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Emission properties of Tm^{3+}-doped CaF$_2$, KY$_3$F$_{10}$, LiYF$_4$, LiLuF$_4$ and BaY$_2$F$_8$ crystals at 1.5 µm and 2.3 µm

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Abstract. Thulium ions (Tm^{3+}) are known for their emissions in the near- and mid-infrared spectral ranges suitable for efficient laser operation. We systematically study the stimulated-emission cross-sections σ_{SE} for the $^3H_4 \rightarrow {}^3F_4$ (at ~1.5 µm) and $^3H_4 \rightarrow {}^3H_5$ (at ~2.3 µm) Tm^{3+} transitions in five low-phonon energy fluoride single-crystals, namely, cubic Tm:CaF$_2$ and Tm:KY$_3$F$_{10}$, tetragonal Tm:LiYF$_4$ and Tm:LiLuF$_4$ and monoclinic Tm:BaY$_2$F$_8$. A promising material is Tm:BaY$_2$F$_8$ which offers broad and intense polarized emission spectra in the mid-infrared (2251 to 2452 nm); the maximum σ_{SE} is 0.39×10^{-20} cm^2 at 2289 nm (for $E \parallel Z$) and the emission bandwidth is exceeding 100 nm (for $E \parallel X$). We also revise the transition probabilities for Tm^{3+} ions in LiLuF$_4$ and BaY$_2$F$_8$ crystals using the Judd-Ofelt formalism and accounting for an intermediate configuration interaction (ICI).

Keywords: fluoride crystals; thulium ions; spectroscopy; stimulated-emission; Judd-Ofelt theory.

1. Introduction

Rare-earth ions (RE^{3+}) are attractive for achieving laser emission in the near and mid infrared (IR) spectral ranges. A clear example is the thulium ion (Tm^{3+}) with the electronic configuration [Xe]4f^{12}. The Tm^{3+} ion is known for its eye-safe emission at ~1.9 μm [1] due to the transition from the lowest-lying metastable excited-state, $^3F_4 \rightarrow {}^3H_6$, Fig. 1. Due to the typically large Stark splitting of the $^3H_6$ ground-state ($\Delta E = 419$ cm^{-1} for Tm:LiYF$_4$ [2]), Tm^{3+}-doped materials provide broadband emissions which are favorable for wavelength-tunable [3] and ultrashort-pulse mode-locked (ML) lasers [4]. Tm^{3+} ions can be efficiently excited at ~0.8 μm, e.g., by commercial AlGaAs laser diodes, according to the $^3H_6 \rightarrow {}^3H_4$ transition [5]. The cross-relaxation (CR) process for neighboring Tm^{3+} ions, $^3H_4 + {}^3H_6 \rightarrow {}^3F_4 + {}^3F_4$, is efficient at moderate Tm^{3+} doping levels. It enhances the pump quantum efficiency for ~1.9 μm lasers up to 2 and reduces the unwanted heat dissipation [6].

Less common but interesting for applications, transitions of Tm^{3+} ions also originate from the $^3H_4$ state, at ~1.5 μm ($^3H_4 \rightarrow {}^3F_4$) [7-10] and ~2.3 μm ($^3H_4 \rightarrow {}^3H_5$) [11-17], Fig. 1. The laser emission at the eye-safe wavelengths around 1.5 μm (in the near-IR) is suited for telecom, range-finding and remote sensing applications. The emission at ~2.3 μm spectrally falls into the mid-IR spectral range known as a molecular fingerprint region; it is thus of practical importance for remote sensing of atmospheric species (such as CO, H$_2$CO or CH$_4$) [18,19], infrared countermeasures and non-invasive glucose (C$_6$H$_{12}$O$_6$) blood measurements [20]. 2.3 μm lasers can be also potentially used as optical pump sources of mid-IR semiconductor lasers and OPOs.

The development of ~2.3 μm Tm lasers is constrained by the search of a suitable gain material. The obvious limitation is the lifetime of the $^3H_4$ level (energy gap to the lower-lying state: ~4100 cm^{-1}). It can be seriously quenched by the multiphonon non-radiative (NR) relaxation, so that the low-phonon energy materials accommodating Tm^{3+} ions are preferable. Fluoride crystals appear as excellent candidates for this aim, as they (i) provide relatively low phonon energies, 400-500 cm^{-1}, leading to weak NR relaxations [21], (ii) have good thermal properties [22] allowing for power scaling [23], (iii) have a broad transparency range and small refractive indices [24], (iv) exhibit long emission lifetimes favorable for energy storage [25], and (v) can be generally doped with large amounts of Tm^{3+} dopants [26].

Among the fluoride laser host crystals, the most developed ones for Tm^{3+} doping are CaF$_2$ [27], KY$_3$F$_{10}$ (both cubic) [28], LiYF$_4$ [29], LiLuF$_4$ (both tetragonal) [30] and BaY$_2$F$_8$ (monoclinic) [31]. In the present work, we limit our considerations to these crystals. Efficient lasers based on these Tm^{3+}-doped fluoride crystals operating on the $^3F_4 \rightarrow {}^3H_6$ transition at ~1.9 μm [27-31] have been already reported. Other crystal compositions such as SrF$_2$, LiGdF$_4$ or KYF$_4$ are known for Tm^{3+}-doping [32-34] while they are rarely used.

Regarding the ~2.3 μm lasers based on Tm^{3+}-doped fluoride crystals, the previous studies focused mainly on the Tm:LiYF$_4$ one, which may be explained by its well-developed growth procedure by the Czochralski (Cz) method [35]. Pinto *et al.* demonstrated the first CW Tm:LiYF$_4$ laser generating 0.22 W at 2.30 μm with a slope efficiency of 15% and a continuous wavelength tunability over the 2.20–2.46 μm range [12]. Loiko *et al.* reported on

power scaling of a similar laser (up to 0.73 W at 2.306 μm) and improvement of the slope efficiency (up to 47.3%) [36]. This was referred to a positive action of energy transfer upconversion (ETU) process, $^3F_4 + {}^3F_4 \rightarrow {}^3H_6 + {}^3H_4$ (Fig. 1), recycling the population of the $^3H_4$ level at high pump intensities. Alternative pumping schemes for ~2.3 μm Tm:LiYF$_4$ lasers were proposed either relying on Yb^{3+},Tm^{3+} codoping (for pumping at ~0.98 μm) [8,37] or based on upconversion pumping and the photon avalanche mechanism (for pumping at ~1 μm or ~1.5 μm) [38,39].

The limited selection of fluoride laser crystals for ~2.3 μm Tm lasers can be attributed to the lack of spectroscopic information about transitions originating from the $^3H_4$ state, and, in particular, the stimulated-emission (SE) cross-sections for principal light polarizations. SE cross-sections, CR and ETU parameters of Tm:LiYF$_4$ crystal were recently reported [36]. Braud *et al.* analyzed the energy-transfer properties of Yb^{3+},Tm^{3+}-codoped KY$_3$F$_{10}$, LiYF$_4$ and BaY$_2$F$_8$ for laser operation at ~1.5 μm and ~2.3 μm [9]. CW laser emission at ~2.3 μm was recently reported in Tm:KY$_3$F$_{10}$ however without the complete spectroscopic information around 1.5 and 2.3 μm [39,40].

In the present work, we aim to perform a comparative spectroscopic study of the main fluoride crystals intended for Tm^{3+} doping, namely, CaF$_2$, KY$_3$F$_{10}$, LiYF$_4$, LiLuF$_4$ and BaY$_2$F$_8$, regarding their stimulated emission (SE) properties at the $^3H_4 \rightarrow {}^3F_4$ and $^3H_4 \rightarrow {}^3H_5$ transitions, which is a prerequisite for further development of mid-infrared light sources.

