研究

Optimization of Glass Composition for Er^{3+} 1.53 μm Emissions

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Energy transfer processes among Nd^{3+}, Yb^{3+} and Er^{3+} ions were investigated. The energy transfer efficiency was calculated from lifetime measurement and compared to the resulting emission intensity. The emission intensity originating from the $^4I_{13/2}$ level of Er^{3+} was mainly determined by the energy transfer efficiency from Yb^{3+} to Er^{3+} in Nb^{3+}, Yb^{3+} and Er^{3+} doped glasses. However, the fluorescence from the $^4I_{13/2}$ level of Er^{3+} was strongly dependent on the concentration ratio of Er^{3+} to Yb^{3+}. The highest emission intensity was obtained in phosphate glass with the optimum ratio of Er^{3+} to Yb^{3+}.

1. Introduction

Erbium (Er^{3+}) is an attractive element for flash lamp- and LD-pumped glass lasers, since it generates radiation of eye-safe wavelength of 1.53 μm.[1] The emission efficiency of an Er^{3+} laser is low since Er^{3+} has weak absorption bands in the visible range, and acts as a three-level system. Codoping with Yb^{3+} sensitizer ions is therefore necessary to obtain laser action at a room temperature.[1] Er^{3+} doped glass lasers sensitized by Nd^{3+} and Yb^{3+} ions or Cr^{3+} and Yb^{3+} ions have been well characterized experimentally, and practical systems have been demonstrated.[2-4]

The present paper is devoted to studying the efficiencies and processes of $Nd^{3+} \rightarrow Yb^{3+}$ and $Yb^{3+} \rightarrow Er^{3+}$ energy transfers in various glasses. Our goal is to discover what type of glass is the best for excitation energy transfer from Nd^{3+} to Yb^{3+} and then Yb^{3+} to Er^{3+} in various glasses.

2. Experimental Procedures

Compositions of base-glasses are listed in **Table 1.**

The aluminate (AL) glasses were melted in an induction furnace at 1500℃ for 1h in N_2 atmosphere. The fluorophosphate (FP) glasses were melted in a Pt crucible at 900℃ for 1 h in N_2 atmosphere. The silicate (SI), germanate (GE) and phosphate (P) glasses were melted in an electric furnace at 1380℃, 1300℃ and 1250℃ respectively for 2h using a Pt crucible.

The absorption measurement was performed with a computer-controlled HITACHI-330 spectrophotometer at a room temperature. The emission spectra were measured by exciting the samples with a SONY-diode laser operating at 800 nm and 980 nm or a Xe-lamp, and by monitoring the fluorescence with a Ge-detector or an R-2228 photomultiplier tube. The fluorescence lifetimes were measured by exciting the samples with a doubled YAG-laser pumped dye laser operating at 800 nm and detecting the fluorescence with an S-1 photomultiplier tube or an InAs-detector.

3. Experimental Results and Discussions

3.1 Spectroscopic characteristics of Nd^{3+}, Yb^{3+} and Er^{3+} doped glasses

For the sake of investigating the interaction of energy transfer among Nd^{3+}, Yb^{3+} and Er^{3+} ions, we should first understand the spectroscopic properties of singly doped active ions in the glasses. We measured the absorption and emission spectra and the fluorescence lifetimes for the singly doped Nd^{3+}, Yb^{3+} and Er^{3+} in the glasses, and then applied the Judd-Ofelt analysis to determine the radiative transition probabilities for Nd^{3+} and Er^{3+} transitions. Details of the theory and method had been well described earlier.[8-10] Hence, only the results will be presented here. The matrix elements $U^{(t)}$ calculated by Weber for Er^{3+} in LaF_3[11] and Carnall, Fields and Rajank for Nd^{3+} in LaF_3[12] were used in the present work. Only the radiative transition probabilities of Yb^{3+} in the glasses were calculated by using Fuchtbauer-Ladenburg equation.[13] The measured values of

Table 1 Compositions of glasses (in cat%).

