Spectroscopic and Dynamic Characteristics of Energy Transfer of $\text{Nd}^{3+} \rightarrow \text{Yb}^{3+}$ and $\text{Yb}^{3+} \rightarrow \text{Er}^{3+}$ in Aluminate Glasses

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アルミネートガラス中の $\text{Nd}^{3+} \rightarrow \text{Yb}^{3+}$ と $\text{Yb}^{3+} \rightarrow \text{Er}^{3+}$ のエネルギー伝達効率に関する分光学及び動力学特性

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The processes of excitation energy transfer among Nd^{3+} , Yb^{3+} and Er^{3+} ions in multicomponent aluminate glasses without any classical glass formers were investigated experimentally, using a conventional spectroscopy and a kinetic model which describes the interactions between active ions. The efficiency of $\text{Nd}^{3+} \rightarrow \text{Yb}^{3+}$ energy transfer is found to be so high as to nearly reach 100%. In Yb^{3+} and Er^{3+} codoped system, a mutual migration of energy occurs. The energy transfer from Yb^{3+} to Er^{3+} is considerably less efficient, owing to the influence of efficient back-energy transfer.

Key-words: Energy transfer efficiency, Aluminate glass, Erbium, Ytterbium, Neodymium, Ion-pair interaction

1. Introduction

Erbium glass lasers have been known since the early days of solid-state laser research. Laser action of trivalent erbium ions in silicate glasses was first discovered by Snitzer and Woodcock.¹⁾ The lasing wavelength of 1.54 μm raised strong interest for reasons of eye safety and easy detection. The disadvantage of only some weak absorption bands of Er^{3+} in the visible range led to the sensitization of fluorescence by codoping with Yb^{3+} and Nd^{3+} or Yb^{3+} and Cr^{3+} .²⁾⁻⁵⁾

The literatures concerning the classical glasses based on silicate, phosphate and fluorophosphate containing Nd^{3+} , Yb^{3+} and Er^{3+} or Cr^{3+} , Yb^{3+} and Er^{3+} ions are very rich. To our knowledge, no optical characteristics of Er^{3+} ions sensitized by Yb^{3+} and Nd^{3+} in aluminate glasses were reported in literature. Recently, we have found that the fluorescences originating from the $^4I_{13/2}$ level of Er^{3+} increased in the order of aluminate > phosphate > fluorophosphate > silicate > germanate glasses. It is expected that this result can lead one to the possibility of finding new fluorescent glass which may be suitable for laser of 1.54 μm , if we can achieve efficient sensitization of fluorescence of Er^{3+} in aluminate glasses by codoping Nd^{3+} and Yb^{3+} .

2. Theoretical background

For multipolar interactions, the transfer rate constant is proportional to an inverse power of the donor-acceptor separation, that is, $W(R) = C_{\text{DA}}R^{-S}$.⁶⁾ This covers the familiar cases of dipole-dipole ($S=6$), dipole-quadrupole ($S=8$), and quadrupole-quadrupole ($S=10$) coupling. An analysis of $\text{Nd}^{3+} \rightarrow \text{Yb}^{3+}$ energy transfer showed that the $\text{Nd}^{3+} - \text{Yb}^{3+}$ interaction is a dipole-dipole and the donor fluorescence decay curves are accurately described by the following equation:^{6),7)}

$$\Phi(t) = \Phi(0) \exp\left(-\frac{t}{\tau_0}\right) \times \exp[-(\alpha t^{-1/2} + W)t] \quad (1)$$

where $\Phi(0)$ is the normalized initial fluorescence intensity, τ_0 is the intrinsic lifetime of donor ions, t is the time after excitation, W is the rate of migrationally limited relaxation,

$$\alpha = \frac{4}{3} \pi^{3/2} N_A (C_{\text{DA}})^{1/2} \quad (2)$$

is direct donor-acceptor static interaction parameter, N_A is the concentration of acceptor ions, $C_{\text{DA}} = R^6/\tau_0$ is the constant that denotes the probability of the interaction of donor-acceptor ions at distance of 1 cm, and R is the critical transfer distance. Similarly, in the case the donor and acceptor is same, so Eq. (2) becomes $\alpha = 4/3 \pi^{3/2} N_D (C_{\text{DD}})^{1/2}$, where N_D is the concentration of active ions and C_{DD} is the donor-donor interaction parameter.

