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Spectroscopy and high-power laser operation of monoclinic Yb³⁺:MgWO₄ crystal

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Monoclinic (wolframite-type) monotonungstate crystals are promising for rare-earth-doping. We report polarized room- and low-temperature spectroscopy, and efficient high-power laser operation of such a Yb³⁺:MgWO₄ crystal featuring high stimulated-emission cross-section ($\sigma_{SE} = 6.2 \times 10^{-20} \text{ cm}^2$ at 1056.7 nm for light polarization $E \parallel N_m$), large Stark splitting of the ground-state (765 cm⁻¹), large gain bandwidth (26.1 nm for $E \parallel N_g$) and strong Raman response (most intense mode at 916 cm⁻¹). A diode-pumped Yb³⁺:MgWO₄ laser generated 18.2 W at ~1056 nm with a slope efficiency of ~89% and a linearly polarized laser output. © 2019 Optical Society of America

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Recently, monoclinic wolframite-type ((Fe,Mn)WO₄, sp. gr. *P2/c*) magnesium tungstate crystals, MgWO₄, have emerged as promising host materials for doping with rare-earth ions (RE³⁺) [1-3]. They belong to the crystal family of monoclinic transition metal monotonungstates M²⁺WO₄ (where M = Mg, Zn, Mn, Fe, Ni, etc.) [4]. So far, MgWO₄ ($a = 4.6889 \text{ \AA}$, $b = 5.6753 \text{ \AA}$, $c = 4.9289 \text{ \AA}$, $\beta = 90.726^\circ$ [5]) crystals were mostly studied for scintillators and for doping with transition-metal ions, e.g., Cr³⁺ [5,6]. MgWO₄ exhibits good thermo-mechanical properties (high thermal conductivity $\langle \kappa \rangle$ of 8.7 W/(mK) [7] and low anisotropy of thermal expansion: $\alpha_a = 11.22$, $\alpha_b = 8.09$ and $\alpha_c = 8.77 [10^{-6} \text{ K}^{-1}]$ [3]). These properties are

superior compared to another well-known crystal family of monoclinic double tungstates, KLn(WO₄)₂ [8], for which $\langle \kappa \rangle \approx 3.5 \text{ W/mK}$ and the thermal expansion tensor shows a significant anisotropy [9]. Besides, RE³⁺-doped MgWO₄ shows attractive spectroscopic properties (broad and intense emission bands for polarized light, large Stark splitting, high luminescence quantum yield and Raman activity) [1-3]. These advantages originate from the low-symmetry structure and the substantial difference in ionic radii of the RE³⁺ dopants and the host-forming Mg²⁺ cations [10].

Regarding laser operation of RE³⁺-doped MgWO₄ crystals, previous studies focused mostly on the spectral range of ~2 μm using thulium (Tm³⁺) [2, 10-12] and holmium (Ho³⁺) [3] ion doping. A diode-pumped continuous-wave (CW) Tm³⁺:MgWO₄ laser generated 3.09 W at 2022-2034 nm with a slope efficiency η of 50% [11]. A graphene mode-locked (ML) Tm³⁺:MgWO₄ laser delivered 86 fs pulses at 2017 nm featuring a bandwidth of 53 nm at a repetition rate of 76 MHz [12].

For laser emission at ~1 μm , ytterbium (Yb³⁺) ion doping holds a huge potential. This is because Yb³⁺ has a simple energy-level scheme eliminating the unwanted energy-transfer processes and leading to high Stokes pump efficiency and weak heat loading [13]. The larger Stark splitting of the ground-state (²F_{7/2}) (as compared to Nd³⁺) is a prerequisite for broader emission at ~1 μm . So far, the growth and preliminary spectroscopy of Yb³⁺:MgWO₄ crystal were reported [1,14]. A semiconductor saturable absorber mirror

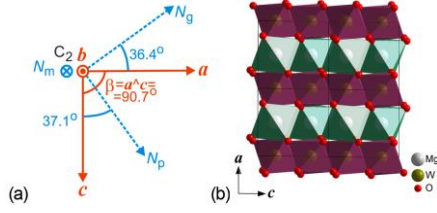


Fig. 1. (a) Orientation of the optical indicatrix axes (N_p , N_m and N_g) in monoclinic Yb:MgWO_4 crystal: \mathbf{a} , \mathbf{b} and \mathbf{c} – crystallographic axes, C_2 – 2-fold symmetry axis; (b) crystal structure in projection to the $\mathbf{a-c}$ plane.

