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One- and two-photon spectroscopy of Pr³⁺-doped YAlO₃ crystals

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Received 17 May 1994, in final form 9 August 1994

Abstract. The energy level position of the Pr³⁺ ion in YAlO₃ and dynamics of the ¹G₄, ¹D₂ and ³P₀ excited states have been analysed. The mechanism of orange and infrared light up-conversion into blue ³P₀-state emission has been elucidated and has been considered for possible use in a blue-wavelength laser. Two-photon absorption transitions from the ³H₄ ground state to the ³P₂ manifold were observed and compared in intensity with the excited-state transitions via the intermediate ¹G₄ manifold.

1. Introduction

Trivalent praseodymium (Pr³⁺) in crystals and glasses is well known for having a very rich emission spectrum extending from the ultraviolet (UV) to the infrared (IR) [1, 2]. Because of the energy level structure, shown schematically in figure 1, and suitable lifetimes of the excited states, Pr³⁺ systems are also attractive as short-wavelength up-conversion laser materials [3, 4]. Continuous-wave stimulated emission at several orange and red wavelengths in Pr³⁺-doped perovskite YAlO₃ (YAP) has been reported [5, 6] and recently we have observed simultaneous blue- and orange-wavelengths lasing in Pr³⁺-doped YAP and also YAG crystals [7]. The optical anisotropy of YAlO₃, enabling one to select favourable crystallographic orientations in order to optimize specific emission performance, makes this system an interesting laser material. The inter-configuration f–d luminescence in the near-UV region observed in Pr³⁺-doped YAP [2], as well as in YAG [2, 8], PrP₅O₁₄ [9] and other Pr³⁺-activated crystals [10], could be used for scintillating detection applications.

In this paper we have analysed the up-conversion processes leading to blue fluorescence from the excited ³P₀ state of the Pr³⁺ ion in YAP. The study and optimization of the up-conversion process demand a detailed knowledge of the energy levels and excited-state dynamics. Some of the energy level positions have been reported earlier [11–14]; however, significant discrepancies between these results and our data prompted us to reinvestigate the YAP: Pr³⁺ emission and absorption spectra and to determine most of the energy levels. We further report the concentration-dependent excited-state dynamics, and we demonstrate and analyse the IR-to-blue- and orange- to- blue-wavelength up-conversion.

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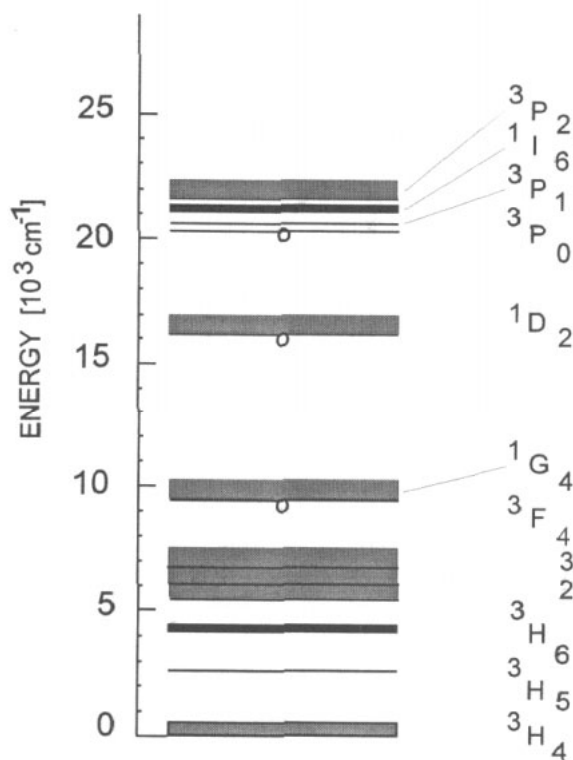


Figure 1. An energy level scheme for Pr³⁺ ions in YAP. The widths of lines represent the extent of the splitting of multiplets determined in this study; levels from which fluorescence has been observed are indicated by open circles.

2. Experimental methods

Two YAP:Pr³⁺ samples of different activator concentrations, 0.3 and 0.1 at.% of Pr³⁺, were examined. The unoriented crystal doped with 0.3 at.% Pr³⁺ was grown using the Czochralski technique at the ITME Laboratory in Warsaw and the sample doped with 0.1 at.% Pr³⁺ was from the IBM Almaden Research Laboratory. Absorption measurements in the range from 195 to 1050 nm, were made using a Cary 2300 Varian spectrometer equipped with a continuous-flow helium cryostat. Fluorescence and excitation spectra were obtained using a tunable dye laser, operating with Coumarine 460 + 480 and Rhodamine 590 dyes, pumped by a nitrogen laser. Excitation in the IR region was achieved with a Ti³⁺:sapphire laser pumped by a frequency-doubled Nd:YAG laser or by the SRS down-shifting in a H₂ cell of an output of a DCM dye laser. The spectra were recorded using a Hilger and Watts or GDM 1000 1 m monochromator with a dispersion of 8 Å mm⁻¹ and detected with an EMI 9789 or RCA C 31034-02 cooled GaAs photomultiplier. For IR detection a highly sensitive model 403L cooled germanium photodetector from Applied Detector Corporation was used. Data acquisition was obtained with an Ortec or Stanford SR 400 photon-counting system controlled with a PC. Fluorescence lifetime measurements were made using a Stanford Research SR 430 multichannel analyser. Sample cooling was provided with a liquid-He optical cryostat.