2. Materials

2.1. Crystal growth

The Tm:KY$_3$F$_{10}$, Tm:LiYF$_4$, Tm:LiLuF$_4$ and Tm:BaY$_2$F$_8$ crystals were grown by the Czochralski (Cz) technique using a resistive heating furnace. The starting materials were prepared from a stoichiometric mixture of KF (or LiF, or BaF$_2$), YF$_3$ (or LuF$_3$) and TmF$_3$ powders with a 4N purity. They were thoroughly mixed and the mixtures were placed into a glassy carbon crucible. The chamber was evacuated to a pressure of 10^{-5} mbar and the crucible was heated to the temperature of 450 °C for 24 h to remove oxygen impurities. Then, the chamber was filled with high-purity Ar and CF$_4$ gases until reaching atmospheric pressure and the crucible was heated up to the melting temperature for few hours. The crystal growth was carried out using an oriented seed of a corresponding undoped crystal. The pulling rate was 1 – 3 mm/h.

In the case of Tm,Y:CaF$_2$, the crystal was grown by using a conventional Bridgman technique. A mixture of CaF$_2$, YF$_3$ and TmF$_3$ powders (purity: 4N) was placed in a graphite crucible within the growth chamber. A good vacuum ($<10^{-5}$ mbar) was then realized before introducing the Ar and CF$_4$ gases to reduce oxygen and water pollution. The crystal growth was carried out with a pulling rate of 3-5mm/h.

After completing the growth process, the grown crystals were cooled down to room temperature within 48 h.

For the spectroscopic studies, we used the crystals with the following composition: 1.5 at.% Tm, 4 at.% Y:CaF$_2$, 5.0 at.% Tm:KY$_3$F$_{10}$, 3.0 at.% Tm:LiYF$_4$, 9.3 at.% Tm:LiLuF$_4$ and 0.5 at.% Tm:BaY$_2$F$_8$. Here, the actual doping concentrations (in the crystal) are specified.

2.2. Crystal structure

The KY_3F_{10} crystals are cubic (fluorite-type structure, sp. gr. O^5_h - $Fm3^-m$). In the structure of KY_3F_{10}, there is one type of substitutional rare-earth ion site: the Y^{3+} one, with the local site symmetry C_{4v} [41]. The lattice constant of undoped KY_3F_{10} is $a = 11.553$ Å.

The CaF_2 crystals possesses the same structure (sp. gr. O^5_h - $Fm3^-m$) but the Tm^{3+} sites in CaF_2 are more complicated because of the charge compensation required [42]. In general, the Tm^{3+} ions replace for the Ca^{2+} cations while the charge compensation is achieved by interstitial F^- anions. We will consider the case of intermediate Tm^{3+} doping level (1–3 at.%) for which the majority of Tm^{3+} ions form clusters with relatively close spectroscopic properties. The introduction of optically passive Y^{3+} cations helps to prevent excessive self-quenching of the Tm^{3+} luminescence from the $^3H_4$ emitting state [43]. Extended discussion about ion clustering and site symmetry for Tm^{3+}:CaF_2 can be found elsewhere [42]. For an undoped CaF_2, $a = 5.451$ Å.

The scheelite-type $LiYF_4$ and $LiLuF_4$ tetragonal crystals are isostructural (sp. gr. C^6_{4h} - $I4_1/a$). They exhibit a single substitutional rare-earth ion site (Y^{3+} and Lu^{3+}, respectively, the local site symmetry is S_4) [26]. The lattice constants for undoped crystals $a = b = 5.164$ Å, $c = 10.741$ Å (for $LiYF_4$) and $a = b = 5.146$ Å, $c = 10.589$ Å (for $LiLuF_4$).

Finally, BaY_2F_8 belongs to the monoclinic crystal class (sp. gr. C^3_{2h} - $C2/m$) [44]. It also has a single rare-earth ion site (the Y^{3+} one with the C_2 local site symmetry). The C_2 symmetry axis is parallel to the b crystallographic axis which determines the anisotropy of the physical properties. The lattice constants are $a = 6.983$ Å, $b = 10.519$ Å, $c = 4.264$ Å and the monoclinic angle is $\beta = a{\wedge}c = 99.7°$.

The Tm^{3+} ion density N_{Tm} corresponding to a 1 at.% doping level for the studied crystals is listed in Table 1.

In Table 1, we also list the maximum phonon frequency hv_{ph}, ranging from 420 cm^{-1} for BaY_2F_8 to ~495 cm^{-1} for CaF_2 and KY_3F_{10}. According to the "energy gap law", which stipulates that the multiphonon NR relaxation is weak when the number of phonons needed to bridge the energy gap to the lower-lying multiplet is over 4 [45], the NR relaxation from the $^3H_4$ emitting state down to the next underlying $^3H_5$ multiplet of the Tm^{3+} ions (of the order of 4000 cm^{-1} [2]) in the studied fluoride crystals should be nearly negligible.

2.3. Optical orientation of samples

The CaF_2 and KY_3F_{10} crystals are optically isotropic. For CaF_2, the dispersion curve was reported yielding $n = 1.422$ at ~2.3 μm [24] and for KY_3F_{10}, only a mean refractive index value $<n> \approx 1.47$ is known.

Both $LiYF_4$ and $LiLuF_4$ are optically uniaxial. The optical axis (O.A.) is parallel to the crystallographic c-axis, so that there are two principal light polarizations, $E \parallel c$ (π) and $E \perp c$ (σ) with the corresponding refractive indices n_e and n_o, Fig. 2(a). For these crystals, $n_e > n_o$ (positive uniaxial crystals). According to the dispersion curves of $LiYF_4$ [46], $n_o = 1.440$ and $n_e = 1.463$ at ~2.3 μm.

The BaY_2F_8 crystal is optically biaxial. Its optical properties are then described in the frame of the optical indicatrix with three orthogonal axes, (X, Y, Z), Fig. 2(b). One of them is parallel to the C_2 symmetry axis (Y ∥ **b**-axis) and the other two are lying in the **a-c** plane. The Z-axis can be found by 21° anti-clockwise rotation from the **c**-axis (in the monoclinic angle, for **b**-axis pointing towards the observer), and the angle X^**a** = 11.3°. Typically for monoclinic laser crystals, the optical indicatrix axes (X, Y, Z) are also labeled as (N_p, N_m, N_g) (a note: not necessarily respectively) according to the relation between the principal refractive indices: $n_p < n_m < n_g$. However, in the literature, there exists some confusion in such assignment for BaY_2F_8 (for example, an exchange of the X and Z axes). In the present work, we follow the notations used in Ref. [47]. Using the dispersion data by Kaminskii *et al.*, we calculated $n_x = 1.466$, $n_y = 1.522$ and $n_z = 1.502$ at ~2.3 μm [48]. Thus, we will simply refer to the **E** ∥ X, Y and Z light polarizations.

3. Experimental

All the measurements were performed at room temperature (RT, 293 K).

The absorption spectra were measured using a spectrophotometer (Lambda 1050, Perkin Elmer) equipped with a Glan-Taylor polarizer. The spectral bandwidth (SBW) was down to 0.1 nm.

The luminescence spectra $W(\lambda)$ at 1.3–1.6 μm ($^3H_4 \rightarrow {}^3F_4$ emission transition) were measured using an optical spectrum analyzer (AQ6375B, Yokogawa, SBW = 1 nm). The $W(\lambda)$ spectra at 2.1–2.7 μm ($^3H_4 \rightarrow {}^3H_5$ emission transition) were measured using a 0.6 m monochromator (HRS2, Jobin-Yvon), a lock-in amplifier (SR810 DSP, Stanford Research Systems) and an InSb photodetector (J10D series, Judson Infrared) cooled by liquid nitrogen (SBW = 4.5 nm). A Glan-Taylor prism was used for polarized measurements. As an excitation source, we employed a CW Ti:Sapphire laser (3900S, Spectra Physics) tuned to the maximum absorption at the $^3H_6 \rightarrow {}^3H_4$ transition. The wavelength calibration was performed using an Hg lamp (Schwabe). The apparatus function of the set-up $X(\lambda)$ was determined using a 20 W quartz iodine lamp providing a luminescence spectrum close to that for a black-body source. The calibrated luminescence spectra were calculated as $W_i'(\lambda) = W_i(\lambda)/X(\lambda)$, where i indicates the light polarization.

4. Results and discussion

4.1. Absorption cross-sections

The absorption cross-sections, σ_{abs}, were calculated from the measured absorption coefficients as $\sigma_{abs} = \alpha_{abs}/N_{Tm}$ where N_{Tm} is the Tm^{3+} ion concentration.

