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Crystal growth, spectroscopic studies and laser operation of Yb^{3+}-doped potassium lutetium tungstate

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Abstract

Single crystals of Yb^{3+}-doped monoclinic potassium lutetium tungstate were grown with several dopant concentrations (0.5%, 5% and 10% in the solution). Optical absorption and emission measurements were performed at room and cryogenic temperatures and the upper level lifetime was estimated. Highly efficient room temperature laser generation in the 1 μm region was achieved with this new Yb-host in the continuous-wave regime, both with Ti:sapphire and diode laser pumping.

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1. Introduction

Yb^{3+} is a promising activating ion possessing a number of advantages over Nd^{3+} for laser operation in the 1 μm spectral region. These advantages are related to the very simple energy level scheme constituted of only two levels: the $^2F_{7/2}$ ground state and the $^2F_{5/2}$ excited state. Effects such as excited state absorption, cross-relaxation and up-conversion, which can lead to reduced laser efficiency through alternative paths for depopulation of the upper level, are absent. The Yb^{3+} ion also has a small quantum defect as a result of the close pump and laser wavelengths, leading to low thermal load. The intense Yb^{3+} absorption lines resulting from the Stark splitting are well suited for laser diode pumping near 980 nm. The splitting depends on the host and in the ground state it determines the thermal population of the lower laser level of the Yb^{3+}-ion operating as a quasi-three-level system, which is related to the laser threshold.

Monoclinic $KRE^{3+}(WO_4)_2$ single crystals (RE: Y and Gd) doped with Yb^{3+} ions have been recognized as an attractive host-dopant combination for diode-pumped solid-state lasers in the 1 μm region [1] due to their anisotropy and capability to adopt very high concentrations of Yb^{3+} reaching the stoichiometric structure $KYb(WO_4)_2$ (KYbW) [2]. Limitations related to the thermo-mechanical properties, however, do not permit the use of an active element thickness matching the absorption length. The latter, depending on the doping level, can be substantially below 100 μm, reaching 13.3 μm for KYbW. Instead, layers of KYbW on passive $KGd(WO_4)_2$ (KGdW) or $KY(WO_4)_2$ (KYW) substrates seem feasible for thin-disk lasers, however, the crystal lattice mismatch seems to be the basic limitation on the achievable interface quality even in the case of

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KYW and KYbW where this mismatch is smaller [3]. The closer ionic radii of Lu and Yb makes the low-temperature monoclinic phase of potassium lutetium tungstate $KLu(WO_4)_2$ (hereafter KLuW) potentially interesting as a passive host due to the possibility not only for doping with very high concentrations of Yb^{3+} but also for the growth of KYbW/KLuW epitaxies. KLuW belongs to the C2/c space group [4] and a summary of some of its physical characteristics (unit cell parameters, density, melting and crystallization temperature, thermal conductivity, hardness and SRS-active vibration modes) can be found elsewhere [5].

In this paper we describe the crystal growth of KLuW and KLuW:Yb^{3+} at several dopant concentrations, characterize the host in terms of transparency window, optical ellipsoid and refractive indices, and provide the results of spectroscopic studies (polarized absorption, emission, and upper level lifetime measurements) of the active ion at room and cryogenic temperatures. Finally, laser operation of KLuW:Yb^{3+}in the continuous wave regime near 1 μm is reported at room temperature.

2. Experimental

The transmission measurements of the undoped host as well as the polarized optical absorption of Yb-doped KLuW at room and cryogenic temperatures were performed with a Cary Varian 500 spectrophotometer (300–3000 nm) and a FTIR 680 Plus Spectrometer (3–8.5 μm) equipped with an Oxford Instruments cryostat (model SU 12) with helium gas flow.

The emission spectra near 1 μm were recorded both at room and low temperatures in 90°-geometry with excitation by a 750 mW diode laser at 940 nm which was modulated at 30 kHz. The fluorescence was dispersed by a 0.46 m monochromator (Jobin Yvon—Spex HR 460). We used a cooled Hamamatsu NIR R5509-72 photomultiplier for detection connected to a lock-in amplifier (EG&G, 7265 DSP) and a closed-cycle helium cryostat (Oxford, Model CCC1104) for sample cooling. The lifetime measurements were performed with the same excitation source and a mechanical chopper.

