Ultraviolet and visible emissions of Er^{3+} in $KY(WO_4)_2$ single crystals co-doped with Yb^{3+} ions

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Abstract

In this paper we studied the luminescence of Er^{3+} in $KY(WO_4)_2$ co-doped with Yb^{3+} at room temperature and at cryogenic temperature in the 360–860 nm range. We found 13 emissions of erbium in the ultraviolet and visible range, and studied the emissions after two pump wavelengths, one at 981 nm resonant to the maximum absorption of ytterbium and one at 798 nm resonant to the $^4I_{9/2}$ energy level of erbium.
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1. Introduction

Interest was increased in compact visible laser sources for data storage and display applications by promising research into the wide-gap semiconductor diode laser [1], harmonic generation by phase matching in non-linear crystals [2] and wave-guides [3] and up-conversion lasers in crystals [4] and fibers [5]. Due to growth and doping problems room-temperature laser opera-

tion is difficult with wide-gap semiconductor diodes. Harmonic generation is a well-known technique, but accurate phase matching requires critical alignment of the non-linear crystals. Lasers that emit at higher frequencies than the pump light are usually called up-conversion lasers. In these lasers, the active ion is usually excited by internal up-conversion of near-infrared or red light via multi-step photon excitation or cooperative energy transfer and emits anti-Stokes visible light. In initial up-conversion laser research, cryogenic temperatures were required and the observed efficiencies were very low [6]. The advent of high-power laser diodes and their rapid improvement in

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the red and near-infrared spectral ranges have created new interest in the development of up-conversion lasers. The output wavelength of laser diodes can be tuned to match the absorption lines of the active laser ion. This results in a substantial fraction of ions being excited into higher energy levels and enhances the up-conversion process. Visible up-conversion lasing at room temperature has already been demonstrated in some lanthanide-doped crystals [7].

Because of its complex energy level scheme with some meta-stable excited states, Er^{3+} leads to multi-step energy transfer and excited-state absorption processes, which can be used for up-conversion pumping. Green laser emission of the transition $^4S_{3/2} \rightarrow {}^4I_{15/2}$ of Er^{3+} has already been carried out with both short-wavelength excitation [8] and up-conversion pumping [9]. The first green room-temperature laser operation of Er^{3+} with direct excitation in the blue spectral range was published in 1993 [10].

The main disadvantage of Er^{3+} is its low absorption cross-section in the laser diodes emission range (0.8–1.5 μm), which limits pump efficiency. A possible improvement is co-dope the material with a second ion that acts as a sensitizer of the active ion. Ytterbium is the ideal candidate for this role because of its high absorption cross-section, the broad absorption band, which offers excitation tuning in the 920–1000 nm wavelength region, and the large overlap between ytterbium emission and erbium absorption, which allows resonant energy transfer from Yb^{3+} to Er^{3+}.

The low-temperature monoclinic phase of potassium rare-earth tungstates, $KRE(WO_4)_2$, can be doped with optical active lanthanide ions, even at a high level of concentration, to constitute solid-state laser materials. The $KY(WO_4)_2$ (hereafter KYW) crystal has a monoclinic crystallographic structure with space group C2/c and lattice parameters $a = 10.64\,\text{Å}$, $b = 10.35\,\text{Å}$, $c = 7.54\,\text{Å}$ and $\beta = 130.5(2)^\circ$ [11].

In this paper we present the spectroscopic study of the optical emission (at RT and 10 K) and lifetime measurements at RT of Er^{3+} in KYW sensitized by Yb^{3+}. Optical emission was studied in the 360–860 nm range, which allowed 13 emissions of erbium under 981 nm pump excita-tion. We also analyzed the emissions under 798 nm pump excitation.

2. Experimental

We grew co-doped erbium, ytterbium $KY_{1-x-y}Er_xYb_y(WO_4)_2$ single crystals, by the top-seeded solution growth slow-cooling method (TSSG), as described in Ref. [12].

