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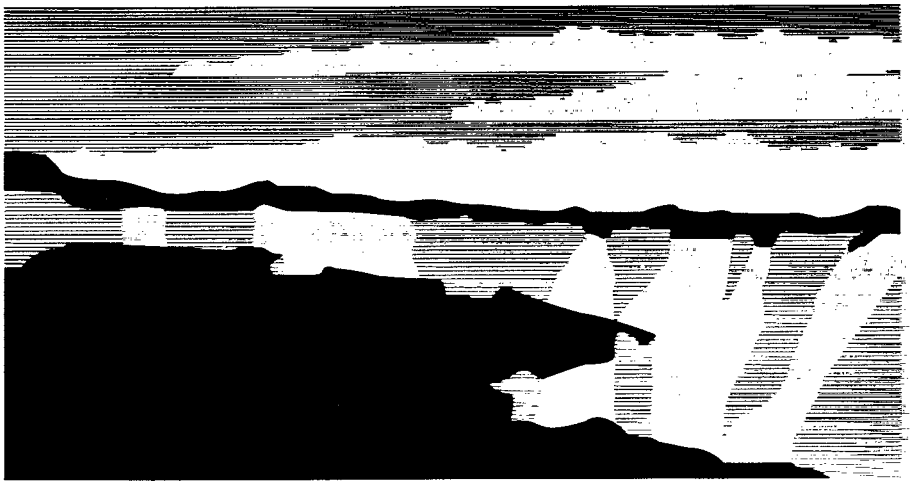

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Upconversion processes in Yb-sensitized Tm:ZBLAN

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ABSTRACT

A systematic spectroscopic study of twenty-two rare-earth-ion doped ZBLAN glass samples was conducted to investigate the feasibility of sensitizing Tm:ZBLAN with Yb to facilitate the development of an efficient and conveniently pumped blue upconversion fiber laser. It was determined that, under conditions of single-color pumping, 480 nm emission from Tm^{3+} is strongest when Yb,Tm:ZBLAN is excited at a wavelength of approximately 975 nm. In this case, the strongest blue emission was obtained from a ZBLAN glass sample with a nominal dopant concentration of approximately 2.0 wt% Yb + 0.3 wt% Tm. Additionally, it was demonstrated that for weak 975 nm pump intensities, the strength of the blue upconversion emission can be greatly enhanced by simultaneously pumping at approximately 785 nm. This increase in upconversion efficiency is due to a reduction in the number of energy transfer steps needed to populate the Tm^{3+} $^1G_4$ energy level. Measurements of fluorescence lifetimes as a function of dopant concentration were also made for Yb^{3+}, Tm^{3+}, and Pr^{3+} transitions in ZBLAN in order to better characterize concentration quenching effects. Energy transfer between Tm^{3+} and Pr^{3+} in ZBLAN is also described.

Keywords: upconversion, ZBLAN, thulium, ytterbium, praseodymium, energy transfer, fluorescence lifetime, spectroscopy, laser

1. INTRODUCTION

Continuous-wave thulium-doped fluorozirconate, or Tm:ZBLAN, fiber lasers have been demonstrated to be efficient devices for the generation of 480 nm blue light. Advantages can include room temperature operation; high gain length times pump intensity products; small, compact packaging; and convenient diode laser pump sources. Demonstrated pump mechanisms in Tm^{3+}:ZBLAN include direct one-color excitation at approximately 1.1 µm[1-5], variations of the 1.1 µm pumping technique that include simultaneous pumping in the red at 645 nm [6] or 680 nm[7], and two-color excitation at 647 and 676 nm[8]. Additionally, avalanche pumping schemes involving single-color excitation in the red have been proposed.[9] It is arguable, however, that convenient, low-cost pump sources at these wavelengths do not currently exist. At present, the most promising results have been obtained using precommercial, tunable, external cavity diode lasers.[3] An alternate approach, yielding more accessible pump wavelengths, involves co-doping the Tm^{3+} doped host with Yb^{3+} ions. This sensitization has resulted in the observation of upconverted blue fluorescence in a variety of materials including silica fiber[10], BaY$_2$F$_8$ [11-12], and a variety of fluoride glasses[13-16], and lasing in BaY$_2$F$_8$ [17]. Several energy transfer mechanisms have been described to explain the upconversion processes. These mechanisms involve either one-color pumping at approximately 780-790 nm or 960-970 nm, or simultaneous two-color pumping at both these wavelengths. For maximum efficiency, the co-dopant concentrations must be optimized for the particular host.

Recent work in Yb^{3+} sensitized Pr^{3+}:ZBLAN has resulted in identification of doping concentrations yielding high Yb^{3+} to Pr^{3+} energy transfer with minimal backconversion.[18] Although the reported goal of that work was the pursuit of a convenient pump mechanism for a 1.31 µm Pr:ZBLAN fiber amplifier, a corollary benefit was the development of an efficient upconversion laser medium.[19] This research was motivated by a desire to determine if a similar optimization scheme could be achieved in Yb,Tm:ZBLAN glass. Towards that goal, we have made fluorescence lifetime measurements for seven optical transitions in a series of Tm:ZBLAN, Yb,Tm:ZBLAN and Tm,Pr:ZBLAN glass samples by direct one-photon excitation. Additionally, we have made both one and two-color excitation measurements in the Tm:ZBLAN and Yb,Tm:ZBLAN samples to determine optimal pumping wavelengths and dopant concentrations. In this paper we will describe the results of that investigation with emphasis on comparisons between our results and previous measurements in the literature, concentration quenching effects, and energy transfer efficiency between sensitizer and activator ions.

2. PULSED EXCITATION EXPERIMENTS

Lifetime measurements were made using a variety of narrow linewidth, nsec pulse duration pump sources to selectively excite specific transitions in bulk glass samples. Yb^{3+} lifetime measurements were made using a Raman upconverted dye laser pumped by the second harmonic output of a Nd:YAG laser. The Tm^{3+} and Pr^{3+} measurements (except for the $^1D_2$ Tm^{3+} transition) were made using an optical parametric oscillator pumped by the third harmonic of a Nd:YAG laser. The Tm^{3+} $^1D_2$ transition was excited directly by the third harmonic of the Nd:YAG laser. In each case, the appropriate emission was isolated using a 1/4 m monochromator in combination with a 10 nm bandwidth dichroic filter. The filtered emission signal was detected using either a Si, Ge, or InGaAs photodiode, sent to a preamplifier with appropriate termination to allow transient resolution, and then to a digital oscilloscope. Oscilloscope traces were then downloaded to a computer for storage.

