

Terbium-based fluoride and oxide crystals for visible lasers

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Terbium-based fluoride and oxide crystals for visible lasers

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Abstract

E. Castellano-Hernández: *Terbium-based fluoride and oxide crystals for visible lasers*

In the course of this thesis, Tb^{3+} -doped fluoride and oxide materials have been investigated with regard to their properties as potential laser active materials with emission in the visible range. Main spectroscopic and laser investigations have been carried out in LiLuF_4 and LiTbF_4 , KY_3F_{10} and $\text{KTb}_3\text{F}_{10}$, BaY_2F_8 , LaF_3 , and TbF_3 as fluorides materials and YAlO_3 and TbAlO_3 , $\text{Y}_3\text{Al}_5\text{O}_{12}$, and $\text{KY}(\text{WO}_4)_2$ as oxide materials. The host material plays a fundamental role in the capacity of Tb^{3+} laser emission as can help to decrease or even avoid detrimental excited state absorption (ESA) processes, unraveling the key to developing efficient Tb^{3+} lasers. Thus, different Tb^{3+} materials were investigated for laser experiments, with a wide range of doping concentrations up to stoichiometric 100 at.%.

Tb^{3+} absorption and emission cross-sections were determined by absorption and fluorescence spectroscopy respectively, exposing the feasible wavelength for pumping and laser emission. Measurements of the fluorescence dynamics indicate the lack of interionic processes between Tb^{3+} ions that could limit the suitable concentration for laser performance. Consequently, high concentrations can contribute to compensate for the low Tb^{3+} absorption and emission cross-sections. Furthermore, pump-probe ESA measurements show gain in the green and yellow spectral regions for Tb^{3+} materials, included the oxide YAlO_3 . This finding is especially relevant as Tb^{3+} laser emission from an oxide material has not yet been demonstrated.

Laser emission with a Tb^{3+} (28 at.%): LiTbF_4 crystal was achieved in cw operation, delivering 0.5 W at 587.5 nm with a slope efficiency of 25%, unprecedented values for any direct emitting yellow laser. Diode-pumped laser emission on this crystal was accomplished with a 52% of slope efficiency at 544 nm in the green and a 22% at 587.4 nm in the yellow, entailing the first demonstration of a diode-pumped Tb^{3+} -based solid-state laser, to the best of the author's knowledge. The present work also demonstrates UV-pumping as a viable solution on a Tb^{3+} (14 at.%): LiTbF_4 crystal, increasing by two the optical-to-optical efficiency of the overall laser system in comparison with cyan-blue pumping. Laser operation was achieved with Tb^{3+} : BaY_2F_8 at 581 nm with a slope efficiency of 16%. To the best of the author's knowledge, this is the first demonstration of laser emission of this crystal.

Kurzfassung

E. Castellano-Hernández: *Terbium-based fluoride and oxide crystals for visible lasers*

Im Rahmen dieser Arbeit wurden Tb^{3+} -dotierte Fluorid- und Oxidmaterialien auf ihre Eigenschaften als potentielle laseraktive Materialien mit Emission im sichtbaren Spektralbereich untersucht. Die wichtigsten spektroskopischen und lasertechnischen Untersuchungen wurden an den Fluoridmaterialien LiLuF_4 und LiTbF_4 , KY_3F_{10} und $\text{KTb}_3\text{F}_{10}$, BaY_2F_8 , LaF_3 , und TbF_3 und den Oxidmaterialien YAlO_3 und TbAlO_3 , $\text{Y}_3\text{Al}_5\text{O}_{12}$, und $\text{KY}(\text{WO}_4)_2$ durchgeführt. Die Wahl des Wirtsmaterial spielt eine grundlegende Rolle für die Laseremission von Tb^{3+} , da es dazu beitragen kann, nachteilige Absorptionsprozesse aus dem angeregten Zustand (ESA) zu verringern oder sogar zu vermeiden, was den Schlüssel zur Entwicklung effizienter Tb^{3+} -Laser darstellt. Daher wurden verschiedene Tb^{3+} -Materialien mit unterschiedlichen Dotierungskonzentrationen bis hin zu stöchiometrischen 100 at.% in Laserexperimenten untersucht.

Die Absorptions- und Emissionsquerschnitte von Tb^{3+} wurden durch Absorptions- bzw. Fluoreszenzspektroskopie bestimmt, wobei die geeignete Wellenlänge für das Pumpen und die Laseremission ermittelt wurde. Die Messungen zur Fluoreszenzdy- namik bestätigen das Fehlen von interionischen Prozessen zwischen den Tb^{3+} -Ionen, welche die nutzbare Dotierkonzentration begrenzen könnten. Folglich können hohe Konzentrationen dazu beitragen, die niedrigen Tb^{3+} -Absorptions- und Emission- querschnitte zu kompensieren. Außerdem zeigen Pump-Probe-ESA-Messungen optische Verstärkung im grünen und gelben Spektralbereich für Tb^{3+} -Materialien, darunter auch das Oxid YAlO_3 . Dieses Ergebnis ist besonders wichtig, da Laseremis- sion von Tb^{3+} mit einem Oxidmaterial noch nicht gezeigt werden konnte.

Die Laseremission mit einem Tb^{3+} (28 at.%): LiTbF_4 -Kristall wurde im cw-Betrieb erreicht und lieferte 0,5 W bei 587,5 nm mit einer differentiellen Effizienz von 25%, beispiellose Werte für jeden direkt emittierenden gelben Laser. Diodengepumpte Laseremission mit dem selben Kristall wurde ebenfalls erreicht. Die differentielle Effizienz lag hierbei bei 52% bei 544 nm im grünen Bereich und 22% bei 587,4 nm im gelben Bereich. Soweit dem Autor bekannt ist, stellt dies die erste Demonstration eines diodengepumpten Tb^{3+} -basierten Festkörperlasers dar. Die vorliegende Arbeit zeigt auch, dass UV-Pumpen eine praktikable Lösung für einen Tb^{3+} (14 at.%): LiTbF_4 - Kristall ist, wodurch sich optisch-optische Effizienz des gesamten Lasersystems im Vergleich zum Cyan-Blau-Pumpen verdoppelt. Der Laserbetrieb wurde mit Tb^{3+} : BaY_2F_8 bei 581 nm mit einer differentiellen Effizienz von 16% erreicht. Soweit dem Autor bekannt ist, ist dies die erste Demonstration der Laseremission dieses Kristalls.

To Miguel Molins Bedriñana,
for making it possible.

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Acronyms

A acceptor

cw continuous-wave

CFD crystal field depression

D donor

DPSSL diode-pumped solid-state laser

ESA excited state absorption

ETU energy transfer up-conversion

GSA ground state absorption

H Hamiltonian

IR infrared

UVA near ultraviolet

2 ω -OPSL frequency-doubled optically pumped semiconductor laser

OPO optical parametric oscillator

PBS polarizing beam splitter

PMT photomultiplier tube

RE rare earth

REE rare earth element

RT room temperature

SHG second-harmonic generation

SSL solid-state laser

VECSEL vertical external-cavity surface-emitting laser

YAG $\text{Y}_3\text{Al}_5\text{O}_{12}$

FWHM full width at half maximum

HR highly reflective

PM pump mirror

OCM output coupler mirror

Introduction

1.1 Motivation

The immense variety of laser sources that have been developed in science and industry comes from the need to fulfill the specific requirements of medical, industrial, research, and daily life applications. The convenience of a laser emitting at a particular wavelength range is in some cases a matter of performance optimization, cost reduction, or market availability. In other cases, the use of a laser with a very specific emission wavelength may be essential and the selection of wavelengths available in existing laser technology limits the possible applications.

Trivalent terbium lasers have the capacity to emit in the green and yellow spectral regions. Visible lasers in these emission ranges are of interest to a variety of applications. Green lasers are used in science for many different purposes such as fluorescence microscopy [Bau00, Con05], interferometry [Zha16], or for pumping other lasers like Ti:sapphire lasers [Har91, McD07]. In medicine, examples of green laser applications include bioinstrumentation, medical scanning, cancer treatment, and surgery [Tsu03, Hol14, Krp10, Baz13]. Industrial applications employ green lasers for material processing, where they are beneficial due to the high absorption coefficient in the green of elements such as copper, gold, or silicon [Eng11, Yua09]. In addition, this quality makes green lasers perfect candidates for engraving and labeling polymeric materials and for copper and gold 3D printers [@CYC19, @Ind18]. Furthermore, green lasers are wide spread in daily life applications, functioning as laser pointers, laser light show systems for entertainment, and in laser printers and laser projectors and displays as part of RGB sources [Hol01].

Well-defined laser emission in the yellow range is also required by a wide variety of applications in science, medicine, and technology. In science, yellow lasers are used for the excitation of the D-lines of absorption of sodium at 589 nm to generate artificial laser guide stars in astronomy [Due09]. In addition, laser emission at this wavelength is also required for sodium detection in spectroscopy and industry [Jun81]. In the field of flow cytometry, laser emitting yellow wavelengths are demanded for the excitation of specific fluorophores that cannot be excited otherwise [Kap07, Tel12]. Another example is the use of yellow lasers in laser-based techniques for enriching of natural uranium to reactor-grade (2.5% to 3.0% ^{235}U) by selective separation of uranium isotopes [Rao03]. In medicine, yellow laser emission has the

highest ratio of oxyhemoglobin absorption vs. melanin absorption, which reduces the laser power needed for macular photocoagulation treatments by 30-40% compared to green lasers and thus decreases the risk of retinal damage [Mai86]. Yellow lasers have also proven their advantageous potential in skin therapies, e.g. in treatments of vascular lesions, among others [Kar19].

The specific wavelengths provided by the energy level scheme of Tb^{3+} are not easy to achieve by using other laser concepts. The absence of available diode lasers emitting in the so-called "semiconductor's green gap" (extending from ~ 535 nm to ~ 620 nm in the green to orange spectral region) leads to the current use of complex setups and limited efficiencies, especially at yellow wavelengths. Therefore, diode-pumped solid-state lasers (DPSSLs) represent the simplest and most power scalable solution to address these wavelengths, as they are characterized by their good beam quality, stability, robustness against misalignment, low handling complexity, and potential for miniaturization.

The demonstration of efficient laser emission of Tb^{3+} -doped materials in the green at wavelengths in the range of 540 – 550 nm and in the yellow at wavelengths of 584 nm and 587 nm [Met16, Met17] brings Tb^{3+} -based solid-state lasers as alternative sources for applications in these emission ranges. However, the complex energy level distribution of the trivalent terbium $4f^n$ and $4f^{n-1}5d^1$ manifolds make it prone to ESA processes, which are detrimental for the laser operation. In consequence, the selection of the host material is critical to achieving efficient laser performance. Hence, this work is dedicated to the study of Tb^{3+} as active ion for solid-state lasers and its behavior in a variety of fluoride and oxide host materials.

1.2 Thesis structure

The thesis begins with a description of the fundamental theory required to understand Tb^{3+} -based lasers, collected in chapter 2. Chapter 3 introduces Tb^{3+} -ions as active ions for visible laser. A description of the host materials and crystalline samples used in the experiments of this work is given in chapter 4. The measurements of the spectroscopic properties of these materials are presented in chapter 5. Chapter 6 deals with the laser experiments which have been carried out with the Tb^{3+} -based crystals. Chapter 7 gives a conclusion and outlook derived from the overall results of the present work.

This chapter introduces the physical concepts necessary to understand the laser processes in the frame of this thesis. Therefore, the properties of rare earth ions will be described, followed by the energy-exchange processes in the ions themselves and with the crystalline matrix, and ending with the basics of the lasers process itself. The exposition of the fundamentals will be only briefly introduced since a more detailed description can be found in books as [Lan65], [Atk11], [Sve89], or [Sol05].

2.1 The rare earth ion

The rare earth elements (REEs) are the group of chemical elements consisting of the lanthanides, from lanthanum with $Z = 57$, to lutetium with $Z = 71$, as well as yttrium ($Z = 39$) and scandium ($Z = 21$). The last two elements are included due to their chemical similarities and because of their presence in the same ores deposits as lanthanides. The term "rare earth" element has a historical origin and it is misleading, as the abundance in the earth's crust of REEs, except the radioactive promethium, is comparable to that of commonly used industrial metals as chromium, nickel, copper, or lead [Hax02]. Among them, the elements from Cerium ($Z = 58$) to europium ($Z = 63$) and from terbium ($Z = 65$) to ytterbium ($Z = 70$) are optically active elements that have demonstrated their potential as dopants on laser gain media.

Lanthanides are usually incorporated in crystals as trivalent cations. The outer electronic configuration is $5s^2 5p^6 4f^n$, with n varying from 1 in Ce^{3+} to 13 in Yb^{3+} . The $4f^n$ electrons, responsible for the optical transitions, are shielded from the electromagnetic field of the crystalline matrix by the full occupation of the 5s and 5p orbitals. Consequently, the energy level structure of trivalent lanthanides does not vary strongly under the influence of the crystal field of different host materials and should be therefore similar to the one expected for the free ion.

2.1.1 Free ion

The energy positions E , of the electronic energy levels in an ion can be determined by solving the time-independent Schrödinger equation

$$H\Psi = E\Psi \quad (2.1)$$

where Ψ represent the wave function of the electronic cluster and the Hamiltonian H determines the different interactions of the valence electrons in the ion and with the crystalline matrix.

Considering an isolated ion with an atomic number Z and an electronic number N , the Hamiltonian can be written as

$$H_{free} = \sum_{i=1}^N \left(-\frac{\hbar}{2m_e} \nabla_{r_i}^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) + \sum_{i<j}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad (2.2)$$

where $\hbar$ is the reduced Plank constant, m_e and e the mass and charge of the electron, ϵ_0 the vacuum permittivity, and r_i and r_{ij} are the distance between the i -th electron and the nucleus and between electrons i -th and j -th respectively. The terms in the parentheses correspond to the kinetic energy of the electron and the Coulomb interaction with the nucleus. The right term corresponds to the Coulomb interaction between each pair of electrons. The spin-orbit interaction is neglected here and will be added as a perturbation later.

Due to the cross-interaction between electrons, equation 2.2 cannot be separated into N equations with an analytic single particle solution for each wave function. Nevertheless, it is possible to apply an ansatz to combine the potential of the nucleus and the interaction of the $N-1$ remaining electrons in an effective central field $V(r_i)$ and add the non-centrosymmetric contribution later on as a perturbation. The solution of such a quantum many-body system can be approximately determined by applying the Hartree-Fock method. In addition, the use of a Slater determinant ensures that the Pauli principle is obeyed. The solution is achieved by adopting iterative algorithms until the result is self-consistent. Thus, the Hamiltonian can be redefined as a formal one-particle operator

$$H_0 = \sum_{i=1}^N \left(-\frac{\hbar}{2m_e} \nabla_{r_i}^2 + V(r_i) \right), \quad (2.3)$$

that depends on the other electrons by means of the self-consistent procedure. The corresponding Schrödinger equation $H_0\Psi_0 = E_0\Psi_0$ have as solution the product of the single electron wave functions

$$\Psi_0 = \prod_{i=1}^N \Psi_i = \prod_{i=1}^N |n_i l_i m_l m_s\rangle \quad (2.4)$$

where the principal quantum number n_i , the angular momentum l_i , and the magnetic and spin quantum numbers m_l and m_s , determine the state of the i -th particle.

Due to the centrosymmetric character of the effective potential, the wave functions Ψ_i are degenerate with respect to the m_l and m_s quantum numbers. Nevertheless, the contribution to the Hamiltonian due to the non-centrosymmetric electron-electron interaction, H_{ee} can be now added as a perturbation

$$H_{ee} = \sum_{i < j}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{i=1}^N \left(\frac{Ze^2}{4\pi\epsilon_0 r_i} + V(r_i) \right) \quad (2.5)$$

as well as the influence of the spin-orbit interaction

$$H_{so} = \sum_{i=1}^N \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{2m_e^2 c^2 r_i^3} (\vec{l}_i \cdot \vec{s}_i), \quad (2.6)$$

where c is the speed of light. Thus, the Hamiltonian for the free ion is describe as

$$H = H_0 + H_{ee} + H_{so}. \quad (2.7)$$

The influence of H_{ee} and H_{so} depends on the atomic number of the ion. For ions with a small Z , the spin-orbit coupling is weak and the spins are coupled all together into a resultant $\vec{S} = \sum_i \vec{s}_i$, as well as all the orbital momenta are coupled into $\vec{L} = \sum_i \vec{l}_i$. The total angular momentum is then defined as $\vec{J} = \vec{L} + \vec{S}$. This configuration is called Russell-Saunders coupling or LS coupling. In heavy ions, the spin-orbit coupling dominates over the Coulomb interaction, and is named as jj-coupling. In this configuration, the spin and the angular momenta of individual electrons are coupled to a combined angular momentum $\vec{j}_i = \vec{l}_i + \vec{s}_i$. Therefore, the total angular momentum is in this case $\vec{J} = \sum_i \vec{j}_i$.

Due to their intermediate size, the influence of the two contributions to the Hamiltonian in rare-earth ions is equivalent, and the ionic states are linear combinations of LS-states with the same total angular momentum J . Nevertheless, the term symbols $^{2S+1}L_J$, based on the Russell-Saunders notation, can be used to label ionic states regardless of the extent of the jj-coupling and will be used to define the ionic states of lanthanides in the following sections. It should be noticed that in the absence of an external field, J is conserved and each energy level of the system is $(2J + 1)$ -fold degenerated.

2.1.2 Lanthanide ions in a crystalline structure

Effect of the crystal field in the $4f^n$ states

Owing to the shielded nature of the $4f^n$ valence electrons in lanthanides, the impact of the crystal field is weak and can be treated as a perturbation of the free-ion Hamiltonian. Therefore, equation 2.7 can be rewritten as

$$H = H_0 + H_{ee} + H_{so} + H_{cf}. \quad (2.8)$$

where H_{cf} implements the interaction with the electrostatic field generated by the surrounding ligands and it is defined as

$$H_{cf} = \frac{1}{4\pi\epsilon_0} \sum_i \sum_l \frac{Z_l e^2}{|\vec{R}_l - \vec{r}_i|}. \quad (2.9)$$

where Z_l and $\vec{R}_l$ are the atomic number and the position of the l -th ligand. This interaction causes the Stark effect and is about one order of magnitude weaker than the previous effects.

In the presence of an external field, the total angular momentum $\vec{J}$ is not longer conserved but only its projection M_J on the direction of the field. Thus, the external field removes the $(2J+1)$ -fold degeneracy of the energy levels. Whether if the degeneracy is completely or partially removed depends on the symmetry of the system as is described by the Kramer's theorem. Accordingly, for ions with an even number of electrons the degeneracy is completely removed and each manifold split into $2J+1$ sublevels, while in ions with an odd number of electrons, a 2-fold degeneracy remains and each manifold split into $(2J+1)/2$ sublevels. In this way, the energy levels of the $4f$ states involved in the laser interactions are determined.

Effect of the crystal field in the $4f^{n-1}5d^1$ states

Transitions into the $4f^{n-1}5d^1$ should be also taken into account as energy transfer processes entailing $5d$ levels can either favor or hinder the laser performance. However, laser transitions involving the $4f^{n-1}5d^1$ configuration are not expected in Tb^{3+} ions and therefore, they are beyond the scope of this thesis and not considered here. In consequence, only a summary of the characteristics of the $4f^{n-1}5d^1$ configuration will be described.

The more external distribution of $5d$ orbitals in comparison with $4f$ orbitals results in a stronger influence of the lattice crystal field in the $5d$ electronic states. This effect exceeds the impact of the electron-electron or spin-orbit interactions ($H_{cf} \geq$

H_{ee}, H_{so}) and cannot be considered a perturbation of the free-ion Hamiltonian. Therefore, as a result of the strong electron-phonon coupling between the ligands and the 5d states, interconfigurational transitions from $4f^n$ states to the 5d states, present in general broad linewidths. In addition, a change of parity makes these transitions parity allowed accordingly with the Laporte rule that forbids electronic transitions that conserve parity, and therefore they are orders of magnitude stronger than intraconfigurational transitions between states in the 4f shell.

2.2 Energy transfer processes in lanthanides

Laser emission from solid-state materials is based on the interaction of electromagnetic radiation with the optically active ions in the material. The processes involved in the laser performance consist of energy exchange between electronic levels and require the interaction of the ion with photons, phonons, or other neighboring ions. When the energy exchange occurs in a single ion, it is denominated intraionic process. In case that two or more ions are involved, the process is then denominated interionic. In the course of this section, it will be considered that the thermalization at room temperature (RT) is fast enough to define multiplets as single levels.

2.2.1 Intraionic processes

Energy exchange involving a single ion must be assisted by the interaction with either photons or phonons. When the interaction results in the emission of a photon, the process is defined as radiative. In the case of an electronic relaxation without the emission of photons, the process is defined as non-radiative.

Absorption

This event takes place when an ion interacts with an incoming photon that matches the energy difference between two states of the ionic system, i.e. $E_{ph} = h\nu = E_2 - E_1$, for two involved electronic levels $|1\rangle$ and $|2\rangle$ with energies E_1 and E_2 such that $E_2 > E_1$. The energy of the photon is transferred to the ion resulting in the excitation of an electron into $|2\rangle$. If the ion is initially in the ground state, the phenomenon is called ground state absorption (GSA). On the other hand, if the electron is already in an excited state when the interaction occurs, the phenomenon is called ESA.

Defining N_1 as the number of electrons of the lower energy level $|1\rangle$, the occupation rate of this level can be described as

$$\left(\frac{dN_1}{dt}\right)_{abs} = -W_{12} \cdot N_1 = -\sigma_{12}FN_1 \quad (2.10)$$

where W_{12} is the rate of the electronic transition $|1\rangle \rightarrow |2\rangle$, σ_{12} is the absorption cross-section, and F is the photon flux of intensity I defined as $F = I/h\nu$.

The absorption cross-section (σ_{abs}) is an especially relevant quantity for laser operation since it determines the capability of the gain media to absorb the pump power. Therefore, this magnitude quantifies the likelihood or rate of that ions in a given cross-sectional area will absorb photons with a particular λ .

Stimulated emission

This radiative process occurs when an excited ion interacts with an incoming photon with energy $E_{ph} = h\nu = E_2 - E_1$ as described in the previous section, stimulating the emission of a second photon that is identical in direction, frequency, phase, and polarization. The electronic occupation N_2 of the upper level $|2\rangle$ changes according to

$$\left(\frac{dN_2}{dt}\right)_{se} = -W_{21} \cdot N_2 = -\sigma_{21}FN_2 \quad (2.11)$$

where W_{21} is the rate of the electronic transition $|2\rangle \rightarrow |1\rangle$ and σ_{21} is the emission cross-section of this process.

As A. Einstein proved in [Ein17], when the two levels involved in the optical transition have the same degeneracy, the probabilities W_{12} and W_{21} are equal and consequently $\sigma_{12} = \sigma_{21} = \sigma$. In these conditions, the variation of flux through a crystal section with a thickness dz is

$$\frac{dF}{dz} = \sigma_{21}N_2F - \sigma_{12}N_1F = \sigma F(N_2 - N_1). \quad (2.12)$$

Equation 2.12 shows that amplification is only possible when $N_2 > N_1$. This condition is called inversion of population, achieved in level $|2\rangle$ in relation to level $|1\rangle$. As W_{12} equals W_{21} , the populations of both levels tend to $N_2 = N_1$ and the aforementioned condition of inversion is not reachable in a pure two-level system.

Spontaneous emission

Excited electrons in a level $|2\rangle$ can also spontaneously decay to a lower level $|1\rangle$ without the interaction of a photon. In this process, the energy lost by the electron results in the emission of photon with energy $E_{ph} = E_2 - E_1$, and random direction, phase, and polarization. Therefore, the population at level $|2\rangle$ decreases due to this process with a ratio

$$\left(\frac{dN_2}{dt}\right)_{sp} = -A \cdot N_2 \quad \text{with} \quad A = \frac{1}{\tau_{rad}} \quad (2.13)$$

where the Einstein coefficient A is proportional to the probability of the decay and it is related to the radiative lifetime τ_{rad} of the excited level.

Analogously to $\sigma_{abs}(\lambda)$, the emission efficiency of an electronic transition is highly relevant for laser performance as it determines the capability of the gain media to emit photons at the laser wavelengths. Therefore, the magnitude $\sigma_{em}(\lambda)$ quantifies the likelihood or rate of that excited ions in a given cross-sectional area will emit photons with a particular λ .

Selection rules

Radiative transitions between electronic states are mainly generated by interaction between dipoles. In a transition between an initial level $|i\rangle$ and a final level $|f\rangle$, the transition dipole moment can be described as

$$\mu_{fi} = \int \psi_f^* \mu \psi_i d\tau \quad (2.14)$$

where $\mu = -e\mathbf{r}$ is the electric dipole moment operator. It should be noticed that μ_{fi} , and therefore the probability that the transition occurs must be zero if the integral in 2.14 is totally symmetric. Thus, under inversion ($\mathbf{r} \rightarrow -\mathbf{r}$) the parity of an atomic orbital is determined by the quantum number l as $(-1)^l$, and consequently the parity of the integrand is $(-1)^{l_f}(-1)(-1)^{l_i}$. Therefore, for states with the same parity, the integrand is odd and the transition probability is zero. The conclusion of this argument is collected in the Laporte selection rule as the only allowed electric dipole transitions are those involving a change in parity.

In rare earth (RE) ions, the radiative transitions between $4f^n$ states are still observed despite being forbidden by the Laporte rule. This anomaly is attributed to contributions of the crystal field that produce an interconfigurational mixing of the $4f$ electronic orbitals with $5d$ orbital. The consequent breaking of the inversion symmetry leads to states of mixed parity that results in partially allowed transitions.

Nevertheless, the probability of these transitions is smaller than for those parity allowed. Thus, interconfigurational transitions between $4f^n$ and $4f^n 5d^1$ states experience a change of parity, and therefore exhibit several orders of magnitude higher cross-sections than those between $4f^n$ states.

In addition, constraints on Δl reveal the following selection rule:

$$\Delta l = \pm 1. \quad (2.15)$$

The origin of this rule can be understood in terms of the conservation of the total angular momentum during the electron-photon interaction. As a boson, the intrinsic spin angular momentum of the photon is an integer and equals to 1. Therefore, during the absorption or the emission of a photon, the orbital angular momentum of the electron in the atom must change by ± 1 , depending on its orientation relative to the angular momentum of the photon.

Furthermore, the total spin angular momentum must also be conserved. The resulting remaining rules can be summarized as:

$$\Delta S = 0, \quad |\Delta L| \leq 2l, \quad |\Delta J| \leq 2l \quad (2.16)$$

Multiphonon decay

Electrons in an excited state may also decay to a lower energy state through non-radiative mechanisms, i. e. without the emission of photons. In such a process, the energy lost by the electron is ultimately transferred into the lattice in the form of heat and therefore can be described as a phonon-assisted decay. Thus, phonons represent quantized microscopic vibrations of the lattice with an effective energy $E_{ph} = \hbar\omega_{eff}$. Consequently, in an electronic transition between an initial state $|i\rangle$ and a final state $|f\rangle$, the energy transfer to the lattice is $\Delta E = E_f - E_i = p \cdot E_{ph}$, where p is the number of emitted phonons. Since phonon quasiparticles behave as bosons, the electron-lattice coupling can be described by means of the temperature-dependent phonon transition rate $W_{ph}(T)$ as [Ris68, Moo70]:

$$W_{ph}(T) = W_0 \cdot e^{-\alpha\Delta E} \left(1 - e^{-\frac{E_{ph}}{kT}}\right)^{-p}, \quad (2.17)$$

where W_0 is the spontaneous transition rate and α describes the coupling strength between electrons and phonons. These parameters are characteristic of each host material, as well as the value of E_{ph} . It should be noticed that the probability of

transition is critically influenced by the number of phonons necessary to cover the energy gap. As an estimation, for values of ΔE that can be covered with a number of phonons $p \leq 5$, the phonon-assisted transition probability becomes comparable to the radiative transition probability. Therefore, for energetically close levels, the contribution of multiphonon relaxation is not negligible and influence the value of the fluorescence lifetime τ_{fl} as

$$\frac{1}{\tau_{fl}} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{nrad}}, \quad (2.18)$$

where $\tau_{nrad} = 1/W_{ph}$ is the lifetime of the non-radiative decay. Moreover, the fluorescence lifetime can be calculated from the relation of the decay in time of the fluorescence intensity:

$$I(t) = I_0 \cdot e^{-\frac{t}{\tau_{fl}}} \quad (2.19)$$

2.2.2 Interionic processes

Several non-radiative processes involve energy exchange including two or more ions. These mechanisms have a big impact on the spectroscopic features of the material as well as on the laser performance. As the interaction of at least two ions needs to take place, these processes are strongly dependent on the density of the optically active ion in the crystalline structure.

Considering an excited ion, the donor (D), that transfers at least part of its energy to another ion, the acceptor (A), the most relevant interionic processes, summarized in figure 2.1, are discussed in this section. If the energy lost by the donor does not equal the energy received by the acceptor, the energy difference can be compensated by phonons.

Energy migration

This process occurs when the donor transfers the totality of its excitation energy to an acceptor that occupies the ground state, as shown in figure 2.1(a). Furthermore, the energy can migrate through several ions of the same species in successive steps. Even though the migration of excitation may conclude in stimulated emission, it can also be transferred to impurities or leave the region of the crystal involved in the laser performance, resulting in losses for the laser process.

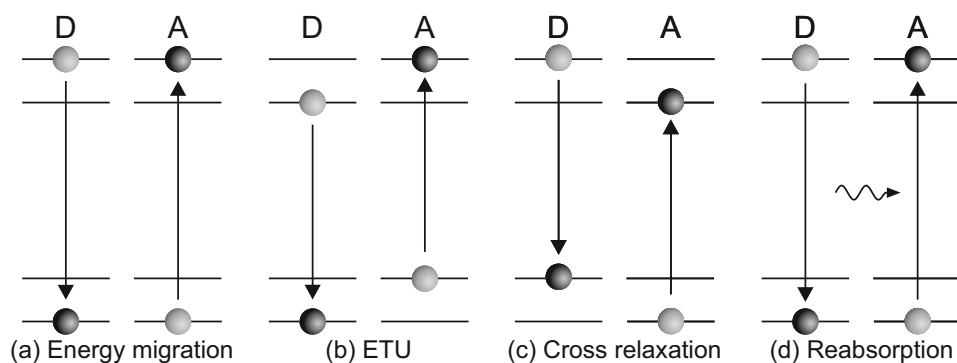


Fig. 2.1.: Schematic representation of possible interionic processes. (a) Energy migration, (b) energy transfer up-conversion, (c) cross relaxation, and (d) reabsorption.

Energy transfer up-conversion

When both ions, donor and acceptor, are in an excited state at the beginning of the energy exchange and the final state of A has higher energy than the initial state of D, the process is called energy transfer up-conversion (ETU), and it is shown in figure 2.1(b). Thereby, the acceptor can relax thereafter, emitting a photon with energy higher than the light that generated the initial excitation of the donor.

Cross relaxation

If the level structure is such that it allows to transfer part of the energy of the donor to the acceptor, maintaining the final position of A lower than the initial position of D, the process is called cross relaxation. Figure 2.1(c) shows an example of this phenomenon, where the acceptor is initially in the ground state, but cross relaxation from an A excited state and also phonon-assisted transitions are possible. Therefore, this process has a strong influence on the spectroscopic characteristics of the active ion by quenching the lifetime of the D initial state and populating the final state of the A.