Aluminate	48 $AlO_{1.5}$-36 CaO-8 MgO-8 BaO-x $ErO_{1.5}$ (x=0. 05-10)
Silicate	50 SiO_2-5 $AlO_{1.5}$-36 ($LiO_{0.5}$+$NaO_{0.5}$)-9 SrO-1 $ErO_{1.5}$
Germanate	57 GeO_2-26 $KO_{0.5}$-16 BaO-1 $ErO_{1.5}$
Phosphate	65. 2 $PO_{2.5}$-8. 6 $AlO_{1.5}$-7. 5 (BaO+MgO)-18. 7 $KO_{0.5}$-1 $ErO_{1.5}$
Fluorophosphate	10 $PO_{2.5}$-33 AlF_3-4 YF_3-48 (MgF_2+CaF_2+SrF_2+BaF_2)-5 NaF-1 $ErO_{1.5}$

0. 3 Nd^{3+}, 2 Yd^{3+} and 1 Er^{3+} were doped.

Table 2 Comparison of spectroscopic properties of Nd^{3+} $^4F_{3/2}$ level in various glasses.

	ν_p(cm^{-1})	N(10^{20} cm^3)	A_R(s^{-1})	τ_M(μs)	$\Delta\lambda$(nm)	σ(10^{-20} cm^2)
Aluminate	11274	0. 97	3452	292	41	2. 33
Germanate	11364	0. 76	1283	348	24	1. 46
Silicate	11377	1. 07	1807	248	23	2. 54
Phosphate	11455	0. 72	2846	255	22	4. 37
Fluorophosphate	11521	0. 71	871	552	24	1. 42

Table 3 Comparison of spectroscopic properties of Yb^{3+} $^2F_{5/2}$ level in various glasses.

	ν_p(cm^{-1})	N(10^{20} cm^3)	A_R(s^{-1})	τ_M(μs)	$\Delta\lambda$(nm)	σ(10^{-20} cm^2)
Aluminate	10225	6. 3	1309	1030	64	1. 07
Germanate	10267	5. 1	750	1190	64	0. 58
Silicate	10256	7. 1	689	1040	63	0. 56
Phosphate	10256	4. 9	913	532	66	0. 79
Fluorophosphate	10267	4. 7	617	2120	67	0. 64

Table 4 Comparison of spectroscopic properties of Er^{3+} $^4I_{13/2}$ level in various glasses.

	ν_p(cm^{-1})	N(10^{20} cm^3)	A_R(s^{-1})	τ_M(ms)	$\Delta\lambda$(nm)	σ(10^{-20} cm^2)
Aluminate	6506	3. 15	117	13. 1	33	0. 92
Germanate	6515	2. 53	95	7. 0	23	1. 09
Silicate	6510	3. 57	98	5. 5	28	1. 04
Phosphate	6532	2. 41	100	8. 1	25	1. 22
Fluorophosphate	6536	2. 35	139	12. 4	55	0. 88

the fluorescence lifetime (τ_M), the average frequency (ν_p) and the bandwidth of emission spectrum ($\Delta\lambda$), the calculated radiative transition probability (A_R) and emission cross section (σ) are shown in **Tables 2-4**.

Comparing the spectroscopic properties of various glasses tabulated in Tables 2-4, it is noticed that the aluminate and phosphate give high radiative transition probabilities and the lifetime decreases in order of FP, GE, AL, SI and P, which corresponds to the increase of phonon energy. For all the investigated samples, the radiative transition probability decreases in order of Nd^{3+}, Yb^{3+} and Er^{3+}, while the fluorescence lifetime increases in order of $^4F_{3/2}$ of Nd^{3+}, $^2F_{5/2}$ of Yb^{3+} and $^4I_{13/2}$ of Er^{3+}.

3.2 Excitation energy transfer between Nd^{3+} and Yb^{3+} ions in the glasses

Until now, as a criterion for the strong energy transfer, a spectral overlap of donor-fluorescence and acceptor-absorption has been usually considered.[5-7] In **Fig. 1**, we show the spectral overlap of Nd^{3+} emission for $^4F_{3/2}\rightarrow{}^4I_{3/2}$ transition and Yb^{3+} absorption for $^2F_{7/2}\rightarrow{}^2F_{5/2}$ transition in the aluminate and phosphate glasses. It can be seen that the spectral overlap in aluminate glass is much higher than in the phosphate glass, from which it is predictable that the efficiency of energy transfer from Nd^{3+} to Yb^{3+} in the aluminate glass will be higher than in the phosphate glass. **Figure 2** exhibits the emission spectra for 0. 3 Nd^{3+} and 2Yb^{3+} (cat%) doped glasses. When

