

## Article

# Spectroscopic Properties of Tb<sup>3+</sup> Ions in TbF<sub>3</sub>-Doped CaF<sub>2</sub> Crystals

Irinuca Bodea <sup>1</sup>, Marius Stef <sup>1,\*</sup> , Carla Schornig <sup>1</sup>, Gabriel Buse <sup>2</sup> , Philippe Veber <sup>1</sup>  and Daniel Vizman <sup>1,2</sup>

<sup>1</sup> Department of Physics, West University of Timisoara, Bd. Vasile Parvan 4, Timisoara 200223, Romania; irinuca.bodea99@e-uvv.ro (I.B.); carla.schornig@e-uvv.ro (C.S.); philippe.veber@e-uvv.ro (P.V.); daniel.vizman@e-uvv.ro (D.V.)

<sup>2</sup> Institute for Advanced Environmental Research, West University of Timisoara, Timisoara 300086, Romania; gabriel.buse@e-uvv.ro

\* Correspondence: marius.stef@e-uvv.ro; Tel.: +40-256-592206

## Highlights

- Tb<sup>3+</sup>-doped CaF<sub>2</sub> single crystals show efficient and stable green luminescence.
- Judd–Ofelt analysis quantifies radiative properties across TbF<sub>3</sub> concentrations.
- Cross-relaxation governs emission from the <sup>5</sup>D<sub>4</sub> level and suppresses <sup>5</sup>D<sub>3</sub> emission.
- Quantum efficiency increases with concentration and reaches the maximum value for highest Tb<sup>3+</sup> content.
- The emission cross-sections and the gain parameter have the highest value for the orange emission (two times higher than green or yellow emission) for 10 mol% TbF<sub>3</sub>.

## What are the main findings?

- Tb<sup>3+</sup>-doped CaF<sub>2</sub> crystals exhibit intense and stable green emission dominated by the <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> transition.
- Judd–Ofelt analysis provides radiative parameters of Tb<sub>3+</sub>-doped CaF<sub>2</sub> crystal.
- The measured quantum efficiency increases from 31.4% (1 mol%) to 71.2% (5 mol%) and 73.9% (10 mol%).

## What are the implications of the main findings?

- Efficient green emission is achieved at moderate–high Tb<sup>3+</sup> concentrations without strong quenching.
- Cross-relaxation (<sup>5</sup>D<sub>3</sub> → <sup>5</sup>D<sub>4</sub>) enables effective population of the <sup>5</sup>D<sub>4</sub> emitting level.
- CaF<sub>2</sub>:Tb<sup>3+</sup> combines millisecond lifetimes (~4.4–6.7 ms) with high QE, suitable for photonic applications.

## Abstract

Tb<sup>3+</sup>-doped CaF<sub>2</sub> single crystals are attractive materials for green photonic applications due to their low phonon energy, high optical transparency, and efficient Tb<sup>3+</sup> emission. In this work, CaF<sub>2</sub> single crystals doped with different TbF<sub>3</sub> concentrations (1, 5, and 10 mol%) were grown and systematically investigated in order to clarify the concentration-dependent spectroscopic behavior of Tb<sup>3+</sup> ions in a fluorite host. Optical absorption spectroscopy, Judd–Ofelt analysis, steady-state and time-resolved photoluminescence, colorimetric evaluation, and emission cross-section and gain calculations were employed. Judd–Ofelt intensity parameters typical of fluoride hosts were obtained, enabling the calculation of radiative transition probabilities and lifetimes. The emission spectra are dominated by intense green luminescence from the <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> transition, while the absence of <sup>5</sup>D<sub>3</sub> emission is attributed to efficient cross-relaxation processes. Fluorescence lifetimes in the millisecond range show slight changes with Tb<sup>3+</sup> concentration. Quantum efficiency increases



Academic Editor: Joanna Pisarska

Received: 28 January 2026

Revised: 10 February 2026

Accepted: 13 February 2026

Published: 18 February 2026

**Copyright:** © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

from low to intermediate concentrations and tends to saturate at higher doping levels. CIE 1931 chromaticity coordinates confirm stable green emission, while emission cross-sections and gain parameters reveal a highest value for orange emission of 10 mol% TbF<sub>3</sub>-doped CaF<sub>2</sub> crystal. These results indicate that CaF<sub>2</sub>:Tb<sup>3+</sup> single crystals are promising materials for photonic applications.

**Keywords:** fluoride crystals; thulium; optical spectroscopy; Judd–Ofelt analysis; luminescence

## 1. Introduction

Rare-earth-doped materials are key enabling materials for a wide range of photonic applications, including solid-state lasers [1–6], wavelength converters [7], magneto-optical components [8,9], scintillators [10–12], and luminescent phosphors [13–19]. In particular, fluorite-type hosts such as CaF<sub>2</sub> [20–25], BaF<sub>2</sub> [26–29] or KY<sub>3</sub>F<sub>10</sub> [30] have attracted sustained interest for visible and near-infrared photonics, due to their low multiphonon relaxation rates and high optical quality, which enable efficient emission and amplification processes, or magneto-optical properties [8]. Tb<sup>3+</sup>-activated fluoride materials are especially relevant for green photonics, optical signaling, and display-related technologies, due to the intense <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>J</sub> (J = 3, 4, 5) emission manifold and the possibility of tailoring radiative properties through dopant concentration control [9,20,31–37].

From a spectroscopic point of view, the performance of rare-earth-activated photonic materials is dictated by the electronic structure of the dopant ions and by their interaction with the host lattice. The optical transitions of Tb<sup>3+</sup> ions arise from the 4f<sup>8</sup> electronic configuration and are characterized by a rich manifold of narrow 4f–4f transitions, whose energies and relative intensities have been thoroughly established through fundamental spectroscopic investigations and tabulations of energy levels and radiative parameters [38–40]. In particular, the <sup>5</sup>D<sub>4</sub> excited state of Tb<sup>3+</sup> is responsible for intense green emission through the <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>J</sub> (J = 6–3) transitions, while the higher-lying <sup>5</sup>D<sub>3</sub> state can contribute blue emission under suitable excitation and concentration regimes, making Tb<sup>3+</sup> a versatile activator for visible photonics [41–44].

Compared to LnF<sub>3</sub> fluorides, CaF<sub>2</sub> offers a cubic crystal structure with higher symmetry, optical isotropy, negligible birefringence, and a broader transparency window, together with superior crystal growth stability and lower scattering losses, making it an excellent host for Tb<sup>3+</sup> ions [40].

When embedded in crystalline hosts, the spectroscopic properties of Tb<sup>3+</sup> are modulated by crystal-field splitting, site symmetry, and phonon-assisted relaxation processes, which together govern emission bandwidths, radiative lifetimes, and quantum efficiencies. Fluoride lattices are particularly advantageous in this respect, as their low maximum phonon energies significantly suppress multiphonon non-radiative decay, thereby preserving high radiative efficiencies of Tb<sup>3+</sup> emission compared to oxide hosts [45–47]. Consequently, fluoride-based systems have been investigated as efficient hosts for Tb<sup>3+</sup>-activated luminescent materials, lasers, and magneto-optical components, with various studies demonstrating the sensitivity of Tb<sup>3+</sup> emission characteristics to the local structural environment and dopant concentration. However, the incorporation of trivalent rare-earth ions into the divalent Ca<sup>2+</sup> sublattice is intrinsically accompanied by charge-compensation mechanisms, most commonly involving fluorine interstitials or complex defect clusters, which profoundly influence the local environment of the optically active centers [22,23,29,48]. As a result, even at relatively low dopant concentrations, CaF<sub>2</sub>:RE<sup>3+</sup> systems may exhibit multiple crystallographic sites and defect-associated centers, leading

to inhomogeneous broadening of optical bands and non-trivial variations in luminescence dynamics [3,22,31]. These defect-related effects become particularly important for  $\text{Tb}^{3+}$ -doped  $\text{CaF}_2$ , where the balance between isolated ions and clustered centers determines the efficiency and spectral distribution of the  $^5\text{D}_4$  and  $^5\text{D}_3$  emissions. Experimental studies have shown that increasing the  $\text{Tb}^{3+}$  concentration can promote ion–ion interactions, cross-relaxation processes, and energy migration toward quenching centers, thereby modifying radiative lifetimes and emission intensities [9,17,20,21,30,36]. Moreover, the spatial distribution of  $\text{RE}^+$  ions—affected by growth conditions, segregation phenomena, and post-growth treatments—has been identified as a key factor governing the reproducibility and performance of photonic materials [49]. These considerations underline the necessity of a detailed spectroscopic analysis that explicitly accounts for defect chemistry and concentration-dependent effects when assessing the optical properties of  $\text{Tb}^{3+}$  in  $\text{CaF}_2$ .

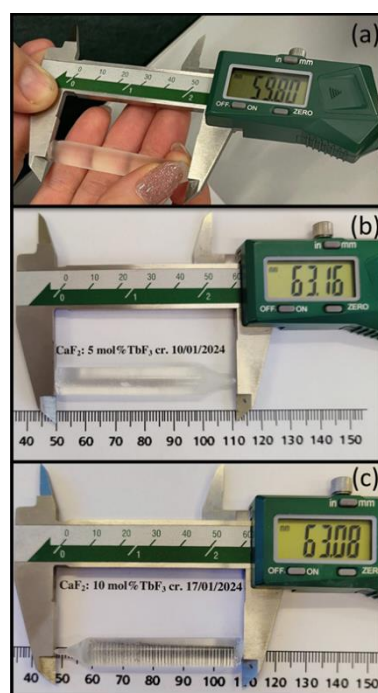
A quantitative assessment of the optical performance of  $\text{Tb}^{3+}$ -doped  $\text{CaF}_2$  requires reliable determination of radiative transition probabilities, branching ratios, and intrinsic lifetimes, parameters that are essential for evaluating the suitability of these materials for photonic applications. In this context, the Judd–Ofelt (J–O) formalism has been widely adopted as a standard theoretical framework to extract radiative properties of rare-earth ions in solids from experimental absorption and emission data [50–54]. When applied to fluoride hosts, the J–O analysis benefits from reduced multiphonon contributions and relatively narrow spectral features, allowing a more direct correlation between intensity parameters and the local symmetry and covalency of the rare-earth sites [3,13,22,24,29].

Nevertheless, the application of the J–O approach to  $\text{Tb}^{3+}$ -doped  $\text{CaF}_2$  is not straightforward and remains subject to several methodological challenges. The coexistence of multiple  $\text{Tb}^{3+}$ -related centers, arising from different charge-compensation schemes and defect complexes, can lead to ambiguities in the assignment of absorption bands and to uncertainties in the extracted intensity parameters [22,26]. Furthermore, recent studies have highlighted that inaccuracies in absorption cross-section determination, spectral overlap between transitions, and the neglect of site multiplicity may introduce significant systematic errors in J–O-derived radiative parameters, particularly in fluorite-type lattices [3,29]. Despite the extensive body of literature dedicated to rare-earth-doped fluorides, the spectroscopic characterization of  $\text{Tb}^{3+}$  in  $\text{CaF}_2$  remains fragmented, with most studies addressing either specific emission features, particular concentration regimes, or selected material forms such as thin films [37,42] and nanostructures [33]. Moreover, recent advances in spectroscopic methodologies and data analysis, including refined absorption cross-section measurements and critical assessments of Judd–Ofelt uncertainties, have highlighted the need for revisiting classical  $\text{Tb}^{3+}:\text{CaF}_2$  systems using updated experimental protocols and interpretative frameworks [53,54]. This is especially relevant in view of the renewed interest in  $\text{CaF}_2$ -based photonic materials for visible emission, laser-related applications, and radiation-resistant optical components, where accurate and reproducible radiative parameters are essential for material optimization and device design.

In this context, the present work aims to provide a systematic spectroscopic analysis of  $\text{Tb}^{3+}$  ions in  $\text{TbF}_3$ -doped  $\text{CaF}_2$  single crystals. By combining steady-state absorption and photoluminescence spectroscopy with time-resolved measurements and a careful radiative analysis, this study seeks to quantify luminescence parameters relevant to photonic applications in the visible spectral region and to investigate the influence of dopant concentration on the optical response of  $\text{Tb}^{3+}:\text{CaF}_2$ . The results are intended to contribute to a more coherent understanding of  $\text{Tb}^{3+}$ -activated fluorite materials and to provide a reliable reference for future developments in fluoride-based photonics.

