Determination of energy transfer parameters in Er^{3+}-doped and Er^{3+}, Pr^{3+}-codoped ZBLAN glasses

Paul S. Golding, Stuart D. Jackson*, Terence A. King
Department of Physics and Astronomy, University of Manchester, Manchester M13 9PL, UK.
paul@fs4.ph.man.ac.uk

Markus Pollnau
On leave from: Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland.

Abstract: A detailed characterization of energy level lifetimes and energy-transfer processes in Er^{3+}-doped and Er^{3+}, Pr^{3+}-codoped ZBLAN bulk glasses is presented. Energy transfer upconversion parameters from the Er^{3+} $^4I_{13/2}$ and $^4I_{11/2}$ levels have been measured and are compared to energy transfer from Er^{3+} to a Pr^{3+} codopant. To assess the practicality of energy transfer a high power, diode pumped, 3 µm, Er^{3+}, Pr^{3+}- codoped ZBLAN fiber laser is presented.
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Introduction

Erbium 3 µm fiber lasers have long been suggested as devices with great potential for surgical use, owing to the strong absorption of radiation by water at this wavelength, and their efficient, compact, design. High output powers from Er^{3+}-doped ZBLAN fiber lasers is often limited, however, by ground-state bleaching arising from undesired excited-state absorption (ESA) from the $^4I_{13/2}$ and $^4I_{11/2}$ laser levels. This can lead to saturation of the 2.7 µm emission by competitive co-lasing at 850 nm [1]. A solution to this problem is the cascade laser system which has been shown to provide unsaturated output but requires high pump intensities and careful mirror selection [2]. Under low-brightness diode laser excitation, however, the cascade laser mechanism is no longer attainable and a different approach is required. Two different operational regimes have been suggested: quenching of the $^4I_{13/2}$ lifetime by energy transfer (ET) to a Pr^{3+} codopant or energy recycling from $^4I_{13/2}$ level by energy transfer upconversion (ETU) (Fig. 1). As part of a study to determine ultimately which of these provides the best approach, we have measured the intrinsic lifetimes of the Er^{3+} $^4I_{13/2}$, $^4I_{11/2}$, and $^4S_{3/2}$ / $^2H_{11/2}$ levels, and investigated the major energy-transfer processes such as ETU from the Er^{3+} $^4I_{13/2}$ and $^4I_{11/2}$ laser levels, ET from these levels to the corresponding levels of a Pr^{3+} codopant, and cross relaxation (CR) from the thermally coupled Er^{3+} $^4S_{3/2}$ / $^2H_{11/2}$ levels in Er^{3+}-doped and Er^{3+}, Pr^{3+}- codoped ZBLAN glass. The macroscopic energy-transfer parameters of all these processes are derived and their dependence on Er^{3+} and Pr^{3+} concentrations is investigated. In addition, the validity of energy transfer for high power laser operation is assessed with the design and construction of a 3 µm, Er^{3+}, Pr^{3+} codoped fiber laser

Method

Lifetimes as well as the parameters of ETU, CR, and ET for Er^{3+}-doped and Er^{3+},Pr^{3+}-codoped in ZBLAN bulk glasses (Le Verre Fluoré, France) were determined by measuring luminescence decay

from the $^4I_{13/2}$, $^4I_{11/2}$ levels, and the thermally coupled $^4S_{3/2}$ / $^2H_{11/2}$ levels to the $^4I_{15/2}$ ground state following direct excitation of these levels at 532, 979, and 1510 nm, respectively.

The excitation source for the spectroscopic measurements was an in-house KTP optical parametric oscillator (OPO) pumped by a frequency-doubled, 10-Hz, Q-switched Nd:YAG laser (Spectron SL802G) at 532 nm. To excite the $^4I_{13/2}$ energy level a center pump wavelength of 1510 nm was selected. For the $^4I_{11/2}$ energy level the center pump wavelength was tuned away from the ground-state absorption (GSA) peak at 973 nm to 979 nm to ensure that GSA was significantly greater that ESA [3]. The lifetime of the thermally coupled $^4S_{3/2}$ / $^2H_{11/2}$ energy levels was measured after direct excitation by the second harmonic of the Q-switched Nd:YAG laser at 532 nm. The luminescence from the samples was imaged onto the entrance slit of a 30-cm monochromator, and the resulting signal was detected using an InGaAs photodiode (Hamamatsu G5746-01) to detect the $^4I_{13/2}$ luminescence at 1560 nm and a silicon photodiode (IPL 10530DAL) to detect the 1010-nm ($^4I_{11/2}$) and 550-nm ($^4S_{3/2}$) luminescences. The spectra were analyzed and ET, ETU and CR parameters were calculated according to a previously published method [4].

