

## Green luminescence of $\text{Er}^{3+}$ in stoichiometric $\text{KYb}(\text{WO}_4)_2$ single crystals

X. Mateos, F. Güell, M. C. Pujol, M. A. Bursukova, R. Solé, Jna. Gavaldà, M. Aguiló, F. Díaz, and J. Massons<sup>a)</sup>

*Laboratori de Física i Cristal·lografia de Materials (FiCMA) and IEA, Universitat Rovira i Virgili, 43005 Tarragona, Spain*

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We grew good-optical-quality  $\text{KYb}(\text{WO}_4)_2$  single crystals doped with erbium ions by the top seeded solution growth slow cooling method. Optical absorption of erbium was performed at room temperature (RT) and at 6 K. Green photoluminescence of erbium was achieved at RT and 6 K after selective excitation of ytterbium ions at 940 nm ( $10\,638\text{ cm}^{-1}$ ). The splitting of all found excited energy levels and the ground energy level of erbium in  $\text{KYb}(\text{WO}_4)_2$  is presented derived from the accurate absorption and emission measurements, respectively. The lifetime of the Stokes and the anti-Stokes green emissions of erbium were measured after excitation at 488 nm ( $20\,490\text{ cm}^{-1}$ ) and 940 nm ( $10\,638\text{ cm}^{-1}$ ), respectively. We propose applying the up-conversion model to the observed green emission. © 2002 American Institute of Physics. [DOI: 10.1063/1.1486477]

Solid-state green light sources are desirable for several applications, including high-density optical storage, color displays, and optoelectronics. Many authors have studied the conversion of infrared radiation into visible radiation in crystals and glasses doped with lanthanide ions.<sup>1–3</sup> Erbium allows this conversion via an up-conversion process, but its low absorption cross section in the 900–1100 nm range, where erbium excitation by diode lasers is possible, limits the pump efficiency. Conversion may be improved by exciting erbium indirectly with a sensitizer ion. Ytterbium is ideal for this, not only because of its high absorption cross section in the abovementioned energy range, but also because of its broad absorption band (which allows excitation in the 900–1000 nm range), and the large energy overlap between ytterbium emission and erbium absorption, which, as in many matrices,<sup>4–6</sup> allows resonant energy transfer from  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$ .

Monoclinic potassium rare-earth wolframate matrices have remarkable optical properties that make them promising hosts for lanthanide-doped optical solid-state lasers.<sup>7,8</sup> Of these, stoichiometric ytterbium tungstate,  $\text{KYb}(\text{WO}_4)_2$  (hereafter KYbW), is also a promising crystalline material for solid-state lasers.<sup>9,10</sup> KYbW doped with erbium may therefore work efficiently in converting infrared into visible light, due to the facility of erbium incorporation substituting ytterbium ions in the structure and due to the necessary high energetic overlap between these two ions that KYbW doped with erbium offers.

Up to now, the most used crystalline host to the generation of green laser radiation<sup>4</sup> by means of the energy transfer between erbium and ytterbium ions is  $\text{YLiF}_4$ . In this work, stoichiometric ytterbium tungstate is studied with the aim of optimizing the energy transfer between the two ions, due to the high quantity of ytterbium.

With this in mind, we made a systematic study of KYbW doped with  $\text{Er}^{3+}$  ions. We grew KYbW single crystals doped with erbium and studied the spectroscopic properties related

to the green emission. Optical absorption was performed at room temperature and at low temperature (6 K). Green emission was also studied at room temperature and at 6 K. We propose a simplified diagram of up-conversion. We measured the decay time of the green Stokes and the anti-Stokes emission of erbium.

