Indium-modified Yb:$KY(WO_4)_2$ crystals. Growth, spectroscopy and laser operation

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Abstract: $KIn_{0.07}Yb_{0.13}Y_{0.8}(WO_4)_2$ monoclinic *C*2/*c* single crystals were grown by the TSSG technique. 500 mW of output power were obtained at 300 K with slope efficiency of 69%. The laser emission was tunable over λ=1020-1047 nm.
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1. Introduction

$KLn(WO_4)_2$ crystals, with Ln= Y, Gd, or Lu, are well established laser materials characterized by a very large absorption and emission cross sections for the so called N_m crystal direction. Laser action in Nd, Yb, Tm or Ho doped $KLn(WO_4)_2$ crystals has been shown under continuous wave (CW), Q-switch and mode-locking operation regimes. [1] More recently, mixed cationic modifications over the optically inert Ln crystal position, i.e $KA_{1-x}B_x(WO_4)_2$, are being studied to produce waveguided lasers. [2]

Although the ordered character of the crystalline structure limits the spectral width of the optical bands and therefore the laser pulse duration, laser pulses near to 100 fs have been obtained for Yb-doped $KLn(WO_4)_2$ crystals.[3] Mixed modifications of the Ln crystal composition (as those mentioned previously for waveguiding purposes) may help to enlarge the width of the optical bands and thus to shorten the pulse duration, which is more critical for Nd or Ho lasers than for Yb and Tm ones. With this purpose, mixed modifications have been tested with success in other types of ordered laser crystals. [4]

So far, little is known on Indium (In) modified $KLn(WO_4)_2$ crystals. *A priori*, In may have a significant influence in the crystal properties because its ionic radius for VIII-coordination, 0.92 Å, is smaller than those of trivalent lanthanides or Y, namely the smallest one for VIII-Ln/Y coordination corresponds to Lu^{3+}, 0.977 Å. In this work we show the successful growth of 10 at% In-modified Yb:$KY(WO_4)_2$ crystals and we report their fundamental spectroscopic and laser characteristics.

2. Crystal growth

$KIn(WO_4)_2$ compound crystallizes either in orthorhombic (low temperature) or in trigonal (high temperature) structures with a polymorphic transformation at 850 ºC, [5] which differs from the desired monoclinic phase of $KY(WO_4)_2$. The stability of the monoclinic (space group *C*2/*c*) crystalline phase characteristic of the low temperature polymorph of $KY(WO_4)_2$ has been studied first in polycrystalline powders synthesized at 860 ºC by solid state reaction with different In concentrations, $KIn_xY_{1-x}(WO_4)_2$, x= 0.1, 0.15, 0.2, 0.25, 0.3 and 0.5. The resulting phase was characterized in a Bruker D8 equipment by powder XRD θ-2θ scans. Figure 1a shows a comparison of selected results with the powder diffraction pattern (PDF) of expected phases. Above x= 0.25 the monoclinic phase coexists with trigonal (hexagonal space group $P\bar{3}c1$, Nº 165) one, as can be deduced from the presence of extra XR reflections, see for instance the XRD pattern of the $KIn_{0.5}Y_{0.5}(WO_4)_2$ composition shown in Figure 1a. We selected 10 at% In composition to minimize phase nucleation competition during crystal growth.

Crystal growth was undertaken by the Top Seeded Solution Growth (TSSG) method using $K_2W_2O_7$ flux. Crystal seeds of the same composition were used. The solute/flux molar composition was 1/8. The nominal saturation temperature of this mixture was found to be 890 ºC and crystal growth was induced by slow (0.05 ºC/h) cooling. Figures 1b and 1c show pictures of two crystals grown without and with pulling (25 μm per day), respectively.

The obtained crystals were characterized at room temperature by single crystal X-ray diffraction using a Bruker SMART CCD 6000 equipment. The monoclinic *C*2/*c* structure of the crystal was confirmed. The crystal lattice parameters obtained were a= 10.625(3) Å, b = 10.334(2) Å, c = 7.5368(16) Å and β= 130.671(8)°, with cell volume 627.6(2) $Å^3$. As expected the crystal volume is slightly smaller than for $KY(WO_4)_2$, V= 629.43 $Å^3$. The refined crystal formula was $KIn_{0.07}Yb_{0.13}Y_{0.8}(WO_4)_2$, i.e. In is incorporated to the lattice (7 at%) in a lower amount that it

was in the growth melt (10 at%), this deficiency is compensated by extra incorporation of Yb (13 at%), that in the melt was only at 10 at%. The Yb density in the crystal calculated from these results is [Yb]= $8.28x10^{20}$ cm^{-3}.