Our equipment for the photoluminescence experiments consisted of a BMI Optical Parametric Oscillator (OPO) pumped by the third harmonic of a seeded BMI SAGA YAG:Nd laser. Fluorescence was dispersed through a Jobin Yvon–Spex monochromator HR460 model. We used a cooled Hamamatsu NIR R5509-72 photomultiplier for the infrared emission of Yb^{3+}, which was also analyzed only under 798 nm excitation, and a Hamamatsu R928 photomultiplier for the visible and UV emissions. The emission spectra were performed at RT and 10 K on a KYW:Er,Yb sample with a composition of 3.15×10^{19} and 2.40×10^{20} ions/cm^3 of erbium and ytterbium, respectively, corresponding to $KY_{0.958}Er_{0.004}Yb_{0.038}(WO_4)_2$. The luminescence signal was analyzed by a EG&G 7265DSP lock-in amplifier and cryogenic temperatures were obtained by an Oxford closed-cycle helium CCC1104 cryostat. Lifetime measurements were taken with the averaging facilities of a computer-controlled Tektronix TDS-714 digital oscilloscope.

3. Results and discussion

The optical emission of erbium ions was carried out in the 360–860 nm range after pumping at 981 nm (overlap in energy between the $^4I_{11/2}$ and the $^2F_{5/2}$ levels of erbium and ytterbium, respectively) at RT and 10 K and at 798 nm ($^4I_{9/2}$ of erbium) at RT. With this pump wavelength we also recorded fluorescence from Yb^{3+} as a probe of back-energy transfer from Er^{3+} to Yb^{3+}.

Fig. 1 shows the emission spectra obtained under excitation in the $^2F_{5/2}$ (Yb) and $^4I_{11/2}$ (Er) energy levels (981 nm). We analyzed the 360–860 nm (27 777–11 628 cm^{-1}) range and found
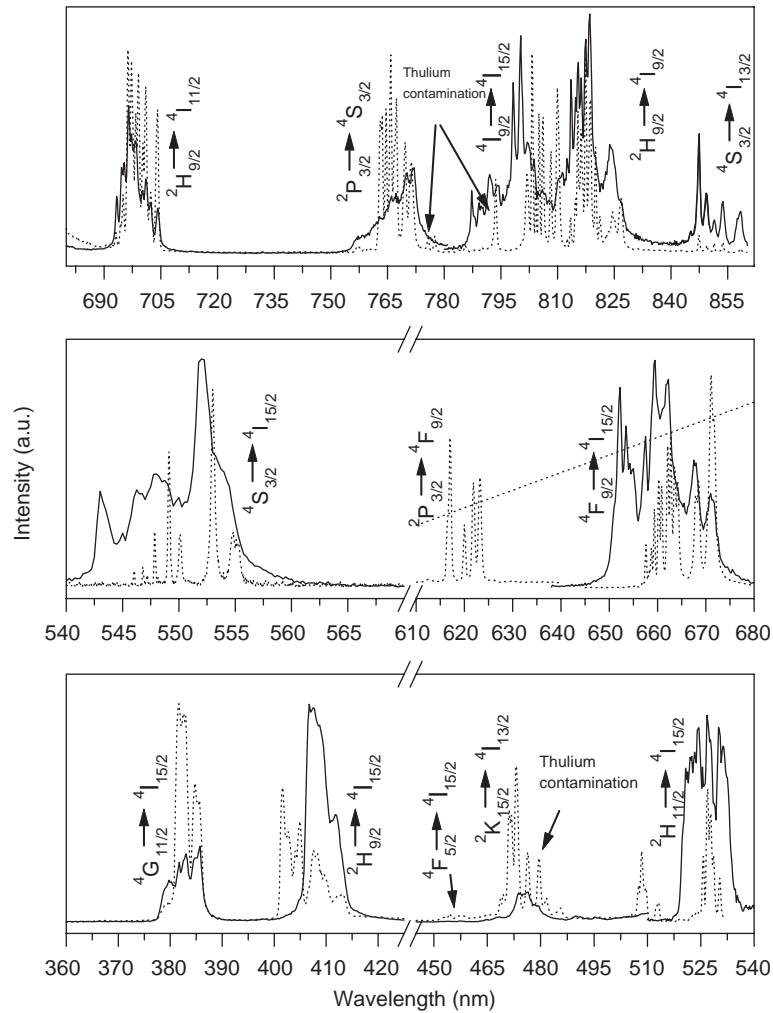
Fig. 1. Emission of erbium in the 360–860 nm range at RT and 10 K.

that the higher intensity signal corresponded to the transition from the $^4S_{3/2}$ level to the ground (emission with maximum intensity at 552 nm). All the achieved signals and the corresponding transition labeling are summarized in Table 1. The assignment were done with the help of low-temperature emission spectra and agree well with the difference in energy between the Stark levels of the excited levels, which are found in Ref. [12].

