Spectroscopic properties of Tb^{3+} as an ion for visible lasers

Sascha Kalusniak¹ · Elena Castellano-Hernández¹ · Hasan Yalçinoğlu¹ · Hiroki Tanaka¹ · Christian Kränkel¹

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Abstract

In recent years, Tb^{3+} -based solid-state lasers with emission in the green and yellow have seen a revival. This was owed to the availability of blue emitting semiconductor-based pump sources and recent findings, which reported more than 60% slope efficiency in the green and about 25% slope efficiency in the yellow. In this paper we review the state of the art of Tb^{3+} -based solid-state lasers. We summarize the spectroscopic properties and present new insights, which enable us to provide valuable guidelines and recommendations for the choice of host materials to further improve the performance of Tb^{3+} -based solid-state lasers.

1 History and state of the art of Tb^{3+} lasers

The outstanding fluorescence properties of Tb^{3+} -doped phosphors are known for decades. Figure 1 shows the various emission lines of Tb^{3+} in the visible spectral range. The most prominent emission peaks are found around 545 nm in the green and 585 nm in the yellow. Further, less intense emission lines are also found in the cyan-blue and red spectral range. The combination of all these lines yields a bright lime-green fluorescence color of phosphors based on Tb^{3+} , which was characteristic for cathode-ray tube-based devices and projection screens [1]. In combination with other rare-earth ions, Tb^{3+} is also an important ion for phosphors for trichromatic light sources [2]. Its intense emission in the visible spectral range made Tb^{3+} thus an interesting ion for the generation of visible laser light ever since then. Green and in particular yellow laser light is highly relevant in medicine for skin and eye treatment [3, 4]. To date, the generation of coherent light in this spectral range remains a challenge: Semiconductor laser diodes suffer from a severe efficiency drop and reduced operational lifetimes at wavelengths beyond 530 nm and below 610 nm, the so called ‘green gap’ [5]. As a consequence, copper vapour laser systems, toxic and inconvenient dye laser systems, or complex nonlinear conversions schemes are still state of the art for the generation of coherent yellow light [6, 7].

However, despite its promising fluorescence properties, Tb^{3+} has not been examined intensively as an active ion for visible lasers for a long time. Though early laser tests date back to the late 1960s and early 70 s [8–10], the laser efficiencies obtained in these pioneering experiments remained low and did not trigger a strong interest in further research on lasers based on Tb^{3+} . Even the demonstration of a Tb^{3+} -based fluoride fiber laser in 2007 did not revive research in this field, as this laser delivered not more than 0.28 mW of output power in the green under 130 mW of argon-ion laser-pumping at 488 nm [11].

Only very recently, upcoming blue emitting semiconductor-based pump sources [12] useful for the direct and efficient excitation of the upper laser level $^5\text{D}_4$ (see Fig. 1) led to a revival of the research on Tb^{3+} as a laser ion with high laser efficiencies for practical applications [13]. Since then, various reports on laser operation of Tb^{3+} -doped laser materials were published. Under pumping with frequency doubled optically pumped semiconductor disk lasers (2 ω -OPSLs) emitting around 485 nm [14, 15], continuous wave laser operation on the green and yellow lines of Tb^{3+} has been achieved. The slope efficiencies in the green were as high as 60% and output powers in excess of 1 W were realized [16, 17]. In the yellow, however, significantly lower efficiencies of only 25% [16–18] are state of the art and the red transition did not allow for laser operation at all. For the red transition excited state absorption (ESA) from the upper laser level was identified as a detrimental factor [16], but to which extent ESA contributes to the reduced efficiency of yellow compared to the green Tb^{3+} lasers is not revealed, yet. Thus, there is still hope that higher efficiencies can be

✉ Christian Kränkel
christian.kraenkel@ikz-berlin.de

¹ Leibniz-Institut für Kristallzüchtung (IKZ), Max-Born-Str.
2, 12489 Berlin, Germany

Fig. 1 Energy level diagram of Tb^{3+} in the host crystal LiLuF_4 (LLF) based on data from [20, 21]. Only the levels possibly involved in laser relevant processes are individually labelled. Black horizontal lines visualize $4f^8$ levels and purple rectangles show $4f^75d^1$ -levels also denoted as $5d$ levels in the text. Relevant absorption and emission channels are indicated by colored arrows. Possible ESA and/or energy transfer upconversion (ETU) transitions are depicted by dashed arrows and the dotted grey arrows indicate cross relaxation channels

reached by the choice of a proper pumping scheme and/or host material.

In recent laser experiments, the low absorption cross sections of Tb^{3+} , caused by the spin-forbidden nature of the absorption around 488 nm were compensated by very high doping concentrations. The best laser efficiencies up to now were obtained with 10–30 at.% doped fluoride crystals. Even at such high doping concentrations, the typical crystal lengths required for efficient pump absorption exceed 1 cm. However, lasing has also been obtained with stoichiometric, i.e. 100 at. % doped, laser crystals such as LiTbF_4 [17] and even TbF_3 [19], which shows the potential for very efficient laser operation at higher doping concentrations. Moreover, there are also promising reports utilizing the higher UV absorption cross sections for optical pumping, which could ultimately reduce the required lengths of gain media to 3 mm or even less, compatible with high power diode pumping [22, 23]. Initial experiments under pumping with an (In,Ga) N-based laser diode emitting at a wavelength of 488 nm enabled very similar laser efficiencies for the green and yellow laser transitions. However, as the diode pump power in these initial experiments was limited to 200 mW, the output power did not exceed 43 mW and 14 mW, respectively [24].

The long fluorescence lifetime of the upper laser level of Tb^{3+} of around 5 ms makes this ion also promising for high energy Q-switched laser operation. In 2020, the first Q-switched Tb^{3+} laser was introduced [25]. This $\text{Tb}^{3+}:\text{LiYF}_4$ laser utilized graphene as the saturable absorber material. At pulse energies on the order of 20 μJ and several 10 kHz repetition rate, the corresponding average output was as high as 0.74 W, but due to the rather long pulse duration of 2.9 μs , the peak power did not exceed 7 W. Improved results were obtained by utilizing $\text{Co:MgAl}_2\text{O}_4$ as the saturable absorber. In this case, stable pulsing was achieved at pulse durations around 150 ns [23, 26]. At an average output power of more than 0.2 W, such a laser delivered 49 μJ pulses at a repetition rate of 5.1 kHz, corresponding to a peak power of 0.36 kW at 544 nm. It is evident, that these lasers exhibit a strong potential for the generation of ultraviolet radiation. Indeed intracavity frequency doubling of this laser yielded more than 200 mW of pulsed output at 272 nm in the UV range [26]. The highest peak powers to date of up to 0.8 kW from Tb^{3+} lasers were obtained recently by electro-optic [27] and acousto-optic Q-switching [28].

