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Tm³⁺-doped calcium lithium tantalum gallium garnet (Tm:CLTGG): Novel laser crystal

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Abstract: We report on the development of a novel laser crystal with broadband emission properties at $\sim 2 \mu\text{m}$ – a Tm³⁺,Li⁺-codoped calcium tantalum gallium garnet (Tm:CLTGG). The crystal is grown by the Czochralski method. Its structure (cubic, sp. gr. $Ia\bar{3}d$, $a = 12.5158(0) \text{ \AA}$) is refined by the Rietveld method. Tm:CLTGG exhibits a relatively high thermal conductivity of $4.33 \text{ Wm}^{-1}\text{K}^{-1}$. Raman spectroscopy confirms weak concentration of vacancies due to the charge compensation provided by Li⁺ codoping. The transition probabilities of Tm³⁺ ions are determined using the modified Judd-Ofelt theory yielding the intensity parameters $\Omega_2 = 5.185$, $\Omega_4 = 0.650$, $\Omega_6 = 1.068 [10^{-20} \text{ cm}^2]$ and $\alpha = 0.171 [10^{-4} \text{ cm}]$. The crystal-field splitting of the Tm³⁺ multiplets is revealed at 10 K. The first diode-pumped Tm:CLTGG laser generates 1.08 W at $\sim 2 \mu\text{m}$ with a slope efficiency of 23.8%. The Tm³⁺ ions in CLTGG exhibit significant inhomogeneous spectral broadening due to the structure disorder (a random distribution of Ta⁵⁺ and Ga³⁺ cations over octahedral and tetrahedral lattice sites) leading to smooth and broad gain profiles (bandwidth: 130 nm) extending well above $2 \mu\text{m}$ and rendering Tm:CLTGG suitable for femtosecond pulse generation.

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1. Introduction

An ordered crystal is an ideal solid state material exhibiting lattice periodicity in all directions. The certain arrangement of atoms in the unit-cell is repeated forming a translationally invariant crystal structure in the long-range. A disorder of the structure denotes some deviation from a perfect crystalline order. Weak disorder can be represented as a perturbation of the crystalline structure, e.g., caused by dopants, defects, vacancies and / or dislocations. Strong disorder is a

46 pronounced departure from the crystalline order. The length scale over which order, or disorder
47 persists is also relevant. The local disorder can be revealed at a length of several unit-cells.

48 In laser physics, structurally disordered crystals constitute an important class of gain
49 materials [1]. In such crystals, one or several host-forming cations are randomly distributed
50 over two or more different crystallographic sites. Two situations for the dopant (laser-active)
51 ions can be thus distinguished: (i) the dopant ions are distributed over several lattice sites [1]
52 or (ii) they are present at one site while other cations experience a random site distribution [2].
53 In both cases, the spectral bands of dopant ions will experience an inhomogeneous broadening
54 either due to the presence of several crystal-fields or due to the different cation multi-ligands
55 around the dopant ions. Such spectral broadening is favorable for broad tuning of the laser
56 wavelength and / or the generation of ultrashort pulses in mode-locked (ML) lasers. Note that
57 there also exists compositional disorder in “mixed” (solid-solution) materials $A_{1-x}B_x$, even
58 when the parent compounds (A and B) are ordered [3]. This also results in spectral broadening.
59 The main drawback of disordered crystals is the deterioration of their thermal properties which
60 justifies the search for such crystals with high thermal conductivity.

61 Among the host crystals for doping with laser-active rare-earth ions (RE^{3+}), cubic
62 multicomponent garnets with general chemical formula $\{A\}_3\{B\}_2\{C\}_3O_{12}$ where A = Y, Gd, Lu
63 or Ca, Mg, Fe, Sr, etc., and B and C = Al, Sc, Ga, Ta, etc., occupy a special position. Note that
64 the ordered garnet $Y_3Al_5O_{12}$ (YAG) is the most widespread laser host crystal. Crystals
65 belonging to the cubic garnet family combine good thermo-mechanical behavior with attractive
66 spectroscopic properties of the dopant RE^{3+} ions. They are optically isotropic. Finally, cubic
67 garnets can be grown by the well-developed Czochralski (Cz) method.

68 Among the structurally disordered multicomponent garnets, calcium niobium gallium
69 garnet (CNGG) is one of the best known representatives [4,5]. The structure disorder of CNGG
70 originates from a random distribution of Nb^{5+} and Ga^{3+} cations over [B] and [C] lattice sites
71 leading to a significant inhomogeneous broadening of the emission bands of the RE^{3+} dopant
72 ions. The latter are expected to replace for the divalent Ca^{2+} cations; the charge compensation
73 is provided by vacancies [6] or by intentional codoping by univalent alkali ions (Na^+ , Li^+ or
74 their combination) [7,8] further affecting the spectral broadening [9].

75 Recently, CNGG-type crystals doped with thulium (Tm^{3+}) [10] and holmium (Ho^{3+}) [11]
76 ions have proven to be very suitable for the generation of sub-100 fs pulses at $\sim 2 \mu m$ owing to
77 their smooth and very broad gain profiles extending beyond the structured water vapor air
78 absorption [12] which is essential for the broadband ML laser performance. Pan *et al.* reported
79 on a Tm,Na:CNGG (Tm:CNNGG) laser mode-locked by a single-walled carbon nanotube
80 saturable absorber (SA) delivering 84-fs pulses at 2018 nm [10]. In the continuous-wave (CW)
81 regime, a broad tuning range of 1879 – 2086 nm was achieved in the same work [10]. Zhao *et al.*
82 achieved shorter pulses (67 fs, i.e., 10 optical cycles at 2083 nm) from a Tm,Ho,Li:CNGG
83 (Tm,Ho:CLNGG) laser ML by the same SA utilizing the combined gain bandwidths from both
84 active ions [13].

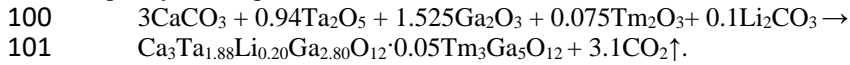
85 There exists another disordered multicomponent garnet similar to CNGG, namely calcium
86 tantalum gallium garnet (CTGG) [14]. Ma *et al.* have shown that CTGG exhibits higher thermal
87 conductivity ($\kappa = 3.76 \text{ Wm}^{-1}\text{K}^{-1}$) as compared to its niobium counterpart [14]. CTGG-type
88 crystals doped with Nd^{3+} and Yb^{3+} ions have been studied for laser operation at $\sim 1 \mu m$ [15,16].
89 However, no lasing in the $\sim 2 \mu m$ spectral range has been reported so far.

90 In the present work, we reveal the potential of Tm^{3+} , Li^+ -codoped CTGG (abbreviated
91 Tm:CLTGG) as a broadband laser gain material at $\sim 2 \mu m$ and beyond.

