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Growth, structure and polarized spectroscopy of monoclinic Er³⁺:MgWO₄ crystal

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Abstract: We report on the growth, structure and polarized spectroscopy of a novel promising laser crystal, erbium-doped magnesium monotungstate, Er³⁺:MgWO₄. 1.01 t.% Er³⁺:MgWO₄ was grown by the Top-Seeded Solution Growth method using Na₂WO₄ as a solvent. The crystal structure was refined by the Rietveld method. Er³⁺:MgWO₄ belongs to the monoclinic class (sp. gr. *P2/c*, wolframite-type structure, lattice parameters: $a = 4.6939(6)$ Å, $b = 5.6747(4)$ Å, $c = 4.9316(6)$ Å and $\beta = 90.7858(4)$ Å. The transition intensities for Er³⁺ ions were determined using the Judd-Ofelt theory accounting for an intermediate configuration interaction (ICI). Er³⁺ ions in MgWO₄ exhibit intense, strongly polarized and broad absorption and emission bands owing to their accommodation in distorted low-symmetry sites (*C*₂). The stimulated-emission cross-section for the ⁴I_{13/2} → ⁴I_{15/2} transition is 0.31×10^{-20} cm² at 1637 nm (light polarization: $E \parallel b$). The radiative lifetime of the ⁴I_{13/2} state is 4.85 ± 0.05 ms. The multiphonon non-radiative relaxation for Er³⁺ excited multiplets is quantified. Er³⁺ ions in MgWO₄ feature large Stark splitting of the ground-state, $\Delta E(^4I_{15/2}) = 435$ cm⁻¹. Er³⁺:MgWO₄ is attractive for low-threshold lasers at ~ 1.64 μm.

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1. Introduction

The Erbium ion (Er³⁺) is well known for its emission in the eye-safe spectral range of $\sim 1.5 - 1.6$ μm originating from the ⁴I_{13/2} → ⁴I_{15/2} electronic transition. The applications of eye-safe erbium lasers are in the fields of range-finding, environmental sensing, aerial navigation and telecom. So far, Er³⁺, Yb³⁺-codoped phosphate glasses represent the state-of-the-art erbium laser media [1]. Here, the Yb³⁺ ion acts as a sensitizer to enhance the pump absorption at $\sim 0.96 - 0.98$ μm, the spectral range addressed by commercial InGaAs laser diodes [2]. Such glasses feature attractive spectroscopic behavior, i.e., broadband Yb³⁺ absorption, efficient Yb³⁺ → Er³⁺ energy transfer and long Er³⁺ upper laser lifetime. Er,Yb:phosphate glass lasers can generate mJ-level nanosecond pulses making them ideal for portable range-finders [3]. At the same time, glasses suffer from poor thermo-mechanical properties limiting the power scaling capabilities.

46 As an alternative to glassy gain media, single crystals can be used. However, so far, only a
47 few materials were found to be suitable for efficient lasers based on the $\text{Yb}^{3+}, \text{Er}^{3+}$ codoping
48 scheme. These include vanadates (YVO_4 [4]), borates ($\text{REAl}_3(\text{BO}_3)_4$ [5,6], $\text{RECa}_4\text{O}(\text{BO}_3)_3$
49 [7]), and silicates (Y_2SiO_5 [8]). Tolstik *et al.* demonstrated an $\text{Er}, \text{Yb}:\text{YAl}_3(\text{BO}_3)_4$
50 ($\text{Er}, \text{Yb}:\text{YAB}$) laser delivering an output power of 1 W at 1555 nm with a slope efficiency of
51 35% [5]. Still, further power scaling of such lasers is limited by severe thermo-optic effects
52 originating from upconversion losses. Moreover, the growth technology of $\text{REAl}_3(\text{BO}_3)_4$
53 borate crystals is far from being mature.

54 An alternative approach is the use of singly Er^{3+} -doped crystals which can be pumped at
55 $\sim 1.54 \mu\text{m}$. This corresponds to excitation directly to the upper laser level (in-band or resonant
56 pumping). Owing to the relatively high absorption cross-sections for the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ Er^{3+}
57 transition, high pump efficiencies can be achieved even for low Er^{3+} doping levels (~ 1 at.%).
58 This leads to weak energy-transfer upconversion, which, together with the low quantum effect
59 inherent to the resonant pumping scheme, determines weak heat loading and high laser slope
60 efficiencies. Contrary to the $\text{Er}^{3+}, \text{Yb}^{3+}$ codoping scheme for which only a few particular host
61 matrices are suitable, single Er^{3+} doping is more advantageous from the material point of
62 view: efficient laser operation can be achieved in many singly Er^{3+} -doped laser materials
63 (crystals) under in-band pumping. In-band pumped $\text{Er}:\text{Y}_3\text{Al}_5\text{O}_{12}$ ($\text{Er}:\text{YAG}$) lasers have
64 delivered multi-watt output at 1617 nm and 1645 nm [9,10]. However, one disadvantage of
65 cubic $\text{Er}:\text{YAG}$ crystals are the depolarization losses appearing at high pump powers in lasers
66 containing polarization-selective elements. Thus, it is still important to search for novel singly
67 Er^{3+} -doped materials offering intrinsic optical anisotropy, broad and intense spectral bands for
68 polarized light, and good thermo-mechanical properties.

