研 究

Dependence of Er^{3+} Emission Intensity on Dopant Concentrations for Yb^{3+} and Er^{3+} Codoped Fluoride Glass

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We have investigated the relationship between erbium emission intensity and dopant concentrations for Yb/Er codoped fluoride glasses pumped with various excited wavelengths. (1) When pumped with a 0.98 μm laser diode (LD), a maximum is found for a 0.55 μm upconversion emission intensity at a high Yb to Er concentration ratio. (2) When pumped with a 0.8 μm LD, a maximum is found for a 0.55 μm upconversion emission intensity at a low Yb to Er concentration ratio. (3) When pumped with a xenon lamp, two maxima are found for a 1.55 μm emission intensity. The emission mechanism is discussed for each case.

1. Introduction

The applications of erbium ion have been well known for visible lasers at 0.55 μm and 0.66 μm,[1] for laser knives at 2.9 μm,[2] and eye safe lasers at 1.54 μm.[3] **Figure 1** shows the energy level diagram of Er^{3+} ions. A 0.55 μm emission is generated by the energy transition from $^4S_{3/2}$ to $^4I_{15/2}$, and a 0.66 μm emission by the transition from $^4F_{9/2}$ to $^4I_{15/2}$ with an upconversion process. A 2.9 μm emission is generated by the transition from $^4I_{11/2}$ to $^4I_{13/2}$ and a 1.54 μm emission by the transition from $^4I_{13/2}$ to $^4I_{15/2}$.

There are some variations in the upconversion process, which depend on the excited wavelength.[4] When pumped with an 800 nm laser diode (LD), a 0.55 μm upconversion emission is generated by excitation state absorption (ESA) involving the energy level transition of $^4I_{15/2} \rightarrow {}^4I_{9/2} \rightarrow {}^4I_{3/2} \rightarrow (\mathrm{ESA}) \rightarrow {}^4S_{3/2} \rightarrow {}^4I_{15/2}$. When pumped with a 980 nm LD, the emission is generated by the process of energy transfer (ET) which involves the energy level transitions of $^4I_{15/2} \rightarrow {}^4I_{11/2} \rightarrow (\mathrm{ET}) \rightarrow {}^4SI_{13/2} \rightarrow {}^4I_{15/2}$.

The absorption cross sections of erbium ion are usually quite small. Therefore, the usage of a proper sensitizer, such as chromium,[5] neodymium,[6] or ytterbium,[7] is necessary for a more effective pumping. Cr^{3+} and Nd^{3+} ions are generally pumped with a xenon lamp and Yb^{3+} ions are pumped with LD. In a Yb^{3+}/Er^{3+} system, the dependence of an Er^{3+} emission intensity on the [Yb^{3+}]/[Er^{3+}] concentration ratio has never been reported with various pumping sources.

We have investigated the dependence of Er^{3+} emission intensities at 0.55 μm and 1.53 μm on the [Yb^{3+}]/[Er^{3+}] concentration ratio under different pumping sources, and investigated the fluorescence mechanism for ytterbium and erbium codoped glasses.

2. Experimental Procedures

We used aluminate-zirco fluoride (AZF) glass as a host glass for the 0.55 μm emission. AZF glass is a kind of aluminum fluoride glass, which has part of its composition being replaced by ZBLAN glass. This glass has the composition of AlF_3 25.1, ZrF_4 12.8, YF_3 11.1, MgF_2 3.7, CaF_2 15.4, SrF_2 13.6, BaF_2 12.6, NaF 6 cat% and 12 cat% for the total content of Yb^{3+} and Er^{3+}. The AZF glass was melted at 950℃ for 30 minutes in an argon atmosphere.