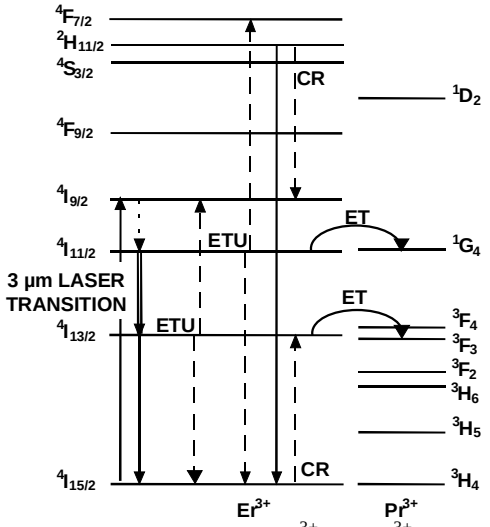

Fig 1. Partial energy-level diagram of Er^{3+} and Pr^{3+} in ZBLAN glass.

Results

Erbium singly doped ZBLAN.

The fluorescence lifetimes of the $^4I_{13/2}$, $^4I_{11/2}$, and $^4S_{3/2}$ erbium energy levels are shown in Fig 2. For the lowest doped samples the measured luminescent lifetimes of the $^4I_{13/2}$ and $^4I_{11/2}$ levels were 9.0 ± 0.2 ms and 6.9 ± 0.1 ms respectively. The effect of the Er^{3+} concentration upon the luminescent lifetime of the $^4S_{3/2}/^2H_{11/2}$ levels is also shown in Fig. 2. The $^4S_{3/2}$ level is in thermal equilibrium with the $^2H_{11/2}$ level, therefore, after excitation, the population relaxes to the Boltzmann distribution within the two levels. At high Er^{3+} concentrations, the luminescent lifetime of these levels is shortened as a result of the CR processes ($^2H_{11/2}$, $^4I_{15/2}$) → ($^4I_{9/2}$, $^4I_{13/2}$) and ($^2H_{11/2}$, $^4I_{15/2}$) → ($^4I_{13/2}$, $^4I_{9/2}$). The observed luminescence from the $^4S_{3/2}$ / $^2H_{11/2}$ levels shows a dramatic reduction in lifetime with a value of 518 ± 6 µs for an Er^{3+} concentration of 4×10^{19} cm^{-3} falling to 21 ± 1 µs for an Er^{3+} concentration of 1.4×10^{21} cm^{-3}.

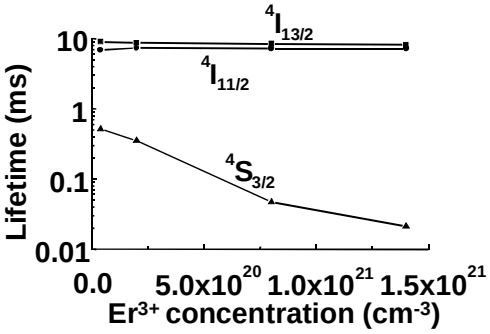

Fig. 2. Erbium energy level lifetimes.

An example luminescence decay curve is shown in Fig. 3. It can be seen that the $\ln(I/I_0)$ versus time curve begins with a nonlinear section which is dependent upon excitation density, N_0, as a result of ion-ion interactions. This is followed by an exponential decay which is the intrinsic decay of the erbium ion. This decay was used to calculate the fluorescence lifetimes shown in Fig. 2. ETU parameters were calculated according to a previously published method [4], as follows. If N represents the time-dependent population density of the excited level, then the rate equation for N is given by:

$$\frac{dN}{dt} = -\frac{N}{\tau} - 2W_{ETU}N^2. \tag{1}$$

where τ is its intrinsic lifetime, and W_{ETU} is the macroscopic ETU parameter. It has been shown [5] that with $N(t=0) = N_0$, integration yields

$$[N_0/N(t)]\exp(-t/\tau) - 1 = 2W_{ETU}N_0\tau[1-\exp(-t/\tau)]. \tag{2}$$

Replotting Fig. 3. with respect to equation (2) gives Fig. 4. From the initial gradient of this curve, which has a value of $2WN_0\tau$, the upconversion parameter can be obtained.

