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Ultraviolet upconversion in Pr^{3+}:Y_2SiO_5 crystal by Ar^+ laser (488 nm) excitation

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Abstract. Ultraviolet upconversion fluorescence band (260–350 nm) has been observed from Pr^{3+}:Y_2SiO_5 pumped by Ar^+ ion laser (488 nm). Power dependence of the fluorescence emitted from $4f5d$, ${}^3P_0$ and ${}^1D_2$ were measured. The upconversion mechanism was analyzed using the rate equations with a simplified three level model. It appears that excited state absorption (ESA) is the dominant upconversion process for lower Pr^{3+} concentration and energy transfer upconversion (ETU) is dominant for higher Pr^{3+} concentration.

PACS. 42.65.Ky Frequency conversion; harmonic generation, including higher-order harmonic generation

1 Introduction

The most common tunable UV lasers are visible lasers followed by frequency doubling or mixing in nonlinear materials, which are usually complicated and need strict phase matching conditions. Therefore, this kinds of UV tunable laser are restricted in practical applications and it is necessary to develop efficient, compact, and reasonable cost tunable UV laser. Recently, there has been an intense interest in the study of new approach to produce tunable UV laser by using the trivalent rare earth (RE) $4f^{n-1}5d \rightarrow 4f^n$ interconfigurational transitions in RE-doped crystals [1–4]. Because of the strong coupling between the $5d$ electron of the active ion and its crystalline environment, the $4f^{n-1}5d$ levels form a broad band and the transitions $4f^{n-1}5d \rightarrow 4f^n$ can produce an UV fluorescence band. The tunable UV lasers of this type have been demonstrated in $LiCaAlF_6$/$LiLuF_4$ crystals doped with Ce^{3+} pumped by direct 4ω or 5ω excitation of Nd^{3+}:YAG laser [5,6]. But, serious problems followed by UV-photon direct pumping are the formation of color centers due to absorption of the pump or the laser radiation into the conduction band. This problem can be solved by upconversion pumping using longer wavelength two-step excitation process. A lot of efforts have been devoted to develop new crystals which could be used for upconversion UV laser materials. Some Pr^{3+}-doped crystals (oxides or fluorides) have received an increasing attention as the candidates, in which the $4f5d$ lowest states are located below the $4f^2$ ${}^1S_0$ manifold and the ${}^1D_2$, ${}^3P_J$ and ${}^1I_6$ manifolds of $4f^2$ configuration can be used as intermediate states for upconversion [7–9]. However, the tunable $4f^{n-1}5d \rightarrow 4f^n$ laser emission by upconversion pumping has never been demonstrated up to now. Therefore, it is necessary to extend this investigation to other crystals.

Pr^{3+}:Y_2SiO_5 crystal, which has high chemical and photochemical stability and suitable energy level structure, provides a potential candidate as UV upconversion laser material. Absorption and emission spectra of Pr^{3+}:Y_2SiO_5 in visible and infrared region have been investigated by Kuleshov et al. [10] and they also studied ESA cross-section.

In this paper we present an observation of UV upconversion luminescence band excited by 488 nm Ar^+ laser in Pr^{3+}:Y_2SiO_5 crystal. To understand the mechanism of the upconversion, we measured the dependence of luminescence intensity on pump power. The rate equations with a simplified three level model have been used to analyze the experimental results.

2 Experiment and results

The single-crystal Pr^{3+}:Y_2SiO_5 samples used in the experiment were provided by the Scientific Materials Corporation of America. The three samples have Pr^{3+} concentration of 1 mol.%, 0.5 mol.%, and 0.02 mol.%, respectively, and an uniformed size of $5 \times 5 \times 5$ mm^3. The space group of Y_2SiO_5 is 12/C (C_{2h}^6) and the cell dimensions are $a = 10.410$ Å, $b = 6.721$ Å, $c = 12.490$ Å and $\beta = 102°39'$ [11]. Y^{3+} ions occupy two different distorted octahedral sites.

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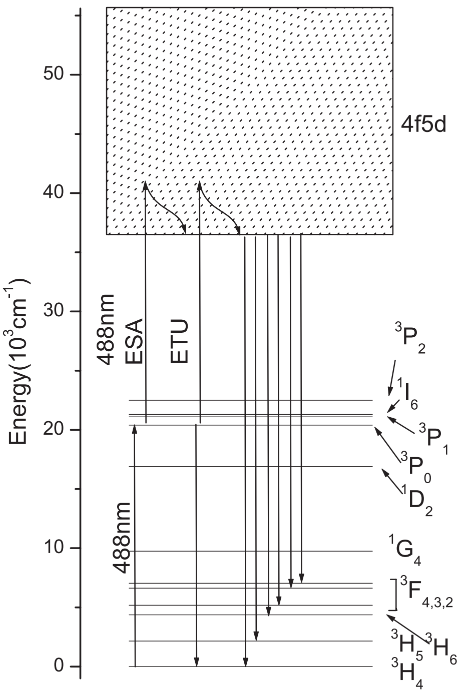

Fig. 1. Energy level diagram of Pr^{3+}:Y_2SiO_5 with indication of excitation and emission process.