69 Magnesium mon tungstate (MgWO_4) has recently emerged as a promising host crystal for
70 doping with laser-active rare-earth ions [11-13]. This crystal is monoclinic and optically
71 biaxial offering strong optical anisotropy. It was found to exhibit good thermo-mechanical
72 properties, i.e., high thermal conductivity of $\sim 8.7 \text{ W m}^{-1}\text{K}^{-1}$ [14] and low anisotropy of thermal
73 expansion [13]. High-power laser operation was demonstrated using such crystals: Loiko *et al.*
74 developed a diode-pumped $\text{Yb}^{3+}:\text{MgWO}_4$ laser delivering 18.2 W at ~ 1056 nm with a high
75 slope efficiency of $\sim 89\%$ and a linearly polarized output [12]. The low-symmetry distorted
76 coordination of rare-earth ions in MgWO_4 leads to broad emission bands [15]. Because of the
77 broadband emission properties, such crystals have been implemented in femtosecond mode-
78 locked lasers [16,17]. Although $\text{Er}^{3+}:\text{MgWO}_4$ has never been studied so far, other monoclinic
79 crystals doped with Er^{3+} ions appear promising for the development of eye-safe lasers: Serres
80 *et al.* reported on a diode-pumped 1 at.% $\text{Er}:\text{KLu}(\text{WO}_4)_2$ laser generating 268 mW at 1610 nm
81 with a slope efficiency of 30% [18].

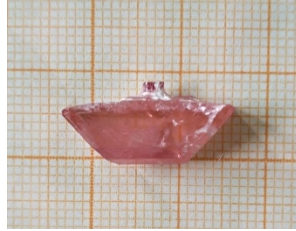
82 In the present work, we report on the growth, structure refinement and a polarization-
83 resolved spectroscopic study of an Er^{3+} -doped MgWO_4 crystal, for the first time, to the best of
84 our knowledge.

85 2. Crystal growth and structure

86 2.1 Crystal growth

87 $\text{Er}^{3+}:\text{MgWO}_4$ was grown by the top-seeded solution growth (TSSG) method [11,19] from the
88 flux with a composition of MgWO_4 : $\text{Na}_2\text{WO}_4 = 5:7$ mol (sodium tungstate, Na_2WO_4 , was
89 used as a solvent) in a vertical tubular furnace. The starting materials were Na_2CO_3 , MgO ,
90 WO_3 (purity: analytical grade) and Er_2O_3 (dopant, purity: 99.99%). They were weighed
91 according to the above-mentioned composition with the initial Er^{3+} concentration of 10 at.%
92 (with respect to Ca^{2+}). The weighed materials were mixed, ground and then put into a Pt
93 crucible with dimensions of $\text{Ø}55 \times 60 \text{ mm}^3$. The crucible was placed into a resistive furnace
94 equipped with a programmable temperature controller, nickel-chrome heating wires and a Pt-
95 Rh/Pt thermocouple. A [010]-oriented seed from an undoped MgWO_4 crystal was used. The
96 solution was kept at 980°C for 2 days to ensure that the starting materials melted completely

97 and homogeneously. The saturation temperature was determined to be 953°C by repeated
 98 seeding trials. The crystal was grown at a cooling rate of 0.6 - 1°C/day and a rotation speed of
 99 10 rpm in the temperature range of 953 - 930°C. Once the growth was completed, the crystal
 100 was slowly pulled out of the solution and cooled down to room temperature (RT, 293 K) at a
 101 rate of 10 K/h. Figure 1 shows an as-grown Er³⁺:MgWO₄ crystal with dimensions of
 102 20 × 8 × 6 mm³. It has a rose coloration due to erbium doping.



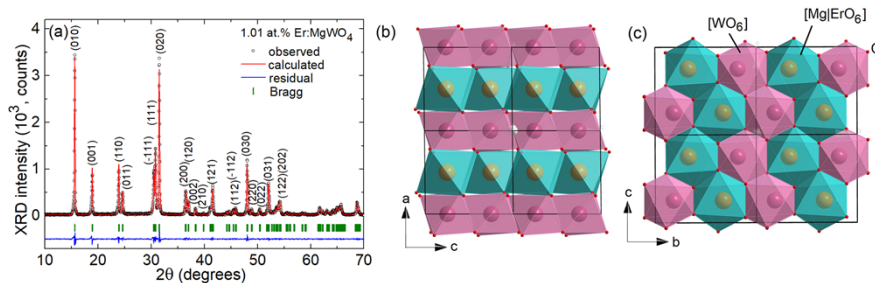
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Fig. 1. A photograph of the as-grown 1.01 at.% Er³⁺:MgWO₄ crystal, the growth direction is along the [010] axis.

106 The actual Er³⁺ doping level was determined by inductively coupled plasma atomic
 107 emission spectrometry (ICP-AES, Ultima2, Jobin-Yvon) to be 1.01 at.% (ion density:
 108 $N_{\text{Er}} = 1.419 \times 10^{20}$ at/cm³). No significant variation of the Er³⁺ doping level across the crystal
 109 boule was observed. The segregation coefficient of Er³⁺ K_{Er} was then 0.1. Such a low value is
 110 due to a significant difference of ionic radii of Mg²⁺ and Er³⁺ (see below). Despite the low K_{Er}
 111 value for MgWO₄, it is relatively easy to access the desired doping level typical for singly
 112 Er³⁺-doped crystals (~1 at.%). Higher doping levels can be accessed by increasing the initial
 113 content of Er³⁺ ions in the growth charge or probably by using other charge compensators
 114 (e.g., Li⁺ cations). However, in in-band-pumped Er lasers, the doping levels above 1 at.% are
 115 usually not used due to the enhanced energy-transfer upconversion.

116 2.2 Structure refinement and electronic structure

117 The X-ray powder diffraction (XRD) data were collected using a Rigaku MiniFlex 600 X-ray
 118 diffractometer with CuK α radiation ($\lambda = 1.5418$ Å) in an angular range of $2\theta = 10$ -80° with a
 119 scan step of 0.02° and a scan speed of 5°/min, as shown in Fig. 2(a). The measured XRD
 120 pattern was well assigned using a standard diffraction pattern of undoped MgWO₄ (JCPDS
 121 card #96-101-0643) and no other phases were found.