All samples were approximately 1 cm dimension cubes. Emission was observed perpendicular to the pump beam direction to reduce the amount of scattered pump light incident on the monochromator. Pump beams were weakly focused, resulting in beam spot sizes of approximately 2 mm diameter in the glass samples. Additionally, pump energies were maintained as low as possible to minimize amplified spontaneous emission. All samples were probed along an edge to minimize reabsorption (especially important for the Yb^{3+} lifetime measurements). Most measurements (see following text descriptions) were repeated five times for each sample, probing a different spot each time, to average out possible lifetime variations caused by concentration inhomogeneities in the glass. For a given measurement condition each sample in the glass series was probed once, before changing the height of the sample holder and probing the series again, to reduce the possibility of pump energy variations, temperature fluctuations, or other unknown effects from causing systematic changes in lifetime measurements.

2.1 Sample description

ZBLAN glass samples were obtained from Infrared Fiber Systems, Inc. All samples were approximately 1 cubic cm in size and were polished on at least three surfaces. Table 1 summarizes the nominal dopant concentration(s) contained in each glass melt . Relative Tm^{3+} concentrations in the bulk samples were independently determined by measuring the absorption coefficient for each sample at 684 nm using a spectrophotometer. It was noted that some samples displayed much greater spatially dependent concentration variations than others. Specifically, the 0.5 wt% Yb + 0.1 wt% Tm sample yielded a 684 nm absorption coefficient approximately 67% larger than that of the other 0.1 wt% Tm samples, and the 0.2 wt% Tm doped sample yielded an absorption coefficient approximately half that of the other 0.2 wt% Tm samples. Relative Pr^{3+} concentrations were similarly evaluated by measuring the strength of the absorption at 587 nm. Pr^{3+} absorption coefficients were found to agree reasonably well with nominal dopant concentration.

	Tm concentration (wt%)							
Co-dopant	0.01	0.05	0.1	0.2	0.3	0.5	1.0	2.0
none	×	×	×	×	×	×	×	×
0.5 wt% Yb			×	×				
1.0 wt% Yb			×	×	×			
1.5 wt% Yb			×					
2.0 wt% Yb			×	×	×	×		
0.1 wt% Pr						×		
0.5 wt% Pr			×		×			
2.0 wt% Pr					×			

Table 1. The grid shows nominal dopant concentrations for the series of ZBLAN glass samples used in this study.

2.2 Fluorescence lifetimes

The following seven figures show measured fluorescence lifetime values for seven different transitions in doped ZBLAN glass. In all cases, the lifetime values were obtained from single exponential fits.

Figure 1 refers to the Yb doped ZBLAN samples. It is apparent that the Yb^{3+} upper state lifetime decreases with increasing Tm^{3+} ion concentration. Inspection of the graph shows fairly large run-to-run variations in measured fluorescence lifetimes. These large variations are probably due to radiation trapping effects in the samples, despite attempts (see experimental description above) to minimize this source of error. Lifetime measurements for Tm^{3+} and Pr^{3+} transitions had *much* smaller standard deviations. Additionally, the 2.0 wt% Yb + 0.3 wt% Tm sample has two "clumps" of measurements, one around 1.6 ms and the other around 1.2 ms. It was noted that the higher values corresponded to one side of the glass cube and the lower values to the opposite side of the cube — implying a concentration variation in the sample. The measurements can be compared to a Yb^{3+} $^2F_{5/2}$ lifetime value of 1.65 ms reported in the literature by Remillieux *et al.*[20] for 2.0 wt% Yb + 0.1 wt% Pr doped ZBLAN fiber.

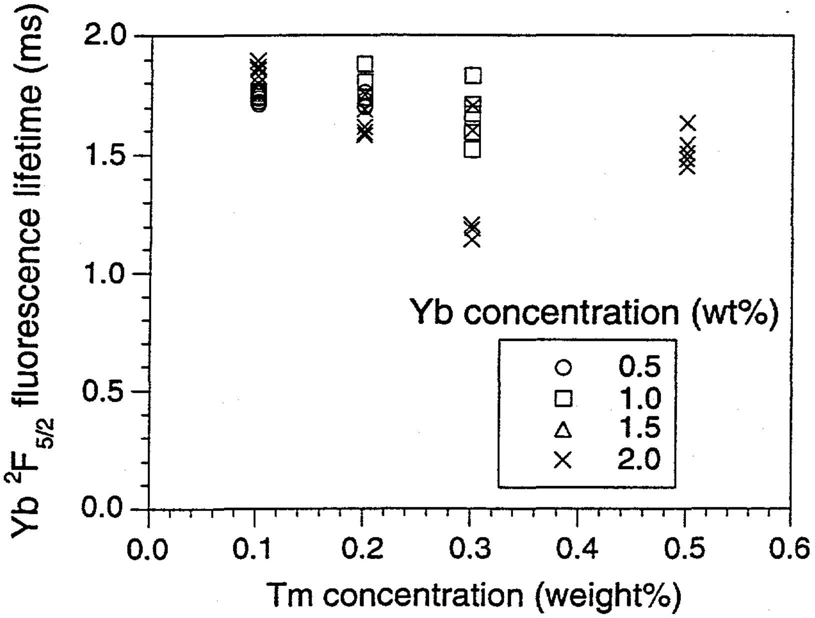


Figure 1. The Yb^{3+} $^2F_{5/2}$ level was excited at 963 nm and emission was monitored at 1012 nm ($^2F_{5/2} \rightarrow {}^2F_{7/2}$). All raw data is shown.