Fluorophosphate glass was used for the Er^{3+} 1.53 μm emission, in which AlF_3 glass was stabilized with $PO_{2.5}$. The fluorophosphate glass gave high emission intensity and the concentration quenching was not observed in our investigation. The glass composition is AlF_3 23, $PO_{2.5}$ 26, ($MgF_2+CaF_2+SrF_2+BaF_2$) 50 cat%. This glass was melted at 950℃ for 30 minutes in an argon

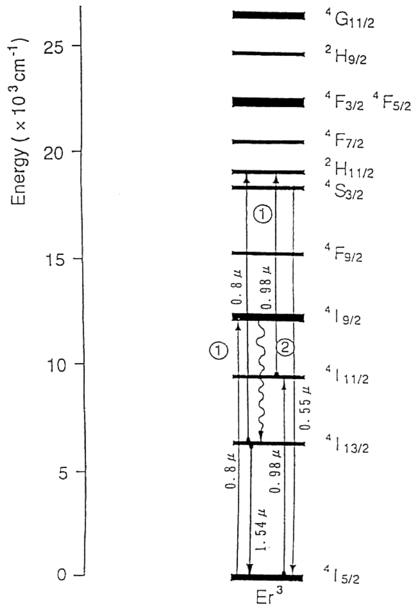

Fig. 1 Er^{3+} energy diagram and 0.55 μm upconversion emission mechanism by 0.98 μm and 0.8 μm pumping. ①0.8 μm pump : ESA, ②0.98 μm pump : ET.

atmosphere.

We used an 840 nm LD and a 980 nm LD as pumping sources for the 0.55 μm emission and a xenon lamp for the 1.53 μm emission. An R 2228 photomultiplier was used as a detector for the 0.55 μm emission and germanium for the 1.53 μm emission. We used an 800 nm dye laser pumped with an Nd : YAG 2 ω laser as a pumping source for the measurement of lifetime, and used an S-1 photomultiplier for detecting the 0.55 μm beam. InAs was used as a detector for the 1.53 μm beams.

When erbium doped glass is pumped with 0.98 μm LD, Er^{3+} ions are excited to the ^{4}I$_{11/2}$ energy level. If Yb^{3+} ions are introduced, the Yb^{3+} ions are excited to the ^{2}F$_{5/2}$ level. When pumped with 0.8 μm LD, Er^{3+} ions are excited to the ^{4}I$_{9/2}$ level in erbium doped glasses as well as ytterbium and erbium codoped glasses.

When pumped with an Xe lamp, Er^{3+} ions are excited to the higher energy levels from the ground state in erbium doped glasses. When ytterbium and erbium codoped glasses are pumped with an Xe lamp, Yb^{3+} ions are excited to ^{2}F$_{5/2}$ and Er^{3+} ions are excited to ^{4}I$_{9/2}$, ^{4}I$_{11/2}$, etc., because both the 980 nm and 800 nm radiations are available from the Xe lamp.

The absorption and emission wavelengths for fluoride and fluorophosphate glass are almost identical. Therefore, the mechanisms of energy transfer or upconversion should be very similar for both glasses. However, since the phonon energy of fluorophoshate glass (1800 cm^{-1}) is higher than fluoride glass (540 cm^{-1}), the energy transfer and upconversion efficiencies should be affected.

3. Results and Discussions

3.1 Enhancement of Er^{3+} 0.55 μm emission by Yb^{3+} ions

When the erbium doped glass was pumped with 980 nm LD, the emission intensity increased with erbium concentration as shown in **Fig. 2**. When Yb^{3+} ions were introduced, the Er^{3+} emission intensity increased drastically in the higher Yb^{3+}:Er^{3+} concentration ratio region, yet it decreased in the lower Yb^{3+}:Er^{3+} concentration ratio region. Fig. 2 shows the tendency that the maximum intensity occurred at 2 cat% of Er^{3+} and at 10 cat% of Yb^{3+}.

When Er^{3+} doped glass was pumped with 800 nm LD, the emission intensity increased with increasing Er^{3+} concentration and then decreased when the ionic concentration became very high as shown in **Fig. 3 a**. This is due to the concentration quenching effect. When Yb^{3+} ions were introduced, the Er^{3+} emission intensity was enhanced for those glasses of higher Er^{3+} concentration and reached a maximum at 8 cat%. It then decreased rapidly for those glasses of low Er^{3+} concentration. This phenomenon is quite different from that of the 980 nm LD.