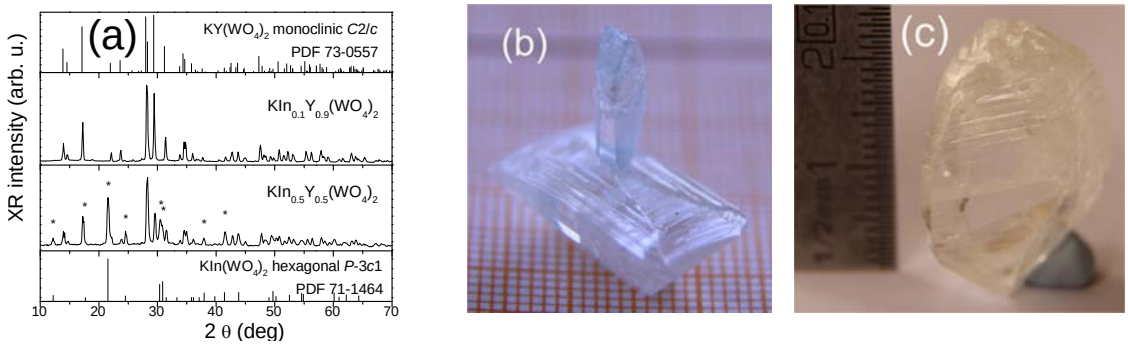

Fig. 1. (a) Comparison of powder XRD scans of $KIn_xY_{1-x}(WO_4)_2$ compounds prepared by solid state reaction with PDF patterns of possible crystalline phases. TSSG crystals with nominal composition $KIn_{0.1}Yb_{0.1}Y_{0.8}(WO_4)_2$ obtained without (b) and with (c) pulling.

3. Spectroscopic characterization

Polarized optical absorption (OA) was measured in a Varian (Cary 5E) spectrophotometer. Photoluminescence (PL) was excited with a Ti-sapphire laser, dispersed by a Spex (f= 34cm) monochromator and detected with a 77 K cooled Ge photodiode. As the peak absorption cross section of *C*2/*c* monoclinic $KLn(WO_4)_2$ crystals is one order of magnitude larger parallel to the N_m direction than that parallel to the orthogonal N_g and N_p directions of the dielectric tensor, we limited most our measurements to N_m polarization.

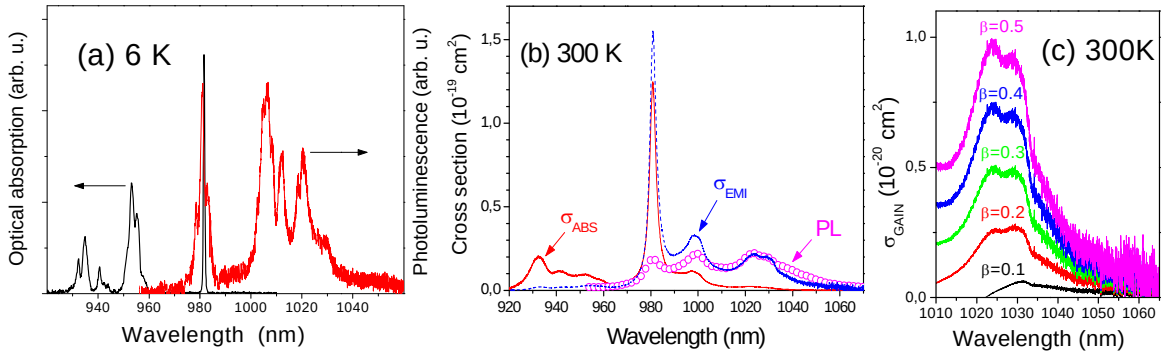

Fig. 2. $KIn_{0.07}Yb_{0.13}Y_{0.8}(WO_4)_2$ crystal. (a) 6 K optical absorption and photoluminescence spectra. N_p-polarization. (b) 300 K absorption (continuous line) and emission (dashed line) cross sections. 300 K photoluminescence (points). N_m-polarization. (b) 300 K gain cross sections for several inversion ratios, β, N_m-polarization.