To generate all the emissions, we excited the $^4I_{11/2}$ and $^2F_{5/2}$ levels of erbium and ytterbium,

respectively. As these ions relaxed to the ground, they emitted the infrared emissions around 1.0 μm, $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} and $^4I_{11/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}. The absorption of a second photon by Yb^{3+} followed by energy transfer to Er^{3+} increased the energy of the electrons in the $^4I_{11/2}$ level to the $^4F_{7/2}$ level. A very fast non-radiative relaxation took place to the $^2H_{11/2}$ and $^4S_{3/2}$, from where erbium generated the 526.5 and 552 nm emissions to the ground state. We also observed a 847.5 nm emission from the $^4S_{3/2}$ level

($^4S_{3/2} \to {}^4I_{13/2}$). Also from the $^4S_{3/2}$ level, a non-radiative relaxation took place to the $^4F_{9/2}$ and generated the 659 nm emission to the ground state. Another non-radiative relaxation to the $^4I_{9/2}$ took place, and from this level, erbium generated the 800 nm emission also to the ground state. Moreover, the absorption of a third photon by Yb^{3+} followed by energy transfer to Er^{3+} increased the

energy of the electrons in the $^4S_{3/2}$ level to the $^2K_{15/2}$ level, from where the 476 nm emission took place from the $^2K_{15/2}$ to the $^4I_{13/2}$. Non-radiative relaxation to the $^4G_{11/2}$ allowed the population of this level and the 385 nm emission to the ground state. The $^2H_{9/2}$ generated emissions at 406.5 nm ($^2H_{9/2} \to {}^4I_{15/2}$), 696 nm ($^2H_{9/2} \to {}^4I_{11/2}$), and 818.5 nm ($^2H_{9/2} \to {}^4I_{9/2}$). We observed the 457 nm emission from the $^4F_{5/2}$ to the ground state. These transitions were corroborated by the difference in energy between the Stark levels of the emitting levels and the arrival levels (see Fig. 2).

We could not observe the $^2P_{3/2}$ level of erbium (around $31350\,cm^{-1}$) by absorption experiments because at this frequency $31350\,cm^{-1}$ (319 nm) the material is not transparent (see Ref. [12]). In Fig. 5 of Ref. [13], Pujol et al. showed the excitation spectrum between 30 000 and $34\,000\,cm^{-1}$ with the UV emission of a Xe lamp in continuous wave mode in an iso-structural host, $KGd(WO_4)_2$. Here there is a band around $31\,350\,cm^{-1}$ that possibly belongs to the $^2P_{3/2}$ level. We related the 772 nm emission to the $^2P_{3/2} \to {}^4S_{3/2}$ transition. The low-temperature 772 nm emission has four signals, the values of which are 13 031, 12 965, 12 993 and $13\,057\,cm^{-1}$. These are labelled in accordance with
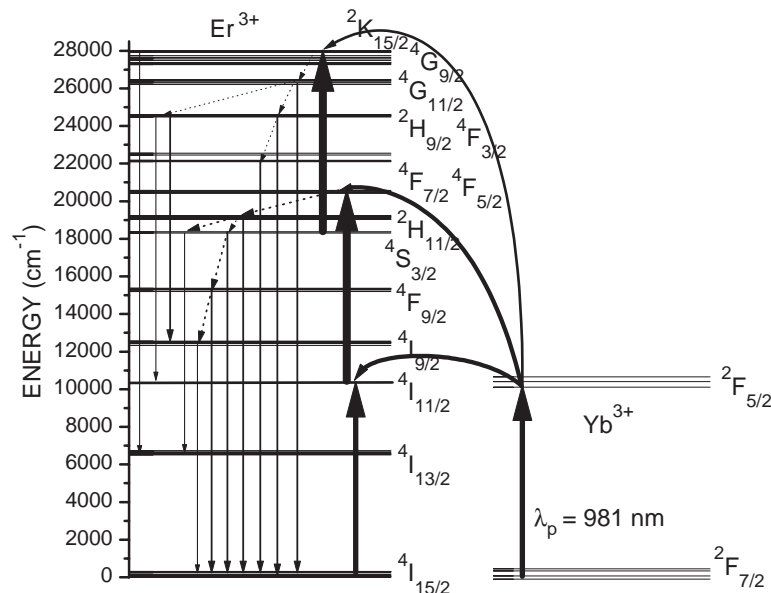
Table 1
Assignment of the emission signals to the corresponding transition

