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Energy transfer upconversion in $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Pr}^{3+}$

J A Capobianco†, N Raspa‡, A Monteil‡ and M Malinowski§

† Department of Chemistry and Biochemistry, Concordia University, 1455 de Maisonneuve Boulevard West, Montreal, Québec, Canada, H3G 1M8

‡ Université de Lyon I, UA442 CNRS, 69622 Villeurbanne, France

§ Institute of Microelectronics and Optoelectronics, Koszykowa 75, 0062 Warsaw, Poland

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Abstract. Excitation of Pr^{3+} -doped $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ crystals at 580 nm ($^1\text{D}_2 \leftarrow ^3\text{H}_4$) produces fluorescence at 486 nm ($^3\text{P}_0 \rightarrow ^3\text{H}_4$) which is attributed to upconversion from interacting Pr^{3+} ions. Based on an analysis of the lifetimes of the levels $^3\text{P}_0$, $^1\text{D}_2$ and the induced fluorescence ($^3\text{P}_0 \rightarrow ^3\text{H}_4$) we conclude that the mechanism responsible for the upconversion process is energy transfer. This mechanism arises from excitation annihilation involving pairs of ions in the $^3\text{H}_6$ and $^1\text{D}_2$ levels.

1. Introduction

In recent years trivalent praseodymium has been the object of increasing interest, since it is an interesting laser activator. The trivalent praseodymium energy level spectrum contains a large number of metastable multiplets ($^3\text{P}_{0,1,2}$, $^1\text{D}_2$, $^1\text{G}_4$) from which laser action has been demonstrated at various wavelengths from the visible to the infrared. Considerable attention has also been paid to the phenomenon of upconversion. Upconverted blue light emission ($^3\text{P}_0 \rightarrow ^3\text{H}_4$) has been reported in $\text{Y}_3\text{Al}_5\text{O}_{12}$ [1], LaF_3 [2], and $\text{KYP}_4\text{O}_{12}$ [3] following orange-yellow excitation ($^1\text{D}_2 \leftarrow ^3\text{H}_4$).

Stimulated emission by upconversion pumping was first reported by Johnson and Guggenheim [4] using infrared light from flash lamps to excite Yb^{3+} ions in BaY_2F_8 doubly doped with $\text{Yb}^{3+}/\text{Er}^{3+}$. Since this report numerous studies have been undertaken in order to achieve laser action via upconversion. Smart *et al* [5] have reported laser action of Pr^{3+} doped fluorozirconate fibres in the blue (491 nm), green (520 nm) orange (605 nm) and red (655 nm) wavelength regions, pumping the $^1\text{G}_4$ with wavelengths around 1.01 μm and 835 nm. Upconversion lasers are potentially attractive short-wavelength sources which can be pumped with the red or near-infrared light produced by III–V semiconductor diode lasers.

Upconversion can be accomplished by several mechanisms: (i) sequential two-photon absorption; (ii) avalanche absorption; and (iii) energy transfer. The latter mechanism proceeds according to a scheme in which two ions excited in an intermediate state in close proximity are coupled by a non-radiative process in which an ion returns to the ground state while the other ion is promoted to the upper level. In most cases, these cross relaxation processes are based on electric dipole–dipole interactions.

In this paper we have undertaken a study of upconversion by the Pr^{3+} ion in the matrix $\text{Gd}_3\text{Ga}_5\text{O}_{12}$. We describe our results of orange-yellow to blue upconversion experiments by pumping the $^1\text{D}_2 \leftarrow ^3\text{H}_4$ transition (580 nm) in order to obtain emission from the