## 2. Materials and Methods

Single crystals of terbium-doped calcium fluoride ( $\text{CaF}_2:\text{Tb}^{3+}$ ) were grown using vertical Bridgman–Stockbarger method under high vacuum conditions ( $10^{-1}$  Pa) in a pure graphite crucible, following procedures optimized for rare-earth doped  $\text{CaF}_2$  crystals [3,24,49]. High-purity  $\text{CaF}_2$  and  $\text{TbF}_3$  powders (optical grade) from Merck (99.99%) were used as the raw material. The nominal terbium concentrations investigated in the present study were 1, 5 and 10 mol%  $\text{TbF}_3$  added to the melt. In the  $\text{CaF}_2$  fluorite lattice,  $\text{RE}^{3+}$  ions predominantly substitute  $\text{Ca}^{2+}$  sites, leading to an extra positive charge. Charge compensation is mainly achieved through the formation of interstitial fluoride ions ( $\text{F}^-_{\text{i}}$ ), resulting in defect complexes of the type  $\text{Tb}^{3+}-\text{F}^-_{\text{i}}$  [22,26]. At higher dopant concentrations, such charge-compensation mechanisms may induce multisite and local structural distortions, while preserving the overall fluorite crystal structure. By using laser-induced breakdown spectroscopy (LIBS), the  $\text{Tb}^{3+}$  concentration in the crystals is determined to be  $2.437$ ,  $11.9$  and  $22.14 \times 10^{20}$  ions/ $\text{cm}^3$  corresponding to the nominal concentration of 1, 5 and 10 mol%  $\text{TbF}_3$ . Crystal growth was performed at temperatures exceeding the melting point of  $\text{CaF}_2$  ( $1381^\circ\text{C}$ ), followed by controlled cooling to promote single-crystal formation and reduce thermal stress. Particular attention was paid to the solidification rate ( $\sim 3^\circ\text{C}/\text{min}$ ) and thermal gradient ( $\sim 12^\circ\text{C}/\text{cm}$ ), as these parameters are known to strongly influence defect formation and dopant distribution in fluorite-type crystals [49,50]. Figure 1 illustrates representative samples corresponding to different terbium concentrations. The crystals exhibit good transparency and no visible cracks, confirming the suitability of the growth conditions for high-quality fluoride crystals. As shown in Figure 1a–c, the absence of visible cracks or strong light scattering indicates a good overall optical quality, which is a prerequisite for reliable spectroscopic investigations.



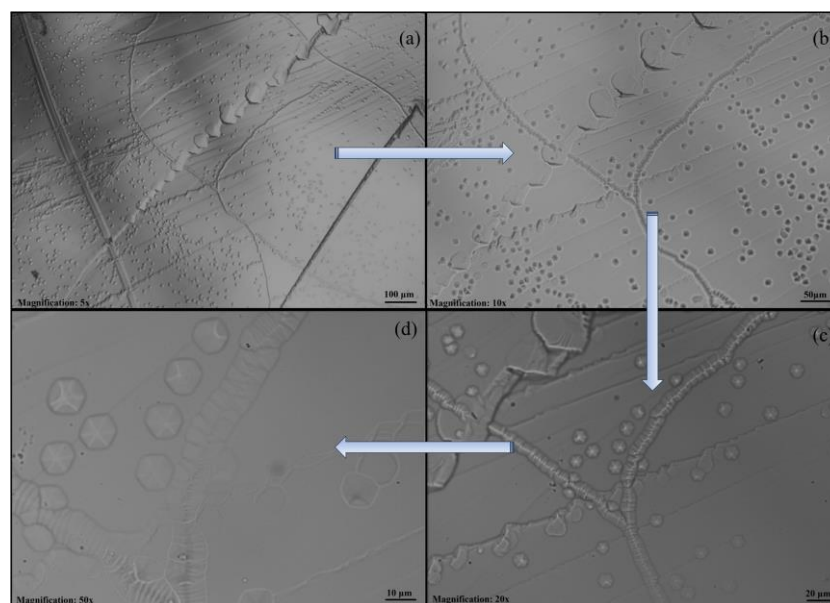
**Figure 1.** Photographs of  $\text{CaF}_2$  single crystals doped with: (a) 1 mol%  $\text{TbF}_3$ ; (b) 5 mol%  $\text{TbF}_3$ ; (c) 10 mol%  $\text{TbF}_3$ . The measured crystal lengths are indicated.

After growth, the as-grown crystals were cleaved along the (111) crystallographic directions into optically flat samples with  $\sim 2$  mm thickness suitable for spectroscopic investigations.

In order to investigate the etch pit morphology and evaluate the dislocation density in  $\text{Tb}^{3+}$ -doped  $\text{CaF}_2$  single crystals, a chemical etching technique was employed. Freshly

cleaved samples with surfaces oriented along the (111) crystallographic plane were immersed in a 4N hydrochloric acid (HCl) solution for 5 min at 60 °C. The etching process was carried out in a temperature-controlled water bath to ensure stable and reproducible conditions. After etching, the samples were thoroughly rinsed with distilled water, immediately dried using filter paper, and subsequently examined by optical microscopy. The etched surfaces were analyzed using an optical microscope equipped with an Olympus UC-30 image acquisition and processing module. This system enabled detailed visualization of etch pits, as well as quantitative measurements of their dimensions and the determination of the dislocation density in the  $\text{Tb}^{3+}$ -doped  $\text{CaF}_2$  crystals.

Figure 2 shows the dislocations in  $\text{CaF}_2$ :1 mol%  $\text{TbF}_3$  single crystals observed on the averaged (111) cleavage plane under various magnifications from  $5\times$  to  $40\times$ .  $\text{CaF}_2$ : $\text{Tb}^{3+}$  single crystals doped with 1, 5, and 10 mol%  $\text{TbF}_3$  exhibited dislocation densities of  $6.3 \times 10^3$ ,  $2.5 \times 10^3$ , and  $17 \times 10^3$  dislocations/cm<sup>2</sup>, respectively, these relatively low values confirming the high crystalline quality of the samples. The etch pit shape observed on the cleavage planes in the vicinity of (111) directions is slightly distorted hexagons, exhibiting thus a 3-fold axis in accordance to the (111) direction of cubic  $\text{CaF}_2$ . They have a quasi-uniform spatial distribution (Figure 2a–d). A similar etch pit shape was previously reported for  $\text{BaF}_2$ : $\text{Tm}^{3+}$  crystals, where the dislocation density reached  $3.9 \times 10^3$  dislocations/cm<sup>2</sup> [29].



**Figure 2.** Dislocations in  $\text{CaF}_2$ :1 mol%  $\text{TbF}_3$  crystal observed on the (111) fresh cleaved plane under various optical magnification: (a)  $5\times$ , (b)  $10\times$ , (c)  $20\times$  and (d)  $40\times$ .

The room-temperature optical absorption spectra, in the UV–VIS domain, were recorded using a Shimadzu 1650 PC from Shimadzu, Kyoto, Japan, spectrophotometer. The IR absorption spectrum was obtained with a Nexus 470 FTIR spectrophotometer. Room-temperature visible luminescence spectra and the time-resolved measurements were recorded by FLS 1000–Edinburgh Instruments spectrofluorometer using Xe lamp as the excitation source and a scan slit of 1 nm.

Such dislocation structures are commonly reported in  $\text{CaF}_2$  crystals [55] and are generally associated with lattice strain induced by aliovalent substitution of  $\text{Ca}^{2+}$  by  $\text{Tb}^{3+}$  ions and the corresponding charge-compensation mechanisms. Although these defects may locally disrupt the crystal field environment of  $\text{Tb}^{3+}$  ions, their overall density in the present samples remains sufficiently low to allow reliable optical and spectroscopic characterization. The combined macroscopic transparency and controlled defect structure

confirm that the grown crystals are appropriate for detailed spectroscopic analysis of Tb<sup>3+</sup> luminescence properties.

Optical absorption spectra were recorded at room temperature using a Shimadzu 1650PC spectrophotometer on cleaved crystal samples with parallel faces in order to minimize scattering losses and interference effects. The absorption measurements were performed in the 190–1100 nm spectral range relevant for Tb<sup>3+</sup> excitation, enabling identification of the characteristic 4*f*–4*f* transitions originating from the <sup>7</sup>F<sub>6</sub> ground state. The near-infrared absorption spectra were registered using a Nexus 470 FTIR spectrophotometer.

Photoluminescence (PL) spectra were measured using FLS1000-Edinburgh Instruments spectrofluorometer under selective excitation into the Tb<sup>3+</sup> absorption bands, using Xe as the excitation source. The emitted light was collected in a right-angle geometry and analyzed with a calibrated detection system to ensure reliable comparison of relative emission intensities. Special attention was paid to the <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>J</sub> emission manifold, which is of primary interest for visible photonic applications.

Time-resolved luminescence measurements were carried out to determine the decay dynamics of the excited Tb<sup>3+</sup> states. Luminescence decay curves were acquired following pulsed excitation provided by a Xe flash lamp and fitted using standard exponential models, providing experimental lifetimes that were subsequently used for radiative and non-radiative analysis. The quantum efficiency measurements were carried out using QYPro integrating a sphere module.

The Judd–Ofelt (JO) analysis was applied to the room-temperature absorption spectra of Tb<sup>3+</sup>-doped CaF<sub>2</sub> crystals to extract the intensity parameters, which were subsequently used to calculate radiative transition probabilities, branching ratios, and radiative lifetimes [51,52].

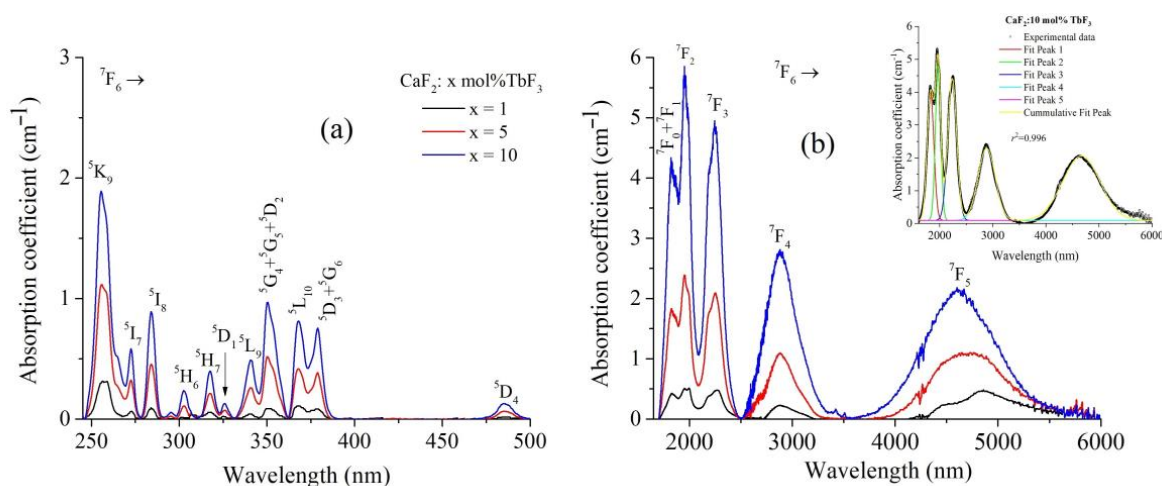
### 3. Results

#### 3.1. Optical Absorption Spectra

The room-temperature optical absorption spectra of Tb<sup>3+</sup>-doped CaF<sub>2</sub> single crystals were recorded in the 240–6000 nm spectral range in order to identify the characteristic 4*f*–4*f* transitions of Tb<sup>3+</sup> ions and to provide the basis for subsequent radiative analysis. The absorption spectra exhibit a series of narrow bands superimposed on a weakly varying background, which is typical for parity-forbidden intra-configurational transitions of trivalent rare-earth ions embedded in wide-bandgap fluoride hosts [9,17,20,36].

