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High-resolution spectroscopic study of Er:YAlO$_3$

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Abstract

The laser crystals' performances being tightly bound to their spectroscopic properties, their continuous study is essential. The paper concerns an investigation, from highly resolved spectra, of erbium in YALO. It presents various conditions that influence the Er emission efficiency, the ways of excitation that lead to an upconversion effect, and the distribution of the active ions inside the host.

Keywords: Laser crystal; Erbium; Energy transfer; Upconversion; High-resolution spectroscopy

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1. Introduction

Rare-earth doped YAlO$_3$ (YALO or YAP) crystals have given rise to numerous spectroscopic studies, mainly motivated by the fact that YALO is a very efficient laser host. Moreover, doped with erbium, it has produced several upconversion laser emissions between 510 nm and 2.7 μm, and in some cases pumping can be achieved with infrared laser diodes.

First observations of the spectroscopic properties and laser action of Er in YALO were reported by Weber and al. [1]. Stimulated emissions occurred around 1.6 μm, arising from transitions between $^4S_{3/2}$ and $^4I_{9/2}$; excitation was produced with a flashlamp at room temperature. Under similar experimental conditions, lasing was also obtained in the region of 2.7 μm ($^4I_{11/2}\rightarrow{}^4I_{13/2}$) [2].

CW laser action at 549.6 nm was achieved in a 1%Er:YALO crystal at low temperatures up to 77 K [3]. Pumping was provided by a resonant two-step excitation using two dye lasers emitting around 800 nm. The population of the $^4S_{3/2}$ level was also realized by a phonon-assisted cooperative energy transfer using a single-pump laser tuned to a $^4I_{15/2}\rightarrow{}^4I_{9/2}$ transition, but did not allow to reach the lasing threshold.

Later, upconversion lasing at 550 nm with a one-color excitation around 800 nm was reported [4], the population mechanism being assigned either to a cross-relaxation between two ions, or to an avalanche process. Optical excitation was performed with a Ti:sapphire laser and the experiments were achieved at low temperature.

Recently green and blue fluorescences were obtained at 300 K with excitation in the 690–810 nm range using a CW Ti:sapphire laser, and assigned to a looping mechanism [5].

In the present work we have considered two aspects that influence the Er emission efficiency: the various ways of excitations leading to an upconversion effect and the distribution of the active ions inside the host. This study is carried out on Er-doped YALO samples. It follows previous studies on Nd spectroscopic properties in Nd-doped and Nd,Er-codoped YALO samples [6].

The experimental techniques are the same as reported in Ref. [6]: absorption, fluorescence and excitation high-resolution spectroscopy. The laser is a tunable single-frequency CW dye laser; its radiation has a bandwidth of about 10 MHz and the wavelength is accurately measured using a lambdascope [7]. Excitations were mainly in the 655–638 nm spectral range. Most of the experiments were realized with the sample cooled at 4 K in a continuous flow cryostat in which the temperature can be varied between 4 and 300 K. The investigated samples are 0.1, 1 and 3% Er, concentrated.

2. Distribution of Er ions

The investigation has been carried out through the study of the profiles of the optical absorption and excitation lines: since the doping ions are usually not quite randomly distributed (they may be in perturbed sites, or belong to pairs or clusters) and therefore not submitted to identical crystal fields, several lines may correspond to the same

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transition. In YALO, the lines are narrow and the ions in non-regular sites give rise to an additional discrete spectrum (satellite structure). In the particular case of Er, the resonance frequencies are almost equal, and most of the satellite lines are buried under the main resonance line. Only a few of them are sufficiently removed from the main line to appear as isolated. In any case, the additional lines are particularly weak compared to the main line.

The lineshapes have been obtained from classical absorption spectra and from excitation spectra of the $^4F_{9/2}$ (1) Stark level. The emitted fluorescence was recorded either on the 972-nm line (transition from the Er $^4I_{11/2}$ level populated after a cascade process), or on the 544 nm line (transition from the Er $^4S_{3/2}$ level populated after an upconversion process). Examples of the recorded spectra are shown in Fig. 1.

