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Upconversion dynamics in Er$^{3+}$-doped YAG

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Abstract

Green, blue, violet and ultraviolet upconversion luminescence is reported at room temperature in a YAG: 10.5%Er$^{3+}$ crystal pumped by one-colour (647 nm) and two-colour (647+618 nm) laser excitation. The upconversion mechanism was studied by means of time-resolved luminescence spectroscopy and the energy flow pathways are described. Based on the results it appears that energy transfer upconversion is the dominant contribution to the upconverted luminescence upon 647 nm excitation, and excited state absorption is the dominating mechanism upon 647+618 nm excitation.

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1. Introduction

The strong interest of upconversion luminescence in rare earth (RE) ion-doped crystals and fibres mainly results from the possibility to obtain new sources for laser emission in different spectral ranges [1–3]. Compared to other techniques for generating laser radiation, upconversion has especially in the short wavelength region the advantage that it does not need as stringent phase matching and high excitation wavelength stability, as second or third harmonic generation do, and it may reduce the photoionization that can induce degradation of the host crystal [4]. Moreover, the advent and rapid improvement, in recent years, of diode lasers in the infrared and red spectral domains provide an opportunity for the development of compact, all solid-state laser sources in the ultraviolet and violet ranges. In upconversion schemes, population in an excited state with an energy exceeding the energy of the pump photon may be achieved either by excited state absorption (ESA), or by energy transfer upconversion (ETU), or by photon avalanche (PA), according to the excitation conditions and the specific pump wavelengths used (see, e.g., Ref. [4]). These
mechanisms can lead to different upconversion luminescence efficiencies, thus, in order to minimise losses in laser or amplifier design, considerable efforts have been devoted to characterise and understand upconversion phenomena of RE ions in various host materials [5–8].

Among the RE ions in which efficient frequency upconversion has been demonstrated, the trivalent erbium ion is very attractive as a laser active ion in the ultraviolet, visible and infrared spectral domains, since its energy-level structure contains several metastable multiplets, $^4I_{13/2}, ^4I_{11/2}, ^4F_{9/2}, ^4S_{3/2}$ and $^2P_{3/2}$. The upconversion luminescence of the Er$^{3+}$ ion has been studied extensively [9–12]. Upconversion laser emission, primarily in the blue, green and infrared region, has also been achieved in several Er$^{3+}$-doped materials, including LiYF$_4$ [13–17], YAlO$_3$ [18], BaY$_2$F$_8$ [19], CaF$_2$ [20], LiKYF$_5$ [21] and LiLuF$_4$ [22], using upconversion schemes based on ESA or ETU processes. However, most upconversion studies in Er$^{3+}$-doped materials have focused on the excitation to three multiplets in the levels $^4I_{13/2}$ ($\approx 1500$ nm), $^4I_{11/2}$ ($\approx 980$ nm), and $^4I_{9/2}$ ($\approx 800$ nm), including one-colour and two-colour laser excitations. The present spectroscopic studies focus on the upconversion luminescence mechanism upon $^4F_{9/2}$ ($\approx 650$ nm) excitation in Er$^{3+}$-doped YAG crystals. In lower concentration crystals, the upconversion will normally be dominated by ESA processes [23,24]. In order to have a strong ETU process, a concentration containing 10.5 at% Er$^{3+}$ was used in this experiment. Although the oxide-based compound YAG in comparison with fluoride crystals has higher phonon energies, which shorten the metastable state lifetimes, it is superior in terms of mechanical hardness, thermal conductivity and optical properties. Moreover, a higher upconversion efficiency may still be achieved; for example, an output power of over 160 mW was reported at 550 nm in an Er$^{3+}$-doped YAlO$_3$ crystal with an upconversion efficiency of 17% [25]. In trivalent erbium-doped compounds, the $^4F_{9/2}$ multiplets can be utilised as an intermediate excited state. Brede et al., for example, demonstrated room-temperature upconversion laser oscillation on the $^4S_{3/2}^{{}^4}\mathrm{I}_{15/2}$ transition by 647 + 800 nm excitation in Er:LiYF$_4$, Er:KYF$_4$ and Er:YAG crystals [26].

Upconversion lasing at 470 nm upon $^4F_{9/2}$ excitation has also been observed in an Er:LiYF$_4$ crystal by two successive ETU processes [27].

