



Comparative study of the spectroscopic and laser properties of Tm^{3+} , $\text{Na}^+(\text{Li}^+)$ -codoped $\text{Ca}_3\text{Nb}_{1.5}\text{Ga}_{3.5}\text{O}_{12}$ -type disordered garnet crystals for mode-locked lasers

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Abstract: Tm^{3+} , X^+ -codoped disordered calcium niobium garnet crystals, $\text{Ca}_3\text{Nb}_{2-x}\text{Ga}_{3+x}\text{O}_{12}$ (CNGG), where X^+ is an alkali cation, Na^+ or Li^+ (shortly Tm:CNNGG and Tm:CLNGG, respectively), are grown by the Czochralski method. A comparative study of their spectroscopic and laser properties is performed. Raman spectra are also studied. For Tm:CNNGG, the Judd-Ofelt parameters for the Tm^{3+} dopant ion are $\Omega_2 = 1.847$, $\Omega_4 = 1.558$ and $\Omega_6 = 0.862$ [10^{-20} cm^2] and the radiative lifetime of the $^3\text{F}_4$ state is 4.11 ms. The absorption, stimulated-emission (σ_{SE}) and gain cross-sections are determined for the $^3\text{H}_6 \leftrightarrow ^3\text{F}_4$ Tm^{3+} -ion transition. For Tm:CNNGG, the maximum σ_{SE} is $0.49 \times 10^{-20} \text{ cm}^2$ at 1867 nm. Both crystals exhibit flat and broad gain spectra extending beyond 2 μm . A compact diode-pumped Tm:CNNGG laser has generated 1.05 W at 2007.7 nm with a slope efficiency of 35%. Broadband tuning of Tm:CNNGG and Tm:CLNGG lasers (tuning ranges of 168 nm and 224 nm, respectively), was demonstrated. The Tm^{3+} , X^+ -codoped CNGG crystals are the promising for sub-100 fs pulse generation at $\sim 2 \mu\text{m}$.

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1. Introduction

In recent years, 2 μm ultrafast lasers based on thulium (Tm³⁺) or holmium (Ho³⁺) ion doped solid state materials are of increasing interest due to their applications in remote sensing, material processing, medical diagnostics, laser surgery, as pump source for synchronous pumping of mid-IR optical parametric oscillators (OPOs) as well as for seeding of near-degenerate near-IR optical parametric chirped-pulse amplifiers (OPCPAs) or laser amplifiers to be used as pump sources for mid-IR OPCPAs. Compared to Ho³⁺-doped materials, the Tm³⁺-doped ones have some advantages, e.g., they usually exhibit strong absorption near 0.8 μm (³H₆ → ³H₄ transition) so that they can be directly pumped by commercial AlGaAs laser diodes [1,2]. A high quantum efficiency approaching 2 can be achieved due to an efficient cross-relaxation (CR) for adjacent Tm³⁺ ions [3]. Tm³⁺-doped materials possess a broad and less structured emission spectrum which is beneficial for tuning of laser emission [4] and generation of ultrashort pulses [5,6].

Up to now, passively mode-locked (ML) 2 μm lasers generating femtosecond pulses have been demonstrated using several Tm³⁺-doped crystals and ceramics [5–9]. However, in contrast to the situation with Yb³⁺-doped materials emitting at ~ 1 μm , sub-100 fs pulses at ~ 2 μm have been reported only with a Tm:MgWO₄ crystal (86 fs, at 2017 nm) and a Tm:(Lu_{2/3}Sc_{1/3})₂O₃ "mixed" ceramic (63 fs, at 2057 nm) [10,11]. For such oscillators, Tm³⁺-doped laser materials should exhibit not only broad and smooth absorption and stimulated-emission (SE) bands but also flat gain cross-section spectra with maxima that are already located or can be shifted by selective cavity mirrors beyond 2 μm , allowing one to avoid the unwanted strong water vapor absorption. Thus, there is still a great demand to develop new Tm³⁺-doped materials with such spectral features.

Cubic multicomponent garnets are very suitable for the design of disordered laser hosts. They have a general formula {A}₃[B]₂(C)₃O₁₂, where {A}, [B], and (C) are dodecahedral (Wyckoff symbol: 24c), octahedral (16a), and tetrahedral (24d) sites, respectively [12]. The coordination number (C.N.) for these sites is VIII, VI and IV, respectively. A stoichiometric disordered calcium niobium gallium garnet (CNGG) has a chemical formula Ca₃Nb_{1.5}Ga_{3.5}O₁₂ = {Ca₃}[Nb_{1.5}Ga_{0.5}](Ga₃)O₁₂ [13]. In a real crystal, its composition deviates from the stoichiometry (mostly, by increased concentration of Nb and decreased – of Ga) and thus some cationic (Ga) vacancies (designated as □) are present to compensate for the charge [13]. This can be represented in the first approximation as Ca₃Nb_{2-x}Ga_{3+x-□}O₁₂ = {Ca₃}[Nb_{2-x}Ga_x](Ga_{3-□})O₁₂ ($x = 0.5$ and $y = 0$ for stoichiometry). More precisely, some amount of vacancies can be present in all three types of sites [12,14]. In CNGG-type crystals, the

disorder in the structure results from the random distribution of Nb^{5+} and Ga^{3+} cations over the same octahedral lattice sites, [B]. When doped with optically active rare-earth ions (RE^{3+}), such as Nd^{3+} , Yb^{3+} or Tm^{3+} , they substitute for the Ca^{2+} ions in dodecahedral sites, {A}, and the local multi-ligands around the RE^{3+} ions contribute to a considerable inhomogeneous spectral line broadening.