(SESAM) ML $\text{Yb}^{3+}:\text{MgWO}_4$ laser delivered 125 fs pulses at 1065 nm at a repetition rate of 117 MHz [15].

In this work, we report a detailed room- and low-temperature polarization-resolved spectroscopy of $\text{Yb}^{3+}:\text{MgWO}_4$ paving the way towards its highly-efficient and high-power diode-pumped laser operation. We consider this work as a first step towards high-power mode-locked bulk and thin-disk lasers based on $\text{Yb}^{3+}:\text{MgWO}_4$.

The 1.25 at.% $\text{Yb}^{3+}:\text{MgWO}_4$ crystal was grown by the Top-Seeded Solution Growth (TSSG) method using Na_2WO_4 as a solvent [1,3]. Its structure (monoclinic, sp. gr. $C_{2h} - P2/c$) [16] was confirmed by using X-ray powder diffraction. In MgWO_4 , the Yb^{3+} ions are replacing the Mg^{2+} ones in a single type of sites (Wyckoff position: $2f$, site symmetry: C_2 , VI-fold oxygen coordination in distorted $[\text{MgYbO}_6]$ polyhedra), Fig. 1(b). Charge compensation is provided by Na^+ cations entering from the melt [3]. The corresponding ionic radii are $R_{\text{Yb}} = 0.868 \text{ \AA}$, $R_{\text{Mg}} = 0.72 \text{ \AA}$ and $R_{\text{Na}} = 1.02 \text{ \AA}$. The concentration of Yb^{3+} ions in the crystal N_{Yb} was $1.82 \times 10^{20} \text{ cm}^{-3}$ (as determined by Inductively Coupled Plasma Atomic Emission Spectroscopy). Note that the increase of Yb^{3+} doping level is mainly limited by the heterovalent doping mechanism; this would also lead to the deteriorated thermal properties of the crystal.

Monoclinic $\text{Yb}^{3+}:\text{MgWO}_4$ is optically biaxial (point group $2/m$). At the wavelength of $\sim 1 \mu\text{m}$, the principal refractive indices are $n_p = 1.97$, $n_m = 2.03$ and $n_g = 2.13 \pm 0.02$ according to the $n_p < n_m < n_g$ convention. One of the optical indicatrix axes (N_m) coincides with the C_2 symmetry axis (the \mathbf{b} -axis) and other two (N_p and N_g) are lying in the orthogonal mirror plane (the $\mathbf{a-c}$ plane), Fig. 1. The angle $N_p \wedge \mathbf{c} = 37.1^\circ$, measured within the obtuse angle β .

Room-temperature (RT, 293 K) absorption, σ_{abs} , cross-sections corresponding to the ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition are shown in Fig. 2(a) for the principal light polarizations $\mathbf{E} \parallel N_p$, N_m and N_g . The maximum σ_{abs} is $6.16 \times 10^{-20} \text{ cm}^2$ at 974.0 nm (the zero-phonon line, ZPL, at RT) and the corresponding full width at half maximum (FWHM) of the absorption peak is 5.6 nm (for $\mathbf{E} \parallel N_g$). The stimulated-emission (SE) cross-sections, σ_{SE} , were calculated using a combination of the Füchtbauer-Ladenburg (F-L) equation [17] based on the measured luminescence spectra, and the reciprocity method (RM) [18] based on the determined Stark splitting). The maximum σ_{SE} reaches $6.2 \times 10^{-20} \text{ cm}^2$ at 1056.7 nm for $\mathbf{E} \parallel N_m$. $\text{Yb}^{3+}:\text{MgWO}_4$ exhibits a strong anisotropy of the SE cross-sections at this wavelength: $\sigma_{\text{SE}}(m) : \sigma_{\text{SE}}(g) = 3.7$ and $\sigma_{\text{SE}}(m) : \sigma_{\text{SE}}(p) = 5.5$, which is a prerequisite for a linearly polarized laser emission. From the luminescence spectra (measured with $\lambda_{\text{exc}} = 972 \text{ nm}$), the emission bandwidth is 18.7 nm ($\mathbf{E} \parallel N_m$) and $>50 \text{ nm}$ (structured spectrum, $\mathbf{E} \parallel N_g$). $\text{Yb}^{3+}:\text{MgWO}_4$ exhibits a single-exponential luminescence decay with a lifetime τ_{lum} of 366 μs , as measured for a powdered sample to avoid radiation trapping. The ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} represents a quasi-three-level laser scheme with reabsorption.