In all these experiments exclusively fluoride crystals served as host materials. Laser action of Tb^{3+} -doped oxides has not been reported up to now. Again, the reasons are not fully understood. One explanation often stated is the strong crystal field of oxides causing a substantial energetic depression of the $4f^75d^1$ states of Tb^{3+} (in the following also referred to as $5d$ states for simplicity) [29]. As a result, the energetic gap between the upper laser level and the energetically lowest $5d$ states can be easily bridged by visible photons and strong parity allowed $4f$ - $5d$ ESA on the pump or even on the laser wavelength is expected. Oxide crystals with similarly low crystal field strength than fluorides exist [29], but their low crystal field strength is in many cases the result of a high coordination number, which often goes along with a high symmetry of the coordination sphere and correspondingly a further reduction of the already low spin-forbidden transition cross sections of Tb^{3+} .

All these results show, that Tb^{3+} is a promising ion for visibly emitting solid-state lasers based on fluoride host materials. In particular for the yellow transition, only very few alternatives for diode-pumped solid-state lasers in this wavelength range exist. However, it is also evident that many spectroscopic properties of Tb^{3+} relevant for the laser process are not yet fully understood and new insights are needed to further improve the performance of Tb^{3+} -based lasers. In this paper, we will summarize the state of the art on the spectroscopy of Tb^{3+} materials relevant for laser operation and introduce various new findings. The conclusions from the spectroscopic properties enable us to provide valuable suggestions and guidelines helpful for the design of future Tb^{3+} -based lasers.

2 Spectroscopic peculiarities of Tb^{3+} with respect to laser applications

2.1 Energy level structure of Tb^{3+} and implications for laser operation

The energy level scheme of trivalent terbium with eight electrons in its optically active $4f$ shell contains 295 Stark multiplets with a total of 3003 Stark sub-levels. Even more energetic configurations become possible, when $4f^7 5d^1$ configurations are considered [30].

Such a complex energy level structure inevitably goes along with difficulties in understanding and describing all relevant processes for trivalent terbium as a laser ion. Figure 1 shows the energy level scheme of Tb^{3+} with all relevant $4f$ and $5d$ states. Due to the large number of energy levels, the energetic distance between most of them is so small, that non-radiative (multi-)phonon relaxation is the dominant depopulation process [31]. Only the levels $^5\text{D}_3 + ^5\text{L}_{10}$ and $^5\text{D}_4$ exhibit gaps to the next lower lying level of ~ 5 and $\sim 15 \times 10^3 \text{ cm}^{-1}$, respectively, which are large enough to prevent non-radiative decay considering typical phonon energies below 1000 cm^{-1} in oxide host materials and even lower values in fluoride crystals.

The $^5\text{D}_3 + ^5\text{L}_{10}$ multiplets (abbreviated as $^5\text{D}_3$ in the following), however, are subject of a strong resonant cross relaxation process (dashed grey arrows in Fig. 1), which effectively depopulates these levels at the doping concentrations required for efficient lasing of Tb^{3+} -based lasers. Thus, only the $^5\text{D}_4$ multiplet of Tb^{3+} exhibits a fluorescence quantum efficiency high enough and thus an upper state fluorescence lifetime long enough to enable laser operation. Pump wavelengths of around 485 nm are required for the direct excitation of this multiplet. In the past, inefficient visible flash-lamps or costly and bulky argon-ion lasers were utilized for this purpose. Only recently high power semiconductor-based devices such as 2ω -OPSLs [14, 15] and even directly blue emitting laser diodes became available [13].

The radiative decay of the $^5\text{D}_4$ multiplet yields various emission lines throughout the visible range with the most prominent emission peaks found at 545 nm in the green and 585 nm in the yellow. All relevant transitions for absorption and emission are electronic $4f$ - $4f$ transitions and as such parity forbidden. Moreover, they all require a spin-flip, which finally yields low transition cross sections on the order of few 10^{22} cm^2 in absorption and roughly an order of magnitude higher emission cross sections (cf. Figure 2). Fortunately, even at high doping ion densities, no concentration quenching of the $^5\text{D}_4$ fluorescence lifetime is observed. In consequence, by utilizing crystals with very high Tb^{3+} doping concentrations of several ten percent

or even stoichiometric crystals, high absorption and gain coefficients can be obtained despite the low transition cross sections.

The spin-forbidden nature of the transitions decreases their cross sections, but in turn, the fluorescence lifetime of Tb^{3+} of 5 ms in fluoride hosts is two orders of magnitude longer than, e.g. for Pr^{3+} [32]. This enables efficient energy storage in Tb^{3+} -doped crystals under blue pumping, which is beneficial for obtaining high-energetic pulses in Q-switched laser operation.

As previously mentioned, in contrast to the $^5\text{D}_4$ multiplet, the $^5\text{D}_3$ multiplet—located at around $27 \times 10^3 \text{ cm}^{-1}$, corresponding to pump wavelengths around 370 nm—is subject to a strong resonant cross relaxation $^5\text{D}_3 \rightarrow ^5\text{D}_4 / ^7\text{F}_6 \rightarrow ^7\text{F}_{0,1}$ (grey arrows in Fig. 1). This cross relaxation efficiently quenches the $^5\text{D}_3$ fluorescence at high doping levels [33]. The resulting low fluorescence quantum yield seriously hampers laser operation from the $^5\text{D}_3$ multiplet, but—as detailed in Sect. 2.4.—it features efficient population of the $^5\text{D}_4$ multiplet upon UV pumping with improved absorption efficiency.

From the energy level scheme, cross relaxation from the $^5\text{D}_4$ multiplet can be excluded. However, there are various energy levels of the $4f$ and even $5d$ configuration of Tb^{3+} , which could serve as acceptor levels for ESA or energy transfer upconversion (ETU) in the range of pump or emission wavelengths (see Fig. 1). It should be noted that in contrast to the ground state absorption, there are several ESA acceptor levels featuring spin-allowed transitions. For the $5d$ levels, the situation is very particular in Tb^{3+} -doped materials: While in Gd^{3+} with its stable half-filled $4f$ shell the first $5d$ bands are found at $\sim 80 \times 10^3 \text{ cm}^{-1}$, corresponding to an excitation wavelength of 125 nm, in Tb^{3+} these bands are located already at roughly half this value ($\sim 40 \times 10^3 \text{ cm}^{-1}$ or 250 nm) due to the loosely bound additional electron. As a consequence, $4f \rightarrow 5d$ ESA at the pump wavelength of 488 nm or potential visible laser wavelengths should be expected. In addition, this $4f \rightarrow 5d$ ESA is parity allowed and thus exhibits high cross sections. This led many researchers to believe that lasing in Tb^{3+} could not be successful [29]. However, the lowest energy levels of the $5d$ configuration are nonet states (^9D) and ESA from the quintet $^5\text{D}_4$ multiplet into these levels requires a double spin-flip. In consequence, despite being parity allowed, the probability for such a transition remains low [16]. Unlike the $4f$ shell, the $5d$ shell is not shielded by outer shells and thus strongly interacts with the crystal field. This results in fairly broad $5d$ bands as compared to the narrow $4f$ absorption lines. Moreover, the energetic position of the $5d$ states depends strongly on the host crystal and a strong crystal field—often found in oxide crystals due to their divalent O^{2-} ligands as compared to the singly charged F^- ligands in fluorides—may depress the ^7D energy levels of the $5d$ configuration to energetic values low