Figure 3 shows the room-temperature optical absorption spectra of CaF<sub>2</sub>:Tb<sup>3+</sup> single crystals with different nominal TbF<sub>3</sub> concentrations (*x* = 1, 5, and 10 mol%), expressed as absorption coefficient as a function of wavelength. The spectra cover a wide spectral range and are presented in two panels: (a) the ultraviolet–visible region (≈240–500 nm) and (b) the near- and mid-infrared region (≈1800–6000 nm). In the UV–Vis range (Figure 3a), the absorption spectra are dominated by a series of narrow, well-resolved bands characteristic of intra-configurational 4*f*–4*f* transitions of Tb<sup>3+</sup> ions originating from the <sup>7</sup>F<sub>6</sub> ground state. The observed absorption features can be assigned to transitions toward the <sup>5</sup>K<sub>J</sub>, <sup>5</sup>L<sub>J</sub>, <sup>5</sup>G<sub>J</sub>, <sup>5</sup>D<sub>J</sub>, <sup>5</sup>H<sub>J</sub> and <sup>5</sup>I<sub>J</sub> multiplets, as indicated in the figure. The spectral positions of these bands remain essentially unchanged with increasing Tb<sup>3+</sup> concentration, indicating that the local crystal-field environment of Tb<sup>3+</sup> ions is not significantly modified within the investigated doping range. On the other hand, the absorption intensity increases systematically with Tb<sup>3+</sup> concentration, reflecting the higher density of optically active centers in the CaF<sub>2</sub> lattice. The relatively narrow bands confirm the weak coupling between the 4*f* electrons and the host lattice phonons, which is typical for rare-earth ions in fluoride hosts [20]. The near-infrared absorption spectra (Figure 3b) show broader absorption bands compared to the UV–Vis region, with bands centered at approximately 1.8 μm, 2.0 μm, 2.2 μm, 2.8,

and a broad band around 4.6  $\mu\text{m}$ . These bands are attributed to transitions from the  $^7\text{F}_6$  ground state to low-lying excited multiplets of  $\text{Tb}^{3+}$ , labeled in the figure as  $^7\text{F}_j$  transitions. As in the UV–Vis region, the absorption intensity in the infrared increases monotonically with  $\text{Tb}^{3+}$  concentration, while no significant spectral shifts are observed, supporting a homogeneous incorporation of  $\text{Tb}^{3+}$  ions into the  $\text{CaF}_2$  host. The inset in Figure 3b presents a representative multi-peak fitting of the infrared absorption spectrum for the  $\text{CaF}_2$ :10 mol%  $\text{TbF}_3$  sample. The experimental spectrum is accurately reproduced by a sum of individual Gaussian components, yielding a very good fit quality (correlation coefficient,  $R^2 \approx 0.996$ ). This reliable deconvolution of overlapping absorption bands enables accurate determination of integrated absorption intensities, which are subsequently used as input parameters for the JO analysis and for the calculation of radiative transition probabilities and branching ratios. The band positions are in good agreement with the energy level scheme reported for  $\text{Tb}^{3+}$  ions in crystalline environments [17,20,36]. No additional broad absorption features attributable to impurity phases or secondary phases were detected, indicating a high optical quality of the investigated crystals.



**Figure 3.** Room-temperature optical absorption spectra of  $\text{CaF}_2$ : $\text{Tb}^{3+}$  single crystals with nominal  $\text{TbF}_3$  concentrations of  $x = 1, 5$ , and 10 mol%. (a) UV–Vis spectra showing the characteristic  $4f-4f$  transitions of  $\text{Tb}^{3+}$  ions from the  $^7\text{F}_6$  ground state. (b) NIR and mid-infrared absorption spectra with assigned  $^7\text{F}_j$  transitions. The inset shows a multi-peak Gaussian fitting of the infrared absorption spectrum for the  $\text{CaF}_2$ :10 mol%  $\text{TbF}_3$  crystal.

### 3.2. Judd–Ofelt Analysis

The Judd–Ofelt (JO) theory is a well-established approach for the quantitative evaluation of  $4f-4f$  transition intensities of rare-earth ions embedded in solid-state hosts [51,52]. Within this framework, the spectroscopic behavior of rare-earth ions is described by three phenomenological intensity parameters,  $\Omega_2$ ,  $\Omega_4$ , and  $\Omega_6$ , which are determined by fitting experimental absorption data. Once obtained, the JO parameters allow the calculation of radiative properties, including electric dipole oscillator strengths, emission cross-sections, radiative transition probabilities, radiative lifetimes, and branching ratios. In the present study, the absorption spectra were used to determine the absorption cross-section,  $\sigma_{\text{abs}}(\lambda)$ , according to:

$$\sigma_{\text{abs}} = \frac{O.D.\ln(10)}{l \times N} \quad (1)$$

where  $l$  is the sample thickness,  $O.D.$  is the optical density, and  $N$  denotes the concentration of  $\text{Tb}^{3+}$  ions. In the JO formalism, the electric dipole line strength for a transition between an initial state  $|J\rangle$  and a final state  $|J'\rangle$  is expressed as:

$$(S_{JJ'}^{\text{DE}})_{\text{calc}} = \sum_{t=2,4,6} \Omega_t |\langle 4f^n \alpha L S J || U^t || 4f^n \alpha' L' S' J' \rangle|^2 \quad (2)$$

The magnetic dipole contribution to the line strength is given by:

$$(S_{JJ'}^{\text{DM}})_{\text{calc}} = \left( \frac{\hbar}{2mc} \right)^2 |\langle 4f^n \alpha L S J || L + 2S || 4f^n \alpha' L' S' J' \rangle|^2 \quad (3)$$

The reduced matrix elements,  $|\langle 4f^n \alpha L S J || U^t || 4f^n \alpha' L' S' J' \rangle|$  required for the evaluation of line strengths were taken from Kaminskii and tabulated in Table 1 [40]. In the present JO analysis, only electric dipole-allowed transitions were considered in the fitting procedure. The experimental line strengths, derived from absorption measurements, are related to the integrated absorption cross-sections by:

$$(S_{JJ'}^{\text{DE}})_{\text{meas}} = S_{JJ'}^{\text{meas}} - \left( \frac{9n^2}{(n^2 + 2)^2} \right) (S_{JJ'}^{\text{DM}})_{\text{calc}} \quad (4)$$

$$\text{where } S_{JJ'}^{\text{meas}} = \left( \frac{9n}{(n^2 + 2)^2} \right) \left( \frac{3hc\epsilon_0}{2\pi^2 e^2} \right) \left( \frac{2J+1}{\lambda_m} \right) \int \sigma_{\text{abs}}(\lambda) d\lambda.$$

where  $n$  is the refractive index of the host material determined by the Sellmeier's equation [56]. The quality of the JO fit was evaluated by calculating the root-mean-square deviation,  $\delta$ , between experimental and calculated line strengths:

$$\delta = \sqrt{\frac{\sum_{i=1}^q \left( (S_{JJ'}^{\text{DE}})_{\text{calc}}^i - (S_{JJ'}^{\text{DE}})_{\text{meas}}^i \right)^2}{q - p}} \quad (5)$$

where  $q = 3$  and  $p = 4$  are the number of absorption transitions strength selected, which correspond to the transitions: Transition,  ${}^7F_6 \rightarrow {}^7F_3, {}^7F_2, ({}^7F_1 + {}^7F_0), {}^5D_4$ . Using the optimized intensity parameters, the total radiative emission probability for a transition was obtained by summing the electric and magnetic dipole contributions:

$$A_{JJ'} = A_{JJ'}^{\text{ED}} + A_{JJ'}^{\text{MD}} \quad (6)$$

from which the radiative lifetime of an excited level was calculated as:

$$\tau_{\text{rad}} = \left( \sum_{JJ'} A_{JJ'} \right)^{-1} \quad (7)$$

Finally, the branching ratio, defined as the relative probability of a radiative transition from a given excited level, was determined using:

$$\beta_{JJ'} = \frac{A_{JJ'}}{\sum_{JJ'} A_{JJ'}} \quad (8)$$

Table 1 summarizes the squared reduced matrix elements,  $[U^{(t)}]^2$  ( $t = 2, 4, 6$ ), associated with the selected optical transitions of  $\text{Tb}^{3+}$  ions originating from the  ${}^7F_6$  ground state, together with the corresponding mean wavelengths.

Table 2 summarizes the experimental and calculated electric dipole line strengths for selected optical transitions of  $\text{Tb}^{3+}$  ions in  $\text{CaF}_2$  crystals with different nominal  $\text{TbF}_3$  concentrations (1, 5, and 10 mol%). The corresponding mean wavelengths and  $\text{Tb}^{3+}$  ion concentrations are also listed. The line strengths were derived from the absorption spectra and subsequently compared with the values obtained from the JO calculations. For all investigated concentrations, a reasonable agreement between the measured and calculated line strengths is observed. The root-mean-square deviation  $\delta$ , reported for each

concentration, decreases with increasing  $\text{Tb}^{3+}$  content, indicating an improvement in the overall quality of the JO fit at higher dopant concentrations. This behavior can be attributed to the enhanced signal-to-noise ratio of the absorption bands at higher terbium contents, which allows a more reliable determination of integrated absorption intensities.

**Table 1.** Mean wavelengths ( $\lambda_m$ ) and squared reduced matrix elements,  $[U^{(t)}]^2$  ( $t = 2, 4, 6$ ), for selected optical transitions of  $\text{Tb}^{3+}$  ions originating from the  $^7\text{F}_6$  ground state, used in the JO analysis.

| Transition, $^7\text{F}_6 \rightarrow$ | $\lambda_m$ (nm) | $[U^{(2)}]^2$ | $[U^{(4)}]^2$ | $[U^{(6)}]^2$ |
|----------------------------------------|------------------|---------------|---------------|---------------|
| $^7\text{F}_3$                         | 2249             | 0             | 0.2142        | 0.3804        |
| $^7\text{F}_2$                         | 1952             | 0             | 0.0479        | 0.4676        |
| $^7\text{F}_1 + ^7\text{F}_0$          | 1826             | 0             | 0             | 0.5178        |
| $^5\text{D}_4$                         | 486              | 0.0007        | 0.0013        | 0.0011        |

**Table 2.** Experimental and calculated electric dipole line strengths for selected optical transitions of  $\text{Tb}^{3+}$  ions in  $\text{CaF}_2$  crystals doped with 1, 5, and 10 mol%  $\text{TbF}_3$ . The mean wavelengths,  $\lambda_m$ ,  $\text{Tb}^{3+}$  ion concentrations, and root-mean-square deviations,  $\delta$ ,  $\delta$  obtained from the JO fitting are also reported.

| TbF <sub>3</sub> Concentration (mol%)                     |                     | 1                                                 |                                                   |      | 5                                                 |                                                   |      | 10                                                |                                                   |      |
|-----------------------------------------------------------|---------------------|---------------------------------------------------|---------------------------------------------------|------|---------------------------------------------------|---------------------------------------------------|------|---------------------------------------------------|---------------------------------------------------|------|
| Transition, <sup>7</sup> F <sub>6</sub> →                 | λ <sub>m</sub> (nm) | (S <sub>JJ'</sub> <sup>DE</sup> ) <sub>meas</sub> | (S <sub>JJ'</sub> <sup>DE</sup> ) <sub>calc</sub> | δ    | (S <sub>JJ'</sub> <sup>DE</sup> ) <sub>meas</sub> | (S <sub>JJ'</sub> <sup>DE</sup> ) <sub>calc</sub> | δ    | (S <sub>JJ'</sub> <sup>DE</sup> ) <sub>meas</sub> | (S <sub>JJ'</sub> <sup>DE</sup> ) <sub>calc</sub> | δ    |
|                                                           |                     | (×10 <sup>−20</sup> cm <sup>2</sup> )             |                                                   |      |                                                   |                                                   |      |                                                   |                                                   |      |
| <sup>7</sup> F <sub>3</sub>                               | 2249                | 1.19024                                           | 1.11444                                           | 0.43 | 2.03022                                           | 1.99188                                           | 0.22 | 1.96614                                           | 1.93776                                           | 0.16 |
| <sup>7</sup> F <sub>2</sub>                               | 1952                | 0.77713                                           | 1.11609                                           |      | 1.37178                                           | 1.54323                                           |      | 1.44786                                           | 1.57478                                           |      |
| <sup>7</sup> F <sub>1</sub> + <sup>7</sup> F <sub>0</sub> | 1826                | 1.42381                                           | 0.84708                                           |      | 1.61265                                           | 1.07274                                           |      | 1.63884                                           | 1.11539                                           |      |
| <sup>5</sup> D <sub>4</sub>                               | 486                 | 0.00936                                           | 0.00936                                           |      | 0.0103                                            | 0.01030                                           |      | 0.01538                                           | 0.01538                                           |      |

Table 3 presents the JO intensity parameters  $\Omega_2$ ,  $\Omega_4$ , and  $\Omega_6$  obtained for  $\text{CaF}_2:\text{Tb}^{3+}$  single crystals with different  $\text{TbF}_3$  concentrations ( $x = 1, 5$ , and 10 mol%), together with the spectroscopic quality factor,  $\chi = \Omega_4/\Omega_6$ . For comparison, previously reported values for  $\text{Tb}^{3+}$ -doped  $\text{CaF}_2$  and selected fluoride and oxide hosts are also included. The  $\Omega_6$  parameter exhibits comparable values across the investigated concentration range, while  $\Omega_2$  and  $\Omega_4$  show more pronounced variations with  $\text{Tb}^{3+}$  content. The  $\Omega_2$  parameter, which is often associated with local symmetry and covalency effects, remains relatively low compared to oxide hosts, consistent with the predominantly ionic character of the  $\text{CaF}_2$  lattice. In contrast,  $\Omega_4$  displays a stronger dependence on dopant concentration, leading to variations in the  $\Omega_4/\Omega_6$  ratio. The spectroscopic quality factor,  $\chi$ , ranges from 0.52 to 1.46 for the  $\text{CaF}_2:\text{Tb}^{3+}$  crystals investigated in this work, indicating moderate changes in the relative contributions of intermediate-rank electric dipole interactions with increasing  $\text{Tb}^{3+}$  concentration. These values are in good agreement with those reported by Liu et al. for 5% Tb doped in  $\text{CaF}_2$  crystals, around 1.18 [36]. When compared with literature data, the obtained JO parameters fall within the typical range reported for  $\text{Tb}^{3+}$ -doped fluoride hosts and differ significantly from those of oxide and tungstate crystals, reflecting the lower phonon energies and reduced covalency of fluoride lattices [47].