The absorption cross-section spectra for the $^3H_6 \rightarrow {}^3H_4$ pump transition of Tm^{3+} ions are shown in Fig. 3 for the studied crystals. The wavelengths of the most intense absorption peak λ_{abs}, the corresponding peak σ_{abs} values and the peak bandwidth calculated as full width at half maximum $\Delta\lambda_{abs}$ (FWHM) are listed in Table 2.

The studied fluoride crystals exhibit very similar σ_{abs} values. The birefringent crystals show a notable anisotropy of absorption in polarized light. The preferable light polarizations

are π (for Tm:LiYF$_4$ and Tm:LiLuF$_4$) and $\boldsymbol{E} \parallel$ Y (for Tm:BaY$_2$F$_8$). For example, for the latter material, $\sigma_{abs} = 0.90 \times 10^{-20}$ cm^2 at 789.3 nm with $\Delta\lambda_{abs} = 2.1$ nm (for $\boldsymbol{E} \parallel$ Y).

4.2. Stimulated-emission cross-sections

The SE cross-sections for the ^{3}H$_4 \rightarrow$ ^{3}F$_4$ and ^{3}H$_4 \rightarrow$ ^{3}H$_5$ transitions were calculated using the Fuchtbauer-Ladenburg (FL) formula [49]:

$$\sigma^i_{SE}(\lambda) = \frac{\lambda^5}{8\pi <n>^2 \tau_{rad} c} \frac{W'_i(\lambda) B(JJ')}{1/3 \sum_i \int \lambda W'_i(\lambda) d\lambda}, \tag{1}$$

where λ is the light wavelength, $<n>$ is the polarization-averaged refractive index at a mean emission wavelength $<\lambda_{lum}>$, c is the speed of light, τ_{rad} is the radiative lifetime of the ^{3}H$_4$ emitting state, $W'_i(\lambda)$ is the luminescence spectrum calibrated for the spectral response of the set-up, $B(JJ')$ is the luminescence branching ratio (assuming purely radiative transitions) for the transitions in emission between the states with the total angular momentum quantum numbers J and J' (J = 4 for ^{3}H$_4$ and J' = 4 and 5 for ^{3}F$_4$ and ^{3}H$_5$, respectively), and i indicates the light polarization. The polarization-averaging (the factor of 1/3) is not performed for isotropic crystals (CaF$_2$ and KY$_3$F$_{10}$). For optically uniaxial crystals (LiYF$_4$, LiLuF$_4$), it is performed as $(2\int_\sigma + \int_\pi)/3$ and for the optically biaxial crystal (BaY$_2$F$_8$), it is $(\int_X + \int_Y + \int_Z)/3$.

In Table 3, we summarize the radiative lifetimes τ_{rad} and the luminescence branching ratios $B(JJ')$ which were used in the present work. For Tm:CaF$_2$, Tm:KY$_3$F$_{10}$ and Tm:LiYF$_4$, there exist reliable literature data on these parameters derived by means of the Judd-Ofelt (J-O) theory [41,50,51]. For Tm:LiLuF$_4$ and Tm:BaY$_2$F$_8$, the present literature data are not satisfactory. For Tm:BaY$_2$F$_8$, Owen *et al.* used a "mixed" crystal, Tm:Ba(Y,Yb)$_2$F$_8$, and did not account for the dispersion of the refractive index [47]. For Tm:LiLuF$_4$, Xiong *et al.* used unpolarized absorption spectra for calculations [52] while Cornacchia *et al.* provided the luminescence branching ratios with a high error [53]. Thus, for the latter materials, we performed such calculations in the present work (Section 4.3).

The results on the SE cross-sections for the ^{3}H$_4 \rightarrow$ ^{3}F$_4$ transition at ~1.5 µm are shown in Fig. 4. The peak emission wavelengths (λ_{em}) and the corresponding σ_{SE} values are listed in Table 4. Among the studied cubic crystals, Tm:KY$_3$F$_{10}$ provides the highest SE cross-section, $\sigma_{SE} = 0.62 \times 10^{-20}$ cm^2 at 1462 nm. The emission properties of the tetragonal Tm:LiYF$_4$ and Tm:LiLuF$_4$ crystals are very close (the cross-sections for the former one are slightly higher). These materials exhibit a remarkable polarization-anisotropy of SE cross-sections with higher σ_{SE} values in π-polarization, namely 1.14×10^{-20} cm^2 at 1452 nm (for Tm:LiYF$_4$). The ratio $\sigma_{SE}(\pi) : \sigma_{SE}(\sigma)$ for this crystal is as high as 3.7. Finally, the monoclinic crystal Tm:BaY$_2$F$_8$ also exhibits some polarization-anisotropy in the σ_{SE} spectra which is however less pronounced. The highest value is observed for light polarization $\boldsymbol{E} \parallel$ Y ($\sigma_{SE} = 0.73 \times 10^{-20}$ cm^2 at 1478 nm), and for other polarizations, a relation σ_{SE} (Y) > σ_{SE} (Z) > σ_{SE} (X) is observed. Note that the peak emission wavelength is the same for $\boldsymbol{E} \parallel$ X and Z but is different for $\boldsymbol{E} \parallel$ Y. This difference originates from the fact that the Y optical indicatrix axis is parallel to the *b*-axis (C$_2$ symmetry axis), and the other two axes (X and Z) are lying in the orthogonal plane. Thus, the polarization selection rules are different in these cases.

For Tm^{3+} ions, there is a strong $^3F_4 \rightarrow {}^3H_4$ excited-state absorption (ESA) transition (cf. Fig. 1) which spectrally overlaps with the emission at ~1.5 μm [38,39]. As the $^3F_4$ multiplet is a metastable level, the probability of such ESA is very high. It should be considered when predicting the possible laser wavelengths for Tm laser operating on this $^3H_4 \rightarrow {}^3F_4$ emission transition.

Now let us discuss the results on the SE cross-sections for the $^3H_4 \rightarrow {}^3H_5$ transition around 2.3 μm, cf. Fig. 5 and Table 4. Such a $^3H_4 \rightarrow {}^3H_5$ emission transition corresponds to a quasi-four level laser scheme and does not overlap with any strong ESA channel. Thus, the local peaks in the σ_{SE} spectra will determine the expected laser wavelengths and the possible emission bandwidths for ML operation [16,17].

Both cubic Tm:KY$_3$F$_{10}$ and Tm,Y:CaF$_2$ crystals exhibit broad and smooth SE cross-section spectra. For the former material, $\sigma_{SE} = 0.34 \times 10^{-20}$ cm^2 at 2342 nm with an emission bandwidth (defined as FWHM) $\Delta\lambda_{em} = 62$ nm. For the Tm,Y:CaF$_2$ crystal, the peak value is smaller, 0.15×10^{-20} cm^2 at 2372 nm, while the emission band is extremely broad ($\Delta\lambda_{em} = 252$ nm), indicating a glassy-like spectroscopic behavior.

For the tetragonal Tm:LiYF$_4$ and Tm:LiLuF$_4$ crystals, the shape of the SE cross-section spectra is similar while slightly higher σ_{SE} values are again determined for the former material, namely 0.44×10^{-20} cm^2 at 2304 nm with $\Delta\lambda_{em} = 34$ nm (for π-polarization). Similarly to the $^3H_4 \rightarrow {}^3F_4$ transition, an anisotropy of the SE properties is detected, however with a smaller ratio $\sigma_{SE}(\pi) : \sigma_{SE}(\sigma)$ of 1.9. This is nevertheless enough to determine a linearly polarized output in **a**-cut Tm:LiYF$_4$ lasers [36].

For monoclinic Tm:BaY$_2$F$_8$ crystal, the highest SE cross-section is observed for light polarization **E** ∥ Z, namely 0.39×10^{-20} cm^2 at 2289 nm with $\Delta\lambda_{em} = 29$ nm. For the other polarizations, a relation σ_{SE} (Z) > σ_{SE} (X) > σ_{SE} (Y) is observed. Much broader emission bandwidths are detected for **E** ∥ Y ($\Delta\lambda_{em} = 86$ nm) and especially for **E** ∥ X ($\Delta\lambda_{em} = 144$ nm). Note that despite a relatively weak anisotropy in the peak σ_{SE} values, Tm:BaY$_2$F$_8$ offers several intense emission peaks at different wavelengths ranging from 2251 to 2452 nm.

