

Visible photon cascade emission from the high energy levels of Er^{3+}

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Abstract

In the past decade quantum cutting phosphors with a visible quantum yield over 100% were investigated. This article describes a method to calculate the maximum visible quantum yield for photon cascade emission of Er^{3+} using Judd–Ofelt theory. A maximum visible quantum efficiency of 112% was calculated. A significant part of the emission intensity is situated in the ultraviolet. If an ion can be co-doped that efficiently converts this ultraviolet into visible light, visible quantum efficiencies between 120% and 190% may be achieved.

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1. Introduction

Luminescent tubes based on phosphors doped with lanthanide ions are very popular for household and other general lighting applications. The phosphors currently applied rely on the UV excitation originating from a mercury discharge. The main emission line of mercury is situated at 254 nm. Mercury is toxic and can be replaced by xenon. The xenon discharge has emissions in the vacuum ultraviolet (VUV), a line at 147 and a band around 172 nm, depending on the pressure, and has the advantage that it requires no start-up time.

The phosphors currently used in luminescent tubes do not absorb the 147 and 172 nm radiation efficiently and/or suffer from degradation upon VUV excitation. Moreover, in the conversion of one VUV photon of the xenon discharge into a visible photon more energy is lost than in the conversion of a UV photon of the mercury discharge into a visible photon. As the energy efficiency of the xenon discharge (65%) is lower than the efficiency of the mercury plasma (75%), phosphors with

a visible quantum efficiency considerably higher than 100% are required in order to make the xenon discharge lamp competitive (i.e. have a higher energy efficiency) with the mercury based luminescent tube.

A visible quantum efficiency of more than 100% can be achieved by the subsequent emission of two visible photons upon excitation at high energy and the theoretical possibility was reported in 1957 by Dexter [1]. In this publication, the possibility of cooperative sensitization of two acceptors by a single donor was discussed for the situation, where the excited state of the donor is at twice the energy of the acceptors. Later, it was experimentally shown that quantum efficiencies exceeding unity can also be achieved by a photon cascade on a single lanthanide ion. In the 1970s, photon cascade emission was observed for Pr^{3+} in YF_3 by Sommerdijk et al. [2,3] and also reported by Piper et al. [4].

The luminescent properties of $\text{YF}_3:\text{Pr}^{3+}$ have been studied extensively as the energy level scheme is suitable for photon cascade emission, where excitation in the $^1\text{S}_0$ level results in the consecutive emission of two visible photons. First, emission from the $^1\text{S}_0$ level to the $^1\text{I}_6$ level yields a photon in the violet region of the electromagnetic spectrum (407 nm). Next, emission from the $^3\text{P}_0$ level to the $^3\text{H}_J$ and $^3\text{F}_J$ levels yields photons in

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the green to red region of the spectrum. A visible quantum efficiency of 140% is reported for $\text{YF}_3:\text{Pr}^{3+}$ [4], but it is not a phosphor suitable for lighting applications as the violet emission results in a low color rendering index [5].

The possibility for photon cascade emission from high energy levels of other lanthanide ions has been considered but was found to yield quantum efficiencies in the visible below 100% [6]. The recent investigations on the VUV energy levels of lanthanide ions has resulted in many new levels from which photon cascade emission is expected, possibly with quantum efficiencies in the visible above 100%. Recently, the VUV energy levels of Er^{3+} were reported [7]. The erbium ion also has a energy level scheme suitable for photon cascade emission in the visible. LiYF_4 and LaF_3 doped with Er^{3+} show emission from several high $4f^{11}$ levels upon excitation in the $4f^{10}5d$ bands. Photon cascade emission was observed, but the most intense emissions were situated in the UV region of the spectrum. It was concluded that a visible quantum efficiency higher than 100% cannot be achieved with a phosphor based on Er^{3+} alone, but this conclusion was not supported by a quantitative analysis. A proper analysis of the maximum visible quantum efficiency requires the calculation of the branching ratios for the emission from the starting level.

Judd–Ofelt theory can be used to predict transition probabilities (and thus branching ratios) for emissions of lanthanide ions using reduced matrix elements for these transitions. To estimate maximum visible quantum efficiencies for photon cascade emission upon excitation in the high-energy (V)UV levels of Er^{3+} the reduced matrix elements for transitions originating from the VUV levels are needed. Carnall et al. [11] reported the reduced matrix elements for transitions on erbium up to the $^4G_{7/2}$ level at $28\,200\text{ cm}^{-1}$. For the transitions involving the higher energy levels the reduced matrix elements have not been reported in the literature. Here, we report the reduced matrix elements for the transitions originating from VUV and UV energy levels of Er^{3+} . In addition to that, we list the reduced matrix elements for absorption from the ground state to all $4f^{11}$ excited states of erbium up to $65\,000\text{ cm}^{-1}$. Using Judd–Ofelt theory, we predict the maximum visible quantum efficiency for photon cascade emission starting from the (V)UV levels of Er^{3+} .

