Disordered Tm:Ca₉La(VO₄)₇: a novel crystal with potential for broadband tunable lasing

Z. ZHANG,1,2 P. LOIKO,3 H. WU,1 X. MATEOS,4,5,10,* J. M. SERRES,4 H. F. LIN,1 W. D. CHEN,1,5,8 G. ZHANG,1 L. Z. ZHANG,1,7 F. DÍAZ,4 M. AGUILÓ,4 V. PETROV,5 U. GRIEBNER,5 Y. C. WANG,5 E. VILEJSHIKOVA,6 K. YUMASHEV,6 AND Z. B. LIN1,7,9

1Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, 350002 Fuzhou, China
2Graduate School of Fujian Normal University, 350117 Fuzhou, China
3ITMO University, 49 Kronverkskiy pr., St. Petersburg 197101, Russia
4Física i Cristal·lografia de Materials i Nanomaterials (FiCMA-FiCNA), Universitat Rovira i Virgili (URV), Campus Sescelades, c/ Marcel·lí Domingo, s/n., E-43007 Tarragona, Spain
5Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy, Max-Born-Str. 2a, D-12489 Berlin, Germany
6Center for Optical Materials and Technologies (COMT), Belarusian National Technical University, 65/17 Nezavisimosti Ave., 220013 Minsk, Belarus
7State Key Laboratory of Structural Chemistry, 350002 Fuzhou, China
8chenweidong@fjirsm.ac.cn
9lzb@fjirsm.ac.cn
10mateos@mbi-berlin.de
*xavier.mateos@urv.cat

Abstract: We report on the crystal growth, structural and spectroscopic investigation of a novel trigonal calcium vanadate crystal, Tm³⁺:Ca₉La(VO₄)₇. Polarized absorption, stimulated-emission and gain cross-section spectra are determined for this material. The maximum σ_{SE} corresponding to the 3F₄ → 3H₆ transition amounts to 1.28 × 10⁻²⁰ cm² at 1854 nm for σ-polarization. The measured lifetime of the Tm³⁺ ions in the 3F₄ state is 1.19 ms. The Judd-Ofelt analysis performed yielded intensity parameters of Ω₂ = 4.682, Ω₄ = 0.659 and Ω₆ = 0.475 [10⁻²₀ cm²]. The polarized Raman spectra indicate a strong and broad band centered at 867 cm⁻¹. Owing to the disordered nature of Ca₉La(VO₄)₇, the Tm³⁺ ions exhibit a broad and smooth gain profile at ~2 μm. The spectroscopic properties of Tm³⁺:Ca₉La(VO₄)₇ are very promising for broadly tunable and ultrashort pulse lasers near 2 μm.

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Vanadate crystals represent an important class of host materials for doping with laser-active trivalent lanthanide ions, $Ln^{3+} = \text{Yb}^{3+}, \text{Nd}^{3+}, \text{Tm}^{3+}, \text{Ho}^{3+}, \text{etc}$. A well-known example is the family of the tetragonal zircon-type REVO$_4$ crystals where RE stands for Y, Gd or Lu [1]. In recent years, REVO$_4$ crystals doped with Yb$^{3+}$ and Tm$^{3+}$ ions were used in efficient and broadly tunable continuous-wave (CW), Q-switched and mode-locked (ML) lasers operating at ~1 and 2 μm [2–6]. Additional broadening of the spectral bands of the $Ln^{3+}$ ions enables shorter pulses to be generated by ML lasers. For this reason “mixed” Y, Gd, Lu, or Bi crystals were also studied [7,8].

There is a different crystal family of trigonal calcium vanadates, with the chemical formula Ca$_9$RE$_3+(VO_4)_7$ where RE = La, Y, Gd, Lu or Bi [9–11]. The first studies of these non-centrosymmetric (point group: 3m) crystals were focused on their nonlinear properties for second-harmonic generation (SHG) [12]. In recent years, they are being studied as laser
host materials for Ln$^{3+}$ dopants [13–15]. A partially disordered structure of the Ca$_9$RE(VO$_4$)$_7$ crystals promotes broadening of the spectral bands of the active ions [11] which is of interest for tunable operation and the generation of ultrashort pulses. The Ca$_9$RE(VO$_4$)$_7$ crystals are uniaxial [16] and they can provide naturally polarized laser output. These materials possess relatively low anisotropy of the thermal expansion ($\alpha_a/\alpha_c \sim 1.5...2$) and they are expected to feature “athermal” thermo-optic behavior [11] which may overcome the disadvantage of its low thermal conductivity (~1 W/mK). The Ca$_9$RE(VO$_4$)$_7$ compounds melt congruently and large-volume crystals can be grown by the Czochralski method [10]. Spectroscopic properties of some of the Ln$^{3+}$ ions in the Ca$_9$RE(VO$_4$)$_7$-type crystals have been studied [11,13–15].

