Upconversion and energy transfer modeling in Er, Yb: CaYAlO₄

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Abstract

This paper models the mechanism of upconversion and energy transfer between Er and Yb ions in diode-pumped Er, Yb: CaYAlO₄ crystal. Rate equations are used for modeling and are solved numerically for the populations of different levels as a function of time. Many input parameters are measured experimentally and the rest of the parameters are predicted from the model. Population inversion is studied for these transitions in Er:

$^4S_{3/2} \rightarrow ^4I_{15/2}$ (green), $^4S_{3/2} \rightarrow ^4I_{13/2}$ (red) and $^4I_{13/2} \rightarrow ^4I_{15/2}$ (IR)

I. Introduction

Diode-pumpable rare earth ions capable of upconversion have been the subject of interest for various applications. One attractive scheme for upconversion is the excitation of Er by pumping Yb. The motivation for selecting CaYAlO₄ crystal is due to the fact that: first, the site has no inversion symmetry therefore making large transition strengths possible and second, Ca and Y sites distances are closer than in YAG, favoring strong energy transfers.

II. Er,Yb Upconversion Model

The most probable path for upconversion in Er is achieved when two excited Yb ions transfer their energy to one Er. This results in excitation from $^4I_{15/2}$ to $^4I_{11/2}$ and from $^4I_{11/2}$ to $^4F_{7/2}$. From $^4F_{7/2}$ the Er relaxes nonradiatively to $^4S_{3/2}$. A rate equation approach has been used to model the population of levels in Er and Yb in order to predict the necessary parameters needed for various applications.¹ The energy levels and processes included in the model are shown in Fig. 1. Er cross relaxation from $^4S_{3/2}$ was not included due to the low Er concentration used in our samples. The corresponding equations are as follows:

$$dN_2/dt = \sigma \cdot \phi \cdot N_1 - A_{21}N_2 + C_{52}N_5N_1 - C_{25}N_2N_3 - C_{26}N_2N_5$$

$$dN_4/dt = A_{54}N_5 - A_{43}N_4 + A_{64}N_6$$

$$dN_5/dt = -(A_{53} + A_{54})N_5 + C_{25}N_2N_3 - C_{52}N_5N_1 - C_{26}N_2N_5 \\ + A_{65}N_6$$

$$dN_6/dt = C_{26}N_2N_5 - A_{65}N_6 - A_{64}N_6 - A_{63}N_6$$

$$N_1 + N_2 = N_{Yb}$$

$$N_3 + N_4 + N_5 + N_6 = N_{Er}$$

Here A_{21} , A_{43} , A_{53} , A_{54} , A_{63} , A_{64} and A_{65} are decay rate constants, N_{Yb} and N_{Er} are the total concentrations of Yb and Er, σ is the Yb absorption cross section at the pump wavelength, and ϕ is the pump flux, which is treated as constant over the pump pulse duration of t_p . C_{25} and C_{26} are forward and upconversion transfer rate constants and C_{52} is the back transfer constant. The parameter values are given in the Table. The back transfer from level 6 was neglected, due to the rapid decay of $^4F_{7/2}$ and $^2H_{11/2}$ to $^4S_{3/2}$. The energy levels of Yb and Er in $CaYAlO_4$, calculated from a quantum mechanical model, show rather small mismatches for all the transfers. Also, the electric dipole strengths of the $^4I_{11/2} \rightarrow ^4F_{7/2}$ and $^4I_{11/2} \rightarrow ^4I_{15/2}$ transitions are predicted by the quantum mechanical model to be about equal. Therefore we assumed that the forward transfer and upconversion rates are equal: $C_{25} = C_{26}$.

III. Experimental Conditions

Transition rates were inferred from a combination of fluorescence lifetime and fluorescence branching ratio measurements. Lifetimes were obtained using pulsed Ti:sapphire, Nd:YAG pumped dye and diode laser pumping. Detection was performed by Ge and InGaAs photodiode detection. Branching ratios were obtained using excitation by Xe lamp and measurement by calibrated monochromator/detector system. Upconversion efficiency was inferred by similar branching ratio measurements, except for the excitation mechanism. Side pumping was performed using two uncooled InGaAs diode arrays, each consisting of three 1 cm bars with average wavelength 971 nm (7nm FWHM), output of 40 W per bar, pulse duration of 1 msec and pulse repetition frequency of 3 Hz.