All the studied Tm^{3+}-doped fluoride crystals exhibit relatively high SE cross-sections on the $^3H_4 \rightarrow {}^3H_5$ transition. The features of Tm:KY$_3$F$_{10}$ are a combination of a moderate σ_{SE} value with a broad emission bandwidth making it very suitable for broadly tunable and ML oscillators. Tm:LiYF$_4$ offers a high peak σ_{SE} value in π-polarization whilst corresponding to a narrower emission band. Tm:BaY$_2$F$_8$ features multiple broad emission peaks up to ~2.45 μm; it is thus attractive for going further into the mid-IR.

4.3. Judd-Ofelt modeling: Tm:LiLuF$_4$ and Tm:BaY$_2$F$_8$

As pointed out above, there is a lack of reliable data on transition probabilities of Tm^{3+} ions in LiLuF$_4$ and BaY$_2$F$_8$ crystals. In the present work, we performed such calculations based on measured absorption spectra for principal light polarizations (π and σ for Tm:LiLuF$_4$ and **E** ∥ X, Y, Z for Tm:BaY$_2$F$_8$). The spectra are displayed in Fig. 6.

The transition probabilities of Tm^{3+} ions were calculated within the standard Judd-Ofelt (J–O) theory [54,55] and its modifications accounting for configuration interaction: the so-called modified Judd-Ofelt theory (mJ–O) and the approximation of an intermediate

configuration interaction (ICI) [56-58]. The J–O formalism was applied to electric-dipole (ED) contributions to the transition intensities. The contribution of magnetic-dipole (MD) transitions (following the selection rule $\Delta J = J - J' = 0, \pm 1$, except $J = J' = 0$) to the transition intensities was calculated separately within the Russell–Saunders approximation on wave functions of Tm^{3+} under an assumption of a free-ion.

A detailed description of such calculations can be found elsewhere [25,59]. Here, we only discuss the different approximations used.

For the standard J-O theory, the ED line strengths of the $J \rightarrow J'$ transitions $S^{ED}(JJ')$ are [54,55]:

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

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

Here, the $U^{(k)}$ are reduced squared matrix elements calculated using the crystal-field parameters from Ref. [60] and Ω_k are the intensity (J–O) parameters (for both, $k = 2, 4, 6$).

For the ICI approximation, the ED line strengths are given by [56,58]:

$$S_{calc}^{ED}(JJ') = \sum_{k=2,4,6} U^{(k)}\Omega_k^*, \tag{3a}$$

$$\Omega_k^* = \Omega_k[1 + 2R_k(E_J + E_{J'} - 2E_f^0)]. \tag{3b}$$

Here, the intensity parameters Ω_k^* are the linear functions of energies (E_J and $E_{J'}$) of the two multiplets participating in the transition $J \rightarrow J'$, E_f^0 is the mean energy of the $4f^n$ configuration and R_k ($k = 2, 4, 6$) are the parameters representing the configuration interaction. Therefore, in the ICI approximation, there are six free parameters, namely Ω_k and R_k ($k = 2, 4, 6$) and the derived Ω_k will be different from those found by using Eq. (2).

If solely the lower-energy excited configuration with the opposite parity ($4f^{n-1}5d^1 = 4f^{11}5d^1$ for Tm^{3+} ions) is considered to contribute to the configuration interaction, then it is possible to write $R_2 = R_4 = R_6 = \alpha \approx 1/(2\Delta)$ where $\Delta \approx E(4f^{n-1}5d^1) - E(4f^n)$ is the average energy difference between the fundamental ($4f^{12}$) and the first-excited ($4f^{11}5d^1$) electronic configurations [56]. In that case, the expression for the ED transition intensities is simplified [56,57]:

$$S_{calc}^{ED}(JJ') = \sum_{k=2,4,6} U^{(k)}\Omega_k^*, \tag{4a}$$

$$\Omega_k^* = \Omega_k[1 + 2\alpha(E_J + E_{J'} - 2E_f^0)]. \tag{4b}$$

Now, there are four free (new) parameters, namely Ω_2, Ω_4, Ω_6 and α. Note that Eq. (4) for the mJ-O theory is transformed into Eq. (2) for the standard one under the assumption of a high-lying $4f^{n-1}5d^1$ excited configuration (i.e., for $\Delta \rightarrow \infty$, thus $\alpha \rightarrow 0$).

Note that the Δ parameter can be estimated from the experimental spectroscopic data and compared to the value which is obtained from the calculations within the mJ-O theory. This was performed in [56] in the case of Pr^{3+} in $KPrP_4O_{12}$. As for the fluorides, there is an extensive literature on the subject including theory and experiments [61]. According to these works, the lower-lying energy levels of the $4f^{11}5d^1$ excited electronic configuration of Tm^{3+} giving rise to the strongest $4f - 4f5d$ ED allowed absorption transitions would be located (by

using Eq. (1) from Ref. [61]) at ~160 nm for all the studied crystals, thus at about the same energy of ~62500 cm^{-1}. Assuming the $4f^{12}$ electronic configuration with an average energy of ~10000 cm^{-1}, it means that it is expected to find a Δ value of the order of 52500 cm^{-1} ($\alpha \approx 1/(2\Delta) = 2\times10^{-5}$ cm).

For both Tm:LiLuF$_4$ and Tm:BaY$_2$F$_8$ crystals, all the calculations were performed by averaging the polarizations, namely $\langle P \rangle = (1/3)(2P_\sigma + P_\pi)$ for the uniaxial Tm:LiLuF$_4$ crystal and $\langle P \rangle = (1/3)(P_X + P_Y + P_Z)$ for the biaxial Tm:BaY$_2$F$_8$ one, where P is the parameter and the subscripts indicate the polarization state.

The measured and calculated absorption oscillator strengths (denoted as $\langle f^\Sigma_{exp} \rangle$ and $\langle f^\Sigma_{calc} \rangle$, respectively) are presented in Table 5 (for Tm:LiLuF$_4$) and Table 6 (for Tm:BaY$_2$F$_8$). Here, the superscript "Σ" stands for the total (ED + MD) value.

A comparison of the root-mean-square deviations (r.m.s. dev.) between $\langle f^\Sigma_{exp} \rangle$ and $\langle f^\Sigma_{calc} \rangle$ indicates that the ICI approximation gives a better agreement between the experimental and calculated values for both crystals. For example, the r.m.s. dev. equals to 0.126 (ICI) and 0.202 (J-O) for the case of Tm:LiLuF$_4$. Moreover, a closer agreement is observed for the absorption oscillator strength for the transition to the first excited state ($^3F_4$). Its value has a direct consequence on the calculated radiative lifetime of this level. Indeed, for Tm:LiLuF$_4$, $\langle f^\Sigma_{exp} \rangle \times 10^6 = 1.436$ while $\langle f^\Sigma_{calc} \rangle \times 10^6 = 1.375$ (ICI) and 1.588 (J–O). Thus, it is expected that the use of the standard J-O approach will underestimate the lifetime of the Tm^{3+} lower-lying excited state while this problem can be avoided when using the ICI approximation. From these considerations, we selected the latter model for further calculations.

The determined intensity parameters giving the minimum r.m.s. dev. (namely, $\{\Omega_k\}$ for the standard J–O theory, $\{\Omega_k$ and $\alpha\}$ for the mJ-O one and $\{\Omega_k$ and $R_k\}$ for the ICI approximation) are listed in Table 7.

The α values which result from the fitting procedure within the framework of the ICI approximation are of the order of 1×10^{-5} for Tm:LiLuF$_4$, which is very close to the above estimated value, and 1×10^{-4} for Tm:BaY$_2$F$_8$, which means that another mechanism (different from a simple configuration interaction one) could contribute.

