Investigation of the interactions between dissimilar ions in (Er, Nd):Y₃Al₅O₁₂

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Unusual fluorescence decay properties of both Er^{3+} and Nd^{3+} ions in (Er, Nd):YAG are reported. Studies reveal that the cross-relaxation-type ion-ion interactions involving Er^{3+} and Nd^{3+} ions are responsible. A rate-equation analysis is used to evaluate the interaction strengths of all the proposed processes. The rate-equation calculation does not fully explain the nonexponential nature of the measured fluorescence decay function of the $^{4}F_{3/2}Nd^{3+}$ ions. As a result, the theory for donor-acceptor energy transfer processes, based on the inverse-power transfer rate model, is adopted to study the mechanism of the interactions between Er^{3+} and Nd^{3+} ions that result in the drastically altered fluorescence decay of Nd^{3+} ions. It is found that the mechanisms governing the energy transfer processes have functional forms different from those for the commonly encountered electric multipolar interactions. The interaction strengths are evaluated by least-squares fitting of the theory to the experimental data. Effects of the ion-ion interactions on lasing properties of the (Er, Nd):YAG are also discussed.

INTRODUCTION

Lasing at 2.94 μ m from highly doped Er:YAG provides an efficient and useful coherent light source. Because the lower level of this laser transition has a longer decay lifetime than the upper level, the laser action at 2.94 μ m is selfterminated. As a result of this bottleneck, the flash-lamppumped Er:YAG laser has been unable to lase in the cw mode, although quasi-cw lasing has been observed from this laser crystal.^{1,2} In an earlier paper,³ we reported our work on vttrium aluminum garnet doubly doped with 15 at. % Er^{3+} and 1 at. % Nd^{3+} ions. In this material, Nd^{3+} ions were added to the Er:YAG crystal in order to relax the $\mathrm{Er}^{3+} \, {}^4I_{13/2}$ state through energy transfer between Er³⁺ and Nd³⁺ ions, as Kaminskii et al. suggested in Ref. 4. This process can be effective because the $Er^{3+} {}^{4}I_{13/2}$ and $Nd^{3+} {}^{4}I_{15/2}$ states are almost isoenergetic in YAG.⁵ In the same paper we also described the large reductions in the $\mathrm{Er}^{3+} \, {}^{4}I_{13/2}$ and Nd^{3+} ${}^4F_{3/2}$ lifetimes and the simultaneous laser action of both ${
m Er}^{3+1}$ and Nd³⁺ ions. Here we describe in more detail the unusual fluorescence decay properties of (Er, Nd):YAG. A rateequation model has been proposed, including cross-relaxation processes between like and unlike ions, and a theory for the donor-acceptor energy transfer processes has been used to analyze the interaction mechanisms. Effects of these processes on fluorescence decay and lasing properties of the material are discussed.

OBSERVATION OF FLUORESCENCE DECAY PROPERTIES OF (Er, Nd):YAG

The fluorescence decay of the lasing levels is one of the most important characteristics of a laser material. To explore the fluorescence decay properties and to reveal the ion-ion interaction mechanisms in (Er, Nd):YAG, experiments were carefully conducted to observe the fluorescence decay from various energy states of both Er^{3+} and Nd^{3+} ions in this material. The sample used in the experiments was a YAG crystal doped with 15 at. % Er and 1 at. % Nd ions. The states from which fluorescence emission was monitored are the $Er^{3+4}I_{11/2}$, $Er^{3+4}I_{13/2}$, and $Nd^{3+4}F_{3/2}$ states. The fluorescence decay properties of the $Er^{3+4}I_{11/2}$ and $^{4}I_{13/2}$ states, between which the 2.94- μ m lasing emission occurred, were revealed through the ~1.007- μ m (${}^{4}I_{11/2} \rightarrow {}^{4}I_{15/2}$) and ~1.63- $\mu m ({}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2})$ transition lines, respectively. Those of the Nd³⁺ ${}^{4}F_{3/2}$ state were studied through the popular 1.06- μ m (${}^4F_{3/2} \rightarrow {}^4I_{11/2}$) line. In our experiments the sample was excited with a Q-switched, frequency-doubled Nd:YAG laser, and the fluorescence transition lines were isolated with a 0.27-m Jarrell-Ash single-grating monochromator. The fluorescence light from the monochromator was collected by a liquid nitrogen-cooled InSb IR detector. The output signals from the detector were stored and processed by a computer-controlled data acquisition system, which could average any preset number of signals for noise reduction. The experimental results obtained are shown in Figs. 1-3. The unusual fluorescence decay properties of the (Er, Nd):YAG crystal are compared with the decay curves of the same states in singly doped 16.6 at. % Er:YAG or 1 at. % Nd:YAG (Figs. 1-3). From Figs. 1-3, the following features were observed:

(1) For the $\text{Er}^{3+4}I_{11/2}$ state (Fig. 1): Fluorescence decay from the singly doped Er:YAG starts out to be linear in a semilog plot that corresponds to an exponential decay and then gradually curves up, which is indicative of a decrease in decay rate. The initial 1/e decay time is 106 μ sec, which corresponds to the measured decay lifetime of the $\text{Er}^{3+4}I_{11/2}$ state in 1 at. % Er:YAG. This nonexponential decay has been demonstrated^{6,7} to be a result of cross-relaxation processes in Er:YAG. It has also been shown^{6,7} that simple exponential fluorescence decay of the $\text{Er}^{3+4}I_{11/2}$ and $^{4}I_{13/2}$ states in Er:YAG could be obtained at low excitation levels when the cross-relaxation processes were not effective. Us-



Fig. 1. Experimentally observed decay curves from $\text{Er}^{3+4}I_{11/2}$ in (a) 16.6% Er:YAG, (b) (15% Er, 1% Nd):YAG.



Fig. 2. Experimentally observed decay curves from $\text{Er}^{3+4}I_{13/2}$ in (a) 16.6% Er:YAG, (b) (15% Er, 1% Nd):YAG.



Fig. 3. Experimentally observed decay curves from $Nd^{3+4}F_{3/2}$ in (a) 1% Nd:YAG, (b) (15% Er, 1% Nd):YAG.

Table 1.	Observed Fluorescence Decay Properties of
	(Er, Nd):YAG

State	Observations
${ m Er^{3+}}{}^4I_{11/2}$	Decay is governed by a simple exponential and is two times faster than in Er:YAG.
Er ^{3+ 4} I _{13/2}	Decay shows slow filling at early times (first 50 μ sec), then becomes an exponential and is approximately 170 times faster than in Er:YAG.
${ m Nd}^{3+} {}^4\!F_{3/2}$	Decay is an exponential at early stage (first 10 μ sec) and is 30 times faster than in Nd:YAG; later it becomes slower and nonexponential.

ing this method, we were able to measure the fluorescence decay lifetime of the $Er^{3+} 4I_{11/2}$ state in Er:YAG as a function of Er concentration. It was found^{6,7} that this lifetime was independent of Er concentration, indicating that the $Er^{3+} 4I_{11/2}$ state in Er:YAG was not subject to concentration quenching.

In comparison, the (Er, Nd):YAG shows a decay governed by a simple exponential over nearly four *e*-folding periods, independent of pump levels. Another important feature of the decay from the $\mathrm{Er}^{3+4}I_{11/2}$ state in (Er, Nd):YAG is that the 1/*e* decay time (53 μ sec) is only one half of that of Er:YAG.

(2) For the $Er^{3+} {}^{4}I_{13/2}$ state (Fig. 2): The decay curves of the $Er^{3+} {}^{4}I_{13/2}$ state in Er:YAG [Fig. 2(a)] and (Er, Nd):YAG [Fig. 2(b)] differ strikingly in that the decay in (Er, Nd):YAG is approximately 170 times faster than that in Er:YAG. This observation confirms the expected reduction of the $Er^{3+} {}^{4}I_{13/2}$ level lifetime. The nonexponential decay of the $Er^{3+} {}^{4}I_{13/2}$ state in Er:YAG is due to the cross-relaxation processes as discussed in feature (1) above. Simple exponential decay was obtained by using low excitation, which allowed us to measure the decay lifetime of the $Er^{3+} {}^{4}I_{13/2}$ state in Er:YAG. This lifetime was found to be 13.7 msec for 16.6 at. % Er:YAG. In addition, the $Er^{3+} {}^{4}I_{13/2}$ state in (Er, Nd):YAG, whose decay pattern was independent of excitation levels, shows a slow decrease in fluorescence strength at the initial stage of the decay.

