

Dynamics of visible-to-ultraviolet upconversion in YAlO_3 : 1% Er^{3+}

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Abstract

The dynamics of visible-to-ultraviolet upconversion in YAlO_3 : 1% Er^{3+} crystal has been investigated using the time-resolved laser spectroscopy when the sample was excited into the $^4\text{S}_{3/2}$ multiplets. It is found that the upconverted luminescence is produced by energy-transfer upconversion or by excited-state absorption depending on the excitation wavelength. The dependence of upconverted luminescence on pump power is presented, and the relative intensities of upconverted luminescence were accounted for by Judd–Ofelt theory.

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1. Introduction

Upconversion phenomena in rare earth (RE) ion-doped crystals and fibers have been studied extensively in the last decades [1,2]. The great interest in study of this kind results primarily from their connection with the possibility of lasing emission in infrared, visible and ultraviolet ranges [3,4]. Among RE ion-doped materials that have demonstrated upconversion phenomena, the Er^{3+} ion-doped ones have been known to be efficient infrared to visible upconverters. In fact, upcon-

version lasing emissions in infrared, visible range have recently been achieved in several Er^{3+} -doped materials. Whitley et al. [5], for example, demonstrated room-temperature upconversion lasing at 546 nm in Er^{3+} -doped fluorozirconate fiber. An output power of 10 mW in Er^{3+} -doped fluorozirconate fiber was also obtained at 548 nm with a slope efficiency of 7% [6]. Both continuous wave (CW) and pulsed laser emission lines have been observed in Er^{3+} -doped YLiF_4 (Er:YLF) crystal at 551 and 544 nm [7,8]. Additional CW upconversion laser emission lines in Er:YLF were also achieved at 468, 470, 561, and 702 nm [9–12]. In Er^{3+} -doped YAlO_3 crystals, green upconversion lasing at 550 nm was reported by Scheps [13,14]. However, most upconversion studies in Er-doped materials were focused on infrared and visible regions. The ultraviolet upconversion phenomena in

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many RE-doped materials remain to be explored [15]. The purpose of this paper is to investigate the possibility of realizing ultraviolet upconversion lasing in Er^{3+} -doped YAlO_3 crystal.

The excitation processes that lead to emission from energy state higher than the terminating state of the first pump-absorption step can be divided into three main classes: excited-state absorption (ESA), energy-transfer upconversion (ETU), and photon avalanche (PA). In a previous paper [16], we have performed an experimental investigation for characterizing and understanding ultraviolet and violet upconversion phenomena in Er^{3+} -doped YAG crystals. It is found that upconversion luminescence could be, depending the excitation wavelengths, contributed by different upconverted mechanisms when the sample was populated into $^4\text{S}_{3/2}$ multiplet. In the present paper we studied dynamic properties of green-ultraviolet and -violet upconversion in Er^{3+} -doped YAlO_3 crystal. Compared with the host material YAG, The compounds (YAlO_3), commonly referred to as YALO or YAP, is similar to YAG in terms of mechanical hardness and thermal conductivity, but superior for upconversion process due to its lower phonon energy, which could efficiently suppress multiphonon relaxation.

In trivalent erbium-doped compounds, the $^4\text{S}_{3/2}$ multiplet is available as an intermediate state for upconversion due to its larger energy gap to next-lower state ($^4\text{F}_{9/2}$). In this paper, a tunable optical parameter oscillator (OPO) laser with 6 ns duration was used as an excitation source. Following $^4\text{S}_{3/2}$ excitation, ultraviolet and violet upconverted signals were found and the mechanisms were investigated in detail using the time-resolved laser spectroscopy.

2. Experiment

The crystal of YALO doped with 1% Er^{3+} , grown by a conventional Czochralski technique, has a size of $1.0 \times 1.0 \times 1.0 \text{ cm}^3$. YALO has a gadolnium orthoferrite structure with the orthorhombic space group D_{2h}^{16} . The Er^{3+} ions substitute for Y^{3+} ions in point group symmetry C_s .

The details of our experimental apparatus have been described elsewhere (see e.g., [16]) and

therefore only a brief description is given here. An injection seeded and Q-switched Nd:YAG laser (Continuum Precision II 8000) with frequency tripling, characterized by a 355 nm wavelength, a 8 ns duration and a 10 Hz repetition rate, were used to pump a tunable OPO laser (Continuum Sunlite EX). To obtained UV radiation, the second harmonic of the OPO laser was produced in two BBO crystals (Continuum FX-1 UV Frequency Extension). The different components of the laser beams from the OPO laser were first isolated with a Pelin–Broca prism, and then the appropriate excitation light passed through an aperture and interacted with the sample. Following pulsed excitation, the fluorescence was collected by a quartz lens and focused to the entrance slit of a 0.5-m monochromator equipped with a Hamamatsu R3896 photomultiplier tube. A transient oscilloscope (Tektronix TDS 620B) and a boxcar integrator (Stanford Research Systems SR250) were used for fluorescence decay and spectra measurements, respectively.