Table 4 shows the radiative parameters associated with the  $^5\text{D}_4 \rightarrow ^7\text{F}_j$  transitions of  $\text{Tb}^{3+}$  ions in  $\text{CaF}_2$  crystals doped with 1, 5, and 10 mol%  $\text{TbF}_3$ . The table lists the transition wavelengths, radiative transition probabilities,  $A_{JJ'}$ , branching ratios,  $\beta_{JJ'}$ , and radiative lifetimes,  $\tau_{\text{rad}}$ , as derived from the JO analysis. For all investigated concentrations, the radiative decay from the  $^5\text{D}_4$  excited state is dominated by transitions to the  $^7\text{F}_5$  and  $^7\text{F}_3$  levels, which exhibit the highest radiative transition probabilities and branching ratios. In particular, the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition shows the largest contribution to the total radiative decay, accounting for more than 50% of the total branching ratio, consistent with the

intense green emission typically observed for  $\text{Tb}^{3+}$ -activated materials [17,20,36,47]. The  $^5\text{D}_4 \rightarrow ^7\text{F}_3$  transition represents the second most significant radiative channel, while transitions to the other  $^7\text{F}_j$  levels contribute more modestly.

**Table 3.** JO intensity parameters  $\Omega_2$ ,  $\Omega_4$ , and  $\Omega_6$  (in units of  $10^{-20} \text{ cm}^2$ ) and the asymmetry ratio  $\chi = \Omega_4/\Omega_6$  for  $\text{CaF}_2:x \text{ mol\% TbF}_3$  crystals at different  $\text{Tb}^{3+}$  concentrations ( $x = 1, 5$ , and  $10$ ). Literature data for related fluoride hosts are included for comparison. The fitting errors obtained from the JO analysis are also presented.

| $\text{CaF}_2:x \text{ mol\% TbF}_3$                           | $\Omega_2$<br>( $10^{-20} \text{ cm}^2$ ) | $\Omega_4$<br>( $10^{-20} \text{ cm}^2$ ) | $\Omega_6$<br>( $10^{-20} \text{ cm}^2$ ) | $\chi = \Omega_4/\Omega_6$ | Ref.       |
|----------------------------------------------------------------|-------------------------------------------|-------------------------------------------|-------------------------------------------|----------------------------|------------|
| $x = 1$                                                        | $7.626 \pm 1.927$                         | $1.178 \pm 0.543$                         | $2.266 \pm 0.378$                         | 0.52                       | This paper |
| $x = 5$                                                        | $2.397 \pm 0.975$                         | $4.202 \pm 0.275$                         | $2.869 \pm 0.191$                         | 1.46                       |            |
| $x = 10$                                                       | $10.319 \pm 0.721$                        | $3.747 \pm 0.203$                         | $2.983 \pm 0.141$                         | 1.26                       |            |
| $\text{CaF}_2:2 \text{ mol\% TbF}_3 + 3.2 \text{ mol\% YbF}_3$ | 4.5708                                    | 0.418                                     | 3.4958                                    | 0.12                       | [41]       |
| $\text{CaF}_2:5\% \text{ TbF}_3$                               | 1.71                                      | 2.65                                      | 2.25                                      | 1.18                       | [17]       |
| $\text{LiYF}_4$                                                | 28.30                                     | 1.65                                      | 2.15                                      | 0.77                       | [40]       |
| $\text{KY}_3\text{F}_{10}$                                     | 3.922                                     | 0.299                                     | 3.022                                     | 0.10                       | [20]       |
| $\text{KYbW}$                                                  | 1.909                                     | 2.414                                     | 4.911                                     | 0.49                       | [47]       |

**Table 4.** Radiative transition probabilities,  $A_{J'J''}$ , branching ratios,  $\beta_{J'J''}$ , and radiative lifetimes,  $\tau_{\text{rad}}$ , for the  $^5\text{D}_4 \rightarrow ^7\text{F}_j$  transitions of  $\text{Tb}^{3+}$  ions in  $\text{CaF}_2$  crystals doped with 1, 5, and 10 mol%  $\text{TbF}_3$ , calculated using the JO formalism. Literature values are included for comparison.

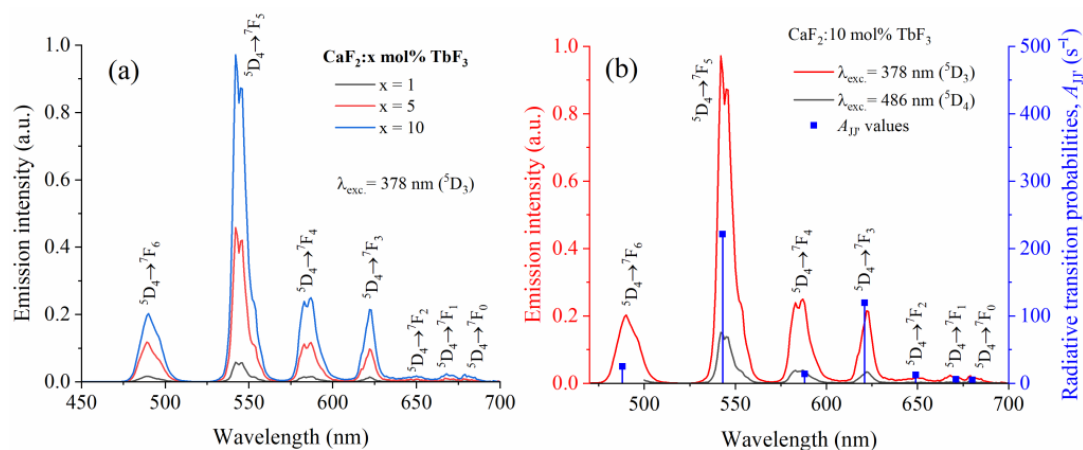
| $\text{TbF}_3$ (mol%)      |                     | 1                                  |                 |                             |                                                            | 5                                  |                 |                             |                                                            | 10                                 |                 |                             |                                                            |
|----------------------------|---------------------|------------------------------------|-----------------|-----------------------------|------------------------------------------------------------|------------------------------------|-----------------|-----------------------------|------------------------------------------------------------|------------------------------------|-----------------|-----------------------------|------------------------------------------------------------|
| $^5\text{D}_4 \rightarrow$ | $\lambda_m$<br>(nm) | $A_{J'J''}$<br>( $\text{s}^{-1}$ ) | $\beta_{J'J''}$ | $\tau_{\text{rad}}$<br>(ms) | $\sigma_{\text{em}}$<br>( $\times 10^{-20} \text{ cm}^2$ ) | $A_{J'J''}$<br>( $\text{s}^{-1}$ ) | $\beta_{J'J''}$ | $\tau_{\text{rad}}$<br>(ms) | $\sigma_{\text{em}}$<br>( $\times 10^{-20} \text{ cm}^2$ ) | $A_{J'J''}$<br>( $\text{s}^{-1}$ ) | $\beta_{J'J''}$ | $\tau_{\text{rad}}$<br>(ms) | $\sigma_{\text{em}}$<br>( $\times 10^{-20} \text{ cm}^2$ ) |
| $^7\text{F}_0$             | 678                 | 1.73                               | 0.0053          | 3.05                        | 0.48                                                       | 6.17                               | 0.0327          | 5.29                        | 0.25                                                       | 5.50                               | 0.0123          | 2.23                        | 0.57                                                       |
| $^7\text{F}_1$             | 668                 | 2.05                               | 0.0063          |                             |                                                            | 7.30                               | 0.0386          |                             |                                                            | 6.51                               | 0.0145          |                             |                                                            |
| $^7\text{F}_2$             | 650                 | 9.88                               | 0.0302          |                             |                                                            | 4.42                               | 0.0233          |                             |                                                            | 14.03                              | 0.0313          |                             |                                                            |
| $^7\text{F}_3$             | 622                 | 98.93                              | 0.3021          | 2.082                       | 0.23                                                       | 39.02                              | 0.2065          | 6.77                        | 0.12                                                       | 134.05                             | 0.2993          | 1.805                       | 0.28                                                       |
| $^7\text{F}_4$             | 585                 | 8.39                               | 0.0256          |                             |                                                            | 13.66                              | 0.0723          |                             |                                                            | 15.40                              | 0.0344          |                             |                                                            |
| $^7\text{F}_5$             | 542                 | 189.46                             | 0.5785          |                             |                                                            | 99.63                              | 0.5271          |                             |                                                            | 244.72                             | 0.5459          |                             |                                                            |
| $^7\text{F}_6$             | 486                 | 17.09                              | 0.0521          | [47]                        | 0.17                                                       | 18.79                              | 0.0994          |                             | 0.10                                                       | 28.06                              | 0.0626          |                             | 0.24                                                       |

The calculated radiative lifetimes of the  $^5\text{D}_4$  level decrease slightly with increasing  $\text{Tb}^{3+}$  concentration, reflecting the combined effect of increasing total radiative rates and concentration-dependent changes in the JO intensity parameters. The obtained lifetime values are in good agreement with previously reported data for  $\text{Tb}^{3+}$ -doped fluoride crystals, as indicated by the literature references included in Table 4.

### 3.3. Emission Spectra

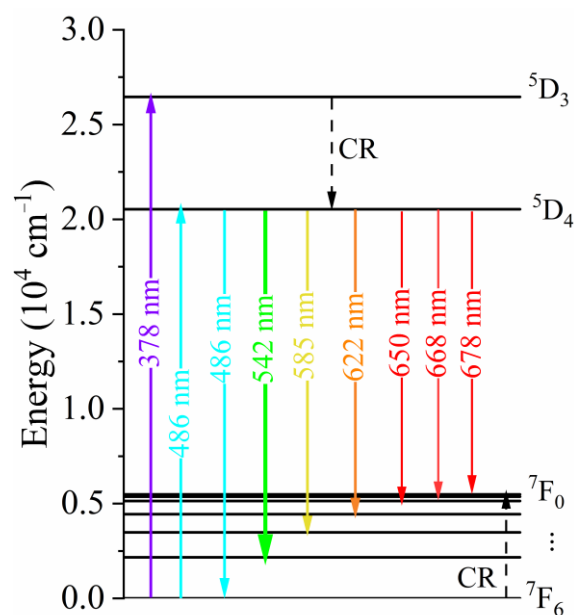
Figure 4 shows the room-temperature photoluminescence spectra of  $\text{CaF}_2:\text{Tb}^{3+}$  single crystals with different  $\text{TbF}_3$  concentrations, recorded under selective excitation at 378 nm, corresponding to excitation into the  $^5\text{D}_3$  level. In Figure 4a, the emission spectra for  $x = 1, 5$ , and  $10 \text{ mol\% TbF}_3$  are compared. All spectra are dominated by the characteristic green emission originating from the  $^5\text{D}_4 \rightarrow ^7\text{F}_j$  ( $J = 6-0$ ) transitions of  $\text{Tb}^{3+}$  ions. The most intense emission band is observed around 542 nm and is assigned to the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition, which is known to be the dominant radiative channel in  $\text{Tb}^{3+}$ -activated materials. Additional emission bands corresponding to the  $^5\text{D}_4 \rightarrow ^7\text{F}_{6-0}$  transitions are clearly resolved. With increasing  $\text{Tb}^{3+}$  concentration, the overall emission intensity increases. The absence of detectable  $^5\text{D}_3 \rightarrow ^7\text{F}_j$  emission bands, under excitation at 378 nm indicates an efficient

non-radiative depopulation of the  $^5D_3$  level toward  $^5D_4$ , consistent with well-known cross-relaxation processes in  $Tb^{3+}$ -doped systems [36]. Figure 4b presents the emission spectrum of the  $CaF_2$ :10 mol%  $TbF_3$  crystal under excitation at both 378 nm ( $^5D_3$  excitation) and 486 nm ( $^5D_4$  excitation), together with the radiative transition probabilities  $A_{J'J''}$  derived from the JO analysis. The spectral shape remains essentially unchanged for the two excitation wavelengths, confirming that the emission originates predominantly from the  $^5D_4$  level, regardless of the excitation pathway. The relative intensities of the emission bands follow closely the calculated radiative transition probabilities, with the  $^5D_4 \rightarrow ^7F_5$  transition exhibiting the highest  $A_{J'J''}$  value. This good agreement demonstrates the internal consistency between the experimental emission spectra and the  $A_{J'J''}$  values.



