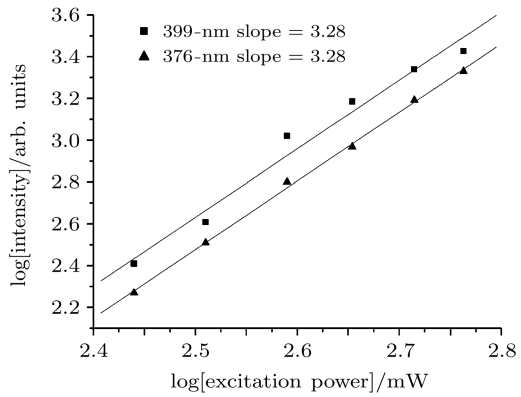



**Fig. 2.** Logarithmic dependence of peak intensity of the ultra-violet up-conversion emissions as a function of the pump power.

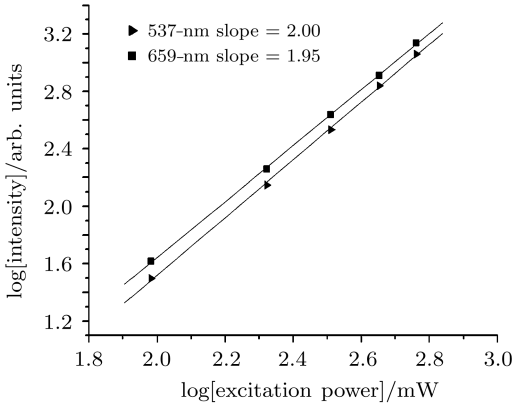



**Fig. 3.** Logarithmic dependence of peak intensity of the green and red up-conversion emissions as a function of the pump power.

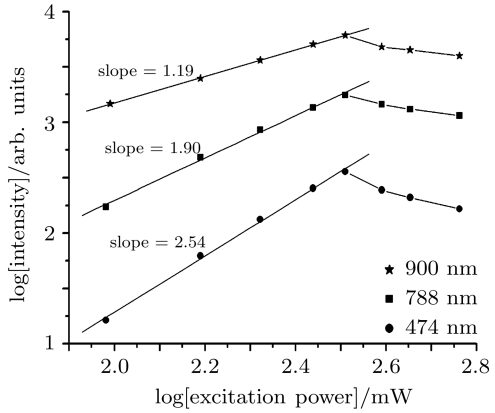



**Fig. 4.** Logarithmic curves of power spectra for 474-, 788- and 900-nm up-conversion emissions.

The strong 900-nm emission spectra can be seen in Fig. 1 for different samples of $Yb^{3+}$:$Er^{3+}$:$Tm^{3+}$ co-doped borosilicate glasses and their emissions are of the one-photon process. The spectrum can also be found from the $Yb^{3+}$:$Er^{3+}$ co-doped borosilicate glasses, but it cannot be found from $Er^{3+}$ single-doped borosilicate glasses, implying that the spectrum at 900 nm comes from the emission of $Yb^{3+}$ ions. As shown in the inset of Fig. 5, $Yb^{3+}$ ions at the ground state $^2F_{7/2}$ are pumped to the lowest Stark energy level 1 of the excitation state $^2F_{5/2}$ by 978-nm laser excitation, and jump into the highest Stark energy level 3 of $^2F_{5/2}$ by recurring to phonons, then radiate a near-infrared spectrum at 900 nm once they transfer to the lowest Stark energy level 1 of the ground state $^2F_{7/2}$. It can be known from Fig. 5 that the spectral intensity at about 900 nm becomes stronger with the increase of temperature because the energy of phonons is enhanced gradually, which conduces to the jump of $Yb^{3+}$ ions into the highest Stark energy level 3 of $^2F_{5/2}$. At the same time, the peak wavelength of spectra shifts towards the shortwave direction as the temperature goes up. The reason is that the electron-vibration energy for $Yb^{3+}$ ions is enhanced at high temperatures, the splitting of the energy level broadens and the highest Stark energy level 3 of $^2F_{5/2}$ shifts towards higher energies, leading to the shift of the spectrum peak.

