Temperature and doping dependence of fluorescence lifetime in Yb:YLF (role of impurities)

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Abstract

We have investigated temperature and doping dependence of fluorescence lifetime in Yb:YLF crystals in the 78-300 K range, for samples with Yb-doping levels of 0.5%, 1 % and 25%. Radiation-trapping prolonged fluorescence lifetimes are first measured to understand the pros and cons of this inevitable process on fractional thermal load and laser gain. Later, pinhole method was used to acquire ideally trapping free fluorescence lifetimes. For the lowly Yb-doped samples, fluorescence lifetime was measured to be 1.97 ms and 2.1 ms at 78 K and 300 K, respectively. For the 25% Yb-doped sample, strong upconversion emission due to the presence of Er, Tm and Ho impurities were observed. A double-exponential decay behavior, combined with excitation intensity dependent decay profile was also revealed for this highly doped sample. Even with the pinhole method, the 300 K fluorescence lifetimes was measured as 4.5 ms, showing the difficulty to acquire radiation-trapping free signals at high doping levels. Time dynamics of upconverted emission in different spectral regions were also recorded, which provides hints on the energy transfer mechanisms between the Yb ion and the other rare-earth impurities.

Keywords: Solid-state lasers; laser crystals; cryogenic lasers; Yb³⁺-doped YLiF₄; fluorescence lifetime.

1. Introduction

Yb:YLF (Yb:LiYF₄) is an interesting material that attracts the attention of optics community, not only as a broadband near infrared laser/amplifier gain medium [1-11], but also as a solid-state optical refrigerating medium [12-18]. From the laser scientist point of view, operating Yb:YLF at cryogenic temperatures enables increased gain and better thermal management, and provides laser sources with 2-3 orders of magnitude higher average power in comparison with room-temperature operation [19-28]. For the optical refrigeration community, solid-state cooling to cryogenic temperatures using Yb:YLF is an important tool to develop nanometer scale quantum optical devices [16]. The Yb-doping of YLF is an important parameter that should be carefully optimized for achieving the desired laser performance [9], and high doping levels are usually required for laser geometries such as thin-disks or slabs [3]. Compared to the other well-known laser materials like Ti:Sapphire and Yb:YAG, Yb:YLF is more forgiving at high doping levels. Relatively efficient lasing/amplification have already been obtained using 20-60% Yb-doped YLF samples [1-5, 9, 20, 29]; however, most of the time at the expense of deleterious thermal effects, which

usually requires quasi continuous-wave operation or amplification at low repetition rates. For optical cooling applications based on anti-Stokes emission of Yb:YLF crystals, one ideally needs very high doping levels to achieve efficient absorption near ~1020 nm (this line lies at the long wavelength edge of the absorption spectrum). On the other hand, efficient cooling of the crystal also requires samples with minimal impurities and minimal parasitic background absorption [15, 17, 18], and so far the optimum doping level stays around 10%. In short, for laser and optical refrigeration communities, it is important to understand the variation of thermo-opto-mechanical parameters of Yb:YLF with doping and temperature [9, 21, 30, 31].

In this work, we have focused our attention on fluorescence lifetime, which is an important parameter for the design of efficient laser/amplifier systems. Fluorescence lifetime could also provide information on the impurities of the crystal, and hence it is potentially important for understanding the optical cooling performance of the crystal. As is well summarized in [32], Yb:YLF has a simple energy level structure, and high-purity samples ideally do not possess excited-state absorption, cross-relaxation, or up-conversion that could all effect the fluorescence lifetime of the laser active level (see Fig. 1 in [32]). On the other hand, the crystal

field is quite weak in YLF, and as a result the absorption and emission spectra strongly overlap, creating radiation trapping effects that could significantly influence the measured fluorescence lifetime [32–40]. The radiation trapping mechanism, which is also known as radiative diffusion, is crystal geometry dependent due to presence of effects such as total internal reflection [40] and is not easy to model accurately [38]. The process involves reabsorption of the emitted fluorescence, creates an additional heat load on the material beyond the quantum defect [41–43], and hence is not desired in terms of thermal behavior. On the other hand, it can be also beneficial for laser amplifiers: enables storage of inversion on a longer timescale than radiative lifetime and facilitates higher small signal gain (if it is reabsorbed in a region that overlaps with the seed). As a side note, a redistribution of inverted ion population might also occur via nonradiative energy transfer process due to electrical interactions such as dipole-dipole activity [38, 44].

