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4f² to 4f5d excited state absorption in Pr³⁺:YAlO₃

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Abstract. Excited-state absorption spectra, from the ³P_J–¹I₆ or ¹D₂ manifold to 4f5d levels, recorded in the 23 000–42 000 cm⁻¹ range and calibrated in units of cross sections, are reported and discussed in the case of Pr³⁺-doped YAlO₃. The 4f5d → 4f²Pr³⁺ emission between 30 000 and 44 000 cm⁻¹ is then observed, showing the possibility of UV laser operation following two-step excitation pumping using near-UV-visible pump photons.

1. Introduction

The broad bands characterizing the 4fⁿ⁻¹5d to 4fⁿ inter-configurational transitions of the trivalent rare earth ions in wide band gap dielectric crystals offer the possibility of using these materials for generating tunable laser radiations in the near-ultraviolet (UV) spectral domain. Positive results have been already obtained with Ce³⁺ ([1, 2] for example) and Nd³⁺ [3] doped fluoride crystals after direct pumping into their 4fⁿ⁻¹5d band. On the other hand no UV laser emission [4] has been observed so far in any Pr³⁺ doped material. However, this ion seems interesting and worth studying in more detail as it can generate intense 4f5d to 4f² emissions in a very broad spectral domain, from about 220 to 450 nm depending on the host matrix, and some hope still remains of obtaining laser emission with it. So far, 4f5d to 4f²Pr³⁺ emissions have been observed essentially in fluoride crystals such as LiYF₄ [5], LiLuF₄ [6], BaY₂F₈ [7], BaF₂ and CaF₂ [4, 8], in oxides such as YAG [9–12], YAlO₃ [8, 11], PrP₅O₁₄ [13], GdBO₃ [14], ScBO₃ [15], LuBO₃ [16], LaB₃O₆ [17], Ca₃La₃(BO₃)₅, Y₂GdAl₅O₁₂ and YOCl [18, 19] and very recently in a chloroelpasolite Cs₂NaYCl₆ [20].

Concerning the Pr³⁺ doped yttrium orthoaluminate YAlO₃ which is considered here, most of the basic optical properties have already been reported in the past. The positions of the energy levels of the Pr³⁺ 4f² ground configuration and the corresponding f–f intra-configurational absorption and emission transitions can be found in [21–23]. According to these papers, the seven lower manifolds ³H_{4,5,6}, ³F_{2,3,4} and ¹G₄ are located in the infrared spectral range whereas the higher lying ones labelled ¹D₂ and (³P_{0,1,2}, ¹I₆) are located in the orange and the blue between about 16 380 and 17 030 cm⁻¹ and between 20 410 and 22 410 cm⁻¹, respectively. In very low concentration crystals, the fluorescence from the ¹D₂ state exhibits exponential decay with a time constant of 165 μs and the fluorescence from the ³P₀ state exhibits exponential decay