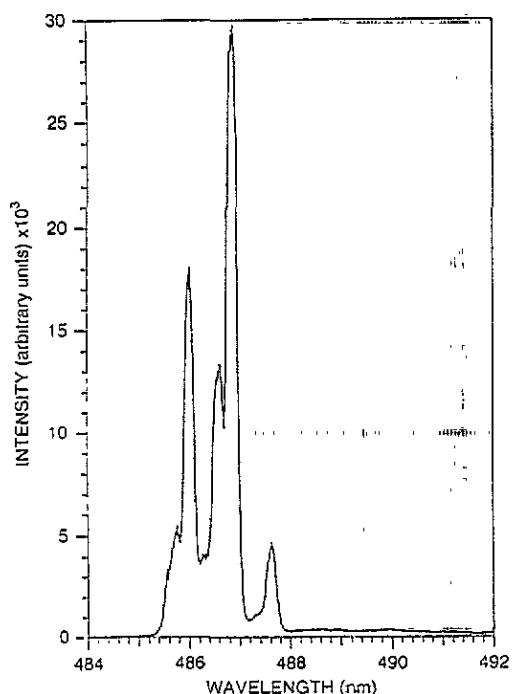


Figure 1. Emission spectrum (4 K) of the transition ${}^3P_0 \rightarrow {}^3H_4$ excited at 580 nm.

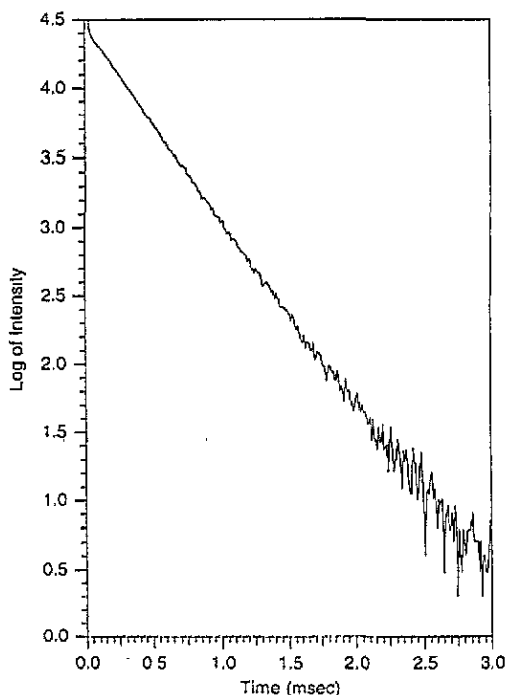
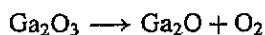


Figure 2. Decay profile (4 K) of the ${}^1D_2 \rightarrow {}^3H_4$ transition for $Gd_3Ga_5O_{12}:Pr^{3+}$. Emission is at 608 nm, and excitation at 580 nm.

${}^3P_0 \rightarrow {}^3H_4$ transition at 486 nm. Investigation of the fluorescence dynamics provides evidence that upconversion occurs via energy transfer.

2. Experimental details

The single crystal of $Gd_3Ga_5O_{12}$ doped with 1% Pr^{3+} was grown using the Czochralski technique in an O_2 atmosphere (flow rate 4.8 l h^{-1}). This was done in order to retard the rate of the forward reaction



thus preventing the decomposition of Ga_2O_3 . The Pr^{3+} ions enter substitutionally for Gd^{3+} . Samples were cut and all faces were optically polished.

The upconverted fluorescence spectrum was obtained by excitation at 580 nm with a tunable dye laser (Spectra Physics 375) operating with rhodamine 6G ($10^{-3} \text{ mol dm}^{-3}$ in ethylene glycol) pumped by a Coherent CR-18, 20 W argon ion laser. The spectrum was recorded using a Jarrell-Ash 1-m Czerny Turner double monochromator using a maximum slit width of $130 \mu\text{m}$.

The fluorescence signal was monitored with an RCA-C 31034-02 photomultiplier in the photon counting mode and recorded under computer control using a Stanford SR 465 software data acquisition and analysis system. The data were acquired at liquid helium temperature (4 K) using a Janis ST-VP-4 continuous flow cryostat.

