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Measurement and Analysis of Upconversion Rates of Er:YAG at Room Temperature

by G. A. Newburgh, T. Sanamyan, and M. Dubinskii

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**A reprint from the 2009 SPIE Defense and Security Symposium,
Orlando, FL, 13–17 April 2009.**

NOTICES

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ABSTRACT

We have measured upconversion fluorescence resulting from the excitation of room temperature 1% and 5% Er:YAG by a 1532 nm nanosecond pump source. Measurements of the fluorescence decay from the $^4I_{13/2}$, $^4I_{11/2}$, $^4F_{9/2}$ and $^4S_{3/2}$ manifolds to the $^4I_{15/2}$ ground state manifold were observed over a wide range of excitation pulse fluence values. A unique set of upconversion parameters were extracted from the measurements using a modification of the traditional rate equation model. Results of calculation are compared to measurement.

Keywords: Er:YAG, upconversion, cooperative upconversion, cross relaxation, experiment, modeling, upconversion coefficients.

1. INTRODUCTION

Upconversion in Er:YAG has been studied for a number of years but recently has acquired new interest due to the design and testing of resonantly pumped high power Er:YAG lasers. Although many have investigated efficiency losses in Er:YAG lasers attributed to upconversion and found that loss fraction is small especially at low Erbium concentrations (< 4%) [1, 2, 3] accurate accounting for upconversion losses remains desirable. In an effort to improve the understanding of the upconversion process, especially in Er:YAG, we have measured the dynamics of the upconversion process in Er:YAG over a range of excitation fluence values (25 – 350 mJ/cm^2) and Erbium dopant concentrations (1% and 5%). The intention of this effort was to extract a single set of cross relaxation and cooperative conversion coefficients applicable over a wide range of 1532 nm pump conditions and low Erbium concentrations. Until now, we believe that published upconversion coefficients were determined from a narrow range of experimental conditions thereby making the extracted upconversion constants less than universal.

As with other authors, the determination of the upconversion constants was approached by fitting calculation to measured fluorescence decay with a variable set of upconversion parameters. During the course of analyzing the experimental results, it was found that the standard rate equation model which served as a basis of the calculations did not allow a single set of constants for fitting. That is, efforts to model the measured fluorescence decay dynamics over the widely varying pump conditions and Erbium dopant concentrations pointed to the impossibility of using a single set of energy transfer (upconversion) coefficients. Therefore a modification to the rate equation model was tried under the assumption that a more accurate model of the distribution of the Erbium ion, one that reflects the physical fact that Erbium ions are not evenly distributed [4] within the YAG crystal would more accurately account for upconversion. The modified model will be presented in this paper.

2. EXPERIMENT

A series of experiments were designed to measure the fluorescence decay of the $^4I_{13/2}$, $^4I_{11/2}$, $^4F_{9/2}$ and $^4S_{3/2}$ manifolds to the $^4I_{15/2}$ ground state manifold in room temperature Er:YAG powder excited by a 1532 nm 10 nanosecond pulse. An OPO was used as a source of the 1532nm radiation. The experiments varied the average fluence of the excitation pulse energy from about 100mJ/cm^2 to 12000 mJ/cm^2 and Er doping concentrations from 1% and 5%.

Care was taken to spatially condition the excitation pulses exiting the OPO for maximum uniformity. A divergent lens was placed in the beam path to expand the beam and a spatial filter placed before and after the divergent lens to reduce the intensity variation across the beam. The 0.7 mJ beam was then focused onto the Er:YAG sample by means of a 50 mm focal length lens. The distance between lens and sample was varied so as to vary the focal spot size from a diameter of 1.5 mm to a diameter of 0.4 mm. Two examples of the beam profile are shown in Figure 1. The profiles were recorded by an NIR Spiricon camera at every setting of the 50 mm fl lens used for excitation of the Er:YAG powder.