Thulium (Tm$^{3+}$) ions are attractive for laser operation around 2 $\mu$m. Such an emission is eye-safe and absorbed in water in the atmosphere and bio-tissues. Tm lasers are thus used in range-finding, remote sensing and medicine. To date, the Tm$^{3+}$ ions have been doped into numerous oxide and fluoride host materials, e.g. Y$_3$Al$_5$O$_{12}$, Lu$_2$O$_3$, YVO$_4$, KLu(WO$_4$)$_2$, YAlO$_3$, LiYF$_4$, etc., and efficient and wavelength-tunable laser operation in the 1.8...2.1 $\mu$m spectral range (depending on the host) has been achieved. In the present work, we report on the crystal growth and a detailed spectroscopic study of a novel trigonal crystal, Tm:Ca$_9$La(VO$_4$)$_7$. Its properties designate Tm:Ca$_9$La(VO$_4$)$_7$ for applications in broadband tunable and ultrashort pulse lasers at ~2 $\mu$m.

2. Crystal growth and structure

The Tm:Ca$_9$La(VO$_4$)$_7$ crystal was grown by the Czochralski method. The raw materials used for crystal growth were synthesized by traditional high temperature solid-state reaction method. The chemicals CaCO$_3$, V$_2$O$_5$ (analytical reagent grade), and La$_2$O$_3$, Tm$_2$O$_3$ with 4N purity, were weighed according to the 9CaCO$_3$ + 0.47La$_2$O$_3$ + 0.03Tm$_2$O$_3$ + 3.5V$_2$O$_5$ → Ca$_9$La$_{0.94}$Tm$_{0.06}$(VO$_4$)$_7$ + 9CO$_2$↑ reaction. The mixtures were ground in an agate mortar for blending well, and extruded to form pellets. Then, these pellets were placed into an alumina crucible and sintered in a muffle furnace at 1000 °C for 48 h. These processes were repeated, and the sintering temperature was raised to 1200 °C to ensure complete reaction. The formation of the trigonal Ca$_9$La(VO$_4$)$_7$ phase was confirmed by X-ray power diffraction (XRD).

The crystal was grown in an iridium crucible with dimensions of 027 × 26 mm$^3$, in a 25 kHz mid-frequency induction furnace (DJL-400) in a N$_2$ atmosphere, with a pulling rate of 1-1.5 mm/h and a rotation rate of 8-12 rpm. A [001] oriented Ca$_9$La(VO$_4$)$_7$ crystal was used as a seed. When the growth process ended, the grown crystal was pulled slowly out of the melt, and cooled to room temperature at a rate of 15-30 °C/h. Large-volume boules of Tm:Ca$_9$La(VO$_4$)$_7$, 30 mm in length and 25 mm in diameter were obtained, Fig. 1(a). The coloration of the as-grown crystals ranged from dark-yellow to green. This is an indication of the presence of color centers which is typical for disordered Ca vanadates grown in anoxic conditions [13]. The formation of color centers is due to the reduction of V$^{5+}$ ions to V$^{4+}$ and V$^{3+}$ and the appearance of oxygen vacancies. In order to eliminate these effects which will be detrimental for potential laser applications, and to reduce the thermal stress, the grown crystal was annealed at 1200 °C for 24 h in air. This improved the transparency of the crystal and its coloration changed to yellowish, Fig. 1(b).

