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ABSTRACT

We systematically study cross-relaxation (CR) and ion clustering in Tm\textsuperscript{3+}:CaF\textsubscript{2} crystals using a spectroscopic approach. For this, the luminescence from the \textsuperscript{3}H\textsubscript{4} and \textsuperscript{3}H\textsubscript{6} states was monitored for a broad range of Tm\textsuperscript{3+} doping concentrations, from 0.01 at.% to 7 at.%. The decay curves were fitted using a model of two ions classes, namely isolated ions showing no energy-transfer processes and ions with neighbors exhibiting both CR and energy-transfer upconversion (ETU), and accounting for energy-migration. The fraction of ions with neighbors and the microscopic concentration-independent CR and ETU parameters are deduced. The critical Tm\textsuperscript{3+} doping level for which at least half of the active ions are clustered is only 0.7 at.%.

The obtained results are relevant for achieving efficient laser operation of Tm\textsuperscript{3+}:CaF\textsubscript{2} crystals at the \textsuperscript{3}F\textsubscript{4} \rightarrow \textsuperscript{3}H\textsubscript{4} (at ~1.9 \textmu m) and the \textsuperscript{3}H\textsubscript{4} \rightarrow \textsuperscript{3}H\textsubscript{5} (at ~2.3 \textmu m) transitions.

Keywords: calcium fluoride, thulium ions, cross-relaxation, ion clustering, luminescence.

1. INTRODUCTION

Cubic (fluorite-type) calcium fluoride (CaF\textsubscript{2}) crystals are well-known for fabrication of optical elements because of their good thermo-mechanical properties (thermal conductivity: \(\kappa \approx 9.7\) W/(mK) for an undoped crystal), broad transparency range (0.13–10 \textmu m) and low refractive index (\(n = 1.424\) at ~2 \textmu m). CaF\textsubscript{2} crystals are also suitable for doping with trivalent rare-earth ions (RE\textsuperscript{3+}) for laser applications [1-3]. They feature a strong RE\textsuperscript{3+} ion clustering even at low doping concentrations about 0.1–1 at.% [4,5] resulting in broad and smooth spectral bands both in absorption and emission (the so-called glassy-like spectroscopic behavior). It is of interest for broadly tunable [6] and mode-locked [7,8] lasers. The good thermal properties of the host matrix allow for power scaling.

Thulium (Tm\textsuperscript{3+}) doped CaF\textsubscript{2} crystals exhibit a broadband emission at ~1.9 \textmu m due to the \textsuperscript{3}F\textsubscript{4} \rightarrow \textsuperscript{3}H\textsubscript{6} electronic transition. Efficient Tm\textsuperscript{3+}:CaF\textsubscript{2} lasers were reported [2,9]. Camy et al. reported on a laser-pumped Tm:CaF\textsubscript{2} laser delivering ~135 mW at 1887 nm with a slope efficiency of 41% and a laser threshold of only 68 mW [2]. Liu et al. reported on power scaling of a Tm:CaF\textsubscript{2} laser under diode-pumping yielding 2.71 W with a higher slope efficiency of 70.1% [9]. The same group of authors demonstrated continuous wavelength tunability for this laser between 1.85 and 2.04 \textmu m (189 nm broad) and mode-locked operation employing a SESAM. In the latter case, 15 ps-long pulses were obtained at a central wavelength of 1886.8 \textmu m with a repetition rate of 96.35 MHz [9]. Thin films of Tm:CaF\textsubscript{2} were grown [10].

It was proven that the ion clustering determines the emission properties of Tm\textsuperscript{3+} ions in CaF\textsubscript{2} [5]. For low doping levels (0.01-0.1 at.%), the Tm\textsuperscript{3+} ions are mostly isolated and they accommodate in sites with different symmetry depending on the charge compensation mechanism involving interstitial F\textsuperscript{-} anions. For higher doping levels, ion clusters are formed. To prevent the clustering of active ions, the CaF\textsubscript{2} crystals were codoped by Tm\textsuperscript{3+} ions and optically passive “buffer” ions Ln\textsuperscript{3+} such as Gd\textsuperscript{3+}, Lu\textsuperscript{3+}, La\textsuperscript{3+} or Y\textsuperscript{3+} [11,12]. Laser operation with such codoped crystals was also demonstrated. Zhang et al. reported on a Tm,La:CaF\textsubscript{2} laser delivering 4.27 W at 1921 nm with a slope efficiency of 67.8% [12].