Excitation experiments have been carried out in geometrical conditions such as the fluorescence resonant radiation is absorbed by non-excited active ions located along the path of the emitted light, which entails that the main line is completely self-reversed. The satellite lines close to the main line are related to much less ions and consequently are subject to a small amount of reabsorption. Therefore the method allows the study of those lines usually hidden in the inhomogeneous profile of the main line. But it has to be noticed that information can be drawn only from the wavelengths of the satellites, the intensities being dependent on parameters (reabsorption, proximity of an intense line, shape of the spectrometer apparatus function) whose effects are out of control.

The absorption spectra exhibit differences only in the intensities of the lines, due to the Er concentration.

The excitation spectra have been recorded for all the available samples in the various possible absorption and emission directions. The following observations have been made: (i) the number and wavelengths of the satellites are

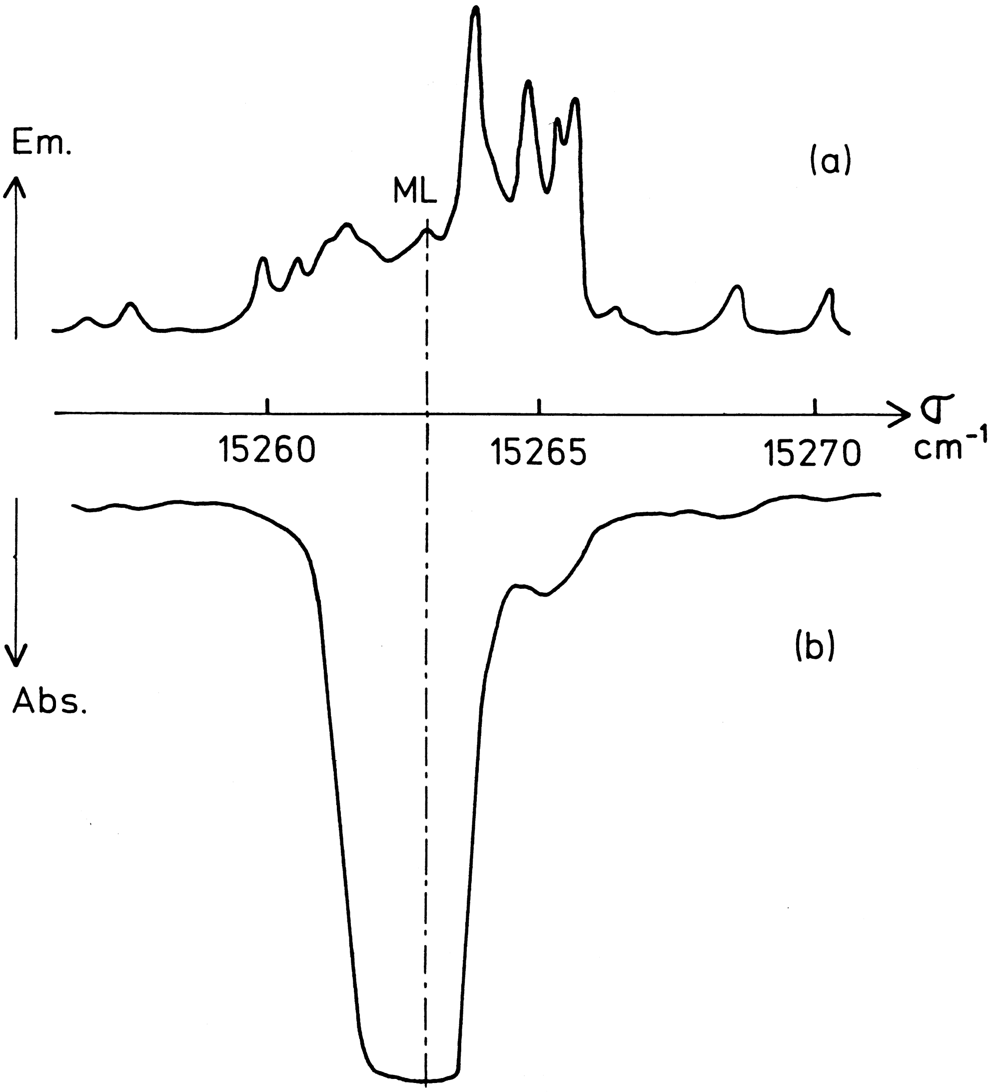

Fig. 1. Profile of the 6550-Å line recorded with a 3% concentrated sample. (a) Excitation spectrum monitored on the 9715-Å line (with reabsorption of the main line). (b) Absorption spectrum (with saturation of the main line).

independent of the concentration; (ii) the upconversion process exhibits a good efficiency only when excitation is in the main line.

