Determination of the Er^{3+} to Ho^{3+} Energy Transfer Coefficient in (Er, Ho):YAG

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The coefficient describing energy transfer from the first excited level of trivalent erbium to the first excited level of trivalent holmium in YAG was obtained from measurement of the relevant material parameters. The value of this coefficient is necessary for estimating the improvement in Er:YAG and/or Ho:YAG lasing when the two ions are co-doped in the same crystal. This coefficient determines the depopulation efficiency of the lower level of the erbium 3-µm transition and the sensitization of the upper level of the 2-µm transition in holmium. Our technique for measuring the energy transfer coefficient, by fluorescence decay measurements in conjunction with computer simulations of the decay and rate equation modeling, resulted in a value of 4.33×10^{-19} cm³s⁻¹, implying that the erbium $\rightarrow$ holmium energy transfer is strong enough to improve the room-temperature holmium 2-µm laser.

We developed a method of determining the $Er^{3+} \rightarrow Ho^{3+}$ energy transfer coefficient through calculations based on the decay of fluorescence from specific levels of Er^{3+} in $Y_3Al_5O_{12}$ (YAG). This method was validated by application to singly-doped Er:YAG. The rate equations of the relevant levels in (Er, Ho):YAG are

$$\frac{\partial n_2}{\partial t} = W_{11} n_1^2 - \frac{n_2}{\tau_2} \tag{1}$$

$$\frac{\partial n_1}{\partial t} = \frac{n_2}{\tau_2} - 2W_{11} n_1^2 - W_{1a} n_1 n_a - \frac{n_1}{\tau_1} \tag{2}$$

$$\frac{\partial n_b}{\partial t} = W_{1a} n_1 n_a - \frac{n_b}{\tau_b} \tag{3}$$

$$\frac{\partial n_a}{\partial t} = \frac{n_b}{\tau_b} - W_{1a} n_1 n_a \quad , \tag{4}$$

where n_j is the volume density of population in level j, τ_j is the lifetime of that level, level 1 is the first excited level of Er^{3+} (the $^4I_{13/2}$), level 2 is the second excited level (the $^4I_{15/2}$), level a is the ground level of Ho^{3+} (the $^5I_8$), and level b is the first excited level (the $^5I_7$). The ion-ion interactions are described by the coefficients W_{11} for two ions in the Er^{3+} $^4I_{13/2}$ level and W_{1a} for one ion each in the Er^{3+} $^4I_{13/2}$ and the Ho^{3+} $^5I_8$ levels. The values of W_{11} and W_{1a} describe the strength of the ion-ion interactions and can be used to predict energy transfer both within Er^{3+} and from Er^{3+} to Ho^{3+}.

The energy transfers are made possible by near-resonant energy level transfers within the materials (Figure 1). The Er^{3+} two-ion energy transfer is fully resonant, while the $Er^{3+} \rightarrow Ho^{3+}$ energy transfer is nearly resonant. The difference between the energy given up by the Er^{3+} ion and the energy received by the Ho^{3+} ion is ~1100 cm⁻¹, 5× higher than the average room-temperature phonon but significantly below the maximum phonon energy supported by the YAG