3. Results

3.1. Optical spectra

Yttrium aluminium perovskite (YAlO₃), otherwise known as yttrium orthoaluminate, has the orthorhombic space group symmetry *Pnma*. The praseodymium ion enters the lattice at yttrium sites having a point symmetry of C_s. For ions in this symmetry, all optical transitions are allowed [13]; table 1 presents the selection rules for electric-dipole transitions. Erickson [13] determined that the ground state of ³H₄ and the lowest level of ¹D₂ multiplet have Γ_1 symmetry. Figure 2 displays the high-energy part of the σ - and π -polarized absorption spectra, corresponding to the ³H₄(1) \rightarrow ³P_J + ¹I₆ transitions, of YAP:0.1 at.% Pr³⁺ measured at 10 K. It can be seen that the crystal-field splitting of ¹I₆ overlaps the splitting of the ³P₁ manifold, making the energy level assignment in this part of spectrum difficult. Figure 3 shows the blue fluorescence spectrum corresponding to the ³P₀ \rightarrow ³H₄ transition (lasing at the strongest 491 nm line has been reported by us previously [7]). Direct excitation of the ¹G₄ state results in a relatively intense emission centred at 1350 nm (figure 4). The IR excitation spectrum of this emission allowed us to determine the positions of several Stark levels of the ¹G₄ manifold [15].

Table 1. Electric-dipole selection rules for C_s symmetry

	Γ_1	Γ_2
Γ_1	σ	π
Γ_2	π	σ

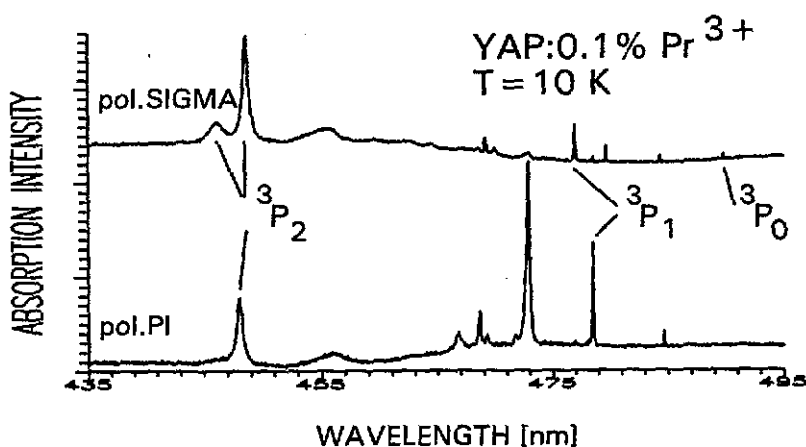


Figure 2. Polarized absorption spectra of the ³P₀, ³P₁, ¹I₆ and ¹I₂ manifolds in YAP:0.1 at.% Pr³⁺ recorded at 10 K.

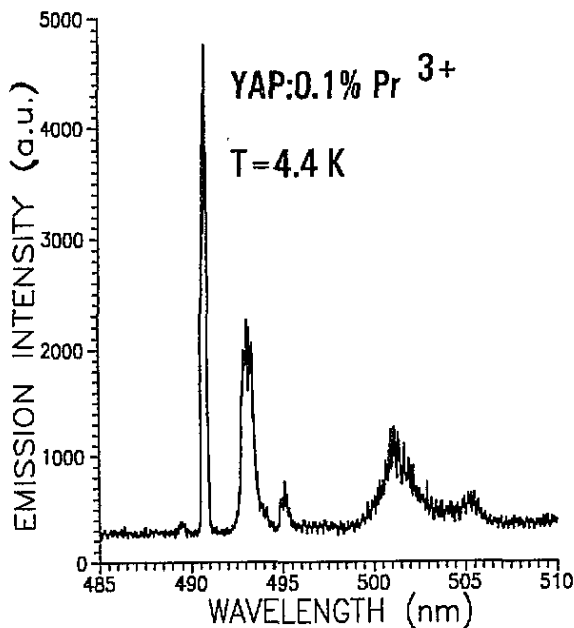


Figure 3. Blue fluorescence spectrum of YAP:0.3 at.% Pr^{3+} corresponding to the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ transition recorded at 4.4 K (a.u., arbitrary units).