Besides radiation trapping, Boulon et al. has already shown that there are radiation quenching effects in highly-Yb-doped Yb:YLF samples [32], where lifetime is shortened by energy diffusion towards traps (quenching centers). These radiation traps are not always well-known [38]: but in the case of Yb:YLF, existence of trace amounts of rare earth impurities (e.g. Er, Tm, Ho) is shown to create radiation quenching channels [17, 32, 45]. The energy transfer from the excited Yb ion into these impurities creates a loss of useful inversion, and results in concentration quenching of the fluorescence lifetime [15]. At elevated temperatures multiphonon relaxation may also create a nonradiative relaxation channel [46], but the YLF lattice is known to be resistant towards this process [47]. Cooperative emission of neighboring Yb ions (pair emission) is also known to create green emission in the 490–510 nm range in Yb:YLF samples [32], but this process has been shown to be quite weak in Yb:YLF. Furthermore, amplified spontaneous emission (ASE) can also play a role in the population dynamics of highly-doped Yb:YLF crystals [48, 49]. As we tried to summarize shortly, despite the simple looking energy structure, the emission dynamics could be rather complex in Yb-doped gain media as well. Unfortunately, despite the importance of the fluorescence lifetime for the design of efficient laser/amplifier systems, to our knowledge, it is so far only investigated in a few studies for Yb:YLF [31, 32, 50].

In this work, to extend the knowledge on this topic, we have investigated the variation of fluorescence lifetime of Yb:YLF with temperature in the 78–300 K range using crystals with doping levels of 0.5%, 1% and 25%. Our initial experiments show the role of temperature and doping in increasing the effective fluorescence lifetime of Yb:YLF crystals via radiation trapping. Later also the pinhole method was used to ideally measure radiation-trapping free intrinsic fluorescence lifetimes, where good agreement with literature was observed for the lowly Yb-doped crystals (1.97 ms at 78 K and 2.1 ms at 300 K). For the 25% Yb-doped YLF sample, radiation trapping effects were very strong and the measured room-temperature fluorescence lifetime was as high as 4.6 ms even when using the pinhole method. We have also identified

the presence of Er, Tm and Ho impurities in this highly doped crystal by observing a strong upconversion spectrum in the visible range. Moreover, fluorescence decay curves with double exponential behavior and excitation intensity dependent fluorescence lifetime behavior were also observed in the 25% Yb-doped YLF sample. The measured intensity dependent behavior, which to our knowledge, reported to the first time in Yb:YLF, might be important for the design of efficient laser amplifier systems. We have further measured the temporal dynamics of the fluorescence emission at different spectral regions of the upconversion spectrum and acquired hints on the energy transfer mechanisms between the rare earth impurities.

The paper is organized as follows: In Section 2, we summarize the experimental setup and the methodology. In Section 3, we present the experimental results in detail, and in Section 4 we close with a brief discussion.

2. Experimental

Several Yb:YLF crystals with Yb-doping of 0.5%, 1% and 25% were available for the experiments. The 0.5% and 1%-doped crystals were 2-cm long, and had an aperture of 10 mm by 15 mm. The 25% Yb-doped crystals were 1.75 mm long and had an aperture of 6 mm by 8 mm. The front and back surfaces of all samples were anti-reflection coated for 1 μ m region, which minimizes trapping of radiation via total internal reflection process. A fiber-coupled, 960 nm laser diode was used as the excitation source. The pump light from the fiber output is collimated and imaged inside the gain medium using a set of appropriate lenses, and a flattop beam profile with a beam diameter of around 2 mm was obtained on the crystals. In typical emission lifetime measurements, Yb:YLF crystals are excited with 200 μ s long pump pulses with 2 kW of peak power at repetition rates between 0.1 to 1 Hz (a low rep rate is used in highly doped crystal). Despite the large peak power, due to the low duty cycle employed, the average absorbed pump power was below 0.5 W in these measurements, and hence the heat load on the crystals was rather low. For measuring the excitation intensity dependence of the fluorescence lifetime, a 2 ms pump pulse was used and the peak power of the pulses has been varied to adjust the incident excitation energy level on the crystals. With that, a maximum incident energy of 4 J (2 kW for 2 ms) was available for the experiments, which corresponds to a fluence of 125 mJ/cm².

Fig. 1 shows a simple schematic of the fluorescence lifetime measurement setup. The fluorescence decay signal was measured at 90° with respect to the direction of excitation beam. A 1000 nm high-pass filter (Thorlabs, FELH1000) was also implemented to cut out any remaining scattered pump signal (which was already at a low level due to usage of high quality crystals and measurement at 90°). The time-dependent fluorescence decay signal was monitored using a free-space 350 MHz Si detector (Thorlabs, DET10A) which possesses a spectral response in the 200–1100 nm range. The signal was recorded with a 600 MHz digital sampling oscilloscope, where a variable resistance terminator was used to adjust the

signal strength on the oscilloscope. The system impulse response was measured to be less than 20 μs even with the largest termination resistance (50 kohm) used in this study. Pinholes with diameters between 10 μm and 2 mm were used for the estimation of radiation-trapping free lifetimes. The high-pass optical filter in front of the detector was replaced by different band-pass and low-pass filters for the measurement of time dynamics of the upconversion spectra in different spectral regions (filters FES0900, FGB37, FB800-40, FB480-10, FB500-40 from Thorlabs).