crystal matrix. Nonetheless, the need to generate this phonon reduces the probability of this transition, and we expect that $W_{1a} \ll W_{11}$.
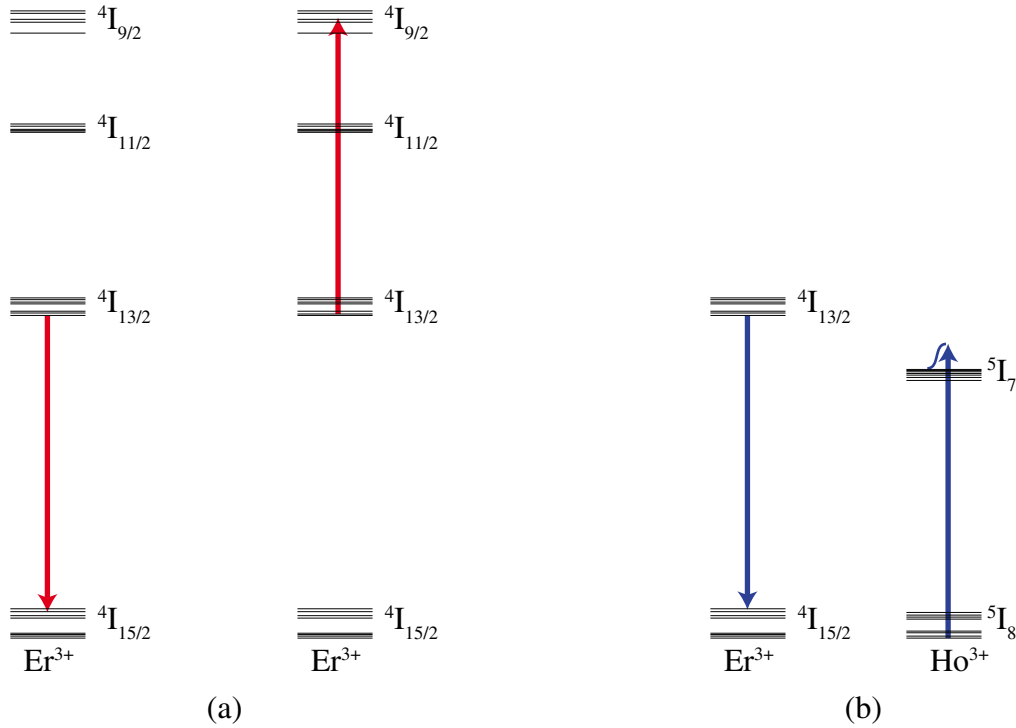
Figure 1. The resonant energy transfer in Er^{3+} (a) has a higher probability than the near-resonant energy transfer from $Er^{3+} \rightarrow Ho^{3+}$ (b).

We began our study of ion-ion interaction strengths with singly doped Er:YAG – with no Ho in the crystal. In this case, both n_a and n_b are 0, so only Eqs. (1) and (2) are needed, and Eq. (2) does not include the term with W_{1a}. The initial conditions for solving these coupled equations are $n_1(0) = 0$ and $n_2(0) = 5.89 \times 10^{18}$ cm^{-3}. The initial condition on n_2 comes from the absorption of a 30.0 mJ Q-switched pulse at 532.1 nm in a 3.5-mm thick piece of 40% (at.) Er:YAG.

Eq. (1) can be rewritten to define an effective lifetime for level 2:

$$\frac{\partial n_2}{dt} = \frac{n_2}{\tau_2^{eff}}; \quad \tau_2^{eff} \equiv \frac{\tau_2}{1 - W_{11}\tau_2} \frac{n_2}{n_1^2} \quad . \tag{5}$$

Eq. (5) can be solved for W_{11}:

$$W_{11} = \frac{\tau_2^{eff} - \tau_2}{\tau_2^{eff} \tau_2} \frac{n_2}{n_1^2} \quad . \tag{6}$$

The effective lifetime asymptotically approaches a constant value (Figure 2). The coupled differential equations (1) and (2) can be solved numerically to match τ_2^{eff} at several times the initial lifetime τ_2. Using the early and late lifetime fits from Figure 2 with the modeled values of

population density in the relevant levels, Eq. (6) yields values of 4.30×10^{-17} cm^{3}s^{-1} for W_{11} at a concentration of 30% and 5.28×10^{-17} cm^{3}s^{-1} for W_{11} at a concentration of 40%.