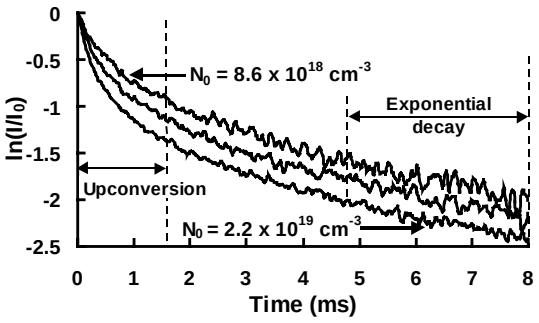

Fig. 3. Luminescence decay curve from the $^4I_{13/2}$ energy level. (Er^{3+} concentration = 1.4 x 10^{21} cm^{-3}). N_0 is the initial excitation density.

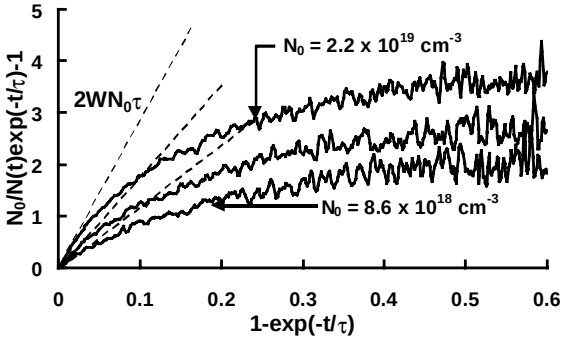

Fig 4. Linearization of Fig. 3 with respect to W. N_0 is the initial excitation density.

The degree of upconversion is dependent upon both the excited-state population density for a given concentration and the Er^{3+} concentration within a sample. Energy transfer upconversion parameters have been calculated for the $^4I_{11/2}$ and $^4I_{13/2}$ and are displayed on Fig. 5. along with the $^4S_{3/2}$ / $^2H_{11/2}$ cross relaxation parameters. The findings from this investigation show strong upconversion parameters for the $^4I_{13/2}$ level with the $^4I_{11/2}$ level parameter being approximately three times lower. These values are comparable to that of crystal hosts, e.g. $LiYF_4:Er^{3+}$ [6], and as such should provide an effective mechanism for energy recycling in ZBLAN, provided that optimum concentrations are available.

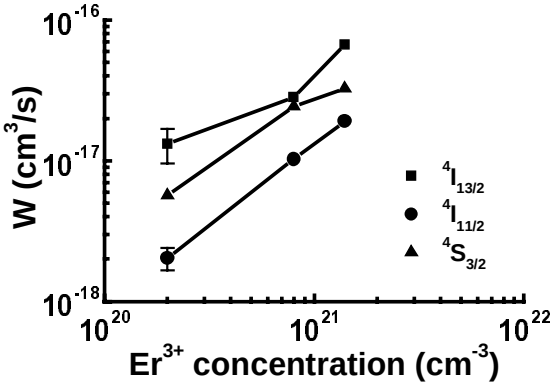

Fig. 5. Energy transfer upconversion and cross-relaxation parameters as a function of Er^{3+} concentration

Praseodymium codoping.

Pr^{3+} has been suggested as a possible codopant for erbium in the crystal host BaY_2F_8 and $LiYF_4$ [6], and in ZBLAN glasses [7], to reduce the lifetime of the $^4I_{13/2}$ lower laser level. The introduction of a small amount of Pr^{3+} to the samples rapidly depletes the $^4I_{13/2}$ level whilst having a much lesser effect on the $^4I_{11/2}$ level (Fig. 6.). Increasing the Pr^{3+} concentration leads to enhanced quenching of both levels whilst retaining the large lifetime difference between them. The overall change in intrinsic lifetime of the energy levels, however, decreases with increasing Pr^{3+} concentration to the maximum level used. Therefore, we suggest that only small amount of Pr^{3+} is necessary in an efficient codoped fiber laser system.

The luminescence decay from the codoped samples can be described by the following equation:

$$1/\tau_{eff}(Er^*) = 1/\tau(Er^*) + W_{ET}\, N(Pr) \qquad (3)$$

where $\tau_{eff}(Er^*)$ is the effective lifetime of the excited level of Er^{3+} in which ET is observed, $\tau(Er^*)$ is the intrinsic lifetime of the same level, N(Pr) is the Pr^{3+} concentration in the sample and W_{ET} is the energy transfer parameter. The ET parameters have been calculated for each of the codoped samples (Fig. 7), where it can be seen that for each energy level the parameters are reasonably insensitive to Pr^{3+} concentration, but increases with erbium concentration in a similar manner to the ETU parameters. This suggests that energy migration within the Er^{3+} $^4I_{13/2}$ and $^4I_{11/2}$ levels is fast.