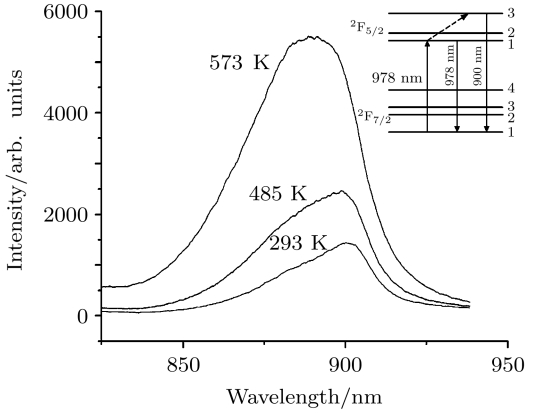



**Fig. 5.** Photoluminescence spectra of the $Yb^{3+}$ ion emissions at 900 nm for different temperatures.

## 3.2. Up-conversion mechanisms

Figure 6 is a schematic diagram of the energy levels and transitions of $Yb^{3+}$:$Er^{3+}$:$Tm^{3+}$ co-doped borosilicate glasses pumped outside by a 978-nm semiconductor laser. The pump wavelengths for $Er^{3+}$ and $Tm^{3+}$ ions, as a matter of fact, are different. That is to say, the energy transfer from $Yb^{3+}$ to $Er^{3+}$ is due mainly to the 978-nm excitation and that from $Yb^{3+}$ to $Tm^{3+}$, however, is owing to 900-nm excitation.

(i) The blue up-conversion emission at 474 nm is ascribed to the transition of $Tm^{3+}$ ions from $^1G_4$ to $^3H_6$. Populations at the $^1G_4$ level are assembled mainly through the energy transfer (ET) ET 1∼ET 4 between $Yb^{3+}$ and $Tm^{3+}$, that is

ET 1: $^3H_6(Tm^{3+})+^2F_{5/2}(Yb^{3+}) \rightarrow ^3H_5(Tm^{3+})+^2F_{7/2}(Yb^{3+})$, then $Tm^{3+}$ ions at $^3H_5$ relax to $^3F_4$,

ET 2: $^3F_4(Tm^{3+})+^2F_{5/2}(Yb^{3+}) \rightarrow ^3F_{2,3}(Tm^{3+})+^2F_{7/2}(Yb^{3+})$, then $Tm^{3+}$ ions at $^3F_{2,3}$ relax to $^3H_4$,

ET 3: $^3H_4(Tm^{3+})+^2F_{5/2}(Yb^{3+}) \rightarrow ^1G_4\ (Tm^{3+})+^2F_{7/2}(Yb^{3+})$. (1)

This is a three-photon process and $Yb^{3+}$ ions act as a sensitizer in it.

ET 4: $^3H_6(Tm^{3+})+2^*\ ^2F_{5/2}(Yb^{3+}) \rightarrow ^1G_4(Tm^{3+})+2^*\ ^2F_{7/2}(Yb^{3+})$. (2)

This is a two-photon process.