The presence of cationic vacancies $\square$ is typically unwanted because they can lead to formation of color centers, crystal coloration and decrease of its optical quality, as well as RE^{3+} luminescence quenching. The vacancies can be eliminated by codoping of the RE^{3+} :CNGG crystals by univalent alkali cations $\text{X}^+ = \text{Li}^+$ or Na^+ which can be distributed over both [B] and (C) sites [12,15]. More recent study indicated the predominant accommodation of Li^+ cations in the tetrahedral sites, (C) [14]. The resulting host crystals are abbreviated as CLNGG and CNNGG, respectively. For CLNGG, $\text{Ca}_3\text{Li}_{0.275}\text{Nb}_{1.775}\text{Ga}_{2.95}\text{O}_{12}$ is the closest composition to the congruent one of the $\text{Ca}_3(\text{LiNbGa})_5\text{O}_{12}$ system [16]. Note that the alkali cations are optically passive and the RE^{3+} , X^+ codoping is different from the case of RE_1^{3+} , RE_2^{3+} one. This is the reason why the Li or Na atoms are included in the host formula. For CLNGG and CNNGG crystals, the RE^{3+} dopant ions are laser-active.

Due to the inhomogeneous spectral broadening, Nd^{3+} and Yb^{3+} doped CNGG-type crystals have proved to be excellent ultrafast laser gain materials [17–21]. For Tm^{3+} -doped CNGG, some spectroscopic properties and laser operation mostly under pulsed pumping have been reported up to now [22–25]. More information is present about Tm^{3+} -doped CLNGG, including spectroscopy, continuous-wave (CW) and ML laser performance [26–30]. Pulses as short as 354 fs were achieved in Ref [28], indicating that this crystal is a promising candidate for ultrafast 2 μm lasers.

Recently, the disordered Yb^{3+} -doped CNNGG crystal has been reported, revealing that the incorporation of Na^+ in CNGG could optimize the crystal properties, namely (i) decrease the temperature of the crystal growth, (ii) promote the Yb^{3+} doping and (iii) enlarge the Yb^{3+} emission bandwidth as compared to Yb :CNGG, which is very important for ultrashort pulse generation [12]. As mentioned above, the Na^+ cations might diminish the effect of the cationic vacancies $\square$. In our recent work, ML pulses with a duration of 45 fs were achieved using Yb :CNNGG [31]. To the best of our knowledge, these are the shortest pulses ever generated from any Yb^{3+} -doped CNGG-type disordered crystal laser.

This motivated us for the present work to grow a Tm :CNNGG (i.e., Tm^{3+} , Na^+ -codoped CNGG) crystal by the Czochralski method for laser operation in the 2- μm spectral range. Its spectral properties, CW and tunable laser performance were also systematically investigated. All these parameters were compared to those of Tm :CLNGG.

2. Crystal growth and structural analysis

A Tm :CNNGG single crystal was grown by the conventional Czochralski (Cz) method under Ar atmosphere containing 2% oxygen (volume/volume percent, v/v) in an iridium crucible. The melting temperature of Tm :CNNGG is ~ 1740 K. The starting materials were CaCO_3 , Na_2CO_3 , Nb_2O_5 , Ga_2O_3 (4N purity) and Tm_2O_3 (5N purity) powders. Figure 1(a) shows the as-grown along the [111] crystallographic direction Tm :CNNGG crystal boule. Its dimensions are $\sim \Phi 25 \times 30$ mm². The surface of the boule contained some dark brown impurities, resulting in small cracks at the bottom of the crystal. We attribute the cracks to the volatilization of the Ga_2O_3 component which could be effectively avoided by optimizing the temperature gradient and atmosphere during the crystal growth. Although there are some impurities on the surface of the as-grown crystal, the internal part of Tm :CNNGG is transparent, see Fig. 1(b). By using the X-ray fluorescence method (fluorescence spectrometer: Primus II), the segregation coefficients of Tm^{3+} and Na^+ ($K = N_{\text{crystal}}/N_{\text{melt}}$) were measured to be 1.21 and 0.67, respectively, corresponding to the concentrations in the Tm :CNNGG crystal of 3.2 at.% and 5.5 at.%, respectively.

The grown Tm:CNNGG crystal was yellow-colored. Pale-green or yellow coloration is typical for CNGG-type crystals and is attributed to the absorption of color centers in the visible due to the cationic vacancies [12].

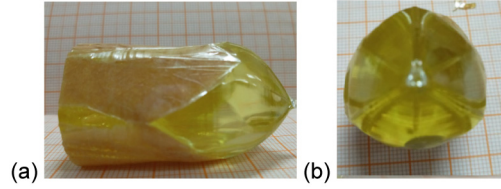


Fig. 1. The as-grown Tm:CNNGG crystal boule: (a) side view and (b) top view.

X-ray powder diffraction (XRD) was used to determine the lattice parameters and phase purity of the as-grown Tm:CNNGG crystal at room temperature. A Bruker D8 Advance diffractometer with Cu K α 1 line ($\lambda = 1.54051 \text{ \AA}$) was used. The results are shown in Fig. 2. They are in agreement with the data for CNGG-type crystals [12], showing a high phase purity of our sample (cubic crystal class, space group $Ia\bar{3}d - O^{10}_h$, No. 230). From the peak 2θ values in the XRD pattern, the cubic unit-cell parameters were calculated to be $a = b = c = 12.4918 \text{ \AA}$, the number of the formula units $Z = 8$. By using the calculated unit-cell parameters, the Tm $^{3+}$ ion concentration N_{Tm} was determined to be $4.46 \times 10^{20} \text{ ions/cm}^3$. For undoped CNGG and CLNGG, the lattice constants were previously determined as $12.4969 \text{ \AA}$ and $12.5066 \text{ \AA}$ [12,14] which is close to our data.