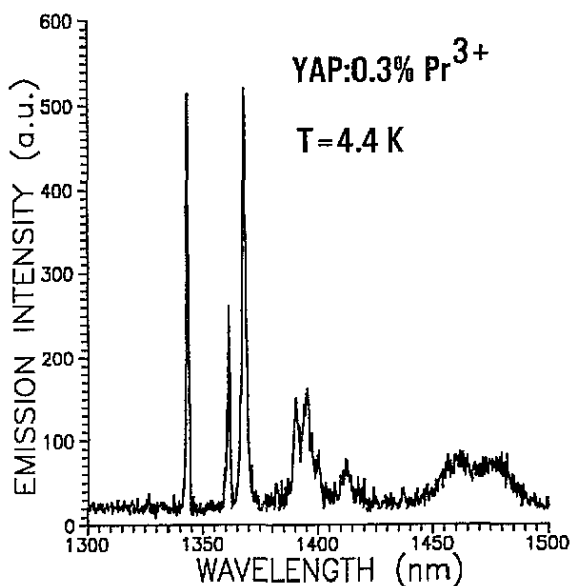


Figure 4. IR fluorescence spectrum of YAP:0.3 at.% Pr corresponding to the $^1\text{G}_4 \rightarrow ^3\text{H}_5$ transition recorded at 4.4 K (a.u., arbitrary units).

3.2. Fluorescence dynamics

In the crystals investigated, emissions from the three excited states of the Pr^{3+} ion, namely $^3\text{P}_0$, $^1\text{D}_2$ and $^1\text{G}_4$, have been observed. The temporal evolution of one-photon (OP), directly excited blue $^3\text{P}_0$ emission is presented in figure 5. In both samples, decays are exponential with time constants of 11.7 μs at 4.4 K, and 10 μs at room temperature.

Fluorescence decay from the $^1\text{D}_2$ state is presented in figure 6. In contrast with the blue $^3\text{P}_0$ fluorescence decay, time evolution of the $^1\text{D}_2$ emission is concentration dependent. In

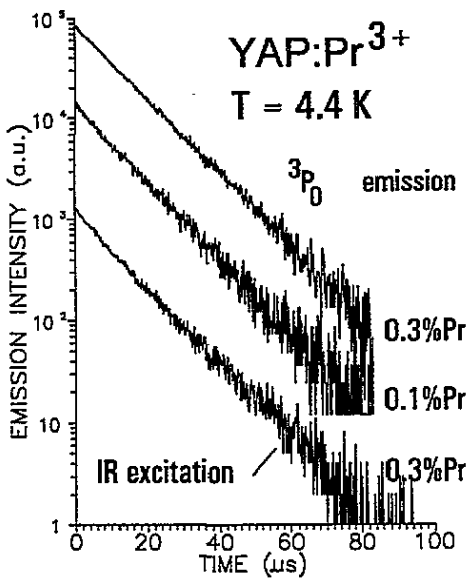


Figure 5. $^3\text{P}_0$ fluorescence decay observed from samples of 0.1 and 0.3 at.% Pr^{3+} -doped YAP after OP (upper traces) and TP IR excitation at 10994 cm^{-1} (910 nm) (lower trace) and $T = 4.4\text{ K}$ (a.u., arbitrary units).

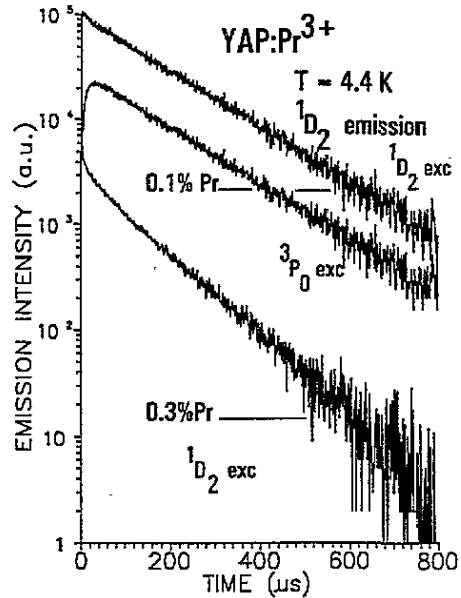


Figure 6. Temporal evolution of the $^1\text{D}_2$ fluorescence after resonant orange ($^1\text{D}_2$) excitation in 0.1 and 0.3 at.% Pr^{3+} samples (curves b) and after blue ($^3\text{P}_0$) excitation in 0.1 at.% Pr^{3+} -doped YAP (curve a) at $T = 4.4\text{ K}$ (a.u., arbitrary units).

the diluted 0.1 at.% Pr^{3+} sample, decay is exponential with a lifetime of $165\ \mu\text{s}$ while, in the 0.3 at.% Pr^{3+} crystal, decay is non-exponential, consisting of a long component and a short component having decay time constants of $128\ \mu\text{s}$ and $40\ \mu\text{s}$, respectively. Figure 6 also shows the low-temperature decay profile of the $^1\text{D}_2$ level excited via the $^3\text{P}_0$ level at 20417 cm^{-1} . It is seen that, in the 0.1 at.% Pr^{3+} doped crystal, decay is exponential with the unchanged (with respect to direct orange excitation) lifetime of $165\ \mu\text{s}$. However, in contrast with the direct excitation, a rise time of $11\ \mu\text{s}$ is measured. This can be attributed to the decay from the $^3\text{P}_0$ level to the $^1\text{D}_2$ level.