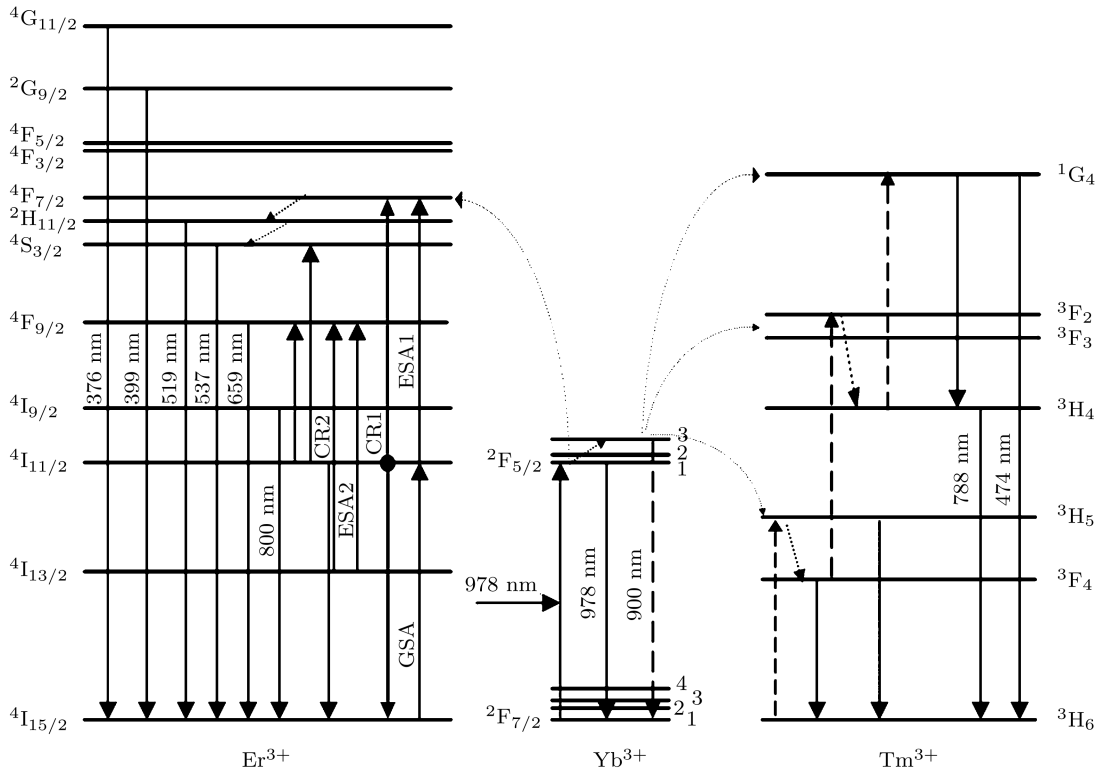



**Fig. 6.** Energy level diagram of $Yb^{3+}$:$Er^{3+}$:$Tm^{3+}$ co-doped borosilicate glass excited by a 978-nm laser beam.

Colligating processes (1) and (2) leads the slope of the power spectrum for 474-nm luminescence in Fig. 3 to be 2.54.

(ii) The up-conversion luminescence of 788 nm comes from the $Tm^{3+}$:$^3H_4 \rightarrow ^3H_6$ transition. Particles are excited to the $^3H_4$ energy level in the following ways: $Tm^{3+}$ ions at the ground state transfer to $^1G_4$ by the energy resonance transition ET4, then relax to $^3H_4$; at the same time, ET2 and ET3 also play an important role.

(iii) The two green up-conversion emission bands at about 519 and 537 nm correspond to the $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions of $Er^{3+}$ ions, respectively. The populations of $Er^{3+}$ at both levels are assembled mainly through energy transfer, ground state absorption (GSA), excited state absorption (ESA) and cross-relaxation (CR) processes. They are

GSA: $^4I_{15/2}(Er^{3+})+h\nu \rightarrow ^4I_{11/2}(Er^{3+})$,

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

and

ESA 1: $^4I_{11/2}(Er^{3+})+h\nu \rightarrow ^4F_{7/2}(Er^{3+})$,

ET 6: $^2F_{5/2}(Yb^{3+})+^4I_{11/2}(Er^{3+}) \rightarrow ^2F_{7/2}(Yb^{3+})+^4F_{7/2}(Er^{3+})$,

CR 1: $^4I_{11/2}(Er^{3+})+^4I_{11/2}(Er^{3+}) \rightarrow ^4I_{15/2}(Er^{3+})+^4F_{7/2}(Er^{3+})$, (4)

then, $Er^{3+}$ ions at $^4F_{7/2}$ relax to $^2H_{11/2}$ and $^4S_{3/2}$.[16]