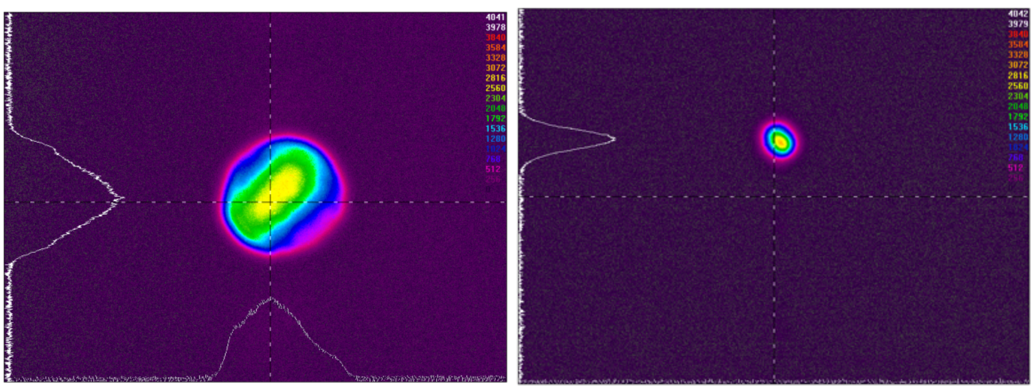

Figure 1 Example of 1532 nsec excitation Pulse Beam Profile: 1.5 and 0.4 mm diameter

Clearly, despite spatial conditioning efforts, the pump spots are non-uniform. As upconversion is a non-linear process, precise analysis of the upconversion dynamics required a precise knowledge of the distribution of pump spot fluence. For accurate fitting of the measured results with calculation, the pump spot intensities were broken down into seven fluence levels. An example of the fluence spot distributions is shown in Figure 2.

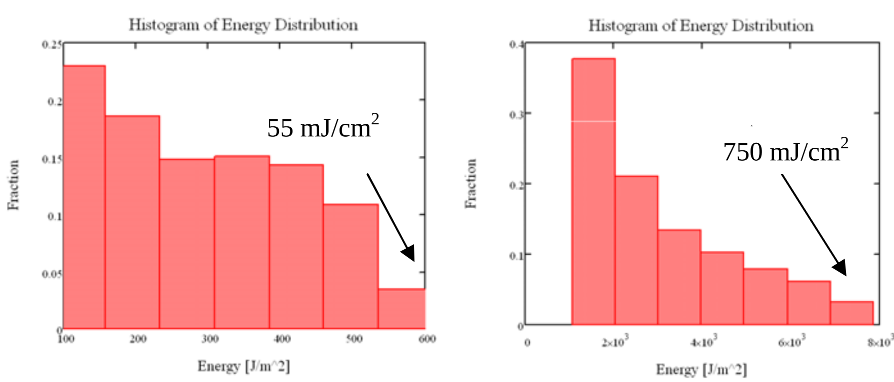

Figure 2 Pump Pulse Fluence Distribution

Samples from Scientific Materials were obtained for this effort at four Er doping concentrations of 0.5, 1.0, 2.0 and 5%. For this paper only the 1% and 5% samples are analyzed as they represent both a large range in Er concentration while allowing for adequately strong fluorescence signals at 550, 650 900 and 1500 nm. Er:YAG powder was selected as a means of avoiding lengthening of fluorescence lifetimes resulting from re-absorption of light by bulk Er:YAG. The powder thickness was estimated to be less than 20 µm. Emission in the 1500 nm range was detected by an amplified InGaAs detector with a 1400 nm long pass filter, while emission at 550, 650 and 900 nm was detected by a S1-like, R5108 TEC cooled PMT using 550, 650 Band pass and 850 long pass filters as appropriate. Response of the PMT signal was recorded by a 1GHz Tektronix oscilloscope.