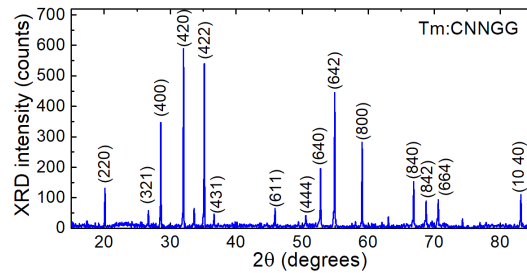


Fig. 2. XRD pattern of the as-grown Tm:CNNGG crystal, numbers denote the Miller's indices, (hkl) .

A Tm $^{3+}$,Li $^{+}$:CNGG (Tm:CLNGG) crystal grown by the Cz method [26] was also studied for comparison. The Tm $^{3+}$ doping was 3.6 at.% ($N_{\text{Tm}} = 4.5 \times 10^{20} \text{ ions/cm}^3$). The melting temperature of Tm:CLNGG is 1723 K.

3. Spectroscopic characterization

Since both CNNGG and CLNGG belong to the cubic system (they are optically isotropic), polished samples with dimensions of $3 \times 3 \times 3 \text{ mm}^3$ were prepared and oriented along the $[111]$ crystallographic direction for the spectroscopic characterization. The studies were performed at room temperature (RT, 293 K).

The RT absorption spectra were measured using a Varian CARY 5000 spectrophotometer (Agilent) with a resolution of 0.2 nm. The absorption spectra of Tm:CNNGG and Tm:CLNGG crystals are shown in Fig. 3(a). In the spectra, the bands related to the transitions from the ground state (3H_6) to the 3F_4 , 3H_5 , 3H_4 , $^3F_{2,3}$, 1G_4 and 1D_2 excited-states are resolved. For Tm:CNNGG and Tm:CLNGG, the UV absorption edge λ_{UV} is at 385 nm ($E_g = 3.22 \text{ eV}$) and 333 nm (3.72 eV), respectively. These values are longer than that for undoped CNGG, $\lambda_{\text{UV}} = 285 \text{ nm}$. The red-shift of the UV absorption edge is most probably due to the X $^{+}$ cation incorporation.

The absorption band corresponding to the $^3H_6 \rightarrow ^3H_4$ transition of Tm^{3+} is shown in Fig. 3(b). For Tm:CNNGG, the maximum absorption cross-section, σ_{abs} , for this transition is $0.38 \times 10^{-20} \text{ cm}^2$ at 785.8 nm and the full width at half maximum (FWHM) of the absorption band is 30.0 nm. The peak σ_{abs} of $0.38 \times 10^{-20} \text{ cm}^2$ at 786.3 nm and a FWHM of 29.3 nm are determined for Tm:CLNGG. Note that Fig. 3(b) clearly indicates various effect of Na^+ or Li^+ cooping on the crystal-field in Tm^{3+} :CNGG. For Tm:CNGG, a similar σ_{abs} value was reported at 786 nm [24] which is close to our data. Compared to widely studied Tm^{3+} -doped laser crystals, such as Tm:YAG (FWHM = 4 nm) and Tm:YVO₄ (FWHM = 5 nm) [32,33], the $^3H_6 \rightarrow ^3H_4$ absorption band of Tm^{3+}, X^{+} :CNGG crystals is much broader, which relaxes the requirements for the wavelength stabilization of the AlGaAs diode laser acting as a pump source.

We attribute this broadening to the disordered structure of Tm^{3+}, X^{+} :CNGG crystals and, partially, to the effect of alkali cation (X^+) incorporation. As mentioned above, the X^+ cations are expected to accommodate in the tetrahedral (C) sites with IV-fold O^{2-} coordination. Their ionic radii are 0.99 Å (Na^+) and 1.37 Å (K^+), compare with that of Ga^{3+} (0.47 Å). A substantial difference in the ionic radii of X^+ and Ga^{3+} cations will promote the alteration of the crystal-field. From the values of the ionic radii, one can also expect stronger effect for Tm:CLNGG crystal as compared to Tm:CNNGG one (for the same X^+ concentration). Note that the difference in ionic radii of Ca^{2+} (1.12 Å) and Tm^{3+} (0.994 Å) for VIII-fold O^{2-} coordination (in the dodecahedral sites {A}) can also contribute to the spectral broadening.

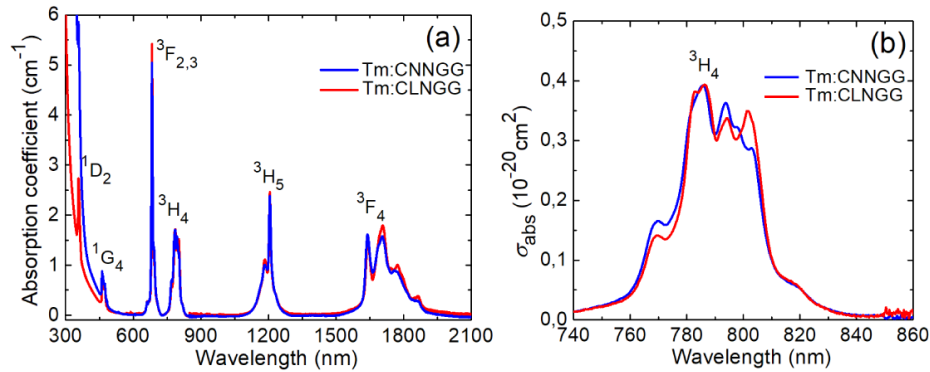


Fig. 3. (a) Comparison of RT absorption spectra of 3.2 at.% Tm:CNNGG and 3.6 at.% Tm:CLNGG crystals; (b) absorption cross-sections, σ_{abs} , corresponding to the $^3H_6 \rightarrow ^3H_4$ Tm^{3+} transition in these crystals.