(3) For the Nd³⁺ ${}^{4}F_{3/2}$ state (Fig. 3): In Nd:YAG the

lifetime of the ${}^{4}F_{3/2}$ state is approximately 240 μ sec, and the decay process is governed by a simple exponential. However, in (Er, Nd):YAG not only is nonexponential decay of the Nd³⁺ ${}^{4}F_{3/2}$ state observed but an initial 1/e decay time of approximately 8 μ sec is recorded. To check this observation and ensure that it is not an artifact of the data acquisition and processing equipment, we also monitored the fluorescence decay at 1.34 μ m, which corresponds to the Nd³⁺ transition from the ${}^{4}F_{3/2}$ to ${}^{4}I_{13/2}$ states. The same nonexponential decay behavior was observed with the same initial 1/e decay time.

As we pointed out in our earlier paper,³ the drastically altered fluorescence decay rates suggest significant unlike ion-ion interactions in the (Er, Nd):YAG crystal. In the section that follows we discuss theoretical models of the ionion interactions as applied to the system under study; these models provide a basic understanding of the mechanisms that result in the observations described above. A summary of the observed fluorescence decay properties from the three Er^{3+} and Nd³⁺ states is listed in Table 1.

THEORETICAL INVESTIGATION OF THE MECHANISMS OF THE ION-ION INTERACTIONS IN (Er, Nd):YAG

To understand the physical processes responsible for the observations described above, we introduced three cross-relaxation processes that involve both Er^{3+} and Nd^{3+} ions. These processes are depicted in Fig. 4, along with the known decay and energy exchange processes. Strong relaxation processes are expected because both energy-state pairs involved in each of the three processes have the same energy difference. A rate-equation analysis, which includes the cross-relaxation processes shown in Fig. 4, was used to calculate the time-varying population distribution of the coupled Er^{3+} and Nd^{3+} states from which fluorescence decays were observed. The coupled rate equations were solved numerically by utilizing the fifth- and sixth-order Runge Kutta-Verner method, and the results were compared with the observed decay data.



Fig. 4. Ion-ion interaction and relaxation processes in (Er, Nd):YAG.

With reference to Fig. 4, W, W₁, and W₂ describe crossrelaxation processes of the Er³⁺ ions in high dopant density Er³⁺-doped materials. They are responsible for the nonexponential decay of the Er³⁺ $4I_{11/2}$ and $4I_{13/2}$ states [Figs. 1(a) and 2(a)] and the quasi-cw laser operation in the 3-µm region of high-concentration Er³⁺:YAG lasers.^{1,6} C₁, C₂, and C₃ in Fig. 4 represent the cross-relaxation processes proposed to account for the drastically altered fluorescence decay functions observed in (Er, Nd):YAG. With reference to Table 1 and Fig. 4, we introduce the following:

(1) The process described by C_1 to account for the faster decay of the $\text{Er}^{3+4}I_{11/2}$ state.

(2) The process described by C_2 to account for the faster decay of the $\mathrm{Er}^{3+} {}^4I_{13/2}$ state and the simple exponential decay of the $\mathrm{Er}^{3+} {}^4I_{11/2}$ state.

(3) The process described by C_3 to account for the faster decay of the Nd³⁺ ${}^{4}F_{3/2}$ state and the filling of the ${}^{4}F_{3/2}$ state Nd³⁺ ions during the early stage of the Er³⁺ ${}^{4}I_{13/2}$ decay.