After IR $^1\text{G}_4$ multiplet excitation, low-temperature $^1\text{G}_4$ 1350 nm fluorescence decay in the 0.1 at.% Pr^{3+} -doped YAP crystal was measured to be less than $1\ \mu\text{s}$ [15].

3.3. Orange-to-blue-wavelength up-conversion

It has been observed that excitation of the $^1\text{D}_2$ Stark levels results in an unexpectedly intense emission from the higher-lying $^3\text{P}_0$ state. The excitation spectrum of this anti-Stokes up-converted emission in the 0.3 at.% Pr^{3+} crystal, presented in figure 7, was recorded when collecting the $^3\text{P}_0$ fluorescence at 491 nm (see figure 3) and tuning the laser frequency over the lowest Stark component of the $^1\text{D}_2$ manifold at 16380 cm^{-1} (610.5 nm). For comparison the excitation spectrum of the $^1\text{D}_2$ emission, measured by monitoring the $^1\text{D}_2 \rightarrow ^3\text{H}_6$ near the IR fluorescence at 825 nm , is also displayed in the same figure. Important differences between the forms of the excitation profiles should be noted. It is seen that the up-converted signal exhibits a pronounced additional satellite line structure. The temporal evolutions of the Stokes and anti-Stokes emissions resulting from the selective excitation of the main line and the satellites are presented in figures 8 and 9. It can be seen that the up-converted

signal decay is strongly excitation wavelength dependent. Excitation at the absorption line centre d produces intense 3P_0 emission with a rise time of $5.5 \mu\text{s}$ and non-exponential decay, approaching at long time delays the decay time of $72 \mu\text{s}$ which is nearly equal to half the 1D_2 fluorescence decay time of $165 \mu\text{s}$. Pumping at wavelengths e and b (see figure 7) results in a faster decay and a shorter rise time of the emission. This type of fluorescence decay has not been observed when exciting satellites a and c: no rise time was detected and decays were unchanged with respect to OP, directly excited 3P_0 decay. Finally, the quadratic dependence of the up-converted 3P_0 fluorescence on incident 1D_2 excitation energy has been determined.

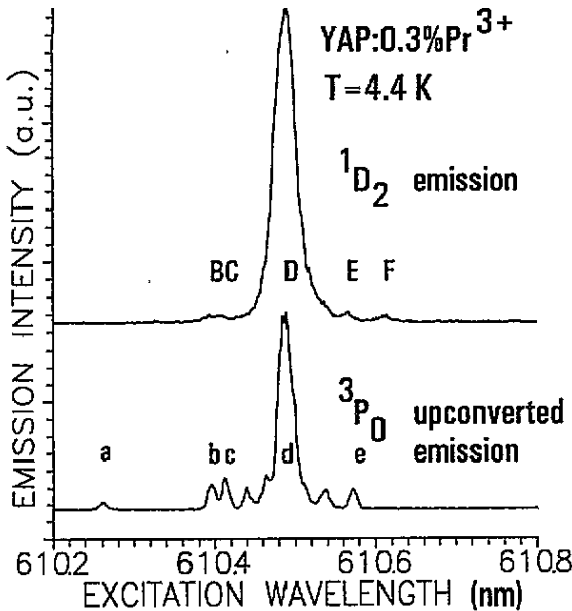


Figure 7. Excitation spectra of the up-converted 3P_0 fluorescence and 1D_2 Stokes emission in YAP:0.3 at.% Pr^{3+} at $T = 4.4 \text{ K}$ (a.u., arbitrary units); the excitation wavelength was tuned around the ${}^3H_4(1) \rightarrow {}^1D_2(1)$ absorption transition.

3.4. IR-to-blue-wavelength up-conversion

Blue emission from the 3P_0 manifold has been observed between 4.4 and 300 K for several excitation wavelengths in the 900 nm band ($11\,000 \text{ cm}^{-1}$). The excitation spectrum of this anti-Stokes fluorescence measured at 10 K in YAP: 0.3 at.% Pr^{3+} is presented in the upper part of figure 10. The polarized IR excitation spectra of the 0.1 at.% Pr^{3+} sample were also measured; however, the blue emission signal was more than one order of magnitude less intense than in the 0.3 at.% Pr^{3+} -doped crystal. The decay profile of the blue emission resulting from the IR excitation at 910 nm (10994 cm^{-1}) is shown in the lower part of figure 5. It can be seen that the decay is exponential with a low-temperature lifetime of $11.5 \mu\text{s}$ and no observable rise-time, as after OP direct excitation (see figure 5). Finally a square intensity dependence of the up-converted 3P_0 emission on IR excitation power was determined.