Figures 2 through 4 show measured fluorescence lifetimes for the Tm^{3+} ion $^1D_2$, $^1G_4$, and $^3H_4$ transitions. Lifetime values in Figures 2, 3 and 4 are averages of 5 measurements taken for each sample. Additionally, measurements on samples with Yb co-doping are only displayed for the 2 wt% Yb case. This is done for clarity, as measurements on samples with other Yb co-doping values were taken and found to fall between the singly doped Tm values and the 2 wt% Yb co-doped sample values. For measurements of the Tm^{3+} $^1G_4$ state (Figure 3), emission was observed at 642 nm for the singly doped and Yb co-doped samples, and at 788 nm for the Pr co-doped samples. Tm^{3+} $^3H_4$ emission was monitored for both direct pumping at 791 nm and for indirect pumping at 689 nm. The latter process involved excitation to the Tm^{3+} $^3F_3$ level followed by rapid phonon assisted relaxation into the $^3H_4$ level. Only data obtained while pumping at 689 nm is show in Figure 4. Within the limits of experimental error, data obtained by pumping at 791 nm appeared identical. It was observed that the lifetime of the Tm^{3+} ion $^1D_2$ state was independent of Yb co-doping, while the corresponding lifetime values for the $^1G_4$ and $^3H_4$ levels were weakly dependent on Yb co-doping. However, all Tm^{3+} ion state lifetimes were strongly affected by Pr co-doping. For instance, the 0.3 wt% Tm^{3+} $^1G_4$ lifetime decreased from 568 μs to 68 μs as the Pr^{3+} ion concentration increased from 0 to 2 wt%. This decrease is probably due to near resonant energy transfer from the Tm^{3+} ion to the Pr^{3+} $^3P_0$ level. Similarly, the 0.3 wt% Tm^{3+} $^3H_4$ lifetime decreased from 1.53 ms to 77 μs (Figure 4, 689 nm excitation) as the Pr^{3+}

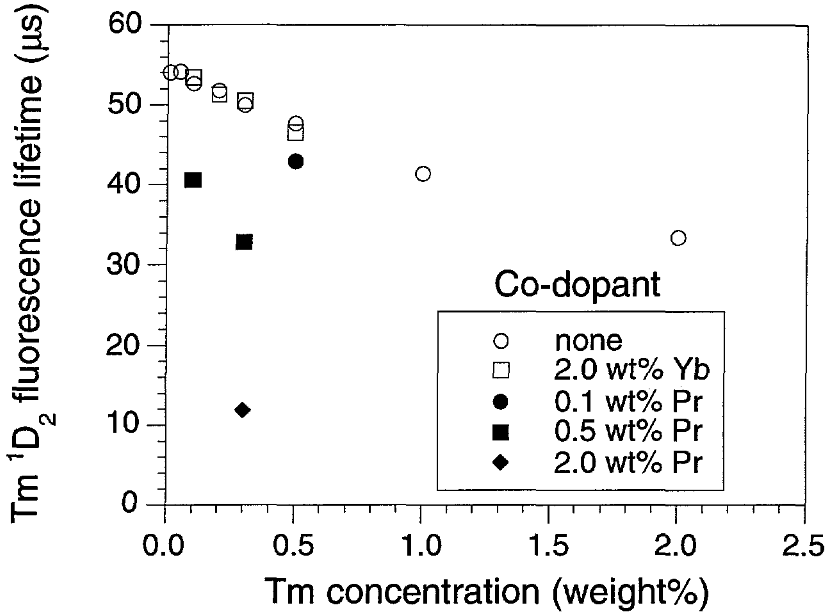


Figure 2. The Tm^{3+} $^1D_2$ level was excited at 355 nm and emission was monitored at 450 nm ($^1D_2 \rightarrow {}^3F_4$). The data shown is an average of five data points taken for each sample.

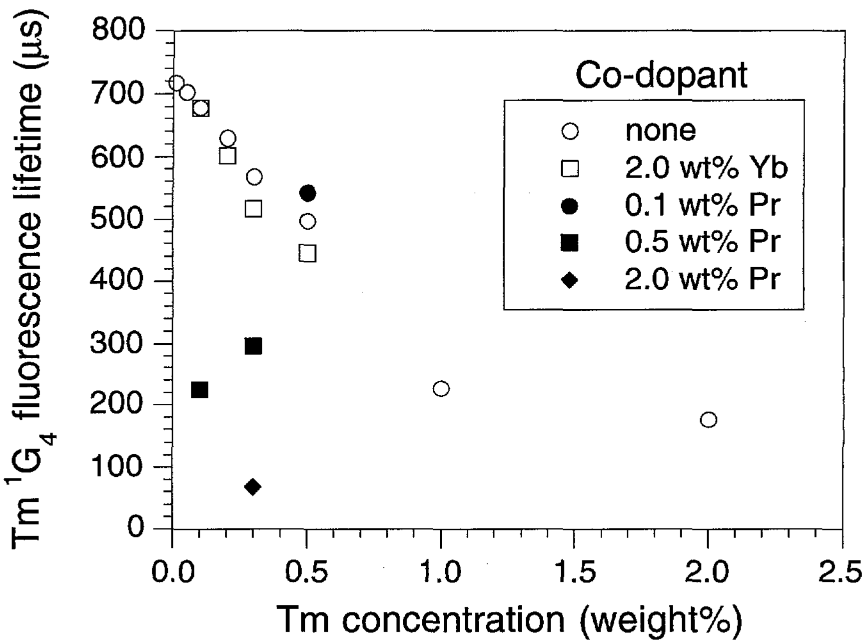


Figure 3. The Tm^{3+} $^1G_4$ level was excited at 468 nm. Emission from the Tm only and Yb co-doped samples was monitored at 642 nm ($^1G_4 \rightarrow {}^3F_4$), while emission from the Pr co-doped samples was monitored at 788 nm ($^1G_4 \rightarrow {}^3H_5$). The data shown is an average of five data points taken for each sample.