3. Crystal growth and optical characterization of KLuW and Yb:KLuW

We used the Top-Seeded Solution Growth slow-cooling method to synthesize undoped KLuW and Yb-doped KLuW single crystals with various dopant concentrations. High-temperature solution with $K_2W_2O_7$ as a solvent, and a composition of 15 mol% solute and 85 mol% solvent was used to grow the crystals. The temperature gradient in the solution was 0.2 K/mm and the saturation temperature was between 1146 and 1162 K. The crystal growth experiments were carried out along the *b* crystallographic orientation. The cooling interval was 20 K at a cooling rate of 0.1 K/h. Inclusion-free crystals of 4 g (typical weigh) and dimensions of $13 \times 7.5 \times 11.5\ mm^3$ along the $c \times b \times a^*$ crystallographic directions, were obtained (Fig. 1).

While previous measurements of the crystal lattice constants were performed with powder diffraction, a very recent crystal X-ray diffraction measurement using our samples yielded in the C2/c space group $a = 10.576(7)$, $b = 10.214(7)$, $c = 7.487(2)$ and $\beta = 130.68(4)°$ [6]. Thus from the comparison of these constants with those of KYW and KYbW it can be concluded that the average mismatch between KLuW and KYbW is about half that of KYW and KYbW which makes KLuW obviously more suitable for growth of Yb-doped-layer/undoped substrate epitaxies.

The composition of the Yb-doped crystals grown was determined by Electron Probe MicroAnalysis (EPMA) and is given in Table 1.

From unpolarized optical transmission measurements of a 1 mm thick plate of KLuW performed at room temperature (Fig. 2), we obtained a clear optical transmission range (1 cm^{-1} absorption level) from 365 to 5110 nm.

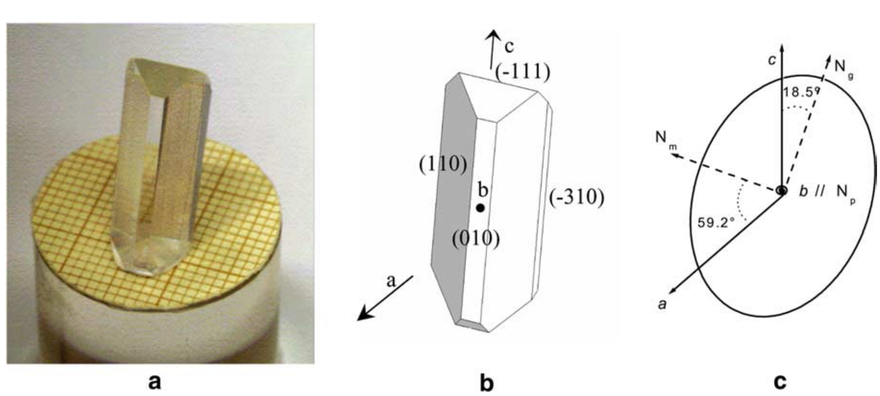

Fig. 1. Photograph of the grown KLuW crystal (a), morphological scheme (b) and optical ellipsoid (c).

Table 1
EPMA results for the composition of KLuW:Yb^{3+}

at.% Yb (solution)	K_{Lu}	K_{Yb}	Yb (cm^{-3})	Crystal composition
0.5	0.998	1.39	4.50×10^{19}	$KLu_{0.993}Yb_{0.007}(WO_4)_2$
5	0.98	1.37	4.30×10^{20}	$KLu_{0.931}Yb_{0.069}(WO_4)_2$
10	0.97	1.30	8.26×10^{20}	$KLu_{0.8700}Yb_{0.1300}(WO_4)_2$

K_{Lu} and K_{Yb} denote the distribution coefficient of the lanthanides in the crystal.