When donor-acceptor energy transfer is active, the luminescence decay does not exhibit a simple exponential dependence on time.⁶⁾ For multipolar interaction, the decay at earlier times ($Wt/\alpha t^{1/2} \ll 1$) is proportional to $1 - \alpha t^{1/2}$.⁶⁾ If the energy migration occurs, the acceptor surrounding of the donors becomes more uniform and the decay approaches the exponential time dependence.

3. Experimental procedures

The samples used in this study were prepared with highly pure materials to eliminate the contamination by impurities. Aluminate glasses were pre-

Table 1. The composition of base-glasses in cationic percent (cat%).

Glass	composition (cat%)
Aluminate	$48\text{AlO}_1, 5-36\text{CaO}-8\text{MgO}-8\text{BaO}-x\text{NdO}_1, 5-y\text{YbO}_1, 5-z\text{ErO}_1, 5$
Silicate	$50\text{SiO}_2-5\text{AlO}_1, 5-24\text{LiO}_0, 5-12\text{NaO}_0, 5-9\text{SrO}-x\text{NdO}_1, 5-y\text{YbO}_1, 5-z\text{ErO}_1, 5$
Phosphate (LHG-8)	$65\text{PO}_2, 5-9\text{AlO}_1, 5-8(\text{MgO}+\text{BaO})-18\text{KO}_0, 5-x\text{NdO}_1, 5-y\text{YbO}_1, 5-z\text{ErO}_1, 5$

pared by melting the batch materials in a platinum crucible at 1500°C for 2 h in N_2 atmosphere and pouring the melts into graphite molds and then annealed. For comparison, the silicate and phosphate glasses were also prepared by melting the batch materials in a platinum crucible at 1400° and 1250°C for 2 h, respectively. The batch compositions of glasses are listed in Table 1. Samples for the optical property measurements were fabricated to the size of $25 \times 25 \times 5$ mm of which four surfaces were optically polished.

The absorption measurements were performed with a computer controlled HITACHI-330 spectrophotometer. The emission spectra were obtained by exciting samples with a SONY-diode laser operating at 800 nm and 980 nm or a Xe-lamp, and monitoring the fluorescence with a Ge-detector or an R-2228 photomultiplier tube. The monochromator-detector combination was calibrated using a helium-neon laser of known spectral output. The emission lifetimes were measured by exciting the samples with a YAG laser pumped dye laser operating at 800 nm and detecting the emission with S-1 photomultiplier tube or InAs-detector. The emission decay curves were recorded and averaged with a computer controlled transient digitizer.

4. Results and discussions

4.1 The efficiency of $\text{Nd}^{3+} \rightarrow \text{Yb}^{3+}$ energy transfer

Room temperature absorption spectra of glass samples containing Nd^{3+} with concentrations range of 0.1 cat% to 2 cat% were obtained. No measurable effect of Nd^{3+} concentration on line strengths of obtained transitions have been found. Decay curves of fluorescence originating from the $^4F_{3/2}$ level of Nd^{3+} were obtained. In the case of samples containing lower concentrations of Nd^{3+} , the decay was exponential time dependence. At higher concentrations the decay became nonexponential time dependence and the corresponding lifetimes became shorter. Figure 1 presents the fluorescence intensity and the lifetime for the $^4F_{3/2} \rightarrow ^4I_{11/2}$ transition of Nd^{3+} versus concentration of Nd^{3+} ions. The dependences of fluorescence intensity and lifetime on concentration can be ascribed to the concentrational quenching effects.