3. MODEL

Upconversion in Er:YAG is a result of energy transfer between excited Erbium ions. Existing models for calculation of cross-relaxation or cooperative conversion between pairs of excited ions assume a homogeneous distribution of ions in the material. Initially, we applied Eq.(1),

$$\frac{dN_j}{dt} = -\frac{N_j}{\tau} + C_{Er} W N_j^{\ 2} \tag{1}$$

as a basis of for modeling the evolution of the Er manifolds (see Figure 5) where N_j, is the excited ion density of the j^{th} manifold, C_{Er} is the Er ion concentration, τ, is the fluorescence lifetime of the excited ion and W is the upconversion rate parameter. However, adequate fitting over the range of excitation fluences and two Er dopant concentrations using this traditional form of the expression proved impossible. Instead, a modification to Eq. (1) was proposed by changing the homogeneous model of N to one that reflected the localization of Er within the YAG host.

Based on the Y coordinates in YAG [5], an excited Er ion may find itself at any of 14 different distances from another excited Er ion in the range of 3 to 12Å. At any of the 14 discrete, R distances, the excited Er may see up to w other excited Erbium ions. As an example, $R_0 = 3.67$ Å may see $w_0 = 4$ other excited Er, while at $R_{14} = 12.01$ Å, $w_{14} = 6$. The distribution of possible inter-Erbium distances is shown in Figure 3.

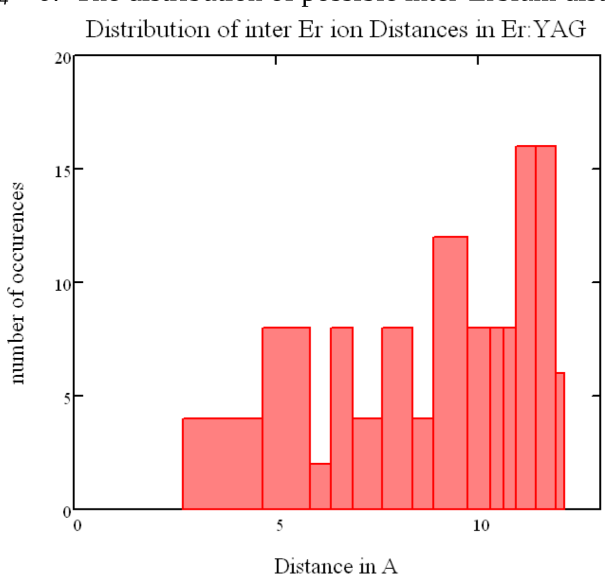

Figure 3 Distribution of Inter-Er Ion Distances in Er:YAG

In calculating upconversion rates, our model assumes that an excited ion can undergo energy transfer only with one other excited Er ion within a radius of 1 lattice constant of 12 Å. That is, an excited ion can see at most one other excited ion. Given this assumption as well as the set of 14 inter-Er distances, R_i, the single, homogeneous ion density model of the j^{th} manifold, N_j, is converted into a set of 14 Er ion "non-homogeneous" densities, $n_{i,j}$ of probability, p_i, which according to Eq. (1) allows us to write,

$$N_j \rightarrow n_{i,j} = N_j \frac{p_i}{R_i^3} \quad where \quad i = 1, 2, ...13, 14 \; and \; p_i = w_i \sum_{k=1}^{14} \frac{R_k^3}{w_k} \tag{2}$$

Such that,

$$N_j \sum_{k=1}^{14} \frac{p_k}{R_k^3} = N_j \sum_{i=1}^{14} n_{i,j} = N_j \tag{3}$$

The results of this calculation are tabulated in Table 2. Note the wide ranging Er-Er ion densities.