In this study, we have observed green, blue, violet and ultraviolet signals in YAG: 10.5% Er$^{3+}$ by one-colour (647 nm) and two-colour (647 + 618 nm) pulsed laser excitation using tunable pulsed dye laser systems. For the interpretation of the upconversion luminescence, the decay profile of the upconverted luminescence using time-resolved spectroscopy was recorded, and a detailed transient analysis and a discussion of the involved upconversion pumping schemes are reported.

2. Experiment

The Er:YAG crystal employed in this work is grown using a conventional Czochralski technique. It is 10 mm long, 8 mm wide, 10 mm high and contains 10.5 at% Er$^{3+}$. The compound YAG has a cubic space-group symmetry $O_h^{10}$ and the Er$^{3+}$ ions substitute for Y$^{3+}$ ions on the dodecahedral sites having $D_2$ symmetry. For the pulsed excitation in the red wavelength region, a dye laser (Continuum Nd-60), operated with a DCM dye, was pumped by a Nd:YAG laser (Continuum NY-82) with a wavelength of 532 nm, an 8 ns pulse duration and a repetition rate of 10 Hz. The beam was slightly focused onto the crystal by a 100-cm focal length lens. The laser spot diameter at the sample was about 2 mm and the energy about 3 mJ. To obtain ultraviolet light for direct excitation, the radiation from the dye laser could be frequency doubled in a KDP crystal. Following the pulsed excitation, the fluorescence was collected by a quartz lens ($f = 15$ cm), filtered by 1/8 m monochromator and finally detected by a Hamamatsu 1564U photomultiplier tube. The spectral resolution of the detected signal was approximately 5 nm. The time-resolved signal from the detector was captured by a digital oscilloscope, and transferred to a computer for the analysis of the decay curves. For two-colour excitation, a second Continuum NY-82 Nd:YAG laser was used to pump another Continuum Nd:60 dye laser, which was also operated with a DCM dye.
The beam was again slightly focused on the crystal \((f=100\ \text{cm})\) and overlapped with the first laser spot. In the two-colour pumping process, the energy of both dye laser pulses was about \(1\ \text{mJ}\). The Nd:YAG lasers were externally triggered by a digital pulse generator (Stanford Research Systems Model DG535), which was used for temporal synchronisation of the two laser pulses. All experiments were performed at room temperature.

3. Results and discussion

When the sample was pumped by a dye laser, tuned to 647 nm, which corresponds to the excitation of the \(4F_{9/2}\) multiplet, upconversion signals around 320, 410, 475 and 560 nm were observed. A relevant part of energy-level diagram of \(\text{Er}^{3+}\) in YAG based on the spectroscopic data reported by Gruber et al. [28] is presented in Fig. 1, together with the excitation schemes described in the following subsections.

### 3.1. Green emission \((\approx 560\ \text{nm})\)

The excitation induces an intense green emission from the \(4S_{3/2}\) multiplet. Firstly, photon avalanche upconversion, i.e., a process that involves cross relaxation to populate the metastable states of two ions followed by ESA from these states, was excluded because none of the typical signatures (e.g. a threshold behaviour) for an avalanche process could be found [4]. The two other upconversion mechanisms, ETU and ESA, can be distinguished by time-resolved measurements [29,30]. ESA consists of two consecutive excitation steps on a single ion and has to occur during the excitation pulse, whereas the ETU process can take place after the pulsed laser excitation and is a two-ion process. Therefore, the lifetime of upconverted luminescence upon ESA exhibits exponential decay behaviour similar to that by direct excitation, while the ETU upconversion process results in a decay behaviour with an observable rise time. Fig. 2 shows a clear rise time of \(1.2\ \mu\text{s}\) in the decay profile by monitoring \(4S_{3/2} \rightarrow 4I_{15/2}\)