(a)   (b)
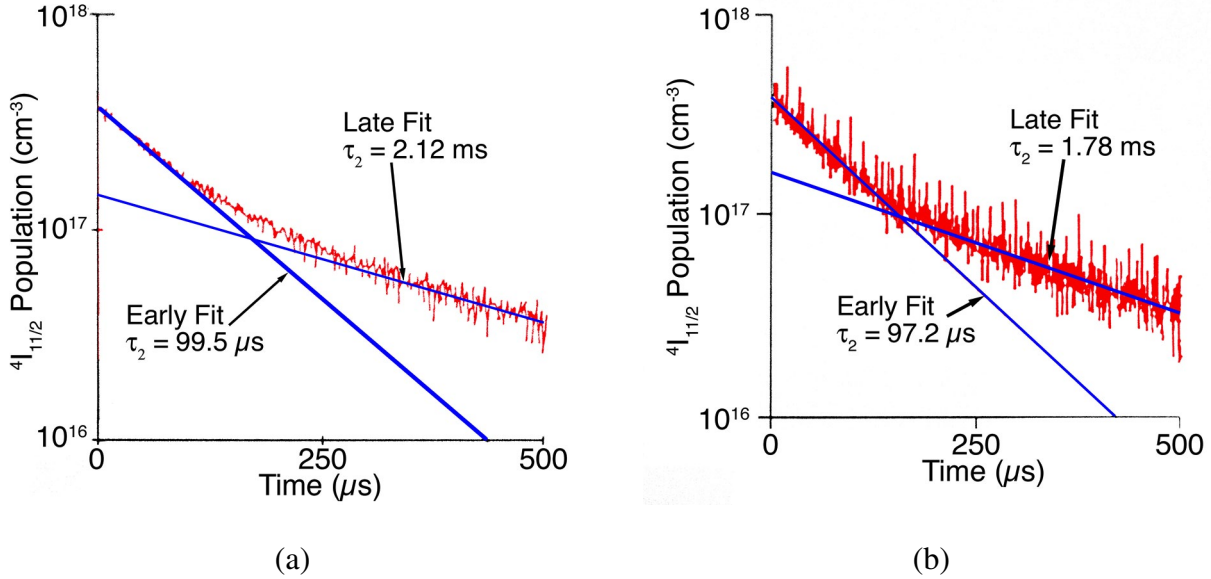
Figure 2. Fluorescence from level 2 of singly-doped Er:YAG with atomic doping levels of 30% (a) and 40% (b) demonstrate the predicted nonlinearities.

For (Er, Ho):YAG, Eqs. (1)-(4) were all used. The critical equation for determining W_{1a} is Eq. (2). At sufficiently long times (Figure 3 demonstrates that times >2 ms are sufficient) the decay of level 1 is controlled by the last two terms. Then