 C_1 , C_2 , and C_3 are the cross-relaxation coefficients and were assumed to be constant in time in our model. The Er^{3+} energy states under consideration are ${}^{4}S_{3/2} + {}^{2}H_{11/2}(4)$, ${}^{4}F_{9/2}(3)$, ${}^{4}I_{11/2}(2)$, ${}^{4}I_{13/2}(1)$, and ${}^{4}I_{15/2}(0)$, and those of Nd³⁺ ions are ${}^{4}F_{3/2}(2)$, ${}^{4}I_{15/2}(1)$, and ${}^{4}I_{9/2}(0)$. The numbers in parentheses are those used to label the energy states of each kind of ion (see Fig. 4).

A set of rate equations is presented below, which includes the various cross-relaxation processes among like or unlike ions in addition to spontaneous emission, multiphonon transitions, and external excitation. The equations involving Er^{3+} states were normalized with respect to the Er^{3+} concentration (C^{Er}), and those dealing with Nd³⁺ states were normalized with respect to the Nd³⁺ concentration (C^{Nd}). This is why C^{Er} and C^{Nd} appear explicitly in the equations. Assume that the initial conditions are n_0^{Er} (t = 0) = 1; $n_i^{Er}(t = 0) = 0$, where i = 1, 2, 3, 4; and $n_0^{Nd}(t = 0) = 1, n_i^{Nd}(t = 0) = 0$, where i = 1, 2. Then the resulting set of eight coupled equations is

$$\frac{dn_0^{\text{Er}}}{dt} = -W_{04}n_0^{\text{Er}} + \frac{n_1^{\text{Er}}}{\tau_1^{\text{Er}}} - (n_0^{\text{Er}}W)n_4^{\text{Er}} + (C^{\text{Er}}W_1)(n_1^{\text{Er}})^2
+ (C^{\text{Er}}W_2)(n_2^{\text{Er}})^2 - C_3n_2^{\text{Nd}}n_0^{\text{Er}}C^{\text{Nd}}
+ C_2n_1^{\text{Er}}n_0^{\text{Nd}}C^{\text{Nd}},$$
(1)

$$\frac{\mathrm{d}n_{1}^{\mathrm{Er}}}{\mathrm{d}t} = \frac{n_{2}^{\mathrm{Er}}}{\tau_{2}^{\mathrm{Er}}} - \frac{n_{1}^{\mathrm{Er}}}{\tau_{1}^{\mathrm{Er}}} + (n_{0}^{\mathrm{Er}}W)n_{4}^{\mathrm{Er}} - (2C^{\mathrm{Er}}W_{1})(n_{1}^{\mathrm{Er}})^{2} -C^{\mathrm{Nd}}C_{2}n_{1}^{\mathrm{Er}}n_{0}^{\mathrm{Nd}} + C^{\mathrm{Nd}}C_{3}n_{2}^{\mathrm{Nd}}n_{0}^{\mathrm{Er}} + C_{1}n_{2}^{\mathrm{Er}}n_{0}^{\mathrm{Nd}}C^{\mathrm{Nd}},$$
(2)

$$\frac{\mathrm{d}n_2^{\mathrm{Er}}}{\mathrm{d}t} = \frac{n_3^{\mathrm{Er}}}{\tau_3^{\mathrm{Er}}} - \frac{n_2^{\mathrm{Er}}}{\tau_2^{\mathrm{Er}}} + (n_0^{\mathrm{Er}}W)n_4^{\mathrm{Er}} + (C^{\mathrm{Er}}W_1)(n_1^{\mathrm{Er}})^2 - (2C^{\mathrm{Er}}W_2)(n_2^{\mathrm{Er}})^2 - C^{\mathrm{Nd}}C_1n_2^{\mathrm{Er}}n_0^{\mathrm{Nd}},$$
(3)

$$\frac{\mathrm{d}n_{3}^{\mathrm{Er}}}{\mathrm{d}t} = W_{43}^{mp} n_{4}^{\mathrm{Er}} - \frac{n_{3}^{\mathrm{Er}}}{\tau_{3}^{\mathrm{Er}}},\tag{4}$$

$$\frac{\mathrm{d}n_4^{\mathrm{Er}}}{\mathrm{d}t} = W_{04}n_0^{\mathrm{Er}} - \frac{n_4^{\mathrm{Er}}}{\tau_4^{\mathrm{Er}}} + (C^{\mathrm{Er}}W_2)(n_2^{\mathrm{Er}})^2, \tag{5}$$