122
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 126

Fig. 2. Structural study of Er³⁺:MgWO₄: (a) X-ray powder diffraction (XRD) analysis: observed (black), calculated (red) and residual (blue) patterns, dashes – Bragg positions, (hkl) – Miller's indices; (b,c) projection of the crystal structure on (b) the *a-c* plane and (c) the *b-c* plane, black lines – unit-cell.

127 The crystal structure was refined by the Rietveld method (Match3 software was used).
 128 The crystallographic data of undoped MgWO₄ [20] were used as a starting model.
 129 Er³⁺:MgWO₄ crystallizes in the monoclinic system with space group $C_{2h}^4 - P2/c$, No. 13, and
 130 centrosymmetric point group $2/m$. The lattice parameters are $a = 4.6939(6)$ Å,
 131 $b = 5.6747(4)$ Å, $c = 4.9316(6)$ Å, monoclinic angle of $\beta = 90.7858(4)^\circ$ (number of formula

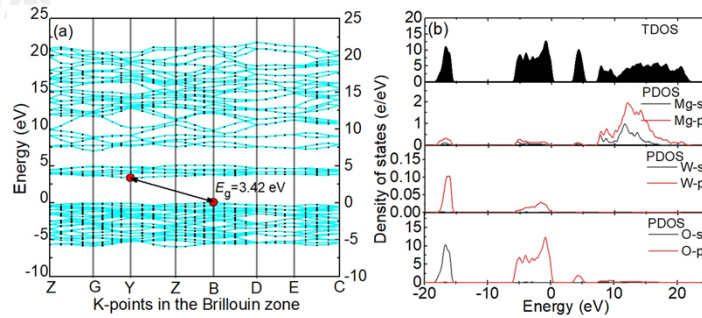
132 units per unit-cell $Z = 2$), unit-cell volume of $V = 131.351 \text{ \AA}^3$ and calculated density
 133 $\rho_{\text{calc}} = 6.078 \text{ g/cm}^3$. The reliability factors are $R_p = 10.5\%$, $R_{\text{wp}} = 14.5\%$, $R_{\text{exp}} = 10.29\%$ and
 134 $\chi^2 = (R_{\text{wp}}/R_{\text{exp}})^2 = 1.98$ indicating good convergence of the fit.

135 The determined fractional atomic coordinates, site occupancy factors (O.F.) and isotropic
 136 displacement parameters B_{iso} are listed in Table 1. Figures 2(b) and (c) present a fragment of
 137 the crystal structure calculated according to the determined atomic positions. $\text{Er}^{3+}:\text{MgWO}_4$
 138 exhibits a wolframite $[(\text{Fe},\text{Mn})\text{WO}_4]$ type structure (MgWO_4 is called huanzalaite in mineral
 139 form). The $\text{Mg}^{2+}|\text{Er}^{3+}$ cations occupy the $2f$ Wyckoff positions with VI-fold O^{2-} coordination;
 140 in the distorted $[\text{Mg}|\text{ErO}_6]$ octahedra, there are two shorter $[1.9392(0) \text{ \AA}]$, two intermediate
 141 $[2.1732(0) \text{ \AA}]$ and two longer $[2.2199(4) \text{ \AA}]$ Mg-O distances. The W^{6+} cations ($2e$ Wyckoff
 142 positions) are also located in distorted octahedra with W-O distances in the range $1.7747(7) -$
 143 $2.1673(4) \text{ \AA}$. The network of $\text{Er}^{3+}:\text{MgWO}_4$ is made up of alternating zig-zag chains of edge-
 144 sharing $[\text{Mg}|\text{ErO}_6]$ and $[\text{WO}_6]$ polyhedra along the c -axis. The shortest distance Mg|Er -
 145 Mg|Er is $3.3323(4) \text{ \AA}$ is observed along the vector $[\text{u v w}]:[0 - 0.3950 0.5]$.

146 In MgWO_4 , erbium ions are expected to replace for the host-forming cations Mg^{2+} in a
 147 single type of sites ($2f$, site symmetry: C_2). The local charge compensation is most probably
 148 ensured by univalent Na^+ cations entering from the Na_2WO_4 solvent ($\text{Er}^{3+} + \text{Na}^+ \leftrightarrow 2\text{Mg}^{2+}$).
 149 The corresponding ionic radii for VI-fold oxygen coordination are: $R_{\text{Mg}} = 0.72 \text{ \AA}$,
 150 $R_{\text{Er}} = 0.89 \text{ \AA}$ and $R_{\text{Na}} = 1.02 \text{ \AA}$ [21]. Large ionic radii of the dopant and charge compensation
 151 cations determine the expansion of the unit-cell [for MgWO_4 , $a = 4.68892(2) \text{ \AA}$,
 152 $b = 5.67529(3) \text{ \AA}$, $c = 4.92891(2) \text{ \AA}$ and $\beta = 90.726(1) \text{ \AA}$] [20]. The difference in the charge
 153 and ionic radii of Mg^{2+} , Er^{3+} and Na^+ is expected to distort the crystal field around the Er^{3+}
 154 ions leading to additional spectral broadening.