Fig. 1. (a) As-grown Tm:Ca$_9$La(VO$_4$)$_7$ boule; (b) annealed in air and polished 1 mm-thick plate cut from this boule; XRD pattern of the powdered Tm:Ca$_9$La(VO$_4$)$_7$ crystal.
The XRD data for the grown crystal were collected at room temperature in the $2\theta = 10$-$80^\circ$ range with a step of 0.02$^\circ$ and a scan speed of 0.13$^\circ$/min, using a Desktop X-ray diffractometer (Rigaku, Miniflex 600) equipped with Cu Kα radiation. The XRD pattern of the powdered as-grown crystal is shown in Fig. 1(c). The diffraction peaks match perfectly the standard pattern of undoped Ca$_9$La(VO$_4$)$_7$ (ICSD card #85104). The concentration of the Tm$^{3+}$ ions in the grown crystal $N_{\text{Tm}}$ was measured by an Inductively Coupled Plasma OES spectrometer (HORIBA Jobin Yvon, Ultima 2), resulting in a value of $N_{\text{Tm}} = 0.88 \times 10^{20}$ at/cm$^3$ or 5.72 at.%. Consequently, the segregation coefficient of Tm$^{3+}$ ions is $K_{\text{Tm}} = 0.95$ which indicates that they can easily substitute the “passive” La$^{3+}$ ions.

The Ca$_9$RE(VO$_4$)$_7$ vanadates are isostructural to the double calcium vanadate, Ca$_3$(VO$_4$)$_2$ or Ca$_{10.5}$(VO$_4$)$_7$ (sp.gr. $R_3c$), which is considered as a parent compound [17]. The trigonal whitlockite-like structure of Ca$_9$La(VO$_4$)$_7$ is formed as a result of a distortion of the Ca$_3$(VO$_4$)$_2$ one when the La$^{3+}$ ions partially occupy the cationic positions of the Ca$^{2+}$ ions [9,18], see Fig. 2(a). Since the difference of the ionic radii of the La$^{3+}$ and Ca$^{2+}$ ions is relatively small, the Ca$_9$La(VO$_4$)$_7$ structure is isomorphic to that of Ca$_3$(VO$_4$)$_2$ while disordering of the cationic positions occurs. The Ca$_9$RE(VO$_4$)$_7$ structure has four cationic sites with different occupancy numbers [9,17,18]: three low-symmetry sites (point group $C_1$): Me(1), Me(2) and Me(3) with coordination numbers 9, 8, and 7, respectively, and a 6-fold coordinated (octahedral) cationic site Me(4), as shown in Fig. 2(b). For an undoped Ca$_9$La(VO$_4$)$_7$, the Ca$^{2+}$ and La$^{3+}$ ions occupy randomly the same Me(1) – Me(4) sites in an overall proportion of 9:1 (the occupancy number for the Me(4) site is close to 1 for the Ca$^{2+}$ ions). In the Ln$^{3+}$-doped Ca$_9$La(VO$_4$)$_7$ crystals, the Ln$^{3+}$ and La$^{3+}$ ions are randomly distributed over the Me(1) – Me(3) cationic positions without inversion symmetry (together with the Ca$^{2+}$ ions). For the Me(1), Me(2) and Me(3) sites, the average Ln$^{3+}$/La$^{3+}$/Ca$^{2+}$–O$^{2-}$ distances are ~2.4, 2.5, and 2.6 Å, respectively. The shortest Ln$^{3+}$–Ln$^{3+}$ distance is ~3.6 Å.

Based on the XRD analysis, we determined the lattice constants for Tm:Ca$_9$La(VO$_4$)$_7$ as $a = b = 10.846$ Å, $c = 37.901$ Å ($V = 3861.2$ Å$^3$ and $Z = 6$), slightly shorter than for the undoped crystal ($a = 10.8987$ Å, $c = 38.1470$ Å) [9]. This is attributed to the difference in ionic radii of the dopant Tm$^{3+}$ and the substituted La$^{3+}$ ions (0.994 Å and 1.160 Å, respectively, e.g., for the 8-fold O$^{2-}$-coordination). The calculated density of Tm:Ca$_9$La(VO$_4$)$_7$ is $\rho = 3.746$ g/cm$^3$.

Fig. 2. (a) Fragment of the structure of the Tm:Ca$_9$La(VO$_4$)$_7$ crystal within one unit-cell; (b) oxygen coordination of metal ions in the four possible sites.