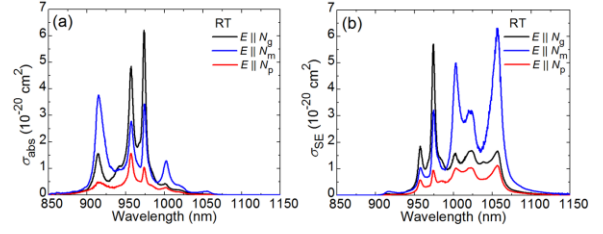


Fig. 2. RT (a) absorption, σ_{abs} , and (b) stimulated-emission, σ_{SE} , cross-section spectra of Yb^{3+} in monoclinic MgWO_4 for $\mathbf{E} \parallel N_p$, N_m and N_g .

Thus, gain cross-sections, $\sigma_{\text{gain}} = \beta \sigma_{\text{SE}} - (1 - \beta) \sigma_{\text{abs}}$, where $\beta = N_2({}^2F_{5/2})/N_{\text{Yb}}$ is the inversion ratio, and N_2 is the upper laser level population, are calculated to predict the spectral properties of laser emission, see Fig. 3 for $\mathbf{E} \parallel N_m$ and $\mathbf{E} \parallel N_g$. For $\mathbf{E} \parallel N_m$, a local peak in the gain spectra is observed at $\sim 1057 \text{ nm}$ and the gain bandwidth $\Delta \lambda_g$ is 15.1 nm (FWHM, for $\beta = 0.1$). For $\mathbf{E} \parallel N_g$, a similar behavior is observed while the gain spectra are broader, $\Delta \lambda_g = 26.1 \text{ nm}$.

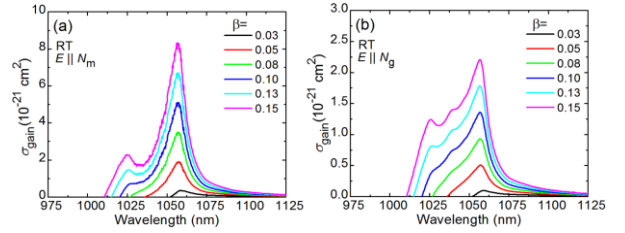


Fig. 3. RT gain cross-sections, $\sigma_{\text{gain}} = \beta \sigma_{\text{SE}} - (1 - \beta) \sigma_{\text{abs}}$, where $\beta = N_2({}^2F_{5/2})/N_{\text{Yb}}$ is the inversion ratio, for Yb^{3+} ions in monoclinic MgWO_4 crystal. The light polarizations are (a) $\mathbf{E} \parallel N_m$ and (b) $\mathbf{E} \parallel N_g$.

The polarized Raman spectra of an N_m -cut $\text{Yb}^{3+}:\text{MgWO}_4$ crystal are shown in Fig. 4 for the $m(ij)m$, where $i, j = p, g$, configurations (using Porto's notation). The excitation wavelength is $\lambda_{\text{exc}} = 514 \text{ nm}$. The most intense vibration is observed at 915.7 cm^{-1} (the FWHM of the Raman band is 15.0 cm^{-1}) and assigned to symmetric stretching W–O vibrations $\nu_1(A_{1g})$ in the WO_6 octahedra [2]. $\text{Yb}^{3+}:\text{MgWO}_4$ is promising for self-Raman frequency conversion.