155 **Table 1. Fractional Atomic Coordinates (x, y, z), Site Occupancy Factors (O.F.) and Isotropic**
 156 **Displacement Parameters B_{iso} (Å^2) for $\text{Er}^{3+}:\text{MgWO}_4$**

Atoms	Wyckoff	x	y	z	O.F.	B_{iso}
Mg	$2f$	1/2	0.6975(1)	1/4	0.98	0.753(7)
Er Na	$2f$	1/2	0.6975(1)	1/4	0.01	0.753(7)
W	$2e$	0	0.1853(6)	1/4	1	0.576(1)
O1	$4g$	0.2325(4)	0.1126(9)	0.9386(7)	1	0.954(1)
O2	$4g$	0.2536(1)	0.3864(1)	0.3864(2)	1	0.991(4)



157 **Fig. 3.** Electronic structure of MgWO_4 : (a) calculated band structure, E_g – bandgap energy; (b)
 158 calculated total and partial densities of states (TDOS and PDOS).
 159

160 The electronic structure of the host matrix, MgWO_4 , was analyzed by the density
 161 functional theory in which the generalized gradient approximation with the Perdew–Burke–
 162 Ernzerhof functional was used to study the exchange–correlation effects. The calculations
 163 were performed using the CASTEP code. The energy cutoff was set to 517 eV. The criterion
 164 for the self-consistent field was eigenenergy convergence within $2.0 \times 10^{-6} \text{ eV}$ per atom. K-
 165 space sampling was performed using a Monkhorst–Pack grid of $4 \times 4 \times 4$ atoms with respect
 166 to k -points in the irreducible Brillouin zone.

167 The results are shown in Fig. 3(a). The top of the valence band (VB) and the bottom of the
 168 conduction band (CB) are located at different points in the Brillouin zone (B and Y,
 169 respectively), indicating an indirect bandgap of $E_{g,calc} = 3.42$ eV. For Er³⁺-doped MgWO₄,
 170 $E_{g,calc}$ is higher, 3.47 eV, in agreement with the optical bandgap derived from the absorption
 171 spectrum using the Tauc plot [22], $E_g = 3.53$ eV. The assignment of electronic bands was
 172 performed with the help of calculated total and partial densities of states, Fig. 3(b). The VB
 173 band in the range from the Fermi energy level around 0 eV to -6.26 eV is mainly derived
 174 from the *p*-states of O. The CB extends from 3.42 to 22 eV and it is mainly due to the *p*- and
 175 *s*-states of Mg.

176 3. Polarized optical spectroscopy

177 3.1 Experimental

178 MgWO₄ is an optically biaxial crystal. For the polarization-resolved study, we have prepared
 179 a six-side polished rectangular sample oriented in the crystallographic frame by means of
 180 single-crystal XRD having the dimensions 4.39(*a*) × 4.15(*b*) × 4.35(*c*^{*}) mm³. Here, *c*^{*} is a
 181 direction being orthogonal to the *a*-axis and lying in the *a-c* plane (as the monoclinic angle of
 182 Er³⁺:MgWO₄ is close to 90°, *c*^{*} ≈ *c* below in the text).

183 The spectroscopic studies were performed at RT and low temperature (LT, 10 K). The
 184 absorption spectra were measured using a spectrophotometer (Lambda 1050, Perkin Elmer)
 185 and the luminescence spectra - by an optical spectrum analyzer (AQ6375B, Yokogawa). For
 186 polarization-resolved studies, a Glan-Taylor polarizer was implemented. The luminescence
 187 decay curves were measured using a nanosecond optical parametric oscillator (Horizon,
 188 Continuum), a 1/4 m monochromator (Oriel 77200), a PMT tube or an InGaAs detector and an
 189 8 GHz digital oscilloscope (DSA70804B, Tektronix). For LT studies, the crystal was mounted
 190 on an APD DE-202 closed-cycle cryo-cooler equipped with an APD HC 2 Helium vacuum
 191 cryo-compressor and a Laceshore 330 temperature controller.

192 3.1 Absorption spectra and Judd-Ofelt analysis

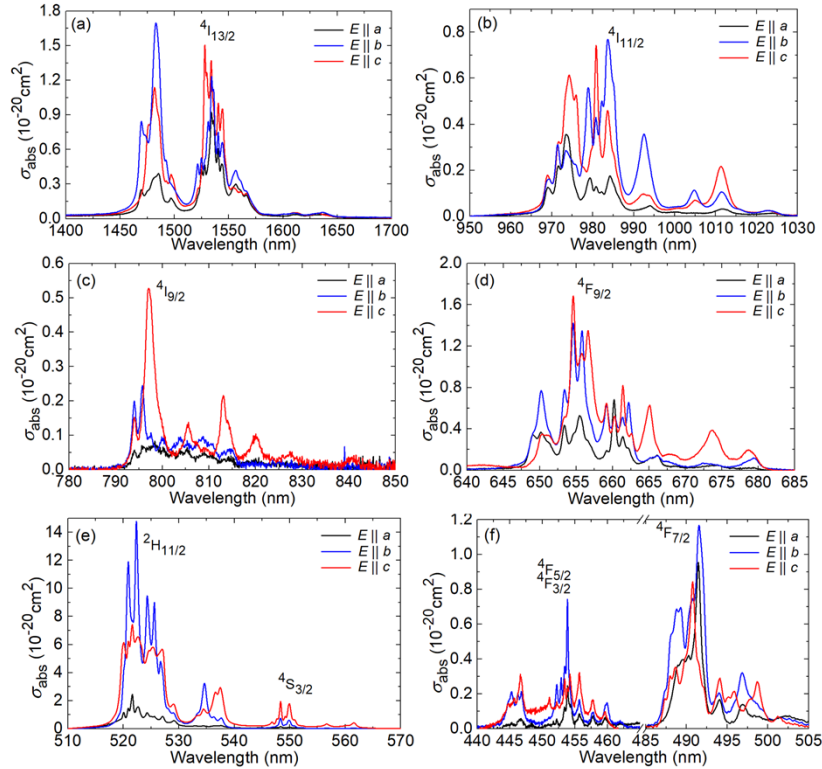
193 The RT polarized absorption spectra of Er³⁺ in MgWO₄ are shown in Fig. 4. The crystal
 194 exhibits a significant anisotropy of the absorption properties. For the ⁴I_{15/2} → ⁴I_{11/2} transition
 195 which can be addressed by commercial InGaAs diode lasers, the maximum absorption cross-
 196 section σ_{abs} is 0.77×10^{-20} cm² at 983.7 nm and the corresponding absorption bandwidth (full
 197 width at half maximum, FWHM) is 4.1 nm (for *E* ∥ *b*). Slightly lower $\sigma_{abs} = 0.74 \times 10^{-20}$ cm²
 198 at 980.8 nm is observed for *E* ∥ *c* at a much narrower bandwidth, 1.4 nm.