Reabsorption

This process, similar to energy migration, occurs when the donor, initially excited, relaxes to the ground state emitting a photon, and the acceptor, initially in the ground state, absorbs the photon and it is promoted to the same excited state where the donor was formerly (see figure 2.1(d)). If the donor was previously excited by a photon of the same energy of the photon emitted, the process is called reabsorption. In this case, the fluorescence emission lines related to the donor's radiative decay will appear weaker than the corresponding emission of photons as the energy is removed. In addition, the fluorescence lifetime of the excited state may be overestimated

as reabsorption processes hold the radiative emission from immediately leave the crystal.

2.2.3 Interaction mechanisms

Non-radiative interionic processes strongly depend on the distance between donor and acceptor and therefore, on the cation density. Two mechanisms govern the energy transfer between ions as a function of the distance: the multipolar interaction and the exchange interaction. In addition, it is worth noticing that the probability of energy exchange increases with the overlap in energies between the emission of the donor and the absorption of the acceptor.

Multipolar mechanism is based on the interaction of the electromagnetic field of the ions involved. The strongest multipolar energy exchange consists of dipole-dipole interaction. Higher-order transitions, such as magnetic dipole transitions are 10^5 times weaker than allowed electric dipole transitions. However, because they follow different selection rules, they may be observed where the electric dipole transitions are forbidden. Electric quadrupole transitions are 10^8 times weaker than electric dipole transitions. In addition, the transfer rate of multipolar interaction dependency on R , the distance between D and A , was calculated by Th. Förster to be proportional to R^{-6} for dipole-dipole interactions, to R^{-8} for dipole-quadrupole interactions, and to R^{-10} for quadrupole-quadrupole interactions [För48]. In consequence, only dipole-dipole interactions are considered here.

Exchange interaction occurs by direct overlapping of the electron wave-functions of donor and acceptor [Lev69]. Therefore, the range of this interaction is limited to a few ångströms. Even though this interaction is stronger than multipolar exchanges, it is very unlikely even for highly doped gain media considered in this thesis.

2.3 Fundamentals of laser physics

A LASER, the acronym of Light Amplification by Stimulated Emission of Radiation, is defined by the generation of light based on the stimulated emission of a gain medium. Due to its impact on technology and its many applications, the acronym has become a standard term that relates to both the principle of operation and the device that generates light based on this principle.

Lasers have three main constituents: an *active medium* that emits the laser light itself, a *pumping system* that introduce energy in the active medium, and a *feedback mechanism* that amplifies the laser emission. The laser phenomenon starts with spontaneous emission, i.e. the fluorescence of the gain medium. The spontaneous emission induces stimulated emission, which in turn requires to be amplified in an

optical resonator, to increase the intensity of the emitted light in a feedback loop, until the laser emission reaches a steady value related to the energy provided to the gain medium by the pump.

There are many different laser concepts, classified by the nature of the gain media that provide the stimulated emission. This thesis is focused on solid-state lasers (SSLs), and particularly those that have crystals as gain media. In SSLs, the optical resonator generally consists of a set of mirrors whose transmission profiles are controlled by layers of coatings optimized for specific wavelengths.

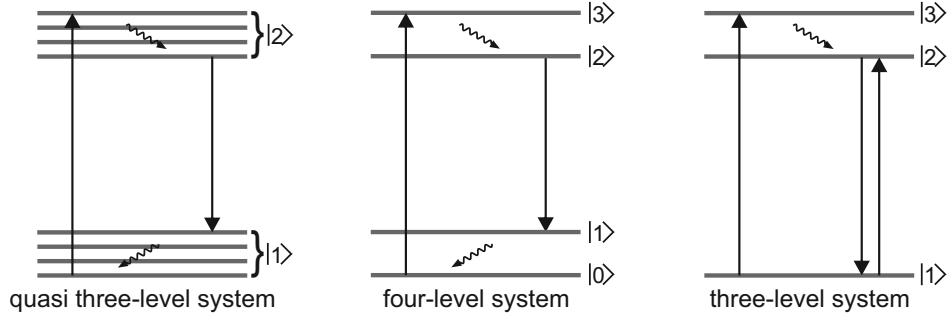


Fig. 2.2.: Schematic representation of the energy levels model for quasi three-level system (left), four-level system (center) and three-level system (right).

2.3.1 Laser schemes and rate equations

Laser active media can be distinguished by the number of energy levels involved in the laser transitions. Accordingly, a simplified model that describes the laser processes is built in the consideration of the electronic occupation of these energy levels. As it was shown in section 2.2.1, it is not possible to achieve inversion, and therefore laser operation, in a system with only two levels. Furthermore, the characteristics of the three- and four-level systems can be extrapolated as particular cases of the quasi three-level system, described in figure 2.2 left.

The dynamics of continuous-wave (cw) lasers are therefore described by the rate equations that determined the change of electron population N_2 in the upper laser level $|2\rangle$ and the growth rate of photon population q in the cavity. For the quasi three-level laser, the upper laser level is the lowest level of the Stark multiplet $|2\rangle$ and the corresponding rate equations can be presented as:

$$\frac{dN_2}{dt} = W_p N_1 - \frac{qc}{V}(\sigma_{em} N_2 - \sigma_{abs} N_1) - \frac{N_2}{\tau} \quad (2.20)$$

$$\frac{dq}{dt} = \frac{lcq}{L'}(\sigma_{em}N_2 - \sigma_{abs}N_1) - \frac{\gamma cq}{L'}. \quad (2.21)$$

The first term in equation 2.20 refers to the increase of population in $|2\rangle$ due to the pump, with W_p as the pumping rate, the second term refers to the stimulated emission, considering reabsorption, and the third term refers to the population losses due to spontaneous emission and phonon decay. In the approximation of single mode operation, the effective cavity mode volume V can be expressed as $V = \pi\omega_0^2 L'/4$, with ω_0 being the radius size of the mode spot at the resonator center, considered approximately constant along the active medium length. The effective length L' is given by $L' = L + (n - 1)l$, where L is the length of the resonator, and n and l the refractive index and the length of the active medium.

In addition, the pumping ratio can be described in terms of the pump power density P_p/V as

$$W_p N_1 = \frac{\eta_p}{h\nu_p} \frac{P_p}{V}, \quad (2.22)$$

where $h\nu_p$ is the energy of the pump photons and η_p is the pumping efficiency.

The first term in equation 2.21 refers to the growth in photon population due to stimulated emission, considering reabsorption, and the second term refers to the removal of photon due to cavity losses per round trip. The logarithmic losses per pass $\gamma = -\ln(1 - T) \cong T$, where T is the output coupling losses, accounts for the internal cavity losses γ_i as well as the transmission of the resonator mirrors γ_1 and γ_2 , with the relation $\gamma = \gamma_i + (\gamma_1 + \gamma_2)/2$. It is worth notice that the approximation $\gamma \cong T$ is only valid for low transmission values.

To deduce the rate equations 2.20 and 2.21, it is necessary to make an additional assumption. Considering that the change in intensity dI when the wave travels a distance dz into the active medium is $dI = (\sigma_{em}N_2 - \sigma_{abs}N_1)Idz$, the change of intensity in a round trip is express as

$$\Delta I = 2[(\sigma_{em}N_2 - \sigma_{abs}N_1)l - \gamma]I, \quad (2.23)$$

hence, beforehand it has been considered that $[(\sigma_{em}N_2 - \sigma_{abs}N_1)l - \gamma] \ll 1$. This assumption is valid for cw laser operation. A more detailed development of the equations can be founded in [Sve89].

Furthermore, defining mirror 2 as the output coupler mirror, the rate of photon losses due to transmission through it is recognizable in the second term of equation 2.21. Thus, the laser output power is

$$P_{out} = \left(\frac{\gamma_2 c_0}{2L'} \right) h\nu_L q, \quad (2.24)$$

with $h\nu_L$ the laser photon energy and $\gamma_2 \cong T_2$, where T_2 is the output coupler transmission.

Therefore, the definition of threshold pump power, P_{th} arises as the pump power necessary to start laser emission, i.e. to achieve a critical inversion of population that allows enough stimulated emission to compensate the total losses of the system. The linear relationship between pump power, P_{pump} and output power is

$$P_{out} = \eta_{sl}(P_p - P_{th}), \quad (2.25)$$

where $\eta_{sl} = dP_{out}/dP_p$ is defined as the slope efficiency of the laser.

Once the cw laser operation starts, the system oscillates in a steady-state condition. If W_p does not vary over time, the electron population at the upper laser level N_2 , as well as the photon population at the laser energy q will remain constant, and therefore $dN_2/dt = dq/dt = 0$. Additionally, at the threshold state q equals 0. By applying these conditions to equations 2.20 and 2.21 and substituting W_p by the expression given in equation 2.22, the threshold pump power is defined as

$$P_{th} = \frac{h\nu_p}{\eta_p \tau} \left[\frac{\gamma V}{\sigma_{em} l} - \frac{\sigma_{abs} V}{\sigma_{em}} (N_{tot} - N_{th}) \right], \quad (2.26)$$

where N_{th} is the population of the upper laser level at the threshold state and $N_{tot} = N_1 + N_2$.

The two factors η_{sl} and P_{th} are commonly used to characterize the behavior of the laser performance, as lower threshold power and higher slope efficiency yields to higher output powers for a determined amount of pump power. In a simple rate equation model, η_{sl} can be defined as

$$\eta_{sl} = \eta_{St} \eta_{ol} \eta_q \eta_{abs} \eta_{res}, \quad (2.27)$$

where the Stokes efficiency $\eta_{St} = 1 - q_d$ is the ratio between the laser and pump photon energies, which can be expressed by means of the quantum defect $q_d = h\nu_p - h\nu_L$. Furthermore, η_{ol} is the mode overlap efficiency between the pump

and the laser mode. The quantum efficiency η_q gives the ratio of laser transition to all transition from the upper laser level, having into account non-radiative decays and other intra- and interionic processes. The absorption efficiency η_{abs} is the ratio of pumped photons that are absorbed. These four efficiencies are grouped into η' , the so-called internal slope efficiency

$$\eta' = \eta_{St}\eta_{ol}\eta_q\eta_{abs}. \quad (2.28)$$

Equation 2.27 concludes with the resonator efficiency η_{res} , that is the ratio of output coupling losses T versus the total resonator losses L with the relation

$$\eta_{res} \propto \frac{T}{T + L}. \quad (2.29)$$

The four- and three-level lasers

In the case of the quasi three-level laser, the population of the Stark multiplets $|1\rangle$ and $|2\rangle$ follows a Boltzmann distribution. Therefore, the thermal coupling between the pump level and the upper laser level in $|2\rangle$ as well as between the lower laser level and the ground state in $|1\rangle$ is included in the rate equations 2.20 and 2.21.

In a four-level laser, the energy levels are separated enough in energies to avoid thermal coupling. Considering in addition a fast decay from the $|1\rangle$ to $|0\rangle$ and from $|3\rangle$ to $|2\rangle$ (see figure 2.2 center), the electronic population of levels $|1\rangle$ and $|3\rangle$ can be neglected. Therefore, $N_3 \cong 0$ favors the pump ratio and $N_1 \cong 0$ favors the inversion of population between the laser levels and thus, decrease the threshold pump power.

On the contrary, in a three-level laser the lower laser level is the ground state, as shown in figure 2.2 (right). Due to this condition, the lower laser level only reduces its population via pumping and higher pump intensities are needed to reach the inversion condition.

Trivalent terbium as laser-active ion

This chapter describes Tb^{3+} as active ion for solid-state visible lasers. As laser emission based on trivalent terbium has been demonstrated in the green and yellow spectral range, a summary of visible lasers emitting in this region gives context for a better understanding of the significance of these lasers. Subsequently, a thorough description of the specific characteristics of Tb^{3+} as RE ion is provided, as well as its properties as optically active ion in gain media for SSL. The chapter concludes with an up to date review of publications related to Tb^{3+} -based lasers, upheld by the substantial amount of research that has been published on this topic in the recent years.

3.1 State of the art of green and yellow lasers

Laser emission in the green and yellow spectral range can be achieved by means of diverse laser concepts. Nonetheless, the emission in these ranges is restricted by the limited availability of suitable gain media, and so the achievable performance is a trade-off between desirable laser properties. Therefore, different types of lasers have been developed to cover the requisites of applications in terms of emission wavelength, output power, operation mode, and cost among others.

It is worth mentioning that the boundaries of the wavelength range for a specific color depend on what the human brain perceives as that color, and therefore they are not rigorously determined. A general convention defines green emission as the wavelength range from 500 to 570 nm and yellow emission from 570 nm to 590 nm.

3.1.1 Green lasers

Here, a summary of the most relevant green-emitting lasers in cw operation is stated. Several gas lasers present green emission lines, such as helium-neon lasers at 543.5 nm, argon lasers at 514.5 nm, or krypton lasers at 520, 531, and 568 nm. While helium-neon lasers are limited to a few mW of output power, krypton lasers can provide hundreds of mW and argon lasers can exceed 20 W, but their wall-plug

efficiency is very poor and the lasers are oversized due to the bulkiness of the cooling system.

Moreover, many dye lasers such as coumarin 6, 7, 153, 334, and 540A among others, have emissions centered in the green region with wide tunability [Bur16]. Nevertheless, green dye lasers in cw are limited to a few watts of output power and dye degradation restricts their operating capacity at these power levels to only a few 100 hours per liter of dye solution [Wel75]. In addition, the toxic and carcinogenic nature of most dyes requires precaution during their exchange. Although diode pumping seems feasible [Bur16], in most cases the pump source itself is a complicated frequency-doubled Nd^{3+} laser system.

For such reasons, many dye lasers have been replaced in recent years by upcoming nonlinear laser systems with visible emission. Frequency-doubled SSL based on lasers emitting at wavelengths around $1\text{ }\mu\text{m}$ convert the infrared (IR) light into green by using nonlinear crystals such as LiNbO_3 , LiB_3O_5 (LBO), or KTiOPO_4 (KTP). The most common of them have $\text{Nd}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG), $\text{Nd}^{3+}:\text{YVO}_4$, and $\text{Yb}^{3+}:\text{YAG}$ as gain media [Mei10, McD07, Die15]. Therefore, the Nd^{3+} lasers deliver 532 nm by doubling 1064 nm and the Yb^{3+} lasers deliver 515 nm by doubling 1030 nm of emission. Frequency-doubled Nd^{3+} lasers at 532 nm deserve special attention due to their extensive use, from compact green laser pointers to pump sources of other lasers such as $\text{Ti}^{3+}:\text{sapphire}$ laser [Har91]. These lasers present a high beam quality and are capable of generating hundreds of watts of green light. Additionally, when the emission wavelength is relevant for applications, fiber laser variants are advantageous due to their higher tunability.

A different approach is given by optically pumped vertical external-cavity surface-emitting lasers (VECSELs), where the IR emission of a semiconductor laser is intra-cavity frequency-doubled. These lasers can deliver tens of watts of output power in the green, with high brightness and relatively compact form-factor [Gui17, Lee06].

However, for all these laser concepts, the nonlinear conversion step to obtain green light from IR light imposes strong requirements on the stability of the fundamental laser wavelength, as well as compromises the efficiency of the system, especially at low powers. Furthermore, the complexity and sensitivity to misalignment manifest in high prices of the commercial high-power systems.

The most straightforward approach to generate laser emission relies on electrically pumped semiconductor materials. Diode lasers are compact, robust, and often inexpensive in comparison with other laser concepts. However, the range of available direct emission wavelengths from semiconductor lasers exhibits a large gap in the visible range from the green to orange spectral region. As shown in figure 3.1, green laser diodes are available at watt level at wavelengths such as 520 nm [@Roi20] or

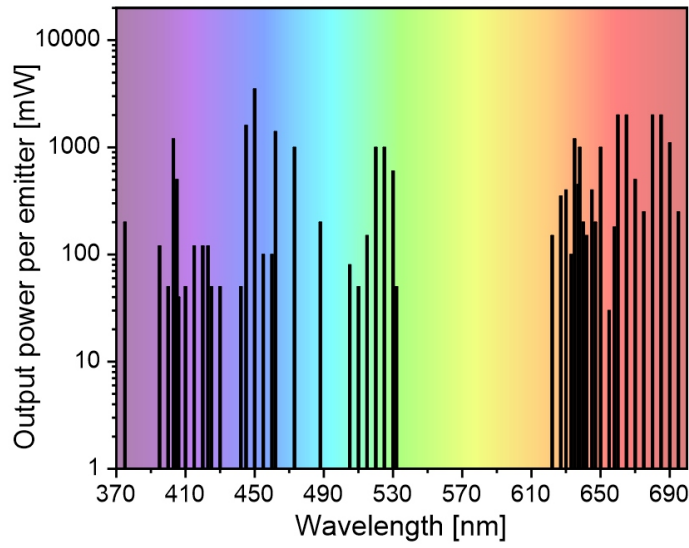


Fig. 3.1.: Output power of single emitter laser diodes provided by different suppliers versus emission wavelength [@Top21, @Nic20, @Fra19, @Las19b, @OSR19, @Tho19, @Las19a, @Roi20].

525 nm [@Nic20], but their efficiency and output power decrease drastically for wavelengths beyond 532 nm [Auf16].

Therefore, diode-pumped SSLs are the simplest alternative to obtain laser emission inside the so-called "green gap" of semiconductor lasers. There are a few RE ions with an energy level configuration suitable to emit green light beyond 532 nm, they are Pr^{3+} , Er^{3+} , Ho^{3+} , and Tb^{3+} [Krä16].

In particular, lasers based on materials doped with Pr^{3+} have been extensively developed, as this RE ion enables remarkably efficient laser operation at several wavelengths within the green. Up to 70% of slope efficiency was demonstrated at wavelengths of 523 nm and 60% at wavelengths of 546 nm under pumping with a frequency-doubled optically pumped semiconductor laser (2ω -OPSL) [Met14b]. Additionally, 1.7 W and 384 mW of output power were obtained at 532 and 546 nm respectively under diode pumping [Luo16, Gün11]. Nevertheless, the energy level system of Pr^{3+} ions allows cross relaxation processes involving the $^3\text{P}_j/{}^1\text{I}_6$ emitting levels. Therefore, the doping concentration feasible for laser operation is limited to $\sim 1.5 \cdot 10^{20} \text{ cm}^{-3}$ (i.e. $\sim 1 \text{ at.}\%$ in LiLuF_4) and the lifetime of the $^3\text{P}_j$ is reduced to $\sim 0.05 \text{ ms}$ for this concentration [Krä16].

Green laser emission around 550 nm can also be achieved in Er^{3+} doped materials by means of upconversion processes [Heb90, Dan94, Mog15] as well as by direct emission from the ${}^4\text{S}_{3/2}$ upper laser level to the ground state ${}^4\text{I}_{15/2}$, where $\sim 200 \text{ mW}$ of output power have been achieved [Mog13]. However, the already shot lifetime of

few 100 μs in typical host materials is quenched at doping concentrations exceeding $\sim 2 \cdot 10^{20} \text{ cm}^{-3}$ (i.e. $\sim 1.5 \text{ at.}\%$ in LiYF_4), due to resonant cross relaxation processes.

Even when laser operation in the green have been demonstrated for Ho^{3+} , less than 10 mW have been achieved at 549 nm by direct pumping [Rei15], and only 40 mW at 550 nm by upconversion pumping [Fun01]. The limitations in the laser performance can be explained by non-radiative phonon-assisted transitions that depopulate the upper laser level. In addition, cross relaxation processes limit the doping concentration.

In publications prior to the work of this thesis, direct laser emission in the green has been demonstrated in various Tb^{3+} -doped fluoride materials [Met16, Met17]. Over 1 W of output power and a slope efficiency of 58% was obtained in a $\text{Tb}^{3+}:\text{LiLuF}_4$ crystal at $\sim 543 \text{ nm}$. Even though the emission cross-sections of Tb^{3+} are about two orders of magnitude lower than for Pr^{3+} -doped materials, Tb^{3+} do not experience cross relaxation processes that could depopulate the upper laser level $^5\text{D}_4$. Therefore, high doping concentrations are possible. Furthermore, the long lifetime of the upper laser level (of $\sim 5 \text{ ms}$ in typical fluoride materials) allows for high storage of energy, which suggests that Tb^{3+} is a favorable active ion candidate for Q-switch laser operation [Dem17].

3.1.2 Yellow lasers

The diversity and power capacity of available lasers are reduced even more in the yellow range. Despite the rapid progress in laser research in the past nearly 60 years, up to now there is no convincing simple and easy to handle solution for generating continuous-wave (cw) laser emission between 570 nm and 590 nm. Many medical applications where yellow laser emission is advantageous still use outdated laser concepts such as dye lasers or cover vapor lasers. Dye lasers like Rhodamine 6G with emission centered around 575 nm, can provide kW pulsed average power e.g. in the yellow [Kli93], but such flashlamp pumped systems are not suited for cw operation. As in the case of green dye lasers, those lasers degrade over time, have a toxic gain media, and their emission in cw operation is limited to a few watts of output power [Wel75, @Sir19]. Even advanced solid-state dye laser concepts are limited to few 10 mW of cw output power due to dye degradation [Bor06]. While copper vapor lasers are able to emit at 578 nm, generating average laser powers of 10 to 100 W, these lasers are confined to pulse operation due to the discharge pumping system, and the overall efficiency of the system does not exceed $\sim 1\%$. In addition, to produce a sufficient density of copper vapor, the vapor tubes are required to run at high temperatures of 1500–1800 $^\circ\text{C}$ [Dye13].

Consequently, progressive nonlinear laser systems have been developed to substitute these outdated laser concepts. In contrast to sources around $1\ \mu\text{m}$ for frequency-doubled green lasers, suitable fundamental sources around $1.2\ \mu\text{m}$ for frequency doubling into the yellow are rare. Semiconductor lasers emitting between 1140 nm and 1180 nm offer a possibility. Even though the need for high spectral and spatial beam quality limits the available fundamental wavelength output power, intracavity frequency-doubled VECSELs have demonstrated powers of 8 W at 575 nm and 20 W at 590 nm [Gui17, Kan14]. Furthermore, second-harmonic generation (SHG) of 1178 nm emitting narrow-band Raman fiber amplifiers have reached 14.5 W at 589 nm in cw [Tay09]. In addition, 1.6 W at 576 nm has been obtained by frequency doubling the emission of a master oscillator power amplifier (MOPA) at 1152 nm in a remarkably compact device [Sah18]. Nevertheless, these frequency-doubled yellow lasers are still fairly complex or limited in cw scaling potential. Yellow laser emission obtained by sum frequency mixing of Nd^{3+} :YAG lasers operating at 1064 nm and 1319 nm have achieved up to 208 W of laser emission at 589 nm [Lu19, Den05, Bie03]. Yet these systems require several conversion and amplification steps, making them intrinsically complex, large in dimensions, highly sensitivity to misalignment, and inefficient particularly at low output power levels where the nonlinear conversion efficiency is low. Together with other nonlinear approaches such as optical parametric oscillators (OPOs) [Str02], photonic structures [Ola10], or Raman shifted fundamental sources [Lee10], the complexity of these systems is increased even further.

Although the ongoing research in the field of semiconductors has produced numerous efforts to create new approaches [Led18, Tan93, Fen15, Nue72, Bou94, Toi14, She15], the development of yellow-emitting semiconductor gain structures remains a challenge (see figure 3.1). The output power of experimental stage laser diodes in the yellow-orange spectral range is limited to mW power levels, mostly operated in pulsed regime, and with very low efficiencies.

Like in the green, diode-pumped SSL with direct emission in the yellow spectral range represents the most simple and scalable solution to address these wavelengths. However, unlike in the green, Pr^{3+} ions do not allow for laser operation at wavelengths between 550 and 600 nm due to ground state absorption losses into the $^1\text{D}_2$ -multiplet [Krä16]. Therefore, Dy^{3+} and trivalent terbium Tb^{3+} are the only RE ions that present yellow emission. As the yellow range is a convention, should be pointed out that laser operation at 593 nm has been demonstrated in a Sm^{3+} -doped material [Mar15]. Nevertheless, the laser operates self-pulsed, and with a slope efficiency of only 1%, the maximum output power remains below 10 mW. In the case of Dy^{3+} -based lasers, emission at 583 and 574 nm have been demonstrated from a Dy^{3+} :YAG and a $\text{Dy}^{3+}, \text{Tb}^{3+}$: LiLuF_4 respectively, under diode-pumping [Bow12,

Bol14]. However, in the first report the laser operates self-pulsed with a limited output power of 150 mW and a slope efficiency of 12%. The second report presents cw laser operation, but the output power is limited to 55 mW and possesses a high laser threshold in excess of 300 mW and a slope efficiency of 13.4%. This insufficient performance is owed to the properties of the ${}^6\text{H}_{13/2}$ terminal level of the respective Dy^{3+} yellow laser transition, which exhibits a significantly long lifetime, even when co-doped by Tb^{3+} for faster depopulation. In addition, cross relaxation processes depopulate the upper laser level ${}^4\text{F}_{9/2}$, limiting the maximum doping concentration to 10 at.% in many host materials. Consequently, the crystals present lengths in the order of centimeters to achieve efficient absorption [Krä16].

Prior to this work, an initial demonstration of efficient laser emission at 587 nm and 584 nm from a few Tb^{3+} -doped fluoride materials confirmed the potential of this ion as active element for yellow emitting SSLs [Met16]. These lasers exhibit an order of magnitude lower thresholds than Dy^{3+} and slope efficiencies of 22% under pumping with a 2ω -OPSL.

3.2 Trivalent terbium as active ion

Terbium is the ninth element of the lanthanide group and carries the atomic number $Z=65$. When doped in a crystalline host, mostly acquires a trivalent oxidation state with the electronic configuration $[\text{Xe}]4f^8$. Hence, the 4f orbitals remain shielded from the crystal field due to complete occupation of the more external 5s and 5d shells. Tb^{3+} ions present a complex energy level diagram of 295 stark multiplets in the $4f^n$ shell [Pei05]. Among them, the ground state is determined by the Hund's rules to be ${}^7\text{F}_6$. Figure 3.2 shows the levels relevant for the visible laser transitions in LaCl_3 . As the influence of the crystal field is weak, this representation gives a qualitative description of Tb^{3+} energy levels applicable to other fluoride and oxide host materials.

Light emission at several lines in the visible range is generated by radiative decay from the ${}^5\text{D}_4$ multiplet into the ${}^7\text{F}_j$ manifold. Photons are emitted in the blue (${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$), green (${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$), yellow (${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$), orange (${}^5\text{D}_4 \rightarrow {}^7\text{F}_3$), and red (${}^5\text{D}_4 \rightarrow {}^7\text{F}_2$, ${}^5\text{D}_4 \rightarrow {}^7\text{F}_1$, and ${}^5\text{D}_4 \rightarrow {}^7\text{F}_0$) [Vas13]. There are two possible channels to electronically populate the ${}^5\text{D}_4$, direct pumping into this level at ~ 485 nm or indirect pumping at ~ 380 nm into the ${}^5\text{D}_3$ multiplet. Further indirect pumping into multiplets higher in energies than ${}^5\text{D}_3$ is also possible as the electronic population will thermally relax into this level [Die63]. On the contrary, the separation between ${}^5\text{D}_4$ and ${}^5\text{D}_3$ is $\sim 5500 \text{ cm}^{-1}$, and therefore multi-phonon relaxation is disregarded as the maximum phonon energies of the most common fluoride materials are

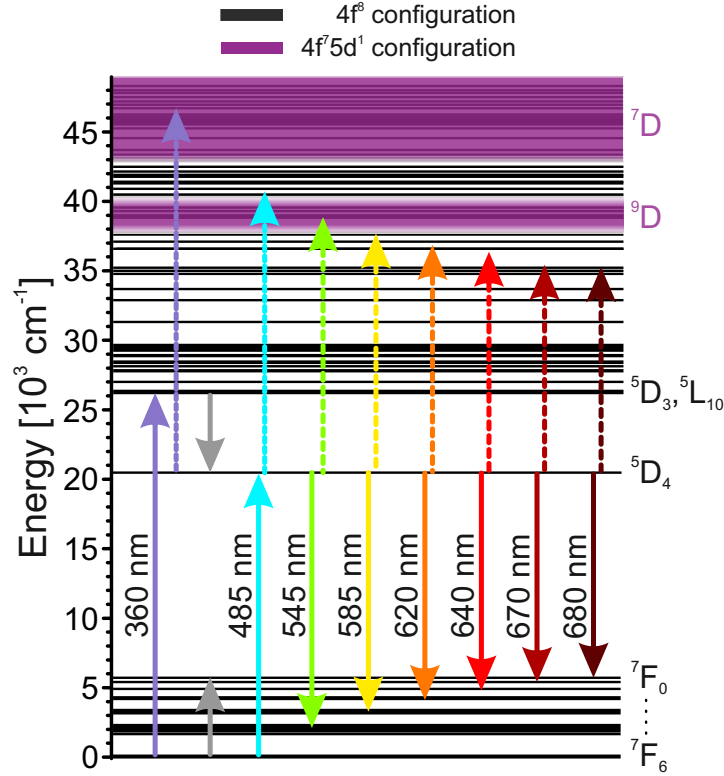


Fig. 3.2.: Energy level diagram of Tb^{3+} in LaCl_3 with $4f^8$ levels represent in horizontal black bars and the lowest $4f^75d^1$ -states represented as purple areas. Solid arrows represent radiative transitions, grey arrows represent a cross relaxation process, and dashed arrows correspond to possible ESA channels [Die63, Met16].

$\leq 500 \text{ cm}^{-1}$ and $\leq 900 \text{ cm}^{-1}$ for oxide host materials. However, due to the similar energy distance between $^5\text{D}_4$ and $^5\text{D}_3$ and between $^7\text{F}_6$ and $^7\text{F}_0$, cross relaxation mechanisms help to transfer the electronic population to the $^5\text{D}_4$ and, at the same time, depopulating the ground state $^7\text{F}_6$. A discussion about the efficiency of this process is held in chapter 5.

Conversely to the $^5\text{D}_3$ manifold, the $^5\text{D}_4$ level cannot be depopulated either by cross relaxation processes or by thermal decay, and therefore the main depopulation mechanism for this level involve radiative transitions. The parity and spin forbidden character of the transitions between the $^5\text{D}_4$ multiplet and the $^7\text{F}_j$ manifold results in absorption and emission cross-sections in the order of 10^{-22} cm^2 . To compensate for the low cross-sections, it is possible to perform laser operation with crystal with a high content of Tb^{3+} . Hereby, laser emission has been previously demonstrated in TbF_3 [Met16], that has a cation density of $2.02 \cdot 10^{22} \text{ cm}^3$. The ion density in this matrix is among the highest possible densities of terbium in a crystalline structure. This fact is an indication that there are no interionic processes between Tb^{3+} ions

that limit their doping concentration for laser operation, as in the case of Dy^{3+} or Pr^{3+} ions. Optimal values of the Tb^{3+} doping concentration for laser performance are discussed in chapter 7.

An additional implication of the forbidden character of these electronic transitions is the long lifetime of the $^5\text{D}_4$ level of ~ 5 ms in typical fluoride host materials. This value is about two orders of magnitude than e. g. for Pr^{3+} in the same matrix. In fact, $^5\text{D}_4$ is the only level with a long enough lifetime at suitable doping concentrations to be the upper laser level for visible emission.

3.2.1 Implications of ESA in the performance of terbium lasers

Contrary to the lack of detrimental interionic processes between Tb^{3+} ions, the energy level distribution of this ion allows for intraionic mechanisms that obstacles the laser performance. The process called excited state absorption, i.e. ESA, occurs when an ion in an excited state absorbs a photon that transfers its energy to the excited electron, promoting it to a state of higher energy than the initial. When ESA takes place at the pump or laser wavelengths, it compromises the efficiency of the laser and may even extinguish the stimulated emission.