The vibrational properties of the Tm:Ca$_9$La(VO$_4$)$_7$ crystal were studied with polarized Raman spectroscopy. The Raman spectra recorded for the $x'(xy)y'$ geometries with $x, y = \pi$ or $\sigma$ and $x' = y' = a$ are shown in Fig. 3. The excitation wavelength was 514 nm. Here we use standard notations where $x'$ and $y'$ represent the direction of propagation of the excitation and
scattered light, and $x$ and $y$ stand for the polarization of the excitation and scattered light, respectively. The Raman bands are observed in two separate ranges: 200–470 cm$^{-1}$ and 740–930 cm$^{-1}$ which are similar to the Raman spectrum of the parent compound, Ca$_3$(VO$_4$)$_2$ [19]. The Raman bands in the low-frequency range are assigned to the O–V–O bending modes and to the Ca$^{2+}$ cation displacements. The high-frequency Raman bands are attributed to the V–O stretching modes and possible vibrations of the V–O...La/Tm chain [20]. The strongest Raman signal is observed for the $a(\pi\sigma)a$ geometry. The most intense band is at 867 cm$^{-1}$ with a full width at half maximum (FWHM) of 26.6 cm$^{-1}$. This stretching mode is assigned as $\nu(A_1)$. The broadening of the Raman bands is due to the disordered nature of the material. The parent compound, Ca$_3$(VO$_4$)$_2$, has been used for stimulated Raman scattering (SRS) of picosecond pulses [21]. The broad and intense Raman bands of Tm:Ca$_9$La(VO$_4$)$_7$ make it also interesting for self-SRS. In addition, the low-energy bands around ~350 cm$^{-1}$ can provide vibronic Tm laser operation as further extension of the tuning capability [22].

![Raman spectra for an $a$-cut Tm:Ca$_9$La(VO$_4$)$_7$ crystal excited at 514 nm](image)

**Fig. 3.** Raman spectra for an $a$-cut Tm:Ca$_9$La(VO$_4$)$_7$ crystal excited at 514 nm: (a) polarization dependence in the $a(xy)a$ geometry; (b) details of the spectrum for the $a(\pi\sigma)a$ geometry.

### 3. Spectroscopic characterization

The Ca$_9$La(VO$_4$)$_7$ crystal is an optically uniaxial birefringent crystal (point group R3c). Its optical axis is parallel to the $c$-axis. At ~1.85 $\mu$m, the two principal refractive indices of Ca$_9$La(VO$_4$)$_7$ are $n_o = 1.841$ and $n_e = 1.808$ [16] (positive uniaxial crystal). The spectral properties are described for the two principal light polarizations, $E \parallel c$ ($\pi$) and $E \perp c$ ($\sigma$).

![Absorption spectrum of the 5.72 at.% Tm:Ca$_9$La(VO$_4$)$_7$ crystal](image)

**Fig. 4.** (a) Absorption spectrum of the 5.72 at.% Tm:Ca$_9$La(VO$_4$)$_7$ crystal; (b) absorption cross-sections $\sigma_{abs}$ for the $^3H_6 \rightarrow ^3H_4$ transition of the Tm$^{3+}$ ion.

The absorption spectrum of the Tm:Ca$_9$La(VO$_4$)$_7$ crystal for the $\pi$- and $\sigma$-polarizations is shown in Fig. 4(a). It was measured at room temperature. For the absorption band related to the $^3H_6 \rightarrow ^3H_4$ transition of the Tm$^{3+}$ ion which is suitable for pumping at around 800 nm with commercial AlGaAs laser diodes, the maximum absorption cross-section is $1.5 \times 10^{-20}$ cm$^2$ at 791.3 nm for $\sigma$-polarization, determined as $\sigma_{abs} = \alpha / N_{Tm}$ where $\alpha$ is the absorption coefficient. The FWHM of the local peak is 8.2 nm. For $\pi$-polarization, $\sigma_{abs}$ is ~3 times lower. The UV absorption edge for the Tm:Ca$_9$La(VO$_4$)$_7$ crystal is at $\lambda_g = 0.44 \mu$m ($E_g = 2.82$ eV).
The absorption oscillator strengths for the Tm\(^{3+}\) ion in Ca\(_9\)La(VO\(_4\))\(_7\) were determined from the measured absorption spectrum:

\[
f_{\text{exp}}(JJ') = \frac{m_e c^2}{\pi e^2 N_{\text{TM}}(\lambda)^2} \Gamma(JJ'),
\]

where \(m_e\) and \(e\) are the electron mass and charge, respectively, \(c\) is the speed of light, \(\Gamma(JJ')\) is the integrated absorption coefficient within the absorption band and \(\langle \lambda \rangle\) is the “center of gravity” of the absorption band. The experimental absorption oscillator strengths were averaged over the principal light polarizations, \(1/3 \times (2f_\sigma + f_\pi)\). The results are shown in Table 1.

The values of \(f_{\text{exp}}\) were used to determine the intensity parameters, \(\Omega_2\), \(\Omega_4\) and \(\Omega_6\), within the standard Judd-Ofelt (J-O) theory [23,24], \(\Omega_2 = 4.682\), \(\Omega_4 = 0.659\) and \(\Omega_6 = 0.475\) \(10^{-20}\) cm\(^2\). Using these parameters, the absorption oscillator strengths were also calculated:

\[
f_{\text{calc}}(JJ') = \frac{8}{3h(2J'+1)(\lambda)} \left(\frac{n^2 + 2}{9n}\right) S_{\text{calc}}(JJ') + f_{\text{MD}}(JJ'),
\]

\[
S_{\text{calc}}(JJ') = \sum_{k=2,4,6} U^{(k)} \Omega_k, \text{ where } U^{(k)} = \langle (4f^s)^{SLJ} \| U^k \| (4f^a)^{SL'J'} \rangle^2.
\]

Here, \(S_{\text{calc}}\) are the line strengths, \(h\) is the Planck constant, \(n\) is the refractive index of the crystal and \(U^k\) are the squared reduced matrix elements [25]. The J-O theory describes electric-dipole (ED) transitions. The contribution of magnetic-dipole (MD) transitions with \(J-J' = 0, \pm 1, f_{\text{MD}}\), was taken from the literature [26].

| Transition \(J\rightarrow J'\) | \(\lambda\) \(\text{nm}\) | \(\epsilon\) \(\text{cm}^{-1}\) | \(f\) \(\text{cm}^{-1}\text{nm}\) | \(f_{\text{exp}} \times 10^6\) | \(f_{\text{cal}} \times 10^6\) |
|-----------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \(^{3}\text{H}_6\rightarrow^{3}\text{F}_4\) | 1667            | 5998            | 118.29          | 3.25            | 3.24\text{ED}  |
| \(^{3}\text{H}_6\rightarrow^{3}\text{H}_5\) | 1214            | 8237            | 31.76           | 2.56            | 1.52\text{ED} + 0.57\text{MD} |
| \(^{3}\text{H}_6\rightarrow^{3}\text{H}_4\) | 792.0           | 12626           | 27.80           | 3.71            | 3.59\text{ED}  |
| \(^{3}\text{H}_6\rightarrow^{3}\text{F}_3\) | 686.0           | 14577           | 10.96           | 1.96            | 1.76\text{ED}  |
| \(^{3}\text{H}_6\rightarrow^{1}\text{G}_4\) | 473.0           | 21141           | 3.83            | 1.41            | 1.32\text{ED}  |

The probabilities of spontaneous radiative transitions were calculated from the corresponding line strengths which, in turn, are derived from the J-O parameters \(\Omega_k\) and squared reduced matrix elements \(U^k\), see Eq. (2b):

\[
A_{\text{calc}}(JJ') = \frac{64\pi^4 c^2}{3h(2J'+1)(\lambda)^3} n \left(\frac{n^2 + 2}{3}\right) S_{\text{calc}}^{(k)}(JJ') + A_{\text{MD}}(JJ')
\]