Monoclinic potassium ytterbium tungstate has the  $C2/c$  space group. The unit cell parameters are  $\mathbf{a}=10.590(4)\text{ \AA}$ ,  $\mathbf{b}=10.290(6)\text{ \AA}$ ,  $\mathbf{c}=7.478(2)\text{ \AA}$ ,  $\beta=130.70(2)^\circ$ .<sup>11</sup>  $\text{KYb}_{1-x}\text{Er}_x(\text{WO}_4)_2$  single crystals, whose atomic erbium concentration is  $3.9\times 10^{19}$ ,  $7.1\times 10^{19}$ ,  $2.3\times 10^{20}$ ,  $3.9\times 10^{20}\text{ at/cm}^3$ , were grown by the top seeded solution growth (TSSG) slow cooling method with  $\text{K}_2\text{W}_2\text{O}_7$  as solvent. The concentration level of  $\text{Er}^{3+}$  in the crystals was measured by electron probe microanalysis (EPMA), with a Cameca SX 50 equipment. These values lead to an average distribution coefficient of roughly 1.1 for the erbium ion in the KYbW host, that ensures the control of the dopant concentration in the crystals.

The three principal optical directions of monoclinic KYbW are located along the crystal, as follows. The principal optical axis,  $N_g$ , with maximum refractive index, can be found by a  $19^\circ$  with respect to the  $\mathbf{c}$  crystallographic axis in the clock-wise rotation, with the  $\mathbf{b}$  positive axis pointing towards the observer. The principal optical axis with intermediate refractive index,  $N_m$ , is  $59.7^\circ$  with respect to the  $\mathbf{a}$  crystallographic axis, being  $N_g$  and  $N_m$  in the  $\mathbf{a}-\mathbf{c}$  plane. Finally, the  $N_p$  principal axis is parallel to the  $\mathbf{b}$  crystallographic axis.<sup>11</sup>

For the spectroscopic characterization we used a crystalline prism of KYbW with an erbium concentration of  $3.9\times 10^{19}\text{ at/cm}^3$ . Its faces were perpendicular to the three principal axes. The thickness was 3.16 mm for the measurements of the optical absorption along the  $N_m$  and  $N_g$  optical directions, and 3.86 mm for the  $N_p$ .

Polarized optical absorption was performed at room temperature and at 6 K with polarized light parallel to the  $N_g$ ,  $N_m$ , and  $N_p$  optical directions using a VARIAN CARY-5E-UV-VIS-NIR 500Scan Spectrophotometer and a Glan-Taylor polarizer. Cryogenic temperatures were obtained by a

<sup>a)</sup>Author to whom correspondence should be addressed; electronic mail: massons@quimica.urv.es

TABLE I. Splitting of the excited energy levels of  $\text{Er}^{3+}$  in KYbW single crystal obtained at 6 K.

$2S+1L_J$	Sublevels energy position ( $\text{cm}^{-1}$ )
$^4I_{13/2}$	65 15, 6543, 6570, 6603, 6670, 6723, 6737
$^4I_{9/2}$	12 336, 12 441, 12 468, 12 498, 12 556
$^4F_{9/2}$	15 201, 15 280, 15 332, 15 341, 15 366
$^4S_{3/2}$	18 308, 18 376
$^2H_{11/2}$	19 035, 19 056, 19 128, 19 170, 19 205, 19 219
$^4F_{7/2}$	20 421, 20 471, 20 497, 20 573
$^4F_{5/2}$	22 104, 22 136, 22 177
$^4F_{3/2}$	22 450, 22 551
$^2H_{9/2}$	24 484, 24 523, 24 569, 24 584, 24 609
$^4G_{11/2}$	26 208, 26 223, 26 326, 26 386, 26 434, 26 457
$^4G_{9/2}$	27 267, 27 293, 27 320, 27 361, 27 378
$^2K_{15/2}$	27 484, 27 568, 27 641, 27 735, 27 936, 27 978, 28 000

Leybold RDK 6-320 cycle helium cryostat. Table I shows the number of absorption peaks, that are clearly consistent with the splitting into the maximum number of Kramers levels  $(2J+1)/2$  expected by the crystalline field, due to the odd number of electrons of  $\text{Er}^{3+}$ , and due to the low symmetry site in which  $\text{Er}^{3+}$  is located ( $C_2$ ) in KYbW host.<sup>11</sup> For the  $^4S_{3/2}$  energy level, two lines are located at 18 308 and 18 376  $\text{cm}^{-1}$  ( $\Delta E = 68 \text{ cm}^{-1}$ ). These correspond to the  $^4I_{15/2}(0) \rightarrow ^4S_{3/2}(0')$  and  $^4I_{15/2}(0) \rightarrow ^4S_{3/2}(1')$  transitions, respectively. This was obtained by polarized optical absorption performed at 6 K. The polarized optical absorption of KYbW:Er at room temperature and at 6 K show that the absorption coefficient depends strongly on the polarization of light, and that the absorption of light along the  $N_m$  optical direction is the most intense and the absorption of light along the  $N_g$  is the least intense.