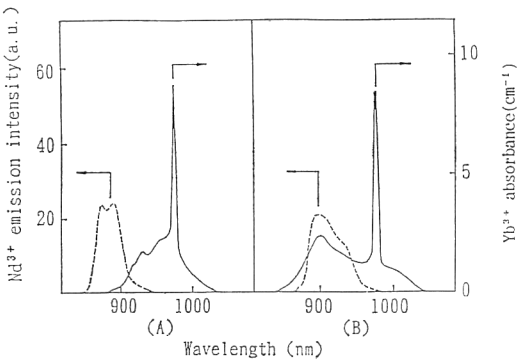

Fig. 1 Spectral overlap of Nd^{3+} emission ($^4F_{3/2} \rightarrow {}^4I_{9/2}$) and Yb^{3+} absorption ($^2F_{7/2} \rightarrow {}^2F_{5/2}$) in (A) phosphate glass and (B) aluminate glass.

the excitation was performed at the $^4F_{3/2}$ level of Nd^{3+}, the Nd^{3+} emission band nearly disappeared in the aluminate glass as a result of energy transfer from Nd^{3+} to Yb^{3+} ions, and the intensities of Nd^{3+} emission bands decreased in order of P, FP, GE, SI and AL. According to the calculation procedure proposed by Reisfeld and Kalisky,[14] where the efficiency of $Nd^{3+} \rightarrow Yb^{3+}$ energy transfer can be approximated by the relation $\eta = 1 - \tau_{Nd-Yb}/\tau_{Nd}$, the efficiencies of the $Nd^{3+} \rightarrow Yb^{3+}$ energy transfer were calculated and they decreased in order of AL, SI, GE, FP and P as shown in **Table 5.**

3.3 Excitation energy transfer between Yb^{3+} and Er^{3+} ions in the glasses

The Yb^{3+} ion has only one excited manifold

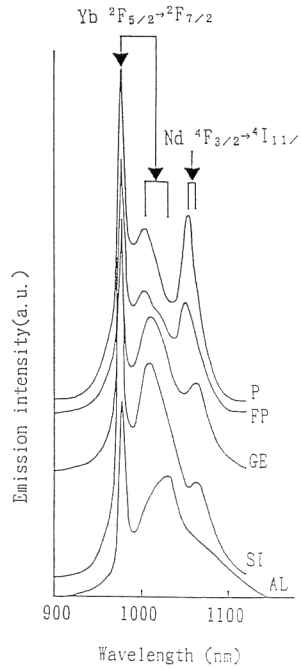

Fig. 2 Emission spectra for Nd^{3+} and Yb^{3+} codoped glasses excited at 800 nm. AL : aluminate, GE : germanate, P : phosphate, SI : silicate, FP : fluorophosphate.

($^2F_{5/2}$ level) located at approximately 10000 cm^{-1}. When the excitation was performed at the $^2F_{5/2}$ level of Yb^{3+} with a diode laser operating at 980 nm, the observed Yb^{3+} emission from $^2F_{5/2}$ just

Table 5 Lifetime of Nd^{3+} (1.06 μm) without and with Yb^{3+} doping in the glasses.

Glass	Nd^{3+}	lifetime (μs)	Nd^{3+}	Yb^{3+}	lifetime (μs)	η (%)
Aluminate	0.3	292	0.3	2	17.2	94
Silicate	0.3	248	0.3	2	40	83
Germanate	0.3	348	0.3	2	80	80
Fluorophosphate	0.3	552	0.3	2	149	73
Phosphate	0.3	252	0.3	2	69	72

Table 6 Emission intensity (I) for Yb^{3+} $^2F_{5/2} \rightarrow {}^2F_{7/2}$ and Er^{+3} $^4I_{13/2} \rightarrow I_{15/2}$ transitions in the glasses. (in cat%)