3. Results and discussion

Fig. 1 shows a partial energy level diagram of Er^{3+} ion based on the spectroscopic data reported by Donlan and Santiago [17], and the relevant upconversion excitation scheme. All experiments were performed at room temperature. When the Er^{3+} ions were excited into the $^4\text{S}_{3/2}$ multiplet, the upconversion signals around 320, 410, and 470 nm were obtained as shown in Fig. 2, where the upper trace corresponds the excitation at 542.4 nm from $^4\text{I}_{15/2}(1)$ to $^4\text{S}_{3/2}(1)$ while the lower one corresponds the excitation at 548.8 nm from $^4\text{I}_{15/2}(4)$ to $^4\text{S}_{3/2}(1)$. The laser spot diameter at the sample was about 3 mm and the energy is about 6 mJ. The spectra presented in Fig. 2 are time-integrated spectra. As the scanning velocity of the monochromator was very slow, the wavelength accuracy of the spectra was mainly determined by the monochromator, which is 0.1 nm. According to the energy level data, we recognized the luminescence transitions: 320 nm ($^2\text{P}_{3/2} \rightarrow ^4\text{I}_{15/2}$), 410 nm ($^2\text{P}_{3/2} \rightarrow ^4\text{I}_{13/2}$), and 470 nm ($^2\text{P}_{3/2} \rightarrow ^4\text{I}_{11/2}$). To explain the intensity ratio of three upconversion

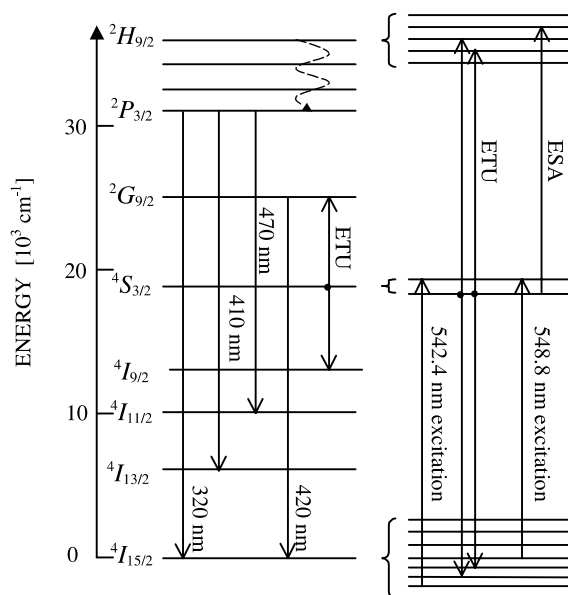


Fig. 1. Simplified energy-level diagram for Er^{3+} ion in YALO crystal showing the excitation and emission transitions in up-conversion processes.

emissions (320, 410, and 470 nm), the transition probabilities from $^2\text{P}_{3/2}$ to $^4\text{I}_{15/2}$, $^4\text{I}_{13/2}$, and $^4\text{I}_{11/2}$, using the Judd–Ofelt theory (see [18,19]), were calculated to be 742, 2854, and 1877 s^{-1} , respectively, where the reduced matrix elements $\langle\langle U^\lambda \rangle\rangle$ and the spectra intensity parameters Ω_t were obtained from [20]. It can be seen that the intensity

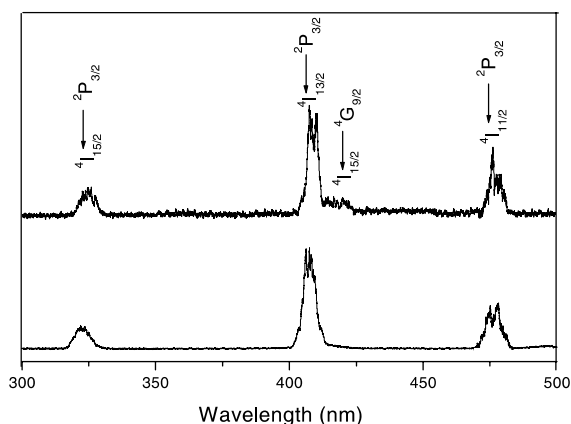


Fig. 2. Upconversion luminescence spectra of YALO: 1% Er^{3+} under 542.4 nm (top) and 548.8 nm (bottom) excitations at room temperature.

ratio of three emission bands (320, 410, and 470 nm) is approximately 1:3.8:2.5, which agree with the experimental results as shown in Fig. 2.