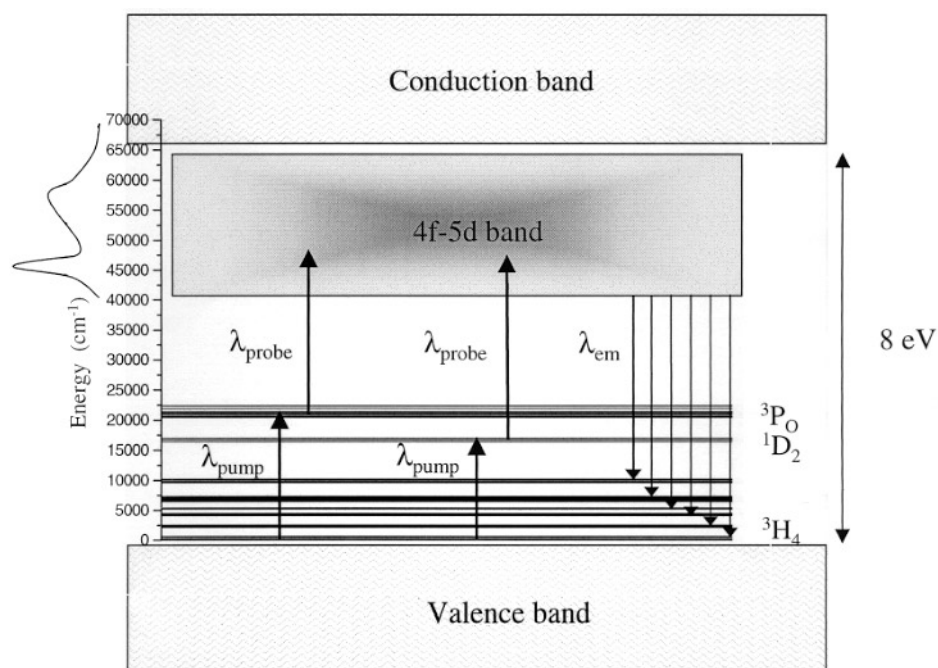


Figure 1. Energy level scheme for YAlO₃:Pr³⁺ showing the transitions used in the pump-probe experiment, the transitions observed in the 4f5d → 4f² emission spectra and the density of states in the 4f5d configuration.

with a time constant of 11 μs [22]. The emission spectrum of the 4f5d first excited configuration was reported for example in [8, 11]; it consists of two broad bands at room temperature peaking around 35 000 and 40 000 cm⁻¹ which are assigned to transitions originating from the lowest 4f5d level and terminating on the low energy manifolds mentioned above. The decay of this emission is nearly exponential with a time constant of 8 ns [8]. A portion of the associated excitation spectrum was also reported in the literature [8]; this spectrum was recorded within the band gap energy (8 eV according to [24]) and it exhibits two groups of bands located around 46 080 and 55 550 cm⁻¹ which are assigned to ³H₄(4f²) → 4f5d transitions.

These energy level considerations (see figure 1) show that up-conversion excitation of the 4f5d UV emission using the ¹D₂ and (³P_{0,1,2}, ¹I₆) energy levels as intermediate excitation steps and visible and near-UV pump photons should be possible in YAlO₃:Pr³⁺, as was reported in the case of YAG:Pr³⁺ [12], and this is the subject of the present investigation. Indeed, such excited-state absorption (ESA) from the higher Pr 4f² levels, which is usually considered as detrimental to laser action from these levels, could be used as an excitation mechanism for the higher 4f5d bands. This could be one way to overcome the solarization problems encountered after direct pumping with short wavelength photons. Moreover, ESA is also a practical experimental method to determine the position and the nature of the 4f5d energy levels.

2. Experimental conditions and spectroscopic results

Several Pr³⁺:YAlO₃ single crystals with different Pr³⁺ activator concentrations between 0.1 and 3 at.% were examined. The 0.1 at.% doped crystal was from the IBM Almaden Research

Laboratory, the 3 at.% doped one was grown using the Czochralski technique in the ITME Laboratory in Warsaw and three other crystals (0.65, 1.3 and 2.6 at.%) were grown with the Czochralski method in the Institute for Physical Research in Ashtarak. Yttrium orthoaluminate YAlO₃ has an orthorhombic structure with space group *Pbnm* and the praseodymium ion enters the lattice at the yttrium sites having the C_s point symmetry [25, 26]. Since YAlO₃ is a biaxial system and only electric-dipole-allowed transitions were expected, spectra had to be recorded with polarization parallel to each of the three principal optical axes (which correspond to each of the crystallographic axes in the case of an orthorhombic structure). Thus, each crystal was oriented and cut in the form of small parallelepipeds of a few mm³ with each face perpendicular to one of these axes *a*, *b* or *c* with *a* = 5.13, *b* = 5.32 and *c* = 7.37 Å.