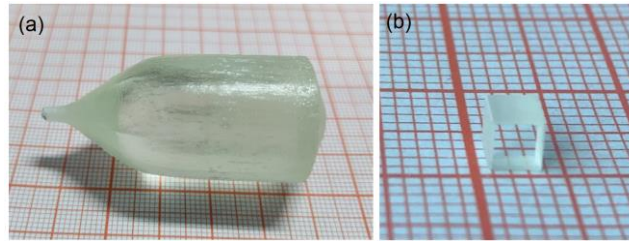
92 2. Crystal growth

93 A Tm:CLTGG single crystal was grown by the Czochralski (Cz) method in an iridium crucible
94 using argon atmosphere. The starting materials, $CaCO_3$ (purity: 4N), Ta_2O_5 , Ga_2O_3 , Li_2CO_3 and
95 Tm_2O_3 (purity: 5N), were weighed according to the following chemical formula:
96 $Ca_3Ta_{1.88}Li_{0.20}Ga_{2.80}O_{12} \cdot 0.05Tm_3Ga_5O_{12}$. To compensate the volatilization of Ga_2O_3 during the

97 synthesis of the polycrystalline material and the crystal growth, an excess of 1.0 wt% Ga₂O₃
98 was used. Larger excess of Ga₂O₃ violates the composition of the crystal and affects its optical
99 quality. The equation of the chemical reaction reads:



102 The raw materials were mixed, ground and heated at 900 °C for 10 h in a platinum crucible
103 to decompose CaCO₃. After cooling down the crucible to room temperature (RT, 20 °C), the
104 mixture was pressed into tablets and reheated at 1200 °C for 15 h to form the cubic garnet phase
105 through a solid-state reaction. The synthesized polycrystalline material was placed in an iridium
106 crucible and melted by an intermediate-frequency heater. The first crystal was grown using an
107 [111] oriented seed from undoped YAG. From this first crystal, another seed with the same
108 orientation was cut and used for the growth of laser-quality crystals. During the crystal growth,
109 the pulling rate varied from 0.5 to 1.0 mm/h and the crystal rotation speed was kept at 8 to 15
110 revolutions per minute. Once the growth was completed, the crystal was removed from the melt
111 and cooled down to RT at a stepped rate of 15 to 25 °C/h. The crystal was annealed in air, the
112 maximum temperature was 1200 °C and the hold duration was 24 h, the heating and cooling
113 rates were about 50 °C/h.



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Fig. 1. (a) Photograph of the as-grown Tm:CLTGG crystal boule, the growth direction is [111];
(b) photograph of a polished laser element.

117 Figure 1 shows a photograph of an as-grown Tm:CLTGG crystal boule. It has a cylindrical
118 shape (diameter: 20 mm, length of the central part: 30 mm). The crystal does not contain cracks
119 and inclusions and no scatter centers are seen under illumination by a He-Ne laser indicating
120 good optical quality. The as-grown crystal shows a light greenish coloration. The surface of the
121 boule is translucent probably due to the volatilization of Ga₂O₃ during the crystal growth (it
122 may attack the surface of the crystal that is pulled over the melt). The internal part of the crystal
123 exhibits excellent transparency, Fig. 1(b).

124 By using X-ray fluorescence, the actual concentration of Tm³⁺ ions was measured to be 3.17
125 at.% with respect to Ca²⁺ ions ($N_{\text{Tm}} = 5.03 \times 10^{20} \text{ cm}^{-3}$) leading to a segregation coefficient K_{Tm}
126 of 0.67. The targeted doping concentration of ~3 at.% Tm was selected due to the spectroscopic
127 considerations. It could be further increased by changing the Tm content in the growth batch
128 considering the determined K_{Tm} value.

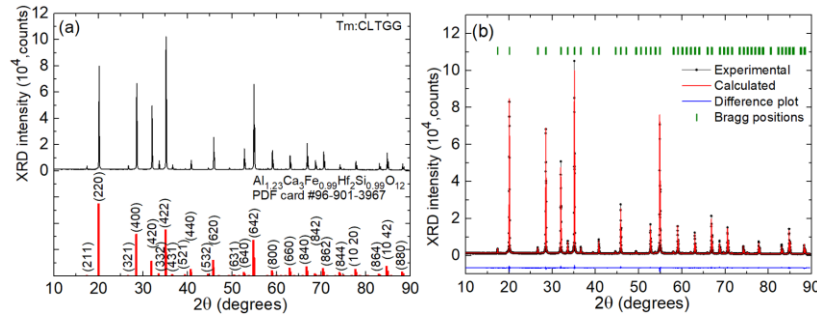
129 3. Crystal structure

130 3.1 X-ray diffraction

131 The X-ray powder diffraction (XRD) pattern was measured at RT using a Bruker D2 Phaser
132 diffractometer, Cu K α 1 radiation (1.54184 Å) with a step size of 0.02° and a step time of 1.0 s,
133 in the range of 2 θ from 10° to 90°. The measured diffraction pattern, Fig. 2(a), agrees well with
134 the theoretical one for cubic Al_{1.23}Ca₃Fe_{0.99}Hf₂Si_{10.99}O₁₂ garnet (Crystallography Open Database
135 (COD) card #96-901-3967). No other phases are found.

136 The structure of Tm:CLTGG was refined using the Rietveld method. The Match3! software
137 was used and a total of 196 reflections were analyzed. The obtained reliability factors are $R_p =$
138 4.94%, $R_{wp} = 6.38\%$, $R_{exp} = 2.21\%$ and the reduced chi squared $\chi^2 = (R_{wp}/R_{exp})^2 = 8.37$.

139 Tm:CLTGG crystallizes in the cubic class (sp. gr. $Ia\bar{3}d$, No. 230) with a lattice constant $a =$
 140 $12.5158(0) \text{ \AA}$, the volume of the unit-cell is $V = 1960.54 \text{ \AA}^3$, the calculated density is $\rho_{\text{calc}} =$
 141 5.893 g/cm^3 and the number of formula units in the unit-cell is $Z = 8$. The fractional atomic
 142 coordinates, the site occupancy factors (O.F.) and the isotropic displacement parameters
 143 obtained during the Rietveld refinement are listed in Table 1.



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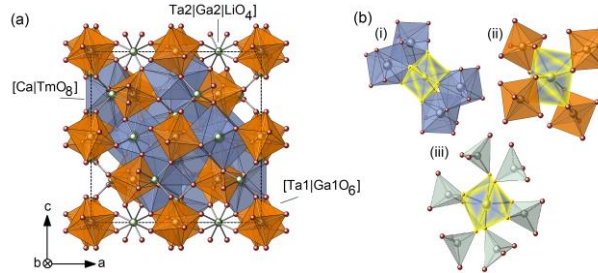
Fig. 2. X-ray powder diffraction study of Tm:CLTGG: (a) XRD pattern, (hkl) are Miller's indices, vertical bars – theoretical pattern for $Al_{1.23}Ca_3Fe_{0.99}Hf_2Si_{0.99}O_{12}$ garnet; (b) Rietveld structure refinement: experimental (black), calculated (red) and differential (blue) XRD profiles, vertical dashes mark the Bragg reflections.