Maximum peak intensity (nm)	Transition
385	$^4G_{11/2} \to {}^4I_{15/2}$
406.5	$^2H_{9/2} \to {}^4I_{15/2}$
457	$^4F_{5/2} \to {}^4I_{15/2}$
476	$^2K_{15/2} \to {}^4I_{13/2}$
526.5	$^2H_{11/2} \to {}^4I_{15/2}$
552	$^4S_{3/2} \to {}^4I_{15/2}$
620	$^2P_{3/2} \to {}^4F_{9/2}$
659	$^4F_{9/2} \to {}^4I_{15/2}$
696	$^2H_{9/2} \to {}^4I_{11/2}$
772	$^2P_{3/2} \to {}^4S_{3/2}$
800	$^4I_{9/2} \to {}^4I_{15/2}$
818.5	$^2H_{9/2} \to {}^4I_{9/2}$
847.5	$^4S_{3/2} \to {}^4I_{13/2}$

Fig. 2. Pump scheme after 981 nm pump.
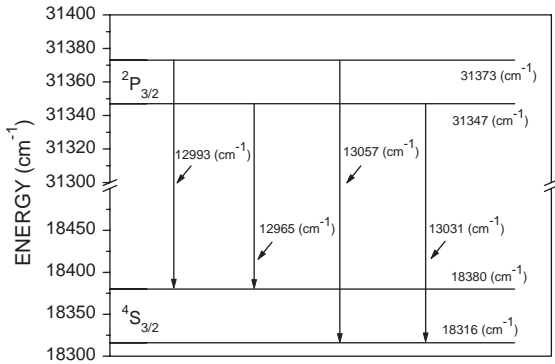
Fig. 3. Schematic view of the transition that generated the 775 nm emission.

Fig. 4. Green emission of erbium at 10 K after pumping at 981 nm. Inset: schematic view of the green channels.

Fig. 5. Emission of Yb^{3+} in the 930–1100 nm range after 798 nm pump at RT (solid line) and 10 K (dotted line).

the scheme of Fig. 3 (the maximum number of Stark levels expected by the crystalline field is two) for $^2P_{3/2}$ and $^4S_{3/2}$.

These signals may be related to the transition from the two Stark levels of $^2P_{3/2}$ to the two Stark levels of $^4S_{3/2}$. Two of these peaks are displaced in accordance with the difference in energy between the two Stark levels of $^4S_{3/2}$ ($\Delta E = 64.6\,cm^{-1}$), which denotes that the arrival level is the $^4S_{3/2}$. From the energy positions of the $^4S_{3/2}$ sublevels, 18 316.1 and 18 380.7 cm^{-1} and by adding the above-mentioned energy values of the emission signals, we found the energy positions of the Starks levels of the $^2P_{3/2}$ level. These were 31 347 and 31 373 cm^{-1}, which were reasonably close to the energy position of the $^2P_{3/2}$ level of erbium in other hosts [14].

To populate this level for the generation of the 772 nm emission, we assumed that, from the $^4F_{7/2}$ level one photon pump 10 193.6 cm^{-1} (981 nm) allowed the population of the $^2P_{3/2}$ level. In this way, we also related the 620 nm emission to the transition from the $^2P_{3/2}$ to the $^4F_{9/2}$ levels of erbium.