Figure 1: A simplified schematic of the fluorescence lifetime measurement setup. The simple system consists of a pulsed high power 960 nm diode (200 μs long pulses with 2 kW peak power) that is used as the excitation source, Yb:YLF crystals with different Yb-doping levels, and a fast Si detector oriented at 90 degrees to the pump line for background-free lifetime measurements. P: Pinhole, F: Filter, BD: beam dump, Det: Detector.

For temperature controlled experiments, the crystals were indium bonded from the top side to a multi-stage pyramidal cold head, which was cooled to cryogenic temperatures by boiling liquid nitrogen. Several silicon-diode based thermal sensors connected to the cold head provided real time temperature information of the cold head with ± 0.1 K accuracy. For temperature dependent fluorescence lifetime measurements, the slow (6-7 hours) dewar cooling cycle is used to acquire the data, as was also employed and described in detail in [51]. During the slow cooling process, the crystals and the cold head are in thermal equilibrium, and the crystal temperature can be accurately measured using the thermal sensors.

In the upconversion emission measurements, the emission spectra were again measured at 90° angle to the pump propagation direction using an Ocean Optics spectrometer with a spectral resolution of 0.5 nm in the 200-1100 nm range. The measured signal is corrected for the overall spectral response of the system (CCD array and grating). The Ho^{+3} ion emission near the 2 μm region is recorded using a 5 nm resolution NIR Quest spectrometer.

3. Fluorescence lifetime measurement results

The results for the fluorescence lifetime measurements are presented in several sub-sections. In Section 3.1, we outline the effect of temperature on lifetime, whereas in Section 3.2 we discuss the results obtained with the pinhole method. Variation of the measured temporal emission dynamics with excitation energy will be elaborated in Section 3.3. Finally, in Sections 3.4 and 3.5, we present the measured spectral and time domain picture for the upconversion mechanism.

3.1 Temperature dependence of fluorescence lifetime

Figure 2: (a) Measured variation of fluorescence lifetime with temperature in the 78-300K range, for 0.5%, 1% and 25% Yb-doped YLF samples. The data is taken without using a pinhole, and at incident excitation energy of around 400 mJ (200 μs long pulses with 2 kW peak power). The results are obtained via making a single exponential fit to the measured decay curves. (b) Sample decay curves and single exponential fit to the data for the 1% Yb:YLF sample. Note that, the limited dynamic range of the measurement system creates the observed noise for signal levels below ~ 0.001 .

We start by presenting our results in Fig.2 (a), which shows the measured temperature dependence of fluorescence lifetime of Yb:YLF gain medium in the 78-300 K range. The measurements were performed at three different Yb-doping levels: 0.5%, 1% and 25%. The data in Fig. 1 (a) is obtained by making a single exponential fit to the measured fluorescence decay curves, in the form:

$$F(t) = C \text{Exp}\left(-\frac{t}{\tau_0}\right). \quad (1)$$

Above, $F(t)$ is the recorded/measured time-dependent decay curve, t is time, C is the amplitude (arbitrary constant), and τ_0 is the fluorescence lifetime of the system that is found by minimizing the sum of the squares of the differences between the measured and predicted decay (known as the method of least squares). For the lowly Yb-doped samples (0.5% and 1%), a single exponential fit matched the experimentally measured decay curves very well. As an example, Fig. 2(b) shows sample decay curves measured for 1% Yb-doped YLF sample taken at temperatures of 78 K and 300 K. As an

exception, for the 25% doped sample, we have noticed that the measured decay curve is better matched by a double exponential decay behavior, and this issue will be discussed using Fig. 3 a little later.

We see from Fig. 2 (a) that, for the lowly Yb-doped samples, the measured fluorescence lifetime decreases slowly and steadily with decreasing temperature, and has a measured value of around 2.05 ms at 78 K (2.07 ms for 1% and 2.02 ms for 0.5%). Note that, the data in Fig. 2 is taken without using the pinhole method that minimizes radiation trapping. Hence, we believe that, the increase of measured fluorescence lifetime with temperature is due to the increasing role of radiation trapping: at higher temperatures the absorption and emission bands overlap more and more, increasing the rate of radiation trapping. Also, as the Yb-doping of the sample increases from 0.5% to 1%, the room-temperature (~300 K) fluorescence lifetime increased from around 2.35 ms to 2.7 ms (due to the increased role of radiation trapping with doping).