We calculated the spontaneous emission probability and the total radiative lifetime for $^4F_{3/2}$ level of Nd^{3+} doped in the aluminate glass and the other several classical glasses for comparison, using Judd-

Fig. 1. Concentrational dependences of $\text{Nd}^{3+} (^4F_{3/2} \rightarrow ^4I_{11/2})$ emission intensity and lifetime in aluminate glass.**Table 2.** Comparison of laser spectroscopic properties of $\text{Nd}^{3+} \rightarrow ^4F_{3/2}$ level in various glasses doped with 1 cat% Nd^{3+} .

Glass	Average frequency (cm^{-1})	Total probability (s^{-1})	Radiative lifetime (μs)	Bandwidth of emission (nm)	Emission cross section (10^{-20}cm^2)
Aluminate	11274	3452	290	41	2.33
Phosphate (LHG-8)	11455	2846	351	22	4.37
Silicate	11377	1807	553	23	2.54

Ofelt theory. The calculated results are tabulated in Table 2. It can be seen that, from Table 2, the spontaneous emission probability for aluminate glass is much higher than in the classical glasses, and the bandwidth of emission spectrum for the $^4F_{3/2} \rightarrow ^4I_{11/2}$ transition of Nd^{3+} in aluminate glass is also broader than in the classical glasses. We also evaluated the $C_{\text{DD}}(\text{Nd-Nd})$ microparameter characterizing the self-quenching of neodymium fluorescence using the results of lifetime measurements and the obtained value of total radiative lifetime ($\tau_{\text{R}} = 290 \mu\text{s}$). The obtained value of $C_{\text{DD}}(\text{Nd-Nd}) = 5.54 \times 10^{-40} \text{cm}^6 \cdot \text{s}^{-1}$ is higher than $C_{\text{DD}}(\text{Nd-Nd}) = 1.6 \times 10^{-40} \text{cm}^6 \cdot \text{s}^{-1}$ for germanate glass,⁸⁾ $C_{\text{DD}}(\text{Nd-Nd}) = 0.3 \times 10^{-40} \text{cm}^6 \cdot \text{s}^{-1}$ for phosphate glass,⁸⁾ and $C_{\text{DD}}(\text{Nd-Nd}) = 5.5 \times 10^{-40} \text{cm}^6 \cdot \text{s}^{-1}$ for tellurite glass⁸⁾ but lower than $C_{\text{DD}}(\text{Nd-Nd}) = 16 \times 10^{-40} \text{cm}^6 \cdot \text{s}^{-1}$ for borate glass.⁹⁾ For the investigation of energy transfer from Nd^{3+} to Yb^{3+} , we used the samples doped with 0.5 cat% Nd^{3+} in order to reduce the self-quenching effects.

A criterion for strong electronic energy transfer is a good spectral overlap donor fluorescence and acceptor absorption. The spectral overlap integral of $\text{Nd}^{3+} (^4F_{3/2} \rightarrow ^4I_{9/2})$ fluorescence and the part of Yb^{3+} absorption is shown in Fig. 2. This good spectral overlap undoubtedly contributes to a better transferring energy from Nd^{3+} to Yb^{3+} . Figure 3 presents the decrease of static Nd^{3+} fluorescence with increasing concentration of Yb^{3+} . Even with small amounts of Yb^{3+} ions (0.5 cat%) the Nd^{3+} fluorescence intensity strongly decreases and nearly vanishes at Yb^{3+} concentration of 1 cat% as shown in Fig. 3. This behaviour means that the energy transfer from Nd^{3+} to

Fig. 2. Spectra overlap of Nd^{3+} emission and Yb^{3+} absorption in the aluminate glass.

Fig. 3. Emission spectra of Nd^{3+} and Yb^{3+} codoped aluminate glass (Yb^{3+} : 0.1, 0.5 and 1.0 cat%, and Nd^{3+} : 0.5 cat%).

Yb^{3+} is very efficient. According to the energy levels of Nd^{3+} and Yb^{3+} ions and the results presented in Fig. 2, the process of energy transfer from Nd^{3+} to Yb^{3+} is considered that, for direct excitation into the absorption bands of Nd^{3+} , the excitation energy can be populated in $^2F_{5/2}$ level of Yb^{3+} through the cross relaxation channel of β as shown in Fig. 4.