From the experimental results, some hypothesis can be drawn concerning the origin of the satellite lines.

(1) The low intensity of the satellites indicates that few ions are in perturbed sites. This means that the substitution of Y ions by Er ions does not induce a deformation of the static crystal field, which agrees with the almost identical sizes of the doping ion and of the host ion ($r(\mathrm{Er})=0.99\ r(\mathrm{Y})$) [8].

(2) Most of the upconversion processes are assigned to an energy exchange between two identical ions. Therefore its probability increases with the proximity of the ions. In Er:YALO, the very weak upconverted emission observed following excitation in satellites implies that they are not induced by the accidental presence of nearby Er ions.

(3) It may also be assumed that the satellite lines are not induced by the presence of unknown impurities in the vicinity of the Er ions. This can be excluded since samples obtained from different sources have been investigated: some Czochralsky crystals were provided by the Institute of Atomic Physics in Bucarest, others by the Livermore Laboratory. Another sample was grown with the containerless technique of the ‘floating zone’ which reduces stress and contamination. All the spectra recorded using these various samples exhibit exactly similar satellite structures.

In conclusion, the Er ions in YALO appear to be distributed mainly in random regular sites. The ions that are in non-equivalent crystal field Er sites and give rise to a satellite structure are very few in number, and the corresponding lines do not seem to be related to the presence of pairs or to defect due to the crystal growth. Under these conditions, the existence of ions in interstitial sites seems likely.

3. Upconversion processes

3.1. Ground state absorption

Laser absorption is performed in the spectral range 655–646 nm, which corresponds to the excitation of the ${}^4F_{9/2}$ Stark levels.

3.1.1. Green emission

Excitation induces an intense green emission from the ${}^4S_{3/2}$ level (18 406 cm^{-1}). The upconversion mechanism is similar to the mechanism reported after excitations in the ${}^4I_{9/2}$ multiplet, i.e. phonon-assisted cooperative energy transfer that involves two ions in the lowest Stark level of the ${}^4I_{11/2}$ state. One ion is produced in the ${}^4F_{7/2}$ state from which a non-radiative relaxation populates the ${}^4S_{3/2}$ lowest Stark level.

The process is not exactly resonant. The emitted radiations relative to transitions to the ${}^4I_{15/2}$ (3–8) levels are absorbed from the metastable ${}^4I_{11/2}$ (1) level with creation of a phonon. On the contrary the ${}^4I_{11/2}(1)\to{}^4I_{15/2}(1, 2)$ radiations are both absorbed with an excess energy, which is a more probable process. Since the fluorescence relative to the transition to level (1) is strongly reabsorbed, in a strictly resonant way, by ions that are out of the laser beam, the corresponding energy is lost for upconversion. Therefore it can be assumed that the most efficient excitation of ${}^4S_{3/2}$ is due to the following cross-relaxation mechanism between two ions (A and B ions in Fig. 2):

$$({}^4I_{11/2}(1)\to{}^4I_{15/2}(2))\Rightarrow({}^4I_{11/2}(1)\to{}^4F_{7/2}(1))+\Delta E$$
$${}^4S_{9/2}$$

with $\Delta E=48$ cm^{-1}

3.1.2. Blue emission

For large enough excitation powers, blue and violet fluorescences are weakly emitted, from ${}^2H_{9/2}$ (22 479 cm^{-1}) and from ${}^2P_{3/2}$ (31 449 cm^{-1}), the population of which necessitates at least three photons.