Table 1. Experimental and Calculated Absorption Oscillator Strengths for a Tm:CNNGG Crystal

Transition	$\langle \lambda \rangle$, nm	$\langle E \rangle$, cm^{-1}	Γ , cm^{-1}	$f_{exp} \times 10^{-6}$	$f_{calc} \times 10^{-6}$
$^3H_6 \rightarrow ^3F_4$	1721.5	5809	244.04	2.09	2.08 ^{ED}
$^3H_6 \rightarrow ^3H_5$	1195.1	8368	90.23	1.60	1.42 ^{ED} + 0.52 ^{MD}
$^3H_6 \rightarrow ^3H_4$	798.7	12520	58.77	2.33	2.16 ^{ED}
$^3H_6 \rightarrow ^3F_{2,3}$	684.9	14601	56.12	3.03	2.73 ^{ED}
$^3H_6 \rightarrow ^1G_4$	468.4	21349	7.29	0.84	0.71 ^{ED}

$\langle \lambda \rangle$ - "center of gravity" of the absorption band, $\langle E \rangle$ - estimated multiplet barycenter energy, Γ - integrated absorption coefficient, f_{exp} and f_{calc} - experimental and calculated absorption oscillator strengths, respectively. ED and MD stand for the electric-dipole and magnetic-dipole contributions, respectively.

The standard Judd–Ofelt (J–O) theory [34,35] was applied to analyze the RT absorption spectrum. More details for the case of Tm^{3+} -doped crystals can be found elsewhere [36]. The dispersion of the refractive index of CNGG was reported in Ref [12]. In particular, $n = 1.93$ at $\sim 2 \mu\text{m}$. The experimental and calculated absorption oscillator strengths f for the Tm:CNNGG

crystal are listed in Table 1. The intensity (J-O) parameters are as follows: $\Omega_2 = 1.847$, $\Omega_4 = 1.558$ and $\Omega_6 = 0.862$ [10^{-20} cm²] for Tm:CNNGG and $\Omega_2 = 1.939$, $\Omega_4 = 1.582$ and $\Omega_6 = 0.754$ [10^{-20} cm²] and for Tm:CLNGG. These values are close to those reported previously for Tm:CNNG, $\Omega_2 = 2.02$, $\Omega_4 = 1.71$ and $\Omega_6 = 0.89$ [10^{-20} cm²] [24].

On the basis of the J-O modelling, the probabilities of spontaneous radiative transitions $A(JJ')$, the luminescence branching ratios $B(JJ')$ and the radiative lifetimes of the excited-states τ_{rad} were calculated, see Table 2 for Tm:CNNGG. The radiative lifetime τ_{rad} of the 3F_4 upper laser level was calculated to be 4.11 and 4.20 ms for Tm:CNNGG and Tm:CLNGG, respectively. These values are longer than that for Tm:CNNG, $\tau_{\text{rad}} = 3.29$ ms [24].

For the pump state 3H_4 , $\tau_{\text{rad}} = 0.74$ ms for both Tm:CNNGG and Tm:CLNGG crystals.

Table 2. Calculated Probabilities of Spontaneous Radiative Transitions of Tm³⁺ Ions in CNNGG Crystal

Exc. state	Final state	$\langle\lambda\rangle$, nm	$A_{\text{calc}}(JJ')$, s ⁻¹	$B(JJ')$, %	A_{tot} , s ⁻¹	τ_{rad} , ms
3F_4	3H_6	1721.5	243.2	100.0	243.2	4.11
3H_5	3F_4	3908.4	$8.5^{\text{ED}} + 1.4^{\text{MD}}$	2.5	391.8	2.55
	3H_6	1195.1	$283.9^{\text{ED}} + 98.0^{\text{MD}}$	97.5		
3H_4	3H_5	2408.0	$29.8^{\text{ED}} + 12.4^{\text{MD}}$	3.1	1344.2	0.74
	3F_4	1490.0	$99.9^{\text{ED}} + 27.5^{\text{MD}}$	9.5		
	3H_6	798.7	1174.6^{ED}	87.4		
$^3F_3 + ^3F_2$	3H_4	4806.9	$6.4^{\text{ED}} + 0.3^{\text{MD}}$	0.2	2975.5	0.34
	3H_5	1604.3	297.4^{MD}	10.0		
	3F_4	1137.4	$76.8^{\text{ED}} + 68.6^{\text{MD}}$	4.9		
	3H_6	684.9	2526.0^{MD}	84.9		
1G_4	3F_2	-	21.2^{ED}	0.8	2573.0	0.39
	3F_3	1481.8	$64.0^{\text{ED}} + 4.1^{\text{MD}}$	2.6		
	3H_4	1132.6	$225.4^{\text{ED}} + 39.5^{\text{MD}}$	10.3		
	3H_5	770.3	$706.1^{\text{ED}} + 177.7^{\text{MD}}$	34.4		
	3F_4	643.5	$198.9^{\text{ED}} + 10.6^{\text{MD}}$	8.1		
	3H_6	468.4	1125.5^{ED}	43.8		

$\langle\lambda\rangle$ - mean wavelength of the emission band, $A_{\text{calc}}(JJ')$ - probability of radiative spontaneous transition, $B(JJ')$ - luminescence branching ratio, A_{tot} and τ_{rad} - total probability of radiative spontaneous transitions and the radiative lifetime of the excited state, respectively. ED and MD stand for the electric-dipole and magnetic-dipole contributions, respectively.

The RT luminescence spectra of Tm:CNNGG and Tm:CLNGG were measured using an optical spectrum analyzer (OSA, Yokogawa, model AQ6375B) under CW excitation by an AlGaAs laser diode at 802 nm, Fig. 4(a). The broad band spanning from 1.6 to 2.05 μm corresponds to the $^3F_4 \rightarrow ^3H_6$ Tm³⁺ transition. Note that due to the reabsorption, the shape of the luminescence spectrum is slightly different for the studied crystals.