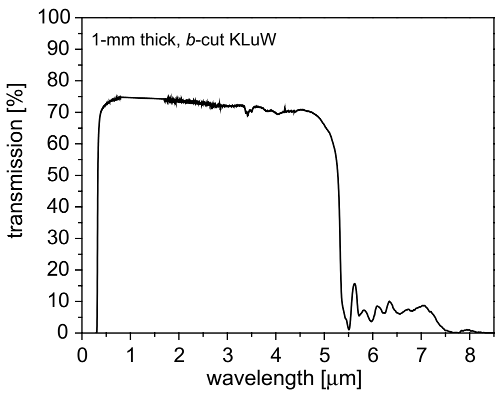

Fig. 2. Unpolarized transmission of KLuW from the UV to the mid-IR.

The notations N_p, N_m and N_g are used for the three principal optical axes of the biaxial KLuW corresponding to the refractive indices $n_p < n_m < n_g$. In monoclinic crystals one of the principal optical axes (in the case of KLuW this is N_p) coincides with the *b* crystallographic axis. We found that N_g, is located at 18.5° with respect to the *c*-axis (clockwise rotation when the *b*-axis is pointing towards the observer), Fig. 1c.

The index of refraction was measured by the minimum angle deviation technique using two prisms and the results are given in Table 2.

The values in Table 2 agree fairly well with the average value of 2.08 at 700 nm reported in Ref. [5]. The angle between the two optic axes amounts to $2V_g = 84.8°$at 630 nm and therefore KLuW is an optically positive biaxial crystal.

4. Spectroscopy of Yb in KLuW

The Stark components of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition in Yb^{3+}:KLuW can be seen as an absorption band in the

Table 2
Dispersion of refractive indices of KLuW, experimental values

λ [nm]	n_g	n_m	n_p
532	2.1413	2.0814	2.0433
630	2.112	2.058	2.016
1064	2.0815	2.0282	1.9939

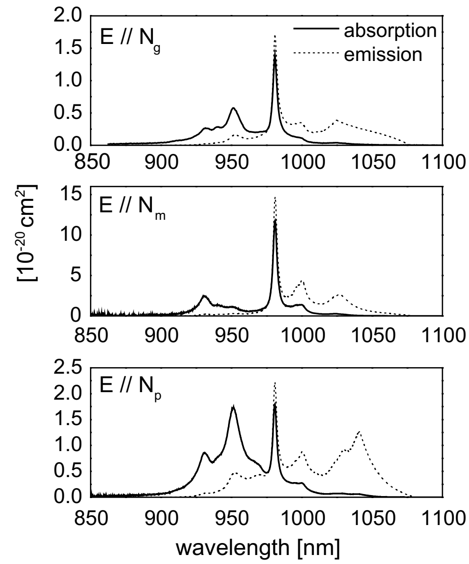

Fig. 3. Polarized optical absorption (solid lines) and calculated emission cross-sections (dotted lines) of Yb^{3+} in KLuW.

polarized room temperature absorption spectra in Fig. 3 stretching from 850 to 1100 nm (11 765–9091 cm^{-1}). Note the high degree of optical anisotropy. The absorption cross-section is maximal for $E \| N_m$ and minimum for $E \| N_g$. The room temperature absorption is characterized by three main peaks which are centered at 981.1 nm (10 193 cm^{-1}), 951.4 nm (10 511 cm^{-1}) and 930.9 nm (10 742 cm^{-1}), and two less intensive peaks near 999.5 nm (10 005 cm^{-1}) and 1024.6 nm (9760 cm^{-1}). The maximum absorption cross-section at 981.1 nm calculated with the Yb^{3+} concentration of 4.50×10^{19} cm^{-3} (0.5 at.% Yb-doped sample) amounts to 1.18×10^{-19} cm^2 for $E \| N_m$ (linewidth: 3.6 nm). Both values are very close to those reported for 5 at.% Yb-doped $KRE^{3+}(WO_4)_2$ (RE = Y and Gd) [7,8] and the stoichiometric KYbW (100 at.% Yb) [2]. Fig. 3 also shows the calculated emission cross-section by means of the reciprocity method [9] which has a maximum of 1.47×10^{-19} cm^2 for $E \| N_m$ at 981.1 nm.