R	Relative ion density	Frequency of occurrence
0.30619	34.83719	0.03571
0.46771	9.77413	0.07143
0.5	8	0.01786
0.55902	5.72433	0.07143
0.5863	4.96176	0.03571
0.68465	3.11593	0.07143
0.70711	2.82843	0.03571
0.77055	2.18572	0.10714
0.84779	1.64109	0.07143
0.86603	1.5396	0.07143
0.90139	1.36542	0.07143
0.91856	1.29027	0.14286
0.98425	1.04878	0.14286
1	1	0.05357

Table 1 "non-homogeneous" Er ion densities

Seen from a standpoint of energy transfer between excited ions, a volume of excited Er:YAG ions is a collection of discrete ion densities of relative magnitudes of 1 to 34 and occurring with relative weights ranging from 0.018 to 0.143.

Application of Eq. (2) leads to a new form of the rate equations governing the occupancy in an Er ion as,

$$\frac{dN_j}{dt} = \sum_{i=1}^{14} p_i \frac{dn_{i,j}}{dt} \quad where \quad \frac{dn_{i,j}}{dt} = -\frac{n_{i,j}}{\tau} + Cn_{i,j}^2 \tag{4}$$

Using the modified rate equation (Eq.4), a new set of rate equations was generated for the calculation of the upconversion and decay dynamics of the Er:YAG ion under 1532 nm pumping. The model accounted for cross relaxation (constant C_{0531}), cooperative upconversion (C_{1103}, C_{2205} , C_{1204} & C_{1305}) and radiative (A_{10}, A_{20},A_{30}, A_{40}, A_{50}) and non-radiative (A_{54}, A_{43},A_{32}, A_{21}) decay between the levels

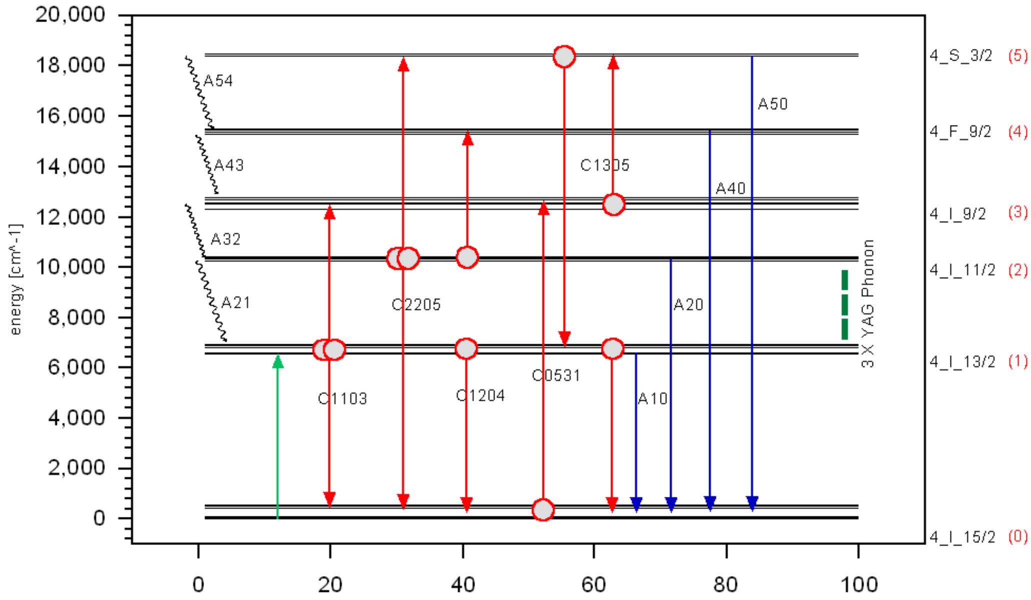

Figure 4 Er Level Scheme with Upconversion

as shown in Figure 4.