A key spectroscopic process which determines the laser efficiency of ~1.9 \textmu m Tm lasers is the cross-relaxation (CR) for adjacent Tm\textsuperscript{3+} ions, \(\text{^3H}_4(\text{Tm}) + \text{^3H}_6(\text{Tm}) \rightarrow \text{^3F}_4(\text{Tm}) + \text{^3F}_4(\text{Tm})\), potentially leading to a pump quantum efficiency of 2 [13]. This means that after an excitation at ~0.8 \textmu m (to the \textsuperscript{3}H\textsubscript{4} pump level), there can be up to 2 excited ions in the upper laser level (\textsuperscript{3}F\textsubscript{4}). CR in Tm\textsuperscript{3+}-doped laser materials increases the laser slope efficiency and reduces the heat dissipation. Up to now, no detailed study of CR for Tm:CaF\textsubscript{2} crystals was performed.

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The aim of the present work is to study the cross-relaxation (and other energy-transfer processes, such as energy-transfer upconversion (ETU)) in Tm:CaF$_2$ crystals accounting for the ion clustering. For this, we involve the spectroscopic model of distinct ion classes which was recently developed [14].

2. EXPERIMENTAL RESULTS

For the spectroscopic studies, we grew a series of Tm$^{3+}$:CaF$_2$ crystals with the doping level ranging from 0.01 at.% to 7 at.%. The Tm:CaF$_2$ crystals were grown using a conventional Bridgman technique with a homemade furnace. A mixture of high purity (4N) CaF$_2$ and TmF$_3$ powders was introduced in a graphite crucible. A good vacuum (<10$^{-5}$ mbar) was realized before introducing Ar and CF$_4$ gases to avoid oxygen pollution. The furnace temperature was set to about 50 K higher than the melting point of CaF$_2$.

After soaking, the charge was thoroughly melted and the crystal growth was carried out with a rate of 2-4 mm/h. When the growth was finished, the crystal was cooled down to room temperature (RT, 293 K) within 48 hours.

2.1 Absorption and luminescence

The RT absorption spectra of Tm$^{3+}$:CaF$_2$ crystals containing predominantly isolated ions (0.05 at.% Tm) and ion clusters (1.5 at.% and 4.5 at.% Tm) are shown in Fig. 1. It is known that in Tm$^{3+}$-doped CaF$_2$ crystals with very low doping levels, the active ions are distributed over three types of sites with the symmetry C$_{3v}$ (trigonal), C$_{4v}$ (tetragonal) or O$_h$ (cubic). The particular symmetry depends on the charge compensation mechanism (as trivalent Tm$^{3+}$ ions are replacing the divalent Ca$^{2+}$ ones). The latter is provided by an interstitial fluorine anion (F$_i^-$). Here, we do not consider the possible charge compensation by oxygen (O$_2^-$) or univalent alkali metal cations (Na$^+$, K$^+$) leading to other types of sites. As a result, the absorption spectra of the 0.05 at.% Tm$^{3+}$:CaF$_2$ crystal represent a superposition of sharp absorption lines of Tm$^{3+}$ ions in all three sites. For high doping levels, the Tm$^{3+}$ ions are mostly arranged in clusters leading to smooth and broad spectral bands. There is no significant change in the absorption spectra of 1.5 at.% Tm and 4.5 at.% Tm-doped crystals, except of the $^3$H$_6 \rightarrow ^3$H$_5$ transition. The small changes may reflect the transition from simple clusters (dimers, trimers) to large agglomerates of active ions.

For the $^3$H$_6 \rightarrow ^3$H$_5$ pump transition, the maximum absorption cross-section $\sigma_{abs}$ is $0.46 \times 10^{-20}$ cm$^2$ at 766.2 nm and the full width at half maximum (FWHM) of the absorption band is 13.2 nm (for the 4.5 at.% Tm doping). For the 0.05 at.% Tm doping, the peak $\sigma_{abs}$ value is much lower, $0.17 \times 10^{-20}$ cm$^2$ at ~768 nm.
The evolution of RT luminescence spectra for the \( ^{3}H_4 \rightarrow ^{3}H_6 \) (at ~0.8 μm) and \( ^{3}F_4 \rightarrow ^{3}H_6 \) (at ~1.9 μm) transitions in emission was studied for a broad range of Tm doping concentrations (0.01–7 at.%). This comparative study revealed a critical Tm concentration (0.5–0.7 at.%) for which a significant change in the shape of the emission bands is observed: the spectra become smooth and broad and they resemble to a great extent those for Tm\(^{3+}\)-doped fluoride glasses. This is an indication of a change in the predominant ion coordination (a transition from isolated ions to clusters). Figure 2 shows such a comparison for the emission from the pump level \( (^{1}H_4) \) at ~0.8 μm.

![Normalized RT luminescence spectra of Tm\(^{3+}\):CaF\(_2\) crystals with different doping concentrations](image)

**Figure 2.** Normalized RT luminescence spectra of Tm\(^{3+}\):CaF\(_2\) crystals with different doping concentrations (the \( ^{3}H_4 \rightarrow ^{3}H_6 \) transition), \( \lambda_{exc} = 769 \) nm (non-selective excitation).