199 Er³⁺:MgWO₄ is also attractive for in-band pumping (directly into the ⁴I_{13/2} manifold): the
 200 maximum σ_{abs} is 1.70×10^{-20} cm² at 1482.9 nm and the absorption bandwidth is as broad as
 201 ~10 nm (for *E* ∥ *b*) and at longer wavelengths addressed by Er fiber lasers, $\sigma_{abs} = 1.51 \times 10^{-20}$
 202 cm² at 1528.0 nm with still broad absorption bandwidth of ~11 nm (for *E* ∥ *c*).

203 The 4fⁿ transition intensities of Er³⁺ were analyzed using the Judd-Ofelt (J-O) formalism
 204 based on the measured absorption spectra. Both the standard J-O theory [23,24] and its
 205 modification accounting for an intermediate configuration interaction (ICI) with an excited
 206 configuration of the opposite parity 4fⁿ⁻¹5d¹ [25,26] were implemented to determine the
 207 electric dipole (ED) contributions. The set of squared reduced matrix elements $U^{(k)}$
 208 (*k* = 2, 4, 6) for Er³⁺ was calculated in the present work based on the free-ion parameters
 209 reported in [27]. The magnetic dipole (MD) contributions to transition intensities (for
 210 transitions following the selection rule $\Delta J = 0, \pm 1$, except of 0 ↔ 0') were calculated here
 211 within the Russell-Saunders approximation on wave functions of Er³⁺ under an assumption of
 212 a free-ion. The refractive index data from [13] were used. More details can be found
 213 elsewhere [28].

214 Table 2 presents the experimental $\langle f_{exp} \rangle$ and calculated f_{calc} absorption oscillator strengths
 215 of Er³⁺ in MgWO₄. The obtained intensity parameters are $\Omega_2 = 11.111$, $\Omega_4 = 3.394$,

216 $\Omega_6 = 0.598 [10^{-20} \text{ cm}^2]$ for the J-O theory and $\Omega_2 = 11.480$, $\Omega_4 = 3.782$, $\Omega_6 = 0.703 [10^{-20}$
 217 $\text{ cm}^2]$, $R_2 = -0.154$, $R_4 = 0.518$, $R_6 = 0.064 [10^{-4} \text{ cm}]$ for the ICI approximation. Note that
 218 these intensity parameters are derived from polarization-averaged absorption oscillator
 219 strengths. The ICI model provided lower root mean square (r.m.s.) deviation between the
 220 $\langle f_{\text{exp}} \rangle$ and f_{calc} values, as well as better agreement between the radiative and measured
 221 lifetimes of the lowest-lying excited-state, $^4I_{13/2}$. Thus, it was selected for further calculations.



222
 223 **Fig. 4.** (a-f) RT (293 K) absorption cross-section, σ_{abs} , spectra of $\text{Er}^{3+}:\text{MgWO}_4$ crystal, the
 224 light polarizations are $E \parallel a, b, c$.

225 **Table 2. Judd-Ofelt Analysis^a of Transitions in Absorption for Er^{3+} in MgWO_4**

$^4I_{15/2} \rightarrow$ $^{2S+1}L_J$	$\langle E_j \rangle$, cm^{-1}	$\langle \Gamma \rangle$, cm^{-1}nm	$\langle f_{\text{exp}} \rangle$, 10^{-6}	f_{calc} , 10^{-6}	
				J-O	ICI
$^4I_{13/2}$	6561.4	69.798	2.427	$1.990^{\text{ED}} + 0.637^{\text{MD}}$	$1.534^{\text{ED}} + 0.637^{\text{MD}}$
$^4I_{11/2}$	10095	11.668	0.962	0.765^{ED}	0.922^{ED}
$^4I_{9/2}$	12226	4.411	0.539	0.876^{ED}	0.194^{ED}
$^4F_{9/2}$	15063	13.095	2.406	4.545^{ED}	2.797^{ED}
$^4S_{3/2}$	18211	3.080	0.813	0.330^{ED}	0.379^{ED}
$^2H_{11/2}$	19002	85.036	24.555	23.092^{ED}	24.379^{ED}
$^4F_{7/2}$	20270	6.024	1.978	2.469^{ED}	2.865^{ED}
$^4F_{5/2,3/2}$	22110	2.754	1.074	0.653^{ED}	0.787^{ED}
$^2G_{9/2}$	24465	1.458	0.696	0.772^{ED}	1.084^{ED}
$^4G_{11/2}$	26095	84.001	45.995	46.721^{ED}	46.095^{ED}
$^4G_{9/2}$	27222	10.841	6.410	3.335^{ED}	6.292^{ED}
r.m.s. dev.				1.590	0.764

226 ^a $\langle E_j \rangle$ - barycenter energy of the absorption band, $\langle \Gamma \rangle$ - polarization-averaged,
 227 $1/3(\Gamma_a + \Gamma_b + \Gamma_c)$, integrated absorption coefficient, $\int \alpha_{\text{abs}}(\lambda) d\lambda$; $\langle f_{\text{exp}} \rangle$ and f_{calc} -
 228 polarization-averaged experimental and calculated absorption oscillator strengths,
 229 respectively, ED - electric dipole, MD - magnetic dipole.
 230

231 The probabilities of spontaneous radiative transitions (A_{JJ}^{Σ} , where Σ indicates both
 232 ED + MD contributions), the mean luminescence wavelength $\langle\lambda\rangle$ calculated from the
 233 barycenter energies of the corresponding multiplets (cf. Table 2), the luminescence branching
 234 ratios B_{JJ} and the radiative lifetimes τ_{rad} are listed in Table 3 (all the values were calculated
 235 within the ICI approximation). For the upper laser level ${}^4I_{13/2}$, $\tau_{\text{rad}} = 4.78$ ms.