The high density of energy levels at $30000\text{--}50000\text{ cm}^{-1}$ allows for both intra-configurational ESA within the 4f orbital and interconfigurational $4f^8 \rightarrow 4f^75d^1$ transitions (see dashed arrows in figure 3.2).

Intraconfigurational ESA

The ESA transitions between 4f levels are parity forbidden and their intensity is, therefore one or two orders of magnitude lower than interconfigurational ESA, that is parity allowed. Nonetheless, pump-probe gain measurements in $\text{Tb}^{3+}:\text{LiLuF}_4$ evidence that intraconfigurational ESA occurs at visible wavelengths and may influence negatively in the laser performance [Met16]. The ESA signal is especially broad and intense in the orange to red spectral range and in consequence the most feasible cause of failure in achieving laser operation at the $^5\text{D}_4 \rightarrow ^7\text{F}_{3-0}$ transitions.

Even when the influence of the crystal field on the positions of the shielded Tb^{3+} -4f energy levels is weak, their location slightly varies depending on the host material within several 100 cm^{-1} . Therefore, the use of different host materials can influence the intensity of the ESA transitions for specific wavelengths and help to allow or improve the laser performance.

Interconfigurational ESA

In contrast to the shielded 4f levels, the position of the 5d-levels depends strongly on the crystalline environment and the difference may imply tens of thousands of cm^{-1} , depending on the host material. To better understand the role that interconfigurational ESA plays in Tb^{3+} ions, it is worth making a comparison of the positions of the 4f ground state and the lower levels of the $4f^7 5d^1$ configuration between the different RE ions. In his work in 2000, Dorenbos developed an empirical expression to determine the energy position of the lowest $4f^{n-1} 5d$ levels of all trivalent lanthanides in one compound, once the position for one of the lanthanides is known in that compound [Dor00c]. The prediction of the energy positions achieves an accuracy of 600 cm^{-1} . By empirical determination of the energy position of this level in Ce^{3+} ions, the positions for the other lanthanides are calculated with the equation

$$E(\text{Ln}, A) = 49340 \text{ cm}^{-1} - D(A) + \Delta E^{\text{Ln}, \text{Ce}}, \quad (3.1)$$

where $E(\text{Ln}, A)$ is the energy of the lowest $4f^{n-1} 5d$ transition of the trivalent lanthanide Ln^{3+} in a host material A, 49340 cm^{-1} is the energy of the transition between the ground state and the lowest 5d-level of the free Ce^{3+} ion, $D(A)$ is defined as the crystal field depression (CFD) of the material A, and $\Delta E^{\text{Ln}, \text{Ce}}$ is the difference in energy between the lowest $4f^{n-1} 5d$ level of the specific Ln^{3+} and of Ce^{3+} . All energies are expressed in cm^{-1} . The CFD is the position shift to lower energies of the $4f^{n-1} 5d$ transition due to the influence of the crystalline matrix, in comparison with the position for the free ion. The stronger the influence of the crystal field in the ion, the larger the splitting between levels of the corresponding 5d-manifold and therefore, the value of $D(A)$. This value is in first approximation, related only to the crystalline structure and not to the ion itself, and therefore can be considered the same for all lanthanides for one specific compound. On the contrary, $\Delta E^{\text{Ln}, \text{Ce}}$ is mostly independent of the host material and therefore only related to the lanthanide. Figure 3.3 collects the values of $E(\text{Ln}, A)$ (circles and x) and the energy positions of the ground state of all trivalent lanthanides (triangles) in YPO_4 . The shape of the trivalent zigzag curves remains unchanged for different host materials and therefore, illustrates the difference in distance for the first interconfigurational transition among the trivalent lanthanides.

As can be observed in figure 3.3, Terbium experiences one of the lowest intrinsic energetic separations between the $4f_n$ and the $4f^{n-1} 5d^1$ configurations. This separation is about double the energy of visible light and therefore, the $4f^{n-1} 5d$ manifold can act as terminal levels for ESA processes. However, the lower 5d

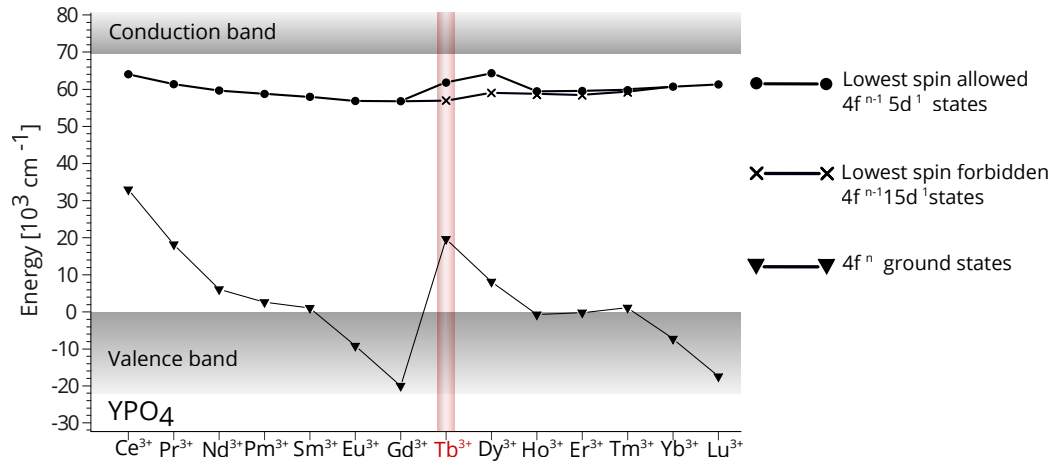


Fig. 3.3.: 4f ground state (triangles) and lowest $4f^{n-1}5d$ spin allowed excited states (circles) and spin forbidden excited states (x) relative to the valence band maximum in YPO_4 [Dor10]

manifold in Tb^{3+} is a ^9D (see figure 3.2). Despite that the transition from the $^5\text{D}_4$ upper laser level to the ^9D manifold is parity allowed, a double spin-flip is required for up-conversion excitation channels of electrons from the ground state $^7\text{F}_6$ to the ^9D . This fact strongly reduces the probability of these transitions to take place and the real values of the corresponding cross-sections are difficult to predict. On the contrary, the ESA transitions to the ^7D -manifold are both parity and spin allowed, and therefore entail strong depopulation channels that may cease the laser operation.

Depending on the exact position of the 5d-manifolds, ESA channels can affect the high-energy pump photons or the photons involved in laser operation. In the first case, this process would decrease the effective pumping capacity of the system and limit the maximum achievable output power of the laser, as well as increase the value of the laser threshold. In addition, it may cause thermal stress, as non-radiative decay processes would be involved. In the case of ESA at the laser wavelengths, the efficiency of the laser would be reduced, hindering or even preventing laser emission.

To decrease the influence or even avoid interconfigurational ESA at the wavelengths involved in the laser operation in Tb^{3+} ions, the choice of the host material is decisive. In previous publications, Tb^{3+} laser operation has been only demonstrated in fluoride materials [Met16]. As can be seen in figure 3.4, fluoride compounds have some of the lowest CFD and therefore the largest energy distance between the 4f ground state and the lower levels of the $4f^{n-1}5d$ configuration. However, figure

3.4 also reveals that certain oxide materials have values of $D(A)$ almost as low as the lowest fluorides. The feasibility of using oxide compounds as host materials for Tb^{3+} -doped lasers is discussed in this work. Typical oxide compounds exhibit higher thermal conductivity and Mohs hardness than typical fluoride compounds, among other properties that make them superior laser material [Agg05].

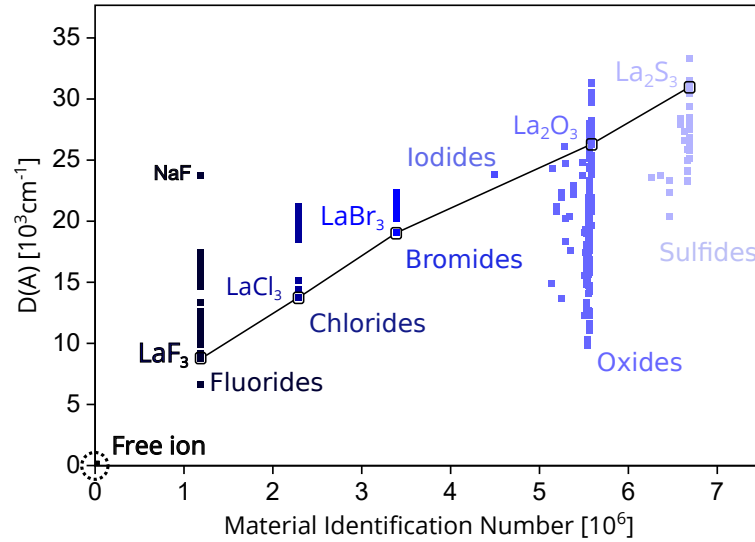


Fig. 3.4.: Crystal field depression values $D(A)$ of 5d-levels of trivalent lanthanides in inorganic compounds [Dor00a].

3.3 State of the art of terbium lasers

The first demonstration of stimulated emission of Tb^{3+} ions was a report on Tb^{3+} -doped glass published as early as in 1967 [And67]. This research was followed by the same year release of a publication on room temperature laser oscillation at 547 nm of terbium- trifluoroacetylacetonate solution under flashlamp pumping [Bjo67]. The next report was published six years later by Jenssen et al. presenting flashlamp pumped laser operation at 545 nm in a Tb^{3+} -doped fluoride crystal for the first time. Even by improving the absorption efficiency by Gd^{3+} -codoping, the laser efficiency was very low. After these early reports, there were no publications in Tb^{3+} -based lasers for 34 years. The next contribution presented in 2007 the first cw Tb^{3+} laser emission at room temperature [Yam07]. In this case, an argon laser pumped fluoride fiber doped with Tb^{3+} delivered less than 1 mW of output power at 543 nm with a slope efficiency of 4%¹. Besides two further reports on random

¹by direct calculation from the data in [Yam07], the correct value of the slope efficiency is 0.4%.

lasing in $\text{Tb}(\text{OH})_3/\text{SiO}_2$ nanoparticles [Lin08, Che09], there are no other results on Tb^{3+} -based lasers until 2016.

The scarce amount of reports on Tb^{3+} lasers in these five decades is mainly attributed to the spectroscopic characteristics of this ion that favor detrimental ESA processes, the low absorption and emission cross-sections, and the lack of cw efficient and powerful pump sources in the blue and near ultraviolet (UVA) [Met14a]. However, a number of publications on the spectroscopic potential of different Tb^{3+} -based active materials arose during these years [Sek94, Sar06, Pra07, Rai08, Bou13, Sha15a, Sha15b].

It is only recently when the first demonstrations of efficient laser emission of Tb^{3+} ions were reported [Met16, Krä16, Met17]. In the work of Metz et al. several fluoride materials were tested as host materials for Tb^{3+} ions. Laser operation was obtained in LiLuF_4 , LiYF_4 , KY_3F_{10} , $\beta\text{-BLu}_2\text{F}_8$, LaF_3 , TbF_3 and, $\text{Tb}^{3+}/\text{Na}^{+}$ -codoped CaF_2 . The best results were obtained with LiLuF_4 and LiYF_4 . Thereby, slope efficiencies of 52% in the green and 22% in the yellow were achieved with output powers of >1 W for the green and 71 mW for the yellow. These outstanding results were possible by the use of 2ω -OPSL pump sources that deliver up to 3 W of pump power in the blue with an excellent beam quality. It must be taken into account that the samples of the host materials tested as laser materials vary in doping concentration, length, and crystal quality, and therefore it is difficult to determine which one is more advantageous. To the starting date of the present work, these publications are the latest contributions on Tb^{3+} -based lasers. The excellent prospects of laser performance proved in these studies set the foundation of this work, which has the aim of evaluating and developing the potential of Tb^{3+} -materials as gain media for SSLs.

Host materials for trivalent terbium

This chapter gives an introduction to the most relevant host materials that were investigated during the development of this thesis. The selected materials are divided between fluorides and oxides. The election of fluoride compounds was made to investigate a variety of materials with different crystal field strengths and because of our insight into their laser properties. Oxide compounds as $\text{KY}(\text{WO}_4)_2$ and especially YAG are well-known laser materials when doped by RE ions. In addition, perovskites as YAlO_3 present among the lowest CFD values among the oxides. These values are comparable to the CFD of the fluorides that were successful in Tb^{3+} -based laser operation. Table 4.1 summarizes the crystals investigated in this work and the values of their CFD, magnitude introduced in section 3.2.1.

Fluoride	CFD (cm^{-1})	Ref.	Oxide	CFD (cm^{-1})	Ref.
LiLuF_4	15140	[Dor00c]	YAlO_3	16537	[Dor00c]
LiTbF_4	~ 15200	[Met14a]	TbAlO_3	16824	[Dor00c]
KY_3F_{10}	16084	[Dor00c]	$\text{Y}_3\text{Al}_5\text{O}_{12}$	26654	[Dor00c]
$\text{KTb}_3\text{F}_{10}$	15140	[Met14a]	$\text{KY}(\text{WO}_4)_2$	(*)	[Dem19]
BaY_2F_8	16047	[Dor00c]			
LaF_3	8751	[Dor00c]			
TbF_3	<i>10000</i>	[Met14a]			

Tab. 4.1.: CFD of selected crystals for investigation. Italic numbers are estimated.

(*) For monoclinic double tungstates such as $\text{KY}(\text{WO}_4)_2$, the CFD value, as well as the position of the 5d levels cannot be easily determined experimentally. This is due to their low bandgap energy of only $\sim 32 \cdot 10^3 \text{ cm}^{-1}$, corresponding to $\sim 315 \text{ nm}$ [Mat06]. In this configuration, the lowest 5d level of Tb^{3+} (^9D) is located inside the conduction band, and therefore its position is not accessible with conventional spectroscopic measurements.

4.1 Requirements for host materials

The host materials need to fulfill a number of requirements in order to be successful for laser operation. First and foremost, it must be possible to grow the compound, and that must be of sufficient size with sufficient crystallographic and optical qualities. Defects and impurities in the crystalline structure will lead to processes such as absorption or light scattering, producing losses in the laser performance and hindering the thermal conductivity. A material with good thermomechanical properties is highly desirable as high thermal conductivity facilitates the dissipation of heat produced by e.g. phonon relaxation, and enables high powers in pumping and laser operation. In addition, the material should be atmospherically stable and robust against degradation. Furthermore, cutting and polishing in the required shape and dimensions should be possible, dismissing materials with high brittleness.

The selection of the host material strongly determines the optical properties and the performance of SSLs. The first requirement is that the host material is optically inert for the pump and laser wavelengths, and due to the high intensities inside the laser cavity, second-order absorption should be unlikely. Therefore, a gap between the valence and the conduction band of at least $40 \cdot 10^3 \text{ cm}^{-1}$ is necessary for visible lasers. Moreover, due to the parity forbidden character of the 4f-4f transitions, an acentric symmetry site for the optically active ion is required to partially loosen the parity constraints and make the transitions possible. Additionally, in the case of Tb^{3+} -doped materials, it is crucial to select crystalline structures that allow for high doping concentrations of the RE ion, required to compensate for the low absorption and emission cross sections. The use of what it is considered overly high concentrations for other RE ions is possible for Tb^{3+} , e.g. 28% in LiLuF_4 or even 100% in TbF_3 , as demonstrated in [Met16]. As discussed in section 3.2.1, the selection of the host material, and its corresponding value of CFD, is as well essential to reduce the influence of ESA. It should be noticed that the distance between the optically active ion and the surrounding ligands tends to increase towards a bigger number of ligands ions, which leads to weaker crystal fields over the central ion for a higher order of coordination spheres [Hen89]. Therefore, it is expected that structures with a higher number of ligands for the RE ion position, as perovskites like YAlO_3 (with coordination number 12), present lower CFD values than structures with a lower number of ligands, like YAG (with coordination number 8) [Sen13]. Finally, it should be noticed that phonon energies, an intrinsic feature of the host material, do not strongly influence the performance of Tb^{3+} lasers. This behavior is due to the large energy distances between the levels involved in the high energetic visible lasers, that prevent multiphonon relaxation. In addition, Tb^{3+} ions lack intermediate

levels that, in the case of e.g. Pr^{3+} , could become a channel of losses by multiphonon decay.

4.2 Fluoride crystals

Fluoride crystals are the only host materials to date that have been proven as suitable for Tb^{3+} -based laser operation. Despite that they typically exhibit less favorable properties than oxide materials, their generally lower CFD causes Tb^{3+} ions to present higher energetic positions for the $4f^n 5d^1$ multiplets, critical for the laser performance. In addition, fluorides can present a negative thermo-optical coefficient that reduces the thermal-lensing effect during laser operation, process that crucially limits the output power and beam quality of high-power lasers.

However, it should be taken into account that fluorides present higher requirements than oxide materials in terms of crystal growth, including high vacuum, use of aggressive gases, and extra purification steps such as fluorination of the starting materials. In addition, they experience lower thermal conductivity, higher thermal expansion and therefore, higher sensitivity to thermal shocks and fractures, higher brittleness, and in some compounds, hygroscopicity.

Nevertheless, the fluoride materials used in this thesis have proved their suitability and good performance as host materials in many works. A short collection of examples can be found here [Heu06, Cor07, Cam07, Met14b, Sch13, Agn04, Rei12, Met16].

4.2.1 Tb^{3+} -doped LiLuF_4 and LiTbF_4

The chemical structure of these two compounds is denominated scheelite, as they belong to the group of LiLnF_4 , with Ln being one of the lanthanides between europium and lutetium, as well as yttrium. These compounds, denominated lithium tetrafluorolanthanates are all isomorphous, presenting a tetragonal structure in $I4_1/a$ symmetry [Tho70]. The unit cell of these compounds is shown in figure 4.1 for LiLuF_4 , with dimensions of 10.55 Å along the c-axis and 5.13 Å along the a-axes [Ran02]. When doped by Tb^{3+} ions, they substitute Lu^{3+} in the dodecahedral sites. Thus, the dodecahedral coordination sphere is formed by eight fluorine ions that are located in a distance of ~ 2.25 Å of the trivalent lanthanide. Consequently, the experimental data from [Dor00a] situate the lowest $4f^{n-1}5d^1$ level above $45 \cdot 10^3 \text{ cm}^{-1}$, and therefore a long enough splitting to avoid interconfigurational ESA at the visible laser wavelengths. Further physical properties of these crystals can be found in table 4.2.

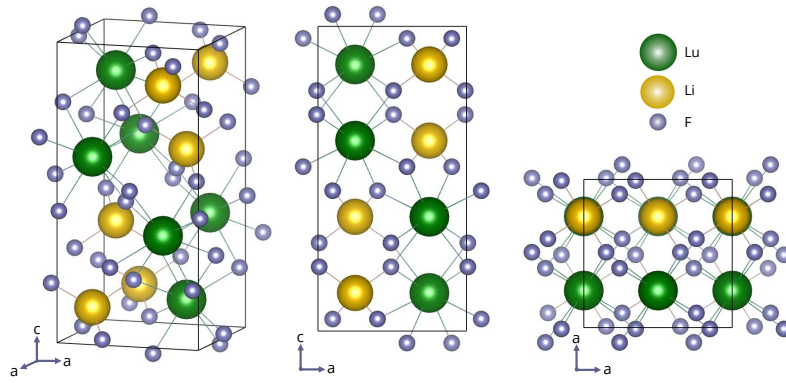


Fig. 4.1.: Scheelite structure of tetragonal LiLuF_4 .

LiLuF_4 presents a congruently melting with a melting point of 850°C and unlike other scheelite structures as LiGdF_4 or LiYF_4 , can be grown from a stoichiometric melt composition [Har83]. The difference between the atomic radius of Lu^{3+} of $1.11 \text{ \AA}$ and of Tb^{3+} of $1.18 \text{ \AA}$ in eight-fold coordination [Kam90a] results in a segregation coefficient of 0.7 for Tb^{3+} ions.

The LiLuF_4 and LiTbF_4 crystals investigated in the frame of this thesis were grown by the Czochralski method at the Institut für Laser-Physik, Universität Hamburg, Germany. A brief description of Czochralski method is presented in appendix A.1. The pulling speed was set to 0.7 mm/h at a rotation rate of 5 rpm , and the started materials had a purity of 5N . The Tb^{3+} -doped LiLuF_4 samples were extracted from two different boules with doping concentrations of $20 \text{ at.}\%$ and $40 \text{ at.}\%$ in the melt ($14 \text{ at.}\%$ and $28 \text{ at.}\%$ in the crystal respectively). They present high crystallographic and optical quality, exhibiting high transparency and no macroscopic defects. On the contrary, the LiTbF_4 boules possess impurities and macroscopic inclusions. Therefore, the size and quality of the samples were not sufficient for laser experiments, and they were used solely for spectroscopic investigations as 100% -doped $\text{Tb}^{3+}:\text{LiLuF}_4$ samples. More information about the growth can be found at [Met14a].

4.2.2 Tb^{3+} -doped KY_3F_{10} and $\text{KTb}_3\text{F}_{10}$

These two compounds present a cubic $\text{Fm}\bar{3}\text{m}$ structure, depicted in figure 4.2. The isotropic character of the cubic structures simplifies sample processing and optical characterization, as there are no strong requirements regarding the orientation with respect to the crystallographic axes. In addition, first-order physical properties as thermal conductivity and thermal expansion are homogeneous in cubic crystals. Unfortunately, their thermal conductivity of $3.5 \text{ W/(m}\cdot\text{K)}$ is about half of the value

for fluoride scheelite crystals. It is worth to mention however, that despite the cubic structure, polarization effects have been observed in KY_3F_{10} when doped with Pr^{3+} [Krä15]. Further physical properties of these crystals are summarized in table 4.2.

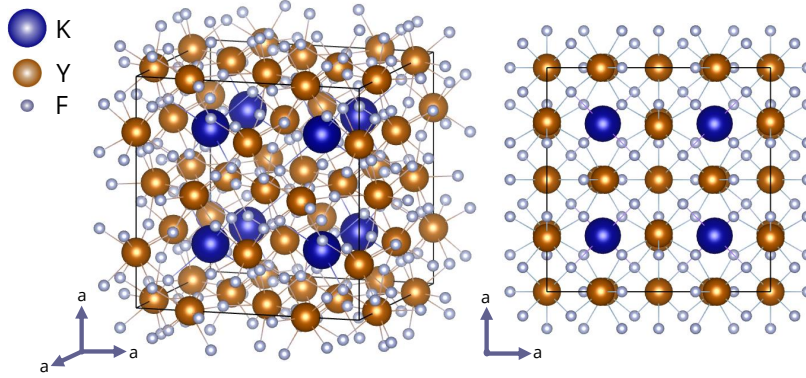


Fig. 4.2.: Two visualizations of the fundamental cell of the cubic structure of KY_3F_{10} .

Tb^{3+} -doped KY_3F_{10} can be grown from a stoichiometric melt at a temperature of $\sim 1030^\circ\text{C}$. The samples investigated here were grown by the Nacken-Kyropoulos technique at the Institut für Laser-Physik, Universität Hamburg, Germany. A brief description of this growth method is presented in appendix A.2. During the growth a dopant concentration of TbF_3 of 20.0 mol% in the melt was used, resulting in 17 at.% of Tb^{3+} in the crystal. More information about the growth can be found at [Met14a]. Due to macroscopic grains and white inclusions, the resultant $\text{Tb}^{3+}:\text{KY}_3\text{F}_{10}$ available samples were only suitable for spectroscopic investigations and not for laser experiments.

The $\text{KTb}_3\text{F}_{10}$ sample used in the frame of this thesis was grown at Synoptics™ (Northrop Grumman Corporation). It presents high crystallographic and optical quality.

4.2.3 Tb^{3+} -doped BaY_2F_8

This compound presents a monoclinic biaxial structure in C_{2m}^2 symmetry, with an angle between the crystallographic *a*- and *c*-axes of 99.7° . Figure 4.3 represents the crystallographic axes (*abc*) in blue, as well as the index ellipsoid orientation (*xyz*) in black, and the optical axes in red. The *y*-axis of the index ellipsoid is by definition oriented parallel to the *b*-axis of the crystalline structure. Therefore, the *x*-, *z*-, *a*- and *c*-axes lay within the plane parallel to the *y*- and *b*-axis. In turn, the *z*- and *c*-axes form an angle of 23° and the *z*-axis is the bisectrix of the 82° angle formed by the optical axes [Gui93, Bai11]. Additionally, figure 4.4 depicts the fundamental cell

of BaY_2F_8 from different perspectives. Further physical properties of this material are described in table 4.2.

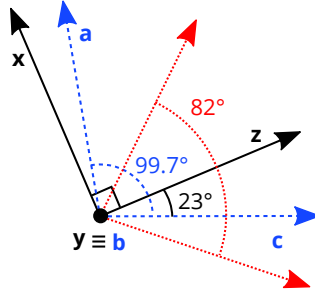


Fig. 4.3.: Crystallographic, refractive index and optic axes in BaY_2F_8 .

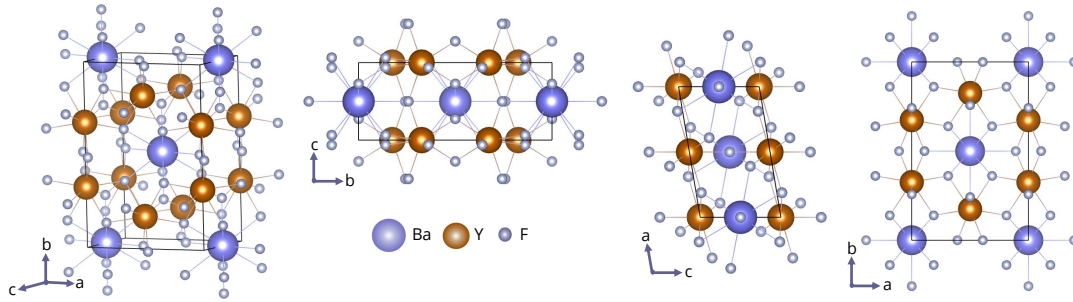


Fig. 4.4.: Different views of the monoclinic structure of BaY_2F_8 fundamental cell.

The samples investigated in the frame of this thesis were grown at the Dipartimento di Fisica, Università di Pisa and MEGA Materials s.r.l., Italy, by Czochralski method (briefly described in appendix A.1). A congruent growth at 980°C with 20 at.% of Tb^{3+} in the melt, resulted on samples with 13 at.% of Tb^{3+} doping concentration in the crystal, determined by x-ray fluorescence (see Appendix A.4). The boule was grown from an a-cut seed at a pulling speed of 0.5 mm/h and a rotation rate of 5 rpm, with a resulting excellent internal optical quality.

4.2.4 Tb^{3+} -doped LaF_3

This compound presents a hexagonal structure in $\text{P6}_3/\text{cm}$ symmetry. Figure 4.5 represent its fundamental cell in different views. LaF_3 is a trifluoride, with only one site for Tb^{3+} ions when doped. Moreover, simple trifluorides as LaF_3 allow for a high concentration of Tb^{3+} and the cation density is comparatively higher than in other fluoride compounds (see table 4.2). Furthermore, one of the most interesting characteristics of LaF_3 when doped with Tb^{3+} is its low CFD of only $\sim 8750 \text{ cm}^{-1}$, that situates this compound as one of the fluorides with lower CFD, as shown in figure 3.4 (cf. also table 4.1).

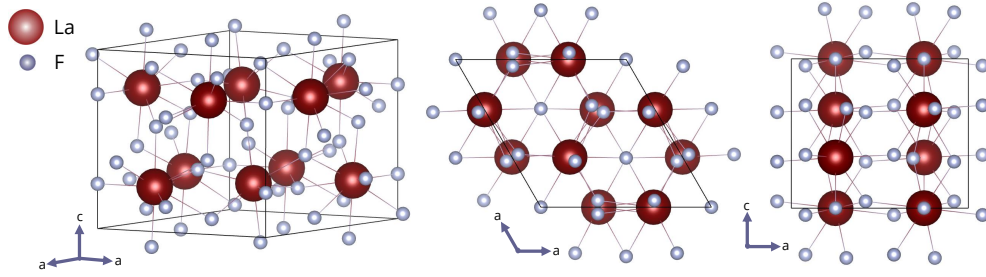


Fig. 4.5.: Fundamental cell of the hexagonal structure of LaF_3 .

Tb^{3+} -doped LaF_3 can be grown from a congruent melt at a temperature of 1487°C , higher than for other fluorides used in this thesis. The samples investigated here were grown by the Czochralski method (see Appendix A.1) at the Institut für Laser-Physik, Universität Hamburg, Germany. LaF_3 powder and crystallites of TbF_3 raw materials had a nominal purity of 5N. A dopant concentration of Tb_3 of 20 at.% in the melt was used, resulting in 12 at.% of Tb^{3+} in the crystal. Due to the insufficient size of the available samples, laser experiments were not realizable.

4.2.5 $\beta\text{-TbF}_3$

This compound presents an orthorhombic structure with space group Pnma and four formulas per unit cell. This kind of simple trifluorides are known as $\beta\text{-YF}_3$ type [Rot93]. Figure 4.6 represent its fundamental cell in different views. As a simple trifluoride, it is expected to have a low CFD with a rough estimated value of $\sim 10000\text{ cm}^{-1}$, as should be comparable to compounds as LaF_3 ($\sim 8750\text{ cm}^{-1}$) or as YF_3 ($\sim 9910\text{ cm}^{-1}$) [Dor00b]. Furthermore, its high cation density of $> 2 \cdot 10^{22}\text{ cm}^{-3}$ together with the stoichiometric 100% of Tb^{3+} in its formula, make this compound to be the fluoride with the highest possible density of Tb^{3+} . Further physical properties of this material are described in table 4.2.

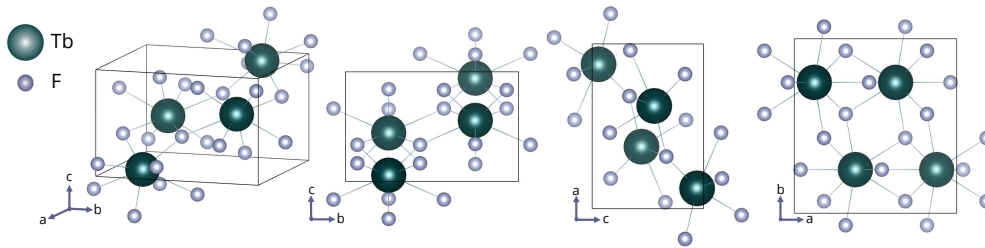


Fig. 4.6.: Fundamental cell of the orthorhombic structure of TbF_3 .

The samples used in this thesis for spectroscopic investigations were selected from crystalline TbF_3 raw material provided by AC materials inc.

	LiLuF ₄ (LiTbF ₄)	KY ₃ F ₁₀ (KTb ₃ F ₁₀)	BaY ₂ F ₈	LaF ₃	TbF ₃
Lattice	tetrag.	cubic	monocl.	hex./trig.	orth.
Space group	I4 ₁ /a	Fm $\bar{3}$ m	C $\frac{2}{m}$	P6 ₃ /cm	Pnma
V _{cell} (Å ³)	277.6 (294.5)	1542.0 (1565.3)	308.8	329.3	198.4
Formula units / unit cell	4	8	2	6	4
Cation density (10 ²² cm ⁻³)	1.441 (1.358)	1.556 (1.533)	1.295	1.822	2.016
Coordination number	8	8	8	9	8
$\partial n / \partial T$ (10 ⁻⁶ K ⁻¹)	-3.6 <i>a</i> -6.0 <i>c</i>	- (-9.7)	-	-	-
$\partial L / \partial T$ (10 ⁻⁶ K ⁻¹)	13.6 <i>a</i> 10.8 <i>c</i>	41.0 (13.7)	17.0 <i>a</i> 18.7 <i>b</i> 19.4 <i>c</i>	~20 <i>a</i> ~10 <i>c</i>	-
κ (W/(mK))	5.0 <i>a</i> , 6.3 <i>c</i>	3.5	3.5 <i>b</i>	2.1 <i>a</i> , 2.6 <i>c</i>	-
Mohs hardness	3.5	4.5	4-5	3.5	-

Tab. 4.2.: Physical properties of fluoride host materials. References for these values can be found in table A.1, appendix A.5.

