

Infrared-to-green up-conversion in Er^{3+} , Yb^{3+} -doped monoclinic $\text{KGd}(\text{WO}_4)_2$ single crystals

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Abstract

Optical spectroscopy of the green emission of erbium in $\text{KGd}(\text{WO}_4)_2$ (KGW) single crystals codoped with ytterbium ions is investigated. To do this, we firstly grew good-optical-quality KGW single crystals doped with Er^{3+} and Yb^{3+} at several dopant concentrations by the Top-seeded-solution-growth slow-cooling method (TSSG). Green photoluminescence of Er^{3+} in KGW host was studied at room temperature (RT) and low temperature (10 K) by means of Yb^{3+} sensitization after infrared excitation at 981 nm (10194 cm^{-1}). We calculated the emission and gain cross-sections and compared these with those of other known Er^{3+} -doped laser materials like $\text{LiYF}_4:\text{Er}$ (YLF:Er) and $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Er}$ (YAG:Er) at RT. Our study also focused on determining the optimal concentration of ions for generating the most intense green emission. We measured the lifetime of the green emission after infrared pump at several Yb^{3+} concentrations. From the low-temperature emission experiments, we determined the energy position of the sublevels of the ground state of erbium.

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1. Introduction

Many researchers into laser systems focus on lasers operating in the visible spectral range, especially in green and blue regions, because of their potential as an alternative to frequency-doubled coherent light. Room temperature (RT) continuous wave (cw) and pulsed up-conversion lasers have been demonstrated in the visible, red, green and blue spectral range, in a variety of lanthanide-doped materials [1–4]. Trivalent Er^{3+} ions operated at 551 nm in YLiF_4 [5] and at 551 nm when this crystal was co-doped with Yb^{3+} [6]. Erbium also generated output laser at 561 nm in YAG [1] at 562 nm in KYF_4 [7] and between 470 nm and 710 nm in $\text{BaY}_2\text{F}_8:\text{Er}$ [8]. The

main disadvantage of single Er^{3+} -doped crystals is the weak optical absorption of the excited energy levels ($^4\text{I}_{11/2}$ to be pumped around 980 nm, $^4\text{I}_{9/2}$ to be pumped around 810 nm, and $^4\text{I}_{13/2}$ to be pumped around 1500 nm), which limits the green output power. On the other hand, Yb^{3+} ions have a strong and broad absorption in the 900–1025 nm range that allows energy transfer between the two ions. This induce a sensitization of erbium observed in many hosts [9–11] and makes the population of the energy levels more efficient. Moreover, the 900–1025 nm pump is suitable for diode lasers. It has the advantage of being inexpensive and can be used to manufacture compact laser devices.

We are interested in researching laser operation in the green spectral region of Er^{3+} -doped monoclinic potassium gadolinium tungstate co-doped with ytterbium, $\text{KGd}(\text{WO}_4)_2:\text{Er},\text{Yb}$ (hereafter KGW:Er,Yb). To do this, we first grew Er^{3+} , Yb^{3+} -doped KGW single crystals at

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several ion concentrations. The method we used was the Top-Seeded-Solution-Growth (TSSG) slow-cooling method. The procedure for applying this method to KGW crystals was published in a previous study [12]. In the present study we report the spectroscopic properties of the green emission of Er^{3+} , as a preliminary study for laser action with up-conversion pumping, in terms of the absorption of the pumping level, the green emission at several concentrations and the gain cross-sections at several population inversion rates. We also measured the lifetime of the $^4\text{S}_{3/2}$ level as a function of Yb^{3+} concentrations. Finally, we analyzed the green emission at 10 K to determine the energy position of the sublevels of the ground state.

We chose KGW crystals as a host because of their well-known laser properties [13,14]. It is relatively easy to substitute gadolinium ions by lanthanides [15], and their crystalline quality is high. The physical anisotropy of KGW crystals, as demonstrated by their thermal [16] and optical [17] behavior, is high.

2. Experimental

The sample used for optical absorption measurements was KGW:Er,Yb (0.5,0.5 mol% of Er_2O_3 and Yb_2O_3 , respectively, substituting Gd_2O_3 in the solution), with a dopant concentration of 1.44×10^{19} at./cm³ for Er^{3+} and 1.73×10^{19} at./cm³ for Yb^{3+} . We chose low concentrations so as not to saturate the detector due to the high absorption cross-section of Yb^{3+} , and because the signal-to-noise ratio of the signals is good. We used the same sample for the luminescence experiments to determine the splitting of the ground at 10 K. Table 1 shows the ions concentration (in at./cm³) of the rest of samples to analyze the green intensity as a function of the dopant concentration. The optical-quality polished samples were prisms cut with their faces perpendicular to the three principal optical axes. We used a 2.21-mm-thick sample to analyze the optical absorption with the electric field of the incident radiation parallel to the N_g and N_m principal optical directions, and a 2.71-mm-thick sample for the $E||N_g$ and $E||N_p$. We performed these experiments at RT and 6 K with polarized