149 **Table 1. Fractional Atomic Coordinates, Occupancy Factors and Isotropic Displacement Parameters for**
 150 **Tm:CLTGG Crystal**

Atoms	Wyckoff	$ x/a $	$ y/b $	$ z/c $	O.F.	$ B_{\text{iso}}, \text{ \AA}^2 $
Ca	24c	1/8	0.0000(0)	1/4	0.963	0.722(7)
Tm	24c	1/8	0.0000(0)	1/4	0.031	0.722(7)
Ta1	16a	0.0000(0)	0.0000(0)	0.0000(0)	0.660	0.253(1)
Ga1	16a	0.0000(0)	0.0000(0)	0.0000(0)	0.340	0.253(1)
Ga2	24d	0.3750(0)	0.0000(0)	1/4	0.789	0.481(4)
Ta2	24d	0.3750(0)	0.0000(0)	1/4	0.068	0.481(4)
Li	24d	0.3750(0)	0.0000(0)	1/4	0.115	0.481(4)
O	96h	-0.0295(1)	0.0492(1)	0.1482(9)	1	0.826(0)

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The structure of Tm:CLTGG is illustrated in Fig. 3. This crystal belongs to the family of multicomponent garnets with a general formula $\{A\}_3\{B\}_2\{C\}_3O_{12}$, where $\{A\}$, $\{B\}$, and $\{C\}$ stand for dodecahedral (Wyckoff symbol: 24c), octahedral (16a) and tetrahedral (24d) sites, respectively [5]. The stoichiometric CTGG, in analogy to CNGG [4], is expected to have a chemical formula of $Ca_3Ta_{1.5}Ga_{3.5}O_{12}$ which is equivalent to $\{Ca_3\}[Ta_{1.5}Ga_{0.5}](Ga_3)O_{12}$. The composition of the real crystal (even undoped) deviates from the stoichiometric one. The Ca^{2+} cations are located in the $\{A\}$ sites.



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Fig. 3. Crystal structure of Tm:CLTGG: (a) a fragment of the crystal structure within one unit-cell (dashed lines) in projection to the $a-c$ plane; (b) the variety of cationic distributions around $Ca^{2+} | Tm^{3+}$ ions occupying the dodecahedral 24c sites: nearest-neighbor cations at: (i) dodecahedral 24c sites, (ii) octahedral 16a sites and (iii) tetrahedral 24d sites.

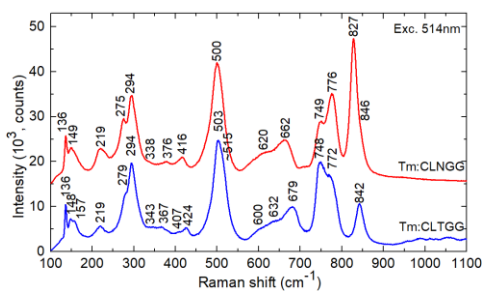
164 The Tm^{3+} ions replace for the Ca^{2+} ones (the corresponding ionic radii are $R_{\text{Ca}} = 1.12 \text{ \AA}$ and
 165 $R_{\text{Tm}} = 0.994 \text{ \AA}$ for VIII-fold oxygen coordination). In the $[\text{Ca}|\text{TmO}_8]$ dodecahedrons, there are
 166 four shorter ($2.3966(2) \text{ \AA}$) and four longer ($2.5577(0) \text{ \AA}$) metal-to-oxygen (M-O) interatomic
 167 distances. The Ta^{5+} and Ga^{3+} cations are randomly distributed over the [B] and (C) sites with
 168 VI-fold and IV-fold oxygen coordination, respectively, according to the occupancy factors
 169 listed in Table 1. The M-O bond lengths are $1.990(0) \text{ \AA}$ ($\times 6$) and $1.8526(1) \text{ \AA}$ ($\times 4$), respectively.
 170 The Li^+ ion incorporation in this garnet takes place only at $24d$ sites. The charge compensation
 171 is ensured by both, Li^+ ions and cationic vacancies \square in the $24c$ and $24d$ sites. Their calculated
 172 percentages are 0.6% and 2.8%, respectively. The chemical formula of the crystal can be thus
 173 expressed as follows:



174 In the Tm:CLTGG structure, each $[\text{Ca}|\text{TmO}_8]$ dodecahedron shares edges with four other
 175 dodecahedra where the shortest interatomic distance $\text{Ca}|\text{Tm}-\text{Ca}|\text{Tm}$ is $3.8321(1) \text{ \AA}$, and it is
 176 surrounded by four corner-sharing octahedra (Ta^{5+} and Ga^{3+} at $16a$ sites) and by six tetrahedra
 177 (Ga^{3+} , Ta^{5+} and Li^+ at $24d$ sites), two of them sharing edges, and the remaining four being
 178 connected by shared corners.
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180 3.2 Raman spectroscopy

181 The Raman spectrum of Tm:CLTGG was measured using a Renishaw inVia confocal Raman
 182 microscope with a $\times 50$ Leica objective and an Ar^+ ion laser (514 nm). It is shown in Fig. 4. In
 183 the same figure, for comparison, we also show the Raman spectrum of its niobium isomorph,
 184 Tm:CLNGG. A total of 18 bands are resolved in the Raman spectrum of Tm:CLTGG. Among
 185 them, the vibrations at high frequencies ($700\text{-}900 \text{ cm}^{-1}$) forming two broad bands are typically
 186 analyzed as they are sensitive to the alteration of the structure of multicomponent garnets [4,5].
 187 They are assigned to internal vibrations (symmetric stretching modes, ν_s) of $[\text{M}_2\text{O}_4]$ tetrahedra
 188 ($\text{M}_2 = \text{Ga}_2$ and Ta_2). In our case, the tetrahedral sites ($24d$) are occupied by Ta^{5+} and Ga^{3+}
 189 cations. The band at lower frequencies with two local maxima at 748 cm^{-1} (C_1) and 772 cm^{-1}
 190 (C_2), is assigned to the $[\text{Ga}_2\text{O}_4]$ groups and it is only slightly distorted with respect to that in
 191 the Tm:CLNGG crystal. The band at higher frequencies, at 842 cm^{-1} (C_4), is due to the $[\text{Ta}_2\text{O}_4]$
 192 groups. The latter does not split, possesses much weaker intensity and is shifted to higher
 193 frequencies as compared to that in Tm:CLNGG crystal with $[\text{Nb}_2\text{O}_4]$ groups. The lack of the
 194 long-frequency component of the second band indicates weak structural distortion of the
 195 $[\text{Ta}_2\text{O}_4]$ tetrahedra and weak content of cationic vacancies, in agreement with the XRD study.
 196 This highlights the positive role of Li^+ ions in the charge compensation.