Figure 3 b shows the Er^{3+} (^{4}I$_{11/2}$–^{4}I$_{13/2}$) 2.7 μm emission intensity versus the dopant concentration when pumped with 800 nm LD. The emission

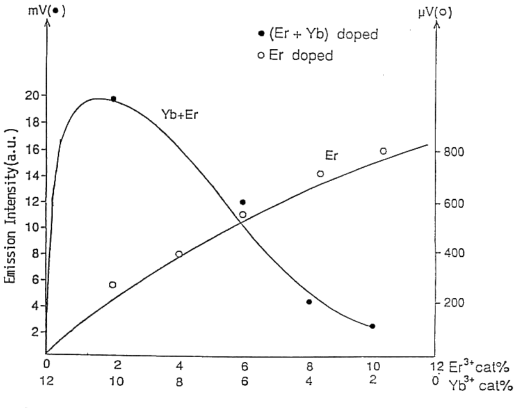

Fig. 2 0.55 μm upconversion emission intensity versus dopant concentration when pumped with 980 nm LD. Host glass : alumino-ziconium fluoride (AZF) glass. Pumping source : 980 nm LD.

intensities of erbium doped glasses increased with Er^{3+} concentration and showed a broad maximum in 8 to 10 cat% of Er^{3+} concentration. This is very similar to that of the 0.55 μm upconversion emission that is shown in Fig. 3 a. This means that both the 0.55 μm and 2.7 μm emission intensities were dominated by the Er^{3+} population at the energy level of $^4I_{11/2}$. This population increased initially with Er^{3+} concentration and then gradually decreased.

When ytterbium was introduced, the Er^{3+} 2.7 μm emission intensity decreased rapidly. This indicates that an energy transfer from Er^{3+} to Yb^{3+} occurred. As a result, the excited Er^{3+} ion population at $^4I_{11/2}$ decreased. Here the energy transfer occurred from $^4I_{9/2}$ to $^2F_{5/2}$ but not from $^4I_{11/2}$ to $^2F_{5/2}$. This is because, as shown in Fig. 2, the energy transfer which occurred between Yb^{3+} and Er^{3+} was from the Yb^{3+} $^2F_{5/2}$ to Er^{3+} $^4I_{11/2}$ transition for those glasses with higher Yb^{3+} concentration. The strong energy transfer from $^4I_{9/2}$ to $^2F_{5/2}$ caused the decrease of the excited Er^{3+} ion population at $^4I_{11/2}$, which was produced by thermal relaxation from $^4I_{9/2}$. Therefore, the enhancement of the Er^{3+} 0.55 μm emission intensity by Yb^{3+} ions when pumped with 980 nm and 800 nm LD are considered (**Fig. 4**).

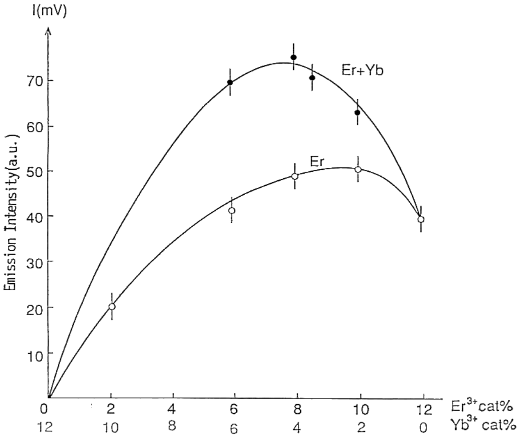

Fig. 3 a 0.55 μm ($^4S_{3/2}$–$^4I_{15/2}$) emission intensity of the AZF glasses pumped with 800 nm LD versus ErF_3 or YbF_3+ErF_3 concentrations. Pumping source : 100 mW 800 nm laser diode. ○ : AZF glasses doped with erbium. ● : AZF glasses doped with ytterbium and erbium.