Using the set of the intensity parameters determined within the framework of the ICI approximation, we calculated the radiative spontaneous emissions probabilities A^Σ_{calc} (here, the superscript "Σ" also stands for the total (ED + MD) value), the luminescence branching ratios $B(JJ')$, the total probability of radiative spontaneous transitions from an excited-state A_{tot} and the radiative lifetime of an excited state τ_{rad}. The summary of results obtained within the ICI approximation is shown in Table 8 (for Tm:LiLuF$_4$) and Table 9 (for Tm:BaY$_2$F$_8$).

For Tm:LiLuF$_4$, the radiative lifetimes of the excited-states of interest for Tm^{3+} laser operation are $\tau_{rad} = 10.99$ ms ($^3F_4$) and 1.34 ms ($^3H_4$). The luminescence branching ratios for the transitions of interest are $B(JJ') = 8.9\%$ ($^3H_4 \rightarrow ^3F_4$) and 2.2% ($^3H_4 \rightarrow ^3H_5$). These values correspond to the ICI approximation.

For Tm:BaY$_2$F$_8$, slightly shorter radiative lifetimes are determined, namely $\tau_{rad} = 8.68$ ms ($^3F_4$) and 1.10 ms ($^3H_4$) while the luminescence branching ratios are similar (compared to Tm:LiLuF$_4$), $B(JJ') = 8.8\%$ ($^3H_4 \rightarrow ^3F_4$) and 3.1% ($^3H_4 \rightarrow ^3H_5$).

Note that the use of a certain approximation in the J–O calculations has a minor effect on the determined luminescence branching ratios $B(JJ')$. Indeed, for the $^3H_4 \rightarrow {}^3H_5$ transition, $B(JJ')$ = 2.65% (J–O), 2.57% (mJ–O) and 2.16% (ICI) for the case of Tm:LiLuF$_4$.

4.4. Analysis of the results

Let us examine the consistency of the determined σ_{SE} spectra for the $^3H_4 \rightarrow {}^3F_4$ and $^3H_4 \rightarrow {}^3H_5$ transitions. For this, a comparison is made between (i) the integrated σ_{abs} values derived from the transformed σ_{SE} spectra via the reciprocity method and (ii) the integrated σ_{abs} values calculated from the respective line strengths of the transitions. Note that both of the considered transitions can be of ED and MD nature. The transitions in absorption (from the $^3F_4$ and $^3H_5$ states) correspond to ESA.

For crystals with a well-defined scheme of Stark levels, the absorption cross-section of a transition between two multiplets is related to the SE cross-section of the reverse transition by the Einstein "reciprocity" expression [1]:

$$\sigma_{abs}^i(\lambda) = \sigma_{SE}^i(\lambda).\frac{Z_u}{Z_l}.\exp\left[\frac{(hc/\lambda)-E_{ZL}}{kT}\right], \tag{5}$$

where h is the Planck constant, k is the Boltzmann constant, T is the crystal temperature (RT, in our case), $E_{ZL} = (hc)/\lambda_{ZL}$ is the energy of the zero line (ZL) transition between the lowest Stark sub-levels of both multiplets, and i indicates the light polarization. Z_m are the partition functions for the lower ($m = l$) and upper ($m = u$) manifolds:

$$Z_m = \sum_k g_k^m \exp(-E_k^m/kT). \tag{6}$$

Here, g_k^m is the degeneracy of the sub-level with the number k and energy E_k^m measured from the lowest sub-level of each multiplet.

From the determined absorption (ESA) cross-sections, we calculate the polarization-averaged integrated σ_{abs} values, $\int<\sigma_{abs}>(\lambda)d\lambda$. The averaging is performed as explained in Section 4.3. Those are compared with the values determined from the line strengths [62]:

$$\int \sigma_{abs}^{calc}(\lambda)d\lambda = \frac{2\pi^2 q^2 \langle\lambda\rangle}{3hc(2J_l+1)\varepsilon_0}\left[\frac{(\langle n\rangle^2+2)^2}{9\langle n\rangle}S_{calc}^{ED} + \langle n\rangle S_{calc}^{MD}\right]. \tag{7}$$

Here, q is the electron charge, $<\lambda>$ is the mean wavelength in absorption, J_l is the total angular momentum quantum number for the lower-lying ($m = l$) multiplet, ε_0 is the vacuum permittivity. The J-O parameters Ω_k for Tm:KY$_3$F$_{10}$ and Tm:LiYF$_4$ [41,49] used to calculate the S_{calc}^{ED} contributions to the line strength of transitions are listed in Table 3. For Tm:LiLuF$_4$ and Tm:BaY$_2$F$_8$, these values were obtained within the ICI approximation using the intensity parameters from Table 7.

Due to the availability of data on the crystal-field splitting for Tm^{3+} ions [2,41,47,63], the analysis is performed for the Tm:KY$_3$F$_{10}$, Tm:LiYF$_4$, Tm:LiLuF$_4$ and Tm:BaY$_2$F$_8$ crystals. The results on the integrated σ_{abs} values obtained by using two approaches, as well as the S_{calc}^{ED} and S_{calc}^{MD} values are listed in Table 10. The agreement between the semi-experimental and theoretical integrated absorption cross sections is quite good. This proves the good choice

of the absorption and emission wavelengths made in the J–O treatment and of the derived intensity parameters, radiative lifetimes and branching ratios.

5. Conclusion

All the studied fluoride crystals exhibit intense and broad emission bands in the near-IR (~1.5 µm) and mid-IR (~2.3 µm) corresponding to the $^3H_4 \rightarrow {}^3F_4$ and $^3H_4 \rightarrow {}^3H_5$ optical transitions, respectively, originating from the same emitting state. The main interest lies in the latter emission which was recently used in a number of continuous-wave and ultrashort-pulse oscillators. So far, only two fluoride crystals have been employed for ~2.3 µm lasers, namely Tm:LiYF$_4$ and Tm:KY$_3$F$_{10}$. The variety of the studied fluoride crystals may allow to address specific requirements for ~2.3 µm lasers, such as (i) broad emission bandwidths (by using Tm:KY$_3$F$_{10}$ and Tm:CaF$_2$) which is of interest for broadly tunable and ML lasers, (ii) high stimulated-emission cross-sections in polarized light (by using Tm:LiYF$_4$, Tm:LiLuF$_4$ or Tm:BaY$_2$F$_8$) or (iii) long emission wavelengths extending beyond 2.4 µm (with Tm:BaY$_2$F$_8$ and combination of crystal orientation and light polarization). Note that all these crystals exhibit rather similar absorption at ~0.8 µm and are suitable for efficient diode-pumping.

For the actual design of the ~2.3 µm lasers, there exist other relevant spectroscopic parameters which need further studies, such as the concentration-dependent rate of the CR energy transfer ($^3H_4 + {}^3H_6 \rightarrow {}^3F_4 + {}^3F_4$) which quenches the upper laser level lifetime, the rate of ETU depopulating the $^3F_4$ metastable level ($^3F_4 + {}^3F_4 \rightarrow {}^3H_6 + {}^3H_4$) and acting as a refilling mechanism for the upper laser level, and, the ESA cross sections at ~1 µm and ~1.5 µm to further explore the recently proposed upconversion pumping scheme.

Separately, one should also comment on the suitability of Tm:CaF$_2$ for laser operation at ~2.3 µm. Just at a glance, this crystal is attractive because of its ultra-broadband emission properties (emission bandwidth of 252 nm, centered at 2372 nm) which are compatible with those for the Cr^{2+}-doped zinc chalcogenides. However, the relatively low SE cross-section and, even more important, the extremely strong clustering of the RE^{3+} dopant ions may be a serious limitation for achieving laser operation. More dedicated study of Tm:CaF$_2$ is required in this regard, focusing on the possible positive role of buffer (optically passive) ions.