Fig. 2 Ground state absorption and stimulated emission cross sections of Tb^{3+} in the hosts YAG, LLF, LaF_3 and CaF_2 . The corresponding doping concentrations are 14 at.% for YAG and LLF, 12 at.% for LaF_3 as well as 10 at.% Tb^{3+} and 10 at.% Na^+ for CaF_2 . Please note the different y-axis scale for the absorption spectra of

$(\text{Tb}^{3+}, \text{Na}^+):\text{CaF}_2$ (g) as well as for the stimulated emission cross sections of $(\text{Tb}^{3+}, \text{Na}^+):\text{CaF}_2$ and $\text{Tb}^{3+}:\text{LaF}_3$ (h, f). The different colored spectra in some of the graphs correspond to the different polarizations with respect to the crystallographic c-axis of these crystals (blue: σ -polarization, red: π -polarization)

enough to enable significant, single spin-forbidden $4f \rightarrow 5d$ ESA. Further experimental results and considerations regarding ESA are found in Sect. 2.5. In particular these ESA considerations explain, why the choice of a proper host material is essential to unveil the full potential of Tb³⁺ as a laser ion for visible lasers.

2.2 Ground state absorption and stimulated emission cross sections in representative host crystals

In the past, numerous Tb³⁺ containing materials have been investigated for their suitability as gain media for visible lasers. Therefore, ground state absorption (GSA) and stimulated emission (SE) cross section data of various Tb³⁺ containing crystals are found in literature. In particular the recent reports on their efficient visible laser operation lead to a revival of spectroscopy on Tb³⁺ doped materials. Just to name a few examples, phosphates [34], borates [35, 36], garnets [37], perovskites [38], tungstates [39, 40] and fluorides [16, 17] were spectroscopically investigated in detail recently.

In the following we will present GSA and SE cross sections of Tb³⁺ ions. For the sake of conciseness, we will restrict ourselves to Tb³⁺ in four representative host crystals, namely Y₃Al₅O₁₂ (YAG), LiLuF₄ (LLF), LaF₃, and CaF₂. As previously discussed, the influence of the crystal field on the $4f$ energy levels is low and mainly impacts the Stark splitting of the multiplets, but it may strongly split the $5d$ levels and thus reduce the energetic positions of the lowest levels. The choice of these four host materials was thus motivated by their significantly different crystal field strengths. Their GSA and SE spectra when doped with Tb³⁺ are shown in Fig. 2. YAG is one of the most frequently used host materials for crystalline solid-state lasers. However, visible lasing of Tb³⁺ ions doped into this host has not been achieved so far, as will be discussed in Sect. 2.5. Nevertheless, with a high crystal field depression (CFD) value of about $26.7 \times 10^3 \text{ cm}^{-1}$ [29], YAG is a useful representative to show the implications of crystalline materials with a high crystal field strength on the electronic transitions of Tb³⁺. The GSA cross section spectrum of Tb³⁺:YAG is shown in Fig. 2a. A pronounced Stark splitting is indicated by clearly separated narrow transition lines of the individual Stark sub-levels. These are spread over a spectral range broader than in other materials. Among the materials discussed here, the GSA cross sections of Tb³⁺:YAG in the cyan-blue are the highest, though they do not exceed $3.7 \times 10^{-22} \text{ cm}^2$. This low value—as mentioned above—is a result of the spin-forbidden nature of the corresponding transition $^7F_6 \rightarrow ^5D_4$. In the GSA spectra, one can also recognize broad and strong unstructured UV absorption bands which are caused by absorption into the lowest $5d$ bands. It is evident that, resulting from the strong crystal

field, the lowest $5d$ band of Tb³⁺:YAG starts at wavelengths around 345 nm, which is the lowest $4f$ - $5d$ energy gap of all materials under investigation here. This transition into the 9D state requires a spin-flip and therefore the absorption peaking around 325 nm is significantly weaker than the next $5d$ absorption bands found around 275 nm and below 250 nm, corresponding to spin-allowed transitions into 7D states.

The SE spectrum shows the typical emission pattern of Tb³⁺ with emission bands in the blue around 480 nm, in the green around 545 nm, in the yellow around 585 nm as well as in the red around 620 nm corresponding to transitions into the lower multiplets 7F_J with $J=6, 5, 4$, and 3 , respectively. The transitions into the multiplets with $J=2$ to 0 can also be found, though much weaker. For Tb³⁺:YAG the emission cross sections in the green are the highest among all materials presented here and peak at around $1.7 \times 10^{-21} \text{ cm}^2$, while none of the other transition cross sections exceeds $0.55 \times 10^{-21} \text{ cm}^2$.

Compared to YAG, LLF possesses a much lower crystal field depression value of $15.1 \times 10^3 \text{ cm}^{-1}$ [41], which is in the intermediate range of materials typically used as laser hosts. The GSA spectra shown in Fig. 2c still exhibit comparably high values of up to $3 \times 10^{-21} \text{ cm}^2$ around 485 nm, but the separation of the individual Stark sub-levels is not as pronounced as for YAG. Finally, the energetic gap between the $4f$ ground state and the lowest $5d$ levels is shifted to significantly higher values as evidenced by the strong absorption peak around 260 nm. The energetic position of the SE lines is not significantly changed compared to Tb³⁺:YAG. While the green emission is comparable, in particular the yellow emission lines of Tb³⁺:LLF (see Fig. 2d) exhibit significantly stronger transition cross sections than Tb³⁺:YAG.

LaF₃ with a crystal field depression value of $8.8 \times 10^3 \text{ cm}^{-1}$ [41] is an example for a low crystal field host. This is caused by the high coordination number of LaF₃, which can be considered to be 9 or 11 [42]. Moreover, the large difference of the ionic radii of Tb³⁺ and La³⁺ of about 20% causes local lattice distortions, resulting in a significant inhomogeneous broadening of the absorption and emission lines [43, 44]. The low crystal field and the broadening result in reduced peak GSA (Fig. 2e) and SE (Fig. 2f) cross sections for Tb³⁺:LaF₃, which amount to roughly half the values found for Tb³⁺:LLF. Moreover, the first transition to be clearly attributed to absorption into a $5d$ band is shifted to even shorter wavelengths below 235 nm, corresponding to a very large $4f$ - $5d$ energy gap.