**Figure 4.** Room-temperature emission spectra of  $CaF_2:Tb^{3+}$  single crystals. (a) Emission spectra of  $CaF_2$ : $x$  mol%  $TbF_3$  ( $x = 1, 5$ , and  $10$ ) under excitation at  $378$  nm ( $^5D_3$  excitation), showing the characteristic  $^5D_4 \rightarrow ^7F_J$  ( $J = 6-0$ ) transitions of  $Tb^{3+}$  ions. (b) Emission spectrum of  $CaF_2$ : $10$  mol%  $TbF_3$  measured under excitation at  $378$  nm ( $^5D_3$ ) and  $486$  nm ( $^5D_4$ ), together with the radiative transition probabilities,  $A_{J'J''}$ , obtained from the JO analysis.

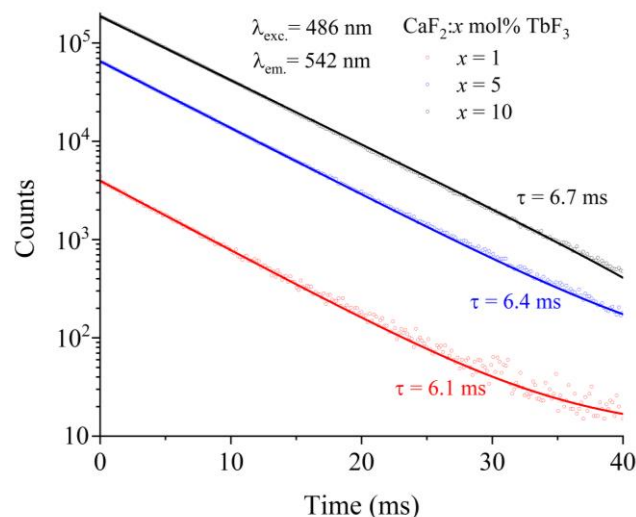
Figure 5 illustrates the simplified energy level diagram of  $Tb^{3+}$  ions in the  $CaF_2$  host, highlighting the main excitation, cross, relaxation (CR), and emission processes involved in the observed luminescence. The diagram includes the relevant excited states ( $^5D_3$  and  $^5D_4$ ) and the lower-lying  $^7F_J$  manifolds, together with the corresponding transition energies expressed in  $cm^{-1}$ . Excitation at  $378$  nm promotes  $Tb^{3+}$  ions to the  $^5D_3$  level, while excitation at  $486$  nm directly populates the  $^5D_4$  level. The diagram emphasizes the efficient non-radiative cross-relaxation (CR) process from the  $^5D_3$  to the  $^5D_4$  level, which leads to a rapid depopulation of the higher-lying  $^5D_3$  state. As a consequence, radiative emission originates from the  $^5D_4$  level, regardless of the excitation pathway. This CR luminescence mechanism has also been reported in  $Tb$  doped in  $CaF_2$  ceramics [20] and  $Gd_2O_3$  glasses [12]. They conclude that the high  $Tb^{3+}$  concentrations make the distance of  $Tb^{3+}-Tb^{3+}$  shorten and thus a fast CR from  $^5D_3$  to  $^5D_4$  energy level occurs. On the other hand, strong quenching of  $^5D_3 \rightarrow ^7F_J$  emissions are observed. The downward arrows indicate the radiative transitions from the  $^5D_4$  excited state to the  $^7F_J$  ( $J = 0-6$ ) ground-state multiplets, corresponding to the characteristic visible emission bands of  $Tb^{3+}$  ions. The strongest emission transitions are observed in the green spectral region, in agreement with the dominance of the  $^5D_4 \rightarrow ^7F_5$  transition in the experimental emission spectra.



**Figure 5.** Simplified energy level diagram of  $\text{Tb}^{3+}$  ions in  $\text{CaF}_2$  showing the main excitation pathways (378 and 486 nm), the cross-relaxation (CR) process between the  $^5\text{D}_3$  and  $^5\text{D}_4$  levels, and the radiative  $^5\text{D}_4 \rightarrow ^7\text{F}_J$  ( $J = 0-6$ ) transitions responsible for the visible luminescence.

### 3.4. Fluorescence Dynamics and Internal Quantum Efficiency

As seen in Figure 6, the photoluminescence decay curves of  $\text{Tb}:\text{CaF}_2$  crystal were obtained for the emissions measured under excitation at 486 nm ( $^5\text{D}_4$  level). After being fitted, all the decay curves exhibit mono-exponential decaying behavior.



**Figure 6.** Decay curves of  $^5\text{D}_4$  level for various concentrations of  $\text{Tb}:\text{CaF}_2$  crystals at room temperature.

Table 5 summarizes the experimentally measured luminescence decay times,  $\tau_{\text{meas}}$ , of the  $^5\text{D}_4$  excited state of  $\text{Tb}^{3+}$  ions in  $\text{CaF}_2$  crystals doped with different  $\text{TbF}_3$  concentrations (1, 5, and 10 mol%). The decay times are reported for the main  $^5\text{D}_4 \rightarrow ^7\text{F}_J$  emission transitions together with the corresponding emission wavelengths. The relative uncertainty associated with the fluorescence lifetime measurements reported in Table 5 ranges between 0.09% and 0.34%, indicating a high precision of the experimental lifetime measurements. For comparison, representative lifetime values reported in the literature for  $\text{Tb}^{3+}$ -doped  $\text{CaF}_2$  and related fluoride systems are also included. The measured decay times lie predominantly in the range of approximately 4.4–6.5 ms, depending on the specific emission

transition and terbium concentration. The  $^5D_4 \rightarrow ^7F_5$  transition, which corresponds to the dominant green emission band, exhibits decay times of 6.1, 6.4, and 6.7 ms for 1, 5, and 10 mol%  $TbF_3$ , respectively. The decay times are relatively similar for the different  $^5D_4 \rightarrow ^7F_j$  transitions and different Tb concentrations. The comparison with literature data reveals that the lifetime values obtained in this work are generally consistent with those reported for other fluorite hosts, while some dispersion can be observed depending on crystal composition, morphology (bulk crystals versus nanostructures), and experimental conditions. Quantum efficiency values are also summarized in Table 5. These data offer a comprehensive understanding of the radiative efficiency and temporal behavior of each doped system, providing valuable parameters for optimizing phosphor performance in practical lighting applications. The internal quantum efficiency (IQE) is determined as a ratio between the number of photons emitted and number of photons absorbed. Number of photons emitted is proportional to the area under the emission spectrum. Number of photons absorbed is proportional to the difference between the area under the scattered band at the 486 nm excitation wavelength from the reference and that from the sample. The measured quantum efficiency of  $CaF_2:Tb^{3+}$  crystals show a pronounced dependence on the  $TbF_3$  concentration. At 1 mol%  $TbF_3$ , a relatively low quantum efficiency of 31.4% is obtained, indicating that non-radiative processes still play a significant role at low dopant concentrations, likely due to incomplete energy transfer and reduced probability of radiative recombination. A substantial increase in quantum efficiency is observed when the  $Tb_3$  concentration is raised to 5 mol%, where  $\eta$  reaches 71.2%. This improvement reflects a more efficient population of the  $^5D_4$  emitting level, consistent with the increased probability of energy migration toward radiative centers and with the effective suppression of competing non-radiative channels. At 10 mol%  $TbF_3$ , the quantum efficiency further increases slightly to 73.9%, suggesting that the system approaches a saturation regime. Loiko et al. calculated the quantum efficiency of about 19% for Tb-doped  $KYb(WO_4)_2$  crystal [47] and Wang et al. obtained 79.2% for Tb-doped  $CaYAlO_4$  crystal [45]. Furthermore, the quantum efficiency in  $LiTbF_4$  and  $TbCaF$  crystals were also calculated at about 65% and 21%, respectively [43], and 89.51% for Tb-doped  $CaF_2$  crystal [36]. This last value is higher than the one measured in this study of about 73.9%. Despite the higher dopant concentration, no significant concentration quenching is observed, indicating that the dominant cross-relaxation processes favor the population of the  $^5D_4$  level rather than introducing additional non-radiative losses. These results demonstrate that  $CaF_2:Tb^{3+}$  crystals maintain high luminescence efficiency at elevated  $Tb^{3+}$  concentrations, which is particularly advantageous for green-emitting photonic applications.

**Table 5.** Experimentally measured luminescence decay times,  $\tau_{meas}$ , of the  $^5D_4$  excited state of  $Tb^{3+}$  ions in  $CaF_2$  crystals doped with 1, 5, and 10 mol%  $TbF_3$ , determined for the main  $^5D_4 \rightarrow ^7F_j$  emission transitions. Literature values reported for  $Tb^{3+}$ -doped related fluoride systems are included for comparison. Quantum efficiency,  $\eta$  (%).

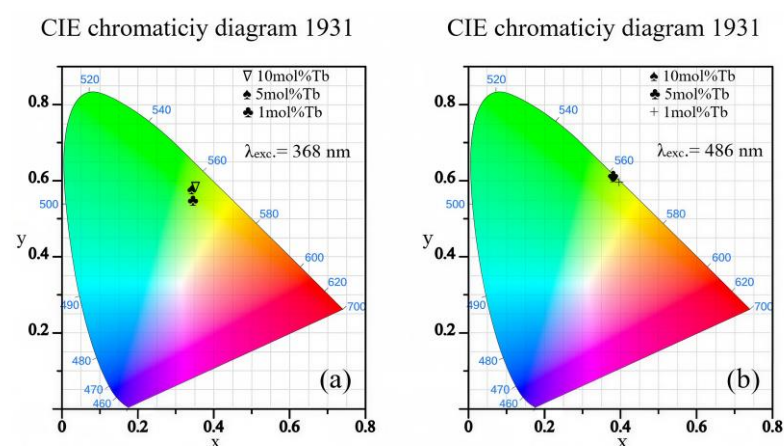
| TbF <sub>3</sub> Concentration (mol%)        |                        | 1   | 5   | 10  | Ref.                       |      |      |      |      |      |      | 1                            | 5    | 10   |
|----------------------------------------------|------------------------|-----|-----|-----|----------------------------|------|------|------|------|------|------|------------------------------|------|------|
|                                              |                        |     |     |     | [35]                       | [33] | [34] | [45] | [36] | [43] | [20] |                              |      |      |
| Transition,<br><sup>5</sup> D <sub>4</sub> → | λ <sub>m</sub><br>(nm) |     |     |     | τ <sub>meas.</sub><br>(ms) |      |      |      |      |      |      | Quantum<br>Efficiency, η (%) |      |      |
| <sup>7</sup> F <sub>0</sub>                  | 678                    | 5.5 | 5.5 | 4.9 |                            |      |      |      |      |      |      |                              |      |      |
| <sup>7</sup> F <sub>1</sub>                  | 668                    | 5.0 | 5.6 | 6.5 |                            |      |      |      |      |      |      |                              |      |      |
| <sup>7</sup> F <sub>2</sub>                  | 650                    | 4.4 | 5.6 | 5.8 |                            |      |      |      |      |      |      |                              |      |      |
| <sup>7</sup> F <sub>3</sub>                  | 622                    | 6.2 | 6.4 | 6.5 |                            |      |      |      |      |      |      | 31.4                         | 71.2 | 73.9 |
| <sup>7</sup> F <sub>4</sub>                  | 585                    | 6.1 | 6.4 | 6.7 |                            |      |      |      |      |      |      |                              |      |      |
| <sup>7</sup> F <sub>5</sub>                  | 542                    | 6.1 | 6.4 | 6.7 | 2.39                       | 7.4  | 8.1  | 1.43 | 6.06 | 4.2  | 6.81 |                              |      |      |

### 3.5. CIE Color Coordinates

The chromaticity characteristics of the Tb-doped  $\text{CaF}_2$  crystals were evaluated using the CIE 1931 color. The corresponding (x, y) coordinates were calculated using CIE 1931 web-based app [33]. These parameters provide information about the visual appearance and practical utility of the emitted light. The CIE color coordinates calculated for each sample are listed in Table 6. In addition, the positions of the emission colors for different dopant concentrations are graphically illustrated in Figure 7.