$$\tau_1^{eff} \approx \frac{\tau_1}{1 + W_{1a}\tau_1 n_a} \quad . \tag{7}$$

Since n_a is the population of the ground level ($^5I_8$) of the Ho^{3+} ion, it is effectively constant with time. The Ho doping concentration in all doubly-doped tests was 1.5%, for a population density $n_a = 2.07 \times 10^{20}$ cm^{-3}. The fluorescence from level 1 ($^4I_{13/2}$) of Er^{3+} is shown in Figure 3. The known fluorescence lifetimes of Er:YAG at 30% and 40% concentrations, together with Eq. (7), result in a value of 4.33×10^{-19} cm^{3}s^{-1} for W_{1a} at both concentration levels.
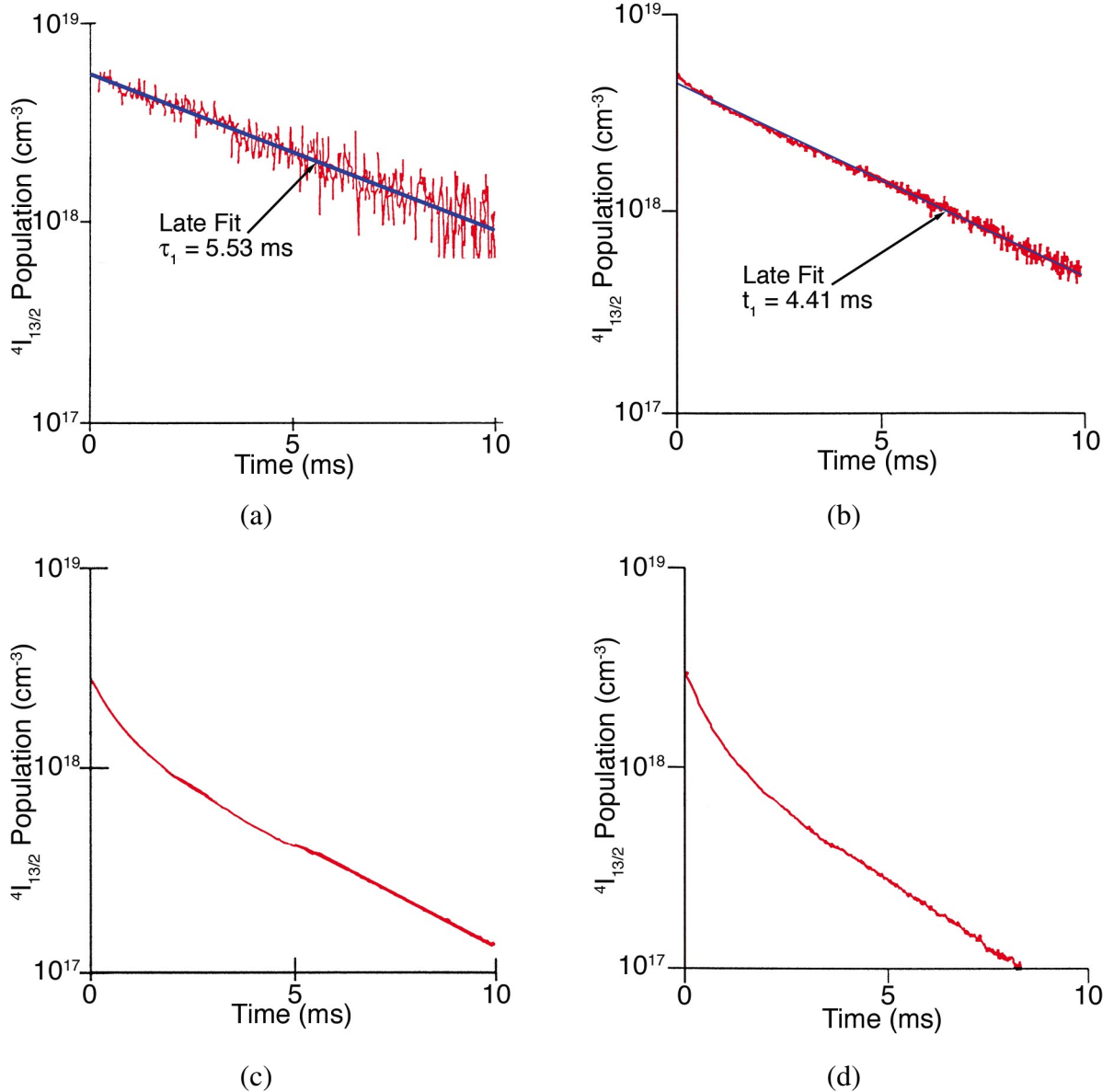
Figure 3. Fluorescence from level 1 of (30% Er, 1.5% Ho):YAG (a) and (40% Er, 1.5% Ho):YAG (b) shows that the Er $\rightarrow$ Ho energy transfer has nearly linearized the fluorescence decay from the first excited level when compared to the singly-doped 30% Er:YAG (c) and 40% Er:YAG (d).

Note that the value of W_{1a} does not vary with Er concentration, indicating that it depends more heavily on Ho concentration. Intuitively, and by the assumptions inherent in the traditional rate equation model, the strength of an ion-ion interaction should not depend on concentration. The value of W_{11}, however, depends strongly on Er concentration. The experiments by which we determined this parameter were designed to eliminate any effects, such as hole burning and reabsorption, that affect the lifetime measurement. It is clear, therefore, that the lifetime variation with concentration is a real effect. This can be explained by recognizing that one of the assumptions made in deriving the rate equation model is that introducing the dopant (Er) into the host (YAG) does not affect any parameters of the host, including its local crystal field. Since the

dopant concentration in these experiments was so high, it is likely that this assumption does not hold, and the lifetime is affected by the concentration. To validate this prediction, we measured lifetimes of the $^4I_{13/2}$ level of Er:YAG for Er concentrations of 1%, 10%, 16.7%, 30%, 33.3%, 40%, 50%, and 60%. Based on these measurements, we propose a third-order equation for the lifetime of this level:

$$\tau_1(x) = 7.88 + 0.763x - 0.0297x^2 + 0.000256x^3 \quad , \tag{8}$$

valid for concentrations from 1% to 60%. Eq. (8) results in lifetimes measured in milliseconds for inputs of concentration (x) in %. Likewise, we have modeled the lifetime of the $^4I_{11/2}$ level as

$$\tau_2(x) = 102 + 0.509x - 0.0300x^2 + 0.000311x^3 \tag{9}$$

with lifetimes measured in microseconds. These two lifetime equations are graphed in Figure 4.

(a)   (b)
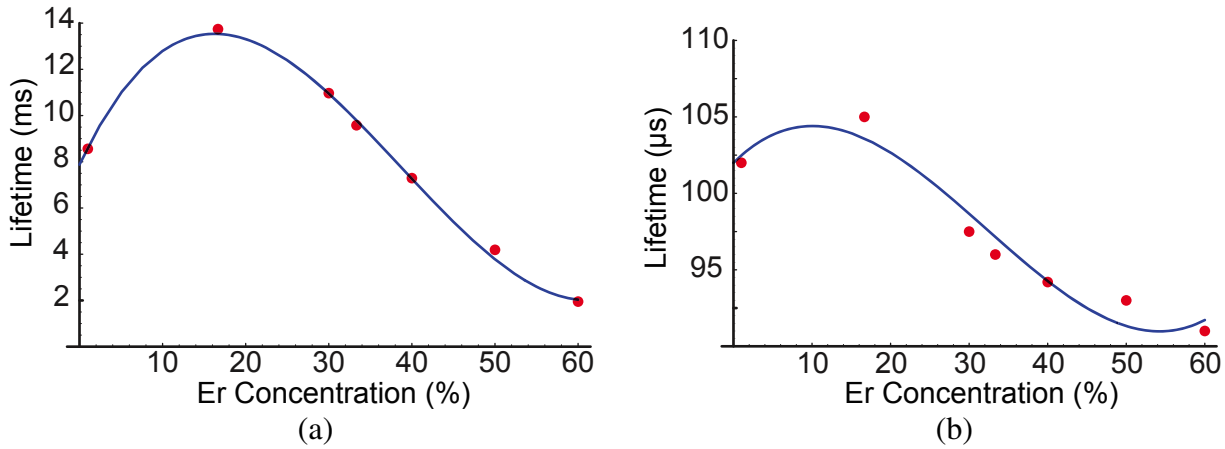
Figure 4. The lifetimes of the Er^{3+} $^4I_{13/2}$ (a) and $^4I_{11/2}$ (b) levels vary significantly with concentration. Lines represent the third-order approximations while dots are measurements.

In conclusion, we have developed a simple method for calculating the strength of ion-ion interactions based on rate equations and lifetime measurements. This technique was used to determine the Er $\rightarrow$ Er $^4I_{13/2}$ cross-relaxation strength at two Er concentrations in singly-doped Er:YAG, and the Er $\rightarrow$ Ho ion-ion interchange strength for two Er concentrations of (Er, Ho):YAG. The value of W_{11}, the Er $\rightarrow$ Er cross-relaxation parameter, was found to be 4.30×10^{-17} cm^{3}s^{-1} for 30% Er:YAG and 5.28×10^{-17} cm^{3}s^{-1} for 40% Er:YAG. The value of W_{1a}, the Er $\rightarrow$ Ho ion-ion interaction strength, was calculated as 4.33×10^{-19} cm^{3}s^{-1} for both (30% Er, 1.5% Ho):YAG and (40% Er, 1.5% Ho):YAG. The Er $\rightarrow$ Ho interaction was sufficient to reduce the lifetime of the Er^{3+} $^4I_{13/2}$ level by ~40%, but not nearly enough to unblock the 2.94-µm Er transition from the $^4I_{11/2}$ to the $^4I_{13/2}$ level. It is sufficient, however, to act as a pump for the Ho^{3+} 2-µm transition from the $^5I_7$ to the $^5I_8$ level.