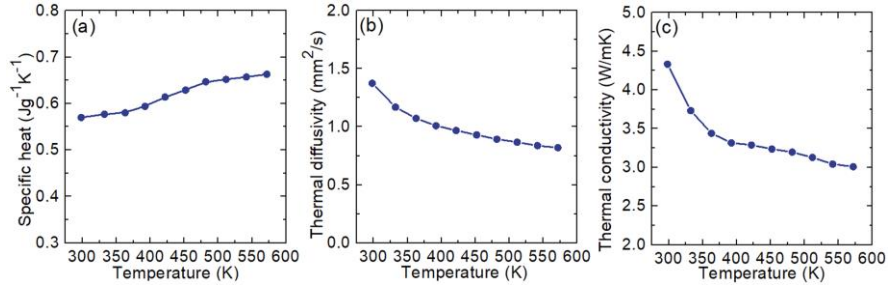
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198 Fig. 4. Unpolarized RT Raman spectrum of the Tm:CLTGG crystal, $\lambda_{\text{exc}} = 514 \text{ nm}$. Numbers
 199 indicate the band frequencies in cm^{-1} . The Raman spectrum of Tm:CLNGG is given for
 200 comparison.

201 4. Thermal properties

202 The specific heat C_p and the thermal diffusivity λ were measured using a laser flash apparatus
 203 (NETZSCH LFA457). For this, a squared wafer with dimensions of $4 \times 4 \times 1 \text{ mm}^3$ was cut from
 204 the Tm:CLTGG crystal along the $[111]$ direction and double side coated with graphite.

205 The dependence of the specific heat (C_p) of Tm:CLTGG on temperature is shown in
 206 Fig. 5(a). The C_p value increases monotonously with temperature, from 0.57 to 0.66 J g⁻¹ K⁻¹,
 207 when the temperature is increased from 298.2 K to 571.9 K. Figure 5(b) shows the measured
 208 thermal diffusivities (λ). The λ value along the [111] direction decreases with temperature. At
 209 298.2 K, it amounts to 1.374 mm²/s. Finally, the thermal conductivity along the [111] direction
 210 was calculated using the formula $\kappa = \lambda \times \rho \times C_p$ where $\rho = 5.53$ g/cm³ is the crystal density
 211 measured using the buoyancy method. The thermal conductivity decreases with temperature,
 212 Fig. 5(c). At room temperature, it amounts to 4.33 Wm⁻¹K⁻¹, which is larger than for CNGG-
 213 type crystals [4,20]. The value of thermal conductivity for Tm:CLTGG is higher than that for
 214 undoped CTGG (3.76 Wm⁻¹K⁻¹) [14]. We refer this to the effect of Li⁺ codoping on eliminating
 215 the cationic vacancies and increasing the thermal conductivity. This effect seems to overcome
 216 the negative role of rare-earth doping which typically tends to decrease κ .



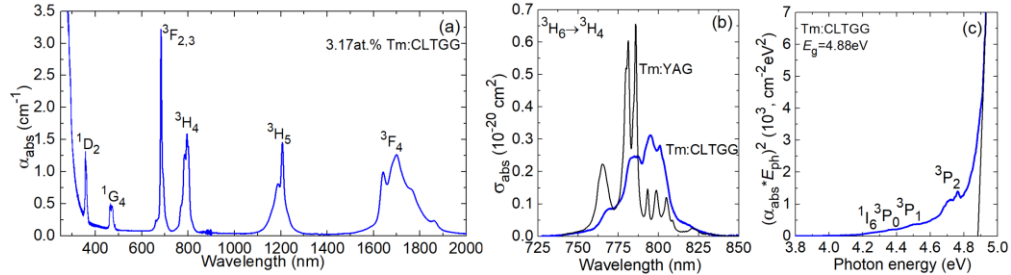
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Fig. 5. Thermal properties of the Tm:CLTGG crystal as a function of temperature: (a) specific heat; (b) thermal diffusivity; (c) thermal conductivity.

220 5. Optical spectroscopy

221 5.1 Optical absorption

222 The absorption spectrum was measured using a Varian CARY 5000 spectrophotometer. The
 223 cubic Tm:CLTGG is optically isotropic. The unpolarized RT absorption spectrum of
 224 Tm:CLTGG is shown in Fig. 6(a). In the spectrum, the well-resolved absorption bands are
 225 related to transitions of Tm³⁺ ions from the ground-state (³H₆) to excited-states (from ³F₄ to ¹D₂,
 226 in increasing energy order).



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Fig. 6. Absorption of the Tm:CLTGG crystal: (a) RT absorption spectrum; (b) absorption cross-sections, σ_{abs} , for the ³H₆ → ³H₄ Tm³⁺ transition; (c) Tauc plot for the evaluation of the optical bandgap (E_g).

231 The absorption cross-sections σ_{abs} for the ³H₆ → ³H₄ Tm³⁺ transition which is suitable for
 232 pumping of laser crystals by AlGaAs diode lasers emitting at ~0.8 μm are shown in Fig. 6(b).
 233 The maximum σ_{abs} is 0.31×10^{-20} cm² at 795.0 nm and the absorption bandwidth (full width at
 234 half maximum, FWHM) is 26.7 nm. Compared to the widespread Tm:Y₃Al₅O₁₂ garnet crystal,
 235 Tm:CLTGG exhibits smoother and broader absorption at the expense of lower cross-section.

236 This represents the effect of inhomogeneous broadening caused by the structural disorder and,
 237 in particular, the different cationic distributions around the Tm^{3+} ions, cf. Fig. 3(b).

238 The absorption spectrum of $\text{Tm}:\text{CLTGG}$ reveals no significant absorption in the visible
 239 from color centers related to cationic vacancies. This indicates charge compensation via Li^+
 240 doping. Figure 6(c) shows the Tauc plot for the determination of the UV absorption edge
 241 (assuming indirect transitions). The optical bandgap energy E_g is 4.88 eV (0.254 μm). At the
 242 onset of the host absorption, weak absorption bands due to transitions of Tm^{3+} ions to higher-
 243 lying $^1\text{I}_6$ and $^3\text{P}_{0,2}$ states are found.