**Table 6.** The CIE color coordinates.

| $\text{CaF}_2:x \text{ mol\% TbF}_3$ | $\lambda_{\text{exc.}} \text{ (nm)}$ | x-Coordinate | y-Coordinate | $\lambda_{\text{exc.}} \text{ (nm)}$ | x-Coordinate | y-Coordinate |
|--------------------------------------|--------------------------------------|--------------|--------------|--------------------------------------|--------------|--------------|
| $x = 1$                              | 378                                  | 0.34270      | 0.54708      | 486                                  | 0.39573      | 0.59402      |
| $x = 5$                              |                                      | 0.34214      | 0.57734      |                                      | 0.37756      | 0.61243      |
| $x = 10$                             |                                      | 0.35118      | 0.58089      |                                      | 0.35118      | 0.58089      |



**Figure 7.** CIE 1931 chromaticity diagrams calculated from the room-temperature emission spectra of  $\text{CaF}_2:\text{Tb}^{3+}$  single crystals with nominal  $\text{TbF}_3$  concentrations of 1, 5, and 10 mol%. The emission points are located in the green region of the chromaticity space, indicating stable green luminescence dominated by the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition of  $\text{Tb}^{3+}$  ions under excitation at (a) 368 nm and (b) 486 nm.

For all investigated samples, the emission points are located in the green region of the CIE 1931 diagram, reflecting the dominant contribution of the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition of  $\text{Tb}^{3+}$  ions. A slight variation in the chromaticity coordinates with  $\text{Tb}^{3+}$  concentration is observed, indicating minor changes in the relative intensities of the individual  $^5\text{D}_4 \rightarrow ^7\text{F}_j$  emission bands as the dopant content increases. However, the overall emission color remains stable and well confined within the green region of the chromaticity space. The comparison between the two panels highlights the reproducibility of the chromaticity coordinates under different excitation conditions, confirming that the emission color is predominantly governed by radiative transitions from the  $^5\text{D}_4$  level, independent of the excitation wavelength. These results demonstrate the good color stability of  $\text{CaF}_2:\text{Tb}^{3+}$  single crystals and their suitability for green-emitting photonic applications. These results are in good agreement with those reported by Liu et al. [14], Kumari et al. [15], Wang et al. [45] and Loiko et al. [47].

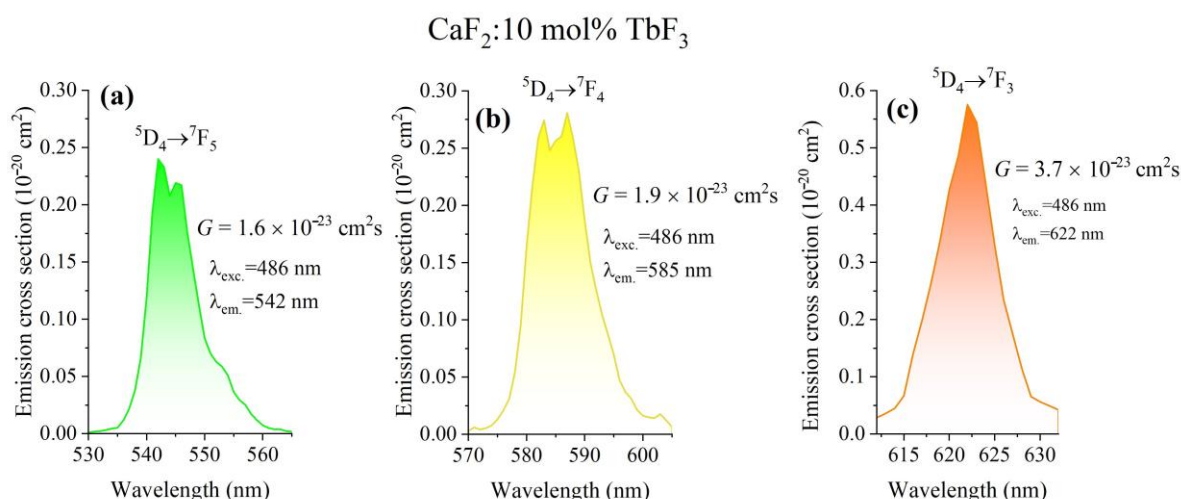
### 3.6. Emission Cross-Section and Gain Parameter

To evaluate the emission cross-section corresponding to the measured luminescence bands, the Füchtbauer–Ladenburg equation [31] was used:

$$\sigma_{\text{em}}(\lambda) = \frac{\lambda^5 I(\lambda)}{8\pi [n(\lambda)]^2 c \tau_{\text{rad}} \int \lambda I(\lambda) d\lambda} \quad (9)$$

where  $I(\lambda)$  is the emission intensity at each wavelength,  $\tau_{\text{rad}}$  is the radiative lifetime of the upper level,  $n$  is the refractive index and  $c$  is the light speed.

Figure 8 shows the emission cross-sections associated with the dominant  $^5D_4 \rightarrow ^7F_J$  transitions of  $\text{Tb}^{3+}$  ions in  $\text{CaF}_2$  crystals ( $J = 5, 4, 3$ ) doped with 10 mol%  $\text{TbF}_3$ . The emission cross-sections were calculated from the experimental emission spectra using the F  chtbauer–Ladenburg approach and are shown for three representative transitions: (a)  $^5D_4 \rightarrow ^7F_5$ , (b)  $^5D_4 \rightarrow ^7F_4$ , and (c)  $^5D_4 \rightarrow ^7F_3$ . The emission bands exhibit well-defined spectral shapes centered at wavelengths characteristic of  $\text{Tb}^{3+}$  transitions. The two times higher emission cross-section is obtained for the orange emission of the  $^5D_4 \rightarrow ^7F_3$  transition (Figure 8c). The emission cross-section data provide a quantitative measure of the radiative potential of the  $^5D_4 \rightarrow ^7F_J$  transitions and confirm that  $\text{CaF}_2:\text{Tb}^{3+}$  crystals show green-, yellow- and orange-emitting capabilities even at high  $\text{Tb}^{3+}$  concentrations (no concentration quenching is observed). To evaluate the laser performance, the optical gain parameter,  $G = \sigma_{\text{em}} \cdot \tau_{\text{meas}}$ , was calculated for the emissions of  $\text{CaF}_2:\text{TbF}_3$  sample under excitation at 486 nm. The gain parameter provides a quantitative measure of the optical amplification potential of the investigated material. In the present study, the gain parameter was evaluated for the main  $^5D_4 \rightarrow ^7F_J$  transitions ( $J = 5, 4, 3$ ) of  $\text{Tb}^{3+}$  ions in  $\text{CaF}_2$  crystals doped with 10 mol%  $\text{TbF}_3$  (Figure 8). The highest gain value of  $3.7 \times 10^{-23} \text{ cm}^2\text{s}$  is obtained for the  $^5D_4 \rightarrow ^7F_5$  transition (orange) of 10 mol%  $\text{TbF}_3$  content, in agreement with its dominant contribution to the green emission and with the JO-calculated radiative transition probabilities.



**Figure 8.** Emission cross-sections of  $\text{CaF}_2:10 \text{ mol\% TbF}_3$ : (a) the green emission around 542 nm, (b) the yellow emission at 585 nm and (c) the orange emission, 622 nm. On the figure are shown values obtained for gain parameter for each transition.

#### 4. Discussions

This comprehensive spectroscopic investigation of  $\text{Tb}^{3+}$ -doped  $\text{CaF}_2$  single crystals reveals a consistent picture in which the optical properties are governed by the interplay between the intrinsic electronic structure of  $\text{Tb}^{3+}$  ions, the fluorite host lattice, and concentration-dependent ion–ion interactions mediated by charge-compensation defects. By combining absorption spectroscopy, Judd–Ofelt analysis, emission measurements, fluorescence dynamics, colorimetric evaluation, emission cross-section and gain parameter calculations, a unified interpretation of the radiative behavior of  $\text{Tb}^{3+}$  in  $\text{CaF}_2$  can be established.

The optical absorption spectra presented in Section 3.1 exhibit the characteristic  $4f-4f$  transitions of  $\text{Tb}^{3+}$  ions originating from the  $^7F_6$  ground state, with band positions that remain essentially unchanged across the investigated concentration range. This behavior indicates that the average crystal-field strength experienced by  $\text{Tb}^{3+}$  ions is not significantly

modified by increasing  $\text{TbF}_3$  content, in agreement with previous reports on  $\text{CaF}_2\text{:RE}^{3+}$  systems [16,20,22,32]. At the same time, the systematic increase in absorption intensity with concentration confirms the proportional incorporation of  $\text{Tb}^{3+}$  ions into the lattice. The absence of additional broad absorption features associated with secondary phases or strong defect-related bands suggests a high optical quality of the grown crystals. However, the observed variations in relative band intensities and linewidths are consistent with the presence of multiple  $\text{Tb}^{3+}$ -related centers associated with different charge-compensation schemes, such as fluorine interstitials or defect clusters, which are known to occur in  $\text{CaF}_2$  doped with trivalent rare-earth ions [22,23,48]. These defect-related effects provide an important microscopic background for interpreting the subsequent radiative and non-radiative processes.

The Judd–Ofelt analysis (Section 3.2) yields intensity parameters  $\Omega_2$ ,  $\Omega_4$ , and  $\Omega_6$  that fall within the typical range reported for  $\text{Tb}^{3+}$ -doped fluoride hosts and differ markedly from those of oxide or tungstate materials. In particular, the relatively low  $\Omega_2$  values reflect the predominantly ionic character and high local symmetry of the  $\text{CaF}_2$  lattice, while the  $\Omega_4$  and  $\Omega_6$  parameters govern the strength of the  $^5\text{D}_4 \rightarrow ^7\text{F}_j$  electric dipole transitions. The moderate variation in the  $\Omega_4/\Omega_6$  ratio with  $\text{Tb}^{3+}$  concentration indicates subtle changes in the local environment and ion–ion interactions, rather than a fundamental alteration in the host lattice. The normalized emission spectra (Figure 4) confirm that the ratio of relative intensities remains relatively unchanged with the concentration of  $\text{TbF}_3$ . Nevertheless,  $\Omega_2$ , being derived from absorption line strengths, remains highly sensitive to band overlap effects (especially due to the overlap of  $^7\text{F}_6 \rightarrow ^7\text{F}_{0,1,2,3}$  absorption bands) and to possible inhomogeneities in dopant distribution along the crystals. The good agreement between experimental and calculated line strengths, together with decreasing rms deviations at higher concentrations, confirms the internal consistency of the JO formalism for describing  $\text{Tb}^{3+}$  absorption in  $\text{CaF}_2$ . These results provide a reliable basis for the calculation of radiative transition probabilities, branching ratios, radiative lifetimes, emission cross section and gain parameter.

The emission spectra discussed in Section 3.3 are dominated by the  $^5\text{D}_4 \rightarrow ^7\text{F}_j$  transitions, with the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  green emission band representing the most intense radiative emission for all investigated concentrations. The absence of detectable  $^5\text{D}_3 \rightarrow ^7\text{F}_j$  emission, even under direct excitation into the  $^5\text{D}_3$  level, indicates an efficient depopulation of  $^5\text{D}_3$  through cross-relaxation processes. This behavior is well explained by the cross-relaxation mechanism  $^5\text{D}_3 + ^7\text{F}_6 \rightarrow ^5\text{D}_4 + ^7\text{F}_j$ , which becomes increasingly efficient with increasing  $\text{Tb}^{3+}$  concentration, as previously reported for  $\text{Tb}^{3+}$ -activated fluoride systems. In  $\text{CaF}_2$  crystal, the low phonon energy of the host lattice does not suppress this process, since cross-relaxation is governed by inter-ionic interactions rather than multiphonon relaxation. As a consequence, excitation energy is funneled efficiently toward the  $^5\text{D}_4$  level, leading to dominant green emission and enhanced radiative output. The close correspondence between the relative emission intensities and the JO-derived radiative transition probabilities further supports this interpretation and demonstrates the consistency between absorption-based modeling and emission measurements.

The fluorescence decay analysis (Section 3.4) reveals millisecond-range lifetimes characteristic of  $\text{Tb}^{3+}$  emission in low-phonon-energy fluoride hosts. The values obtained are close to each other and vary between 4.4 and 6.7 ms, indicating a slight dependence on Tb concentration.