![Fig. 1. Simplified energy-level diagram for the Er\(^{3+}\) ion in YAG showing the excitation and emission transitions in the upconversion processes. For each energy level, the wavenumber (cm\(^{-1}\)) for the highest and lowest Stark levels are given at the right-hand side and the relative lifetimes by direct laser excitations at the left-hand side.](image-url)
luminescence at 561 nm. This demonstrates that the ETU process causes the upconverted luminescence, while the ESA process can be ruled out. Several possible pathways can be considered for the ETU processes populating the $^4S_{3/2}$ state. After ground-state absorption (GSA), the $^4I_{9/2}$ and $^4I_{11/2}$ states will be populated by nonradiative relaxation from the $^4F_{9/2}$ state. Since the $^4F_{7/2}$ lies at almost exactly twice the energy of the $^4I_{11/2}$ state, one ion in the $^4I_{11/2}$ state can be promoted into the $^4F_{7/2}$ state, from which the $^4S_{3/2}$ state can be populated by nonradiative relaxation. It is also possible that energy transfer takes place between one ion in the $^4I_{9/2}$ state and one ion in the $^4I_{11/2}$ state, resulting in one ion into the $^4F_{5/2}$ and another ion in the ground state. The $^2G_{9/2}$ state (yielding blue emission, which will be discussed in next subsection) may also contribute to the population of the $^4S_{3/2}$ state by nonradiative relaxation. This contribution should however be small. The inset of Fig. 2 shows the decay profile of the green emission in a larger scale time, in which we can see that the tail lifetime (>10 μs) of the decay profile is longer than that (1.59 μs) of the $^4S_{3/2}$ state [31]. This strongly indicates that the tail signal of green emission comes from the ETU process by the ions in the $^4I_{11/2}$ state, which has a lifetime of >10 μs, because the lifetimes of the $^4F_{9/2}$ and $^4I_{9/2}$ states are 1.21 μs and 53 ns, respectively. In conclusion, green emission from the $^4S_{3/2}$ state results, during earlier times, from ETU processes with several energy transfer pathways, and during later times, from only the $(^4I_{11/2}→^4F_{7/2}) + (^4I_{11/2}→^4I_{15/2})$ upconversion process.

### 3.2. Violet emission (≈410 nm)

According to the energy-level data, the two transitions: $^2P_{3/2}→^4I_{13/2}$ and $^2G_{9/2}→^4I_{15/2}$ may contribute to the violet emissions. This can be confirmed by the transient emission signal at 410 nm, as shown in Fig. 3, in which a nonexponential decay process was exhibited. The luminescence by the $^2P_{3/2}→^4I_{13/2}$ transition will be discussed in Section 3.3. Here we concentrate on the upconversion luminescence at 410 nm from the $^2G_{9/2}→^4I_{15/2}$ transition. A clear rise time of 130 ns can be observed in the inset of Fig. 3.
demonstrating that the ETU process is the upconversion mechanism responsible for the violet signals. The ESA process, e.g., one ion in the $^4I_{9/2}$ state absorbs a 647 nm photon to populate the $^2K_{15/2}$ state, can be ruled out. There are two possible ETU pathways to populate the $^2G_{9/2}$ state. One is that two Er$^{3+}$ ions in the $^4I_{9/2}$ state interact resulting in that the energy of one ion is transferred nonradiatively onto another ion thereby exciting it into the $^2G_{9/2}$ state. The ETU process involving the ions in the $^4I_{9/2}$ state would occur on a time scale, determined by the lifetime of the $^4F_{9/2}$ state since the lifetime of the $^4I_{9/2}$ state (53 ns) is far shorter than that of the $^4F_{9/2}$ state (1.21 μs). The other pathway to the $^2G_{9/2}$ state is that one ion in the $^4I_{9/2}$ state and one ion in the $^4F_{9/2}$ state interact, leading to one ion in the ground state and one ion in the $^2K_{15/2}$ state, and the $^2G_{9/2}$ state is then populated by subsequent nonradiative relaxation. It is reasonable that ETU is the dominant upconversion process considering the concentration of Er$^{3+}$ ions (10.5 at%) and temperature (300 K) [9,32]. It can also be understood according to the energy-level data, since the two ETU processes are exactly resonant. The thermalisation has the effect that most of the population will be in the lowest Stark levels. Two ions in $^4I_{9/2}$ (Stark level 12297 cm$^{-1}$) can produce one ion into $^2G_{9/2}$ (Stark level 24593 cm$^{-1}$). The other ETU pathway $^4I_{9/2}$ (Stark level 12297 cm$^{-1}$) and $^4F_{9/2}$ (Stark level 15288 cm$^{-1}$) populates $^2K_{15/2}$ (Stark level 27585 cm$^{-1}$), whereas the energy difference for the ESA process is at least tens of cm$^{-1}$.