$$\frac{\mathrm{d}n_0^{\mathrm{Nd}}}{\mathrm{d}t} = \frac{n_1^{\mathrm{Nd}}}{\tau_1^{\mathrm{Nd}}} - W_{02}n_0^{\mathrm{Nd}} + \frac{n_2^{\mathrm{Nd}}}{\tau_2^{\mathrm{Nd}}} - C^{\mathrm{Er}}C_2n_1^{\mathrm{Er}}n_0^{\mathrm{Nd}},\tag{6}$$

$$\frac{\mathrm{d}n_1^{\mathrm{Nd}}}{\mathrm{d}t} = C^{\mathrm{Er}} C_2 n_1^{\mathrm{Er}} n_0^{\mathrm{Nd}} - \frac{n_1^{\mathrm{Nd}}}{\tau_1^{\mathrm{Nd}}} + C^{\mathrm{Er}} C_3 n_2^{\mathrm{Nd}} n_0^{\mathrm{Er}},\tag{7}$$

$$\frac{{\rm d}n_2^{\rm Nd}}{{\rm d}t} = W_{02}n_0^{\rm Nd} - \frac{n_2^{\rm Nd}}{\tau_2^{\rm Nd}} - C^{\rm Er}C_3n_2^{\rm Nd}n_0^{\rm Er},\tag{8}$$

where

- C^{Er} is the concentration of Er^{3+} ions;
- C^{Nd} is the concentration of Nd³⁺ ions;

 W_{04} and W_{02} are the external excitation rates;

- $n_i^{\rm Er}$ is the normalized population of the *i*th ${\rm Er}^{3+}$ state;
- $n_i^{\rm Nd}$ is the normalized population of the *i*th Nd³⁺ state;
- τ_i^{Er} is the fluorescence decay lifetime of the *i*th Er³⁺ state;
- $\tau_i^{\rm Nd}$ is the fluorescence decay lifetime of the *i*th Nd³⁺ state;
- C_i is the coefficient of the *i*th ion-ion interaction process, i = 1, 2, 3;
- W_{43}^{mp} is the multiphonon transition rate from 4 to 3 of Er³⁺ ions;
- $n_0^{\rm Er}W$ is the cross-relaxation rate of the Er ${}^4S_{3/2}$ level;
- $W_1(W_2)$ is the cross-relaxation coefficient for the cross-relaxation process originating from the $\mathrm{Er}^{3+} \, {}^{4}I_{13/2}({}^{4}I_{11/2})$ state.

Several assumptions have been made in writing these equations. They are as follows:

(1) The Nd³⁺ energy levels above the ${}^{4}F_{3/2}$ relax so fast through phonon-assisted processes that the Nd³⁺ ${}^{4}F_{3/2}$ level is effectively directly pumped (a four-level system).

(2) Energy transfer from the $Nd^{3+4}I_{15/2}$ level to the $Er^{3+4}I_{13/2}$ level is negligible compared with the phonon-assisted relaxation of the $Nd^{3+4}I_{15/2}$ level.

(3) $A_{4j}^{\text{Er}} \ll W_{43}^{\text{mp}}$, and $n_0^{\text{Er}} W$ is therefore neglected.

(4) $A_{3j}^{\text{Er}} \ll W_{32}^{\text{mp}}$ and therefore is neglected.

(5) $A_{2j} \ll W_{21}^{mp}$, and the cross-relaxation rate W_2 is therefore neglected. [Note that $\eta_{qe}(\text{Er}^{3+} {}^4I_{11/2})$ is less than 1.5%.⁸]

Here A_{ij}^{Er} is the radiative transition rate from the Er^{3+} state *i* to state *j*, and W_{ij}^{mp} is the multiphonon transition rate from the Er^{3+} state *i* to state *j*.

Our primary objective was to show the validity of our model by comparing the results of the calculation with the experimental data. An iterative fitting procedure leads to the determination of the cross-relaxation coefficients C_1 , C_2 , and C_3 , which are the only unknown parameters in the equations.