ET 7: $^1G_4(Tm^{3+})+^4I_{11/2}(Er^{3+}) \rightarrow ^3H_4(Tm^{3+})+^4S_{3/2}(Er^{3+})$,

ET 8: $^3H_5(Tm^{3+})+^4I_{11/2}(Er^{3+}) \rightarrow ^3H_6(Tm^{3+})+^4S_{3/2}(Er^{3+})$. (5)

(iv) The red luminescence at 659 nm comes from the emission of $Er^{3+}$ ions at $^4F_{9/2}$ level. The up-conversion processes are as follows: first, $Er^{3+}$ ions at the ground state transfer to $^4I_{11/2}$ by GSA and ET5; subsequently, they relax to $^4I_{13/2}$. Then

ESA 2: $^4I_{13/2}(Er^{3+})+h\nu \rightarrow ^4F_{9/2}(Er^{3+})$,

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

CR 2 : $^4I_{11/2}(Er^{3+})+^4I_{13/2}(Er^{3+}) \rightarrow ^4I_{15/2}(Er^{3+})+^4F_{9/2}(Er^{3+})$; (6)

ET 10: $^3H_5(Tm^{3+})+^4I_{13/2}(Er^{3+}) \rightarrow ^3H_6(Tm^{3+})+^4F_{9/2}(Er^{3+})$,

ET 11: $^1G_4(Tm^{3+})+^4I_{13/2}(Er^{3+}) \rightarrow ^3H_4(Tm^{3+})+^4F_{9/2}(Er^{3+})$,

ET 12: $^3F_4(Tm^{3+})+^4I_{11/2}(Er^{3+}) \rightarrow ^3H_6(Tm^{3+})+^4F_{9/2}(Er^{3+})$, (7)

meanwhile, $Er^{3+}$ ions at $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$ also relax to $^4F_{9/2}$.

The green and the red up-conversion luminescences of 537 and 659 nm are two-photon processes as shown in Fig. 3; $Yb^{3+}$ and $Tm^{3+}$ ions act as a sensitizer synchronously.

(v) The ultra-violet up-conversion emission at about 376 nm corresponds to the $^4G_{11/2} \rightarrow {}^4I_{15/2}$ transitions of $Er^{3+}$ ions. The whole up-conversion processes are as follows: $Er^{3+}$ ions are first transferred from the ground state to $^4I_{11/2}$ by GSA and ET 5, subsequently to $^4F_{7/2}$ through ESA 1, ET 6 and CR 1, then through

CR 3: $^4I_{13/2}(Er^{3+})+{}^4F_{7/2}(Er^{3+}) \rightarrow {}^4I_{15/2}(Er^{3+})+{}^4G_{11/2}(Er^{3+})$,

CR 4: $^4I_{9/2}(Er^{3+})+{}^4F_{7/2}(Er^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+})+{}^4G_{11/2}(Er^{3+})$; (8)

ET 13: $^1G_4(Tm^{3+})+{}^4F_{7/2}(Er^{3+}) \rightarrow {}^3F_2(Tm^{3+})+{}^4G_{11/2}(Er^{3+})$,

ET 14: $^3F_4(Tm^{3+})+{}^4F_{7/2}(Er^{3+}) \rightarrow {}^3H_6(Tm^{3+})+{}^4G_{11/2}(Er^{3+})$, (9)

they are excited to $^4G_{11/2}$ level.

As for the violet emission at 399 nm emitted from $^2G_{9/2}$ of $Er^{3+}$, the up-conversion processes from $^4F_{7/2}$ are as follows:

CR 5: $^4I_{11/2}(Er^{3+})+{}^4F_{7/2}(Er^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+})+{}^2G_{9/2}(Er^{3+})$,

CR 6: $^4F_{9/2}(Er^{3+})+{}^4F_{7/2}(Er^{3+}) \rightarrow {}^4I_{11/2}(Er^{3+})+{}^2G_{9/2}(Er^{3+})$; (10)

ET 15: $^3H_4(Tm^{3+})+{}^4F_{7/2}(Er^{3+}) \rightarrow {}^3H_5(Tm^{3+})+{}^2G_{9/2}(Er^{3+})$. (11)

Two violet up-conversion emissions are three-photon processes, and $Yb^{3+}$ and $Tm^{3+}$ ions act as sensitizers in the processes.