From the low-temperature (6 K) absorption spectra we determined the energies of the sublevels of the excited state $^2F_{5/2}$ which are indicated in the inset of Fig. 4. More detailed interpretation of the additional peaks that appear in the absorption spectra can be found in the analysis of the isostructural KYbW [2].

The peaks in the measured fluorescence spectra in Fig. 4 correspond to the emission from the excited $^2F_{5/2}$-manifold to the four sublevels of the ground state manifold $^2F_{7/2}$. The position of the maximum near 10 190 cm^{-1} determines the energy of the $^2F_{5/2}(0')$ sublevel and it agrees well with the value derived from the absorption measurements at 6 K (10 187 cm^{-1}). From the low-temperature emission spectrum, four main lines were found at 10 190.1, 10 015.5, 9755.0 and 9631.5 cm^{-1}

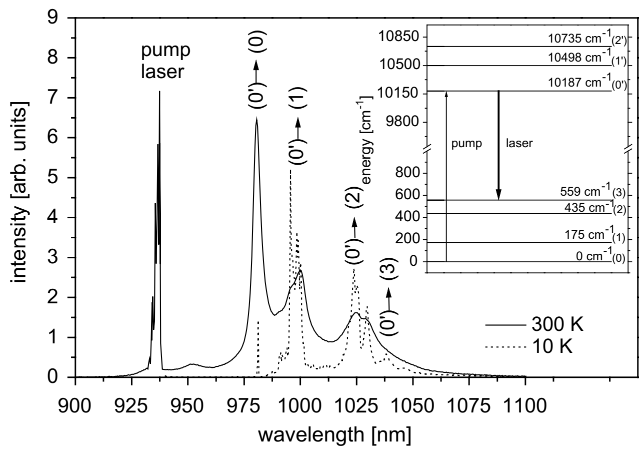

Fig. 4. Room temperature (solid line) and 10 K (dotted line) emission spectra recorded with 0.5%-doped KLuW:Yb^{3+}. Inset: schematic diagram of the Stark levels and laser transition of Yb^{3+} in KLuW.

(981.3, 998.5, 1025.1 and 1038.3 nm, respectively) each of them accompanied by phonon added peaks. These correspond to the electronic transitions $^2F_{5/2}(0') \rightarrow {}^2F_{7/2}(0)$, $^2F_{5/2}(0') \rightarrow {}^2F_{7/2}(1)$, $^2F_{5/2}(0') \rightarrow {}^2F_{7/2}(2)$ and $^2F_{5/2}(0') \rightarrow {}^2F_{7/2}(3)$, respectively. The emission line corresponding to the $^2F_{5/2}(0') \rightarrow {}^2F_{7/2}(0)$ transition is with reduced intensity due to the reabsorption at this wavelength. The Stark sublevels of the ground state manifold $^2F_{7/2}$ derived from the 10 K emission spectrum are at 0, 175, 435 and 559 cm^{-1} (inset in Fig. 4).

The measurement of the fluorescence lifetime was also performed with a low doped (0.5 at.% Yb) KLuW:Yb^{3+} sample to minimize effects like radiation trapping. The measured decay curve could be fitted by a single exponential corresponding to a lifetime value of 375 μs which is larger than the value measured by us and also by others [10] for 0.5% Yb-doped KYW (300 μs). It is expected that this value could be refined in the future by powder measurements since in the case of KYW:Yb and KGdW:Yb very recent such measurements provided shorter lifetimes (233 μs and 243 μs, respectively) than the ones assumed up to now [11]. From the emission cross-sections in Fig. 3 and using the same procedure as in Ref. [2] we obtained by averaging of the three polarizations an estimation of 320 μs for the radiative lifetime of KLuW:Yb^{3+} which is very close to the fluorescence lifetime directly measured.