	Dopant	I(Yb)	Dopant	I(Er)	Dopant	I(Yb)	I(Er)
Aluminate	Yb : 2	265	Er : 1	22	Er : 1+Yb : 2	69	67
Fluorophosphate	Yb : 2	228	Er : 1	22	Er : 1+Yb : 2	37	74
Germanate	Yb : 2	148	Er : 1	11	Er : 1+Yb : 2	22	60
Silicate	Yb : 2	165	Er : 1	18	Er : 1+Yb : 2	9	72
Phosphate	Yb : 2	154	Er : 1	15	Er : 1+Yb : 2	8	55

overlapped the Er^{3+} absorption band for $^4I_{15/2}\rightarrow{}^4I_{11/2}$ transition, which indicates the energy transfer from Yb^{3+} to Er^{3+} ions in the glasses. However, the back energy transfer from Er^{3+} to Yb^{3+} might occur at the same time. In **Table 6**, we list the Yb^{3+} and Er^{3+} emission intensities for $^2F_{5/2}\rightarrow{}^2F_{7/2}(Yb^{3+})$ and $^4I_{13/2}\rightarrow{}^4I_{15/2}(Er^{3+})$ transitions. By codoping Yb^{3+} and Er^{3+} ions in the glasses, the Er^{3+} emission intensity increased and the corresponding Yb^{3+} emission intensity decreased strongly, when the excitation was performed into $^2F_{5/2}$ level of Yb^{3+} and $^4I_{11/2}$ level of Er^{3+} simultaneously. This means that the probability of energy transfer from Yb^{3+} to Er^{3+} was much higher than that of the back energy transfer from Er^{3+} to Yb^{3+}. Absorption of Yb^{3+} ions from $^2F_{7/2}$ to $^2F_{5/2}$ was much stronger than Er^{3+} $^4I_{15/2}\rightarrow{}^4I_{11/2}$ absorption as shown from the A_R coefficient in Tables 2 and 3, so that the excitation of the neighboring Er^{3+} ion :

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

might occur more easily than the excitation of the neighboring Yb^{3+} ion :

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

Adopting the calculation procedure proposed by Reisfeld and Kalisky[14] with the results of lifetime measurement, we evaluated the efficiency of $Yb^{3+}\rightarrow Er^{3+}$ energy transfer and found that the energy transfer efficiency increased in order of P, GE, AL, FP and SI as shown in **Table 7.**

Figure 3 shows the Er^{3+} emission intensity as a function of the efficiency of $Yb^{3+}\rightarrow Er^{3+}$ energy transfer for $2Yb^{3+}$, 1 Er^{3+} cat% codoped various glasses. It is evident that the Er^{3+} emission increased as the $Yb^{3+}\rightarrow Er^{3+}$ energy transfer efficiency became higher.

3.4 Energy transfer between Er^{3+} and Nd^{3+}

For Er^{3+} laser glass sensitized by Nd^{3+} and Yb^{3+}, the disadvantage of back-energy transfer from Er^{3+} to Nd^{3+} or the process,

$$Er^{3+} : {}^4I_{13/2}\rightarrow Nd^{3+} : {}^4I_{15/2}\rightarrow{}^4I_{9/2}$$

was well documented early.[2-4] We measured the emission intensity for the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition of Er^{3+}, and also evaluated the efficiency of energy transfer between Nd^{3+} and Er^{3+} ions on the basis of the lifetime measurement for Er^{3+} and Nd^{3+} doped various glasses pumped by a doubled YAG-laser pumped dye laser operating at 800 nm. The

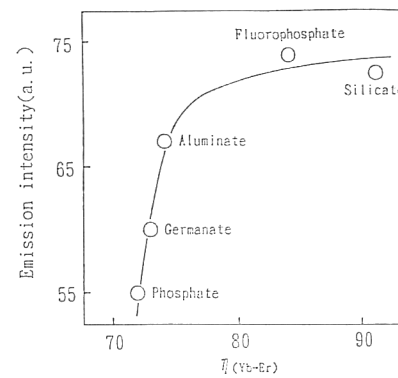

Fig. 3 Dependence of Er^{3+} emission intensity at 1.53 μm on energy transfer efficiency from Yb^{3+} to Er^{3+} in glasses excited by a diode laser at 980 nm.

Table 7 Lifetime of Yb^{3+} (1.03 μm) for Nd^{3+} and Er^{3+} codoped glasses.

Glass	Yb^{3+}	(+Nd^{3+})	lifetime (μm)	Yb^{3+}	Er^{3+}	lifetime (μm)	η (%)
Silicate	2	0.3	1040	2	1	91	91
Fluorophosphate	2	0.3	2120	2	1	338	84
Aluminate	2	0.3	1030	2	1	248	74
Germanate	2	0.3	1190	2	1	320	73
Phosphate	2	0.3	532	2	1	27	72

Table 8 Emission intensity I and the efficiency η of energy transfer between Nd^{3+} and Er^{3+} ions.