Several mechanism can be considered:

(1) an excited state (${}^4S_{3/2}$ (1)) non-resonant absorption of the laser radiation;

(2) a phonon-assisted cooperative energy transfer that involves two ions in ${}^4S_{3/2}$ (1) (one ion is produced in the ${}^2H'_{9/2}$ state from which non-radiative relaxations populate

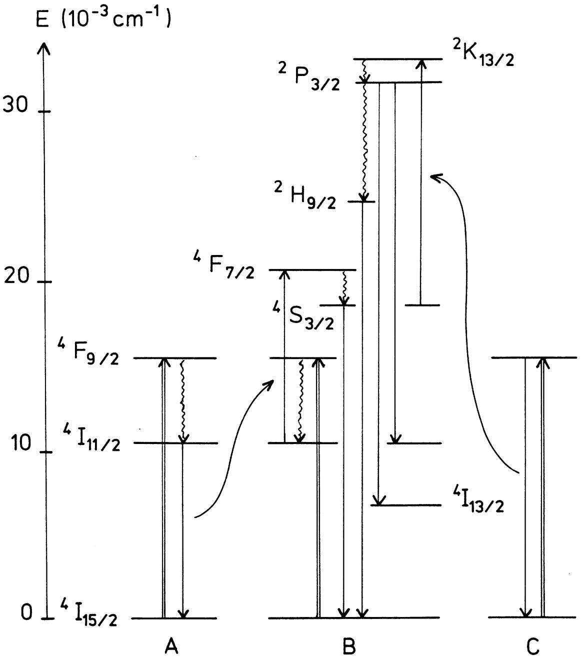

Fig. 2. Schematized resonant GSA upconversion processes. (A,B) Two-ions–two–photons cross-relaxation process, ${}^4S_{3/2}$ emits a green fluorescence. (A–C) Three-ions–three–photons double cross-relaxation process, ${}^4S_{3/2}$ is the starting level for the second cross-relaxation.

the emitting levels; the process is a four-photon one with an excess energy);

(3) a phonon-assisted cooperative energy transfer that involves one ion in the ${}^4S_{3/2}$ (1) state and one ion in the ${}^4F_{9/2}$ (1) state. In this case one ion is produced in the ${}^2K_{13/2}$ state with an excess energy, and the process is a three-photon one.

The ESA process may be ruled out since (i) it is usually about two orders of magnitude less efficient than the cooperative process, (ii) the fluorescence intensity is independent of the excited ${}^4F_{9/2}$ Stark level, i.e. of the laser energy.

To discriminate between the two other possible processes, the obvious way is to determine the number of photons involved. However, in the present case, much attention has to be paid to measuring the emitted fluorescence intensity dependence on the pump power: the error induced by the reabsorption of the emitted light can be avoided by recording the fluorescence relative to transitions to excited levels of the multiplets exclusively. More difficult to settle is the problem due to the large oscillator strengths of the absorption lines relative to the transitions to ${}^4F_{9/2}$; for the five excitation wavelengths, the incident light is absorbed on a short distance and the laser beam is cone-shaped. This means that the space of the crystal–radiation interaction varies with the laser power. As a consequence, the number of photons that is determined is not a constant and decreases when the power increases.

In order to minimize most of the errors, the experiment has been carried out on the 0.1% Er concentrated sample, and the intensity variation of the blue fluorescence from ${}^2P_{3/2}$ was recorded on the more intense non-reabsorbed transition to ${}^4I_{11/2}$. For laser power values as low as possible, a cubic intensity dependence has been obtained. In order to verify that the value was not underestimated, the intensity variation of the green fluorescence from ${}^4S_{3/2}$ has been recorded in similar experimental conditions: a quadratic dependence was actually obtained.

Under these conditions a cross-relaxation mechanism involving three ions can be assumed (Fig. 2):

$$({}^4F_{9/2}\,(1)\rightarrow{}^4I_{15/2})\Rightarrow({}^4S_{3/2}\,(1)\rightarrow\underset{{}^2P_{3/2}}{{}^2K_{13/2}(1)})+\Delta E$$

with detunings between −10 and +300 cm. Moreover, this depletion process agrees with the weak fluorescence emitted from ${}^4F_{9/2}$.

3.2. Excited state absorption

3.2.1. Small detunings

The spectral range 641–638 nm (DCM dye) corresponds to the excited state absorption from ${}^4I_{13/2}$ (1) to the ${}^4F_{5/2}$ multiplet. In this region, absorption from the ground state occurs in the vibrational background of the ${}^4F_{9/2}$ multiplet, with detunings much lower than the phonon cut-off frequency. This entails the existence of a non-zero upconversion effect over the whole investigated spectral range. The three resonances from the excited state appear as a large increase of the emitted green fluorescence.