### 3.3. Ultraviolet and blue emissions ($\approx 320$ and 475 nm)

The ultraviolet and blue emission was assigned to the transitions $^2P_{3/2}\rightarrow^4I_{15/2}$ and $^2P_{3/2}\rightarrow^4I_{11/2}$. To confirm that the signals resulted from the $^2P_{3/2}$ state, a comparison of the decay profiles at 320 and 475 nm was made, as shown in Fig. 4, together with the decay curve at 410 nm ($^2P_{3/2}\rightarrow^4I_{13/2}$). It can be seen in Fig. 4 that the decay profiles of the upconverted luminescence at 320 and 475 nm are very similar, which implies that the ultraviolet and blue emission results from the $^2P_{3/2}$ state. The decay profile of upconverted luminescence at 410 nm also agrees well with those at 320 and 475 nm after a few microseconds (i.e. after
the $^{2}G_{9/2}$ contribution has decayed) and this is an indication that the $^{2}P_{3/2}$ state contributes to the 410 nm signal by means of the $^{2}P_{3/2} \rightarrow ^{4}I_{13/2}$ transition. To populate the $^{2}P_{3/2}$ state several possible processes can be considered. Since two pumping photons at 647 nm do not provide sufficient energy to excite $^{2}P_{3/2}$ at 31480 cm$^{-1}$, at least two upconversion steps must occur. The ESA mechanism can be excluded in this case since, as shown in the inset of Fig. 4, a rise time of 1.2 μs is demonstrated. The ETU processes may take place. The $^{2}P_{3/2}$ state can be populated by ETU to the $^{2}H(2)_{9/2}$ state followed by nonradiative decay to the $^{2}P_{3/2}$ state. Two possible pathways for ETU to the $^{2}H(2)_{9/2}$ state are as follows. Two ions in the $^{4}S_{3/2}$ state produce one ion in the ground state and the other one in the $^{2}H(2)_{9/2}$ state, with subsequent nonradiative relaxation resulting in the upconverted luminescence. Another possibility is that one ion in the $^{2}G_{9/2}$ state and one ion in the $^{4}I_{9/2}$ state populate the $^{2}P_{3/2}$ state by nonradiative relaxation from the $^{2}H(2)_{9/2}$ state. The two ETU processes can be confirmed from the inset of Fig. 4, where two different rise slopes are clearly exhibited (about 120 ns and 1.3 μs).

The ultraviolet emission was very weak since two successive ETU processes were required under 647 nm excitation. A one-step upconversion process will be expected to give a higher upconversion efficiency. Therefore, the ultraviolet emission when using two-colour excitation (647 + 618 nm) was also investigated. The pumping wavelength at 618 nm corresponds to the $^{4}F_{9/2} \rightarrow ^{2}P_{3/2}$ transition. In the experiment, no luminescence was observed when the laser beam at 618 nm alone was used to pump the sample. As expected, an intense ultraviolet emission was observed and can be contributed to an ESA upconversion process, as supported by the data in Fig. 5. The decay profile of the upconverted luminescence at 320 and 475 nm has no rise time and shows an exponential decay similar to that by direct excitation (see e.g., Ref. [30]). However, there is an additional contribution to the 410 nm emission ($^{2}P_{3/2} \rightarrow ^{4}I_{13/2}$) since it shows a nonexponential decay. The higher time resolution in the inset of Fig. 4.
Fig. 5 reveals a contribution from an ETU process. The ETU signal results from the \(^{2}G_{9/2}\) state according to the rise time (130 ns) as discussed above. The ESA process takes place when an \(\text{Er}^{3+}\) ion in the \(^{4}F_{9/2}\) state absorbs another photon (618 nm) to populate the \(^{2}P_{3/2}\) state. From the time scale of the inset in Fig. 5, we can see that, first, the ESA process dominates the 410 nm signal, later on, the contribution from the ETU process appears. Finally, after a few microseconds, the ESA process dominated the signal again.

In summary, we have observed the upconversion luminescence in an \(\text{Er}^{3+}\)-doped yttrium aluminium garnet crystal when optically pumping the \(^{4}F_{9/2}\) state. The upconversion processes were identified by measuring the decay profiles of upconversion emission from different multiplets under one- or two-colour pulsed excitation. With the arguments involved in Section 3, two possible upconversion processes ETU and ESA exist. Under one-colour excitation, \(\text{Er}^{3+}\) ions were excited from the ground-state to the \(^{4}F_{9/2}\) state by a ground-state absorption process, ETU then takes place through different energy-flow pathways. Under a two-colour excitation, \(\text{Er}^{3+}\) ions in the ground state absorb two photons through ESA from the \(^{4}F_{9/2}\) state, which leads to population and upconversion luminescence from the \(^{2}P_{3/2}\) state.

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