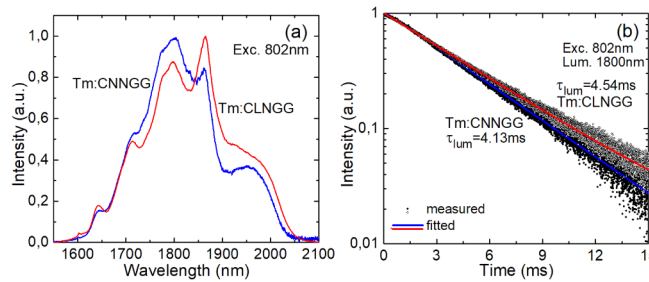


Fig. 4. Emission properties of Tm:CNNGG and Tm:CLNGG crystals: (a) normalized RT luminescence spectra, $\lambda_{\text{exc}} = 802$ nm; (b) luminescence decay curves at RT: symbols - experimental data, solid lines - single-exponential fits for the determination of τ_{lum} , $\lambda_{\text{exc}} = 802$ nm, $\lambda_{\text{lum}} = 1800$ nm.

To measure the luminescence decay curves at RT, we used the same laser diode with a mechanically modulated output, an OSA and a 2 GHz digital oscilloscope. The results are shown in Fig. 5(b). The decay curves were fitted with a single-exponential law leading to a measured decay time τ_{lum} of 4.13 ms and 4.54 ms for Tm:CNNGG and Tm:CLNGG, respectively. These values are slightly longer than the corresponding radiative lifetimes of the 3F_4 state due to the radiation trapping effect. For Tm:CNNGG, the measured τ_{lum} was shorter, 3.31 ms [24].

The absorption and emission properties of Tm^{3+} ions in CNNGG according to the $^3F_4 \leftrightarrow ^3H_6$ transitions were also studied at low temperature (LT, 6 K), see Fig. 5(a). For this, we used an Oxford Instruments Ltd. cryostat (SU 12 model) with helium-gas close-cycle flow. Assuming that the Tm^{3+} ions are located in dodecahedral Ca^{2+} sites {A}, the corresponding site symmetry is D_2 ; it can be distorted due to incorporation of alkali cations and non-uniform multi-ligands around the active ions. Thus, a total of $2J + 1$ Stark sub-levels are expected for each $^{2S+1}L_J$ multiplet, i.e., 13 and 9 for 3H_6 and 3F_4 , respectively. The absorption and emission spectra of Tm^{3+} in CNNGG are rather broad even at LT. A tentative assignment of the LT absorption and emission peaks (according to Ref [37].) yields the scheme of Stark splitting for the Tm^{3+} ions. Three of the most higher-lying Stark sub-levels of the 3H_6 ground-state are not resolved. The zero-phonon-line (ZPL) transition occurs at $E_{\text{ZPL}} = 5554 \text{ cm}^{-1}$ (1801 nm).

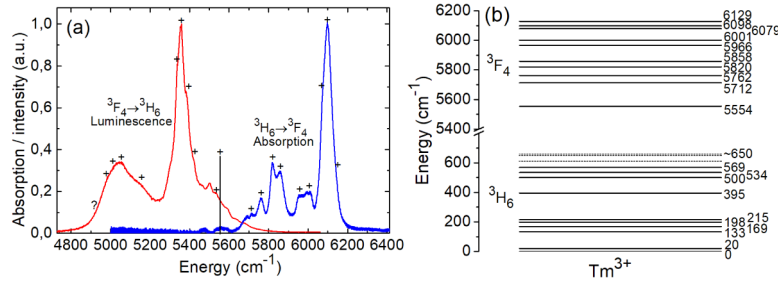


Fig. 5. Low-temperature (LT, 6 K) spectroscopy of Tm^{3+} ions in CNNGG crystal: (a) measured absorption and luminescence ($\lambda_{\text{exc}} = 802 \text{ nm}$) spectra for the $^3F_4 \leftrightarrow ^3H_6$ transitions, “+” indicates the peaks assigned to the Stark-to-Stark transitions; (b) deduced Stark splitting of the 3F_4 and 3H_6 multiplets in D_2 sites, dashed lines – missing Stark sub-levels according to Ref [37], for Tm^{3+} :YSGG.

The RT absorption cross-sections, σ_{abs} , of the Tm^{3+} ions in CNNGG and CLNGG for the $^3H_6 \rightarrow ^3F_4$ transition are shown in Fig. 6(a,c). For Tm:CNNGG, the maximum σ_{abs} is $0.36 \times 10^{-20} \text{ cm}^2$ at 1639 nm and a similar value is observed at longer wavelength of 1705 nm. For Tm:CLNGG, close cross-sections are detected. Previously for Tm:CNNGG, the peak σ_{abs} was determined to be $\sim 0.43 \times 10^{-20} \text{ cm}^2$ at 1.64 μm . The reduction of the $^3H_6 \rightarrow ^3F_4$ absorption and the associated increase of the radiative lifetime of the 3F_4 state (see above) for the $\text{Tm}^{3+}, \text{X}^{+}$ -codoped CNGG crystals as compared to the singly Tm^{3+} -doped one is attributed to the effect of cation incorporation leading to the varied crystal-field strength.

The RT stimulated-emission (SE) cross-sections, σ_{SE} , for the $^3F_4 \rightarrow ^3H_6$ transition of Tm^{3+} ions were calculated by a combination of Füchtbauer-Ladenburg (F-L) formula and the modified reciprocity method (RM) [38,39]. The results are shown in Fig. 6(a,c). For Tm:CNNGG, the maximum SE cross-section is $0.49 \times 10^{-20} \text{ cm}^2$ at 1867 nm. In the spectral range where laser operation is expected, $\sigma_{\text{SE}} = 0.24 \times 10^{-20} \text{ cm}^2$ at 1956 nm. The peak values of the SE cross-sections for Tm:CLNGG are similar to those for Tm:CNNGG. For Tm:CNNGG, the peak σ_{SE} was estimated with the F-L formula to be $0.4 \times 10^{-20} \text{ cm}^2$ at 1.86 μm [24]. This value is however to be underestimated as the reduction of the luminescence intensity due to the strong reabsorption was not taken into account.