244 5.2 Judd-Ofelt analysis

245 The transition intensities for Tm^{3+} ions were calculated from the absorption spectrum using the
 246 standard Judd-Ofelt (J-O) theory [17,18], and its modification accounting for configuration
 247 interaction (mJ-O theory) [19]. This formalism was used to determine the contributions of
 248 electric dipoles (ED). The magnetic dipole (MD) contributions for transitions with $\Delta J = J - J'$
 249 $= 0, \pm 1$ were calculated independently within the approximation of Russell-Saunders on the
 250 wave functions of Tm^{3+} under an assumption of a free-ion. The refractive index of CLTGG was
 251 taken from [20].

252 The detailed procedure of the J-O calculations for Tm^{3+} -doped crystals is described in detail
 253 elsewhere [21]. Here, we only discuss the main approximations. For the standard J-O theory,
 254 the ED line strengths of the $J \rightarrow J'$ transition are given by:

$$255 S_{\text{calc}}^{\text{ED}}(JJ') = \sum_{k=2,4,6} U^{(k)} \Omega_k, \quad (1a)$$

$$256 U^{(k)} = \langle (4f^n)SLJ || U^{(k)} || (4f^n)S'L'J' \rangle^2. \quad (1b)$$

257 Here, $U^{(k)}$ are the reduced squared matrix elements which were calculated using the free-ion
 258 parameters from [22] and Ω_k are the intensity (J-O) parameters (for both, $k = 2, 4, 6$).

259 In the mJ-O theory, it is assumed that only the excited configuration of opposite parity $4f^{n-1}5d^1$
 260 contributes to the configuration interaction. The ED line strengths are then [19]:

$$261 S_{\text{calc}}^{\text{ED}}(JJ') = \sum_{k=2,4,6} U^{(k)} \tilde{\Omega}_k, \quad (2a)$$

$$262 \tilde{\Omega}_k = \Omega_k [1 + 2\alpha(E_J + E_{J'} - 2E_f^0)]. \quad (2b)$$

263 In other words, the intensity parameters $\tilde{\Omega}_k$ are linear functions of energies (E_J and $E_{J'}$) of the
 264 two multiplets, where E_f^0 is the mean energy of the $4f^n$ configuration and $\alpha \approx 1/(2\Delta)$ where $\Delta \approx$
 265 $E(4f^{n-1}5d^1) - E(4f^n)$ is the average energy difference between the fundamental and first excited
 266 configurations.

267 **Table 2. Measured and Calculated Absorption Oscillator Strengths of Tm^{3+} ions in CLTGG crystal^a**

Transition	$\langle E \rangle$, cm^{-1}	Γ , $\text{nm} \times \text{cm}^{-1}$	f_{exp} , 10^{-6}	$f_{\text{calc}}^{\text{ED}}$, 10^{-6}	mJ-O
$^3\text{H}_6 \rightarrow ^{2S+1}\text{L}_J$				J-O	
$^3\text{F}_4$	5823	215.51	1.641	1.649 ^{ED}	1.583 ^{ED}
$^3\text{H}_5$	8363	76.642	1.211	1.317 ^{ED} +0.534 ^{MD}	1.058 ^{ED} +0.534 ^{MD}
$^3\text{H}_4$	12628	51.696	1.859	2.139 ^{ED}	2.810 ^{ED}
$^3\text{F}_{3,2}$	14568	44.848	2.137	3.073 ^{ED}	2.521 ^{ED}
$^1\text{G}_4$	21182	7.750	0.791	0.568 ^{ED}	1.101 ^{ED}
$^1\text{D}_2$	27686	10.607	1.849	1.815 ^{ED}	1.783 ^{ED}
$^1\text{I}_6 + ^3\text{P}_0 + ^3\text{P}_1$	35239	13.677	3.811	1.690 ^{ED} +0.029 ^{MD}	3.017 ^{ED} +0.029 ^{MD}
$^3\text{P}_2$	38067	6.665	2.166	1.958 ^{ED}	2.270 ^{ED}
r.m.s. dev.				1.078	0.689

268 ^a $\langle E \rangle$ - "center of gravity" of the absorption band, Γ - integrated absorption coefficient,
 269 f_{exp} and $f_{\text{calc}}^{\text{ED}}$ - experimental and calculated absorption oscillator strengths, respectively,
 270 ED electric-dipole, MD - magnetic-dipole.
 271

272 Table 2 summarizes the experimental and calculated absorption oscillator strengths f (the
 273 latter are determined by both the J-O and mJ-O theories from the corresponding line strengths).
 274 The intensity parameters are $\Omega_2 = 1.715$, $\Omega_4 = 0.943$ and $\Omega_6 = 0.963$ [10^{-20} cm²] (J-O theory)
 275 and $\Omega_2 = 5.185$, $\Omega_4 = 0.650$, $\Omega_6 = 1.068$ [10^{-20} cm²] and $\alpha = 0.171$ [10^{-4} cm] (mJ-O theory). The
 276 latter theory provides lower root mean square (rms) deviation between the experimental and
 277 calculated f values, so that it was selected for further analysis.

278 The probabilities of spontaneous radiative transitions $A_{\text{calc}}(\text{JJ}')$, the luminescence branching
 279 ratios $B(\text{JJ}')$ and the radiative lifetimes of the excited-states τ_{rad} were calculated using the mJ-O
 280 theory, the results are shown in Table 3. For the $^3\text{F}_4$ and $^3\text{H}_4$ states, τ_{rad} is 5.33 ms and 0.55 ms,
 281 respectively.

282 **Table 3. Calculated Probabilities of Spontaneous Radiative Transitions of Tm^{3+} ions in CLTGG crystal**
 283 **(Obtained from the mJ-O Theory)^a**