4. Discussion

Table 2 summarizes our results of 4.4 K absorption, fluorescence and excitation measurements for Pr^{3+} -doped YAP. Comparison of the low-temperature spectra of the two investigated

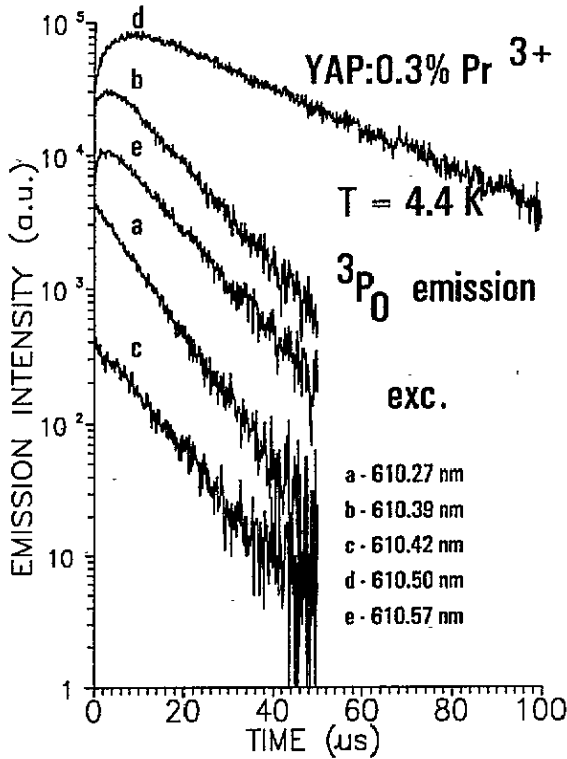


Figure 8. Time evolution of the up-converted $^3\text{P}_0$ fluorescence after selective excitation of the $^3\text{H}_4(1) \rightarrow ^1\text{D}_2(1)$ line centre and the satellites at 4.4 K (a.u., arbitrary units).

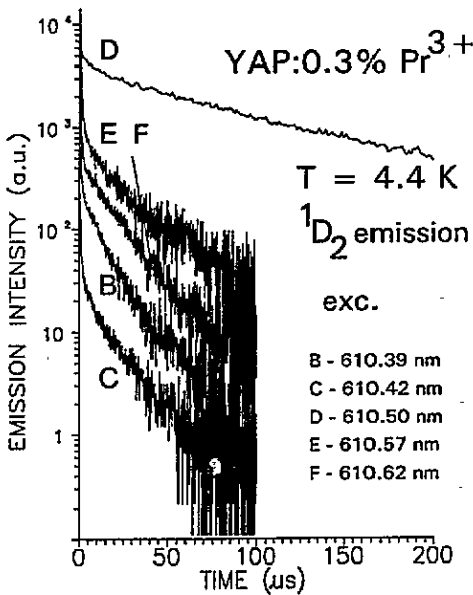


Figure 9. Time evolution of the $^1\text{D}_2$ fluorescence after selective excitation around the $^3\text{H}_4(1) \rightarrow ^1\text{D}_2(1)$ absorption transition at 4.4 K (a.u., arbitrary units); no orange emission was observed when exciting satellite a.

samples did not reveal any dependence of the Pr^{3+} energy level position on active ion concentration. However, slightly larger transition linewidths have been observed for the

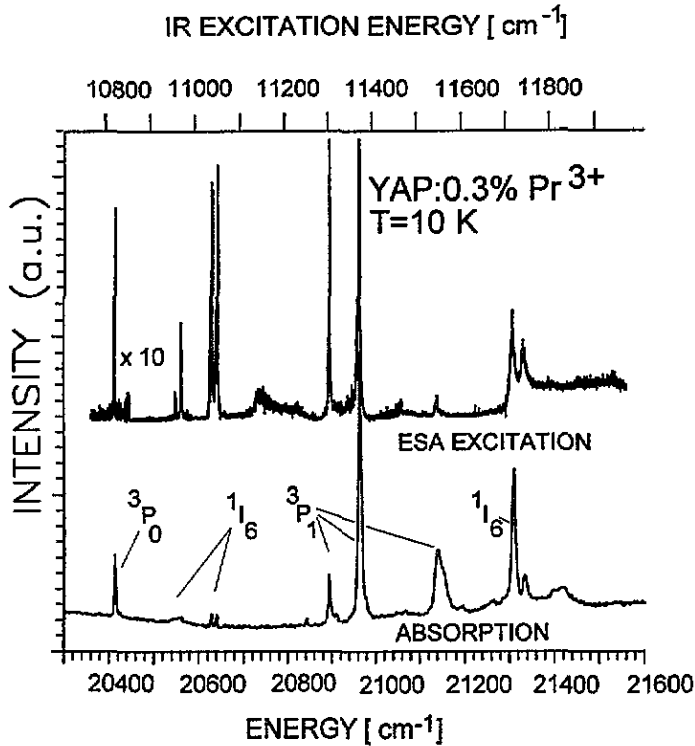


Figure 10. IR excitation spectrum (upper curve and upper energy scale) of the blue P_0 emission for YAP:0.3 at.% Pr^{3+} at $T = 10$ K (a.u. arbitrary units). When considered as the ESA spectrum the curve is plotted against the sum of IR photon energies and 9590 cm^{-1} which is energy of the lowest Stark level of the 1G_4 manifold (lower energy scale). For comparison the lower curve (and the lower energy scale) shows the or absorption spectrum of the same crystal.