The Tm^{3+} ion represents a quasi-three-level laser scheme, and its emission characteristics can be predicted by calculating the gain cross-sections, $\sigma_{\text{gain}} = \beta\sigma_{\text{SE}} - (1 - \beta)\sigma_{\text{abs}}$, where $\beta = N_2(^3\text{F}_4)/N_{\text{Tm}}$ denotes the ratio of the inverted ions to the total Tm^{3+} -ion density. This is shown in Fig. 6(b,d) for different β . For Tm:CNNGG, Fig. 6(b), for relatively high population inversion levels, $\beta > 0.2$, a local peak centered at ~ 1870 nm dominates in the spectrum. In this spectral range, stable ML is possible only in the ps regime due to the presence of strong water vapor absorption lines. For low $\beta < 0.1$, lasing is expected at ~ 2 μm . Such wavelengths are long enough to intrinsically avoid the water vapor absorption. This, together with the broad and smooth gain characteristics of the spectrum are good prerequisites for fs pulse generation. The gain bandwidth (FWHM) of Tm:CNNGG $\Delta\lambda_g$ is 98 nm for $\beta = 0.1$. For Tm:CLNGG, Fig. 6(d), a similar spectral behavior is observed in the gain spectra and the gain bandwidth $\Delta\lambda_g$ is even broader, 105 nm. The $\Delta\lambda_g$ value has not been reported for Tm:CNNG to date.

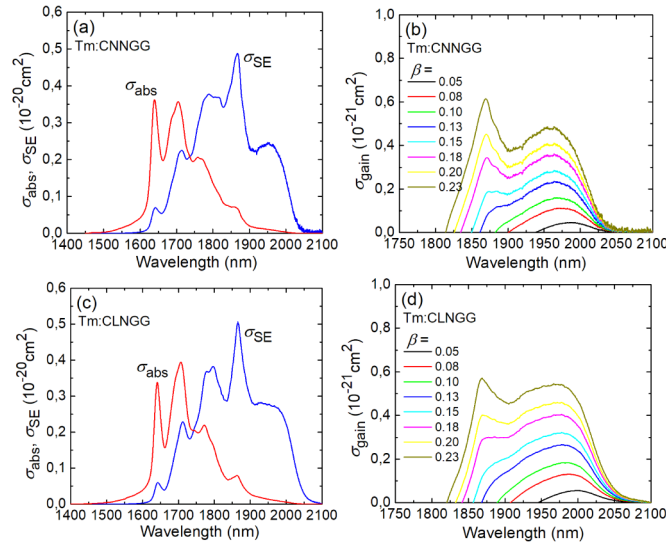


Fig. 6. $^3\text{F}_4 \rightarrow ^3\text{H}_6$ transition of Tm^{3+} ions in (a,b) Tm:CNNGG and (c,d) Tm:CLNGG crystals: (a,c) absorption (σ_{abs}) and calculated (by a combination of the modified RM and F-L methods) stimulated-emission (σ_{SE}) cross-sections, (b) gain cross-sections, $\sigma_{\text{gain}} = \beta\sigma_{\text{SE}} - (1 - \beta)\sigma_{\text{abs}}$, at different inversion rates β . All spectra are at RT.

The vibronic properties of Tm:CNNGG and Tm:CLNGG crystals were characterized with Raman spectroscopy at RT. This method is a sensitive tool to monitor the structure alteration and the possible cationic vacancies for the CNGG-type crystals [12,13]. The Raman spectrum is also relevant for the interpretation of possible side spectral lines under ML operation. The spectrum was measured with a Renishaw inVia confocal micro-Raman microscope with a x50 objective and a 1800 gr/mm grating. The excitation wavelength λ_{exc} was 514 nm (Ar^+ ion laser). The spectral resolution was ~ 1 cm^{-1} . The results are shown in Fig. 7.

For Tm:CNNGG, in the high-frequency range, two intense bands are observed at 725-875 cm^{-1} . They are structured and consist of several components centered at 751, 769 and 786 cm^{-1} (first band) and at 831 and 842 cm^{-1} (second one) which is different from the case of ordered cubic garnets. These two bands correspond to the internal vibrations of the $[\text{GaO}_4]$ and $[\text{NbO}_4]$ tetrahedra, respectively [12,13]. The band splitting is due to the presence of cationic vacancies in the structure, as well as occupation of the same site by various cations (structural disorder) [12,13,15]. In our case, compared to the Raman spectrum of an undoped CNGG [12], the satellite peaks related to the vacancies are notably suppressed. This confirms the positive role of the Na^+ doping. The most intense peak in the Raman spectrum is observed at 502 cm^{-1} .

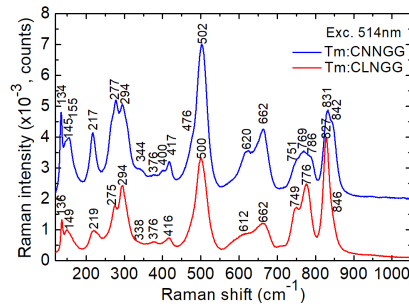


Fig. 7. RT Raman spectra of Tm:CNNGG and Tm:CLNGG: *numbers* – frequencies of the Raman band components (in cm^{-1}).

For Tm:CLNGG, the Raman spectrum is similar. The differences with respect to Tm:CNNGG are (i) a shift of the Raman peaks towards smaller frequencies, (ii) less structured bands at $720\text{--}860\text{ cm}^{-1}$, namely only two (at 749 and 776 cm^{-1}) and one (827 cm^{-1}) well-resolved components assigned to the $[\text{GaO}_4]$ and $[\text{NbO}_4]$ vibrations, respectively, and (iii) almost equal intensity of the Raman peaks at 500 and 827 cm^{-1} . These observations can be interpreted as weaker effect of vacancies on the Tm:CLNGG crystal.