As we will present later, the effect of fluorescence trapping could be minimized by use of aperture method, and fluorescence lifetimes that are closer to the radiative lifetime of the material could be measured (Section 3.2). On one hand, the data in Fig. 2 (a) represents a case close to what we have in laser experiments. It shows that, due to radiation trapping, the emitted photons from the material have a non-ignorable chance of reabsorption, and the rate of reabsorption (radiation trapping) increases with temperature and doping. Of course, as a benefit, the radiation trapping process could be advantageous for laser gain especially for laser amplification studies at low repetition rates where one can pump the system longer than the radiative lifetime, and still improve the stored inversion level and hence gain (e.g. a 25% doped YLF was employed in the 10 Hz regenerative amplifier of [29], and this sample we have seen increased gain for pump pulsewidths as long as 10 ms). On the other hand, each reabsorption event increases the fractional thermal load of the system and for cw operation or higher repetition rate amplification; the additional heat load might be detrimental for laser/amplifier performance. We believe that, the data in Fig. 2 (a) could be used to estimate the increase in fractional thermal load and gain with temperature and doping, and could be beneficial for modeling of inversion and thermal load in Yb:YLF system.

In Fig. 2 (a), we have seen a rather interesting behavior with the fluorescence lifetime data of the 25% Yb-doped YLF sample. First of all, the single exponential fit to the measured fluorescence lifetime has a value of 1.76 ms at 78 K, interestingly a value lower than the known radiative lifetime of the material (~2 ms). Moreover, there is a sudden drop in the lifetime data at 130 K. To understand this behavior we returned back to our experimental findings more carefully, and realized that at 130 K we increased the incident excitation energy of the sample from around 400 mJ to 600 mJ to improve the measured fluorescence signal strength. It is clear from the results that this clearly changed the trend: the measured fluorescence decay curve shape is excitation energy dependent. As mentioned earlier in the subsection, we have further noticed that, a single exponential does not provide a

very good fit to the measured data, and hence we have also tried a double exponential fit to the measured decay:

$$F(t) = A \exp\left(-\frac{t}{\tau_s}\right) + B \exp\left(-\frac{t}{\tau_f}\right). \quad (2)$$

In Equation (2), τ_f and τ_s are fast and slow decay constants of the system, and A and B are their corresponding amplitudes, and other parameters are as defined earlier.

The double exponential fit to the measured decay curves of the 25% Yb-doped YLF sample are summarized in Fig. 3 (the fit searches for values of A, B, τ_f and τ_s that minimizes the sum of the squares of the differences between the measured data and predicted double-exponential decay). Sample experimentally measured decay curves and double exponential fit to the experimental data is shown in Fig. 3 (c). For each temperature we had at least 3 experimentally measured decay curves (similar to the ones shown in Fig. 3 (c)) and the reported decay constant values in Fig. 3 (a) are average values and the error bars in the graph show the standard deviation of the data. Besides showing the best-fit values for fast (τ_f) and slow (τ_s) decay constants obtained using Eq. (2), Fig. 3 (a) also shows the single-exponential fit result (τ_0) acquired using Eq. (1). Furthermore, Fig. 3 (b) shows the ratio of slow decay magnitude (A) to fast decay magnitude (B). We clearly see from Fig. 3 (a) that, the values of single-exponential decay constant (τ_0), as well as the slow (τ_s) and fast (τ_f) components of double-exponential fit increase with increasing temperature. This again we believe is due of the increased role of radiation trapping with temperature.

As we see from Fig. 3 (b), the strength/magnitude of the slow component is 3-6 times higher than the fast component (A/B ratio in Eq. 2). Note also from Fig. 2 (b) that, at 130 K, when the pump excitation intensity is increased, the fast component get stronger (so the ratio of slow/fast decay drops). As a result of increased strength of fast component, the lifetime obtained via a single exponential fit (τ_0) decreases and creates the sharp drop we noticed in Fig. 2 (a).

We believe that the slow component of the decay curve (τ_s) corresponds to the main lifetime of the upper laser level. The slow component has a measured value of 2.15 ms at 78 K, which increases to around 4.5 ms at 300 K. We further believe that this increase is due to the presence of strong radiation trapping in the 25% doped sample. The fast component (τ_f) has a measured value of 0.5 ms at 78 K, which increases to around 1.5 ms at 300 K. Note from Fig. 3 (b) that, the fast component loses strength as the temperature of the sample increases, and we think this is due the decrease of absorption with temperature (or due to decreased inversion of the sample with temperature).

Figure 3: (a) Measured variation of fluorescence lifetime with temperature for the 25% Yb-doped YLF sample. Results for single (τ_0), and double exponential fit are shown. Double exponential fit results in a slow (τ_s) and a fast (τ_f) component. (b) Corresponding variation of the ratio of the slow and fast component strength with temperature for the double exponential fit is shown (A/B ratio in Eq. (2)). The arrow indicates the jump due to increased excitation fluency (from 400 mJ to 600 mJ). (c) Sample double exponential fit to the experimental data at 80 K and 300 K.

We could not find any discussion in the literature related to double exponential decay behavior in Yb:YLF, but we suspect that this fast process (τ_f) is due to the high level of inversion in the sample created by high energy excitation pulse used in our study (pump settings are typical values used in amplifiers). In our view, the observed initial fast decay might be: (i) due to the redistribution of energy from excited Yb³⁺ ions to other rare earth impurities via upconversion,

and/or (ii) due to the amplified spontaneous emission process, as we will discuss further in the coming sections [48, 49].