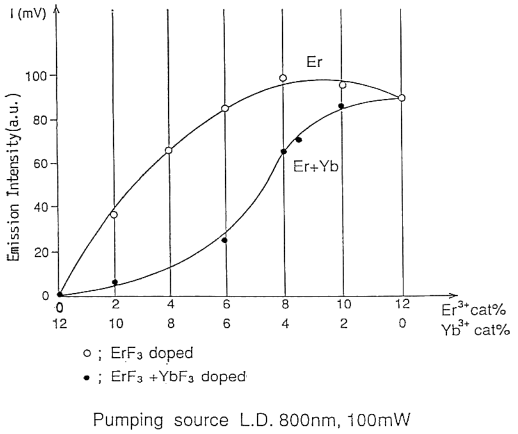

Fig. 3 b $^4I_{11/2}$–$^4I_{13/2}$ emission intensity of the AZF glasses with 800 nm LD versus ErF_3 or YbF_3+ErF_3 concentrations. Pumping source LD 800 nm, 100 mW. ○ : ErF_3 doped, ● : ErF_3+YbF_3 doped.

When pumped with 980 nm LD, the pumping radiation is absorbed by Er^{3+} ions to reach the $^4I_{11/2}$ level for those glasses of high erbium concentration. It is followed by an energy transfer from Er^{3+} $^4I_{11/2}$ to Yb^{3+} $^2F_{5/2}$. Consequently, Er^{3+} 0.55 μm emission decreases by the introduction of ytterbium. But for those glasses of high ytterbium concentration, the pumping radiation is absorbed by Yb^{3+} ions. The energy transfer from Yb^{3+} $^2F_{5/2}$ to Er^{3+} $^4I_{11/2}$ then occurs. As a result, erbium emission is enhanced. Further increase of ytterbium concentration decreases erbium concentration and the emission intensity decreases. Therefore, the maximum emission appears in the higher Yb^{3+} concentration.

When pumped with 800 nm LD, the pumping radiation is absorbed by Er^{3+} to reach the $^4I_{9/2}$ level. Energy transfer from Er^{3+} $^4I_{9/2}$ to Yb^{3+} $^2F_{5/2}$ then occurs. The Er^{3+} 0.55 μm emission is

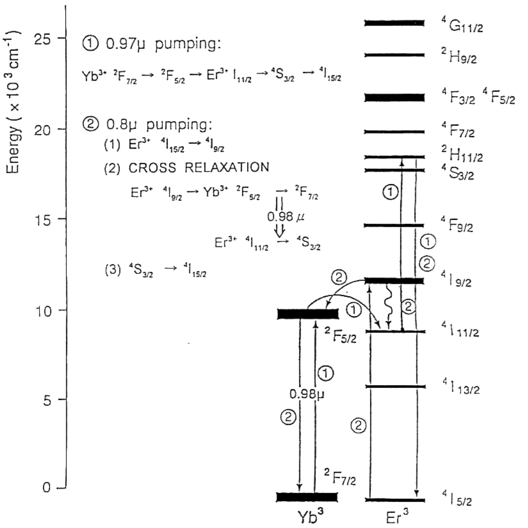

Fig. 4 Er^{3+} 0.55 μm upconversion emission mechanism by 980 nm and 800 nm pumping.

enhanced by the cross relaxation of $({}^2F_{5/2}\ {}^4I_{11/2})$ to $({}^4S_{3/2}\ {}^2F_{7/2})$. But the Er^{3+} ${}^4I_{11/2}$ population decreases with increasing Yb^{3+} concentration as shown in Fig. 3 b. Consequently, the enhancement of the Er^{3+} emission by Yb^{3+} ions decreases rapidly.

3.2 1.53 μm emission

Figure 5 shows the dependence of the Er^{3+} 1.53 μm emission intensity on Er^{3+} and $Yb^{3+}+Er^{3+}$ concentrations, where the total content of $Yb^{3+}+Er^{3+}$ was maintained at 4 cat% .The FCD 1 fluorophosphate glass was used as a host glass and a xenon lamp was used as the pumping source.