Polarized ground state absorption (GSA) spectra were recorded again [23] first to obtain more precise information about the real absorption of our crystals and more particularly in the blue and orange spectral domains corresponding to the ³H₄ → (³P_{0,1,2}, ¹I₆) and ¹D₂ optical transitions since they will constitute the first pumping step of our excited-state absorption (ESA) and excited-state excitation (ESE) measurements. These polarized GSA spectra were registered by using a conventional Cary 2300 Varian spectrometer and Glan–Taylor polarizers.

On the other hand, the excited state absorption (ESA) spectra were recorded at the Centre Interdisciplinaire de Recherche Ions Lasers of Caen by using a pump–probe technique similar to that described in [27] but specifically adapted to the near-UV spectral domain to be investigated here [28]. For that purpose, the pump light was that of an OPO-C-355 laser (GWU) pumped by the frequency tripled pulsed radiation at 355 nm of an Nd:YAG laser (Spectron); this pulsed pump source (5 ns pulsewidth, 10 Hz repetition rate, less than 500 μJ/pulse to avoid optical damage of the crystal) enabled us to populate the ¹D₂ or the ³P_{0,1,2} and ¹I₆ Pr³⁺ states, located in the orange or blue spectral range respectively, from which we wanted to probe absorption towards the 4f5d bands. The probe source was a continuous xenon lamp fed by a stabilized power supply. Both beams were focused into the sample which was sandwiched between two diaphragm plates to ensure a good overlap between the pump and probe beams within the crystal. The probe light transmitted by the sample was analysed through a monochromator (Oriel 77200) and the signal was detected by a photomultiplier (Hamamatsu R3896) and processed into a (PAR 162) boxcar integrator using a gate with a delay of a few μs and a width of 10 μs. In front of the monochromator entrance slit, adequate filters were put in order to eliminate the pump as well as the Pr³⁺ fluorescence light and a Glan–Taylor polarizer was used to record polarized ESA spectra.

All the experiments were performed at room temperature.

As mentioned above, polarized absorption spectra were first recorded in the visible domain and they are reported in figure 2. These spectra are given in units of cross section σ_{GSA} and they were deduced from the measured optical density *D* by using the formula $\sigma_{GSA} = 2.3D/NL$ in which *L* is the sample thickness and *N* the Pr³⁺ concentration. These spectra permitted us to select, for each polarization configuration, the most efficient excitation wavelength to be used as first excitation step in the following ESA experiments.

Two series of ESA experiments were performed. The first one was realized with the pump beam in resonance with one of the ³H₄ → ³P_{*J*} or ¹I₆ optical transitions and the second with the pump beam in resonance with one of the ³H₄ → ¹D₂ transitions. For each series, three spectra were recorded between 23 000 and 42 000 cm⁻¹, each of them with the probe light electric field vector *E* parallel to either the *a*, *b* or *c* crystallographic axis of the crystal. The cross section values σ_{ESA} were deduced from the experiment by using the expression [27]:

$$\sigma_{ESA} = \frac{-\ln(1 - \Delta I/I_0)}{N * L} + \sigma_{GSA}$$

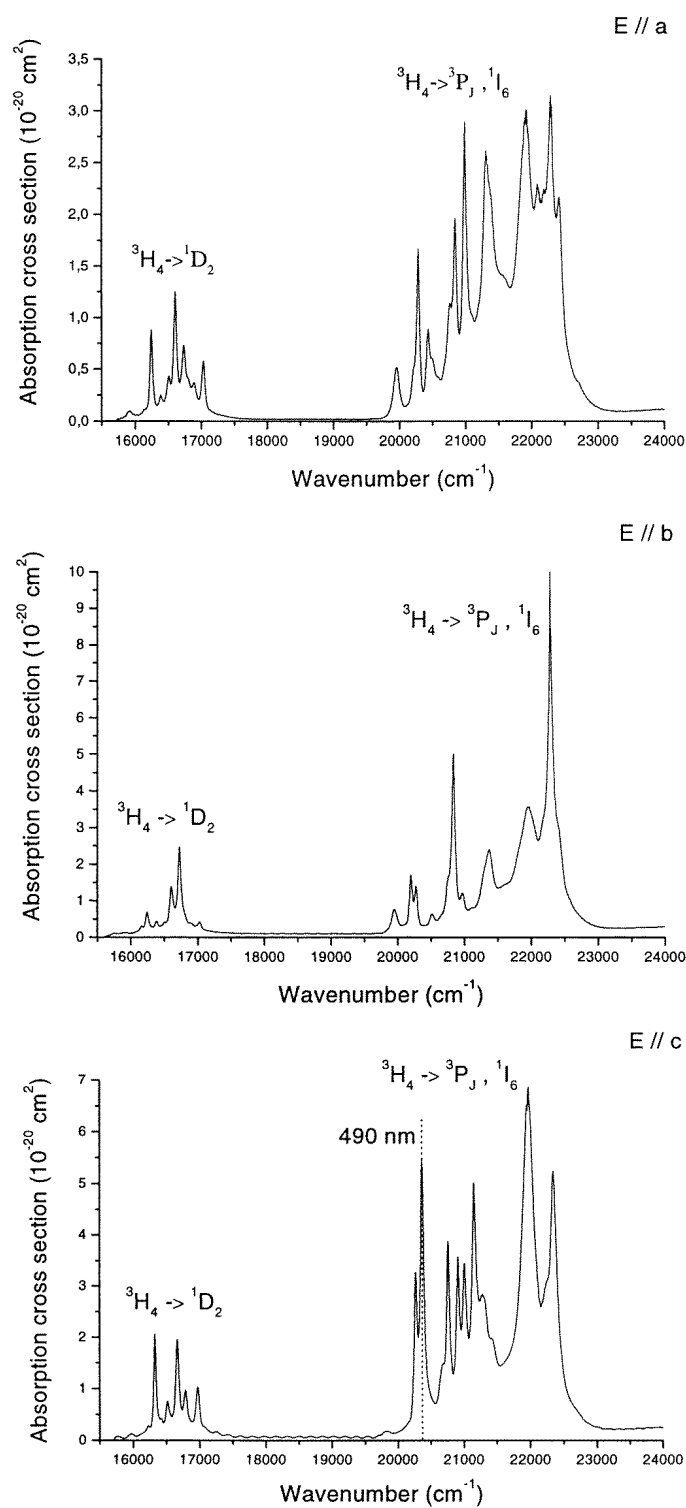


Figure 2. Room temperature absorption cross section of $\text{Pr}^{3+}:\text{YAlO}_3$.

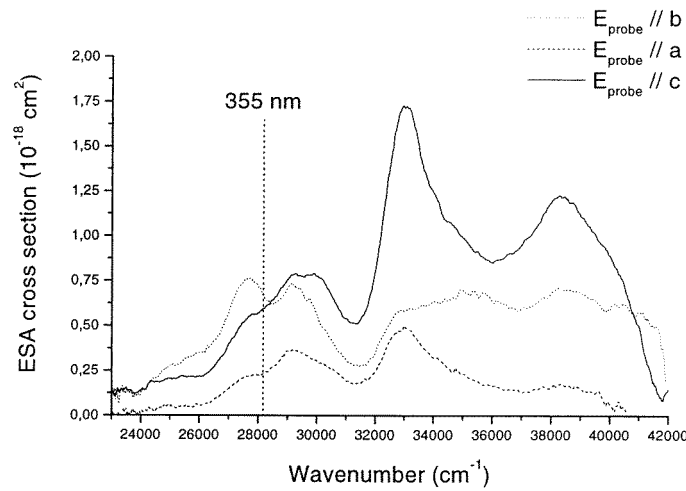


Figure 3. Room temperature ($^3P_J, ^1I_6$) excited state absorption cross section of $Pr^{3+}:YAlO_3$.