3.2 Minimizing radiation trapping

In the earlier section, we have presented measured variation of fluorescence lifetimes with temperature, but the data was taken without care for radiation trapping. In this section, we will present fluorescence lifetime measurements at 78 K and 300 K where we tried to measure the bare fluorescence lifetimes with minimal contribution from radiation trapping. For that, as described in detail in [52-54], we have looked at the variation of measured fluorescence lifetime with the pinhole size used in measurements.

Figure 4: Measured variation of fluorescence lifetime with circular pinhole aperture diameter for the 0.5% and 1% Yb-doped YLF samples at (a) 300 K and (b) 78 K. The reduced pinhole diameter minimizes radiation trapping effects. The data is taken at incident excitation energy of around 400 mJ, and the results are obtained via making a single exponential fit to the measured decay curves.

Figure 4 shows the dependence of measured fluorescence lifetime to pinhole size for the 0.5% and 1% doped YLF samples at 78 and 300 K. For both doping levels, a linear fit to the data shows that, the bare (ideally radiation trapping free) fluorescence lifetime of the samples at 78 K and 300 K is around 1.97 ms and 2.1 ms, respectively. These values are in very good agreement with the values reported by T. Y. Fan et al. for a 5% Yb-doped YLF sample: 1.99 ms at 80 K, and 2.08 ms at 296 K [31]. Recently, similar values are also

presented by Korner et al. for a 10-% doped YLF sample [50]. In our opinion, the slight increase of fluorescence lifetime with temperature from 1.97 ms to 2.1 ms might still be due to remaining radiation trapping effects at higher temperatures. We also don't know the role of non-radiative processes in Yb-doped YLF. Hence, it is not clear if these values can be interpreted as radiative lifetime values. However, radiative lifetime values could also be calculated/estimated using the measured absorption/emission spectrum on the basis of reciprocity method, and reported/calculated values in literature are 2.27 ms [30] and 2.04 ± 0.18 ms [50]. As a result, we see that, within experimental error bars, the measured fluorescence lifetime of the samples with pinholes are close to the calculated radiative lifetimes and can potentially be interpreted as radiative lifetime of the Yb^{+3} ions in the upper laser level.

Figure 5: (a) Measured variation of fluorescence lifetime with circular pinhole aperture diameter for the 25% Yb-doped YLF sample at 300 K. The reduced pinhole diameter minimizes radiation trapping effects. The data is taken at incident excitation energy of around 400 mJ, and the results are obtained via making a double exponential fit to the measured decay curves. (b) Corresponding variation of the ratio of slow and fast component strength of double exponential fit with temperature (A/B ratio in Eq. (2)).

We have also measured the variation of fluorescence lifetime with pinhole diameter for the 25% doped YLF sample at 78 K and 300 K. Fig. 5 and Fig. 6 summarizes the results of single and double exponential fit to the measured data. The 300 K data, which is measured at excitation energy of 400 mJ shows that with the smaller pinhole size, the measured

lifetime decreases in both fast and slow components. The ratio of fast and slow component strengths/magnitudes stays roughly constant, and do not vary with pinhole diameter. The slow and strong component, which we can attribute to the main upper laser level has a lifetime value of around 4.6 ms, which is quite long compared to the low Yb-doped samples. This might be due to the difficulty of getting a completely radiating trapping free measurement in the 25% Yb-doped sample at room-temperature. As another explanation, other rare earth impurity ions such as Er, Tm and Ho with their metastable levels with long lifetimes might also be acting as reservoirs for the Yb-ion (via energy transfer between the ions), effectively increasing the fluorescence lifetime of the system. However, as we will present below, the 25% doped crystal does not possess a long fluorescence lifetime at 78 K, and hence we believe that the long fluorescence lifetime measured at 300 K is most probably due to the inevitable radiation trapping process in this highly doped sample.

Figure 6: (a) Measured variation of fluorescence lifetime with circular pinhole aperture diameter for the 25% Yb-doped YLF sample at 78 K. The reduced pinhole diameter minimizes radiation trapping effects. (b) Corresponding variation of the ratio of slow and fast component strength of double exponential fit with temperature (A/B ratio in Eq. (2)). The data is taken at incident excitation energies of around 400 mJ and 4 J (open markers belong to 4 J measurement). The results are obtained via making a double exponential fit to the measured decay curves.

At 78 K, we have made two different measurements, one at an incident energy of 400 mJ, and another at an incident

energy of 4 J (higher energy measurements are shown with open markers in Fig. 6). Within experimental errors, we did not observe any significant difference on the slow component lifetime of the transition at these different excitation intensities, which remained around 2 ms in the whole measurement range (Fig. 6 (a)). This clearly shows that at 78 K, the absorption and emission bands of Yb:YLF are well separated, and radiation trapping effects are not strong even for highly doped samples. The measured 2 ms lifetime is also in agreement with the earlier measurements with the lowly Yb-doped YLF samples. Note that, compared to the 300 K measurement, the fast component is stronger, and had a lifetime of around 300 μ s. Moreover, within experimental errors, the fast component lifetime (τ_f) is similar for both 400 mJ and 4 J excitation. Contrarily, as we can see from Fig. 6 (b), the increased excitation intensity clearly increases the strength of the fast decay (A/B ratio in Eq. (2)), as it is also observed in earlier measurements.