light parallel to the N_g , N_m and N_p using a VARIAN CARY-5E-UV-VIS-NIR 500Scan Spectrophotometer and a Glan-Taylor polarizer. Cryogenic temperatures were obtained by a Leybold RDK 6–320 cycle helium cryostat. We did the photoluminescence experiments with a BMI OPO pumped by the third harmonic of a seeded BMI SAGA YAG:Nd laser. Fluorescence was dispersed through a HR460 Jobin Yvon-Spex monochromator and detected by a R928 Hamamatsu photomultiplier. We analyzed the signal using an EG & G 7265DSP lock-in amplifier. Low-temperature luminescence was done at 10 K using an Oxford CCC1104 closed cycle helium cryostat. Lifetimes were measured using the averaging facilities of a computer-controlled Tektronix TDS-714 digital oscilloscope.

3. Results and discussion

Fig. 1 shows the absorption and emission cross-section spectra of the $^4\text{I}_{15/2} \rightarrow ^4\text{S}_{3/2}$ and the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transitions, respectively. We calculated the emission cross-section using the Fichtbauer–Ladenburg (F–L) method [18] taking into account an average value of refractive index of 2.06 and the radiative lifetime calculated by the Judd–Ofelt theory previously determined in reference [17]. Note that a maximum emission cross-section value of 1.85×10^{-20} cm² was calculated at 552.8 nm (18089.7 cm⁻¹). This was close to the value in Er:YLF at 561 nm which was the first up-conversion laser in the green spectral range, and also close to the value in Er:YAG at 561 [1]. We calculated the gain cross-section for this transition with the expression, $\sigma_{\text{gain}} = P\sigma_e - (1 - P)\sigma_{\text{abs}}$ where σ_{gain} is the gain cross-section, σ_e is the calculated emission cross-section, σ_{abs} is the absorption cross-section and P is the population inversion rate [19]. The upper inset of Fig. 1 shows the RT-polarized optical absorption of the pump energy level $^2\text{F}_{5/2}$ of ytterbium (overlap in energy with $^4\text{I}_{11/2}$ of erbium). The $E||N_m$ polarization was the most intense, and the $E||N_g$ was the least intense. The lower inset of Fig. 1 shows the gain cross-section for several inversions of population rates (40%, 50% and 60%). Note that for a 60% rate, a positive gain was expected for wavelengths between 545 nm (18349 cm⁻¹) and 564 nm (17730 cm⁻¹), with a maximum gain cross-section of 0.94×10^{-20} cm² at 552.8 nm (18089.7 cm⁻¹).

In Er,Yb systems, the green emission obtained after infrared pump was attributed to the following excitation mechanism. First, Yb and Er are simultaneously excited into the $^2\text{F}_{5/2}$ and $^4\text{I}_{11/2}$ levels, respectively, by absorption of the pump photons (see Fig. 2). A non-radiative energy transfer from Yb^{3+} to Er^{3+} increases the population of the $^4\text{I}_{11/2}$ level of erbium. The indicated up-conversion process ($^2\text{F}_{5/2}(\text{Yb}), ^4\text{I}_{11/2}(\text{Er}) \rightarrow ^2\text{F}_{7/2}(\text{Yb}), ^4\text{F}_{7/2}(\text{Er})$) then takes place, followed by a non-radiative

Table 1
Lifetime of the $^4\text{S}_{3/2}$ level at several dopant concentration

$\text{Er}_2\text{O}_3, \text{Yb}_2\text{O}_3$ in solution (mol%)	$\text{Er}^{3+}, \text{Yb}^{3+}$ concentration in the crystal (at./cm ³)	Lifetime (μs)
0.5, 0.5	$1.44 \times 10^{19}, 1.73 \times 10^{19}$	39
0.5, 1.5	$1.89 \times 10^{19}, 1.26 \times 10^{20}$	83
0.5, 2.5	$1.66 \times 10^{19}, 1.46 \times 10^{20}$	94
0.5, 5.0	$1.89 \times 10^{19}, 2.14 \times 10^{20}$	126
0.5, 7.5	$1.26 \times 10^{19}, 3.72 \times 10^{20}$	132
0.5, 10.0	$2.52 \times 10^{19}, 3.78 \times 10^{20}$	130
0.5, 15.0	$2.52 \times 10^{19}, 6.62 \times 10^{20}$	132