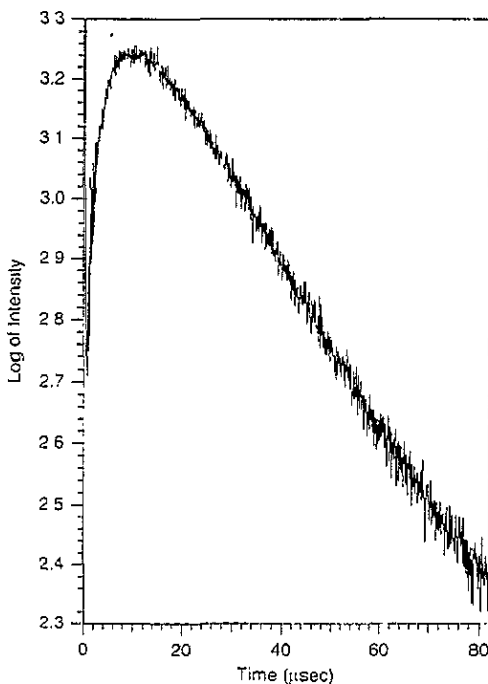


Figure 3. Decay profile (4 K) of the ${}^3P_0 \rightarrow {}^3H_4$ transition for $Gd_3Ga_5O_{12}:Pr^{3+}$. Emission is at 486 nm, and excitation at 580 nm.

Measurements of the fluorescence lifetimes were made using a tunable dye laser operating with Rhodamine 6G (580 nm excitation) pumped by a Molectron UV 1000 N_2 laser. The lifetimes were measured using a 1.5 m SOPRA monochromator, an EMI 96593 cooled photomultiplier and an INEL-MCA3/1 multichannel analyser.

3. Results and discussion

Figure 1 shows the upconverted fluorescence spectrum for the transition ${}^3P_0 \rightarrow {}^3H_4$ at 4 K following orange-yellow excitation (580 nm) into the 1D_2 level. The spectrum consists of a total of at least eight peaks. Knowing that the 3P_0 level consists of a single Stark level (${}^3P_0(\Gamma_1)$) one should theoretically observe, for a single crystal field site, a total of three peaks associated with the (${}^3P_0(\Gamma_1) \rightarrow {}^3H_4(\Gamma_3, \Gamma_1, \Gamma_4)$) transitions. Clearly the additional lines in the emission spectrum must be due to a number of subsites (crystal field sites) differing slightly from one another that are all excited at 580 nm. This will be discussed in greater detail in a subsequent paper.

The upconversion process can proceed via two distinct mechanisms, either a direct two-photon absorption or energy transfer. Within the framework of existing theories [2, 6, 7], lifetime measurements provide invaluable insight into the mechanism that is operative.

Figures 2 and 3 show the decay profiles at 4 K of the 1D_2 and 3P_0 levels, following excitation at 580 nm (${}^1D_2 \leftarrow {}^3H_4$). Temporal dependence of the ${}^1D_2 \rightarrow {}^3H_4$ emission is exponential with a decay time constant of 260 μs . The ${}^3P_0 \rightarrow {}^3H_4$ decay profile is non-exponential, consisting of a long and a short component with decay time constants of

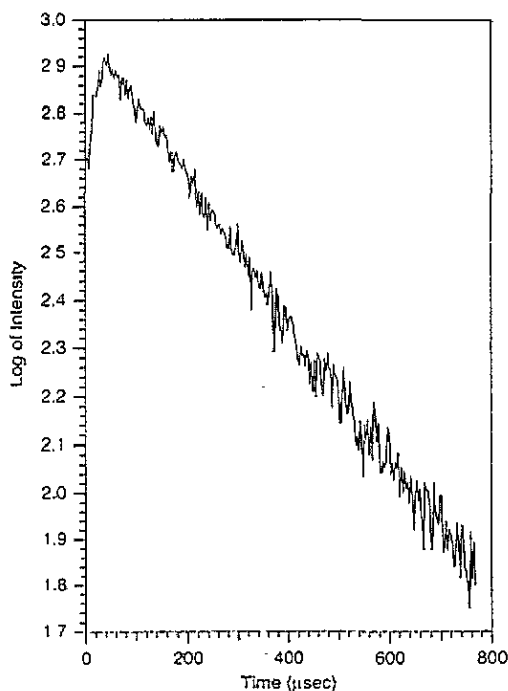


Figure 4. Decay profile (4 K) of the level $^1D_2 \rightarrow ^3H_4$ transition for $Gd_3Ga_5O_{12}:Pr^{3+}$. Emission is at 608 nm, and excitation at 486 nm.