Whatever the Er concentration and whatever the excited ${}^4F_{5/2}$ Stark level, the laser beam is cylindrical-shaped all along the sample length. Under these conditions, the measured value of the fluorescence intensity dependence upon the pump power is expected to be correct. It was found to be strictly quadratic in the entire power range, and neither saturation nor delay were observed. Therefore the energy upconversion is assumed to result from an ordinary one-ion–two photons excited state absorption process (Fig. 3).

The resonant, excited state absorption from the ${}^4S_{3/2}$ (1) Stark level to the ${}^4G_{7/2}$ multiplet is in the same excitation range. An energy upconversion would result from a two-ions–three-photons process, the starting level being populated by the usual cross-relaxation mechanism after a vibronic ground state absorption. As expected, given the available excitation powers, no emission from ${}^2P_{3/2}$ was observed.

3.2.2. Large detunings

The spectral fluorescence range of the rhodamine 590 dye corresponds to the excited state absorption from ${}^4I_{11/2}$

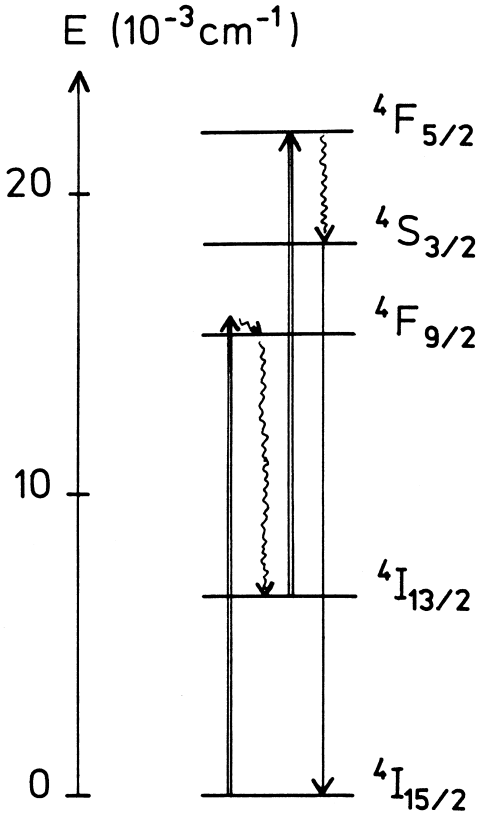

Fig. 3. Schematized one-ion–two-photons resonant ESA upconversion process.

(1) to the $^4G_{9/2}$, $^2K_{15/2}$ and $^2G_{7/2}$ multiplets. Here also the pumping does not correspond to any electronic transition from the ground state, being about 1200 and 1800 cm^{-1} away from the $^4S_{3/2}$ and $^4F_{9/2}$ multiplets. This is the case where an avalanche process may be expected, and was actually obtained in Er:$LiYF_4$ [9].

Experiments were attempted for various excited state absorptions in the most Er-concentrated YALO samples. They were not successful, since none of the characteristics of a photon avalanche (power threshold, long and power-dependent build-up time of the luminescence) were observed, whatever the temperature (4–300 K), and the incident exciting power (in the limits of availability) was. As a matter of fact, a weak green fluorescence was observable only in a Nd,Er-codoped sample for the Er excited state absorptions whose wavelengths were close to the wavelength of a Nd ground state absorption. This transfer of the energy from the few Nd ions excited in the wings of the 17 115-cm^{-1} line to Er ions is in agreement with the results reported in Ref. [6].

Several parameters are involved in a photon avalanche, and the corresponding conditions for its existence have to be simultaneously fulfilled. In the case of Er in YALO, the existence of an efficient cross-relaxation process has been undoubtedly proved, but the absorptions in the one-photon side bands are weak. Compared to $LiYF_4$, the phonon cut-off frequency is particularly large and the lifetimes are appreciably shorter. Under these conditions the power threshold may be much higher than the available excitation power of the laser used in the experiments.

4. Conclusion

The analysis of the profiles of absorption and excitation spectral lines of erbium in YALO samples has shown that the active ions are randomly distributed in the host. Therefore, the energy transfers do not benefit from the presence of clusters, which may account for the low efficiency of the various upconversion processes that have been investigated.

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