3.3 Intensity dependence of fluorescence lifetime in the 25% Yb-doped YLF sample

Figure 7: (a) Measured variation of fluorescence lifetime with incident pump excitation energy for the 25% Yb-doped YLF sample at 300 K. The results are obtained via making a double exponential fit to the measured decay curves. (b) Corresponding variation of the ratio of slow and fast component strength of double exponential fit with temperature (A/B ratio in Eq. (2)). The data is taken using a 50 μ m pinhole aperture to minimize radiation trapping effects.

In the earlier sections, we have seen that, for the 25% Yb-doped sample, the measured fluorescence lifetime decay dynamics shows pump excitation intensity dependence. To

investigate this issue further, we have measured the variation of fluorescence lifetime of the 25% doped YLF sample with excitation intensity at temperatures of 78 K and 300 K. A 50 μ m diameter circular pinhole was used in the measurements to minimize radiation trapping effects.

Fig. 7 summarizes the excitation intensity dependent lifetime measurements at 300 K. The emission decay curves were fitted using single and double exponential assumptions. At low excitation intensities (e.g 100 mJ, see Fig 8 (a)), a single exponential fit provided a very good match to the measured decay. A double exponential fit could also be used, but the strength of additional fast component was rather low (less than 1/10th of the slow decay). On the other hand, at high excitation intensities, we have clearly observed a double exponential behavior, and a single exponential assumption was unable to fit to the experimentally measured decay curve (e.g. 4 J curve in Fig. 8 (b)).

Figure 8: Sample double exponential fit to the measured room-temperature experimental decay curves of the 25% doped YLF sample at an incident energy of (a) 100 mJ and (b) 4 J. The data is taken using a 50 μ m pinhole aperture to minimize radiation trapping effects. The graph clearly shows the contribution of fast and slow component of double exponential fit. Single exponential fit curves are also included to for comparison.

Data in Figs. 7 and 8 clearly show that, as the excitation intensity increases, or as the inversion level of the sample increases, a fast decay path appears in the measured emission decay curves. Moreover, the strength of this decay compared to the slow component increases with increasing excitation energy (Fig. 7 (b)). The rate of fast component also increases slowly with increasing excitation energy: has a value of around 2 ms at low intensities, which decreased to around 900 μ s level at high intensities. So we see that, with increasing inversion, the fast process gets faster and stronger. On the contrary, the slow component, which we attribute to the main transition of the laser level, do not get effected too much, and decays with a lifetime of around 4.5 ms at all intensity levels.

Figure 9: (a) Measured variation of fluorescence lifetime with incident pump excitation energy for the 25% Yb-doped YLF sample at 78 K. The results are obtained via making a double exponential fit to the measured decay curves. (b) Corresponding variation of the ratio of slow and fast component strength of double exponential fit with temperature (A/B ratio in Eq. (2)).

A similar trend is observed for the 78 K data, where the main slow transition decayed with a lifetime of around 2-2.2 ms at all excitation intensity levels (Fig. 9). Comparing Fig. 7 (b) and Fig. 9 (b), we see that, the strength of the fast transition compared to the slow transition was also similar at 78 and 300 K, and followed a similar change with excitation intensity. On the other hand, we have measured a much shorter fast component at 78 K, which decayed within 500 μ s at low intensities and within 200 μ s at high intensities. We believe that this is probably partially due to the increased absorption of the system at 78 K compared to 300 K, enabling higher inversion levels. We also believe that, the fast initial decay of

fluorescence signal is potentially due to (i) the redistribution of energy from the higher lying laser level of the Yb⁺³ ion (²F_{5/2} level) into the other rare earth impurity ions via upconversion mechanism [55-57], and/or (ii) amplified spontaneous emission mechanism that becomes effective at very high inversion levels (gain increases at lower temperatures, which might also fasten the ASE process) [48, 49]. For our case, since the expected level of impurities are quite low (as it will be discussed in the next section), the ASE process is most probably the dominant mechanism in the observed behavior, which underlines the importance of detailed ASE analysis for successful design of Yb:YLF thin-disk and slab lasers/amplifiers.

3.4 Room-temperature upconversion spectrum of 25% Yb-doped YLF sample

As mentioned earlier, we have observed strong upconversion from our 25% Yb-doped samples both at cryogenic and room temperatures. In this sub-section, we will present the spectra of observed emission in different spectral regions.