We compared the energy position of the gravity center of each multiplet of  $\text{Er}^{3+}$  in  $\text{KGd}(\text{WO}_4)_2$  (KGW), and KYbW hosts. It is found that the differences between these gravity centers are smaller in KYbW. Parallel to this, the splitting of each energy level into its sublevels is slightly bigger in KYbW crystals than in KGW (10  $\text{cm}^{-1}$  on average for all energy levels). These two observations allow us to conclude that the crystal field of KYbW is stronger than in KGW. That is in good agreement with the smaller interatomic distances presented in KYbW<sup>11</sup> than in KGW.<sup>12</sup> Additionally, the Judd–Ofelt parameters of erbium in KYbW<sup>13</sup> and those of KGW<sup>14</sup> also demonstrate this crystal field influence. The Judd–Ofelt parameters of erbium in KYbW are bigger than those of KGW. On average the values for KYbW are twice the values for KGW.

Our equipment for the photoluminescence experiments consisted of a BMI OPO pumped by the third harmonic of a seeded BMI SAGA yttrium–aluminum–garnet Nd laser. Pulses of 15 mJ (7 ns in duration, 10 Hz repetition rate) were achieved with a Gaussian beam profile. Fluorescence was dispersed through a HR460 Jobin Yvon–Spex monochromator (focal length 460 mm,  $f/5.3$ , spectral resolution 0.05 nm) and detected by a R928 Hamamatsu photomultiplier. The signal was analyzed by an EG&G 7265DSP lock-in amplifier. Figure 1 shows the high resolution of the low-temperature unpolarized green photoluminescence of  $\text{Er}^{3+}$  performed on the same sample as the optical absorption measurements by selectively exciting ytterbium at 940 nm (10 638  $\text{cm}^{-1}$ ). The signals in the spectrum correspond to

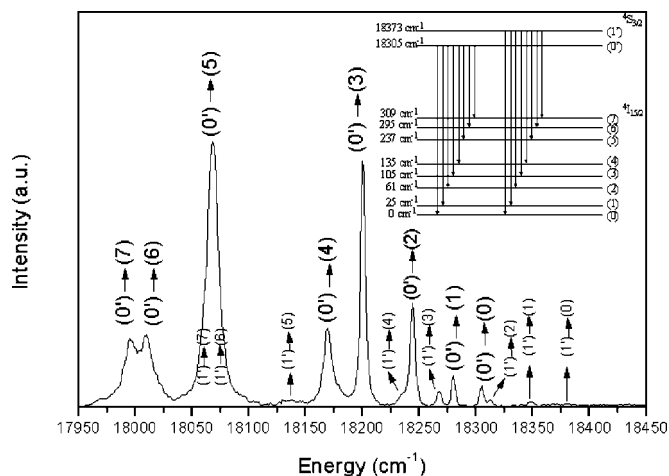


FIG. 1. Low-temperature green emission ( $^4S_{3/2} \rightarrow ^4I_{15/2}$  transition of  $\text{Er}^{3+}$ ) in a KYbW single crystal by pumping resonantly to  $\text{Yb}^{3+}$  at 940 nm (10 638  $\text{cm}^{-1}$ ). Schematic green emission channels and energy sublevels positions of  $\text{Er}^{3+}$  in a KYbW single crystal.