Numerical solutions of the rate equations were obtained by the fifth- and sixth-order Runge Kutta–Verner method.⁹ The results are plotted in Figs. 5 and 6, in which they are compared with the observed decay data. The parameters used for obtaining the results are listed in Table 2, and the fitted values for the cross-relaxation coefficients C_1 , C_2 , and C_3 are summarized in Table 3.



Fig. 5. Calculated decay functions (solid curves) using the rateequation analysis of (a) the $\mathrm{Er}^{3+} \, {}^{4}I_{11/2}$ state and (b) the $\mathrm{Er}^{3+} \, {}^{4}I_{13/2}$ state as compared with experimental data (circles).

From Figs. 5(a) and 5(b), we see that the computed curves agree well with the observed Er³⁺ decay curves, indicating that the proposed cross-relaxation processes and coefficients are appropriate for the unlike ion-ion interactions in this crystal. However, in Fig. 6 a discrepancy was observed between the calculation (solid, straight line) and experimental data for the Nd³⁺ ${}^{4}F_{3/2}$ decay. This, however, by no means suggests that the process governed by C_3 , shown in Fig. 4, does not function as it should. The importance of such a process is indicated by the fact that including the process governed by C_3 can explain the slow filling in the early stage of the $Er^{3+4}I_{13/2}$ state decay, as Fig. 5(b) shows. The difference between calculation and experiment in Fig. 6 comes about because a constant interaction strength was assumed in the calculation. In reality this may not be true because not all Nd³⁺ sites provide the same strength of interaction with Er^{3+} ions in a sample that has 15 at. % Er^{3+} ions but only 1 at. % Nd³⁺ ions. In this case one Nd³⁺ ion can see a spatial distribution of Er³⁺ ions around it, and some Er^{3+} ions may interact with this Nd³⁺ ion with a strength that is different from the strength of interaction between this Nd³⁺ ion and another group of Er^{3+} ions. The overall effect of interactions of this nature is to give rise to the nonexponential decay of the Nd³⁺ ${}^{4}F_{3/2}$ state. In the YF₃:Yb, Ho system, for example, similar nonexponential decay was observed from the Yb³⁺ ions that was due to the energy transfer from Yb³⁺ ions to Ho³⁺ ions.¹³

Because of the difficulty of incorporating a nonconstant interaction strength between Nd³⁺ and Er³⁺ ions, we will use the analytical expression for the donor luminescence of a donor-acceptor system, as derived by Inokuti and Hirayama¹⁴ on the basis of the Förster-Dexter theory of energy transfer,^{15,16} in order to investigate the mechanisms governing the Nd³⁺ $^{4}F_{3/2}$ decay in (Er, Nd):YAG under study.

We begin our analysis with the assumption that the energy diffusion effect among excited Nd^{3+} ions is negligible. This is justified by the fact that our sample contains 1 at. % Nd^{3+} ions, and the excited Nd^{3+} ions in 1 at. % Nd:YAG have a high quantum efficiency. Therefore the mechanism under consideration is energy transfer between donor (excited Nd^{3+}) –acceptor (ground-state Er^{3+}) pairs.

The total rate of transfer from an excited donor to an acceptor at a distance R can be expressed as

$$W_T(R) = \frac{1}{\tau_0} + n(R),$$
 (9)

where τ_0 is the intrinsic lifetime of the excited donors and n(R) is the energy transfer rate of a donor-acceptor pair whose two ions are a distance R from each other. If the energy transfer is governed by a particular electric multipolar term, the transfer rate can be written as

$$n(R) = \frac{1}{\tau_0} \left(\frac{R_0}{R}\right)^s,\tag{10}$$

where s is a positive number and R_0 is, according to Förster,¹⁵ a critical transfer distance such that the transfer rate n(R) is equal to the intrinsic decay rate $1/\tau_0$ of the donor when R is equal to R_0 . Using this model (sometime referred to as the inverse-power rate model), Inokuti and Hiragama¹⁴ were



Fig. 6. Decay functions of the ${}^{4}F_{3/2}$ Nd³⁺ ions calculated by using the rate-equation model (solid, straight line) and energy transfer theory compared with the experimental data (circles).