236

Table 3. Probabilities^a of Spontaneous Radiative Transitions of Er³⁺ in MgWO₄

Transition	$\langle\lambda\rangle$, nm	A_{JJ}^{Σ} , s ⁻¹	B_{JJ}	A_{tot} , s ⁻¹	τ_{rad} , μs
${}^4I_{13/2} \rightarrow$	${}^4I_{15/2}$ 1524.1	122.38 ^{ED} + 86.86 ^{MD}	1	209.24	4779.25
${}^4I_{11/2} \rightarrow$	${}^4I_{13/2}$ 2830.0	35.69 ^{ED} + 17.40 ^{MD}	0.133	400.31	2498.05
	${}^4I_{15/2}$ 990.6	347.22 ^{ED}	0.867		
${}^4I_{9/2} \rightarrow$	${}^4I_{11/2}$ 4692.6	2.76 ^{ED} + 2.42 ^{MD}	0.027	191.42	5223.97
	${}^4I_{13/2}$ 1765.3	57.41 ^{ED}	0.300		
	${}^4I_{15/2}$ 817.9	128.83 ^{ED}	0.673		
${}^4F_{9/2} \rightarrow$	${}^4I_{9/2}$ 3524.8	15.49 ^{ED} + 5.60 ^{MD}	0.006	3303.90	302.67
	${}^4I_{11/2}$ 2012.9	128.34 ^{ED} + 12.56 ^{MD}	0.043		
	${}^4I_{13/2}$ 1176.2	326.51 ^{ED}	0.099		
	${}^4I_{15/2}$ 663.9	2815.40 ^{ED}	0.852		
${}^4S_{3/2} \rightarrow$	${}^4F_{9/2}$ 3176.6	0.79 ^{ED}	0.0003	2382.92	419.65
	${}^4I_{9/2}$ 1670.8	286.84 ^{ED}	0.120		
	${}^4I_{11/2}$ 1232.1	67.60 ^{ED}	0.028		
	${}^4I_{13/2}$ 858.4	633.26 ^{ED}	0.266		
	${}^4I_{15/2}$ 549.1	1394.42 ^{ED}	0.586		
${}^2H_{11/2} \rightarrow$	${}^4F_{9/2}$ 2538.7	79.80 ^{ED} + 0.36 ^{MD}	0.002	34139.01	29.29
	${}^4I_{9/2}$ 1475.8	335.64 ^{ED} + 1.56 ^{MD}	0.010		
	${}^4I_{11/2}$ 1122.7	476.35 ^{ED} + 18.15 ^{MD}	0.014		
	${}^4I_{13/2}$ 803.8	547.22 ^{ED} + 142.88 ^{MD}	0.020		
	${}^4I_{15/2}$ 526.3	32536.54 ^{ED}	0.954		

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^a $\langle\lambda\rangle$ - mean emission wavelength, A_{JJ}^{Σ} - probability of spontaneous transitions ($J \rightarrow J'$), B_{JJ} - luminescence branching ratio, $A_{\text{tot}} = \sum_{J'} A_{JJ'}^{\Sigma}$ - total probability of spontaneous transitions from an excited-state, $\tau_{\text{rad}} = 1/A_{\text{tot}}$ - radiative lifetime, ED - electric dipole, MD - magnetic dipole. ICI model.

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3.2 Emission (spectra and lifetimes)

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The stimulated-emission (SE) cross-sections for the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er³⁺ were calculated using two complementary methods: the Füchtbauer–Ladenburg (F-L) equation [29] and the reciprocity method (RM) [30]. The combined SE cross-section spectra are shown in Fig. 5(a). The maximum σ_{SE} is 1.42×10^{-20} cm² at 1533.9 nm (for light polarization $\mathbf{E} \parallel \mathbf{c}$) corresponding to the zero-phonon line (ZPL) transition at RT (see below). At the wavelengths exceeding ZPL corresponding to the expected Er³⁺ laser emission (see the gain spectra), σ_{SE} is lower, namely 0.26×10^{-20} cm² at 1640 nm ($\mathbf{E} \parallel \mathbf{a}$), 0.31×10^{-20} cm² at 1637 nm ($\mathbf{E} \parallel \mathbf{b}$) and 0.26×10^{-20} cm² at 1633 nm ($\mathbf{E} \parallel \mathbf{c}$).

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A relatively good agreement between the σ_{SE} values calculated by both methods is achieved for a radiative lifetime of the ${}^4I_{13/2}$ state $\tau_{\text{rad}} = 4.85 \pm 0.05$ ms, Fig. 5(b). This value is in line with the J-O analysis. Lower SE cross-sections achieved by the F-L method at shorter wavelengths are due to the reabsorption affecting the measured luminescence spectra.

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Erbium ions represent a quasi-three-level laser scheme with intrinsic reabsorption (the ${}^4I_{13/2} \leftrightarrow {}^4I_{15/2}$ transition). Gain cross-sections, $\sigma_{\text{gain}} = \beta\sigma_{\text{SE}} - (1 - \beta)\sigma_{\text{abs}}$, where $\beta = N_2({}^4I_{13/2})/N_{\text{Er}}$ is the inversion ratio, are thus calculated to conclude about the expected laser wavelength and polarization. The calculated gain profiles for light polarizations $\mathbf{E} \parallel \mathbf{a}$ and $\mathbf{E} \parallel \mathbf{c}$ are shown in Fig. 6. For the high-gain polarization $\mathbf{E} \parallel \mathbf{a}$, a local peak at 1640 nm dominates in the spectra. The gain bandwidth (FWHM) is ~ 17 nm.