### 3.3. Discussion

The up-conversion emissions of $Tm^{3+}$ ions at 474 and 788 nm mainly originate from the energy transfer from $Yb^{3+}$ to $Tm^{3+}$, or in other words, they depend on pumping by the 900-nm transition of $Yb^{3+}$ ions. This can be ensured by the power spectra of the three wavelength bands because of taking on the same trend, which is shown in Fig. 3. When the pump power exceeds 324 mW, the population at the lowest energy level 1 in the excitation state $^2F_{5/2}$ of $Yb^{3+}$ ions increases and the efficiency of the energy transfer from $Yb^{3+}$ to $Er^{3+}$ is effectively enhanced through ET 5, ET 6 and ET 9 processes. As a result, the population at the highest energy level 3 in the excitation state $^2F_{5/2}$ of $Yb^{3+}$ ions decreases accordingly, which weakens the luminescence intensities of not only 900 nm, but also 474 and 788 nm. Therefore, the so-called "power quenching" phenomenon happens.

Comparing the photoluminescence spectra of the samples $Z_1$ and $Z_2$, it can be seen that the up-conversion processes of energy transfer from $Tm^{3+}$ to $Er^{3+}$, such as ET 7, ET 8 and ET 10∼ET 15, are improved remarkably when the $Tm^{3+}$ concentration increases. So, the emissions of $Er^{3+}$ ions, for instance, the green intensities at 519, 537 nm and red 659 nm, become stronger. The emissions of $Tm^{3+}$ itself, however, become obviously weaker, and even disappear for blue up-conversion emission at 474 nm. We can conclude that the concentration of $Tm^{3+}$ ions plays a dominant role in determining the characteristics of up-conversion spectra for Yb:Er:Tm co-doped borosilicate glasses.

## 4. Conclusions

$Yb^{3+}$:$Er^{3+}$:$Tm^{3+}$ co-doped borosilicate glasses are prepared by high-temperature melting, and their photoluminescence characteristics are investigated. Strong up-conversion emissions at 376, 399, 474, 519, 537, 659, 788, 800, 900 nm are obtained under 978-nm laser diode excitation for 0.5at.%$Yb^{3+}$:0.1at.%$Er^{3+}$:0.1at.%$Tm^{3+}$ co-doped borosilicate glass. The energy transfer (ET), the cross-relaxation (CR) and the excited state absorption (ESA) are dominant mechanisms for up-conversion luminescence. The excitation of $Tm^{3+}$ ions mainly originates from the emission of $Yb^{3+}$ at 900 nm because of Stark splitting. Therefore, the power spectra of $Tm^{3+}$ ions at 474 and 788 nm are similar to the spectrum at 900 nm of $Yb^{3+}$, and a "power quenching" phenomenon takes place synchronously once the pump power exceeds 324 mW, due to the fact that the efficiency of the energy transfer from the lowest energy level 1 in the excitation state $^2F_{5/2}$ of $Yb^{3+}$ to $Er^{3+}$ is effectively enhanced, leading to the decrease of population at the lowest energy level 3 at $^2F_{5/2}$ of $Yb^{3+}$ for 900 nm emission. However, 978 nm is an effective pump wavelength for $Er^{3+}$ ions, and $Yb^{3+}$ and $Tm^{3+}$ ions are both sensitizers. When the thulium concentration increases, the photoluminescence intensities at 519, 537 and 659 nm emitted from $Er^{3+}$ become stronger, but up-conversion emissions at 788 and 474 nm emitting from $Tm^{3+}$ become much weaker because of the enhancement of the energy transfer from $Tm^{3+}$ to $Er^{3+}$.

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