Figure 2a shows the 6 K OA and PL spectra of the $KIn_{0.07}Yb_{0.13}Y_{0.8}(WO_4)_2$ crystal. The absorption spectrum shows three main bands corresponding to $^2F_{7/2}(0) \rightarrow {}^2F_{5/2}(0',1',2')$ transitions between Yb^{3+} Stark levels. On the other hand, four band sets are found in the PL spectrum corresponding to $^2F_{5/2}(0') \rightarrow {}^2F_{7/2}(0,1,2,3)$ transitions. This provides the following relative energies for the Yb^{3+} Stark levels: $^2F_{7/2}$, 0, 257, 314, 394 cm^{-1} and $^2F_{5/2}$, 10187, 10491, 10726 cm^{-1}. The crystal field splitting between the barycenters of $^2F_{7/2}$ and $^2F_{5/2}$ multiplets seems slightly larger than in the $KY(WO_4)_2$ crystal, i.e. 10227 cm^{-1} for $KIn_{0.07}Yb_{0.13}Y_{0.8}(WO_4)_2$ *vs* 10167 cm^{-1} for $KY(WO_4)_2$.[6]

Figure 2b shows the N_m-polarized 300 K absorption (σ_{ABS}) and emission (σ_{EMI}) cross sections of Yb^{3+} in $KIn_{0.07}Yb_{0.13}Y_{0.8}(WO_4)_2$ crystal. The latter has been obtained by the reciprocity method taking into account the Z_l/Z_u and E_g values obtained from the Stark level energies given above. It is worth noting that the spectral distribution of σ_{EMI} and the 300 K PL (both for Nm) agree, although at short wavelengths the PL intensity is reduced due to the

emission reabsorption. For the laser wavelengths ($\lambda \approx$ 1030 nm, see later) the emission cross section is $\approx 2\times10^{-20}$ cm^2. Figure 2c shows the gain cross section, $\sigma_{GAIN}= \beta\times\sigma_{EMI} -(1-\beta)\times\sigma_{ABS}$, where β is the ratio of the excited to total Yb densities. For β<0.2 laser emission is expected to be confined in the 1020-1050 nm range.

4. Laser characterization

The room temperature CW laser operation of the $KIn_{0.07}Yb_{0.13}Y_{0.8}(WO_4)_2$ crystal has been pumped with a Ti-sapphire laser tuned at 981 nm. In all cases a sample with 1.163 mm of thickness which absorbed more than 90% of the pump beam was used. The laser operation was first tested in the plane-concave (radius of curvature R= -100 mm) optical cavity. Two output couplers (OC) of transmission at 1050 nm of T_{OC}=2.5% and 5% were tested. A maximum slope efficiency (η) versus absorbed pump power of 69% was obtained with the latter OC. The pump laser threshold was 80 mW and the output power at the maximum pump power was near to 500 mW, see Figure 3a.

A three mirror, V-type, astigmatically compensated optical cavity was used to produce a collimated beam and for laser tuning with a Lyot filter. Best η was also obtained with T_{OC}= 5%, see Figure 3b. The spontaneous laser wavelength decreased with increasing T_{OC}, indicative that the crystal laser operation shifts to higher gain regime, see Figure 2c. With the Lyot filter the laser output was tunable from 1020 to 1047 nm, see Figure 3c.

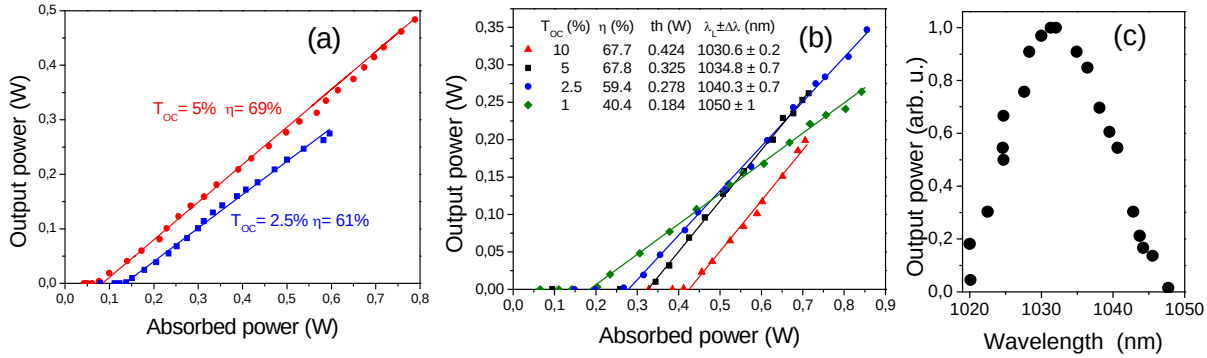

Fig. 3. $KIn_{0.07}Yb_{0.13}Y_{0.8}(WO_4)_2$ crystal. (a) Laser operation in a plane-concave (R= -100 mm) cavity. (b) Laser operation in a V-type cavity. Total length 562 mm. Pump mirror R= -100 mm. High reflector mirror R= -75 mm. Pump- high reflector distance 132 mm. Folding angle 12º. Plane output coupler. T_{OC}= output coupler transmission. η= laser slope efficiency. th= threshold pump power. λ_L= laser wavelength. (c) Laser tuning with a Lyot filter, T_{OC}= 5%.

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5. References

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