Growth and spectroscopy of orthorhombic Yb:KY(MoO$_4$)$_2$ laser crystal with a layered structure

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Abstract. We report on the growth, structure, vibronic and spectroscopic properties of novel Yb$^{3+}$-doped orthorhombic potassium yttrium double molybdate crystal, Yb:KY(MoO$_4$)$_2$. The layered structure of this material determines a strong polarization-anisotropy of absorption and emission bands of Yb$^{3+}$ ions. The maximum stimulated-emission cross-section is $3.7 \times 10^{-20}$ cm$^2$ at ~1.01 μm for light polarization $E \parallel b$ and the lifetime of the $^2$F$_{5/2}$ state is 0.46 ms. Naturally cleaved Yb:KY(MoO$_4$)$_2$ plates are suitable for microchip lasers at ~1 μm.

1. Introduction

Among the oxide host crystals, potassium (rare-earth) double tungstates (DTs) and double molybdates (DMos) with a general chemical formula of KLn(XO$_4$)$_2$ (where X = W or Mo, respectively, and Ln = Y, Gd, Lu, etc.) are attractive for doping with laser-active trivalent rare-earth ions (RE$^{3+}$) [1,2] because they provide ordered structure, high available RE$^{3+}$ doping concentrations, intense and strongly polarized absorption and emission bands, weak non-radiative relaxation and strong Raman response.

Ytterbium (Yb$^{3+}$) ions are well-known for their emission at ~1 μm according to the $^2$F$_{5/2} \rightarrow ^2$F$_{7/2}$ electronic transition. They exhibit a simple energy-level scheme eliminating the unwanted processes such as energy-transfer upconversion or excited-state absorption leading to low heat loading and high laser efficiencies. Yb$^{3+}$-doped materials can be pumped by high-power InGaAs laser diodes emitting at ~0.98 μm. To date, Yb$^{3+}$-doped monoclinic DTs have been implemented for efficient continuous-wave (CW) [3], passively Q-switched [4] and especially mode-locked oscillators at ~1 μm [5,6].

Contrary to DT crystals, their molybdate counterparts, KLn(MoO$_4$)$_2$, are less widespread [2,7]. However, these crystals do not exhibit a polymorphic phase transition below the melting point (like in DTs) and thus they can be grown by the conventional Czochralski (Cz) method [8,9]. KLn(MoO$_4$)$_2$ crystals belong to the orthorhombic class and they feature a layered structure leading to a perfect cleavage feature. This allows one to fabricate thin crystalline films [10] suitable for microchip or thin-disk lasers.

In the present work, we report on the growth, structure, vibronic and spectroscopic characterization of a novel crystal in the orthorhombic DMo family – Yb$^{3+}$-doped potassium yttrium double molybdate, Yb:KY(MoO$_4$)$_2$. 

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2. Crystal growth and structure

KY(MoO₄)₂ crystals are chemically stable, they have a relatively low melting temperature (about 970 °C) and do not show any polychromic transformation below the melting point. In this work, a 3 at.% Yb:KY(MoO₄)₂ crystal was grown by the Cz method using a [100]-oriented undoped seed. 5–7 mol% of potassium trimolybdate (K₂Mo₃O₁₀) were added to the melt to prevent its partial dissociation. The seed rotation speed was 20 rpm, the pulling rate was 1-2 mm/h and the cooling rate was 2 °C/day. The temperature gradient in the melt was below 3 °C/mm. The growth rate was 5–10 g/day.

![X-ray powder diffraction (XRD) pattern of 3 at.% Yb:KY(MoO₄)₂.](image)

The crystalline structure of well-grown crystal of good optical quality was transparent and free of cracks and inclusions, see inset in Fig. 1. No post-growth annealing was applied. The crystal was colorless. The phase purity and the structure of the as-grown crystal were confirmed by X-ray powder diffraction (XRD), see Fig. 1. Yb:KY(MoO₄)₂ is orthorhombic (sp. gr. Pbnm – D14h, No. 60). The Yb³⁺ ions in KY(MoO₄)₂ replace the Y³⁺ ones in a single type of crystallographic sites (symmetry: C₂, VIII-fold O³ coordination). Briefly, the structure of Yb:KY(MoO₄)₂ is as following [8]: continuous belts of edge-sharing distorted [Y/YbO₃] octahedrons are parallel to the b-axis. In the a-b plane, they share corners with the [MoO₄] tetrahedra. The [Y/Yb(MoO₄)₂] radicals form porous layers in the b-c plane. Because of this, the crystal exhibits a perfect cleavage along the (100) plane.

3. Raman spectra

All members of the DT and DMo crystal families are Raman-active [1]. This feature may be used for self-Raman conversion of the laser output. To characterize the vibronic properties of Yb:KY(MoO₄)₂, the room temperature (RT) Raman spectra were measured with polarized light using a Raman microscope (Renishaw inVia). The excitation wavelength was 488 nm (an Ar⁺ laser line). A cleaved crystal plate (i.e., an a-cut) was used and the studied excitation / collection geometries were a(bb)a, a(bc)a, a(cb)a and a(cc)a (according to Porto’s notations).

The Raman spectra are shown in Fig. 2. They are strongly polarized with the most intense Raman response in the a(bb)a geometry. The observed bands are classified into three groups of vibrations [8]. The low-frequency range, 80-272 cm⁻¹, contains translational (T) and rotational (R) modes of the K, Y and Mo cations. Internal bending vibrations (δ) of the oxygen bridged [MoO₄]²⁻ tetrahedral are observed in the intermediate range, 300–435 cm⁻¹. The high-frequency range, 726-944 cm⁻¹, contains intense stretching vibrations (ν) of these tetrahedra.