The MD contributions \(A_{\text{MD}}\) were taken from [26]. On the basis of the probability of spontaneous transitions for the separate emission channels \(J\rightarrow J'\), we calculated the total probability, \(A_{\text{tot}}\), the corresponding radiative lifetime of the excited-state, \(\tau_{\text{rad}}\), and the luminescence branching ratios for the emission channels, \(B(JJ')\):

\[
A_{\text{tot}} = \sum_j A_{\text{calc}}(JJ') \text{ and } \tau_{\text{rad}} = \frac{1}{A_{\text{tot}}},
\]
The results are summarized in Table 2. In particular, the radiative lifetime of the lowest excited-state, $\tau_{\text{rad}}(T^4) = 2.02 \text{ ms}$. The photoluminescence (PL) spectra for the Tm$^{3+}$-doped Ca$_9$La(VO$_4$)$_7$ crystal were measured with unpolarized light under excitation to the $^3H_4$ state at $\sim 0.79 \mu m$ using a tunable Ti:Sapphire laser, see Fig. 5. The PL from the excited level is observed at 0.78-0.82 $\mu m$ ($^3H_4 \rightarrow ^3H_6$ transition) and at 1.4-1.55 $\mu m$ ($^3H_4 \rightarrow ^3F_4$ transition). A broad band spanning from 1.6 to 2.05 $\mu m$ is due to the $^3F_4 \rightarrow ^3H_6$ transition from the upper laser level. In addition, several emissions in the visible (centered at $\sim 0.48 \mu m$ and at $\sim 0.7 \mu m$) and near-IR (at $\sim 1.07 \mu m$) are detected which are related to the radiative transitions from the higher-lying $^1G_4$ and $^3F_{2,3}$ states of Tm$^{3+}$. These states are populated by the excited-state absorption (ESA) process $^3H_5 \rightarrow ^1G_4$ (for the $^1G_4$ state) and the same ESA with a subsequent non-radiative relaxation (for the $^3F_{2,3}$ states). A weak PL of Er$^{3+}$ impurity is also observed at $\sim 0.52$, 0.54 and 1 $\mu m$. The presence of Er$^{3+}$ in the studied crystal may be due to impurities in the Tm$_2$O$_3$ reagent. Then, the Er$^{3+}$ ions are excited by an energy-transfer process Tm$^{3+}(^3H_4) \rightarrow$ Er$^{3+}(^4I_{9/2})$ which is very probable because these two states are resonant in energy. The green emission from Er$^{3+}$ originates from the $^4S_{3/2} + ^2H_{11/2} \rightarrow ^4I_{15/2}$ transition and the near-IR emission from the $^4I_{11/2} \rightarrow ^4I_{15/2}$ one. As a result, visible PL from the Tm:Ca$_9$La(VO$_4$)$_7$ crystal has a green-bluish color.

Table 2. Calculated Emission Probabilities for the Tm$^{3+}$ Ion in Ca$_9$La(VO$_4$)$_7$ Crystal

| Excited state | Final state | $\lambda_{\text{m}}$ (nm) | $B_{\text{r}}$ % | $A_{\text{tot}}$ s$^{-1}$ | $\tau_{\text{rad}}$ ms |
|---------------|-------------|--------------------------|----------------|--------------------------|---------------------|
| $^3F_4$       | $^3H_6$     | 1667                     | 95.4 ED        | 100                      | 495.7               |
| $^3H_5$       | $^3F_4$     | 4467                     | 9.1 ED + 1.5 MD | 1.8                      | 590.2               |
| $^3H_6$       | $^1H_6$     | 1214                     | 426.1 ED + 153.5 MD | 98.2                   | 1.69                |
| $^3H_4$       | $^3H_6$     | 2279                     | 22.4 ED + 17.3 MD | 1.2                      | 3190                |
| $^3H_6$       | $^1H_4$     | 1509                     | 229.1 ED + 42.0 MD | 8.5                      | 0.31                |
| $^3H_6$       | $^3F_4$     | 792.1                    | 2879 ED        | 90.3                     |
| $^3H_4$       | $^4F_4$     | 5121                     | 3.4 ED + 0.2 MD | 0.1                      | 3457                |
| $^3H_4$       | $^1F_4$     | 1166                     | 102.9 ED + 108.1 MD | 6.1                      | 0.29                |
| $^3H_4$       | $^3F_2$     | 686.0                    | 2395 ED        | 69.3                     |
| $^1G_4$       | $^1F_3$     | 1641                     | 16.2 ED        | 44.2                      | 5877                |
| $^1F_1$       | $^1F_3$     | 1577                     | 846.9 ED       | 24.5                      |
| $^1H_4$       | $^1F_3$     | 1166                     | 102.9 ED + 108.1 MD | 6.1                      |
| $^1H_4$       | $^3F_2$     | 686.0                    | 2395 ED        | 69.3                     |
| $^1H_4$       | $^1F_3$     | 1641                     | 16.2 ED        | 44.2                      |