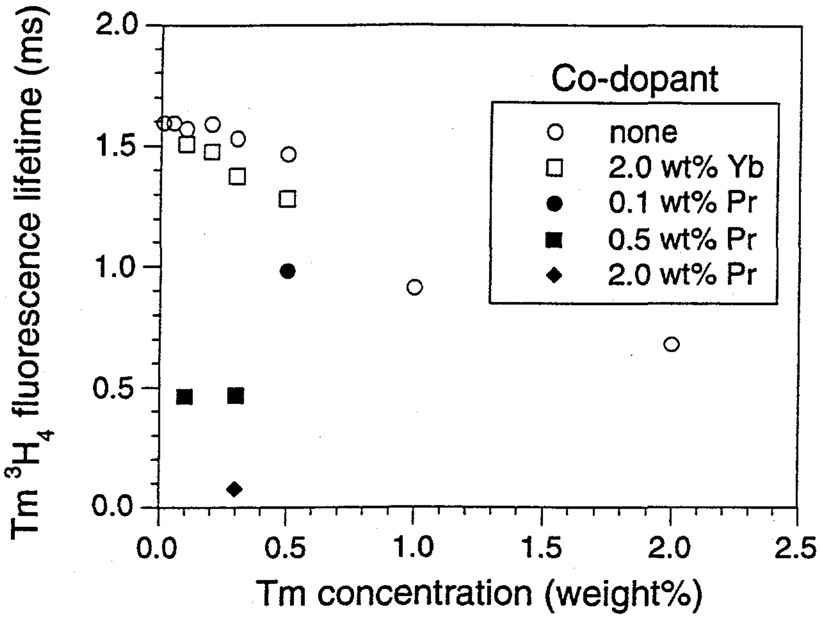


Figure 4. The plot shows the measured fluorescence lifetime of the Tm^{3+} $^3H_4$ level after indirect population of the state by excitation of the Tm^{3+} $^3F_3$ level at 689 nm. The data shown is an average of five data points taken for each sample. Approximately identical results were obtained by exciting the Tm^{3+} $^3H_4$ level directly by pumping at 791 nm. In both cases, emission was monitored at 800 nm ($^3H_4 \rightarrow {}^3H_6$).

ion concentration increased from 0 to 2 wt%, possibly due to energy transfer to the $^1G_4$ Pr^{3+} state. These processes are discussed in greater detail in the next section. The measured lifetime values agree well with the values reported by Sanz *et al.*[21] (55 μs, 630 μs, and 1.42 ms for the Tm^{3+} $^1D_2$, $^1G_4$, and $^3H_4$ states respectively) in 0.15 mol% Tm:ZBLALi glass and by Oomen and Lous[22] (57 μs and 1.7 ms for the Tm^{3+} $^1D_2$ and $^3H_4$ states respectively) in 0.05 mol% Tm:ZBLAN glass.

Lastly, Figures 5, 6, and 7 show measured fluorescence lifetimes for the Pr^{3+} ion $^3P_1$ & $^1I_6$ (too close to distinguish), $^3P_0$, and $^1G_4$ transitions. In each case, five measurements were made on each sample and averaged. Figure 5 indicates that the Pr^{3+} $^3P_1$ & $^1I_6$ levels are weakly depleted by the presence of the Tm co-dopant, presumably due to energy transfer to the Tm^{3+} $^1G_4$ level. However, the Pr^{3+} $^3P_0$ state lifetime (Figure 6) appears unaffected by Tm co-doping since it is lower in energy than the Tm^{3+} $^1G_4$ level and approximately 5750 cm^{-1} higher in energy than the nearest lower lying Tm^{3+} state ($^3F_2$). Finally, Figure 7 indicates that the Pr^{3+} $^1G_4$ state is also affected by the presence of Tm co-doping. In this case, the fluorescence lifetime of the 0.5 wt% Pr^{3+} doped samples decreased from 89 to 60 μs as the Tm^{3+} ion concentration increased from 0.1 to 0.3 wt%. These values agree favorably to those given by Remillieux *et al.*[20] (48 μs, 46 μs, 360 μs and 100 μs for the Pr^{3+} $^3P_1$ & $^1I_6$, $^3P_0$, $^1D_2$, and $^1G_4$ states respectively) for 2.0 wt% Yb + 0.1 wt% Pr doped ZBLAN fiber at 6 K.

2.3 Fluorescence quenching

Peak fluorescence intensities were monitored during lifetime measurements. The normalized fluorescence strength as a function of Tm concentration was then determined by dividing the recorded fluorescence strength by the product of the sample path length and the nominal Tm dopant concentration. It was found that relative Tm^{3+} emission strengths decreased as a function of increasing Tm concentration for all transitions. Emission strengths were essentially independent of Yb or Pr doping levels, although the 0.5 wt% Tm + 2 wt% Pr sample had the weakest emission in all cases. To first order, the emission strengths follow the lifetime trends.

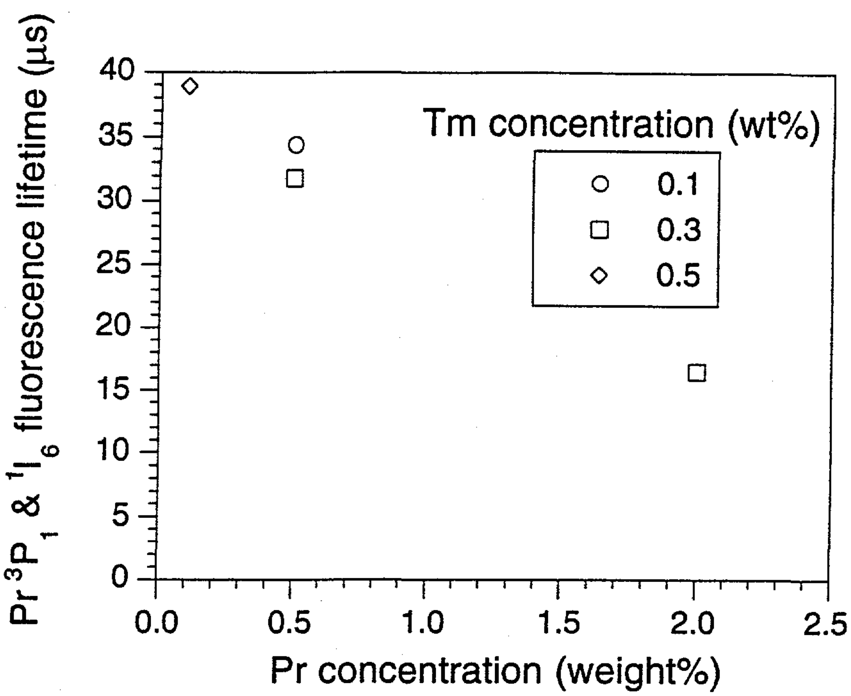


Figure 5. The Pr^{3+} $^3P_1$ and $^1I_6$ levels were excited at 468 nm and emission was monitored at 520 nm ($^3P_1 \rightarrow {}^3H_5$). The data shown is an average of five data points taken for each sample.