the  $^4S_{3/2} \rightarrow ^4I_{15/2}$  transition. The number of energy sublevels of the ground energy level expected by the crystalline field into the maximum number of Kramers levels is eight, that clearly appear in Fig. 1. The energy values of these eight signals are 17 996, 18 010, 18 068, 18 170, 18 200, 18 244, 18 280, and 18 305  $\text{cm}^{-1}$ , and these are labeled according to the scheme in the inset to Fig. 1. The spectrum also shows some minor peaks. These may be related to the transition from the upper sublevel of the  $^4S_{3/2}(1')$  to the ground level. These peaks are displaced in accordance with the difference in energy between the two sublevels of the excited  $^4S_{3/2}$  ( $\Delta E = 68 \text{ cm}^{-1}$ ). From the energy positions of the  $^4S_{3/2}$  sublevels, and by subtracting the abovementioned energy values of emission signals, we found the energy position of the energy sublevels of the ground state. The values were 309, 295, 237, 135, 105, 61, 25, and 0  $\text{cm}^{-1}$ , which were very close to those published in other tungstate matrices such as KGW, KYW, and KErW.<sup>15</sup> From the low-temperature absorption measurements, the  $^4I_{15/2}(0) \rightarrow ^4S_{3/2}(0')$  transition takes the value of 18 308  $\text{cm}^{-1}$ , and from the emission spectrum the value is 18 305  $\text{cm}^{-1}$ . This is due to the Stokes shift by means of the electron-phonon coupling. We consider these values absolutely the same, and, to calculate the energy position of the sublevels of the ground state, we used the value provided by the emission spectrum.

In Er–Yb systems, the green emission obtained after infrared pump can be attributed to a step up-conversion energy transfer process of erbium sensitized by ytterbium involving two or three photons. These absorption-emission mechanisms associated with the step up-conversion energy transfer process depend strongly not only on the pumping wavelength and pumping power but also on the crystalline matrix. The green emission can also be linked to a cooperative sensitization, in which the simultaneous interaction of two excited  $\text{Yb}^{3+}$  ions produces the excitation of  $\text{Er}^{3+}$ . Because of the energy overlap between erbium and ytterbium, the most probable route in KYbW is resonant energy transfer via two-step cross transfers ( $^2F_{5/2} \rightarrow ^2F_{7/2}$ ;  $^4I_{15/2} \rightarrow ^4I_{11/2}$ ) and ( $^2F_{5/2} \rightarrow ^2F_{7/2}$ ;  $^4I_{11/2} \rightarrow ^4F_{7/2}$ ). This mechanism is schematized by the model of Fig. 2. A selective  $\text{Yb}^{3+}$  excitation at 940 nm

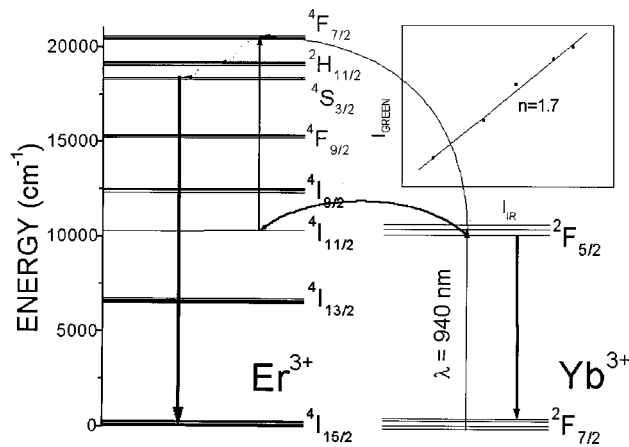


FIG. 2. Simplified energy-level diagram to represent the up-conversion process. Logarithmic representation of  $I_{\text{VIS}}$  vs  $I_{\text{IR}}$  at room temperature by recording the green emission ( ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ ).