5. Laser operation

Laser generation was achieved with the 5 and 10 at.% Yb-doped KLuW samples specified in Table 1. A sample of KYW:Yb^{3+} with 10 at.% Yb in the solution [8.172×10^{20} cm^{-3} Yb-ion density in the crystal or a composition of $KY_{0.8714}Yb_{0.1286}(WO_4)_2$] was available as a reference. The thickness of the 5% and 10% doped KLuW:Yb^{3+} and the 10% doped KYW:Yb^{3+} samples was 2.8, 2.2, and 2.37 mm, respectively. All samples were cut and polished with their parallel faces normal to the N_p-principal optic axis (*b*-cut) and aligned under Brewster angle for polarization parallel to the N_m-principal optic axis in which case maximum absorption and gain are expected (Fig. 3). Two folding mirrors (RC = −10 cm) and two plane mirrors formed a standard, astigmatically compensated Z-shaped resonator with a total length of 140 cm. The pump radiation was focused by a $f = 6.28$ cm lens through one of the folding mirrors which was highly transmitting near 980 nm while the second folding mirror was highly reflecting both at the laser (λ_L) and pump (λ_P) wavelengths. The latter permitted to pump the active medium from the back side in a second pass by 80% retroreflection at the total plane reflector terminating this arm of the pump radiation nonabsorbed in the first pass. No special care was taken to cool the crystal. In the other arm of the cavity a plane output coupler with transmission $T_{OC} = 1.5\ldots10\%$ was used. We applied two pump sources: a broadly tunable cw Ti:sapphire laser with < 1 nm linewidth, delivering more than 2.5 W near 980 nm focused to a beam waist of the order of 30 μm in the position of the crystal and a tapered InGaAs diode laser delivering up to 2 W of output power at 978 nm and tunable between 975 and 982 nm by the temperature, whose M^2 factor for the slow axis emission was <3 ($1/e^2$-value).

With $T_{OC} = 2.8\%$ the KLuW:Yb^{3+} laser threshold could be reached for 965 nm < λ_P < 1005 nm. Results for $\lambda_P = 986$ nm (Ti:sapphire laser) and $\lambda_P = 980$ nm (laser diode) pumping are shown in Fig. 5. The optimum Ti:sapphire laser pump wavelength for the 5% Yb-doped KLuW sample was $\lambda_P = 982$ nm and for the 10% Yb-doped KLuW sample it was shorter ($\lambda_P = 979$ nm) because of the increasing reabsorption. At the optimum pump wavelengths the maximum conversion efficiency

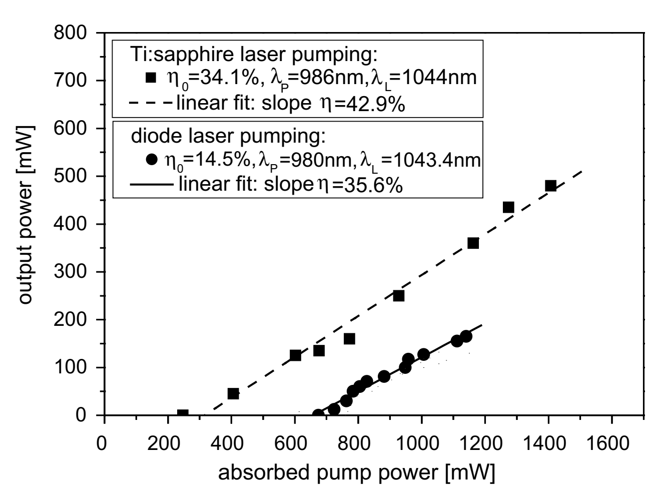

Fig. 5. Laser performance of the 5% Yb-doped KLuW sample with $T_{OC} = 2.8\%$.

both with the 5% and 10% Yb-doped KLuW samples reached 50% and the output power 1 W for an absorbed pump power of ≈2 W (double pass) when the T_{OC} = 10% output coupler was used. The lasing wavelength at maximum output power was λ_L = 1033.3 nm (5% Yb-doping) and longer (λ_L = 1041 nm) for 10% Yb-doping which is also a consequence of the increased reabsorption. For both samples the pump threshold was below 500 mW with the T_{OC} = 1.5% output coupler. In general the performance of both samples was, however, very similar as a function of the absorbed power and also very close to that observed with the 10% Yb-doped KYW reference sample.