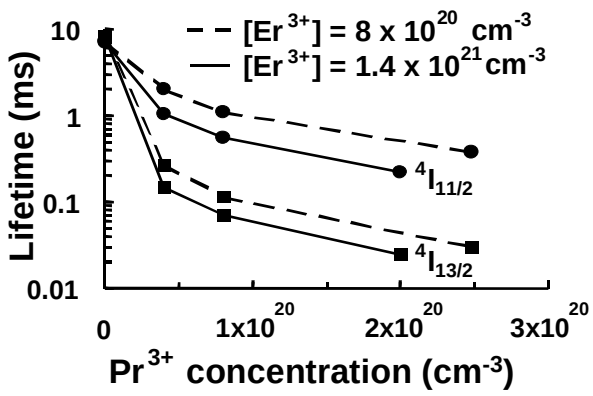

Fig. 6. Effect of Pr^{3+} codoping on Er^{3+} lifetime.

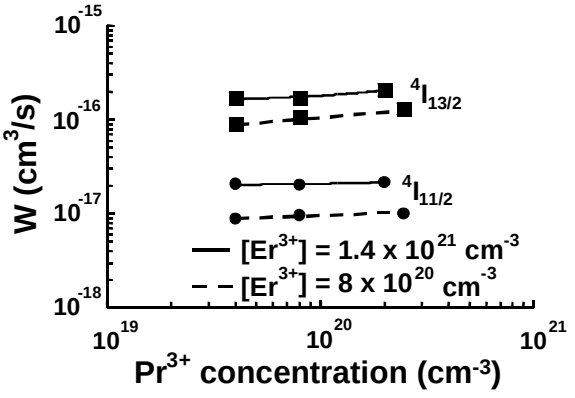

Fig. 7. Energy transfer parameters.

High power Er, Pr – codoped fiber laser.

In order to show the usefulness of the Pr^{3+} as a suitable codopant for Er^{3+} doped fiber lasers, we have demonstrated 1.7W of unsaturated output from a diode pumped Er^{3+}, Pr^{3+}-doped ZBLAN double clad fiber laser [8]. The fiber laser was pumped at a wavelength of 790 nm, which excites the $^4I_{9/2}$ level of Er^{3+}, and the core was doped with 6.3×10^{20} cm^{-3} Er^{3+} and 5.4×10^{19} cm^{-3} Pr^{3+}. The experimental setup is shown in Fig. 8. A mirror which was highly (~99%) reflecting at 790 nm placed at 45° to the pump-light direction steered the pump light onto the input end of the fiber while also effectively transmitting (>99.5%) the fiber-laser output. Two different cavity configurations were used. The first used just the Fresnel reflection at each end of the fiber to provide feedback (denoted resonator A) whilst the second cavity arrangement incorporated a mirror which was highly reflecting at both the pump (>99.9% reflecting) and laser (>99.7% reflecting) wavelengths butted against the distal end of the fiber (denoted resonator B). The performance of this laser is shown in Fig. 9. In the case of resonator A, the counter-propagating output was determined to have a slope efficiency of 12% with respect to the launched pump power and for the co-propagating output this value was 5.2%. The overall threshold launched pump power for this fiber-laser configuration was measured to be 0.52 W. For resonator B, the slope efficiency was determined to be 17.3% with a slightly reduced threshold pump power of 0.47 W.

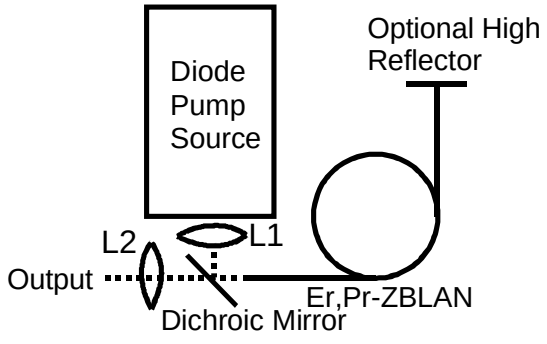

Fig. 8. Experimental setup for fiber laser.

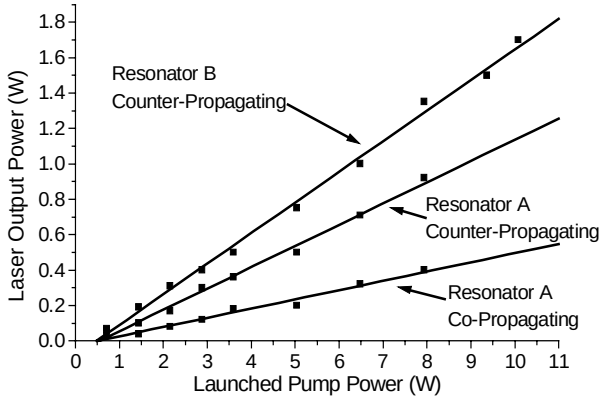

Fig. 9. Laser performance.