At first, we measured the absorption spectrum of the crystals using a Pekin-Elmei-9 UV-VIS-NIR spectrometer with a resolution of 0.2 nm, from which the energy levels positions were obtained as shown in Figure 1. From the absorption spectra it was found that the absorption wavelength of $^3H_4 \rightarrow {}^3P_0$ coincides with Ar^+ laser 488 nm line.

For the upconversion investigation, the samples were pumped by an argon-ion laser in a single-line mode (488 nm). To avoid unwanted plasma lines from the Ar^+ laser entering the crystal a 488 nm narrow band filter was inserted in the pump beam. The fluorescence from crystal was collected at right angle to the incident pump beam by a 4 cm diameter, 10 cm focal length quartz lens onto the entrance slit of a 0.5 m monochromator. The exit slit of monochromator was equipped with a photomultiplier tube (Hamamatsu R3896). To increase detection sensitivity the fluorescence was chopped by a light chopper (Stanford Research System SR540). The signals from the PMT were integrated by a boxcar integrator (Stanford Research System SR250), which was triggered by the reference signal from the chopper. Through GPIB and RS 232 cables the PMT signal was transferred to a personal computer, where the spectra were recorded. All experiments were performed at room temperature.

The fluorescence spectrum measured by 488 nm excitation is shown in Figure 2 and part of the spectral peaks is assigned according to the energy level positions in Figure 1. The different emission bands in Figure 2 were normalized with respect to the spectral line $^3P_0 \rightarrow {}^3H_4$ considering the spectral response of the detection system (calibrated with a standard lamp). As can be seen from Figure 2, besides the spectra lines in visible region which correspond to $4f^2$ intraconfiguration transitions, there is an upconversion UV fluorescence band from 260 nm to 350 nm assigned as the $4f5d \rightarrow 4f^2$ ^3F_J, ^3H_J interconfiguration transitions. The numbers (*40, 6, 4, 1) below the spectrum are the intensity amplifications of the corresponding spectrum. Many transitions between Stark sublevels within $4f^2$ intraconfiguration are resolved.

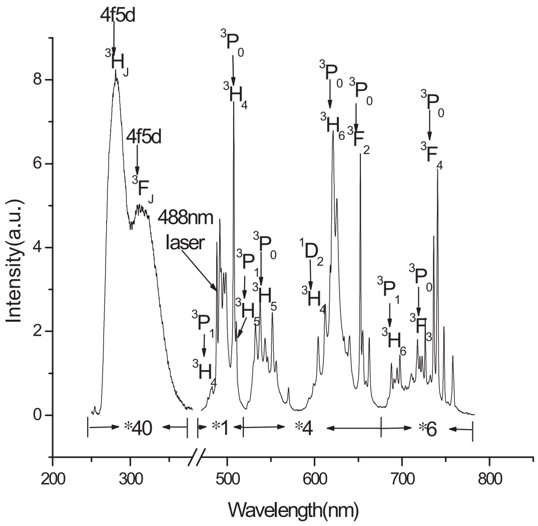

Fig. 2. Fluorescence spectrum of Pr^{3+}:Y_2SiO_5 under 488 nm excitation. The number (*40, 6, 4, 1) below the spectrum are intensity amplification multiplies of the corresponding spectrum.

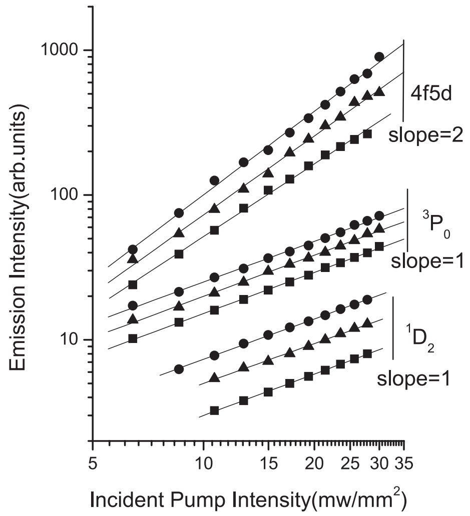

Fig. 3. Dependence of intensity of fluorescence emitted from $4f5d$, $^3P_0$, $^1D_2$ on pump power: (●) 0.02 mol.%, (▲) 0.5 mol.%, (■) 1 mol.%.