$\lambda_{\text{m}}$ - mean wavelength of the emission band, $B_{\text{r}}$ – probability of radiative spontaneous transition, $A_{\text{tot}}$ - luminescence branching ratio, $A_{\text{tot}}$ and $\tau_{\text{rad}}$ – total probability of radiative spontaneous transitions and radiative lifetime of the excited state, respectively; ED and MD stand for the electric-dipole and magnetic-dipole contributions, respectively.
The stimulated-emission (SE) cross-section, $\sigma_{SE}$, spectra corresponding to the $^3F_4 \rightarrow ^3H_6$ transition of the Tm$^{3+}$ ion in Ca$_9$La(VO$_4$)$_7$ were calculated using the modified reciprocity method [27]:

$$
\sigma_i^{SE}(\lambda) = \frac{1}{8\pi n_i^2 \tau_{rad} c} \sum_{j=x,y,z} \int \lambda^3 \sigma_i^{abs}(\lambda) \exp(-hc/(kT\lambda)) \, d\lambda.
$$

Here, $\sigma_i^{SE}$ and $\sigma_i^{abs}$ ($i = \pi$ or $\sigma$) are the SE and absorption cross-sections for the $i$-th principal light polarization, respectively, $\tau_{rad}$ is the radiative lifetime of the emitting state ($^3F_4$ state of Tm$^{3+}$) determined with the J-O theory. The results on the SE cross-sections are shown in Fig. 6(a). The maximum value of $\sigma_{SE}$ is $1.28 \times 10^{-20}$ cm$^2$ at 1854 nm for $\pi$-polarization. This value is ~3 times larger than for $\pi$-polarized light, $0.38 \times 10^{-20}$ cm$^2$ at 1858 nm. The strong polarization-anisotropy of $\sigma_{SE}$ was observed by direct measurement of the luminescence intensity for the two polarizations.

The results on the luminescence decay for the Tm:Ca$_9$La(VO$_4$)$_7$ crystal are presented in Fig. 6(b). By exciting the Tm$^{3+}$ ions at 0.79 $\mu$m, we monitored the decay from the $^3F_4$ upper laser level (at 1.85 $\mu$m) and the $^3H_4$ pump state (at 0.8 $\mu$m). The sample was powdered and immersed in glycerin (10 wt.% of powder in the solution) in order to prevent the effect of reabsorption on the measured lifetime. The decay curves are clearly single-exponential. The determined lifetimes are $\tau_{exp}(^3F_4) = 1.19$ ms and $\tau_{exp}(^3H_4) = 122$ $\mu$s. The shortening of the experimental lifetime of the upper laser level with respect to the radiative lifetime, expressed by a quantum yield of luminescence of $\eta_q = \tau_{exp}/\tau_{rad} = 59\%$, is partially attributed to the non-radiative relaxation probably related to the color centers which are not completely eliminated even after crystal annealing, to the concentration quenching which is also rather strong in, cf. Tm:REVO$_4$ crystals [28], and to the excitation transfer to the Er$^{3+}$ impurities.
An important parameter for quasi-three-level laser materials, e.g. Tm$^{3+}$-doped ones, is the gain cross-section, $\sigma_g = \beta \sigma_{SE} - (1 - \beta) \sigma_{abs}$, where $\beta = N_2/N_{1m}$ is the inversion ratio and $N_2$ is the population of the upper laser level, $^3F_4$. The results on $\sigma_g$ for the Tm:Ca$_9$La(VO$_4$)$_7$ crystal are shown in Fig. 7.

![Fig. 7. Gain cross-sections, $\sigma_g = \beta \sigma_{SE} - (1 - \beta) \sigma_{abs}$, for the $^3F_4 \rightarrow ^1H_6$ transition of the Tm$^{3+}$ ion in Ca$_9$La(VO$_4$)$_7$ crystal for the $\pi$- (a) and $\sigma$- (b) polarizations; $\beta = N_2(Tm)/N_{1m}$ is the inversion ratio.]