Finally, CaF₂ provides a crystal field depression value of $16.5 \times 10^3 \text{ cm}^{-1}$, similar to LLF as also evidenced by the similar energetic position of the $5d$ absorption band in Fig. 2g. In contrast to LLF, in CaF₂ the trivalent Tb³⁺ ions substitute divalent Ca²⁺ ions. Despite co-doping with monovalent Na⁺ for charge compensation, the remaining

disorder in the crystal yields substantially inhomogeneously broadened transition lines of $(\text{Tb}^{3+}, \text{Na}^+):\text{CaF}_2$. This makes Tb^{3+} -doped CaF_2 suitable for wavelength tuning applications [19]. On the downside, this broadening comes at the expense of strongly reduced peak cross sections, which are the lowest among the presented host crystals. The GSA cross sections in the cyan-blue do not exceed $5 \times 10^{-23} \text{ cm}^2$, while the SE cross sections are comparable to those of $\text{Tb}^{3+}:\text{LaF}_3$ (see Fig. 2h).

In all materials, the $4f-4f$ GSA cross sections in the UV-A spectral range exceed those in the cyan-blue by more than a factor of five. As we will discuss in Sect. 2.4, this enables UV-pumped laser operation of Tb^{3+} -doped materials with reduced absorption lengths.

From Fig. 1 it is evident that potential acceptor levels for ESA and ETU are found in the spectral range between 35 and $42 \times 10^3 \text{ cm}^{-1}$ ($\sim 285\text{--}240 \text{ nm}$). Indeed, the GSA spectra exhibit numerous absorption peaks in this spectral range, mostly corresponding to transitions into levels of the $4f$ configuration, but in some materials also $5d$ acceptor levels are found in this range. The influence of these levels on ESA and ETU will be discussed in Sect. 2.5.

2.3 Fluorescence lifetime quenching of the upper laser level $^5\text{D}_4$

The spin-forbidden nature of the transitions from the upper laser level $^5\text{D}_4$ into the lower lying levels of the $^7\text{F}_j$

Fig. 3 Effective fluorescence lifetime of the $^5\text{D}_4$ multiplet of $\text{Tb}^{3+}:\text{LLF}$ for different doping concentrations (with data from [24]). The corresponding fluorescence decay curves were obtained under excitation by a 10 Hz OPO system providing 5 ns long excitation pulses. The black line acts as a guide to the eye with no physical meaning

configuration results in very long upper state lifetimes on the order of 5 ms. Figure 3 with data from our previous publication [24] shows the room temperature fluorescence lifetime of Tb^{3+} in the host LLF for different doping concentrations up to 100% Tb^{3+} , corresponding to LiTbF_4 . For concentrations up to 28 at. %, the fluorescence lifetime is nearly unchanged and remains at about 4.8 ms.

In contrast, for the stoichiometric crystal LiTbF_4 with the highest possible Tb^{3+} concentration in this matrix, the measured lifetime is quenched to about 2 ms. Due to the lack of crystals with Tb^{3+} doping concentrations between 30 at. % and 100 at.% one can only speculate about the onset of this quenching and the investigation of crystals with doping concentrations of around 50 at.% remains an important task to shine more light on this question.

The precise origin of this quenching is also unclear as there are no obvious cross relaxation channels from the emitting $^5\text{D}_4$ multiplet. One possible explanation is the quenching by energy transfer to foreign rare-earth ions, in particular Sm^{3+} , which was previously found in TbF_3 starting materials [45]. In any case, the use of starting materials with higher purities is worth being investigated in more detail in future.

To further investigate the origin of the reduced lifetime in highly doped samples, we performed excitation intensity dependent measurements (see Fig. 4). By utilizing a continuous-wave 2 ω -OPSL at 486.3 nm as the excitation source and chopping the beam at a low frequency of 40 Hz, we ensured that we reached the maximum excitation density achievable with the respective pump intensity.

For very low excitation densities of around 1 Wcm^{-2} a perfectly exponential decay of the fluorescence intensity with a fluorescence lifetime τ_f of 3.3 ms is observed. For increasing pump intensity an increasing deviation from a single exponential decay is observed, finally leading to a

Fig. 4 Fluorescence decay curves of LiTbF_4 for different excitation intensities. The sample was excited by a continuous wave 2 ω -OPSL emitting at 486.3 nm modulated by a 1:1 chopper at 40 Hz

fluorescence decay time as short as 1.2 ms in the first part of the decay curve at the highest pump intensity of 10^5 W cm^{-2} , which increases to 3.3 ms in the tail of the curve. Due to the strong contribution of the first part of the curve to the total number of decays, the effective lifetime for this curve also amounts to 1.2 ms. The data clearly show an inversion level dependent quenching process in LiTbF₄. Similar effects were also observed in other stoichiometric Tb³⁺-containing compounds, e.g., in TbF₃ and were interpreted in terms of exciton-exciton annihilation [46], corresponding to ETU in the terminology used here. These findings are also consistent with the observation, that lasing in TbF₃—with the highest possibly Tb³⁺-density of all fluorides—was only obtained for low output coupler transmissions below 0.5% [19]. Further investigations on these aspects will uncover more details on the nature of the quenching processes in Tb³⁺ and reveal critical interionic distances as identified e.g. for Nd³⁺-doped materials [47, 48] enabling to optimize the doping concentration in Tb³⁺-based gain materials. As discussed in Sect. 2.1 and illustrated by Fig. 1, ETU processes on the longer wavelength transitions are possible loss channels causing quenching at high inversion densities.

Considering the 4-level-laser scheme and intensities of several 100 W/cm² required to reach the lasing threshold in Tb³⁺ lasers [16, 24], we can assume that the actual fluorescence lifetime of highly Tb³⁺-doped samples under lasing conditions is longer than the value reported in [24] and shown in Fig. 3, because the population inversion is clamped at the laser threshold. Nevertheless, even considering the value of 2 ms, the resulting fluorescence quantum efficiency of Tb³⁺ in LiTbF₄ is higher than 40%, which is a remarkable value for such a large active ion density.