When FCD 1 glass was doped with erbium only, the Er^{3+} 1.53 μm emission intensity showed a maximum caused by the increasing excited erbium ion population and the decreasing lifetime with the erbium concentration.[4] When ytterbium ions were introduced, two maxima appeared.

Figure 6 shows the variation of the lifetime of the Yb^{3+} ${}^2F_{5/2}$ with the YbF_3 or YbF_3+ErF_3 concentration. (A very small amount of neodymium ions, 0.3 cat%, were added for the excitation of Yb^{3+} ions.) The upper white circles in Fig. 6 shows the lifetime (τ_0) of Yb^{3+} for the ytterbium doped fluorophosphate glasses. The lower black circles in Fig. 6 shows the lifetime (τ) of Yb^{3+} for ytterbium and erbium codoped fluorophosphate glasses. Yb^{3+} lifetime τ decreases with Er^{3+} concentration which shows that there is an energy transfer from Yb^{3+} to Er^{3+}. We calculated the energy transfer efficiency (η) using the Reisfeld[3] formula of

$$\eta=1-\tau/\tau_0$$

where τ_0 is the Yb^{3+} lifetime in ytterbium doped glass and τ is the Yb^{3+} lifetime in ytterbium and erbium codoped glass. As shown in **Table 1**, the energy transfer efficiency increased with erbium concentration and reached 98.5%.

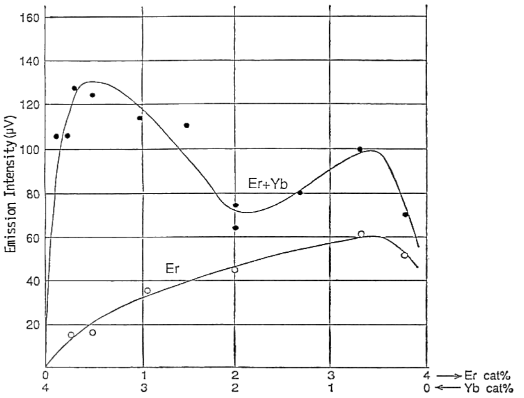

Fig. 5 1.53 μm emission intensity versus ErF_3 or ErF_3+YbF_3 concentrations. Matrix composition: FCD 1, pumping source: Xe lamp, ●: glass doped with $Er^{3+}+Yb^{3+}$, ○: glass doped with Er^{3+}.

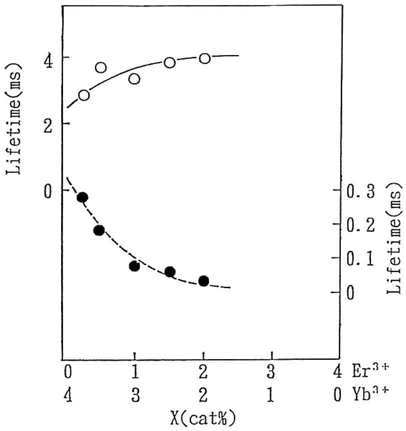

Fig. 6 Lifetime of Yb^{3+} ${}^2F_{5/2}$ in the fluorophosphate glass of FCD 1. ○: FCD 1 doped with Er^{3+}, ●: FCD 1 doped with $Er^{3+}+Yb^{3+}$.

Table 1 Energy transfer efficiency from Yb^{3+} ${}^2F_{5/2}$ to Er^{3+} ${}^4I_{11/2}$.

Yb^{3+} (cat%)	Er^{3+} (cat%)	η (%)
3.75	0.25	90
3.5	0.5	95
3	1	98
2.5	1 5	98
2	2	98.5

Figure 7 shows the variation of the lifetime of the Er^{3+} ${}^4I_{13/2}$ with the Yb:Er concentration ratio. We calculated the energy back transfer coefficiency from Er^{3+} to Yb^{3+}. The results are shown in **Table 2**.