The dependence of the fluorescence intensity emitted from the $4f5d$, $^3P_0$, and $^1D_2$ on the pump power was measured by inserting different neutral density filters in the pump beam. The results are shown in Figure 3 in double logarithmic scale. As can be seen from Figure 3, the slopes of power dependence curve are nearly equal to 2 for the upconversion fluorescence from $4f5d$ and 1 for the fluorescence from $^3P_0$, $^1D_2$, which indicated that the fluorescence was induced by two-photo and one-photon process, respectively.

3 Discussion

The population of the $4f5d$ level responsible for the UV upconversion can be considered from three possible processes. One is referred as excited-state absorption (ESA), which consists of two consecutive excitation steps on a single Pr^{3+} ion, i.e., the process $^3H_4 \rightarrow {}^3P_0 \rightarrow 4f5d$ (as indicated in Fig. 1). The second one is referred as energy transfer upconversion (ETU), in which two Pr^{3+} ions in the $^3P_0$ state interact, resulting in that the energy of an ion is transferred nonradiatively onto another ion thereby exciting it into the $4f5d$ band. The third process is avalanche upconversion, which can be excluded in our case because none of the typical signature (upconversion threshold) for this process could be found as given in [12].

To identify either ESA or ETU is dominant mechanism for the UV upconversion we introduced the population rate equations of the relevant levels as given by Pollnau et al. [13] and assume that the ground-state population is constant. For ESA process the rate equations are given by

$$\frac{dN_2}{dt} = N_1\frac{I\sigma_{12}}{h\nu} - N_2\frac{I\sigma_{23}}{h\nu} - R_2N_2 \tag{1}$$

$$\frac{dN_3}{dt} = N_2\frac{I\sigma_{23}}{h\nu} - R_3N_3 \tag{2}$$

where subscripts 1, 2, 3, refer to the $^3H_4$, $^3P_0$, $4f5d$ states, respectively; N_i, R_i are population density and decay rate of state i, respectively; $h\nu$ is the pump photon energy; I is the pump light intensity; σ_{ij} is absorption cross-section from i to j level. Under the steady-state ($dN/dt = 0$) assumption, equations (1, 2) become

$$N_1\frac{I\sigma_{12}}{h\nu} = N_2\frac{I\sigma_{23}}{h\nu} + R_2N_2 \tag{3}$$

$$N_2\frac{I\sigma_{23}}{h\nu} = R_3N_3. \tag{4}$$

From equations (3, 4), the relation between the population of $^3P_0$, $4f5d$ states and the incident laser power can be obtained by

$$N_2 = \frac{N_1I\sigma_{12}}{I\sigma_{23} + R_2h\nu} = C_1\frac{I}{I\sigma_{23} + R_2h\nu} \tag{5}$$

$$N_3 = \frac{N_1\sigma_{12}\sigma_{23}I^2}{h\nu R_3(I\sigma_{23} + R_2h\nu)} = C_2\frac{I^2}{I\sigma_{23} + R_2h\nu} \tag{6}$$

where C_1, C_2 are constants. From equations (5, 6), one can see that, if $I\sigma_{23} \gg R_2h\nu$, then $N_3 \propto I$ and $N_2 \propto I^0$, if $I\sigma_{23} \ll R_2h\nu$, then $N_3 \propto I^2$ and $N_2 \propto I$. The absorption cross-section σ_{23} can be deduced by

$$\sigma_{23} = \frac{h\nu B_{23}}{c} \tag{7}$$

where B_{23} is the Einstein absorption coefficient from $^3P_0$ to $4f5d$, which can be expressed as [14]

$$B_{23} = \frac{g_3}{g_2}B_{32} = \frac{g_3}{g_2}\frac{c^3}{8\pi h\nu^3}A_{32} \tag{8}$$

where $g_2 = 1$, $g_3 = 7$ are the statistic weight of $^3P_0$ and $4f5d$ states. A_{32} is the spontaneous transition probability of $4f5d \rightarrow 4f^2\ {}^3P_0$, and can be calculated by

$$A_{32} = \frac{64\pi^4e^2\sigma^3}{3hg_3}\frac{n(n^2+2)^2}{9}\left|\langle 4f\,|r|\,5d\rangle\right|^2 \tag{9}$$