The experimentally determined quantum efficiencies show a pronounced increase from low to intermediate  $\text{Tb}^{3+}$  concentrations, followed by a saturation tendency at higher doping levels. This behavior reflects an optimal balance between efficient population of the emitting  $^5\text{D}_4$  level and the onset of concentration-related losses, highlighting the robustness

of  $\text{CaF}_2$  as a host for  $\text{Tb}^{3+}$ -based green emitters. The  $\text{CaF}_2$  host is characterized by a low maximum phonon energy of approximately  $456\text{ cm}^{-1}$ , which effectively suppresses multiphonon non-radiative relaxation processes [57]. This low phonon energy is reflected in the long fluorescence lifetimes of the  $\text{Tb}^{3+} {}^5\text{D}_4$  level ( $\sim 6\text{ ms}$ ) observed in this work and plays a key role in maintaining high optical efficiency by favoring radiative decay channels.

The CIE 1931 chromaticity coordinates (Section 3.5) confirm that all investigated samples emit in the green region of the color space, with only minor variations as a function of  $\text{Tb}^{3+}$  concentration. This color stability is a direct consequence of the dominance of the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$  transition and the suppression of competing emission channels. Such stability is a desirable feature for applications in solid-state lighting, displays, and optical signaling.

The emission cross-sections derived in Section 3.6 further quantify the radiative potential of  $\text{CaF}_2:\text{Tb}^{3+}$  crystals and allow direct comparison with other fluoride and oxide hosts [7–10,12,17,20,32,37]. The obtained values are consistent with the high radiative efficiencies observed experimentally of about 74% and underline the suitability of this system for visible photonic applications.

The obtained gain parameter values demonstrate that  $\text{CaF}_2:\text{Tb}^{3+}$  crystals have a non-negligible optical amplification capability in the visible spectral range, particularly in the orange region associated with the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_3$  transition (two times higher than green or yellow emission). These results indicate that, beyond their luminescent performance,  $\text{Tb}^{3+}$ -doped  $\text{CaF}_2$  crystals may be considered as potential candidates for visible photonic applications requiring moderate optical gain, provided that efficient population inversion can be achieved.

The present results demonstrate that  $\text{CaF}_2:\text{Tb}^{3+}$  single crystals combine favorable spectroscopic properties, making them attractive candidates for photonic devices, magneto-optical components, and scintillation-related applications. The strong role of defect chemistry and cross-relaxation processes suggests that further optimization could be achieved through controlled growth conditions, segregation, co-doping strategies, or post-growth treatments aimed at tailoring the local environment of  $\text{Tb}^{3+}$  ions [7,36]. Future studies should focus on a more detailed correlation between defect structures and luminescence dynamics and the exploration of  $\text{Tb}^{3+}$ -based co-doped systems to enhance emission efficiency and spectral tunability.

## 5. Conclusions

In this work, a comprehensive spectroscopic study of  $\text{Tb}^{3+}$ -doped  $\text{CaF}_2$  single crystals with different  $\text{TbF}_3$  concentrations has been performed, combining optical absorption, Judd–Ofelt analysis, photoluminescence spectroscopy, fluorescence dynamics, colorimetric evaluation, and emission cross-section and gain analysis. The results provide a consistent and detailed picture of the radiative behavior of  $\text{Tb}^{3+}$  ions in a fluorite-type host in the visible spectral range and clarify the role of concentration-dependent effects on their optical performance. The optical absorption spectra reveal well-defined  $4f-4f$  transitions of  $\text{Tb}^{3+}$  ions, indicating that the average local crystal-field environment remains largely preserved. The Judd–Ofelt analysis yields intensity parameters  $\Omega_2$ ,  $\Omega_4$ , and  $\Omega_6$  typical of fluoride hosts, confirming the predominantly ionic nature and relatively high symmetry of the  $\text{CaF}_2$  lattice. The good agreement between experimental and calculated line strengths validates the reliability of the Judd–Ofelt formalism for describing the absorption and radiative properties of  $\text{Tb}^{3+}$  ions in  $\text{CaF}_2$ . The emission spectra are dominated by the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_j$  transitions ( $j = 3, 4, 5$ ), with intense green emission arising from the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$  transition. The absence of  ${}^5\text{D}_3$  emission, even under direct excitation into the  ${}^5\text{D}_3$  level, is attributed to efficient cross-relaxation processes that transmit excitation energy toward the  ${}^5\text{D}_4$  level. This mechanism, together with the low phonon energy of the flu-

oxide host, enables efficient radiative decay and stable green luminescence over a broad concentration range. Fluorescence lifetime measurements show millisecond-scale decay times characteristic of  $\text{Tb}^{3+}$  in low-phonon-energy hosts, which changes slightly with  $\text{Tb}^{3+}$  concentration. The experimentally determined quantum efficiencies increase markedly from low to intermediate  $\text{Tb}^{3+}$  concentrations and tend to saturate at 10 mol% doping level, demonstrating the robustness of  $\text{CaF}_2$  as a host for efficient  $\text{Tb}^{3+}$  emission. The color chromaticity analysis confirms that all samples emit in the green region with good color stability, governed by the dominance of the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition. Emission cross-section and gain parameter calculations further quantify the radiative potential of the investigated crystals, especially for the orange band.

The present study demonstrates that  $\text{CaF}_2:\text{Tb}^{3+}$  single crystals combine favorable intrinsic spectroscopic properties with a high tolerance to dopant concentration, making them attractive candidates for green-emitting photonic applications.

**Author Contributions:** Conceptualization, M.S., G.B. and D.V.; methodology, M.S., C.S., I.B. and P.V.; validation, M.S., C.S. and D.V.; formal analysis, M.S. and I.B.; investigation, M.S., C.S., G.B., I.B. and P.V.; resources, P.V.; data curation, M.S., G.B. and P.V.; writing—original draft preparation, M.S. and I.B.; writing—review and editing, I.B., M.S., G.B., P.V. and D.V.; visualization, M.S.; supervision, M.S. and D.V.; project administration, P.V.; funding acquisition, P.V. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the European Commission within the framework of the National Recovery and Resilience Plan (PNRR), grant number 760080/23.05.2023, ESCARGOT project entitled “Enhanced Single Crystal Applications and Research in the Growth of new Optical rare earth-based compounds for sustainable and efficient Technologies”.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author (e-mail: marius.stef@e-uvr.ro). The data are not publicly available due to privacy reasons.

**Acknowledgments:** Authors would like to acknowledge Ioan Sirbu for his involvement in the crystal growth process.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. Balakrishnan, P.; Suguma, P.; Jayachandiran, M.; Mohammed Abubakkar, M. Comparison of the photoluminescence properties and thermal stability of the metal ions  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$  and the rare earth ions  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  activated in the silicate-based single phosphor for solid-state applications. *J. Mater. Sci. Mater. Electron.* **2026**, *37*, 139. [\[CrossRef\]](#)
2. Bitam, A.; Fartas, R.; Diaf, M.; Boubekri, H.; Cheddadi, A.; Martin, I.R. Investigation of  $\text{Er}^{3+}$ -doped  $\text{BaF}_2$  single crystals for infrared emission and photovoltaic efficiency enhancement. *Luminescence* **2025**, *40*, e70102. [\[CrossRef\]](#)
3. Schornig, C.; Stef, M.; Buse, G.; Poienar, M.; Veber, P.; Vizman, D. Spectroscopic properties of  $\text{TmF}_3$ -doped  $\text{CaF}_2$  crystals. *Materials* **2024**, *17*, 4965. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Sojka, L.; Tang, Z.; Furniss, D.; Sakr, H.; Fang, Y.; Beres-Pawlik, E.; Benson, T.M.; Seddon, A.B.; Sujecki, S. Mid-infrared emission in  $\text{Tb}^{3+}$ -doped selenide glass fiber. *J. Opt. Soc. Am. B* **2017**, *34*, A70–A79. [\[CrossRef\]](#)
5. Kalusniak, S.; Castellano-Hernandez, E.; Yalçinoğlu, H.; Tanaka, H.; Kränkel, C. Spectroscopic properties of  $\text{Tb}^{3+}$  as an ion for visible lasers. *Appl. Phys. B* **2022**, *128*, 33. [\[CrossRef\]](#)
6. Liu, B.; Shi, J.; Wang, Q.; Tang, H.; Liu, J.; Zhao, H.; Li, D.; Liu, J.; Xu, X.; Wang, Z.; et al. Crystal growth, polarized spectroscopy and Judd-Ofelt analysis of  $\text{Tb}:\text{YAlO}_3$ . *Spectrochim. Acta Part Mol. Biomol. Spectrosc.* **2018**, *200*, 58–62. [\[CrossRef\]](#)
7. Terra, I.A.A.; Borrero-González, L.J.; Almeida, J.M.P.; Hernandez, A.C.; Nunes, L.A.O. Judd-Ofelt analysis of  $\text{Tb}^{3+}$  and upconversion study in  $\text{Yb}^{3+}$ – $\text{Tb}^{3+}$  co-doped calibo glasses. *Quim. Nova* **2020**, *43*, 188–193. [\[CrossRef\]](#)