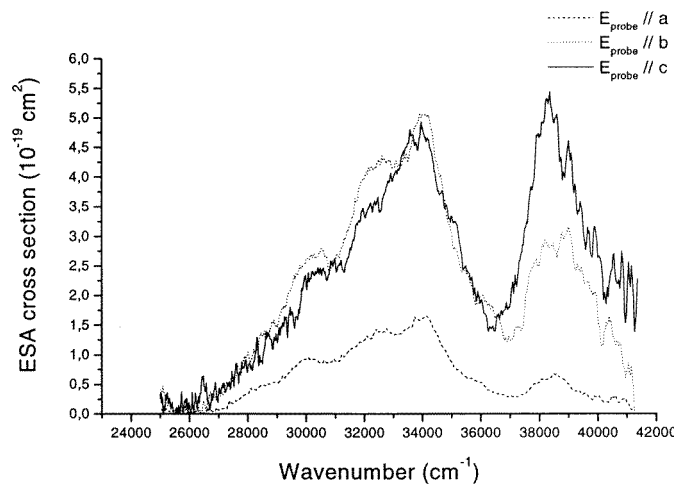


Figure 4. Room temperature 1D_2 excited state absorption cross section of $YAlO_3:Pr^{3+}$.

in which I_0 is the analysed probe light when the pump beam is off, ΔI is the variation of the analysed probe light when the pump beam is on and N^* is the density of Pr^{3+} ions brought into the first excited state by the pump beam.

The resulting ESA cross section spectra are presented in figure 3 for the pump beam energy in resonance with one of the $^3H_4 \rightarrow ^3P_J$ or 1I_6 transitions and in figure 4 for the pump beam energy in resonance with one of the $^3H_4 \rightarrow ^1D_2$ transitions. Several ESA bands are observed and their relative intensities strongly depend on polarization.

As excited state absorption is possible, we also recorded the $4f5d \rightarrow 4f^2$ emission spectrum obtained after two step excitation. The signal output at 490 nm of the OPO-C-355 laser was used for the first step ($^3H_4 \rightarrow ^3P_J$, see figure 2) whereas the 355 nm residual pump output of the same laser was used for the second step ($^3P_J \rightarrow 4f5d$, see figure 3). The resulting unpolarized emission spectrum is presented in figure 5 together with the polarized emission

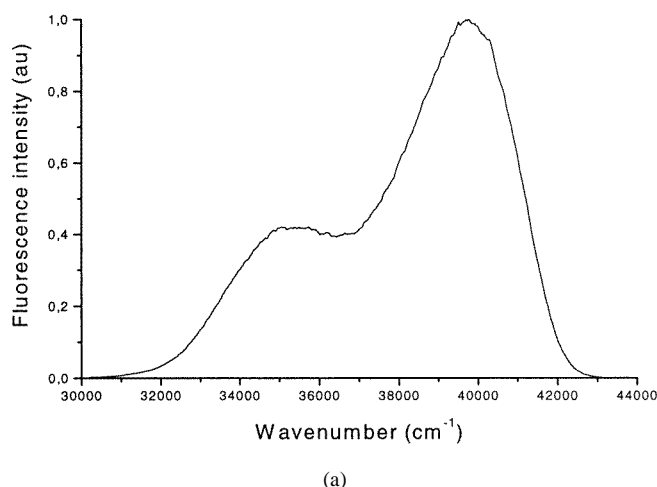


Figure 5. Room temperature $4f5d \rightarrow 4f^2$ fluorescence spectra of $\text{Pr}^{3+}:\text{YAlO}_3$ obtained after (a) two step excitation ($\lambda_1 = 490$ nm and $\lambda_2 = 355$ nm), and after (b) single step UV excitation ($\lambda_{exc} = 217$ nm).

spectra obtained after direct excitation at 217 nm by means of a continuous-wave xenon lamp. All these spectra are similar and it is interesting to note that, in contrast to the ESA absorption spectra, the $4f5d$ to $4f^2$ fluorescence spectra do not exhibit any significant polarization effect.