0.3 at.% Pr^{3+} sample, suggesting a higher degree of lattice strain in this strongly doped crystal.

4.1. Optical spectra and fluorescence dynamics

When comparing the spectroscopic properties of Pr^{3+} ion in different hosts, e.g. the oxides YAG [16, 17], GGG [18] and YAP and the fluorides LaF_3 [20], LiYF_4 [21, 22] and BaY_2F_8 [15], it can be seen that the splitting of most of the J multiplets in YAP is less than in the crystals considered and that the lowest Stark levels of the 3P_0 , 1D_2 and 1G_4 manifolds are considerably lower in energy. For the two oxide crystals YAP and YAG the first $f-d$ bands of the Pr^{3+} ion are also lower in energy, about $33\,000 \text{ cm}^{-1}$ and $40\,000 \text{ cm}^{-1}$, respectively [2], than in fluorides. Despite the apparent differences between the J -level splitting, the energy gaps between the Pr^{3+} multiplets in YAP, YAG and GGG differ only slightly, indicating similar non-radiative transition probabilities in these crystals. Thus, the differences between the fluorescence kinetics are rather related to the character of the cross-relaxation mechanism involved.

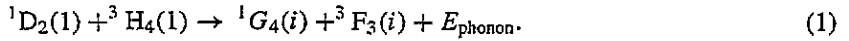
From comparison of the 1D_2 lifetimes it is seen that in YAP: Pr^{3+} the 1D_2 state emission decay is faster and much more strongly affected by fluorescence quenching ($\tau_{\text{fl}}(0.1 \text{ at.}\% \text{ Pr}) = 165 \mu\text{s}$; $\tau_{\text{fl}}(0.3 \text{ at.}\% \text{ Pr}) = 128 \mu\text{s}$) than in YAG [17] and GGG [19].

Table 2. Energy levels of Pr^{3+} in YAP

$2S+1L_J$	($E \text{ cm}^{-1}$)	Γ	$2S+1L_J$	($E \text{ cm}^{-1}$)	Γ
3P_2	22 411.5	1	3F_3	6804	
	22 318	2		6723	
	22 290.5	1		6682	
	21 935	1		6558	
	21 920	2		6515	2
			6482		
			6434		
1I_6	21 422	2	3F_2	5432 ^a	
	21 399.5 ^a	1		5416	
	21 334.5	2		5313	
	21 312 ^a	1		5232	
	21 306 ^a	2		5216	
	21 276.5 ^a	1			
	21 195.5	2			
	21 159.5 ^a	2			
			3H_6	4526 ^a	
3P_1	21 143	2		4441	
	20 963	1		4427	
	20 895.5	2		4396 ^a	
				4352	2
			4322	2	
1I_6	20 647	1		4262	
	20 632	2		5250	
	20 563.5 ^a	1		4179	
	20 551 ^a	2		4128	1
3P_0	20 416.8	1			
			3H_5	2547	
1D_2	17 031	1		2510	
	16 787	2		2491 ^a	
	16 717	1		2449	
	16 651	2		2421	
	16 380	1		2353	
				2281	
1G_4	10 219			2269	
	10 130	1		2243	
	10 081			2236	
	10 006			2143	
	9793 ^a				
	9774		3H_4	639.5	
	9668	1		524 ^a	
9590	1		468		
			229	1	
3F_4	7388 ^a			185 ^a	
	7376 ^a			152	2
	7247			144	1
	7153			52	2
	7142			0	1
	7039				
	7024	2			
	6962				
6934					

^a Less accurate results.

It is well known that in praseodymium compounds this process is attributed to the cross-relaxation between two adjacent ions which could be described by the following mechanism:

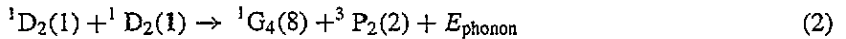


From the energy level scheme presented in table 2, several quasi-resonant processes of this type (with the emission of low-energy phonons) could be pointed out. It is suggested that in YAP:Pr³⁺ this nearly resonant character of cross-relaxation is responsible for the significant reduction in the ¹D₂ lifetime.

4.2. Orange-to-blue wavelength up-conversion

The quadratic dependence of the blue up-converted emission on the incident orange pump intensity indicates a two-photon (TP) excitation process. The TP excited ³P₀ fluorescence dynamics shown in figure 8 are characterized by two distinct sets of decay curves. Pumping at satellites b, d and e resulted in a rise time of the blue emission, which is characteristic for an energy transfer up-conversion (ETU) process. Excitation at satellites a and c resulted in ³P₀ emission with no observable rise time and exponential decay, which for excitation c has the same time constant as under direct resonant pumping (see also figure 3). This type of up-converted kinetics is characteristic of an excited-state absorption (ESA) process.