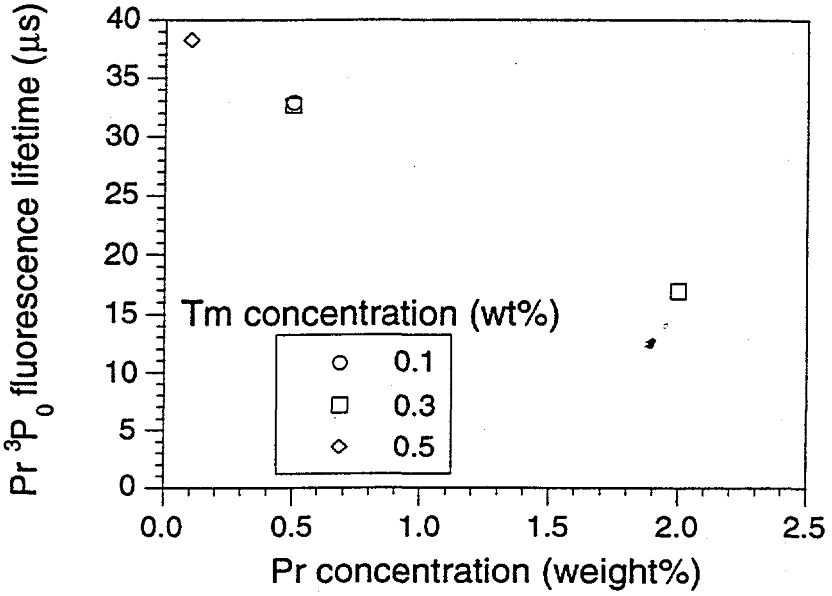


Figure 6. The Pr^{3+} $^3P_0$ level was excited at 468 nm (presumably indirectly by energy transfer from the Pr^{3+} $^3P_1$ and $^1I_6$ levels or by energy transfer from the Tm^{3+} $^1G_4$ state) and emission monitored at 715 nm ($^3P_0 \rightarrow {}^3F_4$). The data shown is an average of five data points taken for each sample.

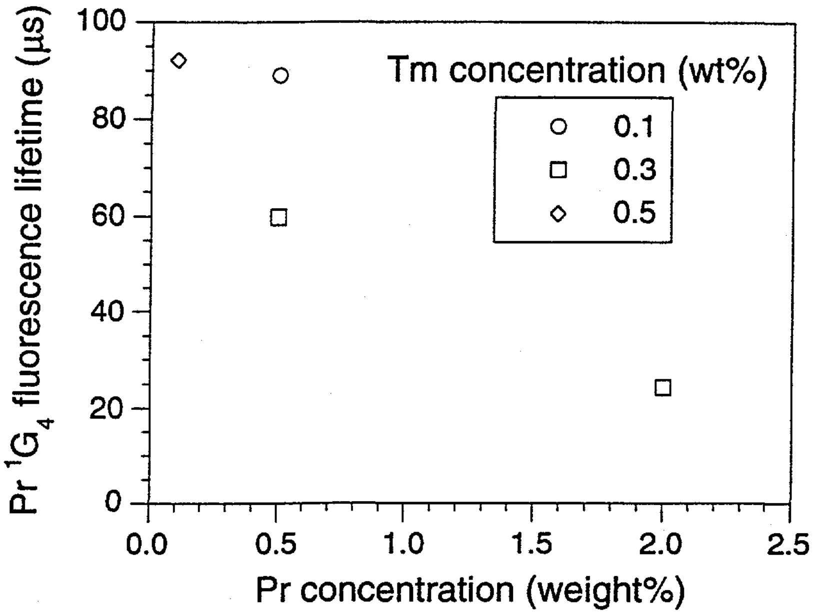


Figure 7. The Pr^{3+} $^1G_4$ level was excited at 1010 nm and emission was monitored at 1313 nm ($^1G_4 \rightarrow {}^3H_5$). The data shown is an average of five data points taken for each sample.

3. CONTINUOUS-WAVE EXCITATION EXPERIMENTS

Upconversion emission strengths were measured while pumping the glass samples using either one or two continuous-wave Ti:sapphire lasers operating at wavelengths between 700 and 1000 nm. In the dual-color pumping case, the pump beams were focused to approximately 500 µm ($1/e^2$) diameter spots in the glass cubes. Furthermore, care was taken to align the two pump beams so that good spatial overlap was obtained in the samples. Emission strengths were monitored using the naked eye, or measured using a photomultiplier tube connected to an oscilloscope. Tm^{3+} ion $^1G_4 \rightarrow {}^3H_6$ emission was isolated using a 480 nm bandpass filter and a 4-94 Corning glass filter.

In the case of some Tm doped samples a weak emission centered at approximately 550 nm was observed. The excitation peak for this emission occurred at 971 nm. This indicates the presence of Er^{3+} ion contamination in those samples.

3.1 Single color excitation

Tm upconversion emission, induced by Yb^{3+} excitation, was examined for each of the Yb^{3+} and Tm^{3+} co-doped samples. Strong visible emissions were observed at 480 nm and 650 nm (corresponding to the $^1G_4 \rightarrow {}^3H_6$ and to the $^1G_4 \rightarrow {}^3F_4$ transitions respectively), while weaker emissions occurred at 450 nm and around 500 nm (corresponding to the $^1D_2 \rightarrow {}^3F_4$ and, possibly, to the $^1D_2 \rightarrow {}^3H_5$ transitions respectively). Upconversion emission was observed for Yb^{3+} ion excitation anywhere in the 915-982 nm range. The optimum excitation wavelength was 974.5 nm. Upconversion emission was not observed from the singly-doped Tm:ZBLAN samples when pumping at 975 nm.

For a fixed excitation density of approximately 250 W/cm^2 (500 mW pump power in an approximately 500 µm $1/e^2$ diameter beam) and for a fixed dopant concentration of 0.2 wt% Tm, the 480 nm emission increased monotonically as the Yb co-dopant concentration was increased from 0.5 to 2 wt%. This is reasonable since at these pumping levels we are not bleaching the fundamental Yb^{3+} absorption and, consequently, the overall energy deposited in the samples increases with increasing Yb concentration. Similarly, we observed that the 650 nm emission exhibited an identical dependence on Yb concentration. The 450 nm emission strength, however, displayed a much greater dependence on Yb^{3+} ion concentration than that of the 480 nm emission. This observation is consistent with the requirement of an additional energy transfer step from Yb^{3+} to Tm^{3+} in order to populate the $^1D_2$ Tm^{3+} state.