Excited state	Terminal state	$\langle\lambda_{\text{em}}\rangle$, nm	$A_{\text{calc}}(\text{JJ}')$, %	$B(\text{JJ}')$, %	A_{tot} , s ⁻¹	τ_{rad} , ms
$^3\text{F}_4$	$^3\text{H}_6$	1717.3	63.62 ^{ED}	1	187.51	5.33
$^3\text{H}_5$	$^3\text{F}_4$	3937.0	8.81 ^{ED} +0.24 ^{MD}	0.027	329.09	3.03
	$^3\text{H}_6$	1195.7	212.78 ^{ED} +107.26 ^{MD}	0.973		
$^3\text{H}_4$	$^3\text{H}_5$	2344.7	16.59 ^{ED} +10.34 ^{MD}	0.015	1801.71	0.55
	$^4\text{F}_4$	1469.5	154.95 ^{ED} +25.61 ^{MD}	0.100		
	$^3\text{H}_6$	791.9	1594.22 ^{ED}	0.885		
$^3\text{F}_2+^3\text{F}_3$	$^3\text{H}_4$	5154.6	22.24 ^{ED} +0.32 ^{MD}	0.005	4760.78	0.36
	$^3\text{H}_5$	1611.6	818.37 ^{ED}	0.172		
	$^3\text{F}_4$	1143.5	1191.94 ^{ED} +74.14 ^{MD}	0.266		
	$^3\text{H}_6$	686.4	2653.77 ^{ED}	0.557		
$^1\text{G}_4$	$^3\text{F}_2+^3\text{F}_3$	1511.9	28.52 ^{ED}	0.030	4524.78	0.22
	$^3\text{H}_4$	1169.0	103.11 ^{ED} +4.17 ^{MD}	0.142		
	$^3\text{H}_5$	780.1	600.49 ^{ED} +39.18 ^{MD}	0.359		
	$^3\text{F}_4$	651.1	1468.80 ^{ED} +156.71 ^{MD}	0.063		
	$^3\text{H}_6$	472.1	273.22 ^{ED} +12.88 ^{MD}	0.406		
$^1\text{D}_2$	$^1\text{G}_4$	1537.5	563.86 ^{ED}	0.008	72495.29	0.01
	$^3\text{F}_2+^3\text{F}_3$	762.3	5710.24 ^{ED} +183.16 ^{MD}	0.081		
	$^3\text{H}_4$	664.1	5340.29 ^{ED}	0.074		
	$^3\text{H}_5$	517.5	218.16 ^{ED}	0.003		
	$^3\text{F}_4$	457.4	50840.29 ^{ED}	0.701		
	$^3\text{H}_6$	361.2	9639.29 ^{ED}	0.133		

284 ^a $\langle\lambda_{\text{em}}\rangle$ - mean emission wavelength, $A_{\text{calc}}(\text{JJ}')$ - probability of radiative spontaneous
 285 transition, $B(\text{JJ}')$ - luminescence branching ratio, A_{tot} - total probability of radiative
 286 transitions, τ_{rad} - radiative lifetime, ED electric-dipole, MD - magnetic-dipole.

287 5.3 Luminescence (emission spectra and lifetime)

288 The RT luminescence spectrum was measured using an optical spectrum analyzer (AQ6375B,
 289 Yokogawa) for which the spectral response was calibrated using a 20 W quartz iodine lamp.
 290 The pump source was a 795 nm Ti:Sapphire laser (excitation to the $^3\text{H}_4$ state). The luminescence
 291 spectrum is shown in Fig. 7(a). The broad and intense band at 1.6 - 2.3 μm is due to the $^3\text{F}_4 \rightarrow$
 292 $^3\text{H}_6$ transition, while the weaker band at 1.35 - 1.55 μm originates from the $^3\text{H}_4 \rightarrow ^3\text{F}_4$ transition.

293 The luminescence decay was studied at RT using an optical parametric oscillator (Horizon,
 294 Continuum), a 1/4 m monochromator (Oriel 77200), an InGaAs detector and an 8 GHz digital
 295 oscilloscope (DSA70804B, Tektronix). The sample was finely powdered to avoid the effect of
 296 radiation trapping. The decay curve from the $^3\text{F}_4$ state is well fitted using a single-exponential
 297 law yielding a luminescence lifetime τ_{lum} of 4.93 ms (for the powdered sample), Fig. 7(b). It is
 298 only slightly shorter than the radiative one, revealing a relatively high quantum yield $\eta_{\text{q}} =$
 299 $\tau_{\text{lum}}/\tau_{\text{rad}} = 92\%$. For the bulk sample, $\tau_{\text{lum}} = 6.50$ ms due to the strong reabsorption. The decay
 300 from the $^3\text{H}_4$ state is not single-exponential revealing the effect of cross-relaxation for
 301 neighboring Tm^{3+} ions. The mean decay time $\langle\tau_{\text{lum}}\rangle = 0.159$ ms, Fig. 7(c).

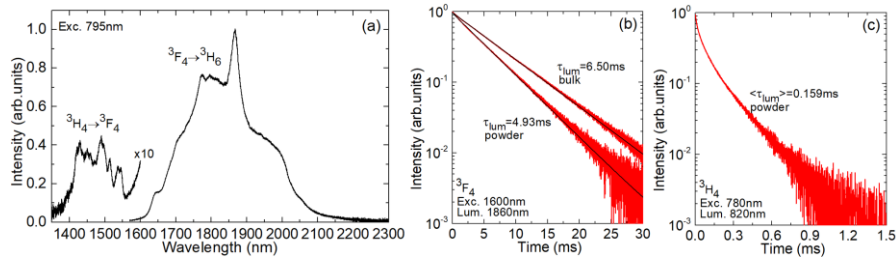


Fig. 7. Near-infrared emission properties of the Tm:CLTGG crystal: (a) luminescence spectrum, $\lambda_{\text{exc}} = 795 \text{ nm}$; (b,c) luminescence decay curves from the (b) $^3\text{F}_4$ and (c) $^3\text{H}_4$ Tm^{3+} states.

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5.4 Low-temperature spectroscopy

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306 The low temperature (LT, 10 K) absorption and luminescence spectra were measured using a
307 cryostat (Oxford Instruments, model SU 12) with helium-gas close-cycle flow. In CLTGG,
308 Tm^{3+} ions replace for the Ca^{2+} ones in dodecahedral sites with D_2 symmetry. These sites are
309 distorted due to the presence of univalent Li^+ cations serving for charge compensation and
310 various cation coordinations around the {A} sites, cf. Fig. 3. Each $2^{S+1}L_J$ multiplet with integer
311 J is thus split into $2J + 1$ Stark sub-levels. For brevity, in Fig. 8, we only show the absorption
312 and luminescence spectra revealing the splitting of the $^3\text{F}_4$ and $^3\text{H}_6$ states relevant for $\sim 2 \mu\text{m}$
313 laser operation. The assignment of electronic transitions is after the work of Lupei *et al.* for
314 ordered Tm^{3+} -doped $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (GGG) garnet [23]. Figure 8 reveals a significant
315 inhomogeneous broadening of the absorption and luminescence bands of Tm^{3+} ions even at 10
316 K when the electron-phonon interaction is suppressed, which is a fingerprint of the structure
317 disorder.

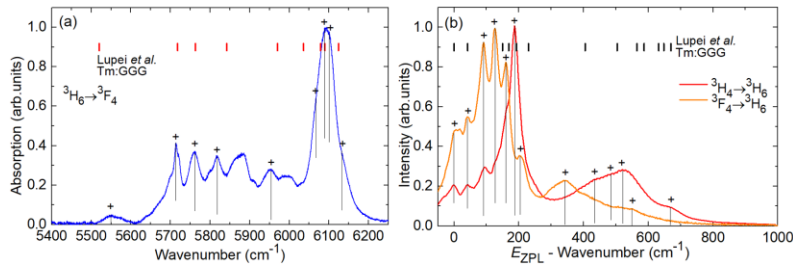


Fig. 8. Low-temperature (LT, 10 K) absorption and emission spectra for Tm^{3+} ions in the CLTGG crystal: (a) absorption, $^3\text{H}_6 \rightarrow ^3\text{F}_4$ transition; (b) emission, $^3\text{F}_4 \rightarrow ^3\text{H}_6$ and $^3\text{H}_4 \rightarrow ^3\text{H}_6$ transitions. The symbol “+” marks the assigned electronic transitions. Vertical dashes – crystal-field splitting in Tm:GGG after [23].