Figure 5 presents the plot of fluorescent intensities of Yb^{3+} versus concentration of Nd^{3+} ions for Nd^{3+} and Yb^{3+} codoped aluminate glasses excited by Xe-lamp. Comparing this plot with the results shown in Fig. 1, it can be found that the fluorescent intensity of Yb^{3+} is almost controlled by the population in emitting level of Nd^{3+} ($^4F_{3/2}$) via excitation, because the variation of Yb^{3+} fluorescence intensities is consistent with that of Nd^{3+} fluorescence intensities against concentration of Nd^{3+} ions. In other words, the higher the intensity of fluorescence from the $^4F_{3/2}$ level of Nd^{3+} for the Nd^{3+} singly doped glass, the higher is the intensity of fluorescence from the $^2F_{5/2}$ level of Yb^{3+} for the Nd^{3+} and Yb^{3+} doubly doped glass, in which there is a linear relationship between them as shown in Fig. 6.

Fig. 4. Energy-level scheme illustrating $\text{Nd}^{3+} \rightarrow \text{Yb}^{3+}$ energy transfer in the aluminate glass.

Fig. 5. Dependence of Yb^{3+} emission intensity on the concentration of Nd^{3+} ions in the aluminate glass containing 5 cat% Yb^{3+} ions.

Fig. 6. Yb^{3+} emission intensity of Nd^{3+} , Yb^{3+} doubly doped versus Nd^{3+} emission intensity of Nd^{3+} singly doped aluminate glass excited by Xe-lamp.

Fig. 7. Plots of Nd^{3+} and Yb^{3+} emission intensities versus concentration of Yb^{3+} ions in the aluminate glass containing 0.5 cat% Nd^{3+} ions.

Figure 7 shows the plots of fluorescent intensities of Yb^{3+} and Nd^{3+} versus concentration of Yb^{3+} . From these plots it is evident that the observed emissions from the $^4F_{3/2}$ level of Nd^{3+} strongly decrease and the observed emissions from the $^2F_{5/2}$ level of Yb^{3+} strongly increase, with increasing Yb^{3+} concentration. In addition, it is also found that, from Fig. 7, when the excitation is performed with Xe-lamp, the fluorescent intensities of Yb^{3+} measured at $1.03 \mu\text{m}$ for 0.5 cat% Nd^{3+} and 0.5–5 cat% Yb^{3+} ions doped glasses are much stronger than that of Nd^{3+} measured at $1.07 \mu\text{m}$ for the sample singly doped with 0.5 cat% Nd^{3+} . This is due to longer lifetimes of the $\text{Yb}^{3+}-^2F_{5/2}$ state compared with that of the $\text{Nd}^{3+}-^4F_{3/2}$ state, and the efficient energy transfer from Nd^{3+} to Yb^{3+} . For example, for 0.5 cat% Nd^{3+} and 0.5–5 cat% Yb^{3+} ions doped glasses the fluorescent lifetimes of $\text{Yb}^{3+}-^2F_{5/2}$ state were from $1080 \mu\text{s}$ to $620 \mu\text{s}$, and for 0.5 cat% Nd^{3+} ions doped glass the fluorescent lifetime of $\text{Nd}^{3+}-^4F_{3/2}$ state was equal to $292 \mu\text{s}$. The fluorescent lifetimes of $\text{Yb}^{3+}-^2F_{5/2}$ state in Nd^{3+} and Yb^{3+} codoped aluminate glass is approximately three times longer than that of Nd^{3+} doped aluminate glass, so that Nd^{3+} and Yb^{3+} codoped aluminate glass may store much higher energy per unit pump power and display stronger fluorescent intensity.