The most intense Raman mode is at 865 cm⁻¹. The full width at half maximum (FWHM) of this mode is 18.8 cm⁻¹. The maximum phonon frequency, hv_max = 944 cm⁻¹.
Figure 2. Polarized Raman spectra of an \textit{a}-cut Yb:KY(MoO$_4$)$_2$, $\lambda_{\text{exc}}$ = 488 nm, \textit{numbers} indicate the frequencies of the Raman peaks in cm$^{-1}$.

4. Optical spectroscopy
Orthorhombic Yb:KY(MoO$_4$)$_2$ crystal is optically biaxial. The optical indicatrix axes coincide with the crystallographic ones while the assignment of the refractive indices is still unknown. We characterized the spectroscopic properties for the principal light polarizations indicated as $E \parallel a$, $E \parallel b$ and $E \parallel c$. All the studies were performed at RT (20 $^\circ$C).

The absorption spectra were measured using a Varian CARY 5000 spectrophotometer and a Glan-Taylor polarizer. The absorption cross-sections, $\sigma_{\text{abs}}$, were then calculated using the Yb$^{3+}$ ion density of $2.29 \times 10^{20}$ cm$^{-3}$, as shown in Fig. 3(a). The maximum $\sigma_{\text{abs}} = 1.77 \times 10^{-20}$ cm$^2$ at 977.1 nm for $E \parallel b$ and the corresponding FWHM of the absorption peak is 19 nm which is advantageous for diode-pumping. Note that the absorption cross-sections for the light polarizations $E \parallel b$ and $E \parallel c$ are much higher than that for $E \parallel a$ (orthogonal to the cleavage plane) which is due to the layered crystal structure. The UV absorption edge $\lambda_{\text{UV}}$ is at 334 nm and in the IR, the transparency window is until 5.3 $\mu$m.

![Figure 3(a, b). Spectroscopy of Yb$^{3+}$ ions in orthorhombic KY(MoO$_4$)$_2$ crystal: (a) absorption, $\sigma_{\text{abs}}$, and stimulated-emission (SE) cross-sections, $\sigma_{\text{SE}}$, for the $^2F_{5/2} \leftrightarrow ^2F_{7/2}$ transition, light polarizations are $E \parallel a$, $E \parallel b$ and $E \parallel c$; (b) the luminescence decay curve.](image)

The luminescence spectra were measured using an optical spectrum analyser (OSA, Hamamatsu, model AQ6373) and a Glan-Taylor polarizer; a Ti:Sapphire laser tuned to 928 and 977 nm was used as an excitation source. The stimulated-emission (SE) cross-section were calculated by the Füchtbauer–Ladenburg (F-L) formula [11]:
\[
\sigma_{\text{se}}(\lambda) = \frac{\lambda^3}{8\pi(n \sqrt{\tau_{\text{rad}}})^3} \sum_{i=a,b,c} W_i(\lambda) \lambda W_i(\lambda) d\lambda,
\]

where, \(i = a, b, c\) is the light polarization, \(\lambda\) is the light wavelength, \(<n> \approx 1.9\) is the mean refractive index of the crystal, \(c\) is the speed of light, \(\tau_{\text{rad}}\) is the radiative lifetime of the emitting state (\(2^7S_2\), see below), \(W_i(\lambda)\) is the measured luminescence spectrum for \(i\)-th polarization. The SE cross-section spectra are shown in Fig. 3(a). The maximum \(\sigma_{\text{se}}\) for the \(2^7S_2 \rightarrow 2^7P_2\) transition of Yb\(^{3+}\) ions is \(3.7 \times 10^{-20}\) cm\(^2\) at 1008.0 nm for the light polarization \(E \parallel b\). The FWHM of the emission band is \(>35\) nm. The strong polarization anisotropy of the SE cross-sections is a prerequisite for linearly polarized laser emission from the Yb:KY(MoO\(_4\))\(_2\) crystal.

The luminescence decay curve for Yb:KY(MoO\(_4\))\(_2\) was measured under ns pulse excitation from an optical parametric oscillator using a fast InGaAs photodetector and an 8 GHz digital oscilloscope. A thin (~100 μm) cleaved film was used to avoid the effect of reabsorption. The excitation wavelength \(\lambda_{\text{exc}}\) was 930 nm, the luminescence from the \(2^7P_{\text{5/2}} \rightarrow 2^7S_{\text{3/2}}\) Yb\(^{3+}\) multiplet was monitored at 1030 nm. The decay curve plotted in a semi-log scale is shown in Fig. 3(b). It is clearly single-exponential in agreement with a single type of sites for Yb\(^{3+}\) ions. The luminescence decay time \((\tau_{\text{num}} = 458\ \mu s)\) was determined according to a single-exponential law, \(I_{\text{num}}(t) = I_{0}\exp(-t/\tau_{\text{num}})\).

5. Conclusion
Orthorhombic Yb:KY(MoO\(_4\))\(_2\) crystals featuring simple growth by the standard Cz method, easy Yb\(^{3+}\) doping, strongly polarized absorption and stimulated-emission cross-section spectra due to the layered structure and a perfect cleavage feature are very promising for microchip lasers based on crystalline films with a thickness of few hundreds of μm and emitting at ~1 μm. Further work will focus on laser characterization of this material.

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