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Table 4. Experimental Energy Levels of Tm^{3+} ions in CLTGG crystal

Multiplet	E, cm^{-1}
$^3\text{H}_6$	0; 42; 91; 126; 160; 187; 206; 342; 433; 484; 522; 549; 668
$^3\text{F}_4$	5538; 5713; 5760; 5813; 5952; 6067; 6091; 6101; 6138
$^3\text{H}_5$	8299; 8314; 8396; 8412; 8426; 8458; 8567; 8606; 8683; 8773; 8809
$^3\text{H}_4$	12577; 12594; 12632; 12703; 12739; 12774; 12916; 12994; 13026
$^3\text{F}_3$	14552; 14573; 14621; 14644 (3 missing)
$^3\text{F}_2$	15096; 15129; 15149; 15230 (1 missing)
$^1\text{G}_4$	21071; 21116; 21205; 21284; 21304; 21461; 21489; 21648; 21707
$^1\text{D}_2$	27662; 27826; 27940; 28044; 28102

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The experimental energy-levels of Tm^{3+} ions in CLTGG are listed in Table 4 for the multiplets from $^3\text{H}_6$ to $^1\text{D}_2$. For the $^3\text{F}_4 \rightarrow ^3\text{H}_6$ transition of interest for $\sim 2 \mu\text{m}$ laser operation, the zero-phonon line (ZPL), i.e., the transition between the lowest Stark sub-levels of both

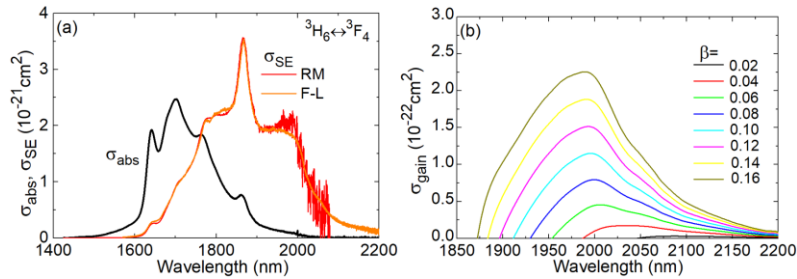
328 multiplets, occurs at 1806 nm ($E_{ZPL} = 5538 \text{ cm}^{-1}$). The partition functions for the ground-state
 329 and the excited-state, calculated at RT, amount to $Z_1 = 4.786$ and $Z_2 = 2.402$, respectively, so
 330 that their ratio $Z_1/Z_2 = 1.992$.

331 5.5 Transition cross-sections

332 The absorption cross-section spectrum for the ${}^3\text{H}_6 \rightarrow {}^3\text{F}_4$ transition is shown in Fig. 9(a), the
 333 maximum σ_{abs} reaches $0.25 \times 10^{-20} \text{ cm}^2$ at 1699 nm.

334 For the ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ transition, the stimulated-emission (SE) cross-section, σ_{SE} , spectra were
 335 calculated by two methods: the Füchtbauer–Ladenburg (F-L) equation [24] and the reciprocity
 336 method (RM) [25]. For the F-L equation, the luminescence spectrum was used, cf. Fig. 7(a),
 337 the radiative lifetime of the ${}^3\text{F}_4$ state was determined from the mJ-O theory ($\tau_{\text{rad}} = 5.33 \text{ ms}$) and
 338 the refractive index of the crystal ($n \approx 1.92$) was taken from [20]. For the RM, we used the
 339 measured absorption spectrum and the determined crystal-field splitting, cf. Table 4. The
 340 results of both methods are shown in Fig. 9(a). They are in good agreement with each other.
 341 The maximum σ_{SE} reaches $0.35 \times 10^{-20} \text{ cm}^2$ at 1866 nm and at longer wavelengths where laser
 342 operation is expected, σ_{SE} reaches $0.18 \times 10^{-20} \text{ cm}^2$ at 1992 nm (both values correspond to the F-
 343 L method).

344 The $\sim 2 \mu\text{m}$ Tm laser represents a quasi-three-level scheme with reabsorption. Thus, gain
 345 cross-sections are usually calculated, $\sigma_{\text{gain}} = \sigma_{\text{SE}} - (1 - \beta)\sigma_{\text{abs}}$, where $\beta = N_2({}^3\text{F}_4)/N_{\text{Tm}}$ is the
 346 inversion ratio. They are useful to conclude about the possible laser wavelength (in the free-
 347 running regime), the potential tuning range as well as the gain bandwidth in ML lasers. The
 348 gain spectra for Tm:CLTGG are shown in Fig. 9(b). The gain profiles of this disordered crystal
 349 are smooth and broad. For small and moderate inversion ratios ($\beta < 0.16$), a single local peak
 350 is observed in the spectra centered at $\sim 1.99 \mu\text{m}$. The gain bandwidth (FWHM) for an
 351 intermediate $\beta = 0.12$ is as broad as 130 nm. The gain profiles extend well beyond $2 \mu\text{m}$ owing
 352 to the large total ground-state splitting ($\Delta E({}^3\text{H}_6) = 668 \text{ cm}^{-1}$) for Tm^{3+} ions and strong electron-
 353 phonon (vibronic) interaction with phonons of the host matrix. The longest purely electronic
 354 transition (neglecting the inhomogeneous broadening) for Tm^{3+} ions is 2053 nm.



355
 356 Fig. 9. ${}^3\text{H}_6 \leftrightarrow {}^3\text{F}_4$ transition of Tm^{3+} ions in CLTGG: (a) absorption, σ_{abs} , and stimulated emission
 357 (SE), σ_{SE} , cross-sections; (b) gain cross-sections, $\sigma_{\text{gain}} = \sigma_{\text{SE}} - (1 - \beta)\sigma_{\text{abs}}$, where $\beta = N_2({}^3\text{F}_4)/N_{\text{Tm}}$
 358 is the inversion ratio.