4.3 Oxide crystals

Oxide compounds are the most widespread host materials for SSLs, due mainly to their advantageous thermomechanical properties. Two of the most common oxide structures used as hosts for laser gain media are sapphire (Al₂O₃) and YAG. Generally, oxides present higher thermal conductivity than fluorides, which protects them against thermal damage. In addition, their higher hardness favors easier handling, especially for cutting and polishing. Furthermore, they present less critical crystal growth requirements, particularly in terms of atmosphere.

Their main disadvantage, when doped by Tb³⁺, is the generally stronger crystal fields, in comparison with fluoride materials (see figure 3.4). Nevertheless, some oxide compounds such as perovskites, present CFDs as low as fluoride materials that have proved to be successful host for Tb³⁺-laser operation. In addition, it is worth to study other oxide materials with higher values of CFD in order to better understand the behavior of Tb³⁺ when doped into this kind of structures. In the work of this thesis, three oxide host materials have been chosen to analyze their spectroscopic and laser properties when doped with Tb³⁺: the perovskite YAlO₃ and the well-known laser materials when doped by RE ions, YAG and KY(WO₄)₂.

4.3.1 Tb³⁺-doped YAlO₃ and TbAlO₃

These two compounds belong to the group of perovskite oxides, with the chemical formula ABX₃. They present an orthorhombic structure with symmetry on the space group Pnma (see figure 4.7). The larger cation, i.e. yttrium or terbium, occupies a 12-coordinate position. As a consequence of this high coordination number, both compounds experience CFDs of $\sim 16700\text{ cm}^{-1}$, only slightly higher than the CFD value of the fluoride materials successful in laser operation (cf. in table 4.1). Further physical properties of this material can be found in table 4.3.

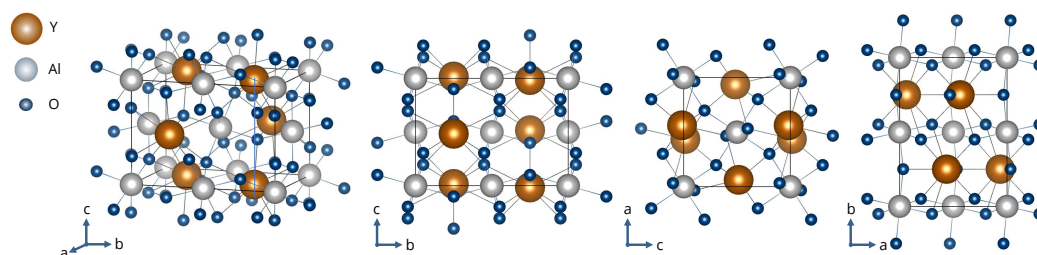


Fig. 4.7.: Fundamental cell of the orthorhombic structure of YAlO₃.

Three boules of Tb³⁺-doped YAlO₃ with dopant concentrations of 20 at.%, 10 at.%, and 5 at.% in the melt were grown in-house, at the Leibniz-Institut für Kristallzüchtung, Germany. YAlO₃ presents a melting point of 1875°C and a description of the Czochralski method used to grow the boules can be found in appendix A.1. The Tb³⁺ concentration in the crystals was determined by x-ray fluorescence to be 19.2 at.%, 9.2 at.%, and 4.5 at.% respectively (see appendix A.4). After being grown, the three crystals presented a light orange-red coloration that was removed by annealing at 900°C for 40 hours in forming gas atmosphere.

The TbAlO₃ sample was grown at the Center for Optical Materials and Technologies of the Belarusian National Technical University, Belarus. The boule was grown by vertical Bridgman method (briefly described in appendix A.3) under Ar/H₂ atmosphere (5 vol.% of H₂).

4.3.2 Tb³⁺-doped Y₃Al₅O₁₂

This compound belongs to the group of garnets with general formula {A₃}[B₂](C₃)O₁₂, presenting a cubic structure in Ia $\bar{3}$ d symmetry. The dodecahedral site {} is occupied by Y³⁺ and the octahedral [] and tetrahedral () sites are occupied by Al³⁺. Figure 4.8 depicts its fundamental cell in different views. This synthetic material became popular as laser crystals already in the 1960s and it is an established laser host materials with widespread use in science and industry. Its resistance against thermal damage makes it especially suitable for high-power lasers and Q-switched lasers.

However, when doped with Tb^{3+} , its high value of CFD suppose a high risk of ESA, that may difficult the laser performance (cf. table 4.1). Further details about YAG can be found in table 4.3.

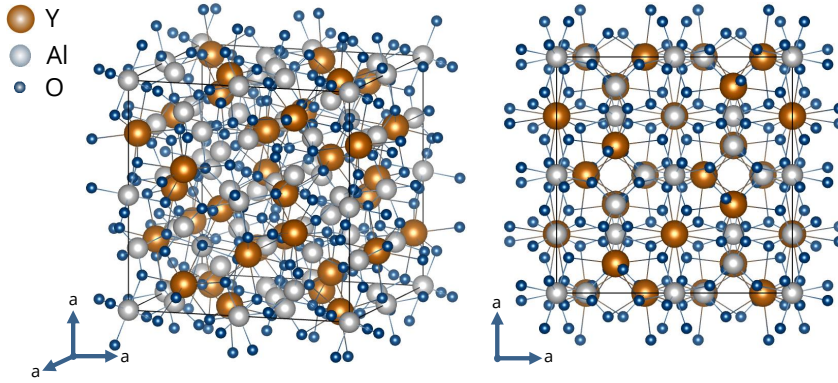


Fig. 4.8.: Two visualizations of the fundamental cell of the cubic structure of $\text{Y}_3\text{Al}_5\text{O}_{12}$.

The Tb^{3+} -doped YAG samples used in the work of this thesis were grown at the Institut für Laser-Physik, Universität Hamburg, Germany. A melting point of 1940 °C permits Czochralski growth when using an iridium crucible. By the use of a 20 at.% of Tb^{3+} in the melt, the crystal presents a 14.4 at.% of Tb^{3+} concentration, determined by x-ray fluorescence (see apendix A.4). The side and optical quality of the available samples only allowed for spectroscopy characterization.

4.3.3 Tb^{3+} -doped $\text{KY}(\text{WO}_4)_2$

The family of potassium double tungstates $\alpha\text{-KRE}(\text{WO}_4)_2$ ($\text{RE} = \text{lanthanide or Y}$) represents a group of well-known host materials for SSL. In particular, $\text{KY}(\text{WO}_4)_2$ presents a biaxial monoclinic structure in C_c^2 symmetry. Figure 4.9 depicts the fundamental cell of this compound. It is possible to incorporate high concentrations of active RE ion in these crystals, even up to a stoichiometric 100% [Klo02]. Unfortunately, their exceptionally small bandgap of $\sim 32 \cdot 10^3 \text{ cm}^{-1}$ implies a strong loss channel for two-photons processes at the pump and laser wavelengths. Further properties of $\text{KY}(\text{WO}_4)_2$ can be found in table 4.3.

The Tb^{3+} -doped $\text{KY}(\text{WO}_4)_2$ crystal was grown by Czochralski method at the Center for Optical Materials and Technologies of the Belarusian National Technical University, Belarus. The boule was grown from a potassium ditungstate ($\text{K}_2\text{W}_2\text{O}_7$) flux at a low-temperature gradient ($\sim 0.1 \text{ K/cm}$) using an $[010]$ oriented $\text{KY}(\text{WO}_4)_2$ crystal seed. Details about the growth method can be found at [Pav93]. The resulting sample contains a 53 at.% of Tb^{3+} , determined by electron-probe microscope analysis.

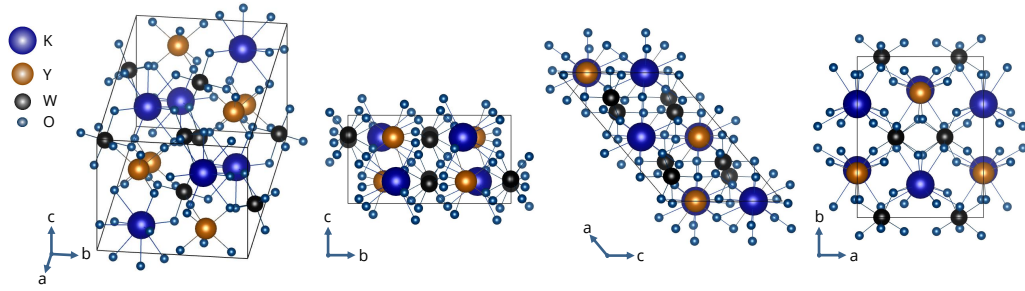


Fig. 4.9.: Fundamental cell of the monoclinic structure of $KY(WO_4)_2$.

4.4 Sample preparation

Most of the samples were prepared in-house in the support lab of Crystal Machining at the Leibniz-Institut für Kristallzüchtung for spectroscopy and laser experiments. After orientation and cutting, the samples surfaces were first lapped and subsequently polished with plane-parallel faces on a PM5 Logitech polishing machine. The lapping process was executed with F800 SiC powder and the polishing was realized in two steps with $3\text{ }\mu\text{m}$ and $1\text{ }\mu\text{m}$ grain size diamond particles.

	YAlO ₃ (TbAlO ₃)	Y ₃ Al ₅ O ₁₂	KY(WO ₄) ₂
Lattice	orthorhombic	cubic	monoclinic
Space group	Pnma	Ia $\bar{3}$ d	C $\frac{2}{c}$
V _{cell} (Å ³)	203.62 (206.44)	1728.14	629.43
Formula units / unit cell	4	8	4
Cation density (10 ²² cm ⁻³)	1.97 (1.94) ¹	1.36	0.64
Coordination number	12	8	8
$\partial n / \partial T$ (10 ⁻⁶ K ⁻¹)	7.7 <i>a</i> , 11.7 <i>b</i>	7.8	-13.1 <i>N_p</i> , -7.6 <i>N_m</i>
$\partial L / \partial T$ (10 ⁻⁶ K ⁻¹)	8.3 <i>c</i> 2.3 <i>a</i> , 8.1 <i>b</i> 8.7 <i>c</i>	6.1	-11.8 <i>N_g</i> 11.0 <i>a</i> , 1.2 <i>b</i> 17.8 <i>c</i>
κ (W/(mK)) (298 K)	11.7 <i>a</i> , 10.0 <i>b</i> 13.3 <i>c</i>	11.2	2.7 <i>b</i>
Mohs hardness	8.5-9	8.5	~4.5

Tab. 4.3.: Physical properties of oxide host materials. References for these values can be found in table A.2, appendix A.5.

¹Considering that there are 4 formula units per unit cell, the correct value of Tb³⁺ density in TbAlO₃ is 1.94×10²² cm⁻³ instead of 4.84 ×10²¹ cm⁻³, as given in [Sek98].

Spectroscopic investigations

This chapter deepens into the spectroscopic properties of Tb^{3+} ions related to laser operation and the influence of the host material in their optical behavior. The spectroscopic measurements carried out in this work give specific information of the optical properties relevant to evaluate the potential of laser performance of the Tb^{3+} -based materials presented in chapter 4.

As an example, emission-cross sections reveal the possible wavelengths for laser emission, absorption cross-sections help to optimize the absorption wavelength of the pump source, and ESA measurements expose detrimental intraionic processes for specific wavelengths. In addition, measurements of the lifetime give valuable information about the dynamic behavior of the electronic population in excited levels, as well as the influence of doping concentration in interionic processes. Additional fluorescence measurements at low temperature help to identify the position of the ground-state Stark levels of Tb^{3+} and show their potential as gain media for cryogenic lasers.

All experimental setups for spectroscopic investigations in the frame of this thesis were built from scratch in a new laboratory facility, by myself to a great extent. Therefore, the selection of laser systems, spectroscopic devices, detectors, and optical and optomechanical components was designed, pursued, and build to satisfy the necessities of the experiments presented here, as well as additional experiments required for further activities of the Center for Laser Materials, at the Leibniz-Institut für Kristallzüchtung. Furthermore, LabVIEW software [Bit06] was developed to control several devices involved in the spectroscopic measurements, in order to fulfill the very specific desired conditions for the experiments. Figure 5.1 shows screenshots of the LabVIEW program developed for fluorescence spectroscopy. The program controls the monochromator and simultaneously records the signal from the detector provided by the lock-in amplifier. A more detailed description of this setup is given in section 5.2.

5.1 Ground state absorption

The GSA was determined by transmission measurements of eight of the materials presented in chapter 4. The transmission spectra were recorded in a Lambda

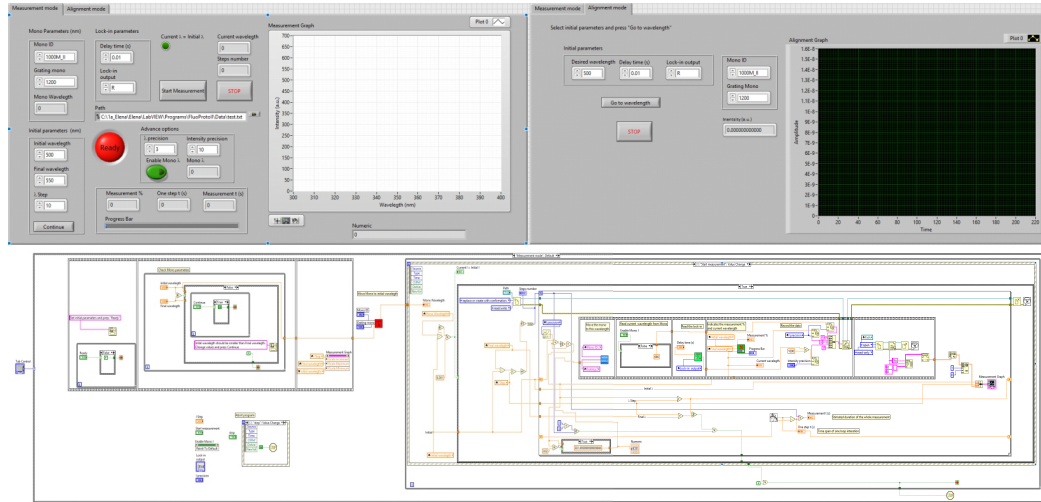


Fig. 5.1.: LabVIEW program for fluorescence spectroscopy. (Up) Two views of the front panel with user settings and controllers. (Down) Main block diagram code.

1050 spectrometer (Perkin Elmer), using a photomultiplier tube (PMT) detector. In addition, crystal holders were designed and manufactured to fulfill the dimensional characteristics of the samples and polarizers were implemented during the polarization-dependent measurements when non-cubic crystals were measured.

The corresponding absorption cross-sections can be calculated by applying the Beer-Lambert law:

$$I(\lambda) = I_0(\lambda) \cdot e^{-\alpha(\lambda)d}, \quad (5.1)$$

where $I_0(\lambda)$ is the initial intensity, $I(\lambda)$ is the remaining intensity after the light has traveled a distance d (crystal thickness) through the crystal, and $\alpha(\lambda)$ is the absorption coefficient, that can be revealed as

$$\alpha(\lambda) = \frac{1}{d} \cdot \ln \left(\frac{I_0(\lambda)}{I(\lambda)} \right). \quad (5.2)$$

The absorption cross-sections (σ_{abs}) are defined as

$$\sigma_{abs}(\lambda) = \frac{\alpha(\lambda)}{[Tb^{3+}]}, \quad (5.3)$$

where $[Tb^{3+}]$ is the concentration of Tb^{3+} in the crystal.

For the transmission measurement to be reliable, it is necessary to perform the experiments in a sample with high optical quality. Defects and impurities in the crystalline structure could induce scattering and parasitic absorption that may result

in unrealistic high values of the cross-sections. Therefore, from the available samples of this work, only eight materials had sufficient optical quality and dimensions to perform reliable absorption measurements on them. The samples were cut and polished with plane-parallel faces to access the main polarization directions. Cubic crystals were measured without polarizers.

The transmission data collected by the Perking Elmer spectrometer was loss corrected having into account the dependency in wavelengths of the Fresnel reflections on the surface of the samples. Additionally, a linear background was removed when necessary.

5.1.1 Absorption spectra of the transition ${}^7F_6 \rightarrow {}^5D_4$

The electronic transition in the wavelength range between 475 and 500 nm, consists of GSA to the level 5D_4 . This direct way to excite electrons into the upper laser level generates minimum losses as the Stokes shift is the smallest. Figure 5.2 depict the absorption cross-section values for this transition. The spectra were recorded with a resolution ≤ 0.3 nm.

All fluoride materials present the blue absorption band in a comparable energetic position, with a similar structure of narrow peaks and alike values of the cross-sections. The only exception is given by $\text{Tb}^{3+}:\text{LaF}_3$, which presents a comparatively less featured spectrum, which broadening results in slightly lower maximum values. This broadening is attributed to the large difference in ionic radii between Tb^{3+} and La^{3+} ions of about a 20% [Kam90b]. The three oxide materials exhibit absorption spectra with comparable features presenting a very structured composition of peaks. However, the value of the cross-sections strongly differ among them, as well as in comparison with the fluoride materials, with absorption cross-sections three times higher for $\text{Tb}^{3+}:\text{YAlO}_3$ and six times higher for $\text{Tb}^{3+}:\text{KY}(\text{WO}_4)_2$. The exact cross-section values of the highest peaks of absorption for each material are specified in table 5.1. In addition, the slightly lower cross-section values of $\text{KTb}_3\text{F}_{10}$ in contrast to the values of the $\text{Tb}^{3+}:\text{KY}_3\text{F}_{10}$ crystal may be due to energy migration to impurities, as the Tb^{3+} concentration is as high as $1.556 \times 10^{22} \text{ cm}^{-3}$, in comparison with $0.265 \times 10^{22} \text{ cm}^{-3}$ for $\text{Tb}^{3+}:\text{KY}_3\text{F}_{10}$.

Additionally, table 5.1 shows the values of one absorption length for the specific Tb^{3+} concentration of the evaluated samples, as it gives relevant information of the dimensions required for the laser samples. When light is absorbed in a homogeneous medium, an absorption length is defined as the length of that medium that reduces its intensity to $\frac{1}{e}$ of its initial value. Optically pumped laser gain media often have a length which is about 2 or even 3 absorption lengths at the pump wavelength, so that the pump absorption is sufficiently effective.

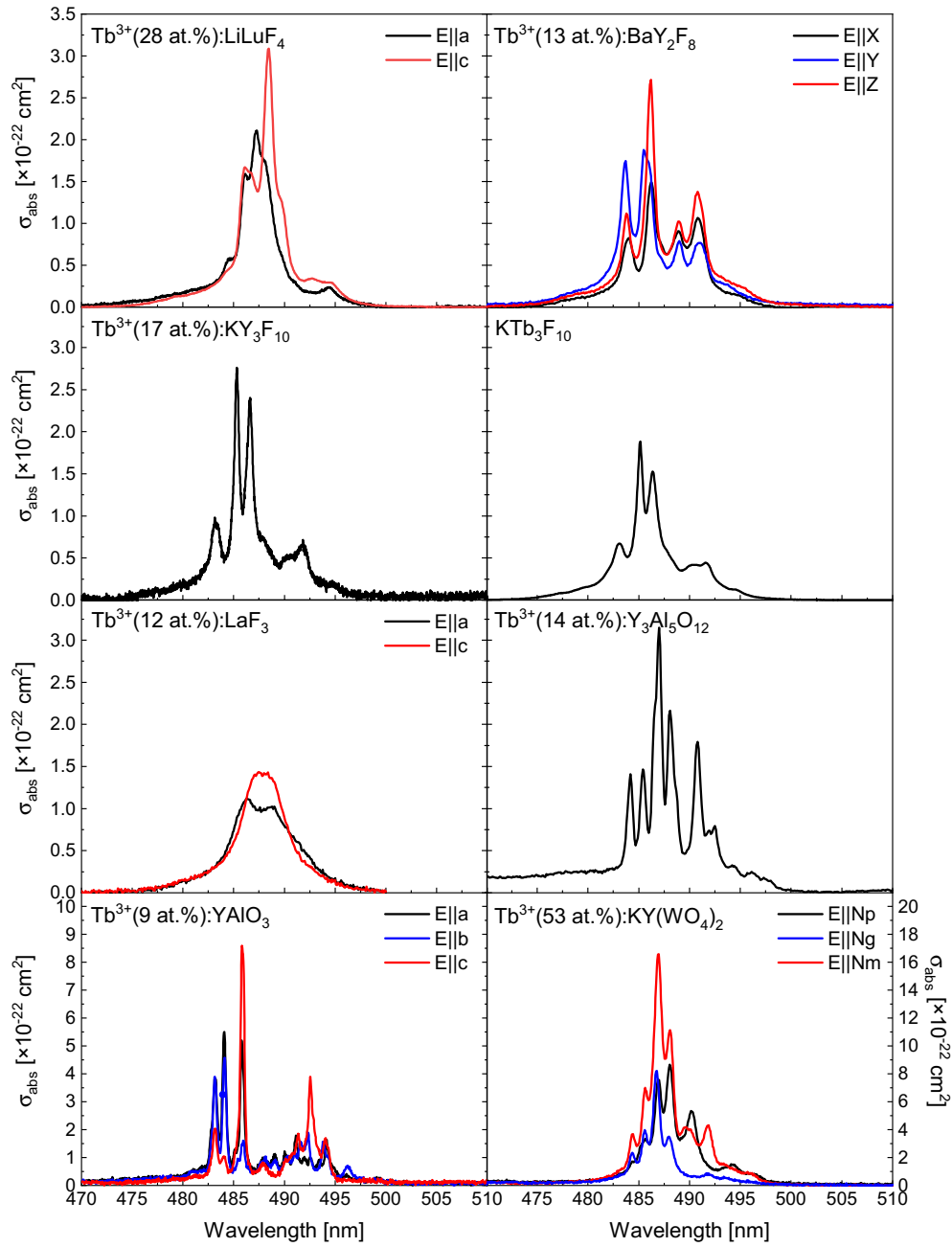


Fig. 5.2.: Effective RT absorption cross-section spectra of transition ${}^7F_6 \rightarrow {}^5D_4$. It is worth notice that the scale of the ordinate axes in the absorption cross-sections graph for the host YAlO_3 are three times higher and for $\text{KY}(\text{WO}_4)_2$ are six times higher than for the rest of the crystals represented in figure 5.2. Therefore, the σ_{abs} values are in the order of 10^{-22} cm^2 for all materials investigated except for these two materials, for which are one order of magnitude higher.

Material Units	Abs. peak (10^{-22} cm^{-1})	λ (nm)	Pol.	Tb ³⁺ (at.%)	Abs. length (mm)
LiLuF ₄	3.088	488.5	E c	28	8.1
BaY ₂ F ₈	2.716	486.2	E c	13	21.9
KY ₃ F ₁₀	2.759	485.3	-	17	13.7
KTb ₃ F ₁₀	1.882	485.2	-	100	3.5
LaF ₃	1.422	488.0	E c	12	32.2
Y ₃ Al ₅ O ₁₂	3.147	487.0	-	14	16.2
YAlO ₃	8.588	485.8	E c	9	6.4
KY(WO ₄) ₂	16.582	487.0	E Nm	53	1.9

Tab. 5.1.: Absorption peak values for Tb³⁺ ions in selected host materials. Value of one absorption length for these crystals.

The values displayed in table 5.1 evidence that the low absorption cross-sections of the $^7\text{F}_6 \rightarrow ^5\text{D}_4$ transitions for Tb³⁺ ions, make in some cases a challenge to manufacture monocrystalline samples with sufficient length for efficient pump absorption. Therefore, alternative absorption transitions in the UVA are evaluated in the following section with the aim of optimizing the pump absorption and reducing the required crystal length.

5.1.2 UV absorption

This section analyzes the possibility of optically pumping Tb³⁺-based lasers into the $^5\text{D}_3$ electronic level in the UV, as an alternative to direct pumping into the $^5\text{D}_4$ upper laser level in the cyan-blue region (see figure 3.2). The GSA into these levels presents ~ 6 times higher absorption cross-sections than the $^7\text{F}_6 \rightarrow ^5\text{D}_4$ transition. In addition, the availability in the market of diodes laser modules that provide several watts of output power, e.g. at 370 nm [Nic20], brings the opportunity for the development of more simple and cost-efficient overall laser setups. The results of this study are published at [Kal20].

The energy level system of Tb³⁺ presents a high density of 4f-levels for energies above 25000 cm^{-1} , corresponding to UVA absorption. The lower energy level of this set of multiplets is the $^5\text{D}_3$ level. As shown in figure 5.3, the wavelengths corresponding to the transition $^7\text{F}_6 \rightarrow ^5\text{D}_3$ are $\sim 380 \text{ nm}$. Due to the denseness of states above $^5\text{D}_3$, pumping at higher wavelengths will result in instantaneous thermalization into this level. Conversely, the energy gap between the $^5\text{D}_3$ level and the $^5\text{D}_4$ upper laser level exceeds 5000 cm^{-1} . Considering that maximum phonon energies are not exceeding 500 cm^{-1} for the fluoride host materials and 900 cm^{-1} for the oxide materials studied here, multiphonon decay processes are regarded

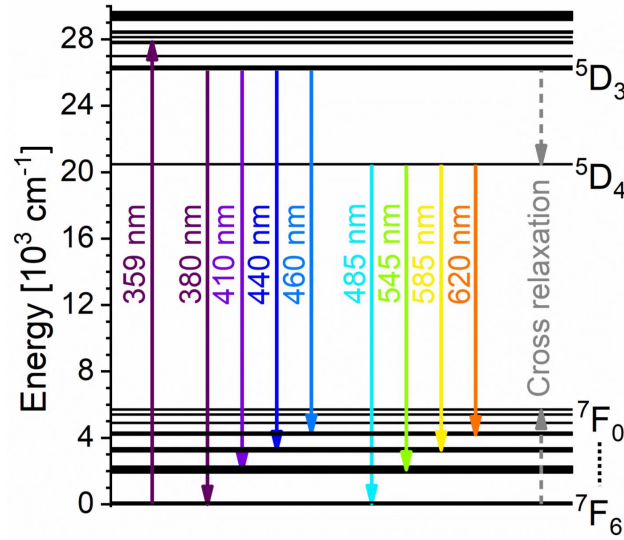


Fig. 5.3.: Energy level diagram of Tb^{3+} in fluoride as host materials. Colored arrows represent absorption and emission transitions and gray dashed arrows correspond to cross relaxation channels.

very unlikely, as exposed in section 2.2.1. In this work, we propose that interionic cross relaxation mechanisms (described in section 2.2.2) involving the resonant transitions ${}^5\text{D}_3 \rightarrow {}^5\text{D}_4$ and ${}^7\text{F}_6 \rightarrow {}^7\text{F}_0$ [Rob76, Jen73], can efficiently populate the upper laser level ${}^5\text{D}_4$ for crystals with a high enough concentration of Tb^{3+} (see figure 5.3).

Even though ultraviolet emission at wavelengths from 375 to 475 nm has been observed for a Tb^{3+} (2 at.%) -doped LiLuF_4 crystal [Kal20], corresponding to direct radiative decay of the ${}^5\text{D}_3$ level into the ground-state multiplet (see figure 5.3), for higher concentrations of Tb^{3+} in this matrix, the cross relaxation processes are proved to be efficient. In fact, for a Tb^{3+} doping concentration of 14 at.%, the UV emission is already quenched by more than two orders of magnitude. In addition, figure 5.4 shows that the excitation spectra recorded at 542 nm closely resemble the absorption spectra. This green emission corresponds to the transition ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$, where the ${}^5\text{D}_4$ level can only be populated by cross relaxation processes when excited at ultraviolet wavelengths. It is worth noticing that the fluorescence intensity of the green emission by exciting at 359 nm is more than 6 times higher than by exciting at 488 nm in the blue. Consequently, we can conclude that the higher absorption of Tb^{3+} ions in the ultraviolet, together with the efficient cross relaxation processes that populate the ${}^5\text{D}_4$ upper laser level, makes pumping in the UV a suitable solution for Tb^{3+} -based visible lasers.

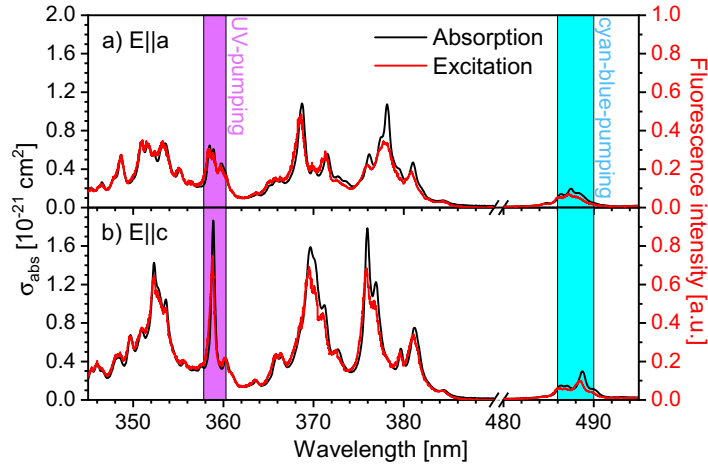


Fig. 5.4.: Tb^{3+} (14 at.%) : LiLuF_4 GSA cross-sections (black) and excitation spectra recorded at 542 nm (red) for a) σ and b) π polarization. Highlighted in purple and blue, wavelengths relevant for pumping Tb^{3+} -based laser [Kal20].

5.2 Emission spectra

This section collects the fluorescence spectra of nine of the Tb^{3+} -crystals described in chapter 4. For these measurements, the crystals were excited at 359 nm into the $^5\text{D}_3$ level of Tb^{3+} . In that way, it was possible to record all the emission lines from the $^5\text{D}_4$ upper laser level to the ground-state multiplet. The excitation source was a frequency-doubled Ti:sapphire laser (M Squared Lasers SolisTiS and ECD-X module) operating at a fundamental wavelength of 718 nm.

The fluorescent detection system was built in-house. The crystal emission was collected for a set of lenses, that focus the light into the entrance slit of an M Series II monochromator (Horiba). An uncoated polarizing beam splitter (PBS) was placed before the entrance slit of the monochromator for the polarization-dependent measurements. Subsequently, an R13456 photomultiplier tube (Hamamatsu) detects the intensity of the light that is amplified in an SR810 DSP Lock-in amplifier (Stanford Research Systems). Then, a LabVIEW (NI Corporation) program that fits the specific needs of these measurements was developed in the frame of this work, to control simultaneously the monochromator wavelengths and the recording of the lock-in amplifier (see figure 5.1). The system response was calibrated in three different ways. The monochromator wavelengths were calibrated by recording the emission of a 2ω -OPSL (Coherent Genesis CX STM) with a known emission of 486.3 nm. The polarization-dependent response of the monochromator was corrected with data provided by Horiba. Additionally, the overall response of the system was calibrated

with the recorded emission spectrum of a tungsten lamp with a known emissivity (OSRAM, WI17G).