These results, however, do also show that the different values for the fluorescence lifetimes of highly Tb³⁺-doped materials reported in the literature have to be carefully interpreted as the experimental conditions may differ. For example, the effective fluorescence lifetime of LiTbF₄ reported in Ref. [24] (see Fig. 3) was obtained under pulsed excitation conditions. As a result of a higher inversion level in this experiment, it amounts to only 2.2 ms which is shorter than the value reported in Fig. 4. Table 1 summarizes the reported fluorescence lifetime values for various Tb³⁺-doped host crystals. For common fluoride host materials with moderate Tb³⁺ doping densities, fluorescence lifetimes around 5 ms are found; the only exception is Tb³⁺:CaF₂ co-doped with monovalent Na⁺, with a fluorescence lifetime as long as 7.1 ms. In the case of stoichiometric Tb³⁺ containing fluoride crystals, the observed fluorescence decay times are typically shorter and found to be in the range between 2 and 3 ms. Among these stoichiometric materials KTb₃F₁₀ (KTF) stands somewhat out with its long fluorescence lifetime [49], which we confirmed to be about 4.3 ms, which is still comparable to the lifetime of the isostructural low

Table 1 Fluorescence lifetime τ_f of Tb³⁺ doped into different host materials

Host	Doping (at. %)	Cation density (10^{22} cm^{-3})	CFD (10^3 cm^{-1})	τ_f (ms)
BaY ₂ F ₈	13	0.168	16.0	5.2
Na ⁺ :CaF ₂	10	0.245	16.5	7.1
LaF ₃	12	0.219	8.8	5.5
LiLuF ₄	28	0.403	15.1	4.9
LiYF ₄	16	0.220	15.3	5.0
KY ₃ F ₁₀	17	0.265	16.1	4.9
KTb ₃ F ₁₀	100	1.56	16.1	4.3
LiTbF ₄	100	1.36	15.1	3.3
TbF ₃	100	2.02	—	2.5
Y ₃ Al ₅ O ₁₂	14	0.190	26.7	3.1
YAlO ₃	9	0.177	16.5	1.9
YAl ₃ (BO ₃) ₄	35	0.206	18.3	1.7 ^a
KY(WO ₄) ₂	53	0.382	—	0.35 ^b
SrAl ₁₁ O ₁₉	14	0.048	11.1	4.2 ^d
Ba ₃ Tb(PO ₄) ₃	100	0.35	17.6	3.17 ^c

To present data recorded under identical conditions all data were re-measured for this work unless referenced otherwise. ^a[37], ^b[39], ^c[34], ^d[53]

doped Tb³⁺:KY₃F₁₀ of 4.9 ms (see Table 1). This cubic crystal is highly interesting for the application in optical isolators [50–52]. During our recent investigations in this respect we studied several crystals from different supplies as well as in-house grown crystals fabricated from high purity and thoroughly fluorinated (i.e. oxide impurity free) starting materials. We found the lifetime of the Tb³⁺ ions in KTF to be strongly dependent on the purity of the starting materials. While this observation on itself does not allow to draw strong conclusions, we assume that also in other highly doped or even stoichiometric Tb³⁺-containing crystals improved fluorescence quantum efficiencies can be obtained by utilizing high quality starting materials.

The situation is somewhat different in oxide host materials. Their larger crystal field strengths [29, 41], increase both, symmetric and asymmetric terms of the crystal field, which are responsible for the crystal field splitting and the transition probability, respectively. As a consequence, the radiative lifetimes of rare earth ions in oxide hosts are in general shorter than in fluoride crystals. For the oxide crystals shown in Table 1, the fluorescence lifetimes are below 3.2 ms in all cases. The only exception is Tb³⁺:SrAl₁₁O₁₉, which exhibits a very high coordination number of 12, causing a large distance between the dopant and the ligands and resulting in a weak crystal field with a relatively high symmetry. In consequence, its lifetime of 4.2 ms is nearly comparable to the values found in fluoride crystals. Unfortunately, the corresponding transition cross sections are very low. In combination with the low possible maximum Tb³⁺

doping concentration, this material does not appear to be a suitable laser host for Tb^{3+} ions [53].

2.4 Resonant cross relaxation $^5\text{D}_3 \rightarrow ^5\text{D}_4 / ^7\text{F}_6 \rightarrow ^7\text{F}_{0,1}$ and prospects of UV pumping

Despite the very complex energy level scheme of Tb^{3+} (cf. Section 2.1), there is only one obvious cross relaxation channel in Tb^{3+} as indicated by the dashed grey arrows in Fig. 1. During this cross relaxation process an excited ion relaxes from the $^5\text{D}_3$ into the $^5\text{D}_4$ multiplet, while a neighbouring ion is excited from the ground state $^7\text{F}_6$ into the $^7\text{F}_0$ or $^7\text{F}_1$ energy levels. The energetic difference between both transitions corresponds to $\sim 5500 \text{ cm}^{-1}$. This cross relaxation was already mentioned in one of the first reports on Tb^{3+} -based lasers [10]. Later reports found it to be predominantly of dipole–dipole character and temperature insensitive in $\text{Tb}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$. Already for low doping concentrations of 2.7 at.%, i.e. a Tb^{3+} density of $3.8 \times 10^{20} \text{ cm}^{-3}$, the emission from the $^5\text{D}_3$ level was significantly quenched and the relative quantum yield of the $^5\text{D}_4$ emission under UV excitation reached 0.97 in this experiment, which reveals the efficiency of the cross relaxation [33]. There are various further reports on this process, but it is not the purpose of this section to review it in all detail. Instead, its relevance for possible laser schemes will be discussed here. For pumping at 488 nm into the $^5\text{D}_4$ multiplet this process can be neglected, as the pump photon energy is not sufficient to populate the $^5\text{D}_3$ multiplet at all. However, the early investigations showed that even at low doping levels cross relaxation efficiently populates the upper laser level $^5\text{D}_4$ following excitation of the $^5\text{D}_3$ level with UV light.

As illustrated in Fig. 5a, even excitation at wavelengths shorter than 380 nm will result in a quick thermalization into the $^5\text{D}_3$ level. Without a cross relaxation process, the energy gap to the $^5\text{D}_4$ level is large enough to effectively prevent multiphonon decay into this level. Thus, one can expect fluorescence at wavelengths between 380 and 460 nm in the UV/VIS range. As the $^5\text{D}_3 \rightarrow ^5\text{D}_4$ radiative transition probability is very low [54], the intensity ratio of the $^5\text{D}_3$ fluorescence vs. the $^5\text{D}_4$ fluorescence can be taken as a measure for the relative steady-state population of these levels. Consequently, the relative change of the UV fluorescence intensity with increasing doping enables conclusions on the concentration dependency of the cross relaxation process.

Indeed, under 353 nm excitation UV fluorescence can be clearly seen in Fig. 5b for the crystal with the lowest doping concentration of 2 at.%, corresponding to a Tb^{3+} density of $2.9 \times 10^{20} \text{ cm}^{-3}$. However it is already weaker than the integrated fluorescence intensity from the $^5\text{D}_4$ level, indicating that significant cross relaxation populates the latter already at such low doping concentrations. At a doping concentration of 14 at.% the intensity of the UV fluorescence is further reduced by about two orders of magnitude and at the highest doping level of 28 at.% the $^5\text{D}_3$ fluorescence in the UV is reduced to only slightly above the detection limit of our setup. At the same time, the fluorescence lifetime of the $^5\text{D}_3$ level measured at around 410 nm is quenched by four orders of magnitude from nearly 1 ms for 2 at.% doping to few tens of ns for 28 at.% doping (cf. Figure 6).