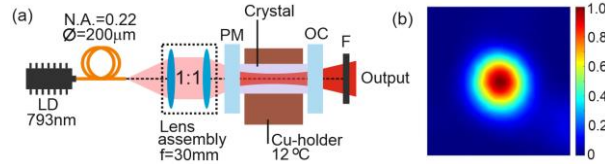
359 6. Diode-pumped laser operation

360 6.1 Laser set-up

361 Figure 10(a) shows the scheme of the compact diode-pumped Tm:CLTGG laser. The laser
 362 element was cut along the [111] direction. It had an aperture of $3.05 \times 3.09 \text{ mm}^2$ and a thickness
 363 of 8.19 mm. Both end faces of the element were polished to laser quality and left uncoated. To
 364 remove the heat released during pumping, the element was wrapped in indium foil and fixed in
 365 a Cu-holder cooled by circulating water; the water temperature was $12 \text{ }^\circ\text{C}$.

366 The laser cavity consisted of a flat pump mirror (PM) coated for high transmission (HT) at
 367 $0.80 \mu\text{m}$ and high reflection (HR) at $1.8\text{--}2.1 \mu\text{m}$ and a set of flat output couplers (OCs) having
 368 transmissions T_{OC} of 1.5%, 3%, 5% or 9% at the laser wavelength. Both mirrors were placed

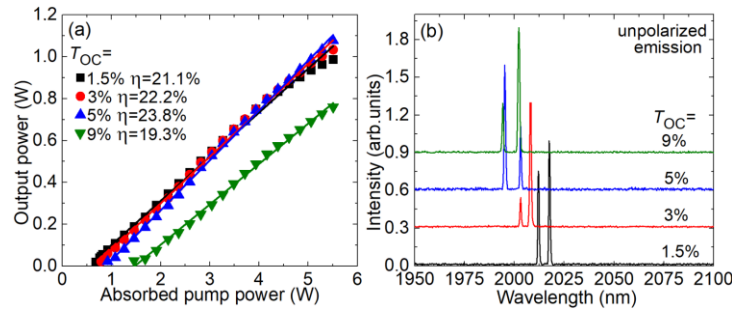
369 close to the crystal resulting in a geometrical cavity length of ~ 8.5 mm. The pump source
 370 comprised a fiber-coupled (fiber core diameter: 200 μm , N.A. = 0.22) AlGaAs diode laser
 371 emitting unpolarized output at a central wavelength of 793 nm (emission bandwidth: 5 nm, M^2
 372 > 80). The pump beam was collimated and focused into the laser element by an AR-coated lens
 373 assembly (reimaging ratio: 1:1, $f = 30$ mm). The pump spot size in the focus $2w_p$ was 200 μm .
 374 The measured pump absorption was $\sim 47\%$. The residual pump was filtered out using a long
 375 pass filter (FEL1000, Thorlabs). The spectra of the laser output were measured using a
 376 spectrometer (WaveScan, APE). The profile of the laser mode in the far-field was captured
 377 using a FIND-R-SCOPE near-IR camera (model 85726).



378
 379 Fig. 10. (a) Scheme of the diode-pumped compact Tm:CLTGG laser: LD – laser diode, PM –
 380 pump mirror, OC – output coupler, F – cut-on filter; (b) far-field output profile of the laser mode,
 381 $T_{OC} = 5\%$, $P_{abs} = 4.0$ W.

382 6.2 Laser performance

383 The input-output dependences of the diode-pumped Tm:CLTGG laser are shown in Fig. 11(a).
 384 The laser generated a maximum output power of 1.08 W at 1995 and 2003 nm with a slope
 385 efficiency η of 23.8% (with respect to the absorbed pump power) and a laser threshold of
 386 0.91 W (for $T_{OC} = 5\%$). At the maximum incident pump power of 11.7 W, the optical-to-optical
 387 conversion efficiency η_{opt} amounted to 9.2%. Further power scaling was limited by the thermal
 388 roll-over in the output dependences. With increasing the output coupling, the laser threshold
 389 increased from 0.68 W ($T_{OC} = 1.5\%$) to 1.46 W ($T_{OC} = 9\%$).



390
 391 Fig. 11. Diode-pumped Tm:CLTGG laser: (a) input-output dependences, η – slope efficiency;
 392 (b) typical spectra of unpolarized laser emission measured at maximum P_{abs} .

393 **Table 5. Laser Performances^a of Tm³⁺-doped Gallium Garnets**

Crystal	Tm, at. %	P_{out} , W	λ_L , nm	η , %	P_{th} , W	Ref.
Tm:CLTGG	3.17	1.08	1995, 2003	23.8	0.91	This work
Tm:CNNGG	3.2	1.05	2008	35.0	0.39	[8]
Tm:CLNGG	3.6	1.32	2002	45.8	0.30	[8]
	~ 3	1.6	1985-2015	37	~ 1	[26]
Tm:CNGG	2.0	0.17	-	3.9	3.5	[27]
	-	0.02	1980-2015	-	4	[28]

^a P_{out} - output power, λ_L - laser wavelength, η - slope efficiency, P_{th} - laser threshold.

394
 395 The laser generated unpolarized emission. The typical spectra of the laser emission are
 396 shown in Fig. 11(b). With increasing T_{OC} from 1.5% to 9%, a blue shift of the emission
 397

398 wavelength was observed from 2012 and 2017 nm to 1994 and 2002 nm. This shift is due to
399 the decreasing reabsorption losses in the crystal typical for quasi-three-level Tm lasers. It also
400 agrees with the gain spectra of Tm:CLTGG, cf. Fig. 9(b). The dual-wavelength emission was
401 due to the etalon effect at the crystal / mirror interface and the broad and smooth gain profile.

402 The laser mode in the far-field, Fig. 10(b), was nearly circular.

403 A summary of output characteristics of CW lasers based on Tm³⁺-doped disordered gallium
404 garnets is presented in Table 5.

405 7. Conclusions

406 To conclude, Tm:CLTGG is a promising crystal for ultrashort pulse generation (sub-100 fs) in
407 the eye-safe spectral range of ~2 μm. It exhibits a structural disorder related to a random site
408 distribution of Ta⁵⁺, Ga³⁺ and Li⁺ cations over the same lattice sites, octahedral (16a) and
409 tetrahedral (24d), which leads to a significant inhomogeneous broadening of the absorption and
410 emission bands of Tm³⁺ ions confirmed at low temperature (10 K). At room temperature, due
411 to a combination of the inhomogeneous broadening and electron-phonon interaction,
412 Tm:CLTGG exhibits smooth and very broad gain profiles owing to the phonon-assisted ³F₄ →
413 ³H₆ transition extending up to at least ~2.2 μm. From X-ray diffraction, Raman spectroscopy
414 and optical transmission, it is evident that Li⁺ ions provide charge compensation during the
415 heterovalent doping (as Tm³⁺ ions are replacing Ca²⁺ ones) and almost eliminate the presence
416 of cationic vacancies. Finally, Tm:CLTGG exhibits attractive thermal properties (for a
417 disordered crystal) being superior to those of the CNGG-type crystals.

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424 **Disclosures.** The authors declare no conflicts of interest.

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

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