Figure 7 and Table 2 show that the back transfer efficiency is about zero when Er^{3+} is less than 1 cat%. It increases rapidly and reaches 77% at 2 cat% of Er^{3+} ions. The existence of the first peak of erbium emission intensity in Fig. 5 can be interpreted as due to the high energy transfer efficiency (98%) from Yb^{3+} to Er^{3+} and negligible back transfer efficiency at Yb^{3+} 3 cat% and Er^{3+} 1 cat%. When Er^{3+} is more than 1 cat%, the back transfer efficiency increases and reaches 77% at 2 cat% of the erbium ion, and the emission intensity shows a minimum. Further increase of erbium concentration causes a decrease of energy back transfer as shown in Fig. 7. Accordingly, the emission intensity increases with erbium ion concentration.

As shown in Fig. 6 and Fig. 7 there is an energy transfer of more than 90% from Yb^{3+} to Er^{3+} and that of 77% from Er^{3+} to Yb^{3+}. The variation

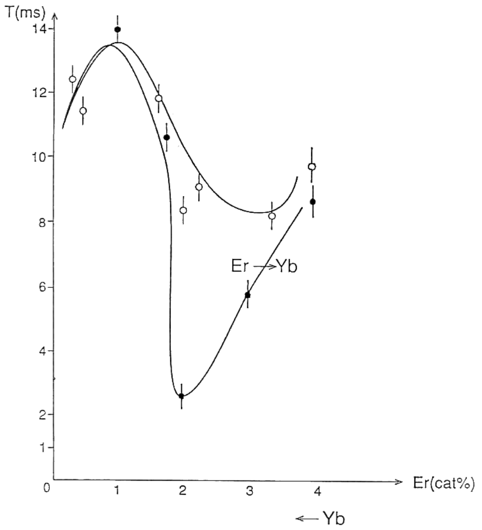

Fig. 7 Lifetime of Er^{3+} $^4I_{13/2}$ in the fluorophosphate glass of FCD 1. ○ : FCD 1 doped with Er^{3+}, ● : FCD 1 doped with $Er^{3+}+Yb^{3+}$.

Table 2 Energy transfer efficiency from Er^{3+} $^4I_{11/2}$ to Yb^{3+} $^2F_{5/2}$.

Yb^{3+} (cat%)	Er^{3+} (cat%)	η (%)
3.75	0.25	0
3.5	0.5	0
3	1	1
2.5	1.5	9
2	2	77

of these energy transfers at different $[Yb^{3+}]/[Er^{3+}]$ concentration ratios causes the maximum and minimum of the Er^{3+} emission intensity. This consequential result is observed in Fig. 5. The two maxima of the 1.53 μm emission observed by the xenon lamp pumping for various Yb/Er concentrations are corresponding to the maxima observed by the 980 nm pumping and 800 nm pumping respectively. The first peak observed in Fig. 5 corresponds to the peak of high ytterbium concentration with 980 nm LD pumping as shown in Fig. 2. The second peak in Fig. 5 corresponds to the peak of high erbium concentration with 800 nm pumping as shown in Fig. 3a. Both the 980 nm and 800 nm radiations are available from the xenon lamp.

4. Summaries

The effect of ytterbium ions on Er^{3+} 0.55 μm and 1.55 μm emission intensities has been investigated. The results are summarized as follows.

(1) The 0.55 μm upconversion emission intensity changed with the pumping wavelength. The maximum emission intensity was found at a higher Yb:Er concentration ratio composition when pumped with 980 nm LD, and it was found at a higher Er:Yb concentration ratio composition when pumped with 800 nm LD. In the former case, 980 nm pumping radiation was absorbed by ytterbium ions. Energy transfer then occured from Yb^{3+} to Er^{3+}, which caused the maximum. In the later case, 800 nm pumping radiation was absorbed by erbium ions. Erbium emission was enhanced through ytterbium ions.

(2) The two 1.53 μm emission maxima observed by the xenon lamp pumping can be synthesized from the peaks that were caused by the 980 nm LD pumping and 800 nm LD pumping respectively.

(3) The highest 1.53 μm emission intensity was observed at the Yb:Er concentration ratio of 3.5 : 0.5. This is because the energy transfer coefficiency from Yb^{3+} to Er^{3+} is very high (95%) and the back energy transfer coefficient is nearly zero at this composition.

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