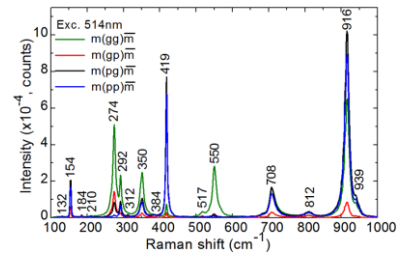


Fig. 4. Polarized Raman spectra for $\text{Yb}^{3+}:\text{MgWO}_4$ for the $m(xy)m$ configurations (Porto's notation), numbers indicate the Raman frequencies in cm^{-1} .

To resolve the Stark splitting of Yb^{3+} multiplets, the absorption and luminescence spectra were measured in the temperature range of 6–300 K, Fig. 5. For Yb^{3+} ions in C_2 symmetry sites, there is a total of $2J + 1$ Stark sub-levels for each $2s+1L_J$ multiplet, numbered as 0..3 for ${}^2F_{7/2}$ and 0'..2' for ${}^2F_{5/2}$. The interpretation of the Stark transitions was carried out accounting for the Raman spectra.

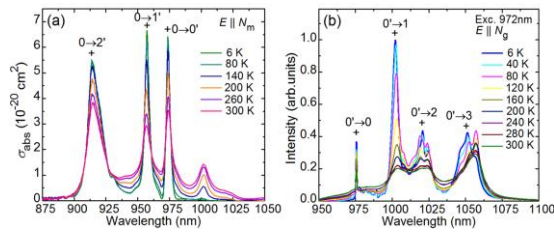


Fig. 5. Low temperature spectroscopy of Yb:MgWO₄: (a) absorption spectra for $E \parallel N_m$; (b) luminescence spectra for $E \parallel N_g$, $\lambda_{exc} = 972$ nm. The “+” marks indicate Stark transitions.

The energy-level scheme of Yb³⁺ ions in MgWO₄ is shown in Fig. 6(a). The ZPL (the transition between the lowest sub-levels of both multiplets) has an energy $E_{ZPL} = 10275$ cm⁻¹. The partition functions for the lower and upper multiplets are $Z_1 = 1.352$ and $Z_2 = 1.469$, respectively ($Z_1/Z_2 = 0.920$). The total Stark splitting of the ground-state, $\Delta E(^2F_{7/2}) = 765$ cm⁻¹, exceeds that in other known tungstate crystals [8,19], Fig. 6(b). For the RE³⁺ ions, the barycenter of any $2S+1L_J 4f^n$ multiplet shows a linear variation vs. the barycenter of any other isolated multiplet, which is expressed as a barycenter plot [20], see Fig. 6(c). The barycenter energies $\langle E(^2F_{5/2}) \rangle$ and $\langle E(^2F_{7/2}) \rangle$ for Yb³⁺:MgWO₄ agree well with this plot.

In Table 1, we compare the emission properties of Yb³⁺:MgWO₄ with other well-known tungstate laser crystals, namely, monoclinic (sp. gr. C2/c) Yb³⁺:KLu(WO₄)₂ [8] and tetragonal disordered (sp. gr. I4₁/a) Yb³⁺:NaY(WO₄)₂ [21]. Yb³⁺:MgWO₄ has higher SE cross-sections, while its gain bandwidths are comparable to those of monoclinic double tungstates.

Table 1. Spectroscopic Properties* of Yb³⁺ in Tungstate Crystals

| Crystal | Site | λ_{em} , nm | $\Delta\lambda_g$, nm | σ_{SE} , 10 ⁻²⁰ cm ² | τ_{lum} , μs | Ref. |
|------------------------------------|----------------|------------------------|---------------------------|--|----------------------|------|
| NaY(WO ₄) ₂ | S ₄ | 1018(π) | 33.9(π) | 1.38(π) | 309 | [21] |
| | | 1024(σ) | 25.9(σ) | 0.86(σ) | | |
| KLu(WO ₄) ₂ | C ₂ | 1026.7(m) | 20.2(m) | 2.6(m) | 275 | [8] |
| | | 1041.2(p) | 28.0(p) | 1.3(p) | | |
| MgWO ₄ | C ₂ | 1056.7(m) | 15.1(m) | 6.25(m) | 366 | * |
| | | 1056.6(g) | 26.1(g) | 1.68(g) | | |

* λ_{em} – emission wavelength, $\Delta\lambda_g$ – gain bandwidth ($\beta = 0.1$), σ_{SE} – SE cross-section, τ_{lum} – reabsorption-free luminescence lifetime.