	Dopant	I(1.53 μm)	Dopant	I(1.53 μm)	η(Nd→Er)	η(Er→Nd)
Aluminate	Er : 1	83	Nd : 0.3+Er : 1	83	27%	88%
Fluorophosphate	Er : 1	49	Nd : 0.3+Er : 1	43	28%	82%
Germanate	Er : 1	32	Nd : 0.3+Er : 1	43	24%	66%
Silicate	Er : 1	50	Nd : 0.3+Er : 1	55	11%	72%
Phosphate	Er : 1	49	Nd : 0.3+Er : 1	33	34%	57%

results are tabulated in **Table 8.** From these results, it is evident that the probability of back-energy transfer from Er^{3+} to Nd^{3+} was much higher than that of energy transfer from Nd^{3+} to Er^{3+}, but the Er^{3+} emission intensity was almost unchanged in any case of doping with or without sensitizer of Nd^{3+} ions. Since the intensity of absorption for $^4I_{9/2}\rightarrow{}^4F_{5/2}$ transition of Nd^{3+} was much higher than that for $^4I_{15/2}\rightarrow{}^4I_{9/2}$ transition of Er^{3+} by introducing Nd^{3+} ions into Er^{3+} doped glasses, the lifetime of $^4I_{13/2}$ level of Er^{3+} decreased strongly but the emission intensity originating from $^4I_{13/2}$ level of Er^{3+} was almost unchanged as the excitation was performed at near 800 nm for the investigated glasses.

3.5 Er^{3+} emission intensity for Nd^{3+}, Yb^{3+} and Er^{3+} codoped glasses

Since introduction of Nd^{3+} ions into Er^{3+} doped glasses does not remarkably change the emission intensity originating from the $^4I_{13/2}$ level of Er^{3+} as mentioned above, the emission intensity of Er^{3+} doped glasses sensitized by Nd^{3+} and Yb^{3+} may be expected to increase due to the $Yb^{3+}\rightarrow Er^{3+}$ energy transfer. **Figure 4** shows that the emission intensity originating from the $^4I_{13/2}$ level of Er^{3+} increased with the efficiency of $Yb^{3+}\rightarrow Er^{3+}$ energy transfer, where the triply doped samples were excited by a Xe-lamp. The best host glass for an Er^{3+} laser is the silicate which has higher probability of energy transfer from Yb^{3+} to Er^{3+}.

However, it should be noted that the donor to acceptor ions ratio has a more important influence on the efficiency of energy transfer from donor to acceptor ions, and for the different glass hosts, the influence of donor and acceptor ion concentrations on the process of energy transfer is also different. **Figure 5** represents the dependence of the emission intensity from the $^4I_{13/2}$ level of Er^{3+} on the ratio of concentration of Er^{3+} to Yb^{3+} in various glasses containing $x$$Er^{3+}$ and $(8-x)$ Yb^{3+} cat%. From these plots, it can be found that there is an emission intensity peak at a certain Er^{3+}/Yb^{3+} ratio for each glass. The reason is as follows: at a lower ratio of Er^{3+} to Yb^{3+}, the increase of Er^{3+} content increases the energy transfer efficiency from Yb^{3+} to Er^{3+}. After it reaches the peak intensity, the further increase of Er^{3+} content causes energy back transfer from Er^{3+} to Yb^{3+}. In **Fig. 6**, we exhibit the dependence of emission intensity of the $^2F_{5/2}$ level of Yb^{3+} on concentration of Er^{3+} doped in the phosphate and aluminate glasses. When the excitation was performed into absorption bands of Er^{3+}, the

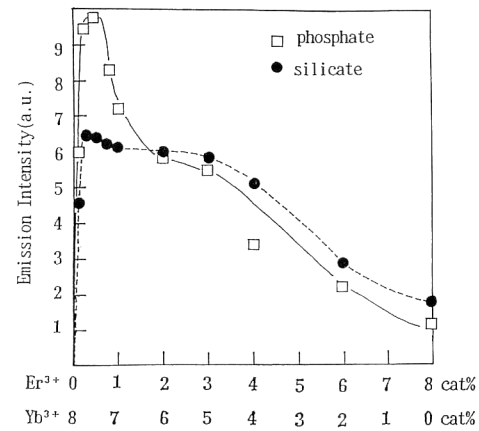

Fig. 5 Emission intensity of Yb^{3+} and Er^{3+} codoped silicate and phosphate glasses at 1.53 μm pumped by a Xe-lamp.