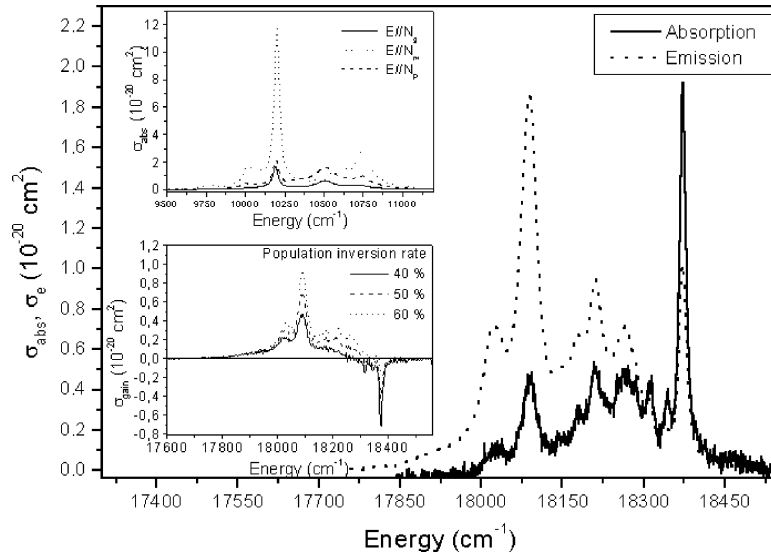


Fig. 1. Comparison between absorption and emission cross-section for the $^4S_{3/2}$ energy level of erbium. Upper inset: Polarized optical absorption of the pump energy level. Lower inset: Gain cross-section for the green emission for several inversion population rates.

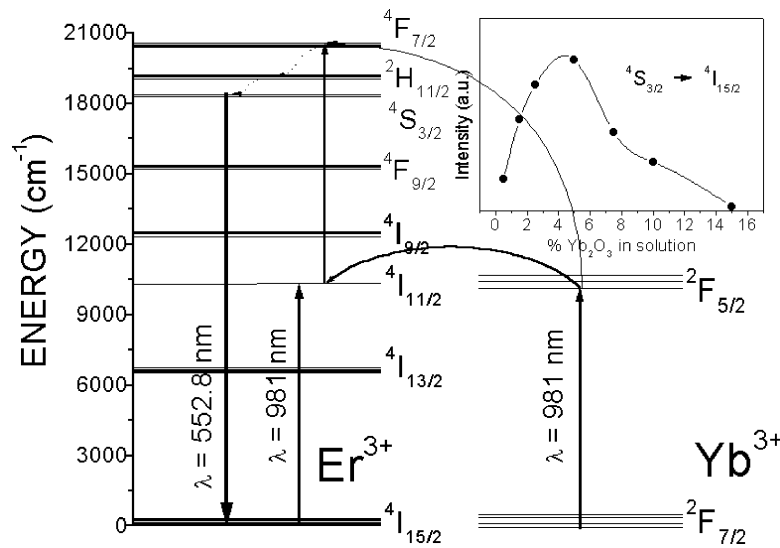


Fig. 2. Schematic diagram of the infrared-to-green up-conversion between Er and Yb ions in KGW. Inset: Green intensity of erbium as a function of the ytterbium concentration.

decay ($^4F_{7/2} \rightarrow ^4S_{3/2}$). The maximum intensity of the green emission takes place on the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition at 552.8 nm (18089.7 cm^{-1}). The quasi-quadratic dependence (slope 1.8), between the pump power and the green luminescence intensity indicated that two photons were involved in this process.

We found that, due to the sensitization, the green emission intensity increased when Er^{3+} was codoped with Yb^{3+} . Also, the green emission intensity decreased for concentrations of erbium above $1.44 \times 10^{19}\text{ at./cm}^3$ (0.5 mol% in solution) due to the quenching between the erbium ions that reabsorbed the green emission. For these two reasons we chose codoped samples by fix-

ing the Er^{3+} concentration around $1.5 \times 10^{19}\text{ at./cm}^3$ (0.5 mol% in solution) and increased the Yb^{3+} concentration in order to analyze the optimal ion concentration for generating the most intense green emission. The inset of Fig. 2 shows that the green intensity increased to 5 mol% of Yb_2O_3 in solution (around $2.14 \times 10^{20}\text{ at./cm}^3$). At higher Yb^{3+} concentrations, this intensity decreased because of the drop in energy transfer efficiency due to the energy-migration among Yb^{3+} ions, which reduced transference to Er^{3+} .