For laser experiments, a rectangular sample was cut from the 1.25 at.% Yb³⁺:MgWO₄ crystal for light propagation along the N_p optical indicatrix axis (N_p -cut). It had a thickness of 3.1 mm and an aperture of 4×4 mm². This crystal orientation was selected because it gives access to the high-gain light polarization ($E \parallel N_m$). The uncoated crystal was mounted in a Cu-holder using Indium foil for better thermal contact from all lateral sides. The holder was cooled to ~14 °C by circulating water. The crystal was inserted in a compact plano-plano (microchip-type) laser cavity, Fig. 7, formed by a flat pump mirror (PM) coated for high transmission (HT) at 0.88-0.99 μm and for high reflection (HR) at 1.02-1.23 μm, and a set of flat output couplers (OCs) with a transmission T_{OC} of 0.5%...10% at the laser wavelength. Both the PM and the OC were placed close to the crystal with minimum air gaps, so that the geometrical cavity length was ~3.1 mm. The microchip laser concept benefits from a robust and compact design and good cavity stability.

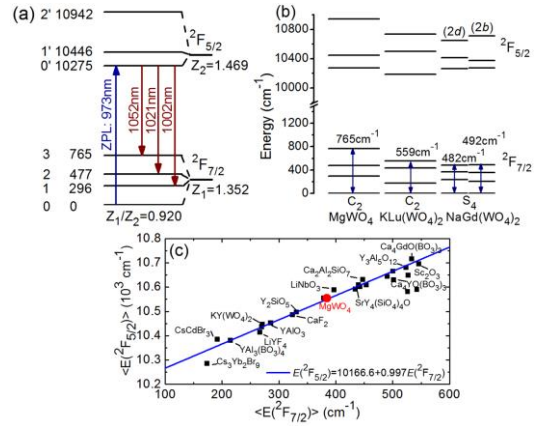


Fig. 6. Stark splitting of Yb³⁺ multiplets in MgWO₄: (a) Energy-level scheme, numbers indicate the energy in cm⁻¹, $Z_{1(2)}$ are the partition functions; (b) Stark splitting of Yb³⁺ in tungstate crystals: MgWO₄, KLu(WO₄)₂ [8], NaGd(WO₄)₂ [19] (C₂ and S₄ – Yb³⁺ site symmetries); (c) barycenter plot [20] for Yb³⁺ ions showing the result for MgWO₄.

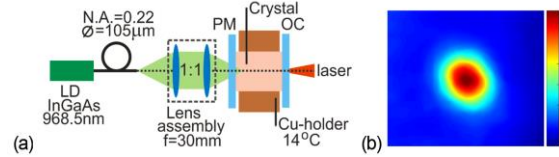


Fig. 7. (a) Scheme of the compact diode-pumped Yb³⁺:MgWO₄ laser: LD – laser diode, PM – pump mirror, OC – output coupler; (b) typical profile of the laser beam in the far-field (the beam ellipticity originates from the astigmatic thermal lens), $P_{abs} \approx 10$ W.

The N_p -cut Yb³⁺:MgWO₄ crystal generated a maximum output power of 18.2 W at ~1056 nm with a slope efficiency η of ~89% (vs. the absorbed pump power P_{abs}), Fig. 8(a). The laser threshold was at $P_{abs} = 0.54$ W and the optical-to-optical efficiency η_{opt} amounted to 33.7% (vs. the pump power incident on the crystal). All these values are specified for $T_{OC} = 10\%$. The laser output was linearly polarized ($E \parallel N_m$) and the polarization was intrinsically selected by the gain anisotropy, Fig. 2(b). For all studied OCs, the emission wavelength was ~1.06 μm, Fig. 3(a), in agreement with the gain spectra. A slight blue-shift of the laser wavelength with increasing output coupling was detected, Fig. 8(b), and ascribed to the quasi-three-level nature of the Yb³⁺ laser scheme exhibiting reabsorption at the laser wavelength. The laser operation in the plano-plano cavity was supported by a positive (focusing) thermal lens. For $T_{OC} < 10\%$, power scaling was limited by a thermal roll-over probably because of too high intracavity laser intensity. The determined laser slope efficiency gives an estimation of the roundtrip passive loss L of 0.35% (loss coefficient: $\delta_{loss} = 0.0056$ cm⁻¹). No crystal fracture was observed up to at least $P_{abs} = 22.5$ W (limited by the available pump).