The ETU process has been investigated in LaF₃:Pr³⁺ crystals [23, 24] and was related to the following mechanism;



where in YAP:Pr³⁺ the excess energy of 43 cm⁻¹ is released. By solving the population equations for the doubly excited ion pair, the time evolution of the ³P₀ emission after ¹D₂ excitation is given by

$$N_3 = \frac{N_2^0 W_t}{W_3 - 2W_2 - W_t} (\exp[-(2W_2 + W_t)t] - \exp(-W_3 t)) \quad (3)$$

where N_2^0 is the initial number of doubly excited ion pairs, W_2 and W_3 are the radiative decay rates of the single ions in the ¹D₂ and ³P₀ states respectively and W_t is the energy transfer rate. It should be noted that according to equation (3) the rise time of the up-converted emission is governed by the lifetime $1/W_3$ of the ³P₀ state, followed by an exponential decay faster than half the intrinsic decay time, i.e. $\frac{1}{2}W$. Our measurements indicated a rise time of 5.5 μs which is much shorter than the ³P₀ decay time of 11.7 μs. The equivalent situation in LaF₃:Pr³⁺ has been explained by Vial *et al* [23] as due to the limitations of the assumed model, i.e. in the concentrated Pr³⁺ systems ¹D₂ decay is no longer exponential and W_3 -values could be different for the specific ion pairs. By fitting the up-converted ³P₀ signal resulting from the excitation of the centre of absorption line d with equation (3) and using $W_2 = 6.06 \times 10^3 \text{ s}^{-1}$ and $W_{\text{up}} = 1.39 \times 10^4 \text{ s}^{-1}$, the transfer rate $W_t = 1.8 \times 10^3 \text{ s}^{-1}$ has been evaluated. The pair origin of satellites b and e responsible for the up-conversion signal is also confirmed by the selectively excited-¹D₂-state decays (see figure 9). On the assumption that the reduction in the ¹D₂ lifetime after excitation at wavelengths B and E is due to cross-relaxation between an excited and unexcited ion (see equation (1)), the quenching rates deduced for lines B and E are $X_B = 1.28 \times 10^6 \text{ s}^{-1}$ and $X_E = 1.42 \times 10^6 \text{ s}^{-1}$, respectively, and are in reasonable agreement with the pair transfer rate of $0.996 \times 10^6 \text{ s}^{-1}$ measured for YAG:Pr³⁺ and the nearest-neighbour interaction rate calculated for this crystal [17].

The energy level scheme for YAP:Pr³⁺ (table 2) shows that the only possible ESA mechanism resulting in the excitation of the ³P₀ state with orange-wavelength photons

should come from the excited ³H₆ state. Thus, the first photon is non-resonantly absorbed in a weak phonon band associated with the ³H₄ → ¹D₂ transition; this is followed by rapid non-radiative relaxation towards ³H₆ manifold from which the second photon excites the ion resonantly to the ¹I₆ manifold. Both satellite a and satellite c lie on the high-energy side of the ³H₄(1) → ¹D₂(1) transition which is consistent with the first-step non-resonant ESA process. It is also seen that excitation a at 16385 cm⁻¹ does not produce any ¹D₂ emission. On the basis of measurements performed at temperatures of 4.4, 10 and 40 K, line a has been identified as the ³H₆(2) + 16385 cm⁻¹ = ¹I₆(2) transition. More intense up-conversion transitions from the strongly populated lowest ³H₆(1) Stark level were observed in the 605–608 nm range. The origin of satellite c could not be unambiguously determined. In the light of the temperature-dependent excitation and decay kinetics results, we suggest that line c results from the ESA transition of some slightly perturbed Pr³⁺ ions.

Thus, we conclude that two different up-conversion processes, ETU and ESA, are simultaneously active in the YAP: 0.3 at.% Pr³⁺ system. Regular ions responsible for the centre of the ³H₃(1) → ¹D₂(1) absorption line d and probably ion pairs related to satellites b and e undergo ETU when for some excitation energies (lines a and c) ESA is responsible for the up-conversion signal.

It can also be seen that the up-conversion emission investigated is comparable in intensity with that of the directly pumped ³P₀ emission. So the high efficiency of up-conversion, which results from the quasi-resonant character of the process, opens up the possibility of blue lasing after orange-wavelength excitation.

4.3. IR-to-blue-wavelength up-conversion

Up-conversion ³P₀ fluorescence after IR pumping could be explained using an excitation scheme similar to that reported by us for Pr³⁺-doped LiYF₄ and YAG crystals [7, 22]. The spectrum in figure 10 corresponds to the second ESA step from the lowest ¹G₄(Γ₁) Stark level at 9590 cm⁻¹ to the levels of the ³P₀ + ¹I₆ + ³P₁ manifolds. The first step is the non-resonant absorption to the phonon band of the ³H₄ → ¹G₄ transition. After rapid non-resonant relaxation, the lowest ¹G₄ Stark level is populated. In figure 10, comparison of the absorption and ESA spectra for YAP:0.3 at.% Pr³⁺ is shown; it can be seen that the ESA spectrum shows an enhanced weak structure between 20500 and 27700 cm⁻¹ observed in OP absorption. In the 0.1 at.% Pr³⁺-doped crystal the ¹G₄ → ³P₀ transition is not observed and the ¹G₄ → ³P₂ lines are very weak. Thus, spin-allowed ¹G₄ → ¹I₆ transitions provided us with better-resolved spectra of the ¹I₆ manifold than was observed for the OP absorption spectra. Polarized measurements performed on the 0.1 at.% Pr³⁺ sample allowed us to determine the position and symmetry of several high-lying praseodymium Stark levels, which are shown in table 2.