### 2.2 Luminescence decay

We monitored the decay of Tm\(^{3+}\) luminescence from the \( ^{3}H_4 \) and \( ^{3}F_4 \) multiplets for a broad range of Tm doping levels (0.01–7 at.%) in CaF\(_2\). Figure 3 shows the measured luminescence decay curves for the \( ^{3}H_4 \rightarrow ^{3}H_6 \) transition in emission (at ~0.8 μm). For very low doping level (0.01 at.% Tm), the luminescence decay curve is close to a single-exponential one with a characteristic lifetime \( t_{num} \) of 3.55 ms. Despite the existence of several species contributing to this emission (namely, isolated Tm\(^{3+}\) ions in various sites), the intrinsic lifetimes of the \( ^{3}H_4 \) state for the \( C_{3v} \) and \( C_{4v} \) coordinated Tm\(^{3+}\) ions in CaF\(_2\) are rather close: 3.03 ms and 3.59 ms, respectively (as determined in site-selective excitation experiments). With increasing Tm doping, the decay from the \( ^{3}H_4 \) state becomes faster and the luminescence decay curves notably deviate from the single-exponential law.

![Luminescence decay curves](image)

**Figure 3.** Luminescence decay curves from the \( ^{3}H_4 \) Tm\(^{3+}\) state in Tm\(^{3+}\):CaF\(_2\): black – experimental data, red – their fitting with the rate-equation model of distinct ion classes, \( \lambda_{exc} = 765 \) nm, \( \lambda_{em} = 820 \) nm. Measured under ns pulse excitation.

To explain this behavior, we used the model of spectroscopically distinct ion classes [14]. A simplified scheme of Tm\(^{3+}\) energy-levels was considered, Fig. 4. The populations of the Tm\(^{3+}\) ground-state \( (^{3}H_6) \) and two relevant excited-states \( (^{3}F_4 \) and \( ^{3}H_4 \)) were monitored; the population of the intermediate \( ^{3}H_5 \) excited-state was assumed to be almost zero as this state is depopulated by very efficient multi-phonon non-radiative (NR) relaxation. The states above \( ^{3}H_4 \) were not taken into account. The following spectroscopic processes were considered: (i) radiative (R) decay from the \( ^{3}F_4 \) and \( ^{3}H_4 \) states, (ii) cross-relaxation (CR) \( ^{3}H_4(Tm_1) + ^{3}H_6(Tm_2) \rightarrow ^{3}F_4(Tm_1) + ^{3}F_4(Tm_2) \), (iii) energy-transfer upconversion, \( ^{3}F_4(Tm_1) + ^{3}F_4(Tm_2) \rightarrow ^{3}H_4(Tm_1) + ^{3}H_6(Tm_2) \), (iv) cross-relaxation (CR) \( ^{3}H_4(Tm_1) + ^{3}H_6(Tm_2) \rightarrow ^{3}F_4(Tm_1) + ^{3}F_4(Tm_2) \),...
$^{3}F_{4}(Tm_{2}) \rightarrow ^{3}H_{6}(Tm_{1}) + ^{3}H_{4}(Tm_{2})$ (ETU$_{1}$) and $^{3}F_{4}(Tm_{1}) + ^{3}F_{4}(Tm_{2}) \rightarrow ^{3}H_{6}(Tm_{1}) + ^{3}H_{5}(Tm_{2})$ (ETU$_{2}$), and (iv) energy-migration (EM) to impurities leading to de-excitation from the $^{3}F_{4}$ and $^{3}H_{4}$ multiplets. We assumed the existence of two distinct ion classes: (a) isolated ions showing no energy-transfer processes (CR and ETU) and (b) ions with neighbors exhibiting both CR and ETU. The fraction of ions with neighbors $f$, the macroscopic rates of CR ($W_{CR}$) and ETU ($W_{ETU_{1}}$ and $W_{ETU_{2}}$) and the $^{3}H_{4}$ level lifetime $\tau$ accounting for EM were used as free parameters of the fitting (for luminescence decay curves shown in Fig. 3). The model gives a satisfactory agreement with the experiment.

![Energy-level diagram](https://example.com/energy-level-diagram.png)

**Figure 4.** The scheme of energy-levels of Tm$^{3+}$ ions (for a free-ion) showing relevant spectroscopic processes associated with the conventional pumping scheme (to the $^{3}H_{4}$ state): R – radiative relaxation, NR – multiphonon non-radiative relaxation, CR – cross-relaxation, ETU – energy-transfer upconversion, EM – energy-migration.