Table 2. Parameters Used in Rate-Equation Calculation

Parameters	Values	Reference
C^{Er}	$2.1 \times 10^{21} \text{ cm}^{-3}$ (15 at. %)	a
${ au_1}^{ m Er}$	13.7 msec	а
${ au_2}^{ m Er}$	106 µsec	а
${ au_3}^{ m Er}$	1.2 µsec	6
${ au_4}^{ m Er}$	1.0 µsec	6
W_{43}^{mp}	$1.8 \times 10^{5} { m sec^{-1}}$	10
$n_0^{\mathrm{Er}} W$	$9.3 imes 10^5 m sec^{-1}$	10
W_1	$2.5 \times 10^{-17} \mathrm{cm^{3/sec}}$	6
W_2	$5.0 imes 10^{-17} { m cm^3/sec}$	6
$C^{ m Nd}$	$1.38 \times 10^{20} \mathrm{cm}^{-3}$ (1 at. %)	11
${ au_1}^{ m Nd}$	$\sim 2 \mu \text{sec}$	12
${ au_2}^{ m Nd}$	237 µsec	a

^a Our results.

Table 3. Cross-Relaxation Coefficients for Unlike Ion-Ion Interaction Processes in (Er, Nd):YAG

Coefficients	Values (×10 ⁻¹⁶ cm ³ /sec)	
C_1	0.7	
C_2	1.2	
<u> </u>	0.5	



Fig. 7. Decay functions of the ${}^{4}F_{3/2}$ Nd³⁺ ions calculated by using the energy transfer theory compared with the experimental data (circles).

able to derive an expression for the donor luminescence that is macroscopically measurable:

$$\phi(t) = \exp\left[-\frac{t}{\tau_0} - \Gamma\left(1 - \frac{3}{s}\right)\frac{4}{3}\pi c_a R_0^{-3} \left(\frac{t}{\tau_0}\right)^{3/s}\right], \quad (11)$$

where $\Gamma(x)$ is the gamma function and c_a is the concentration of acceptor ions (cm⁻³). Equation (11) covers several important situations. Namely, s = 6, 8, 10 corresponds to electric dipole-dipole, dipole-quadrupole, and quadrupolequadrupole interactions, respectively. Equation (11) has been used for analyzing our experiment. The least-squares fits of Eq. (11) to the experimental data, using the most commonly encountered three electric multipolar interaction mechanisns, i.e. s = 6, 8, 10, are plotted in Fig. 6.

As Fig. 6 shows, the best fit is obtained with s = 6, implying a dipole-dipole interaction as expected. However, a better fit is obtained with s = 4 for the initial decay and s = 5 for the subsequent decay. The results are presented in Fig. 7. It is possible that this behavior is a result of the situation in which two or more Er^{3+} ions interact with one Nd³⁺ ion.

The corresponding critical transfer distance R_0 is 7.39 Å for s = 4 and 7.87 Å for s = 5. The interaction strength α , defined as $\alpha = R_0^{s}/\tau_0$, is 1.26×10^{-25} cm⁴/sec for s = 4 and 1.27×10^{-32} cm⁵/sec for s = 5.