Leading to the set of equations to be calculated,

$$\frac{dn_{i,0}}{dt} = \sum_{j=1}^{5} A_{j0} n_{i,j} + C_{1103} n_{i,1}^2 + C_{2205} n_{i,2}^2 + C_{1204} n_{i,1} n_{i,2} - C_{0531} n_{i,1} n_{i,5} + C_{1305} n_{i,1} n_{i,3}$$

$$\frac{dn_{i,1}}{dt} = A_{21} N_2 - 2C_{1103} n_{i,1}^2 - C_{1204} n_{i,1} n_{i,2} + C_{0531} n_{i,1} n_{i,5} - C_{1305} n_{i,1} n_{i,3}$$

$$\frac{dn_{i,2}}{dt} = - A_{21} N_2 + A_{32} N_3 - 2C_{2205} n_{i,2}^2 - C_{1204} n_{i,1} n_{i,2}$$

$$\frac{dn_{i,3}}{dt} = - A_{32} N_3 + A_{43} N_4 + C_{1103} n_{i,1}^2 + C_{0531} n_{i,1} n_{i,5} - C_{1305} n_{i,1} n_{i,3} \qquad (5)$$

$$\frac{dn_{i,4}}{dt} = - A_{43} N_4 + A_{54} N_5 + C_{1204} n_{i,1} n_{i,2}$$

$$\frac{dn_{i,5}}{dt} = - A_{54} N_4 + C_{1204} N_1 N_2 + C_{2205} n_{i,2}^2 - C_{0531} n_{i,1} n_{i,5} + C_{1305} n_{i,1} n_{i,3}$$

which must be calculated for each of the i = 0, 1…13, 14 "non-homogeneous" Er ion densities and summed to give the ensemble average.`

4. ANALYSIS

A rate–equation analysis of the set of fluorescence decay measurements from the $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$ & $^4S_{3/2}$ to the ground state was made based on the application of Eq (5). The data set selected for analysis consisted only of 1% and 5% Er dopant concentrations. The procedure of fitting measurement to calculation consisted of matching the measured and calculated decay slopes as best as possible, based on a single set of upconversion coefficients, *C*. Modeling of the experimental results accounted for the non-uniformity of the 1532 nm beam profile by calculating the initial ion densities of the $^4I_{13/2}$ and $^4I_{15/2}$ levels for seven discrete fluence levels as shown in Figure 2. Examples of the fitting of experiment to calculation are presented in Figures 5 & 6 using the constants as tabulated in Table 2. Although not perfect, comparison of measurement to calculation validates the modification of the upconversion rate equation description based on a non-homogenous Er ion description.

We believe that the modification of the Er ion concentration model from a homogeneous to a non-homogenous description results in a more accurate physical description of upconversion dynamics. Comparison of upconversion constants as derived in this paper compare favorably with previously published results.