4. Laser experiment

Figure 8 shows the laser set-up, which is based on a compact plano-plano (microchip-type) cavity. Laser operation in such a cavity is due to positive thermo-optic coefficients dn/dT ($\sim 8 \times 10^{-6}\text{ K}^{-1}$ at $2\text{ }\mu\text{m}$ being similar to that of $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG)) and, consequently, positive thermal lens for CNGG-type garnets [12].

The samples used in this experiment (Tm:CNNGG and Tm:CLNGG) were cut along the $[111]$ direction with an aperture of $3.0 \times 3.0\text{ mm}^2$ and a thickness of 3.0 mm . Both end faces of the samples were polished to laser grade quality. In order to remove the generated heat during laser operation, the samples were wrapped with indium foil and mounted in a Cu-holder. The cooling water was maintained at a temperature of $15\text{ }^\circ\text{C}$. This cavity consisted of a flat pump mirror (PM), highly transmitting (HT) for $0.77\text{--}1.05\text{ }\mu\text{m}$ and high reflection (HR) coated for $1.80\text{--}2.08\text{ }\mu\text{m}$, and several flat output couplers (OCs) with transmission of $T_{\text{OC}} = 1.5\%$, 3% , 5% or 9% at $1.82\text{--}2.05\text{ }\mu\text{m}$, respectively. Both of the PM and OC were set as close as possible to the crystal. The pumping source was a fiber-coupled AlGaAs laser diode emitting at 802 nm (fiber core diameter: $200\text{ }\mu\text{m}$, numerical aperture, N.A.: 0.22). The diode output was collimated and focused into the crystal through the PM with a lens assembly ($1:1$ reimaging ratio, 30 mm focal length). The pump spot radius in the focus was $100\text{ }\mu\text{m}$. The measured pump absorption under lasing conditions was 28.6% and 27.7% for Tm:CNNGG and Tm:CLNGG crystals, respectively. A dichroic mirror (DM), totally transmitting the pump radiation was employed to separate the laser output beam by reflection.

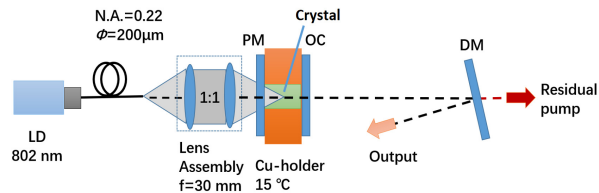


Fig. 8. Scheme of the CW Tm:CNNGG / Tm:CLNGG laser (LD, laser diode; PM, pump mirror; DM, dichroic mirror; OC, output coupler).

In this paper, we report on the first laser operation with Tm:CNNGG. The corresponding input-output characteristics are shown in Fig. 9(a). The maximum output power of 1.05 W at 2007.7 nm was achieved at an absorbed power of 3.4 W , corresponding to a slope efficiency

η of 35.0% (with respect to the absorbed pump power P_{abs}), measured with $T_{\text{OC}} = 3\%$. The laser threshold was at $P_{\text{abs}} = 0.39$ W, and no thermal roll-over was observed with increasing pump power. For higher T_{OC} of 5% and 9%, the laser performance deteriorated due to stronger upconversion losses and the associated heating, resulting in a lower η of only 29.1% and 16.2%, respectively. Figure 9(b) shows the typical laser emission spectra recorded at $P_{\text{abs}} = 3.4$ W, which were strongly dependent on the OC. The peak position of the laser spectra shifted to shorter wavelength with the increase of T_{OC} (a blue-shift behavior), namely from 2010.5 to 1990.1 nm, which agrees with the quasi-three-level nature of the Tm^{3+} laser scheme and with the gain spectra of Tm:CNNGG, Fig. 6(b).

The laser performance of the Tm:CLNGG crystal is presented in Fig. 9(c,d). The maximum output power reached 1.32 W at 2002.1 nm with a maximum η of 45.8% (for $T_{\text{OC}} = 3\%$). The laser threshold was at 0.30 W. A similar blue-shift of the laser emission spectra with T_{OC} , from 2005.5 to 1993.2 nm, was observed, Fig. 9(d). For Tm:CLNGG, the deterioration of laser performance for high output coupling was not so evident as for Tm:CNNGG.

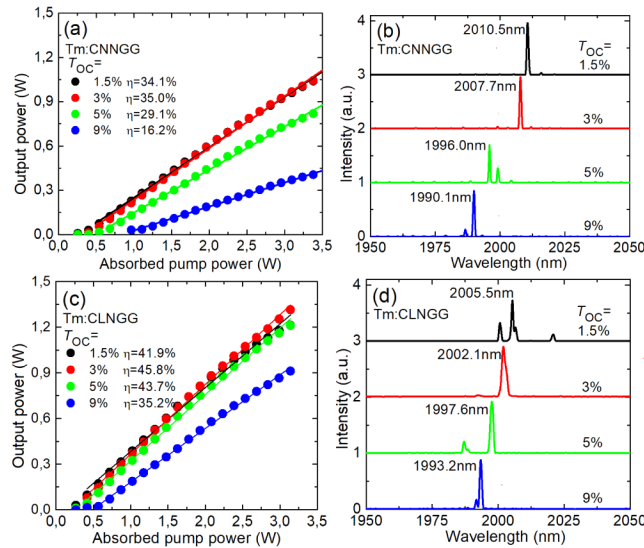


Fig. 9. CW (a,b) Tm:CNNGG and (c,d) Tm:CLNGG lasers: (a,c) input-output dependences, η is the slope efficiency; (b,d) typical laser emission spectra measured at the maximum P_{abs} .