107 and 32 μs respectively. A rise time of 4.4 μs is observed in the upconverted decay profile of the 3P_0 level.

Figures 4 and 5 show the decay profiles at 4 K of the $^1D_2 \rightarrow ^3H_4$ and $^3P_0 \rightarrow ^3H_4$ transitions respectively, excited at 486.3 nm (3P_0 level). The decay profile of the $^1D_2 \rightarrow ^3H_4$ emission is exponential with a lifetime of 250 μs ; however, in contrast with the results shown in figure 2 a rise time of 14 μs is observed. The rise time can be attributed to the decay from the 3P_0 level to the 1D_2 level. The decay profile for the $^3P_0 \rightarrow ^3H_4$ emission is exponential with a lifetime of 14.1 μs , in contrast with the non-exponential decay profile observed upon excitation at 580 nm. The results are summarized in table 1.

Table 1. Decay measurements of the 3P_0 and 1D_2 levels for Pr^{3+} doped $Gd_3Ga_5O_{12}$.

Level excited	Decay level monitored	Rise time τ_r (μs)	Decay time τ_d (μs)
3P_0	1D_2	14	250
3P_0	3P_0	—	14.1
1D_2	1D_2	—	260
1D_2	3P_0	4.4	32
			107

Based on the lifetime measurements, a direct two-photon absorption process is unlikely, since this mechanism would require that the upconverted fluorescence decay of the $^3P_0 \rightarrow ^3H_4$ transition be identical to the lifetime of the directly excited 3P_0 level. As shown in

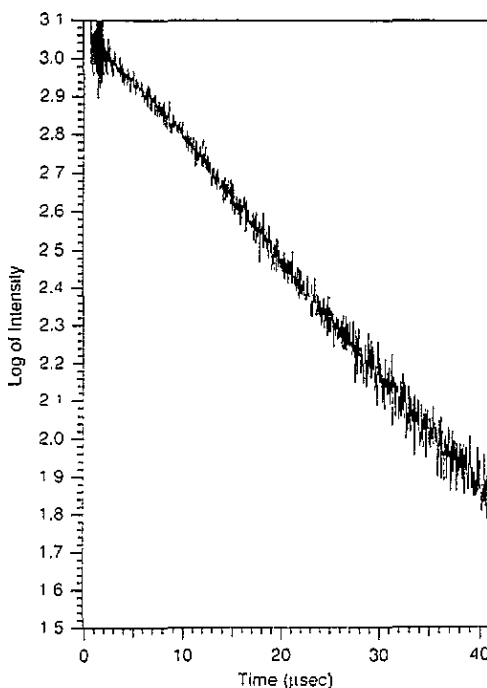


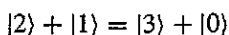
Figure 5. Decay profile (4 K) of the level $^3P_0 \rightarrow ^3H_4$ transition for $Gd_3Ga_5O_{12}:Pr^{3+}$. Emission is at 486 nm and excitation at 486 nm.

table 1, the observed lifetime of the induced fluorescence ($\tau_{up}(^3P_0) = 32 \mu s$) is more than twice the lifetime observed for the directly excited 3P_0 ($\tau(^3P_0) = 14.1 \mu s$).

Further evidence that the direct two-photon absorption process is not operative can be obtained from the energy level diagram shown in figure 6 [8]. We observe that there are no levels lying at approximately twice the excitation energy above the ground state [6]. Absorption of phonons from the crystal lattice is also unlikely due to the large energy gaps involved. In the $Gd_3Ga_5O_{12}$ crystal lattice doped with Pr^{3+} , the upconverted fluorescence is approximately 4000 cm^{-1} above the excitation energy. The effective phonon density for YAG and LuAG doped with Pr^{3+} has been found to be between 200 and 800 cm^{-1} [9]. Assuming the same values for $Gd_3Ga_5O_{12}:Pr^{3+}$ this would require a minimum of five phonons to bridge the energy gap.