Fig. 10 and Fig. 11 show the measured emission spectra from the 25% Yb-doped YLF sample at room temperature at several different excitation intensities in the 200-1100 nm and 1980-2100 nm spectral ranges, respectively. To start with, Fig. 10 (a) shows the strength of upconversion spectra compared to the main 1 μ m emission, where we clearly see that the emission in the main spectrum is much stronger ($>>100$ -1000 times in strength) than the emission in the upconversion spectra. We have also seen that the strength of upconversion spectra roughly scales linearly with inversion (inversion level of the samples were estimated considering pump saturation effects).

Upconversion in Yb:YLF was already reported in [17, 32, 45], and the observed emission spectrum were also identified and the underlying transitions were mostly recovered. Comparing our measurements with the published spectral data in literature, we have noticed that our 25% Yb⁺³-doped YLF sample also possesses fingerprints of Er⁺³, Ho⁺³, and Tm⁺³ ions.

As an example, looking at the measured emission spectrum:

- the broad emission around 2050 nm (Fig. 11, ⁵I₇ to ⁵I₈ decay) clearly indicates the presence of Ho⁺³ ion in our sample [58],
- the emission in the 740-830 nm range (Fig. 10 (f)) possesses fingerprints of Tm⁺³ ion (³H₄ to ³H₆ decay) [58, 59],
- the emission peaks around 550 nm (Fig. 10 (d)) indicates the presence of Er⁺³ (⁴S_{3/2} to ⁴I_{15/2} transition) [59], whereas the emission peak around 540 nm could be attributed to the ⁵S₂ to ⁵I₈ transition of Ho⁺³ ion [58, 59],
- the blue emission band in the 450-500 nm spectral region (Fig. 10 (c)) is due to the ¹G₄ to ³H₆ transition of the Tm⁺³ ion [58, 59],
- the emission spectrum near 650 nm is potentially due to the ¹G₄ to ³F₄ transition of Tm⁺³ ion [58, 59] and the ⁴F_{9/2} to ⁴I_{15/2} transition of Er⁺³ ion [9],

- the weak emission near 410 nm (Fig. 10 (b)) has been attributed to the $^2H_{9/2}$ to $^4I_{15/2}$ transition of Er^{+3} ion [32],
- the weak green emission around 500 nm might be due to Yb^{+3} pair emission [32].

Figure 10: (a-f) Measured room-temperature emission and upconversion spectrum of 25% Yb-doped YLF sample at different pump excitation energies. (a) 200-1100 nm, (b) 350-420 nm, (c) 150-500 nm, (d) 500-575 nm, (e) 620-680 nm, (f) 740-830 nm.

It is clear from the observed emission spectra that, energy transfer from the higher lying laser level of the Yb^{+3} ion ($^2F_{5/2}$ level) into these impurity ions create loss of inversion and gain. Furthermore, besides the radiative decay lines we observe as upconversion emission, the energy levels of the Tm, Er and Tm also possess non-radiative transitions, and via multi-phonon emission impurity ions could also create parasitic heating [60]. Hence, presence of rare-earth

impurities in highly Yb-doped YLF samples might prevent efficient operation of lasers/amplifiers that intrinsically rely on highly-doped samples such as in thin-disk geometry.

Figure 10: (a-f) Measured room-temperature emission and upconversion spectrum of 25% Yb-doped YLF sample at different pump excitation energies. (a) 200-1100 nm, (b) 350-420 nm, (c) 150-500 nm, (d) 500-575 nm, (e) 620-680 nm, (f) 740-830 nm.

In closing we would like to mention that we have also observed very weak green emission from the 0.5% and 1% Yb-doped samples. The emission was easily visible to the eye due to the spectral sensitivity of human eye in this spectral region, but a fast measurement with a spectrometer showed that the green emission strength is more than five orders of magnitude lower than the main $1 \mu m$ emission. We believe some of this emission is due to Yb^{+3} ion pair emission [32], but we have also measured spectral peaks around 540 and 550

nm, indicating trace amounts of Er^{+3} and Ho^{+3} impurity even in these lowly doped samples.

Figure 11: Measured room-temperature emission spectrum of 25% Yb-doped YLF sample around 2050 nm.

3.5 Timing dynamics of different colours of upconversion spectrum

Figure 12: Measured emission time dynamics of 25% Yb-doped YLF sample at different spectral regions. The data is taken at an incident excitation energy of around 4 J, and using a 500 μm pinhole aperture to minimize radiation trapping effects. The 2 ms long pump excitation pulse (with a 2 kW peak power) is also shown.

In order to get a little more insight on the energy transfer process between the laser active Yb^{+3} ion and the other

impurities, we have also characterized the decay dynamics of the different emission wavelengths in the upconversion spectra at room temperature. Fig. 12 shows the measured dynamics of emission at different wavelengths. As mentioned earlier, the emission in the main 1 μm region is orders of magnitude stronger than upconversion emission, and hence in Fig. 12, the magnitude of emission decays at other colors is multiplied to scale them into levels close to the main line. Also, a relatively high excitation energy (4 J) is applied to the sample and a relatively large pinhole (500 μm) was used to achieve enough signal to noise ratio for the upconversion signal decay lines. Hence, the effect of radiation trapping might be strong in the measurements shown in Fig. 12. As a final note, the intensities shown are in arbitrary units, since we did not correct for the spectral response of the Si photodiode, which has a better sensitivity at the upconversion wavelengths.