Fig. 4 shows the low-temperature green luminescence of Er^{3+} after excitation at 981 nm (10 194 cm^{-1}). The expected number of energy sublevels of the ground state of Er^{3+} was eight. These clearly appear in Fig. 4 (marked with crosses), with energy values of 18 011.5, 18 024.5, 18 083.5, 18 179.2, 18 211.6, 18 254, 18 288.2 and 18 315 cm^{-1}. We thus found the energy position of
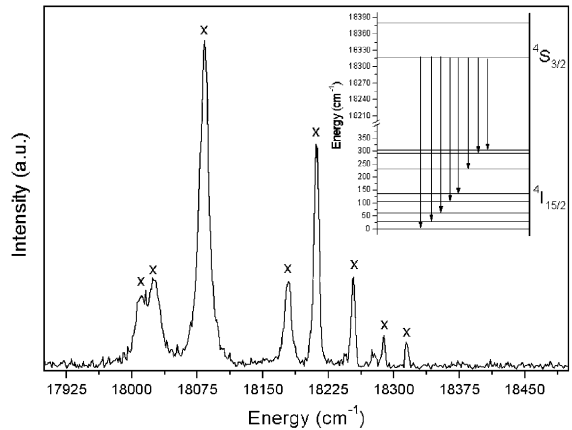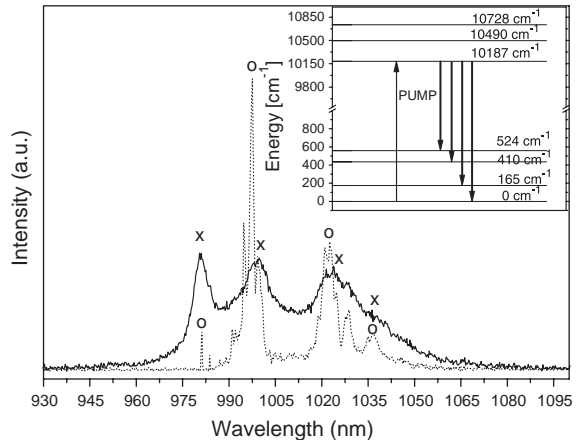
the energy sublevels of the ground state. These were 303.5, 290.5, 231.5, 136, 103.5, 61, 26.8 and 0 cm^{-1}, which are very similar to those found in an isostructural tungstate (KYbW) [15].

We also pumped the crystal at 798 nm resonantly to the $^4I_{9/2}$ level of erbium without direct ytterbium excitation and found a very interesting emission in the 960–1065 nm that corresponded to ytterbium. This is clear proof of the back-energy transfer from erbium to ytterbium. Fig. 5 shows this emission at RT and 10 K, from where we
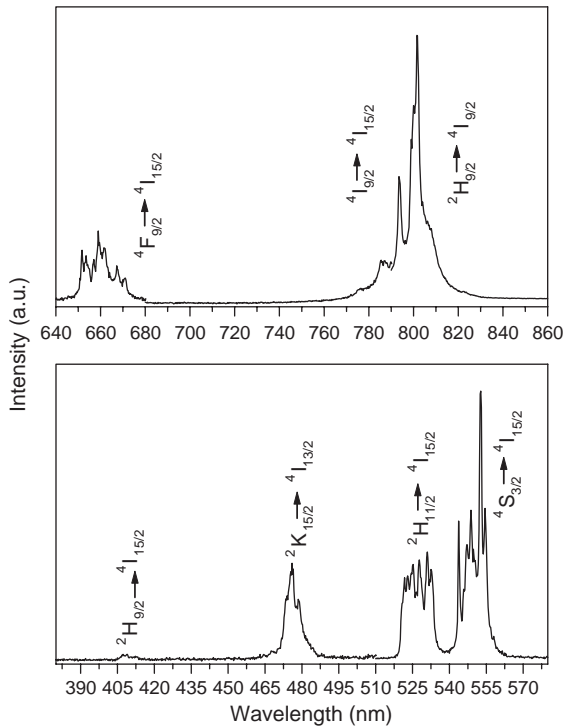
Fig. 6. Emissions of Er^{3+} in the 375–860 nm range after pumping at 798 nm at RT.