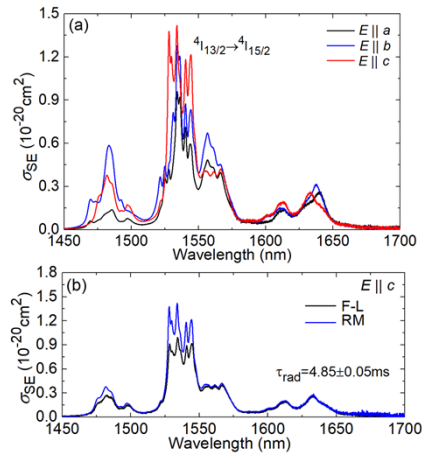


Fig. 5. Stimulated-emission (SE) cross-sections, σ_{SE} , for the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ Er^{3+} transition in $MgWO_4$: (a) combined spectra for $E \parallel a, b, c$; (b) a comparison of spectra calculated by the Fuchtbauer – Ladenburg (F-L) equation and the reciprocity method (RM), for $E \parallel c$.

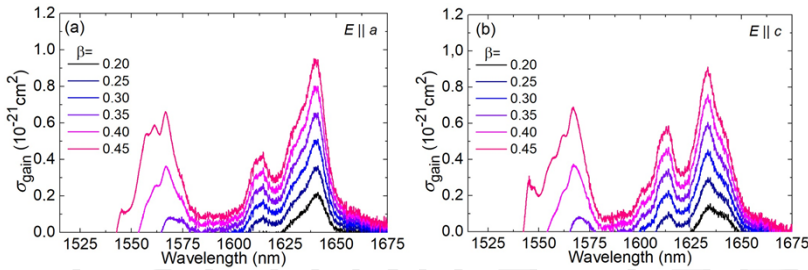
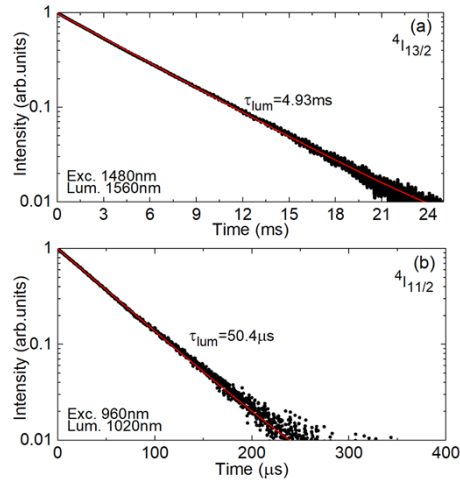


Fig. 6. RT gain cross-section, σ_{gain} , profiles for the ${}^4I_{13/2} \leftrightarrow {}^4I_{15/2}$ transition of Er^{3+} in $MgWO_4$: the light polarization is (a) $E \parallel a$ and (b) $E \parallel c$, β – inversion ratio.

RT luminescence decay curves from the ${}^4I_{13/2}$ and ${}^4I_{11/2}$ Er^{3+} multiplets are shown in Fig. 7. They were measured using a powdered crystal sample to reduce the effect of radiation trapping (reabsorption). The luminescence decay is single exponential in agreement with a single type of sites for Er^{3+} ions in $MgWO_4$ (C_2 symmetry). The luminescence lifetimes τ_{lum} are 4.93 ms and 50.4 μs , respectively. The luminescence lifetime of the ${}^4I_{13/2}$ metastable level is close to the radiative one obtained from the J-O calculations (4.78 ms) and from the evaluation of SE cross-sections (4.85 ms), indicating a luminescence quantum efficiency close to unity. The slightly longer value of τ_{lum} is probably due to residual reabsorption effect.

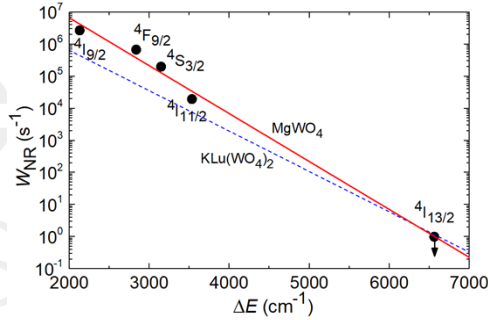
The relatively long lifetime of the upper laser level (for oxide crystals) makes $Er^{3+}:MgWO_4$ attractive for passively Q-switched lasers.

The luminescence lifetimes of five Er^{3+} excited states from ${}^4I_{13/2}$ to ${}^4S_{3/2}$ were measured to determine the rates of multiphonon non-radiative relaxation $W_{NR} = (1/\tau_{lum}) - (1/\tau_{rad})$, cf. Table 4. The values of W_{NR} were plotted vs. the energy gap between the emitting multiplet and the lower-lying manifold, ΔE , as shown in Fig. 8. The experimental points were fitted using the equation $W_{NR} = Ce^{-\alpha\Delta E}$, where C and α are constants characteristic of the material [31,32]. C has the meaning of a rate constant at the limit of zero energy gap ($\Delta E \rightarrow 0$), and $\alpha = -\ln(\epsilon)/(h\nu_{ph})$, where ϵ is the ratio between the probabilities of m -phonon and $m - 1$ -phonon relaxation and $h\nu_{ph}$ is the dominant (maximum) phonon energy of the host matrix. The experimental points in Fig. 8 are well fitted with the above-mentioned equation yielding the values of $C = 6.5 \pm 0.3 \times 10^9 s^{-1}$ and $\alpha = 3.44 \pm 0.1 \times 10^{-3} cm$. The multiphonon relaxation in $MgWO_4$ is slightly stronger than that in the monoclinic $KLu(WO_4)_2$ crystal [31] owing to the high maximum phonon energy of the former material ($h\nu_{ph} = 916 cm^{-1}$ [11]).