These results indicate a very efficient energy transfer to the upper laser level upon UV excitation by the resonant cross relaxation mechanism $^5\text{D}_3 \rightarrow ^5\text{D}_4 / ^7\text{F}_6 \rightarrow ^7\text{F}_{0,1}$ resulting in more than 99% of the fluorescence being emitted from the

Fig. 5 **a** Energy level scheme and possible decay channels of Tb^{3+} upon UV excitation. **b** Normalized and polarization averaged logarithmic fluorescence intensity spectra for three $\text{Tb}^{3+}:\text{LLF}$ crystals

with different doping concentrations of 2, 14, and 28 at.% after excitation at 353 nm. The background colors in both images indicate transitions starting from the same multiplet

Fig. 6 Fluorescence lifetime of the $^5\text{D}_3$ multiplet under 353 nm excitation for LLF crystals of three different doping concentrations. The black solid line acts as a guide to the eye

$^5\text{D}_4$ level for the two higher doping concentrations. To further confirm the efficiency of this mechanism independent of the excitation wavelength, we performed excitation spectroscopy (see Fig. 7). The fluorescence intensity at 545 nm was recorded while the excitation wavelength was scanned between 325 and 515 nm. In both polarizations the excitation spectrum closely follows the absorption spectrum, which shows that the number of green photons generated per pump photon is mainly determined by the absorption efficiency and—due to the efficient cross relaxation process—not or only marginally by the pump wavelength itself.

The Stokes efficiency between pumped and emitted photons decreases with decreasing pump wavelength. Due to the significantly higher absorption of Tb^{3+} in the UV, the fluorescence signal intensity is still much higher under UV pumping and the maximum is found at an excitation

Fig. 7 π -polarized absorption spectrum (black) and excitation spectrum (red) of Tb^{3+} (14 at.%)LLF detected at 545 nm

wavelength of 359 nm as indicated by the purple bar in Fig. 7.

Consequently, we performed laser experiments under pumping at 359 nm using a frequency-doubled continuous wave Ti:sapphire laser. The details of this work are presented in [22], but our main focus here is on the comparison with laser results using a 2ω -OPSL pump source emitting at 486.3 nm (cyan-blue bar in Fig. 7) obtained under almost identical conditions. In the latter case, an 11 mm long Tb^{3+} (14 at.%)LLF crystal yields a slope efficiency of 26% at 587 nm versus the *absorbed* pump power. In contrast, this value is reduced to 20% under 359 nm UV pumping. The main reason for this discrepancy is the reduced Stokes efficiency under UV pumping (61% vs. 83% under 486.3 nm pumping). However, Fig. 8 shows the laser performance versus the incident pump power. One can immediately recognize that due to the significantly increased absorption efficiency, UV pumping reduces the threshold by more than a factor of two and the slope efficiency vs. incident power is more than twice as high under UV pumping. Consequently, the optical-to-optical efficiency for pumping at 359 nm is more than doubled compared to cyan-blue pumping. This effect would be even more pronounced using shorter crystals, which is desirable for pumping with lower beam quality laser diodes with high output powers.

Despite the significantly higher energy of the pump photons, degradation of the optical properties of the laser crystal in these initial experiments, e.g. by color center formation, was not observed and the laser output under 359 nm pumping was stable for a total of several tens of hours [22].

2.5 Excited state absorption channels

Excited state absorption, i.e. absorption from a metastable excited state into higher lying energy levels, is usually

Fig. 8 Laser performance of an 11 mm long Tb^{3+} (14 at.%)LLF at an output coupler transmission of 1.7% vs. incident pump power for two different pump wavelengths

detrimental for a laser. It reduces the achievable gain and thus may ultimately prohibit lasing even at low ESA cross sections. In Tb^{3+} the situation is even more complicated as intra- and interconfigurational transitions as well as a change of the spin quantum number required for several transitions significantly impact the probabilities for the respective transitions. In the following we will first give a short introduction into the particular situation of ESA in Tb^{3+} before we present spectroscopic measurement results on possible ESA on pump and laser wavelengths in this ion.

Figure 9 shows the energy level diagram and the absorption cross sections of $\text{Tb}^{3+}:\text{LLF}$. It can be seen that all black horizontal lines indicating $4f$ energy levels correspond to narrow absorption lines of different intensity in the GSA spectrum, while the purple bars for the $5d$ energy levels correspond to broader and stronger absorption bands. The arrow marked with 1 indicates the typical cyan-blue pump wavelength of 488 nm. As can be seen from the right part of Fig. 9, for the corresponding transition a change of the spin quantum number, thus a spin-flip, from 7 to 5 is required. The corresponding transition is thus spin-forbidden and exhibits low cross sections. Moreover, it is an intraconfigurational transition within the $4f$ shell, which is—according to the Laporte rule [55]—parity forbidden. In consequence, the probability for this transition is very low and the corresponding absorption cross sections are very low. The arrow marked with two indicates a transition from the ground state into the lowest energy level of the $5d$ configuration. This interconfigurational transition is not parity forbidden and should exhibit orders of magnitude stronger transition cross

sections than $4f$ - $4f$ transitions. However, also for this transition a spin-flip is required and thus the transition cross sections are still moderate. In contrast, the transition indicated with 3 is parity- and spin-allowed and the corresponding absorption is very strong. The arrows labelled with the numbers 4, 5 and 6 indicate ESA transitions.

For these transitions we have to consider that the only suitable ESA starting level is the upper laser level $^5\text{D}_4$. As we discussed in the previous section, at the doping concentrations required for lasing, no other level has a sufficiently long lifetime to enable significant population that allows for ESA. While all $4f$ energy levels shown above $20 \times 10^3 \text{ cm}^{-1}$ in Fig. 9 including the upper laser level are quintet states, none of the $5d$ energy levels are quintet states. This has the surprising consequence, that the spin-forbidden but parity allowed ESA indicated by the arrow labelled with four has similar transition probabilities than the parity forbidden, but spin-allowed intraconfigurational $4f$ - $4f$ -transitions indicated by the arrows labelled with five. Finally, the transitions into the lowest energy level of the $5d$ configuration indicated by the arrow labelled with six require a double spin-flip and are thus even more unlikely. Therefore, as opposed to previous belief, the lowest energy levels of the $5d$ configurations are nearly negligible for the laser process, otherwise lasing in the green would be strongly hampered. In contrast, for the example of $\text{Tb}^{3+}:\text{LLF}$ interconfigurational $4f$ - $5d$ ESA should not occur at wavelengths above 400 nm, which is indicated by the energy gap of $25 \times 10^3 \text{ cm}^{-1}$ spanned by the corresponding arrow labelled with four. However, the situation may be different in materials with a stronger crystal field,

Fig. 9 Energy level scheme and GSA spectrum of $\text{Tb}^{3+}:\text{LLF}$ with selection rules and corresponding trends for the transition strengths of the respective GSA and ESA transitions

yielding a stronger depression of the $5d$ states, which—unlike the $4f$ shell—are not shielded by outer shells and thus strongly interact with the crystal field.