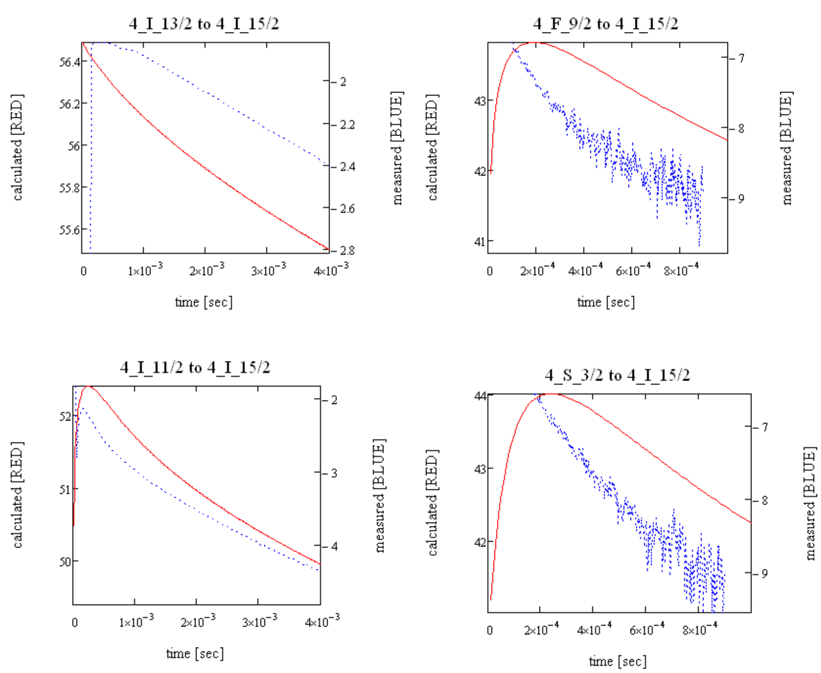

Figure 5 Log-Linear fitting of fluorescence decay in 1% Er:YAG at an average fluence of 380 mJ/cm^2

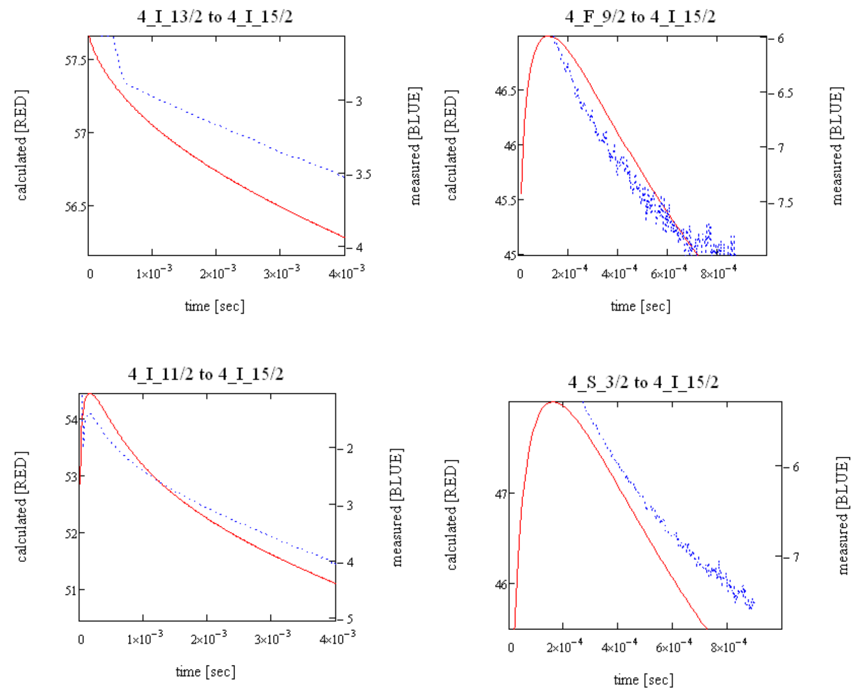

Figure 6 Log-Linear fitting of fluorescence decay in 1% Er:YAG at an average fluence of 1200 mJ/cm^2