The other probable mechanism is the energy transfer upconversion (ETU) process, in which two nearby excited ions undergo energy transfer. It is not unreasonable to expect energy transfer between two neighbouring Pr^{3+} ions in the $Gd_3Ga_5O_{12}$ matrix. We have calculated the average Pr-Pr nearest-neighbour distance to be 6.1 \AA for the sample studied. This value is in good agreement with the value obtained for $Y_3Al_5O_{12}$ where energy transfer has been observed [10].

The fluorescence lifetime results are reminiscent of those reported for Pr^{3+} in LaF_3 and $LaCl_3$ [11, 12]. Therefore, using the energy transfer upconversion model developed for Pr^{3+} ions in $LaCl_3$, the process can be written as



where $|0\rangle$, $|1\rangle$, $|2\rangle$, and $|3\rangle$ represent the Stark levels 3H_4 , 3H_6 , 1D_2 and 3P_0 respectively. A schematic representation for the ETU process is shown in figure 7. First, an ion is initially

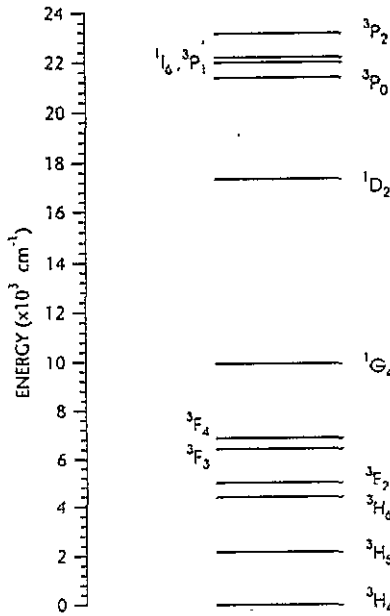


Figure 6. Energy level diagram for $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Pr}^{3+}$.

excited from level $|0\rangle$ to level $|2\rangle$ by absorption of resonance energy, followed by decay to level $|1\rangle$. A second ion near the first is also excited from level $|0\rangle$ to level $|2\rangle$. The two nearby ions undergo an annihilation interaction resulting in one ion in the ground state $|0\rangle$ and the other in state $|3\rangle$ where upconverted fluorescence occurs.

In the framework of the ETU process the time dependent rate equation describing the population of $|3\rangle$ at time t is given by [12]

$$N_3(t) = (N_0 A I_0 / \tau_2^{-1})^2 \sigma_{21} \sigma_u \left(\frac{\exp(-2t/\tau_2) - \exp(-t/\tau_3)}{(\tau_3^{-1} - 2\tau_2^{-1})(\tau_1^{-1} - \tau_2^{-1})} - \tau_2^{-1} \frac{\exp(-t/\tau_1) \exp(-t/\tau_2) - \exp(-t/\tau_3)}{\tau_1^{-1}(\tau_1^{-1} - \tau_2^{-1})(\tau_3^{-1} - \tau_1^{-1} - \tau_2^{-1})} + \exp\left(\frac{-t/\tau_3}{\tau_3^{-1} \tau_1^{-1}}\right) \right) \quad (1)$$

where A is a characteristic constant containing the oscillator strength for the $|0\rangle \rightarrow |1\rangle$ transition, σ_{ij} is the transition probability rate constant of the initial state $|i\rangle$ to the final state $|j\rangle$, σ_u is the rate constant for the ETU process and τ_1^{-1} , τ_2^{-1} , and τ_3^{-1} are the decay rate constants of $|1\rangle$, $|2\rangle$, and $|3\rangle$ respectively.

The steady state population of $|0\rangle$ at the time t is given by

$$N_3(0) = (N_0 A I_0)^2 \sigma_{21} \sigma_u / (\tau_2^{-1})^2 \tau_3^{-1} \tau_1^{-1}. \quad (2)$$

The calculated time dependence of $N_3(t)/N_3(0)$ for the upconversion process is shown in figure 8(a). This was calculated using the following values: $\tau_1 = 14 \mu\text{s}$ (the lifetime of the ${}^3\text{H}_6$ level), $\tau_2 = 260 \mu\text{s}$ (the lifetime of the ${}^1\text{D}_2$ level), and $\tau_3 = 14.1 \mu\text{s}$ (the lifetime of the ${}^3\text{P}_0$ level).