**3. DISCUSSION**

The results on the fraction of Tm$^{3+}$ ions with neighbors $f$ are shown in Fig. 5. With increasing the Tm doping level, the fraction of isolated ions ($1 - f$) gradually decreases. The critical Tm doping level for which at least half of the active ions are clustered is only 0.7±0.1 at.%. This agrees well with our conclusion drawn from the measured luminescence spectra at ~0.8 μm. The dependence of $f$ on the doping concentration was fitted using a statistical approach [14,15]:

$$P_{m,n} = \frac{n!}{m!(n-m)!} p^m (1-p)^{n-m}.$$  

![Fraction of ions with neighbors](https://example.com/fraction-of-ions.png)

**Figure 5.** Ion clustering in Tm$^{3+}$:CaF$_{2}$: fraction of ions with neighbors $f$, symbols – data extracted from the modeling of the experimental luminescence decay curves using the rate-equation model of distinct ion classes, curve – their fit using a statistical approach.

Here, $P_{m,n}$ is the probability for occurrence of neighbor Tm$^{3+}$ ions in the first coordination sphere of the considered Tm$^{3+}$ ion, $n$ is the coordination number (C.N.) by nearest-neighbor rare-earth sites, $m$ is the actual number of Tm$^{3+}$ ions in the first coordination sphere ($m=0$ corresponds to a single ion and $m \geq 1$ - to an ion pair or cluster), and $p = N_{Tm}/N_{max}$ represents the relative doping concentration ($N_{max}$ is the maximum possible concentration). The expression for the fraction of ions with neighbors ($m \geq 1$, not specifying the exact $m$ number) is:
\[ f = 1 - [1 - (N_{\text{Tm}}/N_{\text{max}})]^{\text{CN}}. \]  
\[ \text{(2)} \]

For calculation, we assume \( N_{\text{max}} = 10 \text{ at.}\% \) and C.N. = 10 which gives a good agreement with the data obtained from the measured luminescence curves.

The model also yields the macroscopic rates \( W_{\text{CR}} \), \( W_{\text{ETU1}} \) and \( W_{\text{ETU2}} \) [in s\(^{-1}\)], as shown in Fig. 6. The CR is \( \text{Tm:CaF}_2 \) much stronger than the ETU. \( W_{\text{CR}} \) and \( W_{\text{ETU1(2)}} \) show a quadratic dependence on the Tm doping concentration \( (N_{\text{Tm}}) \):

\[ W_{\text{CR}} = C_{\text{CR}}N_{\text{Tm}}^2, \]  
\[ \text{(3a)} \]
\[ W_{\text{ETU1(2)}} = C_{\text{ETU1(2)}}N_{\text{Tm}}^2, \]  
\[ \text{(3b)} \]

where \( C_{\text{CR}} \) and \( C_{\text{ETU1(2)}} \) are the concentration-independent microscopic energy-transfer parameters. CR in \( \text{Tm}^{3+}:\text{CaF}_2 \) is about one order of magnitude stronger than that in other well-known fluoride crystal, \( \text{Tm}^{3+}:\text{LiYF}_4 \) [16].

Figure 6. Energy-transfer processes in \( \text{Tm}^{3+}:\text{CaF}_2 \): macroscopic rates of cross-relaxation (CR) \( W_{\text{CR}} \) and energy-transfer upconversion (ETU) \( W_{\text{ETU1(2)}} \), symbols – data extracted from the modeling of the experimental luminescence decay curves using the rate-equation model of distinct ion classes, lines – their quadratic fits.

4. CONCLUSIONS

To conclude, we have quantified ion clustering (in terms of fraction of ions with neighbors) and CR and ETU energy-transfer processes (in terms of macroscopic rates and microscopic concentration-independent parameters) in \( \text{Tm}^{3+}\)-doped \( \text{CaF}_2 \) crystals, for the first time, to the best of our knowledge. This information is of key importance for the design of \( \text{Tm:CaF}_2 \) lasers operating on the \( ^4\text{F}_4 \rightarrow ^3\text{H}_6 \) (\( \sim 1.9 \mu\text{m} \)) and \( ^3\text{H}_4 \rightarrow ^3\text{H}_6 \) (\( \sim 2.3 \mu\text{m} \)) transitions. Indeed, for the \( \sim 1.9 \mu\text{m} \) lasers, quantification of CR is important to determine the possibility to reach high pump quantum efficiency of 2 for the upper laser level \( ^3\text{F}_4 \) [13]. For the \( \sim 2.3 \mu\text{m} \) lasers which have not been demonstrated yet in \( \text{Tm:CaF}_2 \), in contrast, CR is a detrimental effect as it quenches the lifetime of the upper laser level \( ^5\text{H}_4 \). However, ETU1 in such lasers can play a key role in refilling the \( ^3\text{H}_4 \) state leading to increased laser slope efficiency [16,18]. The proposed spectroscopic model can be extended to describe the ion clustering in \( \text{Tm}^{3+},\text{Ln}^{3+}:\text{CaF}_2 \) crystals codoped with “buffer” ions.

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REFERENCES