Once the fluorescence spectra are known, the emission cross-sections can be calculated with the Füchtbauer-Ladenburg equation,

$$\sigma_{em}^{\xi}(\lambda) = \frac{1}{8\pi cn^2\tau} \frac{\lambda^5 I^{\xi}(\lambda)}{\frac{1}{3} \sum_j \int \lambda I^{\xi_j}(\lambda) d\lambda}, \quad (5.4)$$

where the fluorescence intensity $I^{\xi}(\lambda)$ corresponding to the ξ polarization, is normalized with the area under the curve of all fluorescence emission to the ground-state multiplet $\frac{1}{3} \sum_j \int \lambda I^{\xi_j}(\lambda) d\lambda$, obtaining an absolute value of the emission cross-sections [Mou86]. In equation 5.4, c represents the speed of light, $n=n(\lambda)$ is the refractive index of the material, and τ the lifetime of the emitting level.

The resulting emission spectra are shown in figure 5.5. The four dominant sets of emission lines at wavelengths from 480 nm to 640 nm corresponds to the main radiative channels from the 5D_4 level into the $^7F_{6,5,4,3}$ multiplets. The remaining emission wavelengths from 640 nm to 705 nm correspond to weaker radiative channels from the 5D_4 level into the $^7F_{2,1,0}$ multiplets. It is worth noticing that the emission cross-sections for TbF_3 and for the three oxide materials are higher than for the rest of the fluoride material, and for that reason, their ordinate axes in figure 5.5 are extended. This enhanced emission is particularly relevant for $KY(WO_4)_2$, host material well known for its high values of absorption and emission cross-sections due to its monoclinic low-symmetry structure that presents a strong anisotropic environment for the optically active ion [Bre01]. Figure 5.6 exhibit the difference on emission of Tb^{3+} on $KY(WO_4)_2$ compare to $LiLuF_4$ for the transition $^5D_4 \rightarrow ^7F_5$.

The values of the fluorescence lifetime (τ_{flu}) of the 5D_4 multiplet used to calculate the emission cross-sections are evaluated in section 5.3. Due to the lack of processes in Tb^{3+} that could quench the lifetime of the 5D_4 -multiplet at RT, it is possible to use τ_{flu} in equation 5.4 as an approximation of the radiative lifetime (τ_{rad}). Consequently, the average lifetime of the 5D_4 multiplet is considered at the temperature that the laser is intended to operate.

5.2.1 Emission spectra at low temperature

Low temperature emission spectra are used to identify the energetic position of the Stark levels of the Tb^{3+} ground-state manifold. These results, in combination with the identification of the energetic positions of the Stark levels of the 5D_4 multiplet by low temperature absorption measurements, contribute to the determination of the partition functions of the Tb^{3+} -ions in each specific host material.

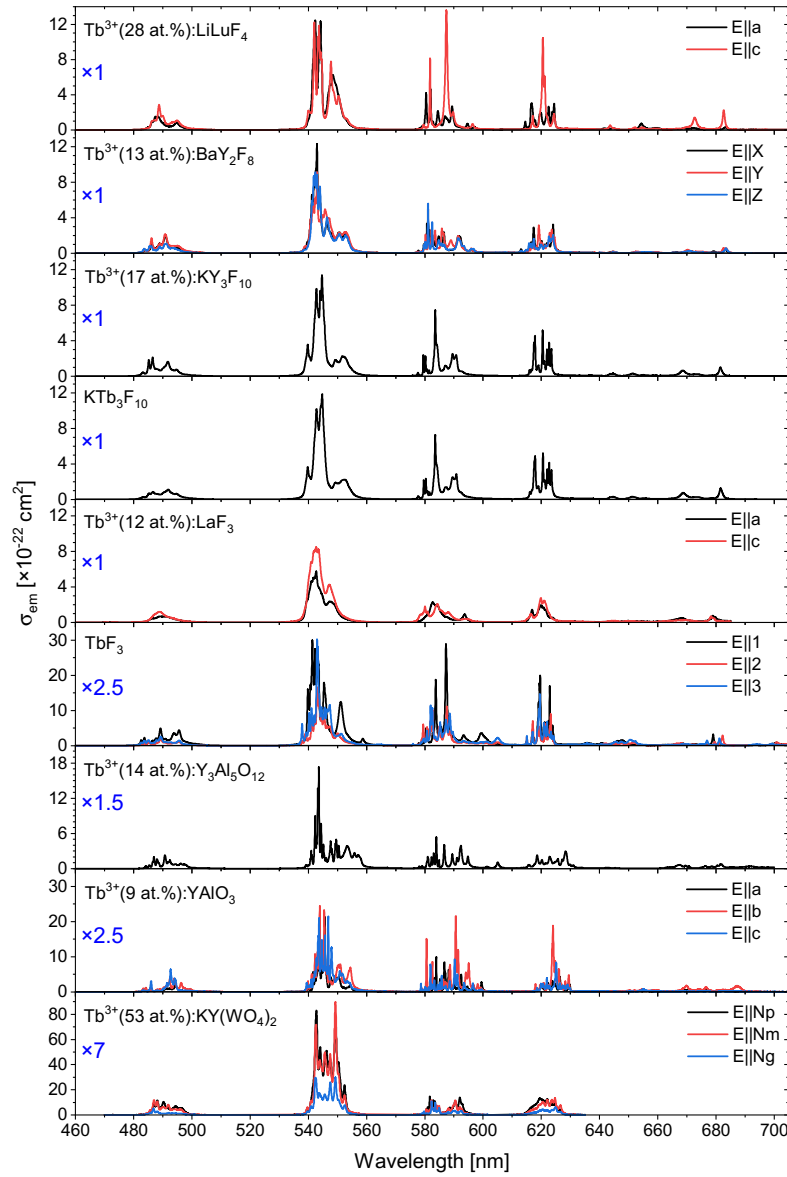


Fig. 5.5.: Effective RT emission cross-section spectra of transition ${}^5D_4 \rightarrow {}^7F_{6...0}$. It is worth notice that the scale of the ordinate axes in the emission cross-sections graph for the host YAG is 1.5 times higher than for the rest of the crystals represented in this figure, for TbF_3 and $YAlO_3$ the scales are 2.5 times higher and for $KY(WO_4)_2$ is 7 times higher. Blue numbers highlight the differences in the axis scales. Nevertheless, the σ_{em} values are in the order of 10^{-21} cm^2 for all materials investigated.

Additionally, low temperature spectra show the potential of these materials to operate as gain media for cryogenic lasers. Figure 5.7 show the emission cross-sections at 12 K. The fluorescence spectra were recorded in the same system described for

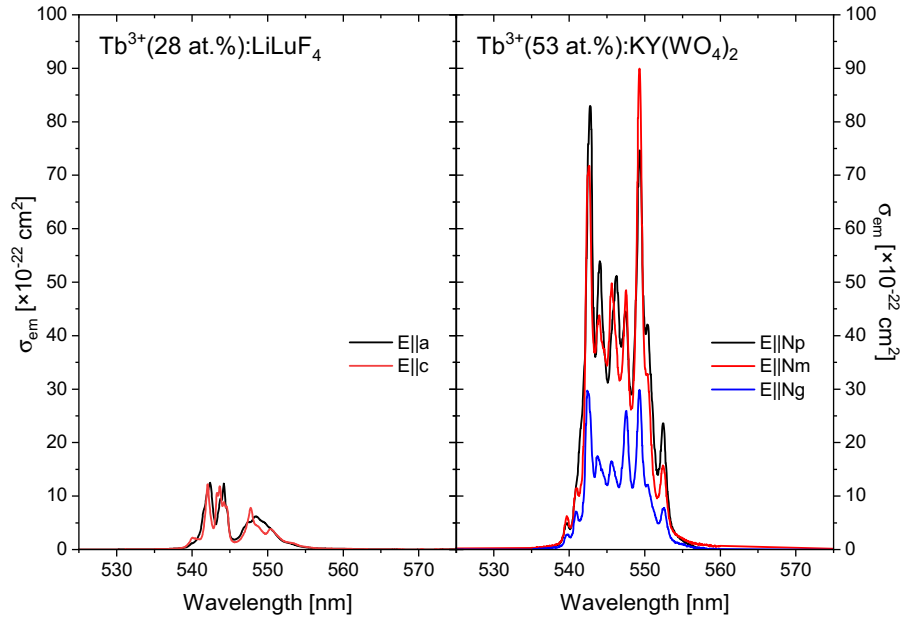


Fig. 5.6.: Comparison between the emission cross-sections of LiLuF_4 and $\text{KY}(\text{WO}_4)_2$ for the transition $^5\text{D}_4 \rightarrow ^7\text{F}_5$.

RT in the previous section, while the samples were set additionally into a cryostat consisting of a DE-204P cold head and an ARS-4HW compressor (Advanced Research Systems, Inc.). The spectra at low temperature present almost 1 order of magnitude higher emission cross-sections than the corresponding spectra at RT.

5.3 Fluorescence dynamics

This section describes the lifetime of the energy levels of Tb^{3+} ions relevant for laser operation. The lifetime of the upper laser level is a key parameter for laser performance that depends on the active medium, i.e. the active ion and the host material. Hence, long lifetime values of the upper laser level contribute to reduced laser thresholds and allow for high storage of energy, convenient for pulsed laser operation. In addition, lifetimes are used to calculate other spectroscopy parameters such as emission cross-sections by the F  chtbauer-Ladenburg equation, in section 5.2.

In the case of a single-exponential decay, the fluorescence intensity decreases over time according to

$$I(t) = I_0 \cdot e^{-\frac{t}{\tau_{fl}}}, \quad (5.5)$$

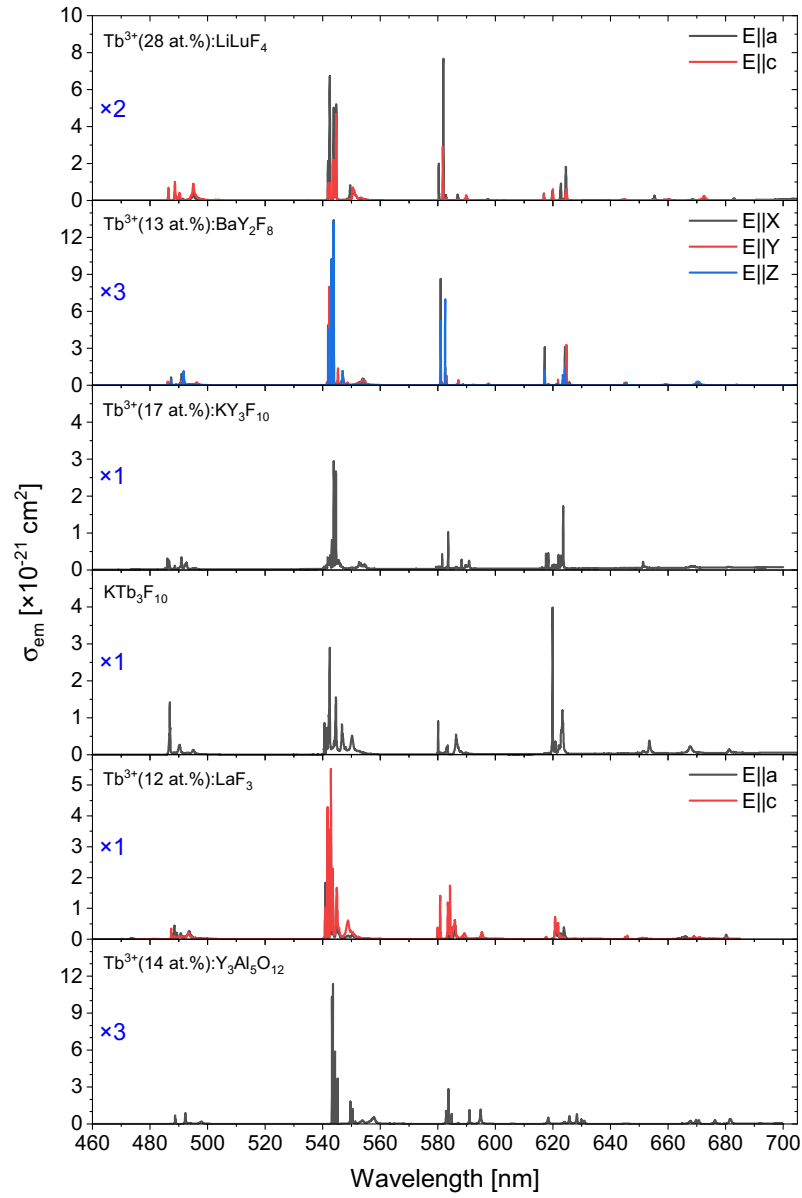


Fig. 5.7.: Effective low temperature emission cross-section spectra of transition $^5D_4 \rightarrow ^7F_{6...0}$. It is worth notice that the scale of the ordinate axes in the emission cross-sections graph differs for the diverse host materials. Blue numbers highlight these differences.

the determination of the fluorescence lifetime τ_{fl} is often calculated by a linear fitting of the decay curve in the logarithmic scale:

$$\ln\left(\frac{I(t)}{I_0}\right) = -\frac{1}{\tau_{fl}} \cdot t, \quad (5.6)$$

In order to measure the lifetime curves, the samples were excited with an optical parametric oscillator (OPO) (GWU-Lasertechnik, VersaScan) with a pulse duration of 5 ns and a repetition rate of 10 Hz. The pulse duration of the pump source is therefore well below the value of the upper laser level lifetime of all crystals measured in this work, which is in general in the order of milliseconds. The fluorescence of the samples was collected by a set of lenses and then imaged onto the slit of an M Series II monochromator (Horiba) equipped with a 1200 g/mm blazed grating optimized for 530 nm. The selected fluorescence from the monochromator was collected either by a silicon diode or by an R5108 photomultiplier (Hamamatsu) and the measured signal was recorded by an RTE1204 oscilloscope (Rohde and Schwarz) and averaged over 1000 decay curves to increase the signal-to-noise ratio. For low temperature and temperature-dependent measurements, the samples were additionally placed into a cryostat consisting of a DE-204P cold head and an ARS-4HW compressor (Advanced Research Systems, Inc.).

5.3.1 Fluorescence lifetime of the 5D_4 multiplet by direct excitation

This section presents the results of the lifetime investigation of the upper laser level 5D_4 in the materials presented in chapter 4. Related to the spin-forbidden character of the fluorescence transitions from this level into the ground state multiplets 7F_J , it yields lifetimes in the order of a few milliseconds. Figure 5.8 collects the values of the average lifetime of the 5D_4 multiplet as a function of the density of Tb^{3+} ions in each compound, measured at RT.

In order to compensate for the low absorption and emission cross-sections of Tb^{3+} ions, high doping concentrations might be beneficial. However, they often come at the expense of detrimental interionic processes which quench the upper laser level lifetime by increasing the probability of non-radiative decay processes. In the following, we present the results of measuring the lifetime of crystals with different doping concentrations of Tb^{3+} for the same host material. Dopant-concentration investigations have been performed for two different host materials, $LiLuF_4$ as a fluoride material and $YAlO_3$ as an oxide material.

For the fluoride host, the available measured Tb^{3+} concentrations correspond to 2%, 14%, 28% and the stoichiometric in Tb^{3+} , $LiTbF_4$ as 100%. The lifetime curves are shown in figure 5.9. For the oxide host, the available measured Tb^{3+} concentrations correspond to 5%, 9%, 19% and the stoichiometric in Tb^{3+} , $TbAlO_3$ as 100%. The lifetime curves are shown in figure 5.10. The excitation wavelengths provided by the OPO were optimized to maximize the fluorescence intensity of the crystals, varying from 486 to 488 nm. In turn, the monochromator was set at 542-543 nm to optimize the detected signal. All curves, except for $LiTbF_4$ and $TbAlO_3$

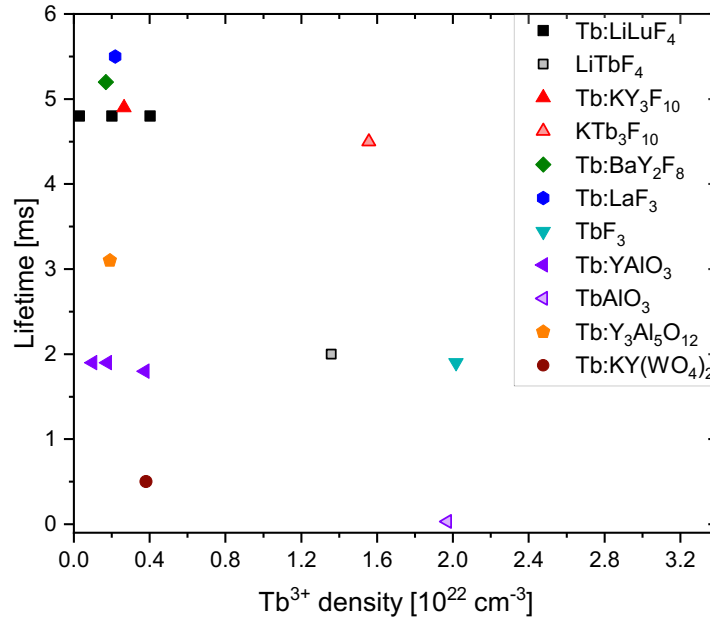


Fig. 5.8.: Fluorescence lifetime values of the 5D_4 multiplet at RT depending on host material and ion density. Hollow symbols correspond to the compounds stoichiometric in Tb^{3+} of the filled symbols series.

exhibit single exponential decays. These results evidence that for concentrations as high as 28% for Tb^{3+} in $LiLuF_4$ and of 19% for Tb^{3+} in $YAlO_3$ there is no quenching of the lifetime and the curves remain single-exponential. This is, therefore, a strong indication that there are no detrimental interionic processes that depend on the distance between Tb^{3+} ions. Consequently, we estimate that the influence of reabsorption in lifetime measurements is negligible.

The significant quenching of the lifetime for the stoichiometric TbF_3 , $LiTbF_4$, and $TbAlO_3$ crystals is attributed to an increase in the density of impurities rather than to interionic processes between Tb^{3+} ions. In particular, RE containing raw materials are often contaminated with small quantities of other REEs, which appear in different proportions on each specific mineral source. The mineral ores from where these raw materials are extracted often contain a mixture of REE that are difficult to separate due to their chemical and physical similarities [Tal13]. Therefore, the high density of Tb^{3+} ions in compounds such as TbF_3 , $LiTbF_4$, or $TbAlO_3$ involve an increase of other RE impurities that favor energy migration. This phenomenon was reported in [Met14a], where emission lines from the $^4G_{5/2}$ -multiplet of Sm^{3+} were observed in TbF_3 and $LiTbF_4$.

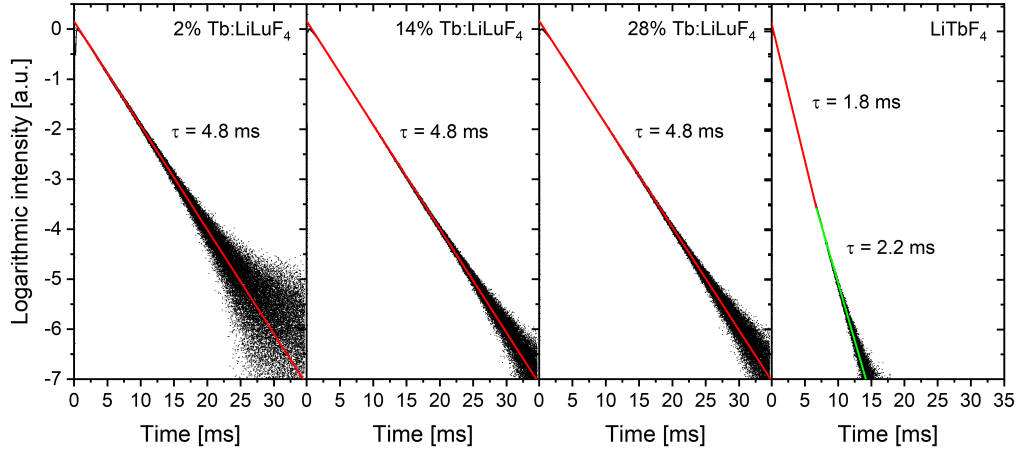


Fig. 5.9.: Fluorescence lifetime curves of the 5D_4 multiplet of Tb^{3+} in $LiLuF_4$ depending on Tb^{3+} concentration. Red and green lines correspond to linear fits following the equation 5.6.

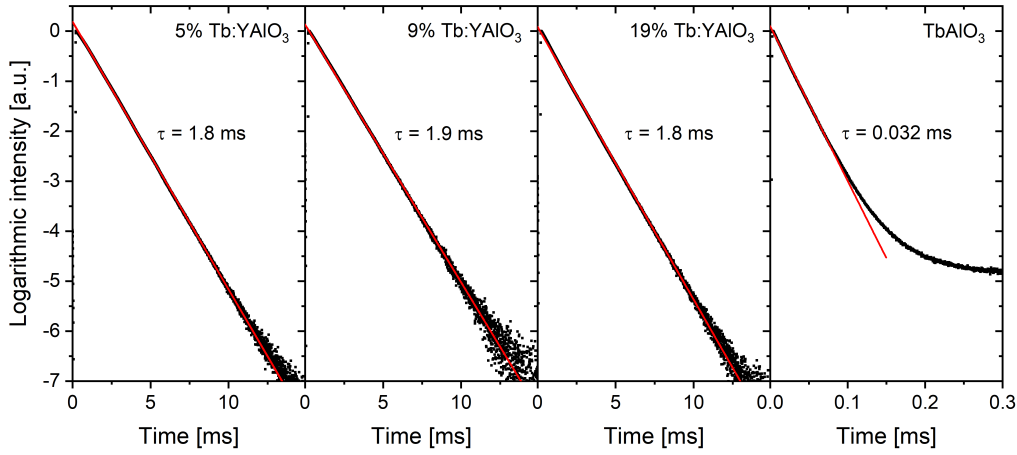


Fig. 5.10.: Fluorescence lifetime curves of the 5D_4 multiplet of Tb^{3+} in $YAlO_3$ depending on Tb^{3+} concentration. Red lines correspond to linear fits following the equation 5.6. It should be notice that the x-axis for $TbAlO_3$ is 50 times smaller than for the rest of the graphs.

5.3.2 Radiative and temperature dependent lifetime

As described in section 2.2.1, the fluorescence lifetime is a combination of the lifetime of both radiative and non-radiative processes. This relationship, given by equation 2.18, allows to calculate the multiphonon decay rate $W_{ph} = 1/\tau_{nr}$ and therefore permits to give an estimation of the quantum efficiency of the process. The τ_{rad} values can be approximated to the fluorescence lifetime measured at low temperature, where the influence of non-radiative processes is minimized.

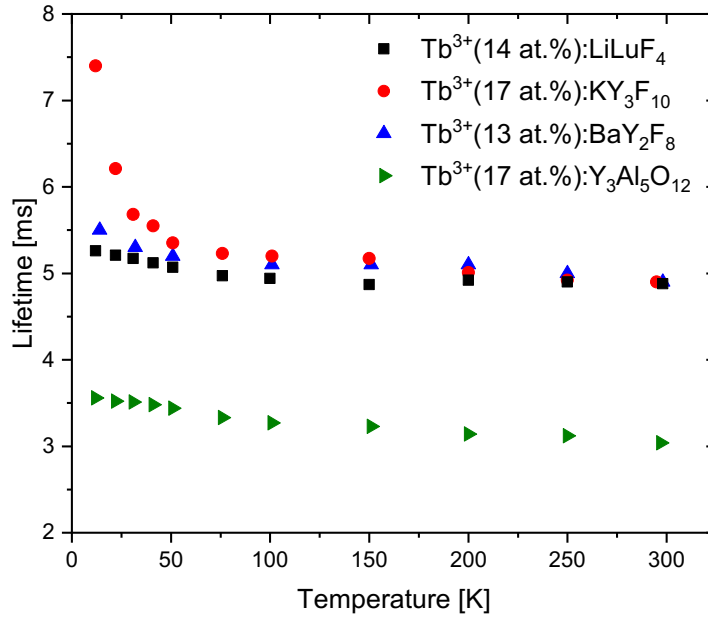


Fig. 5.11.: Temperature-dependent lifetime for four selected host materials.

To evaluate the impact of thermal decay and estimate τ_{rad} values, the lifetime of the 5D_4 -multiplet was measured on Tb^{3+} (14 at.%):LiTbF₄, Tb^{3+} (17 at.%):KY₃F₁₀, Tb^{3+} (13 at.%):BaY₂F₈, and Tb^{3+} (14 at.%):Y₃Al₅O₁₂, for temperatures from 12 K to RT. Figure 5.11 depicts the corresponding results. The difference in lifetimes between 12 K and RT is small for Tb^{3+} (14 at.%):LiLuF₄, Tb^{3+} (13 at.%):BaY₂F₈, and Tb^{3+} (14 at.%):Y₃Al₅O₁₂, and the multiphonon decay W_{ph} entails a $\sim 10\%$ of the totality of depopulation processes of the 5D_4 multiplet. Similarly, the multiphonon decay for Tb^{3+} (14 at.%):Y₃Al₅O₁₂ amounts a $\sim 15\%$. Conversely, in the case of Tb^{3+} (17 at.%):KY₃F₁₀, the increase of the lifetime is significantly higher at low temperature and W_{ph} corresponds to a $\sim 35\%$ of the total decay. Therefore, to determine if the increase at LT on non-radiative decay in KY₃F₁₀ is due to structural reasons or to the quality of the sample, further investigations should be accomplished.

5.3.3 Fluorescence lifetime of the 5D_4 multiplet by excitation at the 5D_3 multiplet

In order to evaluate the viability of pumping Tb^{3+} ions into the 5D_3 multiplet to obtain emission from the $^5D_4 \rightarrow ^7F_{5,4}$ transitions, the lifetime of the 5D_4 multiplet has been measured by exciting the crystals in the UVA. The excitation wavelengths

provided by the OPO were optimized to maximize the fluorescence intensity of the crystals, varying from 375 to 378 nm. At these emission wavelengths the OPO power was limited, and consequently, the recorded signal had a higher level of noise than for excitation at 488 nm. For some of the crystals, the signal was too weak to be recorded. The monochromator was set at 542-543 nm to optimize the detected signal. Table 5.2 collects the lifetime values measured in these conditions. All values are essentially identical to those obtained by direct excitation of the 5D_4 multiplet.

Fluoride	Lifetime (ms)	Oxide	Lifetime (ms)
2 % Tb:LiLuF ₄	4.9	5 % Tb:YAlO ₃	1.8
14 % Tb:LiLuF ₄	4.9	9 % Tb:YAlO ₃	1.9
28 % Tb:LiLuF ₄	4.9	19 % Tb:YAlO ₃	1.8
LiTbF ₄	1.9 / 2.3	TbAlO ₃	No Signal
17 % Tb:KY ₃ F ₁₀	4.9	14 % Tb:Y ₃ Al ₅ O ₁₂	3.0
KTb ₃ F ₁₀	4.1 / 4.7	KY(WO ₄) ₂	No Signal
12 % Tb:LaF ₃	5.5		
TbF ₃	1.9		

Tab. 5.2.: Lifetime values of the 5D_4 multiplet of Tb³⁺ by exciting into the 5D_3 multiplet at RT. Second decays are indicated after a slash.

The reduced efficiency of the cross relaxation process of the resonant transitions $^5D_3 \rightarrow ^5D_4$ and $^7F_6 \rightarrow ^7F_0$ at the low doping concentration of 2% in the Tb:LiLuF₄ crystal, is illustrated in figure 5.12, consistently with the results presented at [Kal20]. Even when the crystals with the three doping concentrations of 2%, 14%, and 28% show decays corresponding to the same lifetime value of 4.9 ms, the crystal with a 2% of Tb³⁺ present a curve with a clear rising time, related to the lifetime of the 5D_3 level. In contrast, the efficient cross relaxation processes for the crystal with a Tb³⁺ concentration of 14% and 28% populate the 5D_4 in a shorter time and therefore, a shortened of the raising time can be appreciated in the lifetime decay curves in comparison with the curve of 2%.

An example of the measured curves is given in figure 5.13 for Tb³⁺ (28 at.%):LiLuF₄ where both curves, the obtained by exciting at 488 nm and 376 nm, are plotted together to emphasize their similarity. The short rising tendency at the beginning of the curve indicates a fast population of the 5D_4 multiplet. These results do not show any detriment when pumping into the 5D_3 multiplet for laser operation.

5.4 Excited state absorption

This section presents the results of ESA measurements in Tb³⁺ (14 at.%):LiLuF₄ and Tb³⁺ (13 at.%):BaY₂F₈ as fluoride materials and in Tb³⁺ (9 at.%):YAlO₃ as oxide

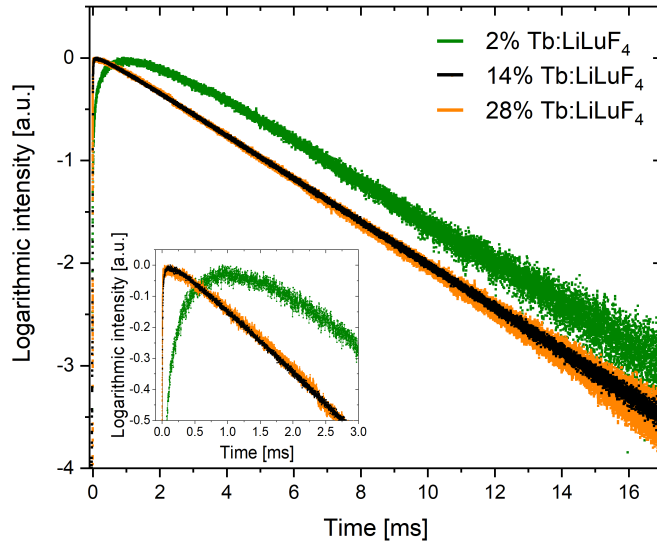


Fig. 5.12.: Lifetime measurements of the 5D_4 level of Tb^{3+} in Tb^{3+} (2 at.):LiLuF₄ (green dots), Tb^{3+} (14 at.):LiLuF₄ (black dots), and Tb^{3+} (28 at.):LiLuF₄ (orange dots) by exciting into the 5D_3 level. The inset graph shows the first few milliseconds of the measurement.

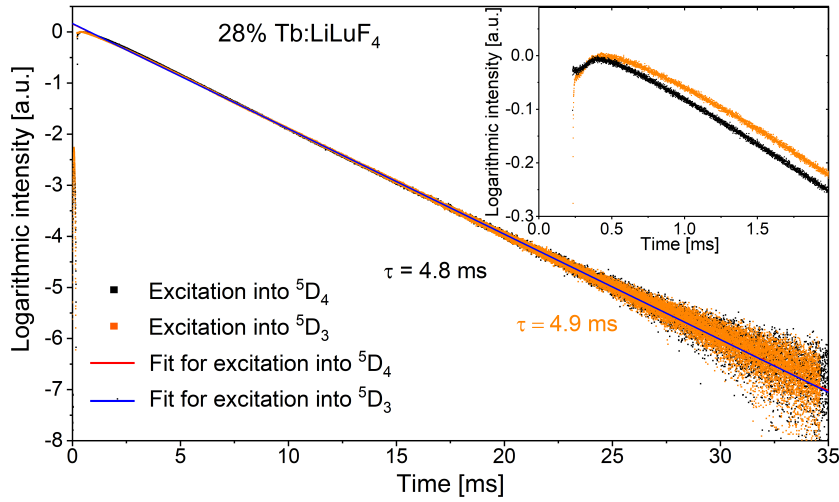


Fig. 5.13.: Lifetime measurement of Tb^{3+} (28 at.):LiLuF₄ by excited into the 5D_3 (orange dots) and 5D_4 (black dots) multiplets. The red and blue lines are the respective linear fits. The superposition of both graphs and fits indicates the similarity of the curves. The inset graph shows the first few milliseconds of the measurement.

material. An extensive description of ESA processes and their influence in Tb^{3+} -based lasers can be found in section 3.2.1. Accordingly, the ESA spectra measured in this work were obtained by implementing a pump-probe technique established

by Koetke et al. [Koe95]. This technique entails the recording of the variations in the intensity of the collected probe light after the sample when it is either excited or not by an additional source of light, denominated pump. When the sample is unpumped, the probe light will be either absorbed or transmitted by the sample. When the sample is pumped, the probe light at emission wavelengths will either cause stimulated emission or ESA, in its interaction with the electronic population of the excited state. The experimental setup is specified in figure 5.14.