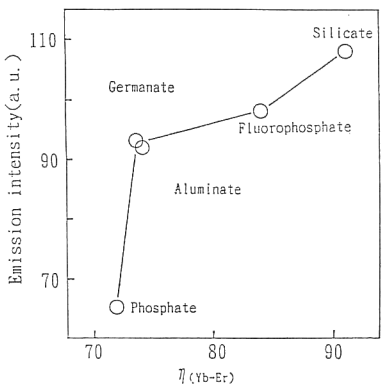

Fig. 4 Er^{3+} emission intensity at 1.53 μm versus energy transfer efficiency from Yb^{3+} to Er^{3+} for Nd^{3+}, Yb^{3+} and Er^{3+} codoped glasses.

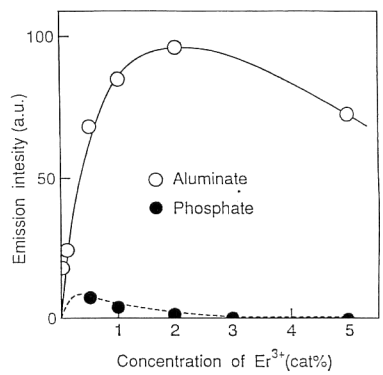

Fig. 6 Intensity of Yb^{3+} $^2F_{7/2}\rightarrow{}^2F_{5/2}$ emission versus concentration of Er^{3+} in aluminate and phosphate glasses.

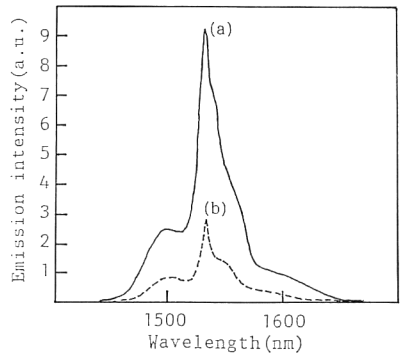

Fig 7 Emission spectrum of the glass (a) in comparison to LEG 30 (b) when pumped by a diode laser at 804 nm.

fluorescence from $^2F_{5/2}$ level of Yb^{3+} was very intense in the aluminate glass while nearly zero in the phosphate glass.

The fluorescent intensity originating from $^4I_{13/2}$ level of Er^{3+} in Nd^{3+}, Yb^{3+} and Er^{3+} codoped glasses was mainly controlled by the efficiency of energy transfer from Yb^{3+} to Er^{3+}. Energy transfer from Yb^{3+} to Er^{3+} ions can be enhanced with Er^{3+} content and back transfer from Er^{3+} to Yb^{3+} can be suppressed by reducing Er^{3+} content. Accordingly the $Yb^{3+} \rightarrow Er^{3+}$ energy transfer efficiency was influenced remarkably by the concentration ratio of Er^{3+} to Yb^{3+} ions.

Based on these experimental results, we selected the ratio Nd^{3+} : Yb^{3+} : Er^{3+} to be 0.5 : 7.5 : 0.5 at its optimum. **Figure 7** shows the Er^{3+} emission intensity at 1.53 μm of the glass with the optimized Nd^{3+} : Yb^{3+} : Er^{3+} ratio in comparison to the LEG 30 which is commercialized by HOYA. The new glass showed 3.6 times higher emission intensity than LEG 30 when pumped by 0.8 μm LD.

4. Conclusions

1. Er^{3+} emission intensity of Nd-Yb-Er doped glasses was very critical to Er^{3+} to Yb^{3+} ratio. The strongest intensity was given for the composition where energy transfer from Yb^{3+} to Er^{3+} occurred with efficiency over 90% and the back transfer was negligible.

2. Optimum content of Nd^{3+} is necessary for absorption of pumping energy.

3. We succeeded to make Nd-Yb-Er doped glass with 3.6 times higher Er^{3+} emission intensity in comparison to the LEG 30 commercialized by HOYA.

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