In Fig. 8 we present the influence of Yb^{3+} concentration on the measured lifetimes of $\text{Nd}^{3+}-^4F_{3/2}$ state and on the $\text{Nd}^{3+} \rightarrow \text{Yb}^{3+}$ energy transfer efficiencies (η). When the Yb^{3+} concentration is over 3 cat%, the efficiencies of energy transfer nearly reaches 100%. We also determined the C_{DA} parameter characterizing the $\text{Nd}^{3+} \rightarrow \text{Yb}^{3+}$ energy transfer through the analysis of fluorescence decay curves. The obtained value of $C_{\text{DA}} = 12.3 \times 10^{-39} \text{ cm}^6 \cdot \text{s}^{-1}$ is higher than $C_{\text{DA}} = 3.8 \times 10^{-39} \text{ cm}^6 \cdot \text{s}^{-1}$ reported for tellurite glass⁸⁾ and $C_{\text{DA}} = 6 \times 10^{-39} \text{ cm}^6 \cdot \text{s}^{-1}$ reported for borate glass.⁹⁾ However, for all acceptor concentrations we have also found the presence of back transfer from Yb^{3+} to Nd^{3+} . Figure 9 exhibits the influence of Nd^{3+} concentration on the fluorescent intensities of Yb^{3+} measured at $1.03 \mu\text{m}$. As the excitation is performed at the

Fig. 8. Variation of $\text{Nd}^{3+}-^4F_{3/2}$ lifetime and the $\text{Nd}^{3+} \rightarrow \text{Yb}^{3+}$ energy transfer efficiency with concentration of Yb^{3+} ions in codoped aluminate glass containing 0.5 cat% Nd^{3+} ions.

Fig. 9. Dependence of Yb^{3+} emission intensity on concentration of the Nd^{3+} ions in the aluminate glass containing 5 cat% Yb^{3+} ions.

Fig. 10. Emission spectra of 3.1 wt% Nd_2O_3 doped LHG-8 glass and 1.0 wt% Nd_2O_3 -8.8 wt% Yb_2O_3 codoped aluminate glass excited by Xe-lamp.

$^2F_{5/2}$ level of Yb^{3+} with diode laser operating at 980 nm, the observed emissions from $^2F_{5/2}$ level of Yb^{3+} decrease slightly with increasing Nd^{3+} concentration, which means the presence of back-energy transfer from Yb^{3+} to Nd^{3+} . Thus it can be seen that although the observed excitation energy transfer from Nd^{3+} to Yb^{3+} is considerably efficient, yet in order to reduce the influence of back-energy transfer from Yb^{3+} to Nd^{3+} on the process, the concentration of Nd^{3+} introduced into the glass should be limited as low as possible.

Figure 10 exhibits emission spectra in region of 900–1200 nm for commercial LHG-8 glass and the Nd^{3+} and Yb^{3+} codoped aluminate glass. The fluorescent intensity of 1Nd : 8.8Yb : aluminate glass (wt%) is approximately 1.25 times stronger than that of 3Nd : LHG-8 glass (wt%), and the bandwidth of emission spectrum of Yb^{3+} is approximately three times broader than that of Nd^{3+} .

4.2 The efficiency of energy transfer from Yb^{3+} to Er^{3+}

When the excitation is performed at the $^2F_{5/2}$ level of Yb^{3+} , the observed emission from $^2F_{5/2}$ level of Yb^{3+} overlaps the Er^{3+} absorption band for the $^4I_{15/2} \rightarrow ^4I_{11/2}$ transition, which is a just reason for transferring the excitation energy from Yb^{3+} to Er^{3+} in the

glass. However, it should be noted here that the Er^{3+} also has a weaker absorption band and corresponding emission band at 980 nm simultaneously as shown in Fig. 11. For this reason, the energy transfer can occur in both directions of $\text{Yb}^{3+} \rightarrow \text{Er}^{3+}$ and $\text{Er}^{3+} \rightarrow \text{Yb}^{3+}$. The energy level scheme for Yb^{3+} and Er^{3+} in aluminate glass, constructed on the basis of absorption measurements, is shown in Fig. 12. Ow-

Fig. 11. Spectral overlaps of absorption (—) and emission (—) of Yb^{3+} and emission (---) of Er^{3+} in the aluminate glass.