DISCUSSION

As Fig. 1(a) shows, the fluorescence decay of the $\text{Er}^{3+} {}^{4}I_{11/2}$ state in Er:YAG is nonexponential. This is due mainly to the cross relaxation of the Er^{3+} ions in the ${}^4I_{13/2}$ state,⁷ which is significant only in high-concentration ${
m Er^{3+}}$ -doped materials. This process has been $shown^{7,17}$ to be responsible for the quasi-cw lasing at $\sim 3 \ \mu m$ from the Er-doped laser crytals. On the other hand, when Nd³⁺ ions are codoped into Er:YAG lattices, the decay of the $\mathrm{Er}^{3+4}I_{11/2}$ state is exponential, and the decay rate becomes twice as fast as in Er:YAG [Fig. 1(b)]. This is, as the investigation in the previous section showed, a result of the two cross-relaxation processes governed by C_1 and C_2 . The process C_2 accelerates the relaxation of the Er^{3+} ${}^4I_{13/2}$ state so that the Er population reservoir in this state is, to a large extent, eliminated. As a result, the cross-relaxation process from this state is prevented from taking place because the cross-relaxation rate is proportional to the number density of the ions in this state. Moreover, the internal pumping process for the $Er^{3+} 4I_{11/2}$ offered by this cross relaxation is disabled, which would otherwise pump the $\mathrm{Er}^{3+4}I_{11/2}$ state. The process C_1 , on the other hand, simply opens up another channel for relaxing the $Er^{3+} 4I_{11/2}$ state in (Er, Nd):YAG in addition to the spontaneous and phonon-assisted emission from this state. Inevitably, this process results in a faster decay rate of the ${
m Er}^{3+} {}^4I_{11/2}$ state. In addition, because this process functions through nonradiative energy transfer, it removes some of the ${}^{4}I_{11/2}$ state Er^{3+} population that would otherwise have been available for stimulated emission. Clearly, both processes described by C_1 and C_2 militate against laser action by the $\mathrm{Er^{3+}}$ ions at 2.94 $\mu\mathrm{m}$.

As far as the decay of excited Nd³⁺ ions is concerned, the calculations in the previous section revealed that this decay is governed predominantly by the dipole-dipole interactions between the excited-state Nd^{3+} ions (${}^4F_{3/2}$) and ground-state Er^{3+} ions (${}^{4}I_{15/2}$). The best fit between calculation and experimental data with s = 4 and s = 5 in the inverse-power rate model represents a special situation of the dipole-dipole interaction, as pointed out by Inokuti and Hirayama.¹⁴ As a matter of fact, the transfer rate n(R) can take a different inverse power of R dependence, which can be either greater than or smaller than 6, depending on whether the effective transfer is of shorter or longer range, if the system under study contains effects that were excluded in the theory. Our result is just an example of this situation. Further study is needed to resolve the detailed physical processes that are involved.

Moreover, the interaction discussed above that occurs between Er^{3+} and Nd^{3+} ions is clearly detrimental to the laser action of Nd^{3+} at 1.06 μ m because the nonradiative interaction removes the Nd^{3+} population in the ${}^4F_{3/2}$ state, which would otherwise be available for lasing action. Actually, we can calculate the relative luminescence yield of the ${}^4F_{3/2}$ Nd^{3+} ions from¹⁴

$$\eta/\eta_0 = \frac{1}{\tau_0} \int_0^\infty \phi(t) \mathrm{d}t, \qquad (12)$$

where η_0 is the luminescence yield of the ${}^4F_{3/2}$ Nd³⁺ ions when Er³⁺ ions are not present and is equal to unity. Numerical evaluation of Eq. (12) gives $\eta/\eta_0 = 3.84\%$. This number matches the 30-times reduction in the lifetime of the ${}^4F_{3/2}$ Nd³⁺ ions in (Er, Nd):YAG as compared with Nd:YAG.

The above analysis helps us to understand the observation of relatively higher-input energy thresholds and lower efficiencies of the laser action from (Er, Nd):YAG at both 1.06 and 2.94 μ m; this observation was made in our early studies of this laser material.³

In conclusion, the unusual fluorescence decay properties of the (Er, Nd):YAG crystal were explained by unlike ionion cross-relaxation mechanisms and energy transfer theory. The lasing performance of this material, as studied earlier elsewhere, is also understandable on the basis of these models. Complete elimination of self-termination in the Er³⁺ 2.94-µm transition has not been accomplished [namely, τ (Er³⁺ $^{4}I_{13/2}$) is still longer than τ (Er³⁺ $^{4}I_{11/2}$)] in (15% Er, 1% Nd):YAG. However, we believe that this bottleneck should be unblocked by means of the combination of Er³⁺ and Nd³⁺ ions in crystals other than YAG in which the Er³⁺ ions have the shortest $^{4}I_{11/2}$ lifetime (~100 µsec). In the next phase of the study of this new class of multiple-wavelength solidstate lasers, hosts with longer Er³⁺ $^{4}I_{11/2}$ lifetimes will be sought.

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