In Table 2, we compare the output characteristics of compact diode-pumped lasers based on Yb³⁺-doped oxide crystals and reported recently. The superior laser results achieved with Yb³⁺:MgWO₄ compared to previous studies with other tungstate crystals, Yb³⁺:NaY(WO₄)₂ and Yb³⁺:KLu(WO₄)₂, are attributed to its better thermo-mechanical properties. crystals, Yb³⁺:NaY(WO₄)₂ and Yb³⁺:KLu(WO₄)₂, are attributed to its better thermo-mechanical properties.

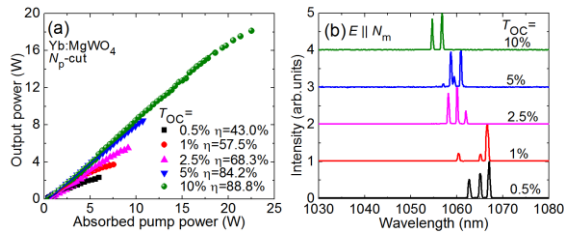


Fig. 8. Diode-pumped compact Yb³⁺:MgWO₄ laser: (a) input-output dependences, η – slope efficiency; (b) typical laser emission spectra. The crystal orientation is N_p -cut, the laser polarization is $E \parallel N_m$.

Table 2. Output Characteristics* of Compact Diode-Pumped Ytterbium Lasers Based on Oxide Crystals Reported So Far

| Crystal | Yb, at. % | P_{out} , W | λ_L , nm | P_{th} , W | η , % | Ref. |
|---|-----------|---------------|------------------|--------------|------------|------|
| Yb:LuVO ₄ | 1.5 | 8.3 | 1031 | 2.6 | 80 | [22] |
| Yb:CaGdAlO ₄ | 8 | 7.79 | ~1061 | 2.0 | 84 | [13] |
| Yb:LuAlO ₃ | 2 | 9.6 | 1041 | ~1.5 | 74 | [23] |
| Yb:NaY(WO ₄) ₂ | 4.8 | 5.2 | 1045 | 1.20 | 50 | [24] |
| Yb:KLu(WO ₄) ₂ | 5.2 | 11.0 | ~1045 | 0.61 | 80 | [25] |
| Yb:MgWO ₄ | 1.25 | 18.2 | ~1056 | 0.54 | 89 | ** |
| Yb:Ca ₄ GdO(BO ₃) ₃ | 10 | 18.2 | 1032 | ~1 | 70 | [26] |
| Yb:YAl ₃ (BO ₃) ₄ | 5.6 | 10.6 | 1042 | 0.79 | 72 | [27] |
| Yb:Lu ₃ Ga ₅ O ₁₂ | 7.1 | 8.97 | 1040 | 1.22 | 75 | [28] |

* P_{out} – output power, λ_L – laser wavelength; P_{th} – threshold pump power, η – slope efficiency (vs. absorbed pump power); **This work.

To conclude, monoclinic Yb³⁺:MgWO₄ is a promising crystal for compact, highly-efficient and high-power lasers at ~1 μ m thanks to a combination of attractive thermal and spectroscopic properties. We report on the first laser operation of Yb³⁺:MgWO₄ in a microchip-type laser cavity yielding >18 W of linearly polarized output at ~1.06 μ m with a slope efficiency (88.8%) almost approaching the Stokes limit, $\eta_{St} = \lambda_p/\lambda_L = 91.7\%$. This is attributed to weak non-radiative relaxation, low optical losses and good mode-matching provided by the positive thermal lens for the selected crystal orientation and the results achieved in this work represent a record for Yb³⁺-doped tungstate laser crystals.

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Disclosures. The authors declare no conflicts of interest.

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