For samples with a fixed Yb concentration of 2 wt%, the 480 nm emission strength was greatest for a Tm dopant concentration of 0.3 wt%. Emission was weaker for both higher (0.5 wt%) and lower (0.2 wt%) Tm dopant concentrations. A possible cause for the observed decrease in 480 nm emission strength at high Tm dopant concentrations is a Tm^{3+} to Tm^{3+} cross relaxation energy transfer process that quenches the $^3H_4$ Tm^{3+} excited state. A well-known example of this effect is the energy transfer between a Tm^{3+} ion in the $^3H_4$ state and a neighbor in the ground state whereby the latter is promoted to the Tm^{3+} $^3H_5$ state and the excited ion is quenched to the Tm^{3+} $^3H_5$ level. This effect, albeit helpful in the design of 2 μm Tm^{3+} lasers, appears to set an upper limit on the Tm dopant concentration suitable for upconversion applications. Finally, we reiterate that of all the samples tested (see Table 1 for listing), the strongest 480 nm upconversion emission — under conditions of single color excitation — was observed in the sample with a nominal doping of 2.0 wt% Yb + 0.3 wt% Tm.

3.2 Two-color excitation

Two color excitation experiments were conducted by simultaneously exciting the Tm^{3+} $^3H_6 \rightarrow {}^3H_4$ transition and the Yb^{3+} $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition. Blue light generation at 480 nm, was most efficient using excitation wavelengths of 974.5 nm (Yb^{3+}) and 794.6 nm (Tm^{3+}). For weak Yb^{3+} excitation pump intensities a significant enhancement of the 480 nm Tm^{3+} upconversion emission, relative to either single-color Yb^{3+} or Tm^{3+} excitation, was observed by adding the second color pump beam. For high Yb^{3+} excitation pump intensities no upconversion enhancement was observed using the dual-color pump scheme.

Upconverted Tm^{3+} emission from Yb,Tm:ZBLAN for single-color 785 nm excitation was typically weak and comprised both blue ($^1G_4 \rightarrow {}^3H_6$) and red ($^1G_4 \rightarrow {}^3F_4$) fluorescence. The addition of a small amount of Yb excitation, at 975 nm, significantly increased the strength of the 480 nm emission. This enhancement, due to two-color pumping, was greatest for samples of higher Tm concentration and lower Yb concentration. Of the samples listed in Table 1, the enhancement effect was greatest for the 0.5 wt% Yb + 0.2 wt% Tm and the 1.0 wt% Yb + 0.3 wt% Tm doped samples. Figure 8 documents this enhancement for the former case. In this instance, the absorbed Tm^{3+} ion excitation power at 794.6 nm was

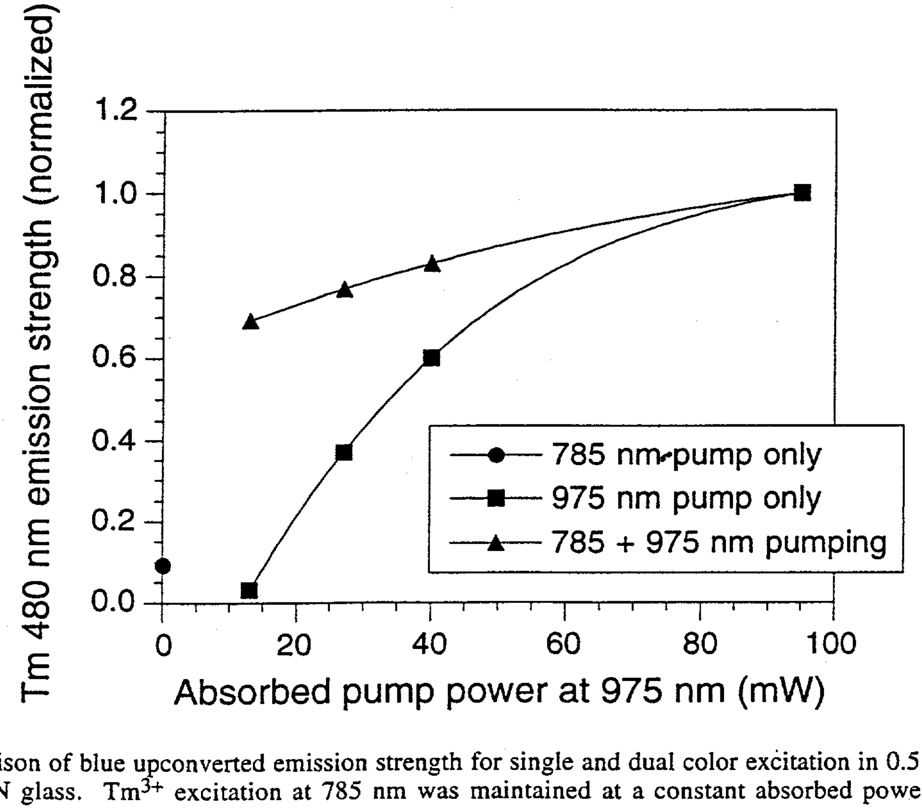


Figure 8. Comparison of blue upconverted emission strength for single and dual color excitation in 0.5 wt% Yb + 0.2 wt% Tm doped ZBLAN glass. Tm^{3+} excitation at 785 nm was maintained at a constant absorbed power of 34 mW. Yb^{3+} excitation at 975 nm was varied from 0 to 100 mW. Pump beams were chopped at a 50% duty cycle.

fixed at 34 mW (134 mW incident pump power) while the absorbed Yb^{3+} ion excitation power was varied from zero to 95 mW (a maximum incident pump power of 140 mW at 974.5 nm). The 480 nm Tm^{3+} ion emission strength for both single-color and dual-color excitation was then monitored and normalized to that observed for the highest power excitation case. The trend shown in Figure 8 is that the greatest enhancement occurs when the Yb^{3+} ion excitation power is small. For example, the use of 34 mW of Tm^{3+} ion excitation increases the blue emission, relative to Yb^{3+} only excitation (with 13 mW of absorbed pump power at 975 nm), by a factor of greater than 20. This enhancement effect is diminished as the amount of Yb^{3+} ion excitation power (at 975 nm) is increased. Finally, examination of the decay of the blue emission, using a mechanical chopper to modulate the pump beam(s), shows that the decay time for the dual-color excitation is much faster than for the Yb^{3+} ion excitation alone.

4. DISCUSSION

4.1 Yb to Tm energy transfer

Figure 9 shows two possible upconversion mechanisms in gain media co-doped with Yb and Tm. The first mechanism involves three sequential energy transfer steps from Yb to Tm and is responsible for the reported laser action in BaY_2F_8.[17] The second scheme involves (1) excitation of the $^3H_4$ level of Tm^{3+}, (2) excitation of the $^2F_{5/2}$ state of Yb^{3+}, and (3) subsequent energy transfer from the $^2F_{5/2}$ state of Yb^{3+} to the $^3H_4$ state of Tm^{3+}.