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Figure 1. Energy level scheme for Tm^{3+} ions (Stark splittings for Tm:LiYF$_4$ can be found in [2]) showing processes relevant for laser operation in the near- and mid-IR: green and red arrows - pump and laser transitions, respectively; R and NR - radiative and non-radiative relaxation, respectively; CR - cross-relaxation, ETU – energy-transfer upconversion, EM – energy-migration.
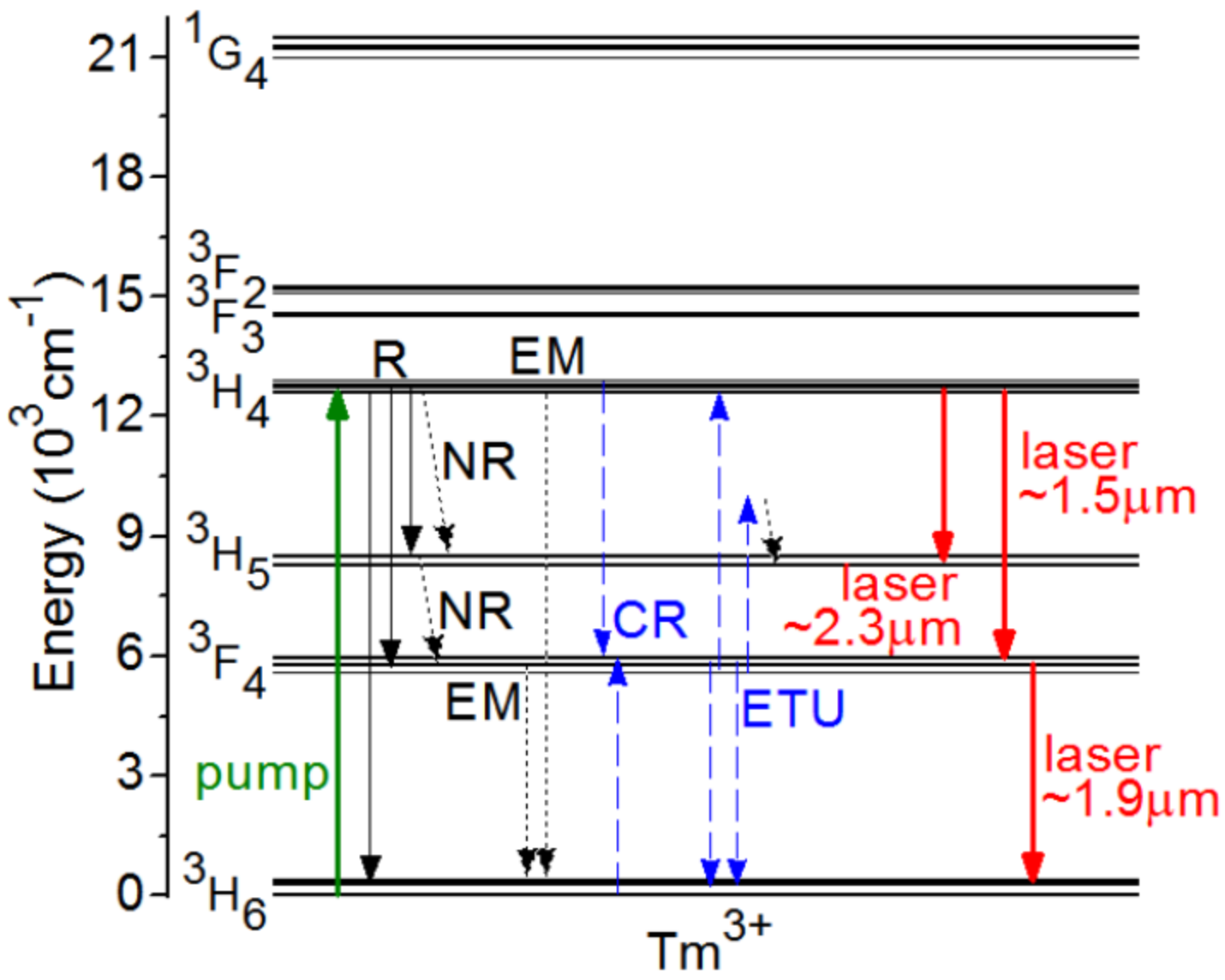
Figure 2. Optical orientation of LiLnF$_4$ (Ln = Y, Lu) and BaY$_2$F$_8$ crystals: (*a*, *b*, *c*) – crystallographic axes, O.A. – optical axis, (X, Y, Z) – optical indicatrix axes, *n* – refractive indices.

Figure 3. Absorption cross-section spectra, σ_{abs}, for the $^3H_6 \rightarrow \, ^3H_4$ pump transition of Tm^{3+} ions in (a) cubic crystals KY$_3$F$_{10}$ and CaF$_2$, (b) tetragonal crystals LiYF$_4$ and LiLuF$_4$ and (c) monoclinic crystal BaY$_2$F$_8$.

Figure 4. Stimulated-emission (SE) cross-section spectra, σ_{SE}, for the $^3H_4 \rightarrow \, ^3F_4$ transition of Tm^{3+} ions around 1.45 µm in (a) cubic crystals KY$_3$F$_{10}$ and CaF$_2$, (b) tetragonal crystals LiYF$_4$ and LiLuF$_4$ and (c) monoclinic crystal BaY$_2$F$_8$.

Figure 5. Stimulated-emission (SE) cross-section spectra, σ_{SE}, for the $^3H_4 \rightarrow \, ^3H_5$ transition of Tm^{3+} ions around 2.3 µm in (a) cubic crystals KY$_3$F$_{10}$ and CaF$_2$, (b) tetragonal crystals LiYF$_4$ and LiLuF$_4$ and (c) monoclinic crystal BaY$_2$F$_8$.

Figure 6. Overview absorption cross-section spectra, σ_{abs}, of (a) Tm:LiLuF$_4$ crystal for light polarizations π and σ; and (b) Tm:BaY$_2$F$_8$ crystal for light polarizations $E \parallel$ X, Y, Z.

(a) cubic crystals
— Tm:KY$_3$F$_{10}$
— Tm,Y:CaF$_2$

(b) tetragonal crystals
Tm:LiYF$_4$
σ
π
Tm:LiLuF$_4$
σ
π

(c) monoclinic crystal
Tm:BaY$_2$F$_8$
X
Y
Z

(a) cubic crystals

Tm:KY$_3$F$_{10}$
τ_{rad}=1.14ms
$B(JJ')$=10.2%

Tm,Y:CaF$_2$
τ_{rad}=2.51ms
$B(JJ')$=8.4%

(b) tetragonal crystals

Tm:LiYF$_4$
τ_{rad}=1.44ms
$B(JJ')$=10.2%
σ
π

Tm:LiLuF$_4$
τ_{rad}=1.34ms
$B(JJ')$=8.9%
σ
π

(c) monoclinic crystal

Tm:BaY$_2$F$_8$
τ_{rad}=1.10ms
$B(JJ')$=8.8%

X
Y
Z

Figure showing spontaneous emission cross-section spectra for (a) cubic crystals, (b) tetragonal crystals, and (c) monoclinic crystal.

(a) cubic crystals

Tm:KY$_3$F$_{10}$
τ_{rad}=1.14ms
$B(JJ')$=2.9%
Tm,Y:CaF$_2$
τ_{rad}=2.51ms
$B(JJ')$=4.6%

(b) tetragonal crystals

Tm:LiYF$_4$
τ_{rad}=1.44ms
$B(JJ')$=2.4%
σ
π
Tm:LiLuF$_4$
τ_{rad}=1.34ms
$B(JJ')$=2.2%
σ
π

(c) monoclinic crystal

Tm:BaY$_2$F$_8$
τ_{rad}=1.10ms
$B(JJ')$=3.1%
X
Y
Z

Axis labels: σ_{SE} (10^{-21}cm^2) vs Wavelength (nm)

(a) Tm:LiLuF$_4$
— π
— σ

$^3P_{0-2}$
$^1I_6$
$^1D_2$
$^1G_4$
$^3F_{2,3}$
$^3H_4$
$^3H_5$
$^3F_4$

(b) Tm:BaY$_2$F$_8$
— X
— Y
— Z

$^1D_2$
$^1G_4$
$^3F_{2,3}$
$^3H_4$
$^3H_5$
$^3F_4$

Table 1. Structural properties of the studied fluoride laser crystals.