Discussion

The 3µm laser transition of erbium is based on a simple 4 level laser scheme. This is complicated, however, by the metastable lifetime of the $^4I_{13/2}$ lower laser level which results in the accumulation of

excited ions. To overcome this problem, erbium crystal lasers are highly doped to exploit upconversion processes. This provides a mechanism that both depletes the $^4I_{13/2}$ lower laser level and recycles some of the energy to the $^4I_{11/2}$ upper laser level. Based on this process, the 3-µm crystal laser is operated CW even for unfavorable lifetime ratios of the laser levels [9] and output powers exceeding 1 W have been obtained. To obtain the highest slope efficiency from such a laser it is important to use optimum Er^{3+} doping levels, which causes the ratio of the probabilities of the $^4I_{11/2}$ and $^4I_{13/2}$ ETU processes to be largest. If this condition is met the slope efficiency may be twice the Stokes efficiency [10,11]. Until recently, ZBLAN glass has been unavailable with high Er^{3+} concentrations and detrimental ESA, rather than ETU, was the dominant factor that affected laser performance. The aim of this research was to investigate whether ETU in Er^{3+} could be exploited to allow for efficient 3µm radiation production, or whether a second operational regime, ET to a Pr^{3+} codopant, would be preferable.

The findings from this investigation show strong upconversion parameters for the $^4I_{13/2}$ level, with the $^4I_{11/2}$ level parameter being approximately three times lower. At the Er^{3+} concentrations investigated here, the ratio of the probabilities of ETU from the $^4I_{13/2}$ lower laser level, which recycles energy to the $^4I_{11/2}$ upper laser level, versus ETU from the $^4I_{11/2}$ upper laser level, which depletes inversion, is more favorable for ZBLAN compared to $LiYF_4$. It is therefore predicted that the optimum Er^{3+} concentration is probably smaller in a fiber laser than the optimum concentration of 2×10^{21} cm^{-3} (= 15 at.%) in $LiYF_4$ [12, 4].

For fibers with lower dopant concentrations, co-doping Er^{3+} with Pr^{3+} allows the system to operate as a four-level laser with short lower and longer upper-state lifetimes. This may be a practical alternative if sufficiently high doping levels are unavailable in optical fibers. This technique allows a doped optical fiber to act as a conventional 4-level laser but limits the slope efficiency [6] to values below the Stokes limit. To demonstrate the effectiveness of praseodymium codoping to enhance the performance of erbium doped ZBLAN fiber lasers, a codoped double clad fiber laser was constructed. This, 790nm diode pumped, device provided up to 1.7 W of unsaturated 2.7 µm output power at a slope efficiency of ~17% with respect to launch pump power (for a 10.5 m long fiber) and a total optical-to-optical efficiency of ~7.6%.

For the future, the possible development of highly Er^{3+}-doped fibers may provide a route to more efficient fiber lasers. Optimized energy transfer upconversion from the lower laser level can recycle ions back to the upper laser level. This energy-recycling regime with its inherent enhancement of the slope efficiency by a factor of two will, thus, be an attractive alternative to Pr^{3+} codoping at higher dopant concentrations.

Conclusion

Energy transfer processes in Er^{3+}-doped and Er^{3+},Pr^{3+}-codoped ZBLAN bulk glasses have been investigated. Energy transfer upconversion parameters for the $^4I_{13/2}$ and $^4I_{11/2}$ energy levels have been found to be comparable to those of $LiYF_4$:Er^{3+}. This should provide an effective mechanism for energy recycling in ZBLAN and possibly enhanced slope efficiencies. Optimum concentrations for this mode of operation are most likely higher than those studied here, but maybe less than that required for $LiYF_4$:Er^{3+} by virtue of a more favorable ratio of the ETU parameters in ZBLAN. Energy transfer from the Er^{3+} $^4I_{13/2}$ and $^4I_{11/2}$ levels to the Pr^{3+} codopant has been shown to effectively reduce the lifetime of the $^4I_{13/2}$, lower, laser level by an order of magnitude more that the $^4I_{11/2}$, upper, level – resulting in a conventional 4-level laser scheme. The validity of co-doping has been demonstrated practical by the production of 1.7W of unsaturated output power from a diode pumped, Er^{3+}, Pr^{3+}- codoped ZBLAN fiber laser.

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* Present address: Optical Fibre Technology Centre, Australian Photonics CRC, 101 National Innovation Centre, Australian Technology Park, Eveleigh NSW 1430, Australia.