A close look at Fig. 12 suggests a few hints on the underlying processes. The excitation source (pump diode signal) is also shown in Fig. 12, and the end of the pump signal initiates a clean observation window for us. First of all, the emissions in the 520-580 nm and 780-820 nm range are mostly in phase with the main emission line in the 1000-1100 nm spectral region (the signal maximum is at the same position and also the decay curves show similar double exponential behavior). Best-fit results to the measured experimental decay curves are summarized in Table 1. For the decays in these 3 spectral regions, we have found a slow response time of around 5 ms and a fast response time of around 1 ms in all cases. Note that, a good fit to the measured data could be obtained for decay curves in this 3 spectral regions, whereas due to the non-exponential nature of the measured decays in the other spectral ranges, the fit to the experimental measured decay were not very good, and the values in Table 1 should be taken as representative decay constants.

Spectral region (nm)	Single exp (ms)	Double exp slow (ms)	Double exp fast (ms)	Double exp slow to fast ratio (a.u.)
1000-1100	2.96 ± 0.04	5.15 ± 0.1	0.97 ± 0.03	1.32 ± 0.03
520-580	3.40 ± 0.06	4.87 ± 0.06	0.90 ± 0.03	2.18 ± 0.04
780-840	3.90 ± 0.06	5.25 ± 0.15	0.74 ± 0.04	2.91 ± 0.12
470-490	6.51 ± 0.15	-	-	-
300-700	6.73 ± 0.18	-	-	-
400-500 & 600-900	6.81 ± 0.03	-	-	-

Table 1: Summary of single and double exponential fit results to the emission decay curves in different spectral regions.

As an example, note that, the peak of the emission signal at 470-490 and 300-700 nm spectral range lags behind the main emission (not in phase). The lag time is around 1 ms for the 300-700 nm band and as large as 2.5 ms for the 470-490 nm transition (a simple single exponential fit gives the rise time of the energy transfer as 1.25 ms). Emission in the blue region (450-500 nm) is believed to originate from the $^1\text{G}_4$ to $^3\text{H}_6$ transition of the Tm^{+3} ion [58, 59]. Matos et al. explains several possible pathways of energy transfer from the Yb ion to the Tm ion [61], including energy-transfer upconversion,

cross relaxation and even a back transfer process (see Fig. 1 in [61]). A Yb-Tm energy transfer process rise-time of around 800 μ s was reported in [61], that is slightly shorter than our measurement (1.2 ms). On the other hand, while analyzing the influence of rare earth impurities in refrigeration efficiency in Yb:YLF, Di Lieto et al. proposed another path [17], the energy transfer from the Yb⁺³ ions to Tm⁺³ is probably not direct, and occurs via the Er⁺³ impurity (energy transfers first from Yb to Er and then from Er to Tm, see Fig. 6 in [17]). The process involves emission of Erbium ion from the ⁴I_{13/2} energy level, which has a long lifetime of 15 ms [62]. Hence, the relatively long delay (2.5 ms) we have measured for the 470-490 nm emission could be potentially explained by this model [17]. This simple example shows that, combined with the effect of radiation trapping that is already strongly present in the highly Yb-doped sample, the overall timing of energy transfer process gets quite complex in the highly Yb-doped YLF sample with Tm, Er and Ho impurities [9].

4. Conclusion

In conclusion, we have presented a detailed study focused on variation of fluorescence lifetime of Yb:YLF with temperature and doping. The data with the lowly doped (0.5-1%) samples using the pinhole method confirmed the earlier literature: fluorescence lifetime is measured to be 1.97 ms and 2.1 ms at 78 K and 300 K, respectively. On the other hand, we have observed a double exponential behavior and excitation intensity dependent decay process in the highly-doped (25%) YLF sample, which is to our knowledge, was not reported earlier. We believe that this double-exponential behavior is mostly due to the amplified spontaneous emission process, and our data shows that suppression of ASE will be a challenge in the design of thin-disk Yb:YLF lasers/amplifiers especially for those operating at cryogenic temperatures. We have further provided detailed upconversion spectrum and initial measurements revealing some insights into the energy transfer process between the Yb ion and the other impurities.

It is clear that, more work is required to understand whether the Yb:YLF crystal growth process could be optimized to minimize the impurities in highly Yb-doped samples. Future work is also required to see the importance of this impurities and parasitic energy transfer process on laser/amplifier performance. We hope the initial findings presented in this work to be useful to laser engineers and scientists working with Yb:YLF systems.

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Disclosures

The authors declare no conflicts of interest.

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