deduced the Stark levels of the ground. These were 0, 165, 410 and 542 cm^{-1}. The Stark levels of the excited were 10 187, 10 490, 10 728 cm^{-1} (see Ref. [12]). For the RT spectrum, the transitions are represented by crosses and for the low-temperature the transitions are represented by circles and both were assigned as it was done previously, for an isostructural material $(KYb(WO_4)_2)$ (see Ref. [16]) taking into account the phonon-coupling features.

Fig. 6 shows the room temperature emissions of erbium after 798 nm pump excitation in the 380–860 nm range. We compared these with the signals that appeared after 981 nm excitation and some bands did not appear for 798 nm excitation. The 385 and 457 nm emissions did not appear because it was impossible to populate the levels above the $^2H_{9/2}$ level in energy with this pump wavelength. We did not observe emissions such as 620, 696 or 847.5 nm. Fig. 7 shows the proposed diagram for the pump at 798 nm.

Table 2 shows the lifetime of the emitting levels of the ultraviolet and visible emissions of Er^{3+}. We also measured the lifetime of the ytterbium emitting level after pumping at 798 nm. This was 260 μs.
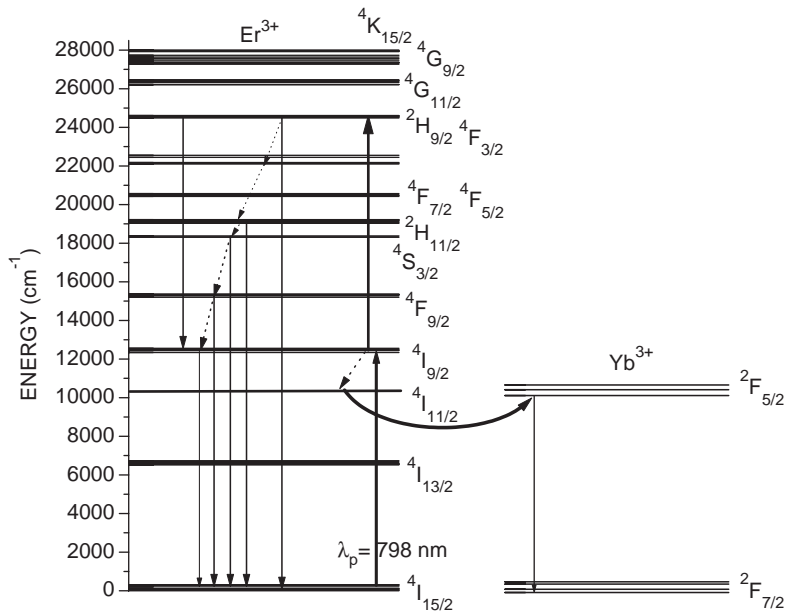

Fig. 7. Pump scheme after 798 nm pump.

Table 2
Measured lifetime of the energy levels of erbium after 981 nm pump at RT

Energy level	Lifetime (μs)
$^2P_{3/2}$	60
$^2K_{15/2}$	160
$^4G_{11/2}$	70
$^2H_{9/2}$	75
$^2H_{11/2}$	115
$^4S_{3/2}$	125
$^4F_{9/2}$	140
$^4I_{9/2}$	155

4. Conclusions

We performed the luminescent characterisation of erbium in $KY(WO_4)_2$ single crystals sensitized by Yb^{3+}. From the experimental RT optical emission, we observed 13 emissions of erbium in the ultraviolet and visible spectral ranges after pumping at 981 nm as a result of the direct energy transfer from ytterbium to erbium. From the 10 K optical emission experiments, we found the energy position of the Stark levels of the ground level by means of the 550 nm emission ($^4S_{3/2} \rightarrow {}^4I_{15/2}$) after pumping at 981 nm.

From the RT optical emission after pumping at 798 nm, we also observed some emissions of erbium and the emission of ytterbium as a result of the back-energy transfer from erbium to ytterbium.

Acknowledgements

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