To first order, Yb^{3+} to Tm^{3+} net energy transfer efficiency in glass hosts, the first step depicted for process one in Figure 9, can be estimated by assuming a direct transfer occurs between donor and acceptor ions. In this case,

$$\eta = 1 - \tau_d / \tau_{d,a} \tag{1}$$

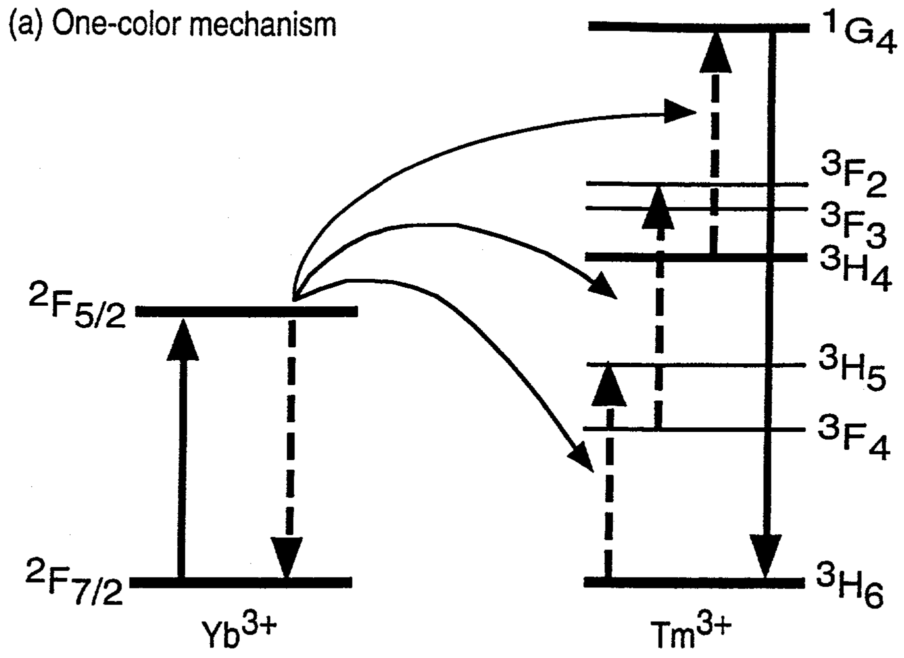
where τ_d is the intrinsic lifetime of the donor state and $\tau_{d,a}$ is the measured fluorescence lifetime of the donor ion in the presence of an acceptor ion. Using the data in Figure 1 (except for the three 0.3 wt% Tm values that appear low) a linear curve fit to the data can be made and extrapolated to 0 wt% Tm to estimate the intrinsic lifetime of the Yb^{3+} excited state. Values for $\tau_{d,a}$ are obtained my averaging all lifetime values measured for a given Tm ion concentration. These approximations assume (1) that the Yb^{3+} ion lifetime is independent of Yb concentration and (2) that radiation trapping effects essentially "wash out". Net efficiencies are then determined using Equation (1), and the results of this calculation are plotted in Figure 10. Two conclusions can be drawn from this graph that are applicable to upconversion laser design: (1) that Yb ion concentration should be selected to achieve a desired absorption in a desired length of fiber, and (2) that Tm ion concentration should be maximized to the extent that concentration quenching effects allow. With regard to the latter it is apparent from Figures 2-4 that decreases in fluorescence lifetimes occur as Tm ion concentrations increase in ZBLAN glass at all doping levels.

The efficiency of the second upconversion mechanism depicted in Figure 9 is more difficult to estimate because of the probable presence of both Yb^{3+} to Tm^{3+} and Tm^{3+} to Yb^{3+} energy transfer. The latter process has been observed in BaY_2F_8 and is an enabling step in achieving single color pumping (at approximately 780-790 nm) of Yb and Tm doped hosts to the Tm^{3+} $^1G_4$ level.[10-11] We note that single-color pumping at 785 nm resulted in blue upconversion emission from the Yb,Tm:ZBLAN samples (see Figure 8), but not from the Tm:ZBLAN samples. Due to the presence of these competing cross-relaxation processes, we have not attempted to quantify the efficiency of the two-color pumping mechanism.

4.2 Tm to Pr energy transfer

From Figures 5-7, it is apparent that lifetimes of both Tm and Pr ions are strongly affected by the presence of the reciprocal co-dopant. All three Tm transitions that were monitored suffered reductions in fluorescence lifetimes due to Pr co-doping. The Tm^{3+} $^3H_4$ to Pr^{3+} $^1G_4$ energy transfer step has been previously described in the literature in $YLiF_4$.[23] Energy transfer from the Tm^{3+} $^1D_2$ level to the Pr^{3+} ^3P manifold has also been previously described in ZBLAN.[22] Energy transfer from the Tm^{3+} $^1G_4$ state to the Pr^{3+} $^3P_0$ state is readily predicted because of the near resonance of the transitions. Due to the minimal number of data points obtained during these measurements, we have not attempted to determine relative transfer efficiencies. We note that Tm to Pr energy transfer is greatest in the 2 wt% Pr co-doped sample. However, such high Pr^{3+} doping levels are presumably unacceptable for laser operation due to strong cross-relaxation processes amongst Pr^{3+} ions.

The data also indicates that the Pr^{3+} $^3P_1$ & $^1P_6$ levels and the Pr^{3+} $^1G_4$ level also suffer fluorescence lifetime reductions due to Tm^{3+} co-doping. In the first case the process presumably involves energy transfer to the near-resonant