After such two step excitation of the $4f5d \rightarrow 4f^2$ emission and using an excitation density of 8.5 mJ mm^{-2} at 490 nm for the first step, solarization of the 0.1 at.% Pr^{3+} -doped sample, with the appearance of a brownish colour, occurred for excitation densities at 355 nm as low as 0.5 mJ mm^{-2} . It is worth noting, however, that the sample could be bleached by exposing it to the 488 nm radiation of a CW Ar^+ ion laser. With the 0.65 at.% Pr^{3+} -doped sample, no such solarization appeared below $E = 0.5 \text{ mJ mm}^{-2}$, and this limit value increased up to 0.7 mJ mm^{-2} for a crystal annealed under hydrogen atmosphere. With the 1.3 at.% Pr^{3+} -doped sample, a 0.7 mJ mm^{-2} excitation density was also necessary to see any solarization effect. For the higher concentration samples (2.6 or 3 at.% Pr^{3+}), no colour centres were created even with an excitation density of 2 mJ mm^{-2} .

3. Discussion

ESA spectra are expected to give complementary information about the structure and the energy position of $\text{Pr}^{3+} 4f5d$ states in $\text{Pr}^{3+}:\text{YAlO}_3$. However, a real interpretation of the observed features will have to await specific theoretical calculations. It is known indeed that the 5d electron is much more sensitive to the crystalline environment than the 4f one which is protected by the outer filled electron shells $5s^2$ and $5p^6$. Thus it is expected that the gross features of the optical transitions to the $4f5d$ electronic configuration should primarily reflect the effect of the ligand field on this 5d electron and the energy level calculations could be done by using a high crystal field scheme in which the crystal field effect on the 4f electron, the spin-orbit and the coulombic interactions would be treated as perturbations, a theoretical approach which was already considered in the past in the case of the $4f^65d$ and $4f^75d$ configurations of the Eu^{2+} [29, 30] and Tb^{3+} [31] ions, respectively. This approach would be essentially the opposite of that recently proposed for example in the case of $4f^25d$ electronic configuration of Nd^{3+} [32]