( $10638 \text{ cm}^{-1}$ ), where no absorption of erbium takes place, excites electrons from the ground energy level of ytterbium to the  ${}^2F_{5/2}$  excited energy level. After excitation, the electrons decay radiatively to the ground state or transfer part of their energy to the  ${}^4I_{11/2}$  energy level of erbium by cross relaxation due to the energetic overlap between these two levels. Once erbium is excited, a second energy transfer from  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$  provokes excitation to the  ${}^4F_{7/2}$  energy level of erbium. In accordance with the small energy gap between the  ${}^4F_{7/2}$  energy level and  ${}^2H_{11/2}$  ( $1350 \text{ cm}^{-1}$ ) and the energy gap between  ${}^2H_{11/2}$  and  ${}^4S_{3/2}$  ( $800 \text{ cm}^{-1}$ ), the  ${}^4F_{7/2}$  multiplet relaxes nonradiatively to the  ${}^4S_{3/2}$  level (via phonon coupling), where the transition is mainly radiative to the ground level (green emission,  ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$  transition). To verify this two-photon process, we measured the ratio between the intensity of the green luminescence and the intensity of the infrared luminescence ( $I_{\text{VIS}} - I_{\text{IR}}$ ) (see the inset of Fig. 2). The linear slope of the logarithmic representation ( $\approx 1.7$ ) indicates that two photons are involved in the up-conversion process.

We measured the emission lifetime of the  ${}^4S_{3/2}$  energy level of erbium ions in  $\text{KYb}_{0.994}\text{Er}_{0.006}(\text{WO}_4)_2$  crystal at room temperature. We achieved Stokes emission in the green region ( ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$  transition) with a lifetime of  $30 \mu\text{s}$  after  $488 \text{ nm}$  ( $20490 \text{ cm}^{-1}$ ) laser pump excitation, which is in good agreement with the lifetime found in the  ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$  transition of erbium in other wolframate matrices such as KGW and KYW.<sup>2,16</sup> The position of the monochromator is at  $553 \text{ nm}$ , just in the wavelength of the maximum signal. This lifetime value is also in agreement with the expected by the Judd–Ofelt calculations.<sup>13</sup> We achieved anti-Stokes emission, after  $940 \text{ nm}$  ( $10638 \text{ cm}^{-1}$ ) laser pump excitation, also in the green region, but with a lifetime of  $140 \mu\text{s}$ . This increase in the lifetime confirms the energy transfer from ytterbium to erbium, because a new excitation channel to the erbium ions is activated. Figure 3 shows the Stokes and anti-Stokes decay curves of these two luminescent emissions, with single-exponential behavior. The necessary time (rise time) to excite erbium ion via energy transfer from ytterbium is observable in the anti-stokes decay curve.

In conclusion, we have shown that potassium ytterbium wolframate doped with erbium can be successfully grown by

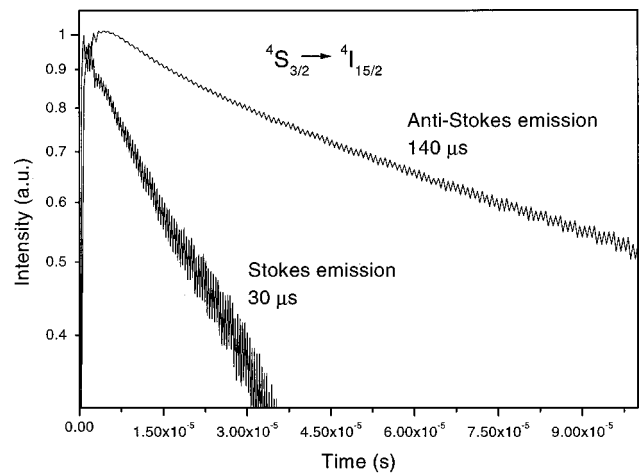


FIG. 3. Temporal evolution of the Stokes and anti-Stokes green luminescence of the  ${}^4S_{3/2}$  energy level of  $\text{Er}^{3+}$  in  $\text{KYb}$  single crystal after pump excitation at  $488 \text{ nm}$  ( $20490 \text{ cm}^{-1}$ ) and  $940 \text{ nm}$  ( $10638 \text{ cm}^{-1}$ ), respectively.

the TSSG-slow cooling method. From low-temperature optical absorption and emission measurements we determined the splitting of the excited energy levels of  $\text{Er}^{3+}$  and the ground level ( ${}^4I_{15/2}$ ), respectively. Conversion from IR to VIS radiation took place and the green luminescence is explained by a step up-conversion energy transfer process involving two photons.

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