Fig. 3 shows the low-temperature green luminescence of Er^{3+} after excitement at 981 nm (10194 cm^{-1}). The expected number of energy sublevels of the ground energy

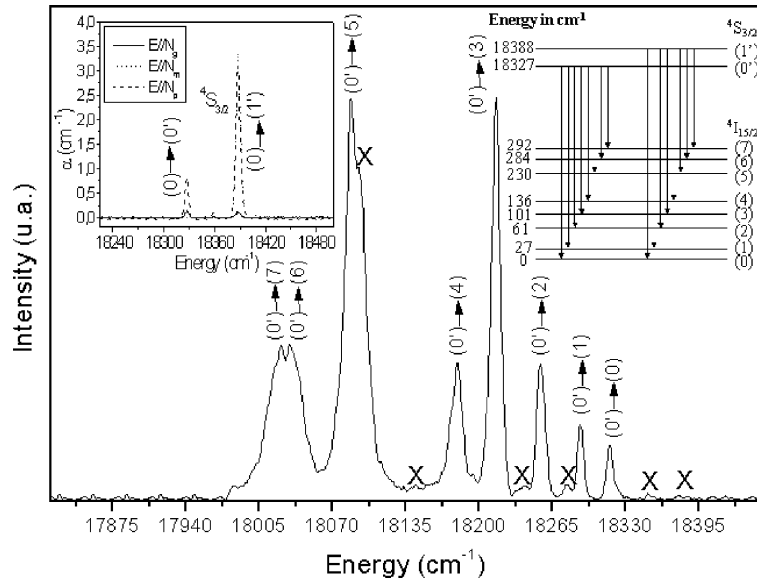


Fig. 3. Low-temperature green emission of erbium after energy transfer from ytterbium. Left inset: Low-temperature polarized optical absorption of the $^4S_{3/2}$ level. Right inset: Schematic green emission channels of Er^{3+} in KGW:Er,Yb.

level of Er^{3+} was eight. These, clearly appear in Fig. 3, with energy values of 18024 cm^{-1} , 18032 cm^{-1} , 18086 cm^{-1} , 18180 cm^{-1} , 18215 cm^{-1} , 18255 cm^{-1} , 18289 cm^{-1} and 18316 cm^{-1} , and are labelled according to the scheme in the right inset of Fig. 3. The spectrum also shows some minor peaks which are represented by crosses. These may be related to the transition from the upper sublevel of the $^4S_{3/2}(1')$ to the ground level, because they were displaced in accordance with the difference in energy between the two sublevels of the excited $^4S_{3/2}$ ($\Delta E = 61\text{ cm}^{-1}$, see left inset of Fig. 3). From the energy positions of the $^4S_{3/2}$ sublevels, and by subtracting the above-mentioned energy values of emission signals, we found the energy position of the energy sublevels of the ground state. The values were 292, 284, 230, 136, 101, 61, 27 and 0 cm^{-1} , which are very close to those published in other tungstate matrices such as KYW, KErW [20] and KYbW [21].

We measured the lifetime of the green emission as a function of the ytterbium concentration (from 0.5% to 15%) for a fixed erbium concentration (0.5%) (see Table 1) and concluded that, due to greater sensitization, the lifetime of the $^4S_{3/2}$ level increased to an ytterbium concentration of 5 mol%. We observed that at higher Yb^{3+} concentrations the lifetime maintained constant. We related this phenomenon to the large degree of overlap between absorption and emission of Yb that derived in radiation trapping among Yb^{3+} ions that blocked the up-conversion efficiency, and consequently, the lifetime of the green emission did not increase. To have evidence of such energy transfer from Yb to Er, we analyzed in a previous work the decrease of the Yb lifetime when increasing the Er concentration [21].

4. Conclusions

In conclusion, we grew good-optical-quality monoclinic Er,Yb-doped KGW single crystals at several dopant concentrations and studied the green emission of erbium after simultaneous excitation of the two ions at 981 nm. It was observed an increase in the green emission of erbium after co-doping the samples with Yb^{3+} as a test of the energy transfer between ions. We calculated the emission cross-section of the visible emission. This was close to the emission cross-sections in YLF:Er and in YAG:Er. The experiments revealed 0.5%–5%, (1.89×10^{19} , $2.14 \times 10^{20}\text{ at./cm}^3$) Er,Yb concentration, respectively, as the optimal dopant concentration for achieving the most intense green emission. We used the low-temperature green emission of Er^{3+} to determine the splitting of its ground state and measured the lifetime of the $^4S_{3/2}$ energy level for several Yb^{3+} concentrations. Our results suggest that this emission is suitable for laser action and would constitute a very interesting (diode-pumped) solid-state laser in the green of the spectral range.

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