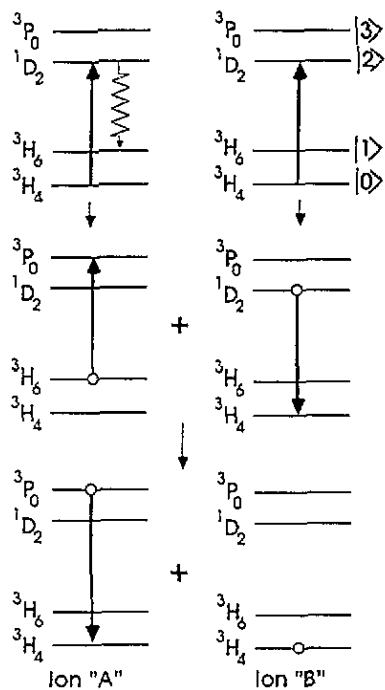


Figure 7. ETU mechanism.

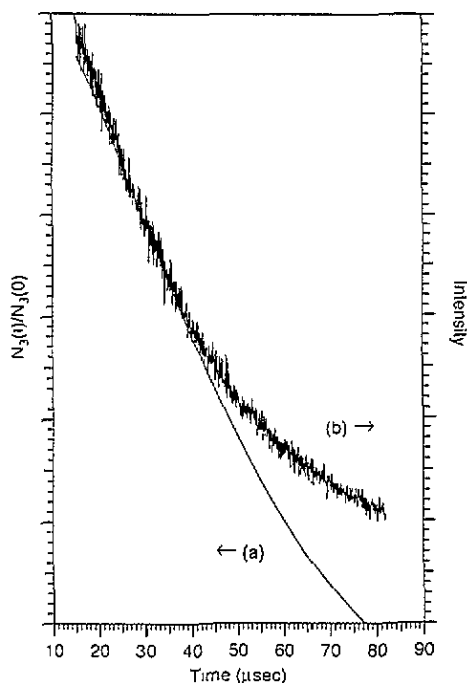


Figure 8. (a) Calculated ETU decay ($N_3(t)/N_3(0)$) for the $|^1D_2\rangle + |^3H_6\rangle \rightarrow |^3P_0\rangle + |^3H_4\rangle$ process and (b) experimental decay of the upconverted 3P_0 fluorescence.

The decay time calculated from the negative reciprocal of the slope of $\ln[N_3(t)/N_3(0)]$ versus time is $40.6 \mu\text{s}$. This value is in good agreement with the experimental value, $32 \mu\text{s}$, obtained for the decay time of the upconverted $^3P_0 \rightarrow ^3H_4$ fluorescence (figure 8(b)) induced by the 580 nm pump. This is consistent with the interpretation that upconversion occurs via energy transfer and that the process is adequately explained by the ETU model. Consequently the rise time of $4.4 \mu\text{s}$ associated with the upconverted 3P_0 fluorescence can be attributed to the time required to populate the 3H_6 level.

4. Conclusions

Upconverted blue light emission in $Gd_3Ga_5O_{12}:Pr^{3+}$ is observed ($^3P_0 \rightarrow ^3H_4$) when the system undergoes orange-yellow excitation into the 1D_2 manifold. A rise time was found to be associated with the 3P_0 decay pattern showing that the 3P_0 level is fed from lower-lying levels. This evidence points to an ETU process between two neighbouring ions. In this case, two neighbouring ions in close proximity are coupled by a non-radiative process in which one ion returns to the ground state manifold 3H_4 while the other ion is promoted to the upper level 3P_0 . Time dependent rate equations derived for the ETU process were applied to the experimental decay data of the upconverted 3P_0 fluorescence and a good fit was obtained, thus providing further evidence that upconversion is occurring via energy transfer.

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