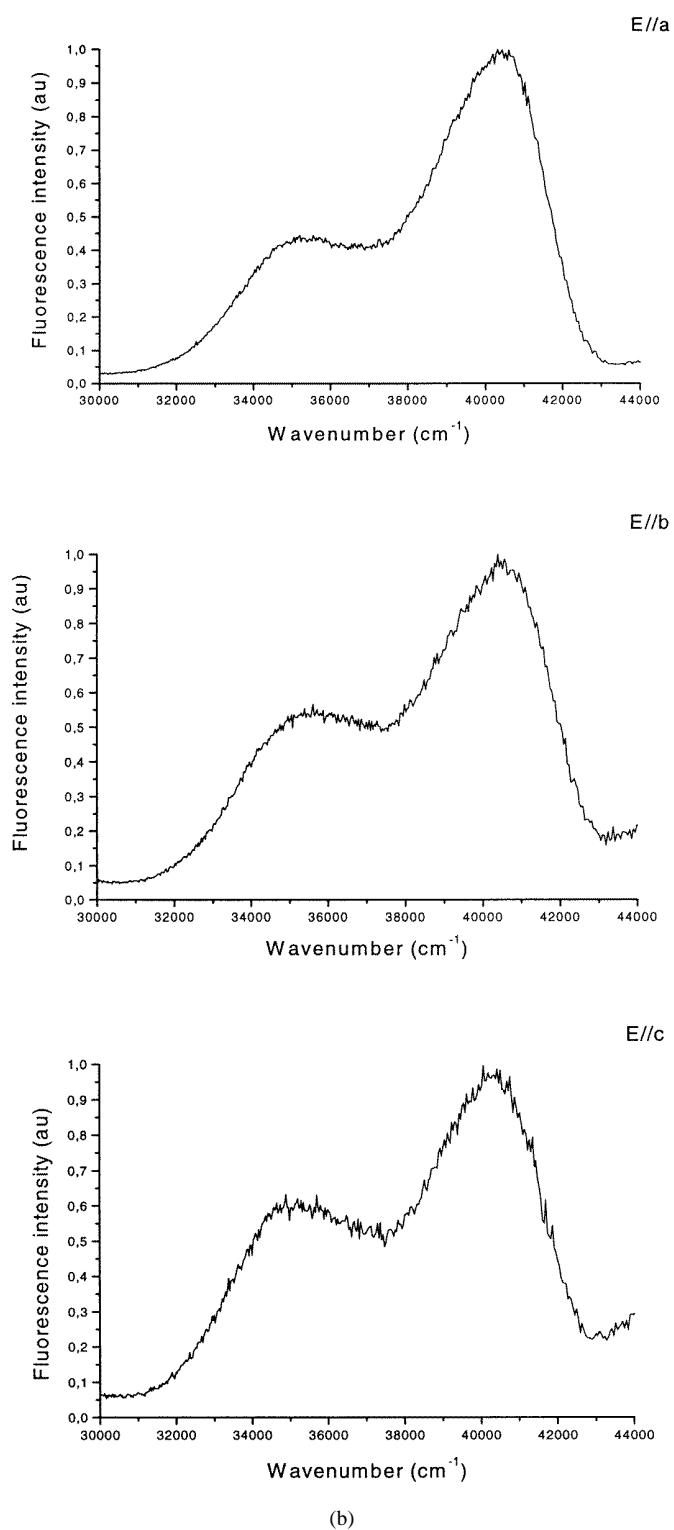


Figure 5. (Continued)

in YLiF_4 and K_2YF_5 . In this article, indeed, the electrostatic interaction is considered first, in which case the $4f^25d$ electronic configuration splits into various spectral terms with energies ranging over $25\,000\text{ cm}^{-1}$ (as in the free ion case); the tetragonal crystal field is only considered than as a perturbation which splits further each of these spectral terms by a few hundreds of cm^{-1} . This method may appear very practical to interpret the various optical bands but the results may be completely unrealistic, especially if the crystal field splits the $5d$ electronic energy levels by several thousand cm^{-1} , which is generally the case.

In our opinion, both approaches could be valid as long as the discussion of the results is restricted to the description and the interpretation of the lowest energy levels of the $4f5d$ configuration since it is likely to be constructed from the 2F state of the $4f$ electron and the lowest crystal field component of the $5d$, i.e. 2E or 2T_2 , depending on the symmetry of the crystal host. However, the question is not so straightforward for the other energy levels. It is likely that the crystal field effect on the $5d$ electron, the $4f$ – $5d$ coulombic interaction and the spin–orbit coupling among the $4f$ and $5d$ electrons have to be treated all together, which is not the purpose of this paper but which we are now examining very seriously.