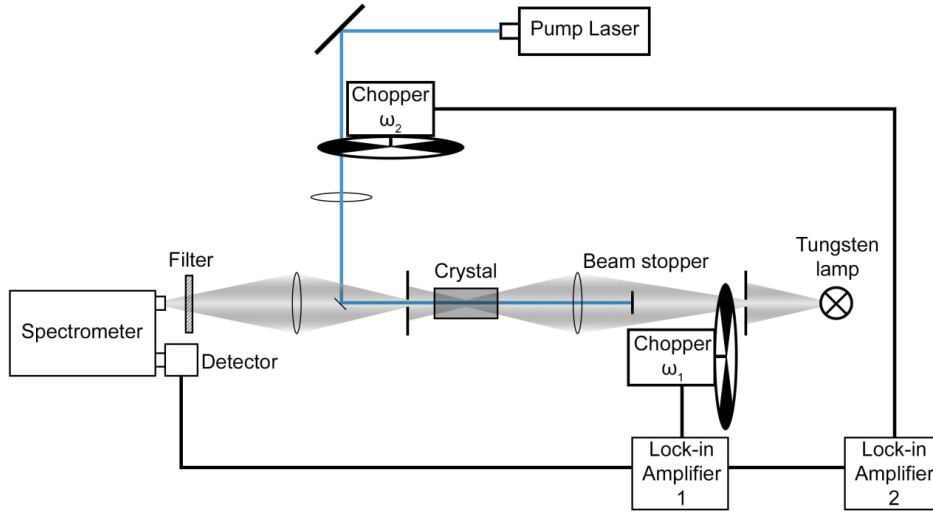


Fig. 5.14.: Experimental setup for ESA measurement with a pump-probe technique.

According to Lambert-Beer law, an unpumped crystal, with length d and Tb^{3+} -concentration N , transmits the probe beam of intensity I_0 as

$$I_u = I_0 e^{-\sigma_{abs} N d}, \quad (5.7)$$

In the case of Tb^{3+} , by using a pump source at 486.2 nm, only the $^5\text{D}_4$ level is excited. Therefore, the corresponding relation for the pumped crystal is

$$I_p = I_0 e^{-\sigma_{abs}(N-N_e)d + (\sigma_{em} - \sigma_{esa})N_e d}, \quad (5.8)$$

where N_e is the fraction of Tb^{3+} ions in an excited state. Combining both expressions, the difference in intensity after the crystal depending on if it pumped or not $\Delta I = I_p - I_u$, can be expressed as

$$Ln[1 + \frac{\Delta I}{I_u}] \approx \frac{\Delta I}{I} = N_e d(\sigma_{abs} + \sigma_{em} - \sigma_{esa}), \quad (5.9)$$

as ΔI is very small and I is the slightly modulated probe beam intensity. Considering an amplification factor "a", the signal of the second amplifier $\Delta I' = a\Delta I$ can be expressed as

$$\frac{\Delta I'}{I} = aN_e d(\sigma_{abs} + \sigma_{em} - \sigma_{esa}). \quad (5.10)$$

Thus, the ESA influence at the emission wavelengths from the 5D_4 level was evaluated in three Tb^{3+} -based crystals: Tb^{3+} (14 at.%) $LiLuF_4$, Tb^{3+} (13 at.%) BaY_2F_8 as fluoride materials, and Tb^{3+} (9 at.%) $YAlO_3$ as oxide material. During the measurements, a 2ω -OPSL (Coherent Genesis CX STM) with emission at 486.3 nm served as a pump. The probe source consists of a tungsten lamp with a known emissivity (OSRAM, W117G). A polarizing beam splitter cube was set in front of the M Series II monochromator (Horiba), for polarizing dependent measurements. The signal from the monochromator was recorded by an R13456 photomultiplier tube (Hamamatsu) and sent to two lock-in amplifiers (SR810 DSP and SR830 DSP, Stanford Research Systems) set in series. The probe signal was chopped at ~ 600 Hz (reference frequency for the first amplifier) and the pump signal at ≤ 10 Hz (reference frequency for the second amplifier). The resulting spectra are shown in figure 5.15.

At the wavelength evaluated, there are no absorption transitions in Tb^{3+} ions. Therefore, if the resultant signal $\Delta I'$ is positive, the σ_{em} are stronger than the σ_{esa} , and laser operation is possible. Conversely, when $\Delta I'$ is negative, the ESA processes dominated over stimulated emission, and laser operation is not expected. In agreement with the results presented at [Met14a], there is no presence of a negative broadband signal which indicates that there is no interconfigurational ESA into the lowest $4f^7 5d^1$ -levels (9D -multiplet). This fact suggests that the ESA process is strongly suppressed due to the double spin-forbidden character of the transitions. This fact is as well truth for Tb^{3+} (9 at.%) $YAlO_3$, confirming that oxide materials with low CFD are potential candidates as host materials for Tb^{3+} -based laser operation. With respect to intraconfigurational ESA from the 5D_4 level into $4f$ -multiplets with energies above 35000 cm^{-1} , the three evaluated crystals present an equivalent behavior. For the wavelength corresponding to the transitions $^5D_4 \rightarrow ^7F_{5,4}$, the stimulated emission dominates over ESA processes, allowing laser emission in the green and yellow spectral range. It should be noticed, however, that ESA transitions are not completely excluded at these wavelengths and therefore, particular host materials with different values of CFD could be beneficial or detrimental for the laser

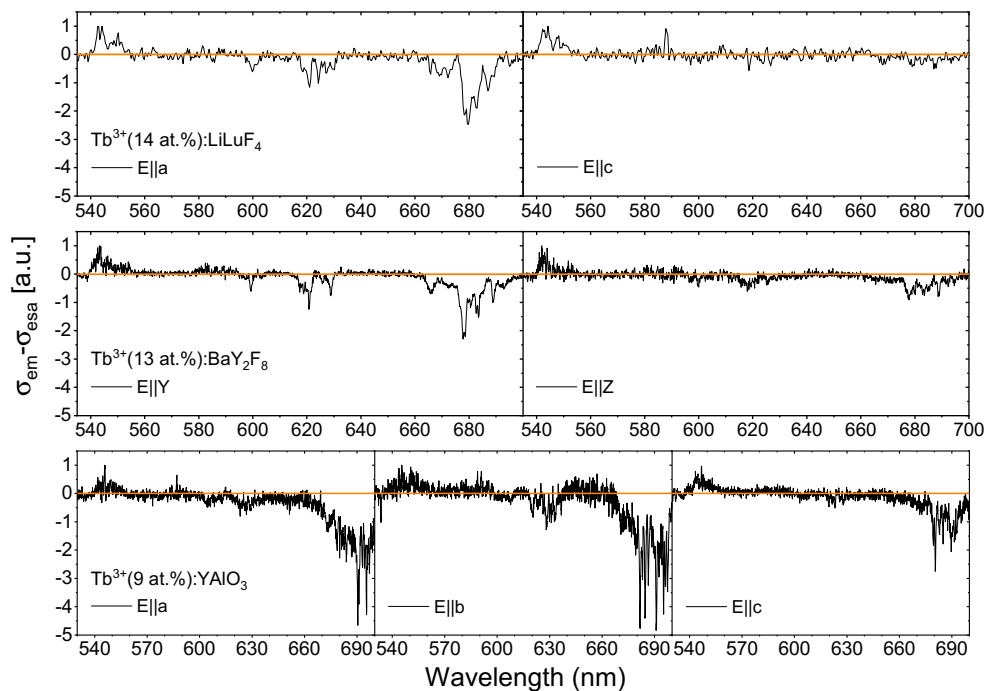


Fig. 5.15.: Polarized ESA measurements of Tb^{3+} (14 at.%) LiLuF_4 , Tb^{3+} (13 at.%) BaY_2F_8 , and Tb^{3+} (9 at.%) YAlO_3 . The spectral resolution of the monochromator was 0.3 nm. The orange grid line marks the zero as help to the eye.

operation. On the contrary, for the transitions $^5\text{D}_4 \rightarrow ^7\text{F}_{3,1,0}$, ESA prevails over gain, and laser emission is not expected in the orange and dark red transitions. For the transition $^5\text{D}_4 \rightarrow ^7\text{F}_2$ at red wavelengths around 640 nm, the indications of presence of ESA are not determinant, but the absence of clear peaks of gain made as well the laser operation at these wavelengths very unlikely.

5.5 Summary

The spectroscopic investigations presented in this chapter suggest the potential of the studied fluoride materials as suitable host materials for Tb^{3+} -based lasers in the green and yellow spectral range. The appearance of consistent ESA peaks in the transitions for longer wavelengths for the studied crystals suggest that laser operation at these wavelengths is probably depleted and appears unlikely. However, the narrow ESA peaks for the $^5\text{D}_4 \rightarrow ^7\text{F}_3$ and particularly for $^5\text{D}_4 \rightarrow ^7\text{F}_2$ transitions, brings the possibility of finding a suitable host material with a slightly different CFD (i.e. slightly different position of the ESA transitions) that could allow laser operation in the orange and red. The broader ESA signal for transitions $^5\text{D}_4 \rightarrow ^7\text{F}_{1,0}$ makes very unlikely the possibility to find a suitable host material.

Owing to these results, laser experiments have been accomplished in several of the studied host materials when samples with sufficient optical quality and dimensions were available. Results are shown in the following chapter of this work.

The spectroscopic investigations in Tb^{3+} -doped YAlO_3 reveal the high potential of this material to be a suitable oxide host material for Tb^{3+} -based laser operation. According to the theoretical considerations, the similar features of the ESA spectra in comparison with those for fluoride materials point to a similar energy level distribution that could allow laser operation in the green and yellow spectral range. The lifetime values of the $^5\text{D}_4$ -level in this material in the order of milliseconds are not quenched for Tb^{3+} -concentrations of 19 at.%, allowing for feasible crystal dimensions for laser operation.

Despite the high absorption and emission cross-sections of $\text{KY}(\text{WO}_4)_2$ in comparison with other Tb^{3+} -based host materials (about three times higher σ_{abs} and about seven times higher σ_{em} than e.g. LiLuF_4), this material has been found to be not suitable for laser operation. The low bandgap of energy attributed to $\text{KRE}(\text{WO}_4)_2$ corresponding to only ~ 315 nm, situates the conduction band in a very low position, that even embed the ^9D -multiplet of the 5d-configuration [Mat06]. In these conditions, intervalence charge transfer processes quench the emission of the $^5\text{D}_4$ level, promoting excitation from the ground state to the bottom of the host material conduction band [Bou10], and preventing laser operation. A more detailed dissertation on this subject can be found at [Dem19].

In order to determine the suitability of Tb^{3+} -doped YAG as laser material, further ESA measurements are required. Despite that the lifetime of the $^5\text{D}_4$ -level in this material of >3 ms is longer than for TbF_3 , material that has demonstrated laser operation [Met16], the strong CFD presented in garnets make this material very likely to suffer from ESA depletion of the $^5\text{D}_4$ upper laser level. Unfortunately, the dimensions of the available samples during the course of this work did not allow this kind of measurements.

In addition, lifetime investigations confirm the absence of detrimental interionic processes between Tb^{3+} ions that could disturb laser operation. Therefore, materials with high concentrations of Tb^{3+} are beneficial for efficient laser operation, compensating the low absorption and emission cross-sections and loosening the requirements on the gain media dimensions.

In order to reduce even more the dimensions of Tb^{3+} -based gain media, the possibilities of ultraviolet pumping into the $^5\text{D}_3$ -level have been investigated. The over 6 times higher absorption cross-sections in the UV in comparison with the absorption cross-sections of direct pumping into the $^5\text{D}_4$ upper laser level reduces the required crystal length for sufficient absorption of the pump. In combination with the evidence of efficient cross relaxation processes from $^5\text{D}_3$ to $^5\text{D}_4$ already

in materials with a Tb^{3+} concentration of 14 at.%, presents UV pumping as a very promising alternative to blue pumping, encouraging laser experiments under these conditions.

Laser experiments

This chapter exposes the laser experiments performed in Tb^{3+} -based materials in the frame of this thesis. Laser operation was successfully achieved in $\text{Tb}^{3+}:\text{LiLuF}_4$ under different pumping conditions, as well as in $\text{Tb}^{3+}:\text{BaY}_2\text{F}_8$ for the first time in this material. Laser experiments were accomplished in other Tb^{3+} -containing gain media such as $\text{KTb}_3\text{F}_{10}$, $\text{Tb}^{3+}:\text{KY}(\text{WO}_4)_2$, and $\text{Tb}^{3+}:\text{YAlO}_3$, where laser emission was not obtained. The prospects of laser emission of these materials are investigated.

6.1 Laser setups

This section introduces the resonators that were built to evaluate the laser materials, as well as the pump sources that excited Tb^{3+} -ions during the laser experiments.

6.1.1 Resonators

As the purpose of this work focus on the evaluation of the laser properties of the crystals, with the additional aim of finding alternatives to simplify the laser technology in order to make it more accessible for applications, the configuration of the laser resonators was kept fairly simple. All setups were constituted by a set of two mirrors, a plano-convex lens to focus the pump beam into the crystalline gain medium, and a filter to separate the residual pump power from the laser output.

In these kinds of resonator configurations, the absorbed pump power of the gain media is not accessible during laser operation. Therefore, the absorbed pump power was estimated from the absorption value at the laser threshold pump power. At this pump power level, the transmitted power through the crystal inside the resonator was measured, and the total absorption was calculated from this value and corrected by losses from Fresnel reflections. Corrections of second-pass absorption from the transmitted light reflected from the output-coupler mirror back into the crystal were also considered. This value depends on the output-coupler mirror transmission for the pump. The fraction of absorbed pump power value was considered to remain constant during laser operation at higher incident pump powers.

All crystals were placed on a water-cooled copper heatsink with a temperature of 20°C , directly contacted to the bottom of the crystal. In some cases, when the

shape of the crystalline samples was regular, an extra water-cooled copper cover was placed on top of the crystal, for extra cooling.

Nearly concentric resonator

This kind of resonator consists of two mirrors of equal radius of curvature, separated by a distance slightly shorter than twice the radius, while the crystalline gain media is placed in the middle of the cavity. The exact distance between mirrors is influenced by the length and refractive index of the gain media as they affect the effective optical path of the laser light, and therefore, the optimized distance slightly differs from crystal to crystal. Figure 6.1 depicts a scheme of the resonator and pump system. In all experiments performed in this type of resonator, the radius of curvature of the mirrors was 100 mm. These radius and distance between mirrors are optimal for large gain media of 1 to 2 cm long. Shorter radii, i.e. 50 mm, would make a bigger difference between the size of the pump beam and the cavity mode, the second one being larger than the first. This configuration entails a decrease in the overlap between them and therefore in the laser efficiency. For longer radii of curvature, such as 200 mm, a lens with a longer focal length must be used to be able to place the focus in the center of the cavity, and therefore, the optical density of the pump in the crystal decreases consequently. The pump mirrors (PMs) had high transparency for the pump wavelength, while they were highly reflective (HR) for the respective laser wavelength. Several output coupler mirrors (OCMs) with different transmissions at the laser wavelengths were used to evaluate the laser performance at variable population densities of the upper laser level of Tb^{3+} ions. In turn, several lenses were tested to maximize the output power, depending on the length of the crystal.

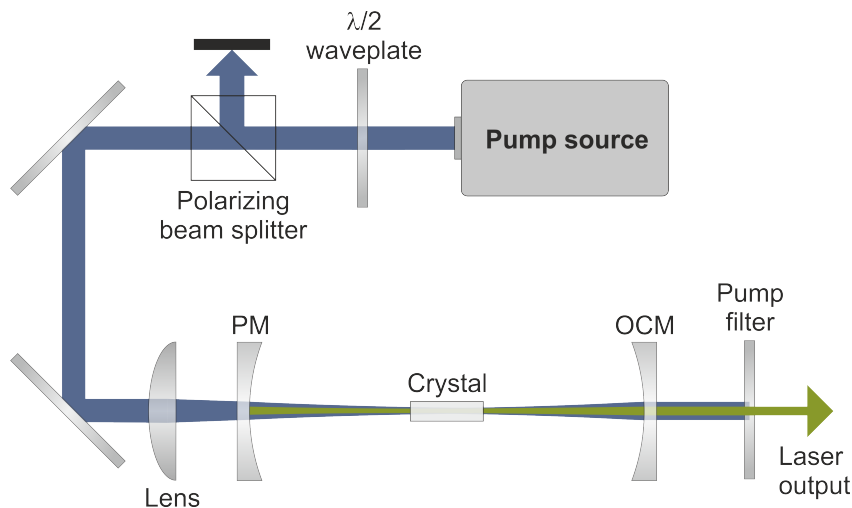


Fig. 6.1.: Schematic of the nearly concentric resonator and pump system. The pump beam is depicted in blue and the laser beam is represented in green.

Hemispherical resonator

This kind of resonator consists of a planar PM and a curved OCM. The PM was selected with high transmission for the pump wavelengths and highly reflective for the laser wavelengths. Several OCM with a radius of curvature of 100 mm and different transmission profiles for the laser wavelengths were tested to evaluate the laser capability of the crystals at different population densities of the upper laser level of Tb^{3+} ions. The distance between the two mirrors is slightly shorter than the radius of curvature of the OCM and depends on the length and refractive index of the gain media. In this configuration, the crystal is situated as close as possible to the PM. This position is the closest to the focus of the resonator mode, which is located on the surface of the PM. A schematic of this resonator is shown in figure 6.2. In the laser experiments with hemispherical cavities of this work, several lenses were tested to maximize the output power, assisted by matrix calculations. For the 11 mm long crystal used in this cavity, the pumped light was focused by a lens with a focal length of 250 mm resulting in a pump waist diameter of $\sim 50 \mu\text{m}^2$.

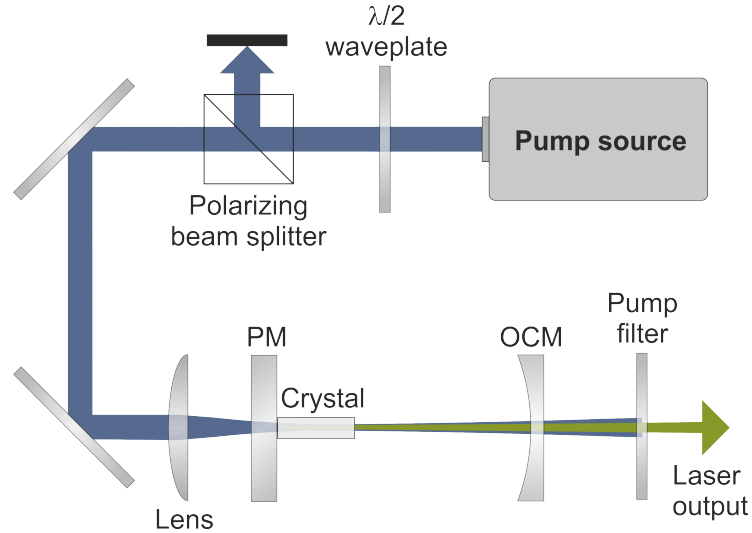


Fig. 6.2.: Schematic of the hemispherical resonator and pump system. The pump beam is depicted in blue and the laser beam is represented in green.

6.1.2 Pump sources

Different laser concepts have been used as pump sources for Tb^{3+} -material during the laser experiments. In order to keep the pump emission as stable as possible, they were operated at maximum power. Therefore, since all pump sources used in these experiments are linearly polarized, the incident pump power onto the crystal was adjusted by a set of $\lambda/2$ -plate and PBS (see figures 6.1 and 6.2).

Frequency-doubled optically pumped semiconductor lasers

Optically pumped semiconductor laser (OPSL) technology consists of a multi-quantum well semiconductor structure that is optically pumped in a thin disc laser-like external cavity. This kind of light source, presented at [Kuz97], combines the advantages of solid-state and semiconductor lasers. The laser emission has high beam quality due to the external cavity architecture and can achieve high-power levels. In turn, it shares the broad and diverse emission bandwidth of semiconductor gain media [Gui17]. The close to diffraction-limited beam quality allows for highly efficient intracavity frequency-doubling, enabling emission at UV and blue wavelengths. The laser experiments of this work employed an InGaAs-based 2ω -OPSL emitting at 486.3 nm. This source, a Genesis CX laser from Coherent inc., can achieve up to 4 W of output power with a beam quality factor of $M^2 < 1.1$. The emission exhibits a divergence of < 0.5 mrad (FW, $1/e^2$) and an emitted beam diameter of 2.25 mm (FW, $1/e^2$). Figure 6.3 shows the emission of this pump source in comparison with the absorption profile of $\text{Tb}^{3+}:\text{LiLuF}_4$.

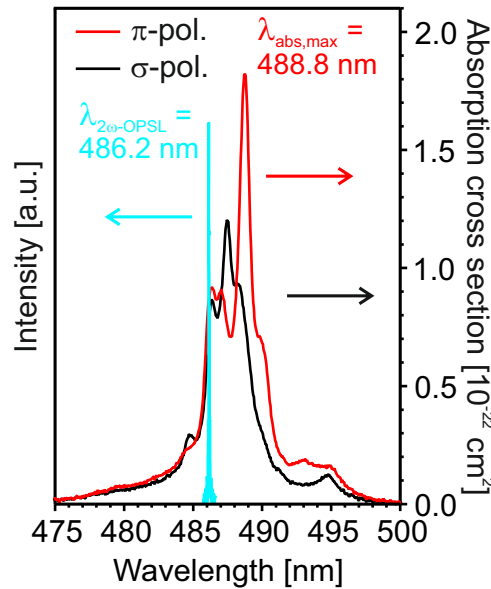


Fig. 6.3.: Emission of the 2ω -OPSL pump source (cyan line) in comparison with the polarization dependent absorption cross-sections of $\text{Tb}^{3+}:\text{LiLuF}_4$ (black and red lines).

InGaN-based laser diodes

Laser diodes are electrically pumped semiconductor lasers in which the gain is generated by an electrical current flow through a p-n junction. In such a heterostructure, electrons and holes are recombined, generating photons in the process. The use of

this kind of lasers as pump source for SSL is especially advantageous due to their high electrical-to-optical efficiency sometimes $> 60\%$, which leads to a high overall wall-plug efficiency and low cooling demands [Pas21b]. In addition, the relatively narrow optical bandwidth of the laser diodes allows to directly target pumping of certain transitions of laser-active ion, further improving efficiency and reducing thermal issues. These features, together with the industrialized production, the compactness, and the long lifetime of the diodes, establish these pump sources as a very cost-efficient solution, suitable for market laser products. Although the beam quality of high-power diode lasers is generally low, it often allows for pumping a laser medium in the direction along the laser beam (so-called end pumping) with a very good overlap of laser mode and pumped region, leading to high-power efficiency of the SSL [Pas21a]. Moreover, the large variety of semiconductor materials developed as laser diodes allows for the production of a broad range of emission wavelengths that are determined by the bandgap of each semiconductor material. More concretely, indium-gallium-nitride (InGaN) diode lasers can provide emission in the range from UVA to green wavelengths [Mou19]. This kind of semiconductor lasers were first demonstrated in 1996 with a pulsed mode operation at 417 nm by S. Nakamura [Nak96], awarded with the Nobel prize in physics for the invention of efficient blue light-emitting diodes in 2014.

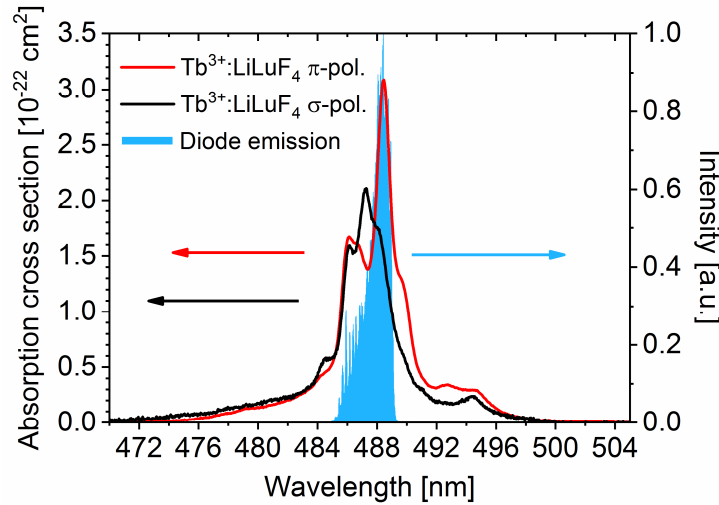


Fig. 6.4.: Emission of the diode laser pump source (blue area) in comparison with the polarization dependent absorption cross-sections of $\text{Tb}^{3+}:\text{LiLuF}_4$ (black and red lines).

In this work, an indium-gallium-nitride InGaN-based diode laser (iBeam Smart, Toptica Photonics) with an emission wavelength of 488.2 nm presenting a full width at half maximum (FWHM) emission bandwidth of 1.3 nm, and a maximum output power of 200 mW served as a pump source for the laser experiments. Its emission

wavelength was chosen to match the highest peak of the ${}^7F_6 \rightarrow {}^5D_4$ ground state absorption of Tb^{3+} in π -polarization into the upper laser level (see Figure 6.4). The diode emission exhibits a divergence of < 1 mrad and a beam quality of $M^2 < 1.2$ at an emitted beam diameter of $1 \text{ mm} \times 0.97 \text{ mm}$ ($1/e^2$). In addition, the laser stability exhibits a standard deviation of 0.2%. These features qualify the diode laser as a suitable pump source for highly efficient laser performance. It should be noted that the emitted beam diameter is smaller than the beam diameter of the 2ω -OPSL pump source, resulting in different optimum focusing conditions.

A Faraday isolator (Qioptiq Photonics) placed after the diode output prevents potentially harmful optical feedback into the laser diode. To avoid wavelength drift of the diode emission with current, the diode was operated at maximum power at all times.

Frequency-doubled Ti:sapphire laser

In order to reach further pump wavelengths, a frequency-doubled Ti:sapphire laser (SolsTiS, MSquared Lasers) was used as pump source. An ECD-X cavity, provided with five different frequency-doubling crystals, allows for laser operation in the range of 350 - 485 nm with an output power from 0.5 W up to ~ 2 W for some of these wavelengths. The broad tunability range together with the excellent quality of the beam close to diffraction-limited ($M^2 < 1.1$), makes this pump source very versatile for the research investigation of UV-pumping of Tb^{3+} ions.

6.2 Lasers based on $LiLuF_4$

6.2.1 OPSL-pumped $Tb^{3+}:LiLuF_4$

This section presents the results of laser experiments on a Tb^{3+} (28 at.%): $LiLuF_4$ sample by 2ω -OPSL excitation. The crystal employed in the experiments is described in section 4.2.1 and the outcome of this specific work is published at [Cas18]. Hereby, the cw laser emission at 587.5 nm exposes the power scaling of Tb^{3+} -lasers in the yellow range to 0.5 W at an efficiency of 25%. These were to the date of publication the highest values obtained for any direct emitting yellow SSL, to the best of our knowledge.

The laser sample was prepared in a-cut orientation for the laser experiments. The as-grown boule enabled the preparation of a 21 mm long sample with an irregular outer shape and a clear aperture of ~ 5 mm. This orientation of the tetragonal crystal gives access to both π - and σ -polarization. The crystal was placed on a water-cooled copper heat sink with direct contact only to the bottom of the crystal. The 2ω -OPSL

described in section 6.1.2 served as the pump source. Figure 6.3 shows that its wavelength does not match the highest absorption peak of $\text{Tb}^{3+}:\text{LiLuF}_4$, which reduces the absorption efficiency. The polarization of the pump beam was optimized for maximum laser output power by a $\lambda/2$ waveplate, which was found when the polarization of the pump beam was at $\sim 45^\circ$ between both crystal axes. However, as expected from figure 6.3, the laser was not very sensitive to the polarization of the pump beam. Subsequently, a PBS was placed behind the waveplate and optimized for maximum laser output, too. In this way, we were able to adjust the incident pump power by rotating the waveplate, as explained in section 6.1.2. A plano-convex lens with a focal length of 100 mm served to focus the pump beam into the crystal. The beam waist diameter was calculated to be $\sim 40 \mu\text{m}$ in the center of the crystal and $\sim 100 \mu\text{m}$ at its end facets. In this configuration, we achieved a single-pass pump absorption efficiency of 74%. The nearly concentric laser cavity was formed by two mirrors with radii of curvature of 100 mm separated by about 195 mm depending on the respective alignment conditions. An absorptive glass filter (Schott OG515) with a transmission of 90.9% for 587 nm and $\sim 0\%$ for 486 nm was placed behind the output coupling mirror to separate the residual pump light from the laser output.

The 486.3 nm pump wavelength directly excites the upper laser level $^5\text{D}_4$ of Tb^{3+} (see figure 3.2). The laser transition $^5\text{D}_4 \rightarrow ^7\text{F}_4$ corresponds to yellow emission centered at 587.5 nm. Figure 6.5 shows that the emission cross-sections of $\text{Tb}^{3+}:\text{LiLuF}_4$ in the green spectral range around 544 nm are of comparable strength than in the yellow at around 587.5 nm. In order to favor yellow laser emission independent of the output coupler properties, the pump mirror provides a transmission greater than 70% for the green, while it is highly reflecting for the yellow spectral range. The transmission for the pump wavelength is as high as 98%.

Several output coupling mirrors with transmissions between 0 and 12% at 587.5 nm were tested in the experiments. Figure 6.6 exhibits the laser efficiency curves for a selection of them. The emission peak was found at 587.5 nm, measured by a wavelength meter WS-6 (HighFinesse), and the laser output was found to be polarized parallel to the optical c-axis of the crystal (π -polarization) as expected, as it corresponds to the highest emission peak at this wavelength (see figure 6.5).

The best performance was obtained at an output coupler transmission of 5.5%. In this case, the maximum output power amounted to 0.50 W at an absorbed pump power of 2.16 W, only limited by the available pump power. The beam presented a TEM_{00} mode. A record slope efficiency of 25% was achieved in this configuration. The optical-to-optical efficiency, defined as the percentage of absorbed power that is converted to output power at maximum output power, was 20% with a laser threshold of 208 mW of absorbed pump power. Stability measurements at maximum

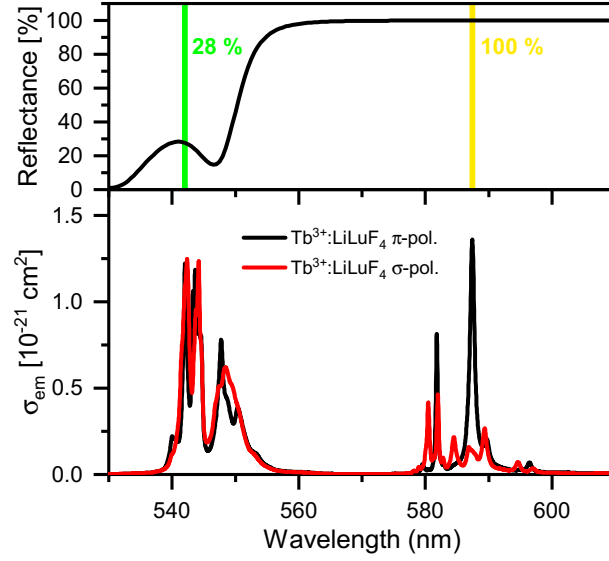


Fig. 6.5.: Pump mirror reflectance and polarization dependent stimulated emission cross-section spectra of $\text{Tb}^{3+}:\text{LiLuF}_4$.