Crystal	Growth *	$T_{melting}$, °C	Crystal class (sp. gr.)	Optical behavior	Tm^{3+} site	N_{Tm},** 10^{20} cm^{-3}	$h\nu_{ph}$, cm^{-1}
CaF_2	Br	1360	cubic (O^5_h - $Fm3^-m$)	isotropic	cluster	2.45	495
KY_3F_{10}	Cz	1030	cubic (O^5_h - $Fm3^-m$)	isotropic	C_{4v} (Y^{3+})	1.56	495
$LiYF_4$	Cz	842	tetragonal (C^6_{4h} - $I4_1/a$)	uniaxial	S_4 (Y^{3+})	1.38	446
$LiLuF_4$	Cz	825	tetragonal (C^6_{4h} - $I4_1/a$)	uniaxial	S_4 (Lu^{3+})	1.43	435
BaY_2F_8	Cz	960	monoclinic (C^3_{2h} - $C2/m$)	biaxial	C_2 (Y^{3+})	1.30	421

*Cz – Czochralski method, Br – Bridgman method.

**For 1 at.% doping level.

Table 2. Absorption properties of Tm^{3+} ions in fluoride crystals corresponding to the $^3H_6 \rightarrow {}^3H_4$ transition at around 0.8 μm.

Crystal	σ_{abs}, 10^{-20} cm^2	λ_{abs}, nm	$\Delta\lambda_{abs}$, nm
CaF_2	0.77	766.1	11.9
KY_3F_{10}	0.79	778.6	2.8
$LiYF_4$	0.85 (π),	779.9 (π),	7.6 (π),
	0.39 (σ)	790.3 (σ)	16.5 (σ)
$LiLuF_4$	0.81 (π),	781.8 (π),	7.1 (π),
	0.40 (σ)	790.1 (σ)	16.6 (σ)
BaY_2F_8	0.40 (X),	780.7 (X),	3.4 (X),
	0.90 (Y),	789.3 (Y),	2.1 (Y),
	0.69 (Z)	780.7 (Z)	4.3 (Z)

*σ_{abs} – absorption cross-section, λ_{abs} - peak absorption wavelength, $\Delta\lambda_{abs}$ - absorption bandwidth. The light polarization is indicated in brackets.

Table 3. Radiative lifetime of the $^3H_4$ state τ_{rad} and the luminescence branching ratios $B(JJ')$ used for calculating the SE cross-sections for the $^3H_4 \rightarrow {}^3H_5$ and $^3H_4 \rightarrow {}^3F_4$ transitions of Tm^{3+} ions in fluoride crystals.

Crystal	$\tau_{rad}(^3H_4)$, ms	$B(JJ')$, %		*$\Omega_k \times 10^{20}$, cm^2			Ref.
		$^3H_4 \rightarrow {}^3H_5$	$^3H_4 \rightarrow {}^3F_4$	Ω_2	Ω_4	Ω_6	
CaF$_2$	2.51	4.6	8.4	0.891	1.251	0.959	[51]
KY$_3$F$_{10}$	1.14	2.9	10.2	1.907	1.531	1.465	[41]
LiYF$_4$	1.44	2.4	10.2	1.96	1.17	1.38	[50]
LiLuF$_4$	1.34	2.2	8.9	**			This work
BaY$_2$F$_8$	1.10	3.1	8.8	**			This work

*The J-O parameters Ω_k (k = 2, 4, 6) corresponding to the τ_{rad} and $B(JJ')$ values are given.

**Spectroscopic parameters calculated within the ICI approximation, cf. Table 7 for the full list of intensity parameters.

Table 4. Emission properties of Tm^{3+} ions in fluoride crystals corresponding to the $^3H_4 \rightarrow {}^3H_5$ and $^3H_4 \rightarrow {}^3F_4$ transitions in emission at ~1.5 µm and ~2.3 µm, respectively.

Crystal	$^3H_4 \rightarrow {}^3H_5$			$^3H_4 \rightarrow {}^3F_4$	
	σ_{SE}, 10^{-20} cm^2	λ_{em}, nm	$\Delta\lambda_{em}$, nm	σ_{SE}, 10^{-20} cm^2	λ_{em}, nm
CaF_2	0.15	2372	252	0.16	1478
KY_3F_{10}	0.34	2342	62	0.62	1462
$LiYF_4$	0.52 (π),	2303 (π),	34 (π),	1.14 (π),	1452 (π),
	0.28 (σ)	2306 (σ)	34 (σ)	0.31 (σ)	1498 (σ)
$LiLuF_4$	0.44 (π),	2304 (π),	35 (π),	1.01 (π),	1452 (π),
	0.23 (σ)	2307 (σ)	36 (σ)	0.26 (σ)	1500 (σ)
BaY_2F_8	0.32 (X),	2341 (X),	144 (X),	0.49 (X),	1468 (X),
	0.20 (Y)	2421 (Y)	86 (Y),	0.73 (Y),	1478 (Y),
	0.39 (Z)	2289 (Z)	29(Z)	0.58 (Z)	1468 (Z)

*σ_{SE} - stimulated-emission cross-section, λ_{em} - peak emission wavelength, $\Delta\lambda_{em}$ - emission bandwidth. The light polarization is indicated in brackets.

Table 5. Experimental and calculated absorption oscillator strengths*
for Tm^{3+} ions in the $LiLuF_4$ crystal.

$^3H_6 \rightarrow$ $^{2S+1}L_J$	E_J, cm^{-1}	$\langle f_{exp} \rangle$ $\times 10^6$	$\langle f^\Sigma_{calc} \rangle \times 10^6$ J-O	mJ-O	ICI
$^3F_4$	5700	1.436	1.588^{ED}	1.565^{ED}	1.375^{ED}
$^3H_5$	8335	1.571	$1.150^{ED}+$ 0.406^{MD}	$1.134^{ED}+$ 0.406^{MD}	$1.212^{ED}+$ 0.406^{MD}
$^3H_4$	12594	1.970	1.842^{ED}	1.865^{ED}	2.033^{ED}
$^3F_{2,3}$	14504	2.619	2.563^{ED}	2.539^{ED}	2.568^{ED}
$^1G_4$	21160	0.593	0.558^{ED}	0.568^{ED}	0.593^{ED}
$^1D_2$	27944	1.596	1.839^{ED}	1.832^{ED}	1.699^{ED}
$^1I_6+{}^3P_0$	35084	0.769	$0.699^{ED}+$ 0.021^{MD}	$0.729^{ED}+$ 0.021^{MD}	$0.617^{ED}+$ 0.021^{MD}
$^3P_1$	36368	0.214	0.522^{ED}	0.551^{ED}	0.288^{ED}
$^3P_2$	38009	2.125	1.916^{ED}	1.941^{ED}	2.084^{ED}
r.m.s. dev.			*0.202*	*0.219*	*0.126*

*E_J – barycenter energy of the absorption band, $\langle f_{exp} \rangle$ and $\langle f^\Sigma_{calc} \rangle$ -
experimental and calculated absorption oscillator strengths, respectively
(ED + MD), the brackets $\langle .. \rangle$ indicate polarization-averaging, $1/3(2\sigma+\pi)$.
ED and MD stand for electric-dipole and magnetic-dipole contributions,
respectively.

Table 6. Experimental and calculated absorption oscillator strengths* for Tm^{3+} ions in the BaY_2F_8 crystal.

$^3H_6 \rightarrow$ $^{2S+1}L_J$	$E_J,$ cm^{-1}	$\langle f_{exp} \rangle$ $\times 10^6$	$\langle f^\Sigma_{calc} \rangle \times 10^6$ J-O	mJ-O	ICI
$^3F_4$	5812	1.596	2.007^{ED}	1.670^{ED}	1.602^{ED}
$^3H_5$	8381	1.832	1.372^{ED}+ 0.417^{MD}	1.210^{ED}+ 0.417^{MD}	1.366^{ED}+ 0.417^{MD}
$^3H_4$	12738	2.289	1.905^{ED}	2.236^{ED}	2.295^{ED}
$^3F_{2,3}$	14733	2.974	3.177^{ED}	3.058^{ED}	2.987^{ED}
$^1G_4$	21164	0.751	0.715^{ED}	0.864^{ED}	0.765^{ED}
$^1D_2$	28120	3.234	3.017^{ED}	3.199^{ED}	3.232^{ED}
r.m.s. dev.			*0.319*	*0.154*	*0.054*

*E_J – barycenter energy of absorption band, $\langle f_{exp} \rangle$ and $\langle f^\Sigma_{calc} \rangle$ - experimental and calculated absorption oscillator strengths, respectively (ED + MD), the brackets <..> indicate polarization-averaging, 1/3(X+Y+Z). ED and MD stand for electric-dipole and magnetic-dipole contributions, respectively.