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Fig. 7. RT luminescence decay curves from the $^4I_{13/2}$ (a) and $^4I_{11/2}$ (b) multiplets of Er^{3+} in $MgWO_4$: circles – experimental data, lines – single-exponential fits.



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Fig. 8. The rate of multiphonon non-radiative relaxation W_{NR} vs. the energy gap to the lower-lying manifold ΔE for Er^{3+} in $MgWO_4$: circles – data obtained from luminescence lifetime measurements, red solid line – their fit, blue dashed line – fit for $KLu(WO_4)_2$ [31].

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Table 4. Evaluation^a of Non-Radiative Relaxation Rates for Er^{3+} in $MgWO_4$

Excited state	ΔE , cm^{-1}	τ_{rad} , μs	τ_{lum} , μs	W_{NR} , s^{-1}
$^4I_{13/2}$	6561	4779.25	4930	<1
$^4I_{11/2}$	3534	2498.05	50.4	1.94×10^4
$^4I_{9/2}$	2131	5223.97	0.37	2.70×10^6
$^4F_{9/2}$	2837	302.67	1.47	6.77×10^5
$^4S_{3/2}$	3148	419.65	4.94	2.00×10^5

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^a τ_{lum} and τ_{rad} – luminescence and radiative lifetimes, respectively, ΔE – energy-gap between the barycenters of the emitting state and the lower-lying manifold, W_{NR} – non-radiative relaxation rate.

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3.3 Low-temperature spectroscopy

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LT absorption and luminescence spectra were measured to determine the Stark splitting of the upper ($^4I_{13/2}$) and lower ($^4I_{15/2}$) laser multiplets of Er^{3+} , cf. Fig. 9(a,b). The assignment of the electronic transitions followed previous work on Er^{3+} -doped $KLu(WO_4)_2$ crystal [33]. For C_2 symmetry sites, each $2S+1L_J$ multiplet with non-integer J is split into $J + 1/2$ Stark sub-levels. All the sub-levels are identified from the measured spectra leading to the energy-level scheme shown in Fig. 9(c). The partition functions for the lower and upper laser manifolds are $Z_l = 4.534$ and $Z_u = 4.343$, respectively, and their ratio $Z_l/Z_u = 1.044$ (these data were used for the calculation of SE cross-sections via RM).

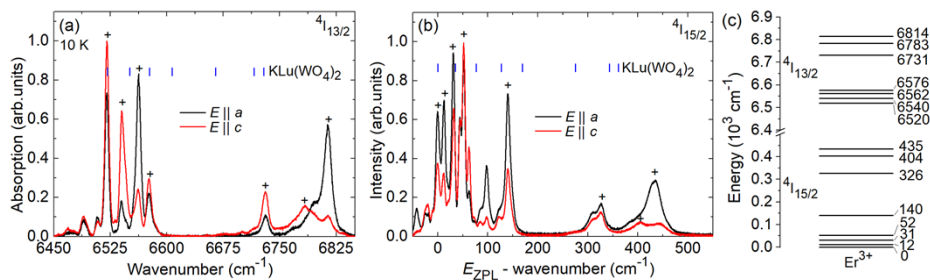


Fig. 9. (a,b) LT (10 K) (a) absorption and (b) luminescence spectra of Er^{3+} in the MgWO_4 crystal corresponding to the ${}^4I_{15/2} \leftrightarrow {}^4I_{13/2}$ transition, “+” - assigned electronic transitions, *dashes* – electronic transitions for Er^{3+} in $\text{KLu}(\text{WO}_4)_2$ crystal [33]; (c) experimental Stark splitting of the ${}^4I_{15/2}$ and ${}^4I_{13/2}$ Er^{3+} multiplets, *numbers* indicate the sub-level energies in cm^{-1} .

The energy of the ZPL transition occurring between the lowest Stark sub-levels of both multiplets E_{ZPL} is 6520 cm^{-1} (1533.7 nm). The total Stark splitting of the lower laser level (${}^4I_{15/2}$) is 435 cm^{-1} which is larger than that for Er^{3+} in $\text{KLu}(\text{WO}_4)_2$, 361 cm^{-1} [33]. This is attributed to the stronger crystal field for distorted C_2 sites in MgWO_4 . Large total Stark splitting of the ground-state explains the relatively long emission wavelengths (cf. Fig. 5) and is beneficial for low threshold laser operation.

4. Conclusion

To conclude, Er^{3+} -doped MgWO_4 is a promising gain material for eye-safe lasers emitting at $\sim 1.6 \mu\text{m}$. It exhibits (i) relatively intense and broad absorption bands around $\sim 1.54 \mu\text{m}$ which is attractive for in-band pumping, (ii) high stimulated-emission cross-sections for polarized light potentially leading to naturally polarized laser emission, (iii) broad emission bands making it feasible to access laser wavelengths at $\sim 1.62 - 1.64 \mu\text{m}$ similarly to $\text{Er}:\text{YAG}$ and (iv) relatively long upper laser level lifetime and high luminescence quantum efficiency which is attractive for low-threshold operation, as well as generation of giant pulses in Q-switched lasers. In addition, as shown in previous work, MgWO_4 features good thermal properties. The observed broad, intense and polarized spectral bands for $\text{Er}^{3+}:\text{MgWO}_4$ are assigned to low-symmetry (C_2) coordination of Er^{3+} ions replacing for the host-forming Mg^{2+} cations which is distorted by the heteroallene doping mechanism involving univalent Na^+ cations, i.e., the difference in the charge and the ionic radii of Mg^{2+} , Er^{3+} and Na^+ .

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Data availability. Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

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