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


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

(Received 23 January 2002; accepted for publication 23 April 2002)

We grew good-optical-quality KYb(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 ($10.638\unit{cm}^{-1}$). The splitting of all found excited energy levels and the ground energy level of erbium in KYb(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 ($20.490\unit{cm}^{-1}$) and 940 nm ($10.638\unit{cm}^{-1}$), respectively. We propose applying the up-conversion model to the observed green emission.

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.$^{1-3}$ 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 900–1000 nm range, and the large energy overlap between ytterbium emission and erbium absorption, which, as in many matrices,$^{4-6}$ allows resonant energy transfer from Yb$^{3+}$ to Er$^{3+}$.

Monoclinic potassium ytterbium tungstate has the C2/c space group. The unit cell parameters are $a=10.590(4)\unit{Å}$, $b=10.290(6)\unit{Å}$, $c=7.478(2)\unit{Å}$, $\beta=130.70(2)^\circ$. KYb$_{1-x}$Er$_x$(WO$_4$)$_2$ single crystals, whose atomic erbium concentration is $3.9\times10^{19}$, 7.1$\times10^{19}$, 2.3$\times10^{20}$, 3.9$\times10^{20}\text{at/cm}^3$, were grown by the top seeded solution growth (TSSG) slow cooling method with K$_2$WO$_4$ as solvent. The concentration level of 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° with respect to the $c$ crystallographic axis in the clock-wise rotation, with the $b$ positive axis pointing towards the observer. The principal optical axis with intermediate refractive index, $N_m$, is 59.7° with respect to the $a$ crystallographic axis, being $N_g$ and $N_m$ in the $a$–$e$ plane. Finally, the $N_p$ principal axis is parallel to the $b$ crystallographic axis.

For the spectroscopic characterization we used a crystalline prism of KYbW with an erbium concentration of $3.9\times10^{19}\text{at/cm}^3$. 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
TABLE I. Splitting of the excited energy levels of Er$^{3+}$ in KYbW single crystal obtained at 6 K.

<table>
<thead>
<tr>
<th>$^{2S+1}L_J$</th>
<th>Sublevels energy position (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4I_{15/2}$</td>
<td>65 15, 6543, 6570, 6603, 6670, 6723, 6737</td>
</tr>
<tr>
<td>$^4I_{13/2}$</td>
<td>12 336, 12 441, 12 468, 12 498, 12 556</td>
</tr>
<tr>
<td>$^4F_{9/2}$</td>
<td>15 201, 15 280, 15 332, 15 341, 15 366</td>
</tr>
<tr>
<td>$^4S_{2}$</td>
<td>18 308, 18 376</td>
</tr>
<tr>
<td>$^2H_{15/2}$</td>
<td>19 035, 19 056, 19 128, 19 170, 19 205, 19 219</td>
</tr>
<tr>
<td>$^2H_{13/2}$</td>
<td>20 421, 20 471, 20 497, 20 573</td>
</tr>
<tr>
<td>$^2F_{9/2}$</td>
<td>22 104, 22 136, 22 177</td>
</tr>
<tr>
<td>$^2F_{7/2}$</td>
<td>22 450, 22 551</td>
</tr>
<tr>
<td>$^4G_{15/2}$</td>
<td>24 848, 24 523, 24 569, 24 584, 24 609</td>
</tr>
<tr>
<td>$^4G_{13/2}$</td>
<td>26 086, 26 223, 26 326, 26 386, 26 434, 26 457</td>
</tr>
<tr>
<td>$^4G_{11/2}$</td>
<td>27 267, 27 293, 27 320, 27 361, 27 378</td>
</tr>
<tr>
<td>$^2K_{15/2}$</td>
<td>27 484, 27 568, 27 641, 27 735, 27 936, 27 978, 28 000</td>
</tr>
</tbody>
</table>

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

Leybold RDK 6-320 cycle helium crystal. 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 Er$^{3+}$, and due to the low symmetry site in which Er$^{3+}$ is located (C$_2$) in KYbW host.\footnote{11} For the $^4S_{3/2}$ energy level, two lines are located at 18 308 and 18 376 cm$^{-1}$ ($\Delta E = 68$ cm$^{-1}$). These two observations allow us to conclude that the crystal field of KYbW is stronger than in KGW. That is in agreement with the smaller interatomic distances presented in KYbW\footnote{11} than in KGW.\footnote{12} Additionally, the Judd–Ofelt parameters of erbium in KYbW\footnote{13} and those of KGW\footnote{14} 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 ml (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 Er$^{3+}$ performed on the same sample as the optical absorption measurements by selectively exciting ytterbium at 940 nm (10 638 cm$^{-1}$). The signals in the spectrum correspond to 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 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 $^4S_{3/2}$ ($\Delta E = 68$ 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 cm$^{-1}$, which were very close to those published in other tungstate matrices such as KGW, KYW, and KErW.\footnote{15} From the low-temperature absorption measurements, the $^4I_{15/2}(0) \rightarrow ^4S_{3/2}(0')$ transition takes the value of 18 308 cm$^{-1}$, and from the emission spectrum the value is 18 305 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 Yb$^{3+}$ ions produces the excitation of 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 Yb$^{3+}$ excitation at 940 nm
(10 638 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 Yb$^{3+}$ to Er$^{3+}$ provokes excitation to the $^4I_{7/2}$ energy level of erbium. In accordance with the small energy gap between the $^2F_{7/2}$ energy level and $^2H_{11/2}$ (1350 cm$^{-1}$) and the energy gap between $^2H_{11/2}$ and $^4S_{3/2}$ (800 cm$^{-1}$), the $^2F_{7/2}$ 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$_{VIS}$/I$_{IR}$) (see the inset of Fig. 2). The linear slope of the logarithmic representation ($\approx 1$) 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 KYb$_{0.994}$Er$_{0.006}$(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 $\mu$s after 488 nm (20 490 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. The position of the monochromator is at 553 nm, just in the wavelength of the maximum signal. This lifetime value is also in agreement with the expected by the Judd–Ofelt calculations. We achieved anti-Stokes emission, after 940 nm (10 638 cm$^{-1}$) laser pump excitation, also in the green region, but with a lifetime of 140 $\mu$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 the TSSG-slow cooling method. From low-temperature optical absorption and emission measurements we determined the splitting of the excited energy levels of Er$^{3+}$ and the ground level ($^2I_{15/2}$), 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.

The authors acknowledge financial support from CICyT under Project Nos. MAT99-1077-C02, 2FD97-0912-C02, and FIT-070000-2001-477, and from CIRIT under Project No. 2001SGR00317.