This is evidenced by Fig. 10, where we show the SE from the upper laser level 5D_4 in the positive range of the graph and the UV GSA in the negative range. The energetic difference between same positions on the upper and lower wavelength scale was chosen to correspond to the energy of the 5D_4 level ($\sim 20.55 \times 10^3 \text{ cm}^{-1}$). Therefore, this plot directly shows the UV levels relevant for possible ESA in the vicinity of the main SE peaks of Tb³⁺ (see also Fig. 9).

From Fig. 10a one can expect by the spectral match that the green emission around 545 nm could be subject to strong ESA into the lowest $5d$ level. However, this transition is double spin-forbidden (cf. Figure 9). For the yellow emission around 580 nm one can see a weak overlap with a narrower $4f$ line which might influence the laser performance. Finally, the red emission around 620 nm perfectly overlaps with a $4f$ ESA absorption line, so that efficient laser operation appears

range around 250 nm, in Tb³⁺:LLF (Fig. 2c) only the strong $5d$ band is seen, but in Tb³⁺:LaF—due to its weaker crystal field—this $5d$ band is shifted to below 230 nm and reveals ‘hidden’ $4f$ lines, which are less sensitive to the crystal field and thus do not change significantly in energy.

2.5.1 Excited state absorption at laser wavelengths

The presence of excited state absorption is detected by measuring the transmission characteristics of a crystal pumped into the level of interest. This pump-probe measurement is similar to a gain measurement, and indeed gain may amplify the probe beam, while ESA attenuates it. ESA and gain can take place at the same wavelength, thus a negative signal indicates dominating ESA, while for a positive signal the gain is stronger. The calibration of the signal to ESA cross sections requires a GSA or SE transition at wavelengths free of ESA. Unfortunately, all transitions in Tb³⁺ could be subject of ESA due to its complicated energy level scheme.

Figure 10 SE (positive signal) and UV GSA (negative signal) cross section spectra of **a** Tb³⁺:LLF and **b** Tb³⁺:YAG.

unlikely. Notably, one can also expect an effect of ESA in the blue, which may affect the pump. In contrast, the $5d$ bands in Tb³⁺:YAG are so strongly depressed, that the whole visible emission overlaps with the single spin-forbidden $5d$ ESA into the 7D level, which can be expected to inhibit lasing completely. While these considerations are very useful to make first estimations about the possible laser performance, direct ESA measurements are required to quantitatively determine the transition probabilities for the respective transitions. As an example, the comparison of Fig. 2c, e shows that strong $5d$ GSA absorption bands can overlap with weak $4f$ GSA absorption bands, which then cannot be seen in the GSA spectra, but may be more relevant for ESA. In the

Consequently, the signal referred to as ‘ESA signal’ in our measurements is actually the gain cross sections minus the ESA cross sections in arbitrary units. Details on the methodology used for the measurements shown here are found in [56].

Despite this drawback, we performed polarization dependent pump-probe measurements on Tb³⁺(14 at.):LLF as shown in Fig. 11 to further confirm the qualitative picture discussed above. For comparison, the figure also shows the stimulated emission signal normalized to the 545 nm peak of the ESA signal.

The strongest optical gain (i.e. positive ESA signal) is found in the green spectral range around 545 nm. It mainly

Fig. 11 ESA signal (blue) and stimulated emission cross sections (red) of Tb^{3+} (14 at. %):LLF in the range of possible laser wavelengths

follows the shape of the corresponding stimulated emission, which proves the absence of $4f$ - $4f$ ESA, but a weak broad band $4f$ - $5d$ ESA cannot be fully excluded. In contrast, the gain in the yellow around 585 nm—in particular in π -polarization—is significantly lower than the stimulated emission, which indicates an influence of ESA. However, the signal is still positive and lasing can be expected. This measurement confirms the conclusions drawn from Fig. 10 and explains the generally lower laser efficiency of the yellow compared to the green laser transition in Tb^{3+} -based lasers. It should, however, be noted that different host crystals may result in slightly shifted positions of the corresponding $4f$ absorption line, which could contribute to greatly improving the efficiency of the yellow laser. The situation is different around 620 nm. While the height of the SE peaks is comparable to that of the yellow, the ESA signal hardly shows any positive amplitude, which must be caused by strong ESA.

Finally, around 680 nm a strong negative signal is found, which indicates ESA cross sections much stronger than the stimulated emission in this range. It is remarkable that except for the peak around 600 nm ESA is only found at wavelengths, where also stimulated emission takes place. This strong resonance favours ETU processes and might explain the inversion level dependent quenching process found in LiTbF_4 in Sect. 2.3.

Interestingly, the cross sections for $5d$ ESA into the ^9D state seem to be very low, even though this level would be within reach for ESA from the upper laser level and should cause a broad negative background signal. This strongly relaxes the requirements on the crystal field depression value of the host material and even oxide hosts possessing larger crystal field depression values might be suitable hosts for Tb^{3+} .

2.5.2 Excited state absorption at cyan-blue pump wavelengths

The energy level scheme of Tb^{3+} gives also rise to ESA in the region of the cyan blue pump wavelengths around

488 nm. However, it is not straight-forward to record the spectrum of the ESA signal in this wavelength range as the pump signal cannot be separated from the probe signal. To avoid this effect, in the measurements shown in Fig. 12a the upper laser level $^5\text{D}_4$ was populated via pumping at 359 nm and successive cross relaxation. Due to the high efficiency of this process, the population of the $^5\text{D}_3$ multiplet is very low and ESA from this level can be safely excluded. Therefore, this measurement gives reliable insights into possible ESA in the spectral range relevant for cyan-blue pumping.

However, in particular at the pump wavelength the data must be interpreted carefully. Here, due to the measurement conditions [56], bleaching of the GSA contributes to the ESA signal and might be even misinterpreted as gain. Nevertheless, a few strong ESA transitions can be identified unambiguously, with the most relevant transition at about 490 nm very close to the main absorption peak.

To assess the presence of ESA at possible pump wavelengths, we detected the UV/VIS fluorescence at wavelengths below 460 nm emitted from the $^5\text{D}_3$ multiplet in a low doped Tb^{3+} (2 at. %):LLF crystal. As seen in Fig. 5 b), the quenching of the $^5\text{D}_3$ fluorescence is rather weak in this crystal and energy migration processes such as ETU are also unlikely. On the other hand, emission from this level upon blue excitation must be the result of ESA. Thus, the intensity of the $^5\text{D}_3$ fluorescence is a useful measure for the strength of ESA at blue pump wavelengths. Figure 12b shows this fluorescence for two different π -polarized pump wavelengths of 479 nm and 486.3 nm. Despite the much lower absorption at 479 nm, under the same incident pump power the $^5\text{D}_3$ fluorescence intensity increases by an order of magnitude which confirms strong ESA at 479 nm, but also weak ESA at 486.3 nm. With increasing 479 nm pump power we even found the absorption efficiency of the crystal to increase by more than an order of magnitude. To understand this, we must remember that following the ESA most of the energy is transferred back into the $^5\text{D}_4$ level via thermalization and cross relaxation from the $^5\text{D}_3$ level. Therefore, the population of the $^5\text{D}_4$ is increasing despite ESA, which—at ESA

Fig. 12 **a** Polarized ESA signal of a Tb^{3+} (14 at. %):LLF crystal around 490 nm and GSA spectra. **b** Polarization averaged fluorescence from the $^5\text{D}_3$ level obtained under excitation of the $^5\text{D}_4$ level at 479 nm (red) and 486.3 nm (black) in Tb^{3+} (2 at. %): LiLuF_4

cross sections much stronger than the GSA (see Fig. 12a)—results in the observed nonlinear increase of the absorption at high pump intensities. Unfortunately, this process comes with a significant heating of the sample.