To understand the physical mechanisms responsible for the observation described above, the dependence of intensity of upconverted luminescence emitting from $^2\text{P}_{3/2}$ state on pump power was investigated experimentally at first. The intensity of upconverted luminescence at 321.8 nm was measured under different exciting laser power. The results are shown in Fig. 3 in double logarithmic scale, and the slopes of plots for two excitation wavelengths (542.4 and 548.8 nm) are 1.8 and 1.9, respectively. This indicated a two-step upconverted process taking place under the two wavelengths excitations. The possible upconversion mechanisms (ESA and ETU) upon $^4\text{S}_{3/2}$ excitation are shown in Fig. 1, where PA upconversion was excluded in our case because none of the typical signature for this process [21]. When Er^{3+} ions in excited state $^4\text{S}_{3/2}$ were transformed to $^2\text{H}_{9/2}$ state by means of the ESA or the ETU mechanism, subsequent nonradiative relaxation from the $^2\text{H}_{9/2}$ populates the $^2\text{P}_{3/2}$ resulting in the upconverted luminescence.

ESA and ETU can be distinguished by the time-dependent measurements [16,22–24]. Following a pulsed excitation from ground state, ESA takes place during the excitation pulse, whereas the ETU

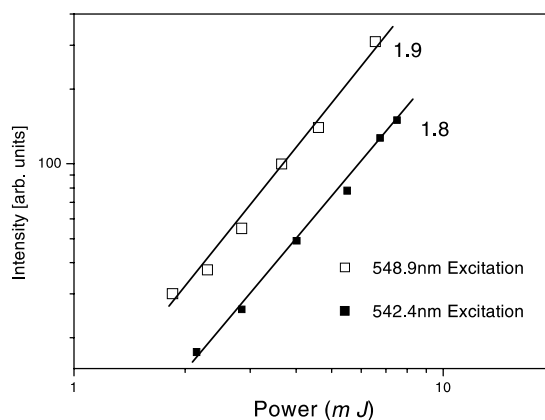


Fig. 3. The intensity of upconverted fluorescence at 321.8 nm as a function of pump power. The numbers denote the slopes in double-logarithmic representation under 542.4 nm (1.8) and 548.8 nm (1.9) excitations, respectively.

process can process after the pulse. Therefore, the lifetime of upconverted luminescence upon ESA exhibits an exponential decay behavior similar to that by direct excitation, while ETU upconversion process results in a decay behavior with an observable rise time. In the experiment, we measured the decay curves of the $^2P_{3/2}$ state under 542.4 and 549.8 nm excitations by monitoring $^2P_{3/2} \rightarrow ^4I_{13/2}$ luminescence at 406.8 nm, as shown in Fig. 4. The top curve (542.4 nm) exhibits a clear rise time, whereas the bottom curve (548.8 nm) has no rise time but an exponential decay with the lifetime of 50 μs , which is in good agreement with the lifetime (49 μs) of the $^2P_{3/2}$ state measured by direct excitation at 316.6 nm (31586 cm^{-1}). This confirms that ESA is dominant upconversion mechanism for 542.4 nm excitation, while ETU is dominant for 548.8 nm excitation.

The difference of upconverted mechanisms between 542.4 and 548.8 nm excitations can also be understood from the crystal-field levels of Er^{3+} : YALO. Table 1 listed the relevant Stark levels taken from [17] together with lifetimes of these multiplets measured in the present experiment by direct excitation. Following the ground state ab-

Table 1

The Stark levels of relevant multiplets taken from [17] and the lifetimes of excited states measured in this work by direct excitation in YALO: 1% Er^{3+}

State	Energy (cm^{-1})	Lifetime (μs)
$^4I_{15/2}(0)$	0.0	
(1)	50.7	
(2)	170.7	
(3)	217.6	
(4)	265.9	
(5)	388.0	
(6)	443.1	
(7)	516.4	
$^4S_{3/2}(0)$	18,406.2	114
(1)	18,486.7	
$^2P_{3/2}(0)$	31,449.0	49
(1)	31,585.2	
$^2H_{9/2}(0)$	36,315.0	
(1)	36,389.0	
(2)	36,462.7	
(3)	36,630.5	
(4)	36,662.5	