At the moment, our experimental results can be analysed just by confronting the position and the structure of the $4f5d$ bands which can be derived from our ESA spectra with those known from the ground-state excitation spectrum already reported in the literature [8] and obtained by using synchrotron radiation. Considering the energies of the lowest Stark levels of 1D_2 in Pr:YAlO_3 (around $16\,400\text{ cm}^{-1}$) the ESA spectra of figure 4 would locate the probed portion of the $4f5d$ electronic configuration between about $44\,000$ and $58\,000\text{ cm}^{-1}$, with four maxima around $46\,400$, $48\,400$, $50\,400$ and $54\,760\text{ cm}^{-1}$. These four maxima are also identified on the ($P_{0,1,2}$, 1I_6) ESA spectra (figure 3) and a new one appears on the high energy side leading to a probed $4f5d$ level at $58\,910\text{ cm}^{-1}$; concerning the peak position of the central ESA band, it is clearly shifted to lower wavenumbers for polarization of the probe beam parallel to either a or c , relative to the spectrum recorded with the probe beam parallel to b (see figure 3). These probed $4f5d$ levels are in a spectral domain ranging from 230 to 160 nm. According to [8] the totality of the energy levels of the $4f5d$ configuration would lie within this spectra range, the two groups of excitation bands which are clearly observed, though certainly poorly resolved, being tentatively assigned to the cubic crystal field splitting with a value of about $11\,000\text{ cm}^{-1}$. In a high crystal field scheme, the observed five components in our ESA spectra could correspond to the five expected crystal field states. Also, once this interpretation is confirmed, which still remains to be clearly demonstrated, our ESA spectra, since they are polarized and much better resolved spectra than the corresponding unpolarized ground-state absorption/excitation spectra and since they are associated with transitions originating from spin singlets 1D_2 , 1I_6 or spin triplets 3P_J , should help considerably in the understanding of the fine structure of the $4f5d$ electronic configuration, in particular in the determination of the respective magnitude of the crystal field strength and of the coulombic and spin–orbit interactions.

Regarding photochemical stability (absence of colour centre formation) of the $\text{Pr}^{3+}:\text{YAlO}_3$ single crystals used in the two step excitation experiments, it is clear that it increases with Pr^{3+} concentration. This is in agreement with a previous work [33] in which it has been shown that the colour centre formation in YAlO_3 mainly comes from the formation of electron (e^-)–hole (e^+) pairs. As holes are preferentially trapped by Pr^{3+} ions, with the formation of Pr^{4+} ($\text{Pr}^{3+} + e^+ \rightarrow \text{Pr}^{4+}$), the probability of their capture by other type of hole trap decreases. Moreover, the adverse electron capture process at Pr^{4+} ions ($\text{Pr}^{4+} + e^- \rightarrow \text{Pr}^{3+}$) may occur. So Pr^{3+} ions, serving as additional traps, change the direction of processes of charge carrier release and capture which results in an increase of the material stability to short wavelength radiation.

Finally, the UV emission spectrum $I(\lambda)$ of Pr³⁺ in YAlO₃ can be worked out to give an estimate of the peak emission cross section $\sigma_e(\lambda)$, for example at $\lambda = 252$ nm, by using the usual expression:

$$\sigma_e = \frac{\lambda^5}{8\pi n^2 c \tau_R} \frac{I(\lambda)}{\int \lambda I(\lambda) d\lambda}.$$

Assuming a radiative lifetime equal to the measured fluorescence lifetime at room temperature $\tau_R \approx 8$ ns [8], thus a fluorescence quantum efficiency close to unity, it is found $\sigma_e(\lambda) \approx 4.25 \times 10^{-18}$ cm².

4. Conclusion

Excited state absorption from the ³P_J-¹I₆ (20 410–22 410 cm⁻¹) or ¹D₂ (16 380–17 030 cm⁻¹) manifold is demonstrated to be a possible pumping mechanism of the Pr³⁺ 4f5d states in YAlO₃:Pr³⁺ single crystals. The excited state absorption spectra show several maxima located in the range 24 000–42 000 cm⁻¹ with ESA cross sections of the order of 10⁻¹⁸ cm². They strongly depend on polarization and reveal a very clear structure which can be assigned to the predominant effect of the crystal field but which still needs to be analysed in more detail. In particular, registration of liquid helium temperature ESA spectra and specific calculations are now under way to complete these very important but preliminary results. Finally, the laser potential of such an up-conversion UV emitting system appears quite reasonable due to a decreasing solarization effect observed with increasing dopant concentration and a high stimulated emission cross section.

Acknowledgments

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