It can be seen that the excitation energy of about 11150 cm⁻¹ (see figure 10) does not correspond to any absorption feature around 20740 cm⁻¹ expected from the ESA mechanism. From table 2, it is shown that 11150 cm⁻¹ is half the energy of the ³P₂ manifold of YAP:Pr³⁺. Figure 11 gives a comparison of the polarized absorption spectrum of YAP around the ³P₂ energy with the double IR excitation energy. It is concluded that the structure observed in the IR excitation spectrum is due to two-photon absorption (TPA) transitions from the ³H₄ ground state to the ³P₂ manifold. Thus, two distinct types of transition, ESA and TPA, have been observed in YAP:Pr³⁺. As both processes have a quadratic dependence on excitation intensity and exhibit the same excited-state dynamics, they could only be separated here on the basis of a precise energy level analysis. Contrary to the weak inter-configuration 4f-4f5d TPA transitions reported recently for YAG:Pr³⁺ [25, 26] which are forbidden in first order by the parity selection rules, the intra-4f²-configuration TPA transitions observed here

for YAP:Pr^{3+} are only about one order of magnitude lower in intensity than the OP absorption transitions are. A similar observation has been reported recently by de Mello Donega *et al* [27] who compared the intensities of TPA and ESA transitions between the $^3\text{H}_4(1)$ and $^3\text{P}_0$ states of the Pr^{3+} ions in Sr MoO_4 .

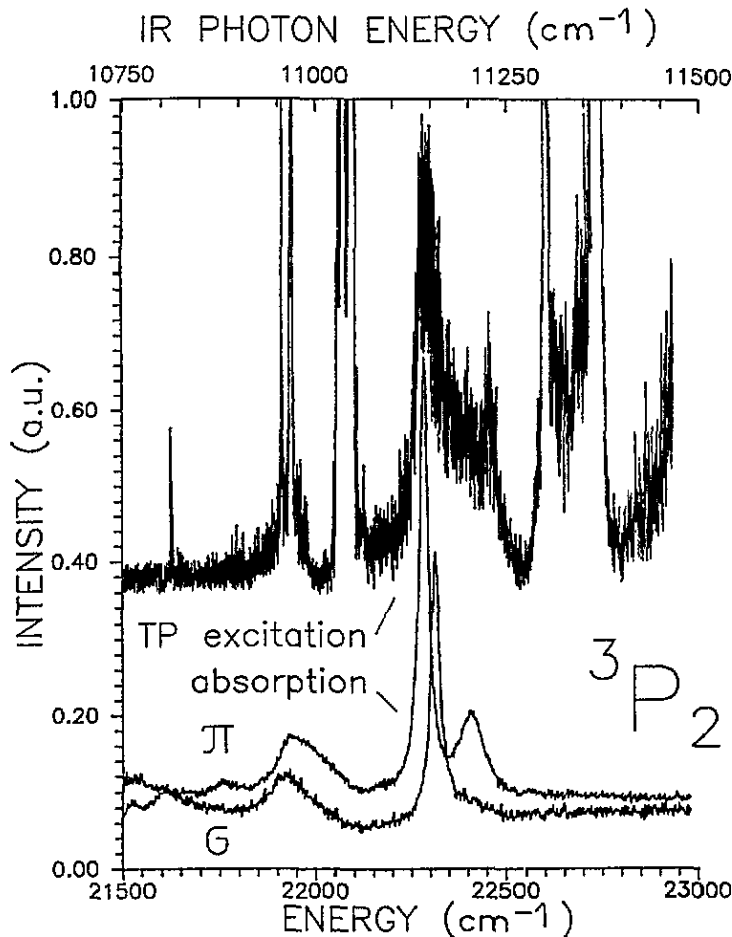


Figure 11. Comparison of polarized OP absorption (lower trace) and TP excitation spectra (upper trace) around the $^3\text{P}_2$ manifold energy (a.u., arbitrary units).

In summary, three different mechanisms of up-conversion leading to blue $^3\text{P}_0$ emission have been studied in $\text{YAlO}_3 : \text{Pr}^{3+}$ crystals: energy transfer between two ions in the $^1\text{D}_2$ state after orange-wavelength excitation, ESA via intermediate $^1\text{G}_4$ manifold after IR excitation, and TPA from the $^3\text{H}_4$ ground state to the $^3\text{P}_2$ manifold. Comparison of the ESA and TP excitation spectra provided information on the TPA transition intensities. These experiments allowed us for the first time to establish a complete energy level scheme for Pr^{3+} ion in a YAP crystal.

Acknowledgments

We are indebted to R M Macfarlane (IBM, Almaden) for providing the 0.1 at.% Pr^{3+} -doped

YAP sample. One of the authors (MM) would like to thank Region Rhone-Alpes and CNRS for supporting him as a visiting scientist.

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