8. Vasyliev, V.; Molina, P.; Nakamura, M.; Vllora, E.G.; Shimamura, K. Magneto-optical properties of Tb<sub>0.81</sub>Ca<sub>0.19</sub>F<sub>2.81</sub> and Tb<sub>0.76</sub>Sr<sub>0.24</sub>F<sub>2.76</sub> single crystals. *Opt. Mater.* **2011**, *33*, 1710–1714. [\[CrossRef\]](#)
9. Du, Z.; Liu, Q.; Hou, T. The effects of Tb<sup>3+</sup> doping concentration on luminescence properties and crystal structure of BaF<sub>2</sub> phosphor. *Bull. Mater. Sci.* **2015**, *38*, 805–809. [\[CrossRef\]](#)
10. Kawano, N.; Nakauchi, D.; Nakamura, F.; Yanagida, T. Scintillation and dosimetric properties of Tb-doped CaF<sub>2</sub> translucent ceramics synthesized by the spark plasma sintering method. *J. Asian Ceram. Soc.* **2020**, *8*, 484–491. [\[CrossRef\]](#)
11. Dodson, C.M.; Zia, R. Magnetic dipole and electric quadrupole transitions in the trivalent lanthanide series: Calculated emission rates and oscillator strengths. *Phys. Rev. B* **2012**, *86*, 125102. [\[CrossRef\]](#)
12. Chewpraditkul, W.; Sheng, Q.; Chen, D.; Beitlerova, A.; Nikl, M. Luminescence of Tb<sup>3+</sup>-doped oxide glasses with high Gd<sub>2</sub>O<sub>3</sub> concentration under UV and X-ray excitation. *Phys. Status Solidi A* **2012**, *209*, 2578–2582. [\[CrossRef\]](#)
13. Wang, C.-X.; Li, Y.; Liu, Z.-F.; Valeev, E.F.; Moskaleva, L.V. Combined relativistic ab initio multireference and experimental study of the electronic structure of terbium luminescent compound. *J. Phys. Chem. A* **2020**, *124*, 82–89. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Liu, J.; Zhang, Y.; Yao, R.; Ren, H.; Wang, W.; Feng, H.; Li, W.; Miao, Z. Enhanced circularly polarized green luminescence metrics from new enantiopure binary tris-pyrazolonate-Tb<sup>3+</sup> complexes. *Molecules* **2024**, *29*, 5887. [\[CrossRef\]](#)
15. Kumari, P.; Lather, V.; Malik, A.; Ahlawat, P.; Kumar, R. Study of luminescence phenomena of Tb (III) containing fluoroquinoline for application in optoelectronic devices. *J. Fluoresc.* **2024**, *35*, 6279–6296. [\[CrossRef\]](#)
16. Sun, L.; Liu, E.; Fan, J.; Hu, X.; Wan, J.; Li, J.; Li, H.; Hu, Y. Fabrication and luminescence properties of Tb<sup>3+</sup> and Tb<sup>3+</sup>/Ag-doped CaF<sub>2</sub> microcubes. *J. Lumin.* **2015**, *166*, 361–365. [\[CrossRef\]](#)
17. Boubekri, H.; Diaf, M.; Labbaci, K.; Guerbous, L.; Duvaut, T.; Jouart, J.P. Synthesis and optical properties of Tb<sup>3+</sup> doped CdF<sub>2</sub> single crystals. *J. Alloys Compd.* **2013**, *575*, 339–343. [\[CrossRef\]](#)
18. Kuboniwa, S.; Hoshina, T. Luminescent properties of Tb<sup>3+</sup> in oxygen-dominated compounds. *J. Phys. Soc. Jpn.* **1972**, *32*, 1059–1068. [\[CrossRef\]](#)
19. Sardar, D.K.; Nash, K.L.; Yow, R.M.; Gruber, J.B.; Valiev, U.V. Absorption intensities and emission cross sections of Tb<sup>3+</sup> (4f8) in TbAlO<sub>3</sub>. *J. Appl. Phys.* **2006**, *100*, 83108. [\[CrossRef\]](#)
20. Zhan, C.; Mei, B.; Sun, Z.; Li, W.; Yang, Y.; Liu, X.; Zhang, Y. Fabrication and spectroscopic properties of hot-pressed Tb:CaF<sub>2</sub> transparent ceramics with different doping concentrations. *Opt. Mater.* **2022**, *126*, 112128. [\[CrossRef\]](#)
21. Tachihante, M.; Zambon, D.; Arbus, A.; Zahir, M.; Sadel, A.; Cousseins, J.C. Optical properties of trivalent terbium doped calcium fluorapatite. *Mater. Res. Bull.* **1993**, *28*, 605–613. [\[CrossRef\]](#)
22. Kumar, R.; Joseph, D. Spectroscopic studies of Tm-doped CaF<sub>2</sub> single-crystal. *Eur. Phys. J. Plus* **2024**, *139*, 105902. [\[CrossRef\]](#)
23. Zehelesnov, D.S.; Starobor, A.V.; Palashov, O.V. Characterization of the terbium-doped calcium fluoride crystal. *Opt. Mater.* **2015**, *49*, 526–529. [\[CrossRef\]](#)
24. Siebold, M.; Bock, S.; Schramm, U.; Xu, B.; Doualan, J.L.; Camy, P.; Moncorge, R. Yb:CaF<sub>2</sub>—A new old laser crystal. *Appl. Phys. B* **2009**, *97*, 327–338. [\[CrossRef\]](#)
25. Aballea, P.; Suganuma, A.; Druon, F.; Hostalrich, J.; Georges, P.; Gredin, P.; Mortier, M. Laser performance of diode-pump Yb:CaF<sub>2</sub> optical ceramics synthesized using an energy-efficient process. *Optica* **2015**, *2*, 288–291. [\[CrossRef\]](#)
26. Brown, E.E.; Fleischman, Z.D.; McKay, J.; Dubinskii, M. Spectroscopic characterization of low-phonon Er-doped BaF<sub>2</sub> single crystal for mid-IR lasers. *Opt. Mater. Express* **2021**, *11*, 575–584. [\[CrossRef\]](#)
27. Madirov, E.I.; Kuznetsov, S.V.; Konyushkin, V.A.; Busko, D.; Richards, B.S.; Turshatov, A. Pushing the limits: Down-converting Er<sup>3+</sup>-doped BaF<sub>2</sub> single crystals with photoluminescence quantum yield surpassing 100%. *Adv. Opt. Mater.* **2024**, *12*, 2303094. [\[CrossRef\]](#)
28. Pisarska, J.; Kowal, M.; Kochanowicz, M.; Zmojda, J.; Dorosz, J.; Dorosz, D.; Pisarski, W.A. Influence of BaF<sub>2</sub> and activator concentration on broadband near-infrared luminescence of Pr<sup>3+</sup> ions in gallo-germanate glasses. *Opt. Express* **2016**, *24*, 2427–2435. [\[CrossRef\]](#)
29. Shi, C.; Xie, Z.; Deng, J.; Dong, Y.; Yang, X.; Hu, Y.; Tian, Y.; Kan, Y.; Chen, G. Termoluminescence of BaF<sub>2</sub>:RE (Ce, Dy, Eu) crystals. *J. Electron. Spectrosc. Relat. Phenom.* **1996**, *79*, 87–90. [\[CrossRef\]](#)
30. Zhang, L.; Chen, B.; Sun, J.; Li, X.; Cheng, L.; Zhong, H. Spectroscopy and calculations for f–f transitions of Tb<sup>3+</sup> ions in KY<sub>3</sub>F<sub>10</sub> nanocrystal. *J. Nanosci. Nanotechnol.* **2015**, *15*, 4717–4721. [\[CrossRef\]](#)
31. Racu, A.; Stef, M.; Buse, G.; Nicoara, I.; Vizman, D. Luminescence properties and Judd–Ofelt analysis of various ErF<sub>3</sub> concentration-doped BaF<sub>2</sub> crystals. *Materials* **2021**, *14*, 4221. [\[CrossRef\]](#)
32. Zong, Z.; Wang, Y.; Zhang, Z.; Liu, J.; Zhao, L.; Liu, J.; Su, L. High-power 2.8 μm lasing in a lightly-doped Er:CaF<sub>2</sub> crystal. *J. Lumin.* **2022**, *250*, 119089. [\[CrossRef\]](#)
33. Hasabeldaim, E.H.H.; Swart, H.C.; Kroon, R.E. Luminescence and stability of Tb doped CaF<sub>2</sub> nanoparticles. *RSC Adv.* **2023**, *13*, 5353–5366. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Kawano, N.; Kato, T.; Nakauchi, D.; Takebuchi, Y.; Fukushima, H.; Shiratori, D.; Luiz, G.; Jacobsohn, L.G.; Yanagida, T. TSL, OSL and scintillation properties of Tb-doped barium fluoride translucent ceramics. *Opt. Mater.* **2023**, *141*, 113948. [\[CrossRef\]](#)

35. Huang, X.-F.; Yang, X.-B.; Zhao, D.; Ma, L.-P.; Bao, Y.-Z. Effect of BaF<sub>2</sub> and CaF<sub>2</sub> on properties of Tb<sup>3+</sup>-doped yellow phosphorus slag luminescent glass-ceramics. *Opt. Mater.* **2022**, *126*, 112134. [[CrossRef](#)]
36. Liu, J.; Shi, Z.; Song, Q.; Li, D.; Li, N.; Xue, Y.; Xu, J.; Xu, J.; Wang, Q.; Xu, X. Judd-Ofelt analysis and spectroscopic study of Tb:CaF<sub>2</sub> and Tb/Pr:CaF<sub>2</sub> co-doped single crystals. *Opt. Mater.* **2020**, *108*, 110219. [[CrossRef](#)]
37. Calixto, M.E.; Méndez-Blas, A.; Soucase, B.M. CaF<sub>2</sub> thin films obtained by electrochemical processes and the effect of Tb<sup>3+</sup> doping concentration on their structural and optical properties. *J. Solid State Electrochem.* **2018**, *22*, 2465–2472. [[CrossRef](#)]
38. Carnall, W.T.; Fields, P.R.; Rajnak, K. Electronic energy levels of the trivalent lanthanide aquo ions. III. Tb<sup>3+</sup>. *J. Chem. Phys.* **1968**, *49*, 4447–4449. [[CrossRef](#)]
39. Carnall, W.T.; Crosswhite, H.; Crosswhite, H.M. *Energy Level Structure and Transition Probabilities in the Spectra of the Trivalent Lanthanides in LaF<sub>3</sub>*; Argonne National Laboratory (ANL): Argonne, IL, USA, 1977. [[CrossRef](#)]
40. Kaminskii, A.A. *Laser Crystals: Their Physics and Properties*; Springer: Berlin/Heidelberg, Germany, 1990. [[CrossRef](#)]
41. Huang, L.; Qin, G.; Arai, Y.; Jose, R.; Suzuki, T.; Ohishi, Y.; Yamashita, T.; Akimoto, Y. Crystallization kinetics and spectroscopic investigations on Tb<sup>3+</sup> and Yb<sup>3+</sup> codoped glass ceramics containing CaF<sub>2</sub> nanocrystals. *J. Appl. Phys.* **2007**, *102*, 093506. [[CrossRef](#)]
42. Méndez-Blas, A.; López-Cruz, E.; Palestino, G.; Calixto, M.E. Synthesis and characterization of CaF<sub>2</sub> thin films doped with Tb<sup>3+</sup>. *MRS Adv.* **2017**, *2*, 147–152. [[CrossRef](#)]
43. Vasyliiev, V.; Vllora, E.; Sugahara, Y.; Shimamura, K. Judd-Ofelt analysis and emission quantum efficiency of Tb-fluoride single crystals: LiTbF<sub>4</sub> and Tb<sub>0.81</sub>Ca<sub>0.19</sub>F<sub>2.81</sub>. *J. Appl. Phys.* **2013**, *113*, 203508. [[CrossRef](#)]
44. Rai, S.; Hazarika, S. Fluorescence dynamics of Tb<sup>3+</sup> and Tb<sup>3+</sup>/Ho<sup>3+</sup> doped phosphate glasses. *Opt. Mater.* **2008**, *108*, 1343–1348. [[CrossRef](#)]
45. Wang, Y.; Cheng, J.; Wang, Z.; Gong, Y.; Tu, C.; Huang, J.; Sun, Y.; Yu, Y. Study of the optical features of Tb<sup>3+</sup>:CaYAlO<sub>4</sub> and Tb<sup>3+</sup>/Pr<sup>3+</sup>:CaYAlO<sub>4</sub> crystals for visible laser applications. *Crystals* **2022**, *12*, 1729. [[CrossRef](#)]
46. Huang, L.-L.; Fu, Y.-B.; Wu, L.-N. Analysis of the laser performance of Tm<sup>3+</sup>, Tb<sup>3+</sup> (Ho<sup>3+</sup>):YVO<sub>4</sub> crystals at ~1.5 μm wavelength. *Chin. Phys. B* **2003**, *12*, 1417–1422. [[CrossRef](#)]
47. Loiko, P.; Mateos, X.; Dunina, E.; Kornienko, A.; Volokitina, A.; Vileshnikova, E.; Maria Serres, J.M.; Baranov, A.; Yumashev, K.; Aguiló, M.; et al. Judd-Ofelt modelling and stimulated-emission cross-sections for Tb<sup>3+</sup> ions in monoclinic KYb(WO<sub>4</sub>)<sub>2</sub> crystal. *J. Lumin.* **2017**, *190*, 37–44. [[CrossRef](#)]
48. Nicoara, I.; Munteanu, M.; Pecingina-Girjoaba, N.; Stef, M.; Lighezan, L. Dielectric spectrum of rare-earth-doped calcium fluoride crystals. *J. Cryst. Growth* **2006**, *287*, 234–238. [[CrossRef](#)]
49. Chani, V.I.; Boulon, G.; Zhao, W.; Yanagida, T.; Yoshikawa, A. Correlation between segregation of rare earth dopants in melt crystal growth and ceramic processing for optical applications. *Jpn. J. Appl. Phys.* **2010**, *49*, 75601. [[CrossRef](#)]
50. Zhang, Y.; Liu, J.-M.; Liu, M.-H.; Zhang, Z.-B.; Wong, W.-H.; Zhang, D.L. Error evaluation of Judd-Ofelt spectroscopic analysis. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2020**, *239*, 118536. [[CrossRef](#)]
51. Judd, B.R. Optical absorption intensities of rare-earth ions. *Phys. Rev.* **1962**, *127*, 750–761. [[CrossRef](#)]
52. Ofelt, G.S. Intensities of crystal spectra of rare-earth ions. *J. Chem. Phys.* **1962**, *37*, 511–520. [[CrossRef](#)]
53. Luo, W.; Liao, J.; Li, R.; Chen, X. Determination of Judd-Ofelt intensity parameters from the excitation spectra for rare-earth doped luminescent materials. *Phys. Chem. Chem. Phys.* **2010**, *12*, 3272–3282. [[CrossRef](#)] [[PubMed](#)]
54. Luo, M.; Chen, B.; Li, X.; Zhang, J.; Xu, S.; Zhang, X.; Cao, Y.; Sun, J.; Zhang, Y.; Wang, X.; et al. Fluorescence decay route of optical transition calculation for trivalent rare-earth ions and its application for E<sup>3+</sup>-doped NaYF<sub>4</sub> phosphor. *Phys. Chem. Chem. Phys.* **2020**, *22*, 25177–25183. [[CrossRef](#)] [[PubMed](#)]
55. Motzer, C.; Reichling, M. High resolution study of etch figures on CaF<sub>2</sub> (111). *J. Appl. Phys.* **2009**, *105*, 064309. [[CrossRef](#)]
56. Li, H.H. Refractive index of alkaline earth halides and its wavelength and temperature derivatives. *J. Phys. Chem. Ref. Data* **1980**, *9*, 161–289. [[CrossRef](#)]
57. Richman, I. Longitudinal optical phonons in CaF<sub>2</sub>, SrF<sub>2</sub>, and BaF<sub>2</sub>. *J. Chem. Phys.* **1964**, *41*, 2836–2837. [[CrossRef](#)]

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.