where $\sigma = 1.7 \times 10^4\ \text{cm}^{-1}$ the wave number of the transition, e electron charge, $n = 1.793$ refractive index of the crystal, and $\langle 4f|r|5d\rangle = 0.900$ a.u. [15]. From equations (7, 8, 9) we calculated $\sigma_{23} = 8 \times 10^{-19}\ \text{cm}^2$. With the lifetime of the $^3P_0$ state measured previously in our lab, $R_2 = 4.2 \times 10^5\ \text{s}^{-1}$ is obtained. In terms of the laser power used here (see Fig. 3), it is found that $I\sigma_{23}$ (about $10^{-17}\ \text{Js}^{-1}$) $\ll R_2h\nu$ (about $10^{-13}\ \text{Js}^{-1}$). The UV upconversion fluorescence intensity should be proportional to N_3 and therefore to I^2, whereas the fluorescence from $^3P_0$ should be proportional to N_2 and therefore to I. These results are in agreement with the experiments (see Fig. 3).

For ETU process, the rate equations have the forms

$$\frac{dN_2}{dt} = N_1\frac{I\sigma_{12}}{h\nu} - 2WN_2^2 - R_2N_2 \tag{10}$$

$$\frac{dN_3}{dt} = WN_2^2 - R_3N_3 \tag{11}$$

where W is the upconversion rate. All other symbols have the same meanings as in the case of ESA. Under steady-state excitation, these relations lead to

$$N_1\frac{I\sigma_{12}}{h\nu} = 2WN_2^2 + R_2N_2 \tag{12}$$

$$WN_2^2 = R_3N_3. \tag{13}$$

To compare WN_2^2 with R_2N_2, the following formula given by Nicolas et al. [16] was used

$$\frac{WN_2^2}{R_2N_2} = 1 - \frac{\int_0^\infty I(t)dt}{I_0\tau_0} \tag{14}$$

where $I(t)$ is the fluorescence intensity decay profile from the $^3P_0$ level, τ_0 is the lifetime measured in the less concentrated crystal. The decay curves $I(t)$ for the three Pr^{3+} concentration were obtained by exciting $^3P_0$ state with a pulsed tunable laser. The resulting values of WN_2^2/R_2N_2 are 0.17, 0.06, and 0 for 1 mol.%, 0.5 mol.%, and 0.02 mol.% Pr^{3+} concentrations, respectively, which indicate that $WN_2^2 \ll R_2N_2$ for all of the three Pr^{3+} concentration. According to equations (12) and (13) we can get

$$R_2N_2 \approx N_1\frac{I\sigma_{12}}{h\nu}, \quad N_2 \propto I \quad \text{and} \quad N_3 \propto I^2.$$

These are also in agreement with experiments.

However, if comparing upconversion rate for ETU process $WN_2^2 = R_3N_3$ (Eq. (13)) with ESA rate $N_2I\sigma_{23}/h\nu = R_3N_3$ (Eq. (4)), we found

$$\text{ETU rate/ESA rate} = \frac{WN_2^2}{N_2I\sigma_{23}/h\nu} = \frac{h\nu WN_2}{I\sigma_{23}}. \qquad (15)$$

From (14) yields

$$WN_2 = \left(1 - \frac{\int_0^\infty I(t)dt}{I_0\tau_0}\right) R_2. \qquad (16)$$

Therefore

$$\text{ETU rate/ESA rate} = \frac{h\nu}{I\sigma_{23}} \left(1 - \frac{\int_0^\infty I(t)dt}{I_0\tau_0}\right) R_2. \qquad (17)$$

Inserting all of date into (17), we obtained ETU rate/ESA rate = 10^3, 10^2, 0, for the Pr^{3+} concentration 1 mol.%, 0.5 mol.%, 0.02 mol.%, respectively. The results indicate that ETU process is the predominant upconversion mechanism for higher Pr^{3+} concentrations, whereas ESA is the predominant for lower Pr^{3+} concentrations.

4 Summary

The ultraviolet upconversion fluorescence band from 260 nm to 350 nm in the Pr^{3+}:$\mathrm{Y_2SiO_5}$ by 488 nm Ar^+ laser excitation has been observed, which corresponds the transitions $4f^{n-1}5d \rightarrow 4f^2\ ^3\mathrm{F_J}$, $^3\mathrm{H}_J$. In order to understand the mechanism of the upconversion process, the power dependence of the fluorescence was measured. Two possible upconversion mechanisms ESA and ETU were analyzed based on the rate equations with a simplified model for the three Pr^{3+} doped concentrations.

To achieve ultraviolet laser oscillation with this material needs more comprehensive research work on it. One of the crucial problems is the excited state absorption from the $4f5d$ level to the conduction band. We are just making the investigation on this subject now using pump-probe technique.

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