Previously, the output power of a diode-pumped CW Tm:CLNGG laser reached 1.6 W at ~ 2000 nm with $\eta = 37\%$; however, the laser element was cooled to 5°C [27]. We report on even higher laser slope efficiency while operating the laser at around RT. For Tm^{3+} ions, the lower limit of η is set by the Stokes efficiency $\eta_{\text{St}} = \lambda_{\text{p}}/\lambda_{\text{L}}$ which is 40.0% for Tm:CLNGG. Higher slope efficiency is possible due to CR. Figure 9(c) provides the evidence of efficient CR in Tm:CLNGG. Voronko *et al.* determined the CR microparameter in Tm:CNNGG C_{CR} as $2.29 \times 10^{-39} \text{ cm}^6/\text{s}$ [23]. Following Ref [40], we estimated the pump quantum efficiency for Tm:CLNGG η_{q} as 1.25, so that the upper limit for the laser slope efficiency is $\eta_{\text{q}}\eta_{\text{St}} = 50\%$ which is only slightly higher than the experimental value.

The wavelength tuning performance of the disordered Tm:CNNGG and Tm:CLNGG crystals was studied by employing a standard X-folded laser cavity, Fig. 10. A Lyot filter was used as a wavelength tuning element in the cavity. It was a 3.2-mm-thick quartz plate with the optical axis at 60° to the surface. It was located close to the 0.5% OC. The crystal sample was placed at Brewster angle between two folding concave mirrors M_1 and M_2 with the same radii of curvature (RoC) of -100 mm. Both mirrors were dichroic: HR at the laser wavelength and HT at the pump wavelength. The pump source used was a CW Ti:Sapphire laser with a

maximum output power of 3.6 W at 785.3 nm. The pump beam was focused into the crystal with a spot radius of 30 μm by using a focusing lens with a focal length of 70 mm. The laser emission spectra and the corresponding output powers were recorded at $P_{\text{abs}} \sim 0.8$ W.

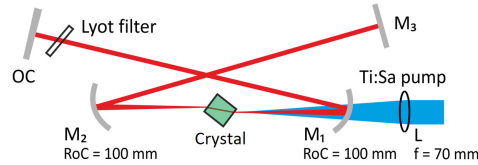


Fig. 10. Scheme of the tunable Tm:CNNGG / Tm:CLNGG laser (L, lens; $M_1 - M_2$, dichroic folding mirrors; M_3 , plane mirror; OC - output coupler).

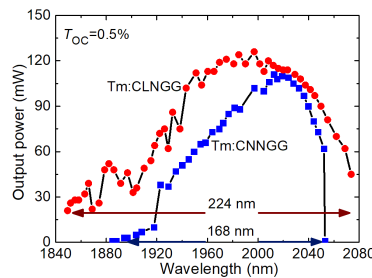


Fig. 11. Wavelength tuning performance of the Tm:CNNGG and Tm:CLNGG lasers.

The wavelength tuning performance of the Tm:CNNGG and Tm:CLNGG lasers is shown in Fig. 11. For Tm:CNNGG, a maximum output power of 111 mW was achieved at 2013 nm. A wavelength tuning range of 168 nm, from 1885 to 2053 nm, was obtained. For Tm:CLNGG, the tuning range was even broader, 224 nm, from 1848 to 2072 nm, representing an improvement over the previous paper [26]. These results indicate that the disordered $\text{Tm}^{3+}, \text{X}^{+}$:CNGG crystals are the promising gain material to generate sub-100 fs pulses in ML lasers.

5. Conclusion

In conclusion, we report on a detailed comparative study of spectroscopic and laser properties of Tm^{3+} ions in $\text{Tm}^{3+}, \text{Na}^+(\text{Li}^+)$ codoped disordered CNGG-type crystals (CNNGG and CLNGG, respectively). The Tm:CNNGG crystal is grown by Czochralski method and characterized for the first time. The studied crystals are promising for femtosecond pulse generation in mode-locked lasers at ~ 2 μm . They exhibit broad absorption bands for pumping at ~ 0.8 μm (FWHM ~ 30 nm), broad and smooth emission bands extending beyond 2 μm (the gain bandwidth is about 100 nm). This spectral behavior is ascribed partially to the disordered structure of CNGG-type crystals and partially – to the effect of alkali cation incorporation modifying the crystal-field. Codoping by $\text{Na}^+(\text{Li}^+)$ also ensures partial elimination of the unwanted cationic vacancies. Note that very recently, we achieved mode-locking of a Tm:CNNGG laser resulting in sub-100 fs (84 fs) pulses at 2018 nm [41].

Comparing the Tm:CNNGG and Tm:CLNGG crystals, the latter has some advantages in terms of broader gain bandwidth leading to wider wavelength tuning range in CW lasers and possibly shorter pulses in ML lasers, as well as lower losses leading to more efficient laser operation in the CW regime. This can be attributed to the role of Li^+ cations which efficiently prevent the formation of cationic vacancies, as confirmed by Raman spectroscopy. The Tm:CNNGG crystal has similar spectroscopic properties but the use of Na^+ codoping has some advantages in terms of crystal growth. Further improvement of the spectroscopic and laser characteristics of Tm:CNNGG is expected by increasing both the Tm^{3+} and Na^+ concentrations (up to 10 at.%). The former will lead to more efficient CR for Tm^{3+} ions and the latter – to further modification of the crystal-field.

First free-running and tunable CW laser operation is achieved with Tm:CNNGG. A compact (microchip-type) diode-pumped Tm:CNNGG laser generated about 1 W of output at $> 2 \mu\text{m}$ with a slope efficiency of 35%. A tuning range of 168 nm extending well above $2 \mu\text{m}$, until 2053 nm, has been demonstrated with Tm:CNNGG.

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