Table 7. Intensity parameters for Tm^{3+} ions in the $LiLuF_4$ and BaY_2F_8 crystals obtained within the standard J-O theory, the modified J-O theory (mJ-O) and the intermediate configuration interaction (ICI) approximation.

Crystal	Model	$\Omega_k \times 10^{20}$, cm^2			$\alpha \times 10^4$, cm	$R_k \times 10^4$, cm		
		Ω_2	Ω_4	Ω_6		R_2	R_4	R_6
Tm:LiLuF$_4$	J-O	2.224	1.602	1.042	-	-	-	-
	mJ-O	2.370	1.556	1.062	0.011	-	-	-
	ICI	2.920	1.331	1.006	-	0.072	0.099	-0.134
Tm:BaY$_2$F$_8$	J-O	1.709	2.736	1.035	-	-	-	-
	mJ-O	3.396	2.358	1.345	0.110	-	-	-
	ICI	2.746	2.285	1.028	-	-0.012	0.211	-0.160

Table 8. Probabilities of radiative spontaneous transitions* for Tm^{3+} ions in $LiLuF_4$ (as calculated within the ICI approximation).

Excited state	Terminal state	$\langle\lambda\rangle$, nm	$A_\Sigma^{calc}(JJ')$, s^{-1}	$B(JJ')$, %	A_{tot}, s^{-1}	τ_{rad}, ms
$^3F_4$	$^3H_6$	1754	91.0^{ED}	100	91.0	10.99
$^3H_5$	$^3F_4$	3795	$4.6^{ED}+0.1^{MD}$	2.4	192.9	5.18
	$^3H_6$	1200	$141.0^{ED}+47.2^{MD}$	97.6		
$^3H_4$	$^3H_5$	2348	$11.6^{ED}+4.5^{MD}$	2.2	745.0	1.34
	$^3F_4$	1451	$54.4^{ED}+11.9^{MD}$	8.9		
	$^3H_6$	794	662.6^{ED}	88.9		
$^3F_2+^3F_3$	$^3H_4$	5236	$4.7^{ED}+0.1^{MD}$	0.2	2087.0	0.48
	$^3H_5$	1621	231.7^{ED}	11.1		
	$^3F_4$	1136	$320.9^{ED}+31.0^{MD}$	16.9		
	$^3H_6$	689	1498.4^{ED}	71.8		
$^1G_4$	$^3F_2+^3F_3$	1502	$36.1^{ED}+2.1^{MD}$	3.2	1192.8	0.84
	$^3H_4$	1167	$111.8^{ED}+17.8^{MD}$	10.9		
	$^3H_5$	780	$314.0^{ED}+70.5^{MD}$	32.2		
	$^3F_4$	647	$83.1^{ED}+5.4^{MD}$	7.4		
	$^3H_6$	472	552.0^{ED}	46.3		
$^1D_2$	$^1G_4$	1474	140.9^{ED}	0.8	17396.4	0.058
	$^3F_2+^3F_3$	744	$1576.7^{ED}+91.4^{MD}$	9.5		
	$^3H_4$	651	896.8^{ED}	5.2		
	$^3H_5$	510	39.5^{ED}	0.2		
	$^3F_4$	450	9628.4^{ED}	55.4		
	$^3H_6$	358	5022.7^{ED}	28.9		

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

Table 9. Probabilities of radiative spontaneous transitions* for Tm^{3+} ions in BaY_2F_8 (as calculated within the ICI approximation).

Excited state	Terminal state	$\langle\lambda\rangle$, nm	$A_\Sigma^{calc}(JJ')$, s^{-1}	$B(JJ')$, %	A_{tot}, s^{-1}	τ_{rad}, ms
$^3F_4$	$^3H_6$	1721	115.2^{ED}	100	115.2	8.68
$^3H_5$	$^3F_4$	3893	$5.1^{ED}+0.1^{MD}$	2.3	224.0	4.47
	$^3H_6$	1193	$167.6^{ED}+51.2^{MD}$	97.7		
$^3H_4$	$^3H_5$	2295	$22.7^{ED}+5.1^{MD}$	3.1	906.4	1.10
	$^3F_4$	1444	$67.1^{ED}+12.9^{MD}$	8.8		
	$^3H_6$	785	798.6^{ED}	88.1		
$^3F_2+^3F_3$	$^3H_4$	5012	$5.9^{ED}+0.0^{MD}$	0.2	2501.7	0.40
	$^3H_5$	1574	299.5^{ED}	12.0		
	$^3F_4$	1121	$351.3^{ED}+31.4^{MD}$	15.3		
	$^3H_6$	679	1813.6^{ED}	72.5		
$^1G_4$	$^3F_2+^3F_3$	1555	$56.0^{ED}+2.2^{MD}$	4.1	1406.1	0.71
	$^3H_4$	1187	$93.1^{ED}+18.0^{MD}$	7.9		
	$^3H_5$	782	$305.2^{ED}+74.4^{MD}$	27.0		
	$^3F_4$	651	$108.4^{ED}+5.6^{MD}$	8.1		
	$^3H_6$	473	743.2^{ED}	52.8		
$^1D_2$	$^1G_4$	1438	195.0^{ED}	0.9	22610.8	0.044
	$^3F_2+^3F_3$	747	$2399.3^{ED}+100.1^{MD}$	11.0		
	$^3H_4$	650	736.0^{ED}	3.2		
	$^3H_5$	506	46.4^{ED}	0.3		
	$^3F_4$	448	9022.0^{ED}	39.9		
	$^3H_6$	356	10112.0^{ED}	44.7		

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

Table 10. Comparison of the semi-experimental and theoretical integrated absorption cross sections* for the $^3H_4 \leftrightarrow ^3F_4$ and $^3H_4 \leftrightarrow ^3H_5$ transitions of Tm^{3+} ions in fluoride crystals.

Material	Transition	S^{ED}_{calc} $\times10^{20}$, cm^2	S^{MD}_{calc} $\times10^{20}$, cm^2	$\int\sigma_{abs,calc}(\lambda)d\lambda$ $\times10^{20}$ $cm^2\times nm$	Z_u/Z_l	λ_{ZL}, nm	$\int<\sigma_{abs}>(\lambda)d\lambda$ $\times10^{20}$, $cm^2\times nm$
Tm:KY$_3$F$_{10}$	$^3F_4\rightarrow^3H_4$	0.788	0.139	18.7	1.07	1443	22.9
	$^3H_5\rightarrow^3H_4$	0.767	0.245	27.8	1.22	2258	38.7
Tm:LiYF$_4$	$^3F_4\rightarrow^3H_4$	0.705	0.139	17.4	1.56	1428	17.1
	$^3H_5\rightarrow^3H_4$	0.597	0.245	22.7	0.90	2317	29.0
Tm:LiLuF$_4$	$^3F_4\rightarrow^3H_4$	0.752	0.147	18.5	1.61	1428	17.7
	$^3H_5\rightarrow^3H_4$	0.690	0.237	24.9	0.89	2320	24.1
Tm:BaY$_2$F$_8$	$^3F_4\rightarrow^3H_4$	0.856	0.147	21.5	1.12	1431	16.7
	$^3H_5\rightarrow^3H_4$	1.173	0.237	39.7	1.07	2286	39.3

*S^{ED}_{calc} and S^{MD}_{calc} – ED and MD line strengths, respectively, $\int\sigma_{abs,calc}(\lambda)d\lambda$ - calculated integrated absorption cross-section according to Eq. (7), Z_u/Z_l - the ratio of partition functions, Eq. (6), λ_{ZL} - ZL wavelength, $\int<\sigma_{abs}>(\lambda)d\lambda$ – polarization-averaged integrated absorption cross-section determined from the SE cross-sections with Eq. (5).