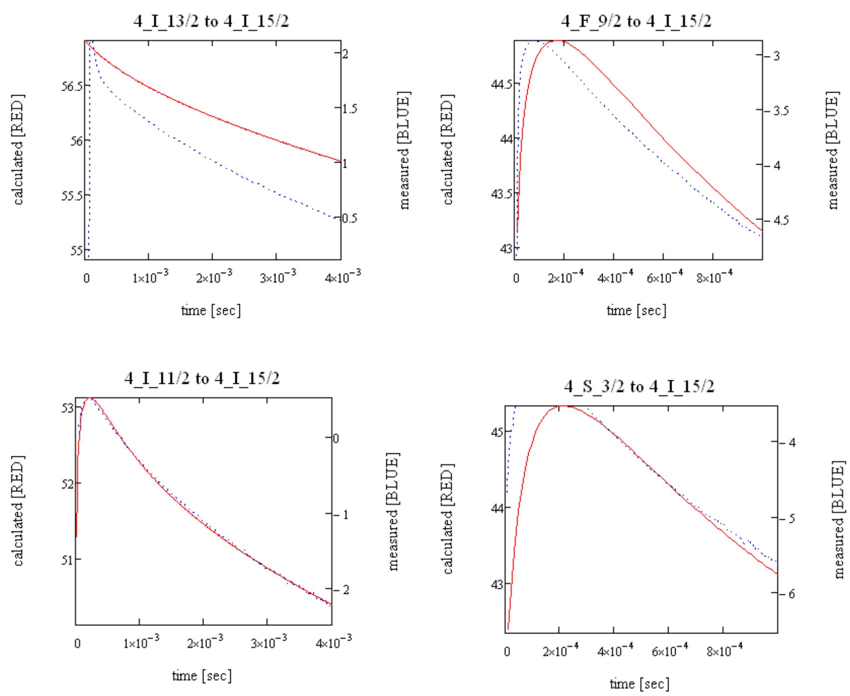

Figure Log-Linear fitting of fluorescence decay in 5% Er:YAG at an average fluence of 110 mJ/cm^2

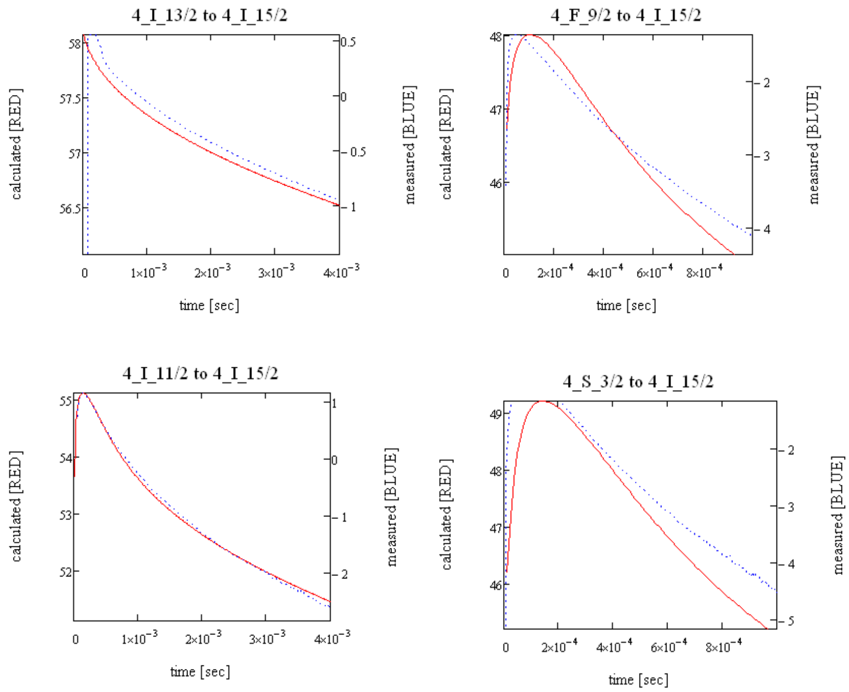

Figure 7 Log-Linear fitting of fluorescence decay in 5% Er:YAG at an average fluence of 380 mJ/cm^2

Upconversion Constant	This work [cm^3/sec]	Previous Authors [cm^3/sec]
C_{1103}	1.5 *10^{-17}	(1.5 – 2.5) *10^{-17} [6,7]
C_{2205}	1.0 * 10^{-17}	(3-5) 10*10^{-17} [7]
C_{1204}	5 * 10^{-18}	1.8 * 10^{-18} [8]
C_{1305}	3 * 10^{-17}	3.8 * 10^{-18} [8]

Table 2 Upconversion List

5. CONCLUSION

We have presented upconversion fluorescence measurements of 1% and 5% Er:YAG over a wide range of pulse excitation fluences. A modified form of the traditional rate equation model expressing the inversion of the Er:YAG ion has been proposed based on a discrete distribution of Er ions in the YAG host. Upconversion constants are extracted from measurement using the new rate equation model and compared to published values.

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