cences from the $^4\text{S}_{3/2}$ and $^4\text{I}_{11/2}$ levels decrease with increasing Yb^{3+} concentration, due to the cross relaxations from the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{13/2}$ and $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$ transitions of Er^{3+} to the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition, respectively. However, from Fig. 15 it can be found that introducing Yb^{3+} into the Er^{3+} doped system, the intensity of fluorescence originating from the $^4\text{I}_{13/2}$ level decreases but the fluorescent lifetime of the $^4\text{I}_{13/2}$ level is unchanged. These results indicated that the back-energy transfer from Er^{3+} to Yb^{3+} only occurs in the higher energy levels than the $^4\text{I}_{13/2}$ level of Er^{3+} , namely the excitation energy is transferred from the $^4\text{S}_{3/2}$ and $^4\text{I}_{11/2}$ levels but no from the $^4\text{I}_{13/2}$ level of Er^{3+} to the $^2\text{F}_{5/2}$ level of Yb^{3+} . The presence of back-energy transfer is considered to be due to the relatively low energy of Al-O vibrations which can reduce multiphonon relaxation rate from the $^4\text{I}_{11/2}$ level to the $^4\text{I}_{13/2}$ level of Er^{3+} , and comparatively enhancing the probability of cross relaxation from the $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$ transition of Er^{3+} to the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition of Yb^{3+} . In Table 3 we present the experimental lifetimes and the quantum efficiencies of $^4\text{I}_{11/2}$ level of Er^{3+} ions in aluminate, silicate and phosphate glasses. The lifetime and the quantum efficiency of the $^4\text{I}_{11/2}$ level in aluminate glass are much higher than those in the silicate and phosphate glasses. This shows that the multiphonon relaxation rate from the $^4\text{I}_{11/2}$ level in the aluminate glass is much lower than that in the silicate and phosphate glasses. The lower multiphonon relaxation rate from the $^4\text{I}_{11/2}$ level may be a serious obstacle in the population buildup on the $^4\text{I}_{13/2}$ level which plays the role of upper laser state in an Er^{3+} doped laser glass, but it may promote transferring energy from the $^4\text{I}_{11/2}$ level of Er^{3+} to the $^2\text{F}_{5/2}$ level of Yb^{3+} . For this reason, although the emission intensity of singly Er^{3+} doped aluminate glass is higher than that of singly Er^{3+} doped silicate and phosphate glasses, the Er^{3+} doped aluminate glass sensitized by Yb^{3+} and Nd^{3+} is not more efficient than the Nd^{3+} , Yb^{3+} and Er^{3+} codoped silicate and phosphate glasses for the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition of Er^{3+} .

Table 3. The observed lifetimes (τ) and quantum efficiencies (η) of the $^4\text{I}_{11/2}$ level of Er^{3+} in various glasses.

	Aluminate	Silicate	Phosphate
τ (μs)	160	14	~3
η (%)	2.3	0.13	~0.03
Er^{3+} (cat%)	1.0	1.0	1.0

5. Conclusions

Presented experimental results indicated that the high efficiency of energy transfer from Nd^{3+} to Yb^{3+} may result from the good spectral overlap of Nd^{3+} fluorescence and Yb^{3+} absorption. The electronic energy transfer efficiency approaches 100%. The fluorescent efficiency of Yb^{3+} doped aluminate glass sensitized by Nd^{3+} is higher than that of Nd^{3+} doped LHG-8 glass that is the famous Nd^{3+} laser glass.

In Yb^{3+} , Er^{3+} codoped aluminate glasses, the excitation energy is transferred in both directions of $\text{Yb}^{3+} \leftrightarrow \text{Er}^{3+}$. The back-energy transfer from Er^{3+} to Yb^{3+} depletes the populations of the excited $^4\text{S}_{3/2}$, $^4\text{I}_{11/2}$ and $^4\text{I}_{13/2}$ states. The Er^{3+} doped aluminate glass sensitized by Yb^{3+} and Nd^{3+} , consequently, is not a good candidate for 1.54 μm erbium laser glass.

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