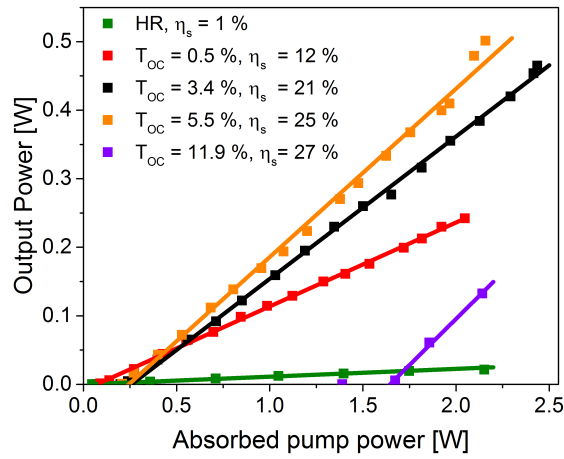


Fig. 6.6.: Laser characteristics of a 21 mm long a-cut $\text{Tb}^{3+}:\text{LiLuF}_4$ crystal under pumping at 486.3 nm utilizing various output coupling mirrors.

output power present a standard deviation of 2.7%. This value is partly due to mechanical instabilities caused by the cooling water flow and pump instabilities caused by back-reflections due to the absence of an optical isolator. The laser does not present “self-pulsing” behavior. For output coupler transmissions below 2%, we observed laser thresholds well below 100 mW with a minimum threshold of 47 mW for the HR mirror (see figure 6.7).

It is furthermore worth noting that laser operation was achieved even for an output coupling mirror with a transmission as high as 11.9%. Nonetheless, during

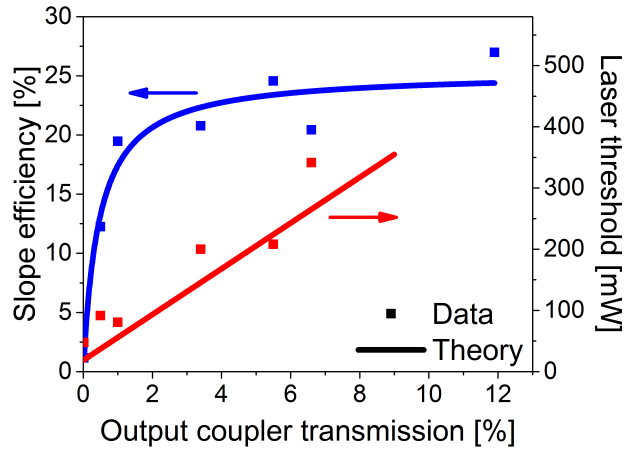


Fig. 6.7.: Slope efficiency (blue) and laser threshold (red) as a function of the output coupler transmission. The solid blue line is a Caird fit according to equation 6.1. The solid red line is a theoretical estimation of the threshold values given by equation 6.2.

the performance with this output coupler, the laser operated in a highly unstable regime. However, the capability to achieve laser operation at such high cavity losses without an obvious reduction of the laser efficiency is another indicator for the absence of detrimental interionic processes. Such an efficient operation at high inversion levels in combination with the long lifetime of ~ 5 ms of the upper laser level 5D_4 (see figure 5.9) allows for high storage energies. This makes Tb^{3+} -doped materials very promising for Q-switched laser operation with high pulse energies.

The blue data in figure 6.7 show the slope efficiency of the laser vs. the output coupler transmission. The solid blue line represents a Caird fit of the experimental points [Cai88] according to

$$\eta_s = \eta' T (T + L)^{-1}, \quad (6.1)$$

where T is the output coupler transmission, L the cavity losses, and η' the internal slope efficiency. In this way, we estimate the cavity losses to be $\sim 0.5\%$, which is a reasonably low value for a cavity incorporating a 21 mm long crystal. The internal slope efficiency η' is estimated to be 25%. This value is much lower than the Stokes efficiency that amounts to 83%. Due to the length of the crystal, we cannot fully exclude a low overlap between the pump and the laser mode being partially responsible for the low internal slope efficiency. However, results obtained previously for green Tb^{3+} -lasers with similar lengths of the gain media [Met16] yielded efficiencies exceeding 50%. Therefore, other reasons for a low internal slope efficiency must be present for the yellow transition of Tb^{3+} . A possible cause for

the decrease in efficiency is intraconfigurational ESA between 4f levels at the laser wavelength, as explained in section 3.2.1, that does not prevent laser operation but reduces its efficiency. This hypothesis is confirmed by comparing the σ_{em} of $\text{Tb}^{3+}:\text{LiYF}_4$ (see figure 5.5) with the ESA measurements shown in figure 5.15. The emission cross-sections at 587.5 nm in the yellow are slightly higher than at 544.2 nm in the green, whereas the results from the ESA pump-probe measurement show that the gain signal at 544.2 nm is stronger than for 587.5 nm.

The red data in figure 6.7 depict the laser threshold power vs. the output coupler transmission. The solid red line is a theoretical estimation of the threshold values assuming a perfect pump and laser mode overlap, given by

$$P_{th} = h\nu_p A \gamma / (\eta_p \tau \sigma_{em}), \quad (6.2)$$

where $h\nu_p$ is the photon energy of the pump source, A is the beam area in the crystal, $\gamma = T + L$ is the total power losses per round trip, η_p is the pump efficiency, τ is the lifetime of the upper-state, and $\sigma_{em} = 1.1 \times 10^{-21} \text{cm}^2$ is the emission cross-section at 587.5 nm [Cai88]. We omitted the 11.9% output coupling mirror result due to a significantly increased laser threshold and the incapability of giving an accurate value because of the laser operation instabilities. For the remaining data, the laser threshold increases linearly up to output coupler transmissions of 6.6%. We again conclude that there are no inversion dependent loss processes up to this output coupling level, whereas at similar values a significant decrease in efficiency is observed in other lasers, such as the green transition at 523 nm in $\text{Pr}^{3+}:\text{LiYF}_4$ [Met14b].

6.2.2 Diode-pumped $\text{Tb}^{3+}:\text{LiLuF}_4$

This section presents the results of laser experiments on a Tb^{3+} (28 at.%): LiLuF_4 sample by diode laser excitation. The crystal employed in the experiments is described in section 4.2.1 and the outcome of this work is published at [Cas20b]. This first demonstration of a Tb^{3+} -based DPSSL has been, to the time of publication, the simplest and most efficient direct yellow emitting solid-state laser. The first diode-pumped $\text{Tb}^{3+}:\text{LiLuF}_4$ laser exhibits a slope efficiency of 22% at a wavelength of 587 nm in the yellow spectral range under diode pumping emitting up to 200 mW at 488 nm. An even better performance was obtained at 542 nm in the green with a slope efficiency of 53%. The whole setup utilizes no nonlinear conversion processes and power scaling is only limited by the available pump power at the time of the experiments.

For the laser experiments accomplished in this work, we utilized a sample with a length of 18.5 mm. The a-cut orientation of the tetragonal crystal structure gives access to both, π - and σ -polarization of the sample. The plane-parallel polished faces provide a clear aperture of ~ 5 mm. The sample orientation was verified by Laue and pole-figure measurements with an x-ray diffraction system (GE Inspection Tech.). The diode laser used as pump source during the laser experiments is described in section 6.1.2, and the description of the nearly concentric resonator configuration can be found in section 6.1.1. For focusing the pump light into the crystal, different plano-convex lenses were tested, with the best results obtained for the focal lengths of 150 mm and 100 mm for green and yellow laser operation, respectively. The resulting focal diameters in the center of the crystal were $165\text{ }\mu\text{m}$ for the green and $102\text{ }\mu\text{m}$ for the yellow laser and increased to $167\text{ }\mu\text{m}$ and $111\text{ }\mu\text{m}$, respectively, at the crystal surface. Our simulations showed that with these pump beam waists a close to perfect match with the fundamental TEM_{00} laser mode can be achieved in the nearly concentric resonator design. Again, it should be noted that due to the smaller diameter of the diode beam the pumped area is different than for the previous results under 2ω -OPSL pumping [Met16, Cas18]. The stronger focus for the yellow laser turned out to be advantageous for the achievable output power in view of the moderately higher thresholds at this transition. In both cases, the single-pass absorption efficiency of the crystal amounted to $\sim 77\%$ of the incident beam. The simple nearly concentric laser cavity consisted of two mirrors with radii of curvature of 100 mm separated by a distance of ~ 200 mm. Different OCMs with transmissions of up to 3.3% for the laser wavelength were tested. A dichroic mirror (DMLP505 Thorlabs) separates the green laser beam from the residual pump light, and an absorptive glass filter (Schott OG515) made the same service for the yellow laser. The dichroic mirror, placed at an angle of 45° with respect to the incident beam, has a transmission of 98.8% for 542 nm and 0.8% for 488 nm. The glass filter has a transmission of 90.9% for 587 nm and $\sim 0\%$ for 488 nm.

Diode-pumped green laser emission

The green laser emission corresponds to the Tb^{3+} transition $^5\text{D}_4 \rightarrow ^7\text{F}_5$ (see figure 3.2). This transition at a wavelength of 542 nm has an emission cross-section of $1.22 \times 10^{-21}\text{ cm}^2$ for π -polarization and $1.25 \times 10^{-21}\text{ cm}^2$ for σ -polarization. A second peak at 544.1 nm exhibits emission cross-sections of $1.19 \times 10^{-21}\text{ cm}^2$ for π -polarization and $1.23 \times 10^{-21}\text{ cm}^2$ for σ -polarization (see figure 5.5).

The laser experiments were performed using several OCMs with transmissions between $< 0.2\%$ (HR) and 2.6% (see figure 6.8 (left)). The laser operates at a center emission wavelength of 544.1 nm for the two OCMs with the lowest transmission,

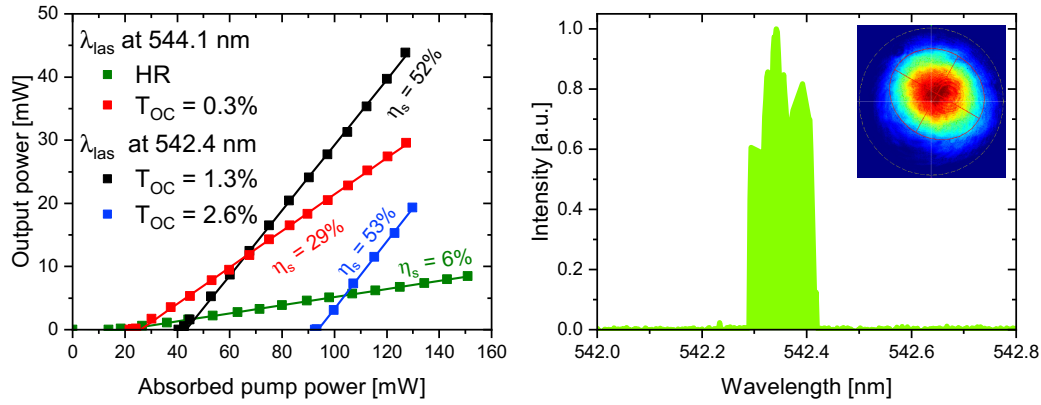


Fig. 6.8.: (Left) Laser characteristics of an 18.5 mm long diode-pumped Tb^{3+} (28 at.%) $LiLuF_4$ crystal for different output coupler transmissions T_{oc} and different laser emission wavelengths λ_{las} in the green spectral range. (right) Laser emission spectra for green emission centered at 542.4 nm at maximum output power with an output coupler transmission of 1.3%. Inset: Beam profile of the laser under the mentioned conditions.

HR and 0.4%, and at 542.4 nm for the two OCM with the higher transmissions, 1.3% and 2.6%. This variation in the emission wavelength is attributed to the detailed transmission characteristics of the mirror coatings rather than to the change in population of the respective energy levels. For the HR and the 0.4% OCM, the transmission between 542.4 nm and 544.1 nm is fairly plain slightly favoring the emission at 544 nm. However, for the 1.3% and the 2.6% OCM, the transmission of the mirrors increases with wavelength, making the conditions more favorable for the laser to operate at the emission peak at 542 nm. As expected from the emission spectra (see figure 5.5), in all cases the laser emission was found to be polarized perpendicular to the c-axis of the crystal. Even though $Tb^{3+}:LiLuF_4$ is reported to support laser operation at output coupler transmissions as high as 11.9% [Cas18], the maximum diode laser emission of 200 mW did not allow to reach the laser threshold for OCM transmissions higher than 2.6%. This transmission yielded the highest slope efficiency of 53%, but the maximum output power was limited to 19.2 mW by the available pump power. At a similar slope efficiency of 52%, the highest output power of 44 mW was obtained with the OCM with a transmission of 1.3% at a corresponding absorbed pump power of 127 mW. The resulting optical-to-optical efficiency amounted to 34.5% and the laser threshold was as low as 40 mW. Stability measurements of the laser output showed a standard deviation of 2.5% under these conditions. The minimum laser threshold achieved with the HR mirror was as low as 14 mW of absorbed pump power. The laser emission spectrum at maximum output power shown in figure 6.8 (right) was measured by an optical spectrum

analyzer (AQ6374, Yokogawa) with a spectral resolution below 0.05 nm. The FWHM of the emission is around 0.1 nm. The emission in the green spectral range is centered at 542.4 nm. The inset shows the output beam profile at maximum power, recorded by a CinCam-CMOS-1202 (Cinogy Tech.) camera, revealing Gaussian power distribution in fundamental mode TEM_{00} .

Diode-pumped yellow laser emission

The yellow laser emission of Tb^{3+} ions corresponds to the transition $^5D_4 \rightarrow ^7F_4$ (see figure 3.2) located at a wavelength of 587.4 nm. This transition exhibits a peak emission cross-section of $1.36 \times 10^{-21} \text{ cm}^2$ for π -polarization and the peak cross-section of $0.14 \times 10^{-21} \text{ cm}^2$ for σ -polarization is found at 582 nm (see figure 5.5).

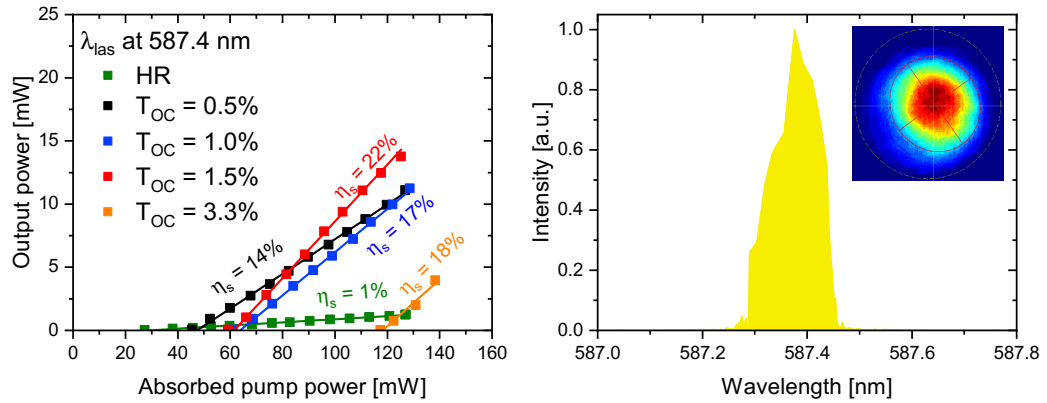


Fig. 6.9.: (Left) Laser characteristics of an 18.5 mm long diode-pumped Tb^{3+} (28 at.%) $LiLuF_4$ crystal for different output coupler transmissions T_{oc} at $\lambda_{las} = 587.4$ nm in the yellow spectral range. (right) Laser emission spectra for yellow emission centered at 587.4 nm at maximum output power with an output coupler transmission of 1.5%. Inset: Beam profile of the laser under the mentioned conditions.

The laser experiments were performed with several OCMs with transmissions between $< 0.2\%$ (HR) and 3.3% (see figure 6.9 (left)). The laser operates around 587.4 nm for all OCMs. As in the case of green emission, the maximum pump power of 200 mW did not allow for laser operation with higher output coupler transmissions. The laser emission was always polarized parallel to the c-axis of the crystal. The best performance of the yellow Tb^{3+} : $LiLuF_4$ laser in terms of maximum output power and slope efficiency was obtained using the OCM with a transmission of 1.5%. The corresponding slope efficiency was 22% and the maximum output power amounted to 13.8 mW at an absorbed pump power of 125.3 mW. The resulting optical-to-optical efficiency was 11.0% and the laser threshold was reached at 59

mW of absorbed pump power. The laser emission spectrum and the beam profile can be found in figure 6.9 (right). Stability measurements of the laser output yielded a standard deviation of 4.1% for this configuration. The lowest laser threshold of 27 mW was found for the HR mirror.

In addition, during the operation with the HR mirror, it was possible to force the laser to operate at a wavelength of 582.0 nm by cavity alignment. Under these conditions, the maximum output power was 0.6 mW with a slope efficiency of 1.6% and a laser threshold of 86 mW of absorbed pump power.

Discussion

The results of these first experiments on diode pumping of a Tb^{3+} doped solid-state laser are comparable to those obtained previously under 2ω -OPSL-pumping as can be seen in figure 6.10 for the example of the green laser transition. In all cases including the yellow laser, the slope efficiencies and laser thresholds at comparable output coupler transmissions are very similar to the values obtained under 2ω -OPSL-pumping [Met16], which is enabled by the good beam quality of the single emitter laser diode used here. Even though the best optical efficiencies that were obtained under 2ω -OPSL-pumping in the order of 38% are higher than the results of up to 25% presented here, it should be taken into account that the 2ω -OPSL itself is a diode-pumped frequency doubled laser with an internal efficiency below 25%. Therefore, the authentic optical-to-optical efficiency (and also the wall-plug efficiency) are much higher under diode pumping.

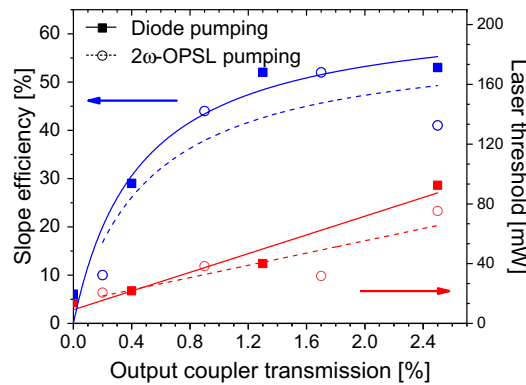


Fig. 6.10.: Comparison of laser performance of Tb^{3+} (28 at.%) : LiLuF_4 under 2ω -OPSL and laser diode pumping in the green spectral range. Here, the respective fit curves (blue: Caird [Cai88] (cf. figure 6.11, same data for diode pumping), red: linear) mainly serve as a guide to the eye. It should be noted that different focusing conditions and crystal lengths were used during 2ω -OPSL pumping [Met16] (21.1 mm) and diode pumping (18.5 mm).

In addition, these results, and in particular the low pump threshold powers, give rise to the prediction that significant further scaling of the output power of diode-pumped Tb^{3+} lasers is feasible even with high-power multi-mode laser diodes with lower beam quality. In this context, it should be noted that the available efficiency is not limited by the spatial overlap between the pump and the laser mode or the losses in the 18.5 mm long gain medium. Figure 6.11 shows the laser slope efficiency versus the output coupler transmission for the green and the yellow emission. The solid lines correspond to Caird fits according to equation 6.1 [Cai88], yielding low cavity losses of 0.3% for both wavelengths. The slope efficiency η_{slope} of a laser is determined by the equation

$$\eta_{\text{slope}} \leq \eta_{\text{Stokes}} \cdot \eta_{\text{overlap}} \cdot \eta_{\text{quantum}} \cdot \eta_{\text{resonator}} \quad (6.3)$$

where the Stokes efficiency η_{Stokes} is the ratio of the laser and pump photon energy, η_{overlap} is the mode overlap efficiency between pump and laser mode, the quantum efficiency η_{quantum} is the ratio of laser transitions to all transitions from the upper laser level (i.e. including possible non-radiative or ESA transitions) and the resonator efficiency $\eta_{\text{resonator}}$ is the ratio of the output coupling losses to the total resonator losses. The right term of this equation corresponds to the internal slope efficiency η' . A more developed description of the rate equation is given in section 2.3.1.

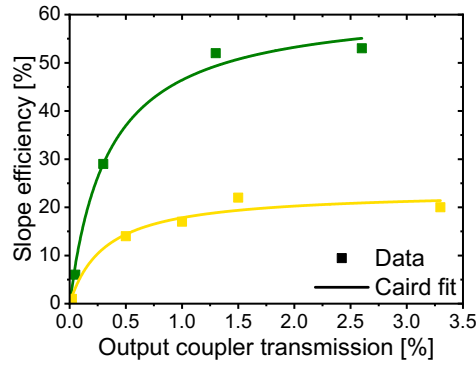


Fig. 6.11.: Slope efficiencies for different output coupler transmissions. The green dots correspond to laser emission at 542.4 and 544.1 nm and the yellow dots to laser emission at 587.4 nm. The solid lines represent the respective Caird fits according to equation 6.1.

The resulting η' of 62% for the green emission and 23% for the yellow are clearly below the respective Stokes efficiencies of 90% and 83%. The deviation between the internal slope efficiency and the Stokes efficiency is much larger for the yellow laser, while – as mentioned above – the mode overlap is very similar for both

lasers. Consequently, the ratio of the internal slope efficiencies depends only on the Stokes efficiency and the quantum efficiency. With the known values for the Stokes efficiency, the resulting ratio between the quantum efficiencies in the green and the yellow amounts to 0.4. We attribute this lower quantum efficiency of the yellow $\text{Tb}^{3+}:\text{LiLuF}_4$ laser to remaining intraconfigurational 4f-4f ESA processes that do not fully prohibit laser operation but decrease the efficiency of this transition. We can nearly exclude ESA into 5d levels, as this would also affect the green laser with its even higher photon energies.

6.2.3 UV pumping of $\text{Tb}^{3+}:\text{LiLuF}_4$

This section presents the results of laser experiments on a Tb^{3+} (14 at.%) LiLuF_4 sample by UV laser excitation into the $^5\text{D}_3$ multiplet. The crystal employed in the experiments is described in section 4.2.1 and the outcome of this specific work is published at [Kal20]. This new pump concept for Tb^{3+} -lasers allows making use of the ~ 6.5 times higher absorption cross-sections into the UV in comparison with the absorption cross-sections of the transition $^7\text{F}_6 \rightarrow ^5\text{D}_4$. By pumping at 359 nm in the UV, we obtained efficient laser operation in the green and yellow spectral range with optical-to-optical efficiencies doubling those obtained at 486 nm in the blue, under the same conditions.

These experiments were performed in an 11 mm long a-cut sample placed in a 95 mm long hemispherical cavity (see section 6.1.1). The plane input coupling mirror was transparent for both pump wavelengths in the UV and cyan-blue range and highly reflective for green and yellow light. The OCMs had a radius of curvature of 100 mm and different transmissions between $< 0.2\%$ (HR) and 4.2% for the respective laser wavelength. As a pump source, we used the output of a cw Ti:sapphire laser described in section 6.1.2, which was tuned to emit at the peak absorption wavelength of $\text{Tb}^{3+}:\text{LiLuF}_4$ at 359 nm. This is the wavelength of strongest absorption in the UV (cf. figure 5.4), but the choice of this pump wavelength was further motivated by the observation of ESA from the upper laser level $^5\text{D}_4$ in the 370 nm range in the previous work [Met16]. The pump light with a maximum power of ~ 300 mW was attenuated by a combination of a $\lambda/2$ -plate and a PBS and focused into the crystal by a lens with a focal length of 250 mm resulting in a pump waist diameter of ~ 50 μm . The polarization of the pump beam was optimized for the highest absorption, i.e. parallel to the c-axis of the crystal. In the laser experiments at the green transition shown in figure 6.12 (left), we obtained the highest slope efficiency of 41% at 542 nm using an output coupler transmission of 4.2%. The highest cw output power of 78 mW was obtained with a lower mirror transmission of 1.7%, owed to the lower laser threshold here. Utilizing a highly reflective output

coupling mirror, the laser threshold was found to be as low as 15 mW of absorbed pump power.

For the yellow transition at 587 nm, the highest slope efficiency amounted to 20% at a maximum output power of 34 mW and an output coupler transmission of 1%. Using a highly reflective OCM, the lowest absorbed pump power laser threshold was found to be 24 mW. As mentioned in the previous section, the inferior performance of the yellow transition in comparison with the green transition is attributed to intraconfigurational ESA in this wavelength range. The laser characteristics of the yellow laser are shown in figure 6.12 (right). During the entire experiment, the output of the UV-pumped laser was stable and we did not observe a decrease of the output power. This result rules out significant short-term degradation of the optical properties of this gain material, e.g. by color center formation, under pumping at 359 nm.

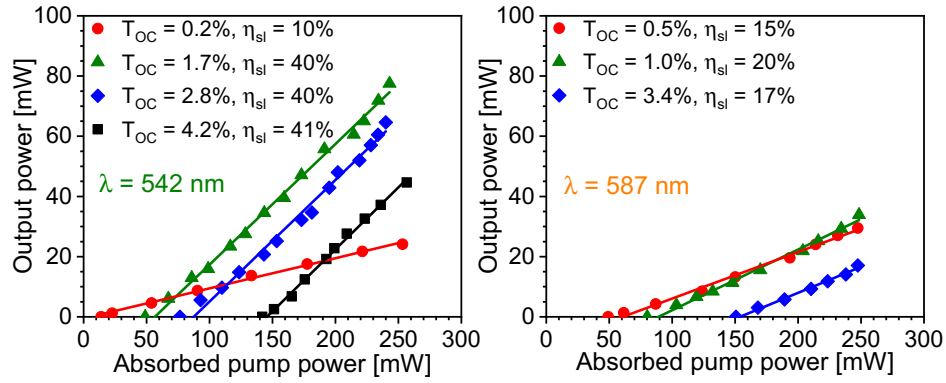


Fig. 6.12.: Laser characteristics of an 11.4 mm long Tb^{3+} (14 at.%) : $LiLuF_4$ sample under UV-pumping at 359 nm. The left graph shows the transitions ${}^5D_4 \rightarrow {}^7F_5$ around 542 nm and the right graph shows the transition ${}^5D_4 \rightarrow {}^7F_4$ around 587 nm.

Further experiments were performed to compare these values to the results obtained under 2ω -OPSL pumping at 486 nm in the blue (pump source described section 6.1.2). These experiments were performed in an identical cavity, i.e. the same mirrors and laser sample as for UV-pumping. The obtained pump waist diameter was $\sim 60 \mu m$. This pump source provides an output power of up to 4 W, but the pump power was limited to 650 mW to obtain similar absorbed pump power values of ~ 250 mW to the previous experiments under 359 nm pumping.

Discussion

The results of both experiments are compared in table 6.1. As expected, the lowest observed laser thresholds using highly reflective mirrors ($P_{thr,HR}$) under UV pumping are increased by about a factor of 1.35, corresponding to the ratio of the pump

wavelengths. For the laser wavelength λ_{las} of 542 nm as well as for 587 nm, with both pump sources we obtain a similar fraction of the maximum achievable slope efficiency, in agreement with equation 6.3. This fraction is determined by the ratio of the slope efficiency with respect to the absorbed pump power $\eta_{sl,abs}$ and the Stokes efficiency $\eta_{St} = \lambda_{pump}/\lambda_{las}$. This allows the conclusion that ESA is either not present or influences the laser performance equally at both pump wavelengths. Due to the significantly higher fraction of absorbed pump power under UV pumping, finally the total optical-to-optical efficiency with respect to the incident power, defined here as $\eta_{opt,inc} = \eta_{sl,abs} \cdot \eta_{abs}$, is more than a factor of 2 higher under UV pumping as compared to cyan-blue pumping. It should be noted that this is an intrinsic advantage of our UV-pumping scheme and does not depend on the available pump power. Also, we intentionally chose a sample originally used for cyan-blue pumping [Met16]. A shorter laser sample would have even more pronounced the advantage of UV pumping.

λ_{las}	542 nm		587 nm	
λ_{pump}	486 nm	359 nm	486 nm	359 nm
$P_{thr,HR}$	11 mW	15 mW	18 mW	24 mW
η_{St}	90%	66%	83%	61%
$\eta_{sl,abs}^*$	59%	40%	26%	20%
$\eta_{sl,abs}/\eta_{St}$	60%	61%	31%	33%
η_{abs}	32%	97%	32%	97%
$\eta_{opt,inc}$	19%	39%	8%	19%

Tab. 6.1.: Laser parameters of an 11 mm long Tb^{3+} (14 at.%): $LiLuF_4$ crystal at different pump wavelengths.

6.3 Lasers based on BaY_2F_8

This section presents the results of laser operation on a Tb^{3+} (13 at.%): BaY_2F_8 crystal under 2ω -OPSL pumping. The crystal employed in the experiments is described in section 4.2.3 and the outcome of this work was presented at [Cas20a]. The result of these experiments supposes the demonstration of laser emission of a Tb^{3+} -doped BaY_2F_8 crystal for the first time. Furthermore, the laser emission of this crystal at 581 nm entails the first demonstration of direct emission of an SSL at 581 nm in the yellow range.

The laser experiments were performed in a 195 mm long nearly concentric laser cavity (see section 6.1.1) with mirrors with radii of curvature of 100 mm. Additionally, the crystal was water-cooled at 20°C through a copper heatsink with

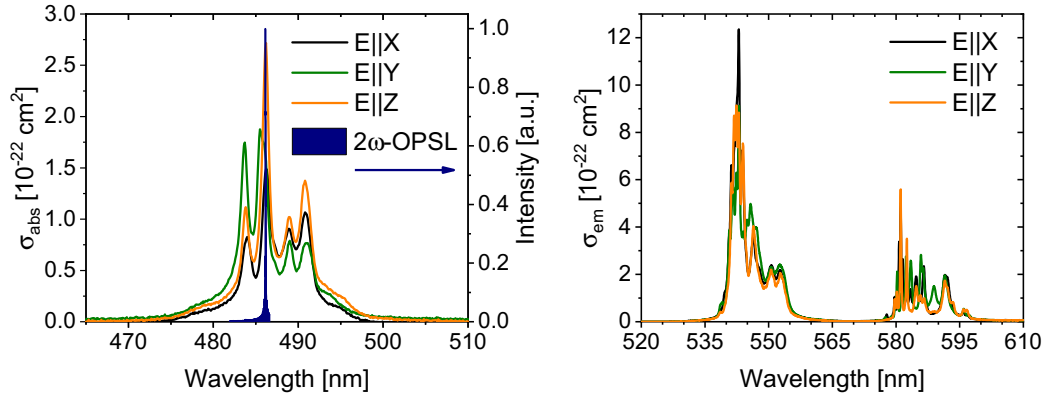


Fig. 6.13.: (left) Polarization dependent absorption cross-sections of $\text{Tb}^{3+}:\text{BaY}_2\text{F}_8$ in comparison with the emission of the 2ω -OPSL pump source. (right) Polarization dependent emission cross-sections of $\text{Tb}^{3+}:\text{BaY}_2\text{F}_8$.

water flow on both the top and bottom of the crystal. As a pump source, a 2ω -OPSL at 486.3 nm (see section 6.1.2) directly excited the $^7\text{F}_6 \rightarrow ^5\text{D}_4$ transition of Tb^{3+} ions in the 4f shell. As shown in figure 6.13 left, for this material the pump source perfectly matches the highest peak of absorption of Tb^{3+} for this transition, corresponding to a polarization parallel to the z-axis. The sample used in the experiments had a length of 16 mm and an x-cut orientation. As shown in table 5.1, this length is shorter than one absorption length for this crystal at the pump wavelengths, where it presented a single pass absorption efficiency of 52%. The emission of the laser at 581.1 nm was polarized parallel to the z-axis of the index ellipsoid of the monoclinic BaY_2F_8 crystal and corresponds to the highest emission peak of the $^5\text{D}_4 \rightarrow ^7\text{F}_4$ transition at this polarization (see figure 6.13 right).