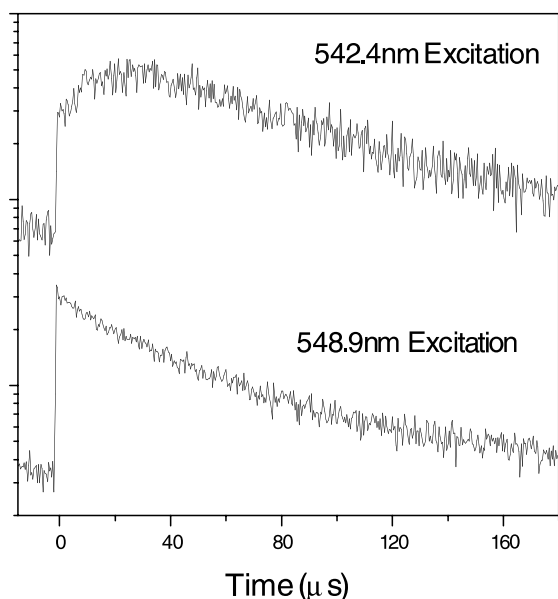


Fig. 4. Decay profiles of the upconverted luminescence at 406.8 nm in YALO: 1% Er^{3+} by 542.4 nm (top) and 548.8 nm (bottom) excitations in a semilogarithmic representation.

sorption (GSA) as shown in Fig. 1, the subsequent thermalization of the $^4S_{3/2}$ state takes place on a picosecond time scale, which results in population of the lowest Stark level of $^4S_{3/2}$. Because the duration of the excitation pulse (6 ns) is significantly longer than the thermalization process, upconversion process can occur from the lowest Stark level of $^4S_{3/2}$ for the second excitation step regardless of ESA or ETU. We found that for 548.8 nm excitation the photon energy ($h\nu = 18,221.6\text{ cm}^{-1}$) is very close to the energy difference between the $^4S_{3/2}(0)$ and the $^2H_{9/2}(3)$ levels, that means near resonant with this wavelength. However, for 542.4 nm excitation ($h\nu = 18,436.6\text{ cm}^{-1}$), the energy difference between the photon and the interval between the $^4S_{3/2}$ and the $^2H_{9/2}$ levels is at least 180.3 cm^{-1} , that is far away from resonant. Therefore, ESA responsible for the upconverted fluorescence at 548.8 nm excitation is reasonable.

An additional signal around 420 nm under 542.4 nm excitation was also observed as can be seen from Fig. 2. We found a possibility to produce this signal as follows. According to spectroscopic data, the energy difference between the multiplets $^4I_{9/2}-^4S_{3/2}$ and $^4S_{3/2}-^2G_{9/2}$ is almost

equal. Therefore the ETU upconversion process ($^4S_{3/2} \rightarrow ^4I_{9/2}$) + ($^4S_{3/2} \rightarrow ^2G_{9/2}$) is possible, and a subsequent radiation from $^2G_{9/2}$ to $^4I_{15/2}$ results in 420 nm fluorescence.

In the experiments, we found that, under the same excitation intensities, the upconverted signal at 548.8 nm excitation is stronger than that at 542.4 nm excitation. This indicated that ESA is a better mechanism for practical pumping for lasers in YALO: Er³⁺ (1 at.%) crystal.

4. Summary

In this paper, we observed the ultraviolet and violet upconversion luminescence in YALO: Er³⁺ (1 at.%) crystal upon $^4S_{3/2}$ excitation. In order to distinguish the mechanism of the upconverted luminescence, we measured the decay profile of upconverted luminescence by means of time-resolved laser spectroscopic technique. The dependence of luminescence intensity versus pump power was also measured. With the evidence presented in Figs. 1–4 and arguments developed in Section 3, two possible upconversion processes ETU and ESA were analyzed. Er³⁺ ions were excited from the ground state to $^4S_{3/2}$ state with GSA. At 542.4 nm excitation, ETU takes place between two ions in the $^4S_{3/2}$ state to produce an ion in the $^2H_{9/2}$ state and the other into the ground state. Subsequent nonradiative relaxation from the $^2H_{9/2}$ state populates the $^2P_{3/2}$ state. Another ETU process (($^4S_{3/2} \rightarrow ^4I_{9/2}$) + ($^4S_{3/2} \rightarrow ^4G_{9/2}$)) could also take place at this wavelength excitation. At 548.8 nm excitation, an Er³⁺ ion in the $^4S_{3/2}$ state near resonantly absorbs another photon and leads to population of $^2H_{9/2}$. Subsequent nonradiative relaxation from the $^2H_{9/2}$ state populates the $^2P_{3/2}$ state resulting in the ESA upconversion luminescence. This demonstrated that the mechanism for upconversion could be determined to be different by only a small variation of the excitation wavelength.

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