IV. Results

This set of differential equations was solved numerically using a Runge-Kutta routine. The values of C_{25} and C_{52} were constrained to obey $C_{52}/C_{25} = 1.4$, consistent with experimental data, and their magnitude varied to fit the experimental population ratio $N_6/N_4 = 0.028$. The resulting value $C_{25} = 6.0 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ is plausible, being above the lower limit given in the Table and comparable to the values reported for Yb to Er

transfer in glass. We found that the Er concentrations in our samples are too high to permit population inversion for any potential laser transition for a realistic pump flux. To determine the likelihood of achieving laser oscillation in Er,Yb:CaYAlO₄ we have repeated the calculations with the Er concentration reduced to $1 \times 10^{19} \text{ cm}^{-3}$, a value typical of Er,Yb:glass. The resulting threshold flux is still quite high (Fig. 2), $1.4 \times 10^{23} \text{ cm}^{-2} \text{ s}^{-1}$ to invert the green $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transition. The infrared $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition inverts at about $1 \times 10^{23} \text{ cm}^{-2} \text{ s}^{-1}$. It should be noted, however, that in this model each manifold is treated as a single level.

The Er $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition exhibits advantages of smooth, broad emission and a stimulated emission cross section substantially larger than that of Er:glass. The Yb absorption and Yb-Er transfer rates are also satisfactorily large. However, the 1.5 μm laser threshold estimated from the upconversion model is quite high. This is attributable to the relatively long Er $^4\text{I}_{11/2}$ fluorescence lifetime, which promotes both back transfer to Yb and upconversion. CaYAlO₄ is thus not very attractive as a laser host for sensitized Yb,Er 1.5 μm operation. Due to the large cross section and inhomogeneous broadening, Er:CaYAlO₄ may still perform well in laser applications where the $^4\text{I}_{13/2}$ state is pumped directly.

We observe the effectiveness of upconversion in populating the Er³⁺ $^4\text{S}_{3/2}$ state upon pumping the Yb³⁺ $^2\text{F}_{5/2}$ manifold to be considerably better in CaYAlO₄ than in YAG. However, under diode array sidepumping conditions similar to those for realistic laser experiments, the ratio of the total emission photon flux for all the Er $^4\text{S}_{3/2} \rightarrow ^4\text{I}_J$ transitions to the photon flux for the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition is still quite small, 0.028, due in part to nonradiative decay of the $^4\text{S}_{3/2}$ manifold. The prospects for upconversion laser operation in Er,Yb:CaYAlO₄ depend on the cause of this decay. If it is due to cross relaxation rather than multiphonon emission, proper choices of Er and Yb concentration may reduce the decay rate. In such a case this material may be an interesting candidate for upconversion laser operation.

V. Conclusions

This model predicts pump and concentrations needed for population inversion. Due to rapid decay of $^4\text{S}_{3/2}$ more pump flux is needed for this level to be inverted. The threshold for $^4\text{I}_{13/2}$ to $^4\text{I}_{15/2}$ transition needs a lower pump flux than for the $^4\text{S}_{3/2}$ level. However the long lifetime of $^4\text{I}_{11/2}$ promotes back transfer and upconversion, thus keeping the IR (1.5 μm) threshold higher than desired.

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Reference

1. Johnson, Guggenheim, Rich and Ostermayer, J. Appl. Phys., Vol. 43, No. 3, March 1972.

Fig. 1

Table . Parameters for Er,Yb:CaYAlO₄ upconversion model.
The symbols are defined in the text and Fig.1
Standard deviations are given where known.

measured:	A ₂₁	1245 s ⁻¹
	A ₄₃	220 ± 20 s ⁻¹
	(A ₅₃ + A ₅₄)	2520 ± 94 s ⁻¹
	A ₅₃	405 ± 327 s ⁻¹
	A ₅₄	2115 ± 327 s ⁻¹
	A ₆₃	450 ± 215 s ⁻¹
	A ₆₄	1350 ± 635 s ⁻¹
	A ₆₅	8000 ± 850 s ⁻¹
	C ₂₅	≥ 3 × 10 ⁻¹⁷ cm ³ s ⁻¹
	C ₅₂	(1.40 ± 1.34) × C ₂₅
	N _{Yb}	1.05 × 10 ²¹ cm ⁻³
	N _{Er}	1.33 × 10 ²⁰ cm ⁻³
	σ	7.3 × 10 ⁻²¹ cm ²
upconversion		
experimental		
conditions:	φ	4.0 × 10 ²⁰ cm ⁻² s ⁻¹
	t _p	1 ms
upconversion		
fitting		
results:	C ₂₅ = C ₂₆	6.0 × 10 ⁻¹⁷ cm ³ s ⁻¹
	C ₅₂	8.4 × 10 ⁻¹⁷ cm ³ s ⁻¹