The gain cross-sections are much higher for $\sigma$-polarization as compared with $\pi$-polarization. The uniaxial crystals offer two principal orientations of the laser elements, denoted as $a$-cut and $c$-cut. For a laser based on an $a$-cut Tm:Ca$_9$La(VO$_4$)$_7$ crystal and containing no polarizing elements, we expect linearly ($\sigma$-) polarized laser output; and for a $c$-cut crystal, it will be unpolarized. For the $\sigma$-polarization at low $\beta < 0.05$, a broad gain spectrum spanning from 1.9 to 2.05 $\mu$m is observed. With an increase of $\beta$, a local peak is formed in the gain spectra shifting from $\sim$1.93 $\mu$m ($\beta \sim$0.1) to 1.86 $\mu$m ($\beta >$0.1). In contrast, the $\pi$-polarization impresses by a broad gain smoothness up to high inversion levels of $\beta \sim$0.3. In general, the gain spectra for Tm:Ca$_9$La(VO$_4$)$_7$ are broad and structureless. Thus, one can expect broad tuning of the laser emission from $\sim$1.8 to 2.05 $\mu$m.

From the point of view of the spectroscopic properties, both $a$- and $c$-cut Tm:Ca$_9$La(VO$_4$)$_7$ crystals are attractive for laser operation as they offer access to the high-gain $\sigma$-polarization. The thermo-optic coefficients are negative for the Ca$_9$La(VO$_4$)$_7$ crystal: $dn_o/dT = -13.2$ and $dn_e/dT = -12.4 \times 10^{-6}$ K$^{-1}$ at $\sim$1.85 $\mu$m [11]. However, for an $a$-cut crystal, one can expect a positive thermal lens due to an “athermal” compensation of the negative contribution of $dn_e/dT$ and the positive contribution of the large thermal expansion along the $a$-axis, $\alpha_a = 17.5 \times 10^{-6}$ K$^{-1}$ [11]. This may potentially enable microchip laser operation where the positive thermal lens plays a key role in the mode stabilization in a plano-plano laser cavity [29]. For a $c$-cut crystal, the thermal lens is expected to be negative due to much weaker thermal expansion along this direction, as $\alpha_a/\alpha_c \sim$1.9. Thus, one can conclude that $a$-cut Tm:Ca$_9$La(VO$_4$)$_7$ crystals are more attractive for laser operation.

4. Conclusion

We report on the Czochralski growth and detailed spectroscopic characterization (including study of absorption, emission and Raman spectra, luminescence decay, transition cross-sections and Judd-Ofelt modeling) of a novel trigonal crystal, Tm$^{3+}$:Ca$_9$La(VO$_4$)$_7$. This work represents the first description of the optical properties of the Tm$^{3+}$ ion in calcium vanadate single crystals. The disordered multi-site structure of Ca$_9$La(VO$_4$)$_7$ results in broad and structureless absorption and emission bands of the Tm$^{3+}$ ions while preserving the polarization anisotropy of the optical properties. According to the analysis of the spectroscopy and thermo-optics of Tm:Ca$_9$La(VO$_4$)$_7$, the preferred orientation for laser operation is $a$-cut ($\sigma$-polarization). The maximum SE cross-section corresponding to the $^3F_4 \rightarrow ^1H_6$ transition is $1.28 \times 10^{-20}$ cm$^2$ at 1854 nm for the $\sigma$-polarization. According to the gain spectra in both polarizations, broadband tunable laser emission at 1.8-2.05 $\mu$m and ultrashort
pulse generation may be achieved. Tm:Ca₉La(VO₄)₇ possesses relatively long storage time in
the upper laser level, ~1.2 ms for 5.72 at.% Tm doping, which is beneficial for passive Q-
switching. Future work on Tm:Ca₉La(VO₄)₇ should be focused on the reduction of non-
radiative quenching via proper annealing and purification of the raw materials which may
provide higher luminescence quantum yield. In addition, Tm:Ca₉La(VO₄)₇ crystals are
promising Raman and self-Raman frequency shifters.

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