2.5.3 Excited state absorption at UV pump wavelengths

With respect to the investigation of the most suitable UV pumping scheme (see Sect. 2.4) we also discuss ESA in the range of possible UV pump wavelengths. According to the laser results presented in [22], at a pump wavelength of 359 nm the influence of ESA can be expected to be low. However, this wavelength is not yet covered by suitable semiconductor laser diodes. In contrast, diodes with emission in the wavelength range between 370 and 385 nm are more mature (see e.g. [57]) and may thus be better suited for diode-pumped laser operation of Tb^{3+} . The ESA signal shown in Fig. 13 indicates that in Tb^{3+} :LLF significant ESA is only present around 370 nm. The corresponding transition is relatively broad and can be attributed to ESA into the ^7D levels of the 5d configuration,

possibly with underlying 4f levels. From these findings, one could conclude that ESA in the range of available UV pump laser diodes may hinder the development of UV-diode-pumped solid-state lasers based on Tb^{3+} . However, we would like to remind here, that the energetic position of the ^7D level of the 5d configuration can be shifted by a proper choice of the host material.

Fig. 13 ESA signal of a 14% doped Tb^{3+} :LLF crystal in the range of possible UV pump wavelengths and corresponding GSA spectra (with data from [19])

3 Conclusion

We have reviewed the spectroscopic properties of Tb^{3+} in different host materials with respect to its application as a laser ion for visible lasers with emission in the green and yellow spectral range. Our findings reveal several peculiarities of this novel laser ion. Current state-of-the-art Tb^{3+} lasers operate at slope efficiencies around 60% in the green and 25% in the yellow. These results are among the most efficient laser transitions in their respective wavelength ranges, but the performance is still well below the Stokes limit in excess of 80% for both transitions. Even

though not all processes limiting the laser performance are fully understood, yet, we believe that optimized pump wavelengths, increased doping concentrations and the choice of more suitable host materials can contribute to further improving the laser performance of Tb^{3+} based gain materials.

In particular the investigation of novel host crystals bears significant potential. For the up to now most efficient host materials YLF and LLF, intraconfigurational $4f-4f$ ESA significantly reduces the laser efficiency on the yellow transition and completely prevents laser operation in the red. The reason is an accidental, but almost perfect spectral match of the main SE peaks with ESA in these hosts. With this finding it is surprising, that YLF and LLF enabled the best laser performance so far. At the same time, it motivates the investigation of alternative host materials with a stronger Stark splitting of the individual multiplets to shift the stimulated emission peaks away from the corresponding ESA transition or vice versa. On the other hand, it is evident that a shift of the ^7D state of the $4f^75d^1$ configuration to values within reach for parity allowed ESA on the pump or laser wavelength is strongly detrimental for the laser performance. We assume that crystal field depression values up to $21 \times 10^3 \text{ cm}^{-1}$ could still be sufficiently low to prevent this effect. Notably, various oxide host materials provide crystal field depression values in this range [29]. These would usually provide improved thermal and mechanical properties, which is beneficial for further power scaling of Tb^{3+} based lasers.

One obvious drawback of Tb^{3+} is the spin-forbidden nature of all transitions relevant for the laser process, leading to very low cross sections of ground state absorption and stimulated emission. However, this can be compensated to a large extent by utilizing higher doping levels. Whereas for Nd^{3+} or Pr^{3+} typical cross sections are the range of 10^{-19} – 10^{-20} cm^2 , the doping concentration of these ions is usually limited to below 1 at.% to avoid strong quenching. In contrast, even stoichiometric Tb^{3+} containing compounds enable lasing and achieve absorption efficiencies comparable to those of 1 at.% Pr^{3+} or Nd^{3+} doped crystals. Further research is required to find the best suited Tb^{3+} doping concentrations for efficient lasing. In particular, crystals with doping concentrations between ~30 at.% and 100 at.% are not investigated, yet. This shows that there is a strong potential to reduce the required gain material length for efficient operation of Tb^{3+} -based lasers. In particular when pumping with low beam quality high power laser diodes such short laser crystals are indispensable. The absorption efficiency can be even further improved by making use of several times higher absorption cross sections in the UV range for pumping. As an example, even a 2 mm short 50 at.% Tb^{3+} -doped crystal exhibits more than 90% single pass

Fig. 14 Tentative future development schedule of Tb^{3+} -based lasers

absorption efficiency at several pump wavelengths between 350 and 380 nm.

With all these improvements, we can predict some possible future developments in the field of Tb^{3+} based lasers (see Fig. 14). Already at the current state of the art, multi-mode laser diodes with up to 2 W of output power are commercially available at wavelengths around 488 nm [57]. At the efficiencies of Tb^{3+} lasers reported hitherto, this should allow for few hundred mW of output power from green and yellow emitting Tb^{3+} -based diode-pumped solid-state lasers (DPSSLs), enough to achieve tens of mW in the UV at wavelengths of 273 nm or 293 nm by intra-cavity frequency doubling.

An even stronger potential is seen in Q-switched operation: Due to the higher photon energy and much lower cross sections, the saturation energy of Tb^{3+} :YLF is more than two orders of magnitude higher than e.g. for Nd :YLF, which should enable the generation of high energetic pulses. With a careful adjustment of the saturable absorber parameters e.g. of $\text{Co:MgAl}_2\text{O}_4$ [23, 26] in passive Q-switching or by active Q-switching [27, 28], kW peak powers are within reach from such lasers. The combination of further increased doping concentrations and the use of UV diodes as pump sources will enable to reduce the thickness of the gain media to below 2 mm. It should also be noted, that meanwhile up to 6 W of output power are available around 375 nm from laser diode modules [57]. Such short gain media may allow to further reduce the pulse duration to few 10 ns while even further increasing the peak power in microchip geometry Tb^{3+} lasers. Ultimately, Tb^{3+} -based lasers have the potential for UV-pumped DPSSLs with kW peak power and few 10 ns pulse duration in the UV-B and UV-C range.

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Declarations

Conflict of interest The authors have no conflicts of interest to declare that are relevant to the content of this article.

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