(a) One-color mechanism

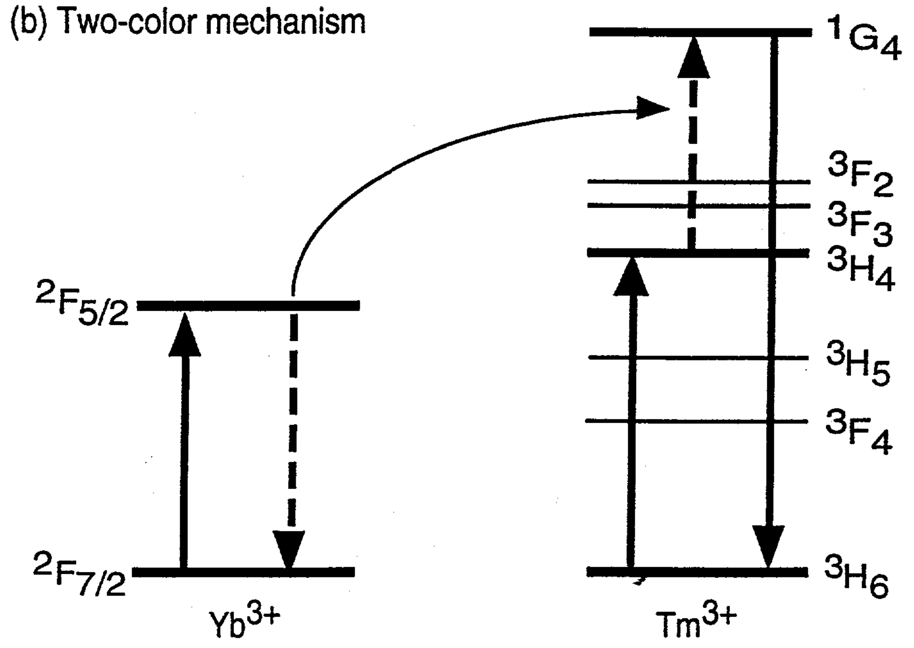

(b) Two-color mechanism

Figure 9. The top drawing (a) shows a sequential three-step energy transfer from Yb^{3+} to Tm^{3+} resulting in population of the Tm^{3+} $^1G_4$ level (the one-color mechanism). The Yb ions can be pumped anywhere in the 915-982 nm range. The lower drawing (b) shows a one-step energy transfer from Yb^{3+} to Tm^{3+} that also results in population of the Tm^{3+} level. This (two-color) mechanism requires direct excitation of both Yb^{3+} and Tm^{3+} at approximately 975 nm and 785 nm respectively.

Tm^{3+} $^1G_4$ level. No reduction in lifetime was observed for the Pr^{3+} $^3P_0$ level due to Tm^{3+} co-doping. This is understandable since the Pr^{3+} $^3P_0$ state is lower in energy than the Tm^{3+} $^1G_4$ state nd approximately 5750 cm^{-1} higher in energy than the Tm^{3+} $^3F_2$ state. No attempt was made to quantify Pr to Tm energy transfer rates.

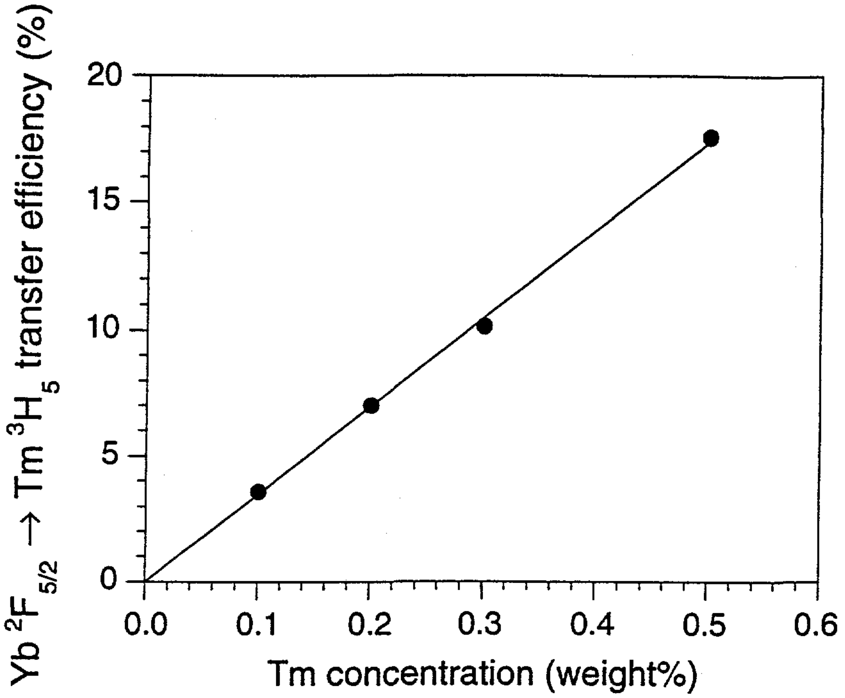


Figure 10. The graph shows the estimated energy transfer efficiency from the Yb $^2F_{5/2}$ level to the Tm $^3H_5$ level.

4.3 Dual-color excitation of Yb,Tm:ZBLAN

Figure 8 shows that the dual-color excitation upconversion mechanism offers significant advantage over single-color Yb^{3+} ion excitation (at low pump intensities) since it reduces the number of Yb to Tm energy transfer steps required to populate the Tm $^1G_4$ state from three to one. Specifically, population of the Tm^{3+} $^3H_4$ level can be accomplished in one direct step rather than two energy transfer steps. The observation that the dual-color enhancement is greatest for samples with lower Yb concentration, or for the case of lower Yb^{3+} ion excitation power (Figure 8), is consistent with this mechanism. As Yb^{3+} excitation intensity or Yb dopant concentration is increased, the Tm^{3+} ions are more likely to receive the three quanta of energy required to populate the $^1G_4$ level. Additionally, the observation of reduced fluorescence decay time for the Tm^{3+} $^1G_4$ state in the dual excitation scheme is consistent with a reduced energy transfer population time due to the single, rather than the triple, step energy transfer process.

4.4 Summary

We have investigated the effects of Yb^{3+} sensitization of Tm^{3+} activators in ZBLAN. The results indicate that it should be possible to use Yb^{3+} to Tm^{3+} energy transfer mechanisms to enable the development of more conveniently pumped blue upconversion fiber lasers. For single-color excitation it was observed that the highest upconversion efficiency was obtained from the sample with a nominal dopant concentration of 2.0 wt% Yb + 0.3 wt% Tm. These dopant levels are comparable to those employed in Yb sensitized Pr:ZBLAN fiber lasers.[19] Additionally, we have compared the efficiency of the single-color pump scheme to that of dual-color excitation and determined the latter to be more efficient at low pump power densities. An advantage of the dual-pump approach is greater flexibility in choosing the Yb and Tm doping levels.

We have also investigated energy transfer between Pr and Tm ions in ZBLAN. Strong coupling was noted between ions resulting in energy transfer in both directions. The observations may indicate that Tm sensitization of Pr:ZBLAN fiber lasers is possible, although more research needs to be conducted in this area.

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