Several output coupling mirrors were tested with transmissions between 0.1 and 0.9% around 581 nm. The corresponding laser characteristics are depicted in figure 6.14. Under these conditions, lasing was achieved with a maximum slope efficiency of 16% at an output coupler transmission of 0.9%. The minimum threshold was found to be 117 mW of absorbed pump power at an output coupler transmission of 0.46%.

Laser emission at green wavelengths was observed. However, it was too weak and unstable to be characterized, even during laser operation with an output coupler mirror highly reflective for the laser wavelength. As the crystalline sample was x-cut oriented, only polarization parallel to the y- and z-axes were accessible. Despite the emission cross-sections in the green are higher for the polarization parallel to the x-axis, these cross-sections almost double in strength the emission cross-sections for yellow wavelengths for the accessible orientations. In addition, figure 5.15 shows that the gain for the green is higher than for the yellow. Therefore, ESA

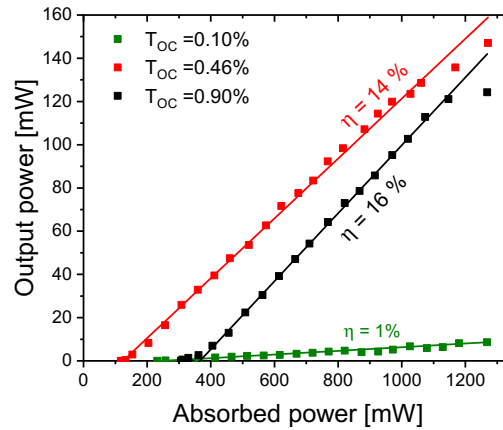


Fig. 6.14.: Laser efficiency curves of Tb^{3+} (13 at.%): BaY_2F_8 for different output coupler transmissions (T_{OC}).

processes are not considered to be the reason for the difficulties to obtain stable and efficient laser operation in the green. However, the low thermal conductivity of BaY_2F_8 of $\kappa=3.5$ W/mK (see table 4.2) may be reduced even further due to the high concentration of Tb^{3+} that amounts to 13 at.% in this sample. Therefore, detrimental processes due to heat cannot be excluded. Among them, thermal depolarization is disregarded, as all polarizations have sufficient emission cross-sections at this wavelength. The lack of operation in the green, which presents higher emission cross-sections than in the yellow, may be related to the also unexpected high laser threshold for the yellow laser operation by the use of the output coupler mirror with the lowest transmission of 0.1%. This threshold value of 230 mW is higher than for the mirror with transmission of 0.46%, which amounts to 117 mW, as shown in figure 6.14. Further investigations, such as measurement of thermal conductivity in the doped crystal could not be performed due to the lack of samples with the required dimensions.

6.4 Laser tests on further Tb^{3+} -containing materials

Further laser experiments were performed in the Tb^{3+} -based materials $\text{KTb}_3\text{F}_{10}$, $\text{Tb}^{3+}:\text{KY}(\text{WO}_4)_2$, and $\text{Tb}^{3+}:\text{YAlO}_3$ where laser emission was not obtained. Table 6.2 summarize some of the parameters relevant for these experiments. In all cases, a 2ω -OPSL with emission at 486.3 nm (see section 6.1.2) served as pump source. The nearly concentric resonator (as presented in section 6.1.1) was prealigned by utilizing a $\text{Tb}^{3+}:\text{LiLuF}_4$ sample as gain media and subsequently laser experiments

were attempted in the mentioned materials for the green and yellow emission, by the use of OCMs highly reflective for the laser wavelengths.

Crystal	KTb ₃ F ₁₀	Tb ³⁺ :KY(WO ₄) ₂	Tb ³⁺ :YAlO ₃
[Tb ³⁺] (at.%)	100%	53%	19%
Description	4.2.2	4.3.3	4.3.1
Sample length (mm)	9.2	5.15	20.0
Orientation	<001>	Ng	a-cut
η_{abs} (single pass)	87%	-	81%

Tab. 6.2.: Parameters relevant for laser experiments. In this case, η_{abs} indicates the single-pass percentage of absorption of the pump.

Even though, there is no clear evidence from the spectroscopic results that dismiss KTb₃F₁₀ as suitable gain media, the larger decrease of the fluorescence lifetime with respect to the radiative lifetime in comparison with other Tb³⁺-doped materials (see figure 5.11), is an indication of non-radiative processes that partially quench the lifetime at room temperature and may be detrimental for laser operation. In addition, further ESA measurements of this material could help to clarify the lack of laser emission experimented in this work.

In the case of Tb³⁺:KY(WO₄)₂, the absence of laser emission was a confirmation of the conclusions drawn from the spectroscopic investigations that disregard KY(WO₄)₂ as host material for Tb³⁺-based laser operation, as discussed in chapter 5 and in [Dem19].

On the contrary, the spectroscopic investigations made on Tb³⁺:YAlO₃ materials indicate the potential of YAlO₃ as a host material for Tb³⁺-lasers. In particular, the ESA measurements presented in figure 5.15 show gain at the laser wavelengths, especially in the green spectral range. However, achieving laser emission was not possible during the laser experiments. Therefore, ESA at the pump wavelengths was considered as a possible detrimental process for the laser operation. To prove this hypothesis, a simple measurement was realized as a proof of concept. A Tb³⁺ (19 at.%):YAlO₃ was excited in the blue at 486.3 nm and the fluorescence emission was recorded in the ultraviolet range. Figure 6.15 shows that the crystal was emitting around 415 nm. Therefore, by exciting the transition $^7F_6 \rightarrow ^5D_4$ we obtain emission of the transition $^5D_3 \rightarrow ^7F_5$, i.e. at higher wavelengths (see figure 5.3). Additionally, we cannot completely exclude that it may still be some residual absorption in the visible that was not completely removed during the annealing process mentioned in section 4.3.1. In conclusion, ESA processes at the pump wavelengths are a feasible cause that prevents laser operation for Tb³⁺:YAlO₃ materials. In particular, intraconfigurational ESA to the ⁹D levels cannot be discarded, as the position of 5d levels is affected more strongly for the CFD than 4f levels. ESA measurements

at the pump wavelengths and pumping at alternative wavelengths could help to understand and overcome these detrimental processes to achieve laser emission with $\text{Tb}^{3+}:\text{YAlO}_3$ materials.

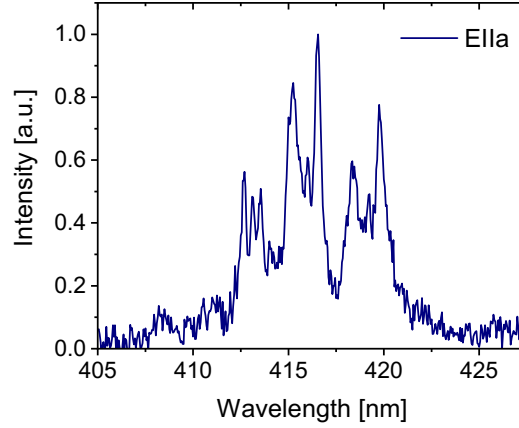


Fig. 6.15.: Tb^{3+} (19 at.%): YAlO_3 fluorescence emission in the UV by excitation at 486.3 nm.

6.5 Summary

Laser experiments were conducted in $\text{Tb}^{3+}:\text{LiLuF}_4$ crystals, where the use of different pump concepts was evaluated. Under 2ω -OPSL-pumping, a Tb^{3+} (28 at.%): LiLuF_4 crystal delivered up to 0.5 W of output power with a slope efficiency of 25% at a wavelength of 587.5 nm. Additionally, laser operation of the same crystal under diode-pumping was successful in the green and yellow spectral region. In this case, the laser performance reached similar efficiencies than by 2ω -OPSL-pumping, and the output power was only limited by the available power of the diode. These results represent the first demonstration of a Tb^{3+} -based DPSSL. Furthermore, laser operation of a Tb^{3+} (14 at.%): LiLuF_4 crystal under UV-pumping was achieved with laser emission in the green and yellow regions. In these conditions, the slope efficiencies of the laser decreased only proportionally to the Stokes efficiencies and the yielded optical-to-optical efficiencies were almost double than under blue-cyan pumping.

The laser experiments on Tb^{3+} (13 at.%): BaY_2F_8 of this work represent the first demonstration of laser emission in a Tb^{3+} -doped BaY_2F_8 crystal. Laser emission was achieved at 581 nm in the yellow with a maximum slope efficiency of 16% and output power over 100 mW. Laser emission at green wavelengths was observed but stabilization of the emission was not possible in this range.

Additional experiments were performed on $\text{KTb}_3\text{F}_{10}$, Tb^{3+} (53 at.%): $\text{KY}(\text{WO}_4)_2$, and Tb^{3+} (19 at.%): YAlO_3 where laser emission was not achieved. Further investigations in the influence of ESA processes in $\text{KTb}_3\text{F}_{10}$ would help to clarify the lack of emission for this material. In the case of $\text{KY}(\text{WO}_4)_2$, the very low position of the lowest 5d level of Tb^{3+} that is located inside the conduction band of this material, allow for intervalence charge transfer processes that quench the emission from the $^5\text{D}_4$ multiplet, and laser operation is not expected. On the contrary, the lack of laser operation of Tb^{3+} (19 at.%): YAlO_3 is attributed to ESA on the pump-wavelengths, preventing inversion of population. Pumping at alternative wavelengths could help to avoid this detrimental process making feasible laser operation for this material.

Conclusion and outlook

In the course of the presented work Tb^{3+} -based materials have been investigated regarding their spectroscopic and laser properties. The crystals, grown in-house or by external collaborators, were characterized by several spectroscopic techniques, focusing on the properties relevant for laser operation. Laser experiments in the visible spectral range were performed on selected material, when the dimensions, optical quality, and doping concentration were suitable to fulfill the requirements as gain media. Hereby, laser emission in the yellow range was achieved with unprecedented efficiency and simplicity of the laser system.

The spectroscopic investigations present absorption cross-sections in the order of 10^{-22} cm^{-1} and emission cross-sections in the order of 10^{-21} cm^{-1} for Tb^{3+} ions. The lifetime investigations do not present quenching for high doping concentrations, confirming the absence of interionic processes detrimental for laser operation. As an example, figure 7.1 collects the fluorescence lifetimes for Tb^{3+} -doped LiLuF_4 shown in figure 5.9. For the highest possible concentration of Tb^{3+} in this matrix, LiTbF_4 , the measured fluorescence lifetime of $\sim 2 \text{ ms}$ still yields a radiative quantum efficiency of more than 40%, which is remarkably high for such a large active ion concentration. Therefore, investigations of Tb^{3+} concentrations between 40% and 75% could allow for further significant improvement of the laser performance. Consequently, the low cross-sections can be compensated by high doping concentrations of Tb^{3+} in the host material, as well as by increasing the length of the gain media. In order to improve the absorption of the pump power and reduce the constrictive requirements of the crystals, UV-pumping benefits from the 6.5 times higher absorption cross-sections in this range. Additional ESA investigations point out to strong depletion of the emission for wavelengths in the orange to red spectral region in the investigated crystals. In addition, the reduced quantum yield of yellow laser transitions in comparison with the green transitions suggests that there is weak intraconfigurational ESA at the yellow wavelength that does not prevent laser operation but reduces its efficiency.

With a Tb^{3+} (28 at.%): LiLuF_4 crystal as gain medium, the most efficient direct emitting cw yellow SSL have been demonstrated, to the time of publication. The laser delivers 0.5 W of output power with a slope efficiency of 25% at a wavelength of 587.5 nm. These values exceed those of previous yellow Tb^{3+} -lasers by nearly

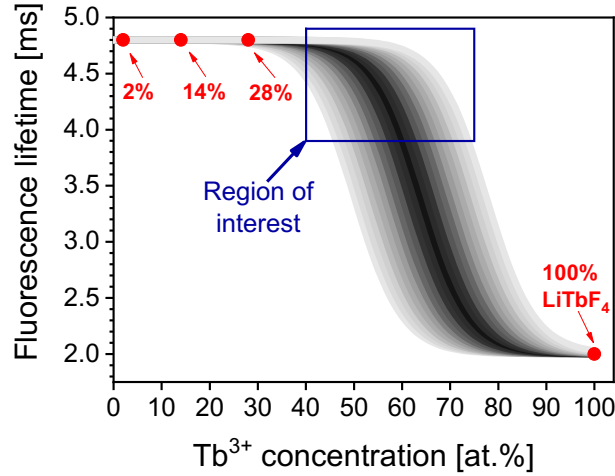


Fig. 7.1.: Measured fluorescence lifetime of the excited state 5D_4 in $Tb^{3+}:LiLuF_4$ for different Tb^{3+} concentrations in the crystal (red dots). The gray shaded regions show possible tendencies for the lifetime quenching of $Tb^{3+}:LiLuF_4$ toward higher doping concentrations.

a factor of two [Met16] with the output power being only limited by the available pump power. Moreover, the prospects for further improvement are good, since $LiLuF_4$ is a well-established host crystal known to withstand high pump powers when doped with other rare-earth ions [Ber18]. These results are comparable with the best efficiencies obtained by complex nonlinear approaches to generate yellow laser emission and even higher at low output power.

By the use of the same crystalline matrix, the first diode-pumped laser operation of a Tb^{3+} -doped material and the most efficient diode-pumped direct-emitting yellow solid-state laser have been demonstrated. The simple approach of this work does not involve any nonlinear wavelength conversion process, neither in the pump source nor in the laser cavity. The laser emission at 542.4 nm in the green spectral range exhibits a high slope efficiency in excess of 50%, and in the yellow at 587.4 nm the maximum slope efficiency amounts to 22%. In all cases, the output power was only limited by the available pump power. Therefore, the future progress in cyan-blue emitting diode lasers at 488 nm should enable further improvement of the laser performance, which will be supported by the use of higher doping concentrations possible due to the late onset of concentration quenching of the emitting level lifetime demonstrated here. In addition, this DPSSL exhibits low laser thresholds below 30 mW of absorbed pump power. Hence, these systems are a convenient, efficient, and possible to miniaturize alternative to nonlinear systems, in particular in the low power range, where nonlinear conversion efficiencies are intrinsically lower.

Additionally, literature results on tunable laser operation over several nanometers have been previously demonstrated for the green spectral range in Tb^{3+} -doped laser materials [Met17]. Thus, our preliminary results on laser operation at 582 nm also render it possible to achieve wavelength tuning in the yellow spectral range and to improve the performance at 582 nm by the use of optimized mirror coatings.

The presented work demonstrates UV pumping as a viable solution to reduce the required length of Tb^{3+} -doped gain media for efficient absorption. In a Tb^{3+} (14 at.%) : LiLuF_4 crystal, reducing the length of 11 mm long gain medium by a factor of two would still yield more than 80% single-pass absorption compared to below 20% under cyan-blue pumping. Moreover, as efficient laser operation was obtained with samples with twice the Tb^{3+} concentration, it would allow to reduce the required gain medium length by another factor of two to below 3 mm as compared to 21 mm crystals used for blue-cyan pumping, while still achieving a higher absorption efficiency. As the visible emission cross-sections of Tb^{3+} -doped materials are typically one order of magnitude higher than the absorption cross-sections in the cyan-blue, this approach should still enable efficient laser operation at gain medium dimensions well compatible with high power low beam quality laser diodes. For example, diode laser modules with several watts of output power exist at 370 nm [Nic20] providing a good spectral overlap with the FWHM absorption bandwidth of more than 3 nm of the peaks in this spectral range. While initial measurements indicated detrimental ESA in this wavelength range [Met16], further investigations are required to confirm its influence on the laser efficiency. This also involves the potential formation of color centers which are more likely to appear under short wavelength excitation. However, the choice of different host materials for terbium ions may strongly vary the position of the 5d-levels supposedly responsible for ESA at these wavelengths [Dor00a, Dor01].

Laser emission of a Tb^{3+} : BaY_2F_8 crystal was demonstrated for the first time in the frame of this work. With a Tb^{3+} concentration of 13 at.% the laser delivers over 140 mW of output power with a maximum slope efficiency of 16% at a wavelength of 581 nm. Even though laser emission was observed at green wavelengths, the laser operation was unstable and further characterization is necessary to fully understand the origin of the involved detrimental processes.

To date, there is no report on Tb^{3+} -doped SSLs based on oxide materials. However, Tb^{3+} : YAlO_3 is a very promising candidate for laser emission in the green and yellow spectral range. The low CFD of YAlO_3 of $\sim 16500 \text{ cm}^{-1}$ is comparable with the CFD of other fluoride materials that have demonstrated laser emission, such as Tb^{3+} -doped BaY_2F_8 [Cas20a] or KY_3F_{10} [Met16]. In addition, ESA pump-probe experiments show gain in the green and yellow spectral regions. The lack of emission during the laser experiments of this work is attributed to ESA at the pumping wavelengths of

486.3 nm, corresponding to direct pumping into the upper laser level 5D_4 . Therefore, by pumping at alternative wavelengths, laser operation with this material seems feasible.

The revealed outstanding potential of Tb^{3+} ion for efficient laser emission has caused an ongoing quest for further suitable host materials, inducing a considerable quantity of publications in the following years. Examples of these reports are cited here [Loi17, Che18, Liu18, Shi18, Szt18, Din18, Dem19, Qin19, Che20c, Liu20, Din21, Dem21]. Among them, it is worth to highlight the report of H. Chen et al. on laser operation of $Tb^{3+}:LiYF_4$ at 544 nm and 582 nm, with a slope efficiency as high as 63% in the green [Che20a] and laser operation of a $LiTbF_4$ crystal, demonstrated for the first time in the same contribution.

It should also be noted that the long upper state lifetime of Tb^{3+} gives rise to high energy storage, beneficial for high pulse energies in experiments on Q-switched laser operation using visible saturable absorber materials [Dem17, Tan20]. Very recent work, published during the writing phase of this manuscript, has presented the first demonstrations of a Q-switched Tb^{3+} laser [Che20b], utilizing graphene as saturable absorber material, and further improved results were obtained by utilizing $Co:MgAl_2O_4$ as saturable absorber achieving a pulse duration of ~ 150 ns [Tan21, Che20d]. At an average output power of more than 0.2 W, such a laser delivered $49 \mu J$ pulses at a repetition rate of 5.1 kHz, corresponding to a peak power of 0.36 kW at 544 nm. Additional experiments have been recently published on intracavity frequency doubling of this laser, yielding more than 200 mW of pulsed output at 272 nm in the UV range [Che20d]. Last, the highest peak powers to date of up to 0.8 kW from Tb^{3+} lasers were obtained recently by electro-optic [Yan21] and acousto-optic Q-switching [Che21].

The work presented in this thesis has taken part in the development of Tb^{3+} lasers with several contributions. Hereby, substantial improvement of laser operation in the yellow was reported [Cas18], as well as DPSSL operation [Cas20b], laser operation under UV-pumping [Kal20], the first laser emission demonstration of a $Tb^{3+}:BaY_2F_8$ crystal [Cas20a], and several spectroscopic investigations of different features of Tb^{3+} containing materials [Kal21, Dem19, Tan21]. In the future, the investigation of further host materials, pump alternatives, and doping concentrations of Tb^{3+} could reduce the detrimental impact of ESA on the laser efficiency and enable alternative laser configurations and emission wavelengths that improve the laser performance and their suitability for applications.

Appendix

A.1 Crystal growth by Czochralski method

The Czochralski method was developed by the Polish chemist Jan Czochralski in 1916 and published in 1918 [Czo18]. Since then, it has become the most common process for commercial production of high-quality laser crystals, due to the capability of this technique to produce large single-crystal boules with a low level of defects.

In the most commonly used variant of this technique, the premixed raw materials are placed in a crucible surrounded by an isolation structure that holds the crucible and ensures the required temperature profile optimal for the growth. A high-frequency coil applies inductive heat to melt the raw materials. The whole system is set in a sealed chamber where vacuum or atmospheric conditions can be controlled. In order to start the growth, the melt is cool down until the temperature is lowered to just below the melting point of the material. A non-reactive wire with a higher melting temperature than the raw material is introduced in the melt. This wire acts as a crystallization nucleus as the melt solidifies on it. More reproducible and higher quality results are obtained when a seed crystal is attached to the wire for better control of the crystallographic direction of the growth. By slowly lifting the wire that is attached to a rotating pull rod, the material solidifies atomic layer by atomic layer, in a monocrystalline structure.

To ensure the monocrystallinity and the high structural quality of the crystal, a few parameters must be precisely controlled: the heating power, the pulling rate, and the rotation rate. These parameters determine the diameter of the boule. At the beginning of the growth, a thin neck reduces the number of crystal nuclei, preventing polycrystallinity, as well as reducing the proliferation of dislocations. Subsequently, lower heating powers and slower pulling rates increase the overall size of the final boule.

The Czochralski method allows growing crystals with diameters of 450 mm and a weight exceeding 300 kg for silicon materials. Other crystals commonly grown by this technique are germanium crystals, as well as oxide and fluoride crystals like garnets, niobates, tantalates, vanadates, aluminates, silicates, and germanates.

A.2 Crystal growth by Nacken-Kyropoulos method

The Nacken-Kyropoulos method was developed in the early 20th century independently by the two scientists that give it its name [Nac15, Kyr26]. It entails a growth alternative to the Czochralski method that is advantageous for the growth of certain oxides (e.g. Al_2O_3), and fluorides.

This technique can be easily implemented in a Czochralski growth system, as the growth process is similar and simplified. In the same conditions described in appendix A.1, the premixed raw materials are melted and a wire or a seed crystal is introduced into the melt. Subsequently, instead of slowly pulling the wire or seed out of the melt, the temperature of the melt is directly decreased. The crystal nucleation starts on the surface of the wire (or seed) that is colder than the melt and propagates through the whole volume of the melt.

The Nacken-Kyropoulos method is advantageous compared to the Czochralski method, for crystals which growth is troublesome due to difficulties in pulling the material or maintaining the contact between the melt and the growing crystal. In contrast, this method has the disadvantage of a worse control of the crystallization process, as the surface of the melt and the crucible may act as nucleation points, promoting polycrystallinity and inducing stress. The use of carbon crucibles favors the growth of fluorides, as they generally exhibit very low wetting to this material.

A.3 Crystal growth by vertical Bridgman method

The vertical Bridgman method was developed by Percy W. Bridgman and presented for the first time in [Bri23]. In this technique, the raw materials are placed in a crucible and heated up until melted. Subsequently, the crucible is slowly lowered, displacing it from the heated zone to a colder zone. In this way, crystallization starts from the bottom of the crucible. The crystal boule grows by further moving the crucible away from the heated region.

As for the Nacken-Kyropoulos growth (appendix A.2), there is a risk of parasitic crystallization and stress induced by the contact between the melt and the crucible walls. A seed placed at the bottom of the crucible contributes to controlling the crystallization in the desired direction.

A.4 Micro X-ray fluorescence measurements

Micro X-ray fluorescence (μ -XRF) measurements were carried out under low vacuum conditions (about 1 mbar) using a Bruker M4 TORNADO spectrometer to investigate

the chemical compositions of the prepared samples. The measurement system was equipped with a Rh X-ray source operated at 50 kV and 200 μ A. Polycapillary X-ray optics were used to focus the bremsstrahlung at the surface of the samples which results in a high spatial resolution of about 20 μ m. Using a measurement time of 60 s per point, three measurements per sample were conducted. The signals were detected using a circular silicon drift detector with a high energy resolution (<145 eV). The element quantification (of Tb and Y) was conducted by using the fundamental parameter (FP) approach.

A.5 References for Chapter 4 tables

	LiLuF ₄ (LiTbF ₄)	KY ₃ F ₁₀ (KTb ₃ F ₁₀)	BaY ₂ F ₈	LaF ₃	TbF ₃
Lattice	[Tho70]	[Grz02]	[Gui93]	[Udo08]	[Met14a]
Space group	[Tho70]	[Grz02]	[Gui93]	[Udo08]	[Met14a]
V_{cell} ($\text{\AA}^3$)	[Ran02] [Met14a]	[Grz02] [Pod76]	[Gui93]	[Udo08]	[Met14a]
Cation density (10^{22} cm^{-3})	this work this work	this work this work	this work	this work	this work
Coord. number	[Ran02]	[Grz02]	[Kam90a]	[Udo08]	[Met14a]
$\partial n / \partial T$ (10^{-6} K^{-1})	[Agg05]	[Sch17]	-	-	-
$\partial L / \partial T$ (10^{-6} K^{-1})	[Agg05]	[Fri06]	[Bar93]	[Kle67]	-
κ (W/(mK))	[Agg05]	[Pop09]	[Agg05]	[Rei13]	-
Mohs hardness	[Kam93]	[Web03]	[Kam90a]	[Rei13]	-

Tab. A.1.: References for the values given in table 4.2.

	YAlO ₃ (TbAlO ₃)	Y ₃ Al ₅ O ₁₂	KY(WO ₄) ₂
Lattice	[Die75]	[Dob04]	[Kam01]
Space group	[Die75]	[Dob04]	[Kam01]
V_{cell} (Å ³)	[Die75] [Sek98]	[Dob04]	[Cas15]
Cation density (10 ²² cm ⁻³)	[Web69] this work	[Web69]	this work
Coordination number	[Sen13]	[Sen13]	[Kam01]
$\partial n / \partial T$ (10 ⁻⁶ K ⁻¹)	[Agg05]	[Agg05]	[@EKS21]
$\partial L / \partial T$ (10 ⁻⁶ K ⁻¹)	[Agg05]	[Agg05]	[Puj01]
κ (W/(mK)) (298 K)	[Agg05]	[Agg05]	[Agg05]
Mohs hardness	[Liu18]	[Jia13]	[Emm19]

Tab. A.2.: References for the values given in table 4.3.

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Journal publications

- E. Castellano-Hernández, P. W. Metz, M. Demesh, and C. Kränkel. "Efficient directly emitting high-power $\text{Tb}^{3+}:\text{LiLuF}_4$ laser operating at 587.5 nm in the yellow range". *Opt. Lett.* 43.19 (2018), pp. 4791–4794.
- M. Demesh, A. Yasukevich, V. Kisel, E. Dunina, A. Kornienko, V. Dashkevich, V. Orlovich, E. Castellano-Hernández, C. Kränkel, and N. Kuleshov "Spectroscopic properties and continuous-wave deep-red laser operation of Eu^{3+} -doped LiYF_4 ". *Opt. Lett.* 43.10 (2018), pp. 2364-2367.
- M. Demesh, A. Mudryi, A. Pavlyuk, E. Castellano-Hernández, C. Kränkel, and N. Kuleshov "Cross sections and transition intensities of Tb^{3+} in $\text{KY}(\text{WO}_4)_2$ ". *OSA Continuum* 2.4 (2019), pp. 1378–1385.
- E. Castellano-Hernández, S. Kalusniak, P. W. Metz, and C. Kränkel. "Diode-Pumped Laser Operation of $\text{Tb}^{3+}:\text{LiLuF}_4$ in the Green and Yellow Spectral Range". *Laser Photon. Rev.* 14.2 (2020), p. 1900229.
- S. Kalusniak, H. Tanaka, E. Castellano-Hernández, and C. Kränkel. "UV-pumped visible Tb^{3+} -lasers". *Opt. Lett.* 45.22 (2020), pp. 6170–6173.
- S. Kalusniak, E. Castellano-Hernández, H. Tanaka, H. Yalcinoglu, and C. Kränkel. "Spectroscopic properties of Tb^{3+} as an ion for visible lasers". *Appl. Phys. B* 128.33 (2022).

International conferences. Oral contributions

- S. Kalusniak, H. Tanaka, E. Castellano-Hernández, and C. Kränkel. "Enhanced absorption efficiency in UV-pumped $\text{Tb}^{3+}:\text{LLF}$ " presented at CLEO/Europe-EQEC Conference, talk CA-1.2 (2021), Munich, Germany.
- S. Kalusniak, H. Tanka, E. Castellano-Hernández, and C. Kränkel. "UV pumping of Tb-based solid-state lasers with visible emission" The 10th Advanced Lasers and Photon Sources (ALPS), talk ALPS-14-03 (2021), Online Conference.
- C. Kränkel, E. Castellano-Hernández, S. Kalusniak, and H. Tanaka "Tb-Lasers: Current state and future prospects" The 10th Advanced Lasers and Photon Sources (ALPS), invited talk ALPS-14-02 (2021), Online Conference.

- H. Tanaka, S. Kalusniak, E. Castellano-Hernández, and C. Kränkel "UV-pumping and passive Q-switching of visible Tb:LiLuF₄ lasers" SPIE Photonics West, talk 11664-11 (2021), Online Conference.
- E. Castellano-Hernández, E. Damiano, S. Kalusniak, M. Tonelli, and C. Kränkel. "Laser emission of Tb³⁺:BaY₂F₈ at 581.1 nm in the yellow range" 9th German-French Workshop on Oxide, Dielectric, and Laser Crystals (2020), Berlin, Germany.
- C. Kränkel, E. Castellano-Hernández, S. Kalusniak, and H. Tanaka "New In-GaN diode-pumped solid-state laser materials", Advanced Solid-State Lasers Conference (ASSL), invited talk ATu2A.1 (2020), Online Conference.
- S. Kalusniak, H. Tanaka, E. Castellano-Hernández, C. Kränkel "Prospects of UV diode pumping of Tb-based solid-state lasers with visible emission" 8th EPS-QEOD Europhoton Conference, talk We-A3.4 (2020), Online Conference.
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- H. Tanaka, D. Schulz, E. Castellano-Hernández, S. Kalusniak, D. Klimm, C. Kränkel, and M. Bickermann "Terbium-containing fluoride crystals for laser and photonics applications" 8th German-French Workshop on Oxide, Dielectric, and Laser Crystals (2019), Villeurbanne, France.
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- E. Castellano-Hernández and C. Kränkel. "Diode-pumped visible laser operation of Tb³⁺:LiLuF₄". Conference on Lasers and Electro-Optics (CLEO/Europe-EQEC), talk CA-4.1 (2019), Munich, Germany.
- E. Castellano-Hernández, A. Uvarova, M. Demesh, H. Tanaka, and C. Kränkel "Tb³⁺-doped materials for efficient lasing at 588 nm" 8th EPS-QEOD Europhoton Conference, talk 29.2 (2018), Barcelona, Spain.
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- M. P. Demesh, E. Castellano-Hernández, V. E. Kisel, A. S. Yasukevich, V. I. Dashkevich, V. A. Orlovich, C. Kränkel, and N. V. Kuleshov "Spectroscopy and laser operation of $\text{Eu}^{3+}:\text{LiYF}_4$ " 18th International Conference on Laser Optics (ICLO), talk ThR1-39 (2018), St. Petersburg, Russia.
- C. Kränkel, E. Castellano-Hernández, and A. M. Heuer "Tailored crystals for solid-state lasers" 18th International Conference on Laser Optics (ICLO) invited talk ThR1-35 (2018), St. Petersburg, Russia.
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