With the laser diode at the optimum λ_P = 980 nm no saturation of the absorption took place because of the lower pump intensity and the total pump power incident on the sample was absorbed in the first pass. This, together with the imperfect overlap of the pump and laser waists in the crystal, resulted in increased reabsorption losses and therefore in lower slope and maximum pump efficiencies, and higher oscillation thresholds (Fig. 5). With the T_{OC} = 5% output coupler the maximum pump efficiency reached with the 5% Yb-doped KLuW was η_0 = 14.9% at an output power of 170 mW (λ_L = 1041 nm). The slope efficiency was η = 41.9%.

6. Conclusion

In conclusion we doped for the first time to our knowledge KLuW crystals with Yb^{3+} ions and performed polarized absorption and emission studies at room and cryogenic temperatures in order to determine the Stark splitting of the two electronic states. The upper level lifetime amounts to 375 μs at room temperature. Lasing in the 1 μm range of Yb^{3+} in the monoclinic host KLuW was demonstrated achieving conversion efficiencies as high as 50% and output powers of the order of 1 W in the cw regime without active cooling of the crystal. Diode pumping of KLuW:Yb^{3+} at 980 nm was also demonstrated. Work is in progress to grow KLuW crystals with higher Yb doping level and also epitaxial composites based on KLuW.

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References

[1] N.V. Kuleshov, A.A. Lagatsky, V.G. Shcherbitsky, V.P. Mikhailov, E. Heumann, T. Jensen, A. Diening, G. Huber, Appl. Phys. B 64 (1997) 409.
[2] M.C. Pujol, M.A. Bursukova, F. Güell, X. Mateos, R. Sole, J. Gavalda, M. Aguilo, J. Massons, F. Diaz, P. Klopp, U. Griebner, V. Petrov, Phys. Rev. B 65 (2002) 165121:1.
[3] A. Aznar, R. Sole, M. Aguilo, F. Diaz, U. Griebner, R. Grunwald, V. Petrov, Appl. Phys. Lett. 85 (2004) 4313.
[4] L.I. Yudanova, O.G. Potapova, A.A. Pavlyuk, Inorg. Mater. 23 (1987) 1657 (transl. from Izv. Akad. Nauk SSSR, Neorg. Mat. 23 (1987) 1884–1887).
[5] A.A. Kaminskii, K. Ueda, H.E. Eichler, J. Findeisen, S.N. Bagaev, F.A. Kuznetsov, A.A. Pavlyuk, G. Boulon, F. Bourgeois, Jpn. J. Appl. Phys. 37 (1998) L923.
[6] X. Mateos, A. Aznar, R. Solé, X. Solans, J. Massons, F. Díaz, M. Aguiló, J. Appl. Cryst., in preparation.
[7] A.A. Lagatsky, N.V. Kuleshov, V.P. Mikhailov, Opt. Commun. 165 (1999) 71.
[8] N.V. Kuleshov, A.A. Lagatsky, A.V. Podlipensky, V.P. Mikhailov, G. Huber, Opt. Lett. 22 (1997) 1317.
[9] S.A. Payne, L.L. Chase, L.K. Smith, W.L. Kway, W.F. Krupke, IEEE J. Quant. Electron. 28 (1992) 2619.
[10] A.A. Demidovich, A.N. Kuzmin, G.I. Ryabtsev, M.B. Danailov, W. Strek, A.N. Titov, J. Alloys Compd. 300–301 (2001) 238.
[11] V.E. Kisel, A.E. Troshin, V.G. Shcherbitsky, N.V. Kuleshov, Advanced Solid-State Photonics 2004, paper WB7, TOPS Vol. 94, Optical society of America, Washington, DC, 2004.