2. Theory

In the 1960s Judd [8] and Ofelt [9] independently developed a theory for the calculation of transition probabilities between J -multiplets of lanthanide ions. This theory is known as the Judd–Ofelt theory and has played an important role (and still does) in the

understanding and interpretation of lanthanide spectra. The derivations in this theory are not easy to understand as they involve complex mathematics. The resulting formulas describing the transition probabilities, however, are surprisingly simple, which makes the Judd–Ofelt theory easy to use. For a review of Judd–Ofelt theory, see [10].

The Judd–Ofelt theory explains the intensity of the ‘forbidden’ $4f^n-4f^n$ transitions by taking into account the admixture of configurations of opposite parity (for example $4f^{n-1}5d$ configurations) into the $4f^n$ configuration. One of the approximations used is that the admixing configuration is totally degenerate (the closure approximation) and its energy is set equal to the mean energy of this configuration. The position of the opposite-parity configuration is considered to be far above the $4f^n$ configuration. For lanthanide ions showing emission from a $4f^n$ level for which the lowest $4f^{n-1}5d$ absorption is close to the $4f^n$ level like, for example, the 1S_0 level of praseodymium this approximation is not valid and can cause a discrepancy between theory and experiment.

A second approximation used in the Judd–Ofelt theory is that transition probabilities are calculated for transitions between J -multiplets. In a crystal the J -levels are split by the crystal field and transitions between individual crystal field levels will be different (depending on M_J). Only for situations in which the various crystal field components of the initial state are equally populated (which is true if the crystal field splitting is much smaller than kT) the transition probability is correctly determined with the Judd–Ofelt theory. If this is not the case, the transition probabilities between individual crystal field components have to be evaluated and there will be an influence of temperature due to a variation of the thermal population of the various crystal field components with temperature.

For a general description of transition probabilities, independent of crystal structure, the Judd–Ofelt theory gives a good indication of branching ratios for emission from an initial level to all lower energy levels. In the calculation of transition probabilities it is essential to calculate the reduced matrix elements $U^{(\lambda)}$ between all possible initial and final $4f^n$ states.

Carnall et al. [11] tabulated the (squares of the) reduced matrix elements $U^{(\lambda)}$ for transitions up to about $40\,000\text{ cm}^{-1}$ for all lanthanide ions.

The electric dipole strength S_{ed} for a transition from the initial level $f^n[\gamma, S, L]J$ to a final level $f^n[\gamma', S', L']J'$ is defined as

$$S_{\text{ed}} = \sum_{\lambda=2,4,6} \Omega_{\lambda} |\langle f^n[\gamma, S, L]J || U^{(\lambda)} || f^n[\gamma', S', L']J' \rangle|^2, \quad (1)$$

where the term Ω_{λ} is called a Judd–Ofelt parameter and the squared term between brackets is referred to as the reduced matrix element $U^{(\lambda)}$. The transition probability

A for a transition can be calculated from the dipole strength S_{ed} by

$$A = \frac{64\pi^4 e^2 n (n^2 + 2)^2 v^3}{27 h (2J + 1)} S_{\text{ed}}, \quad (2)$$

where n is the refractive index, v is the frequency of the photon emitted and $(2J + 1)$ is the degeneracy of the initial level.

The Judd–Ofelt parameters Ω_λ are lattice dependent and can be obtained from absorption and emission spectra. Ω_λ values have been reported for the lanthanide ions in many host lattices. This allows the prediction of intensities for transitions that have not yet been observed and the Judd–Ofelt intensity parameters can be used to compare intensity ratios for emissions of a lanthanide ion in different host-lattices. See, for instance, [12]. Judd–Ofelt theory is used to determine transition probabilities and oscillator strengths for forced electric dipole transitions. The strength for magnetic dipole transitions can be calculated exactly, but these transitions are generally much weaker. If the reduced matrix elements are known for all intraconfigurational transitions of a lanthanide ion, then transition probabilities and subsequently branching ratios for emissions can be calculated, using the Ω_λ values as parameters.

Using Judd–Ofelt theory a visible quantum efficiency of 157% was calculated for YF_3 by Pappalardo [6]. We present a similar calculation method to predict the maximum visible quantum efficiency for photon-cascade emission of a lanthanide ion upon excitation at different energies, but our method requires less calculation steps as it omits the calculation of radiative lifetimes and non-radiative decay rates.

3. Method

As discussed in the Section 2 the transition probabilities for the emission from an initial $4f^n$ state to final states depends on the squares of the reduced matrix elements $(U^{(\lambda)})^2$ as follows:

$$A' \propto v^3 \sum_{\lambda=2,4,6} \Omega_\lambda (U^{(\lambda)})^2 \quad (3)$$

with v being the frequency of the photon being emitted for this transition. In Eq. (3) no correction for the wavelength dependence of the refractive index n is applied. This introduces a negligible error since the wavelength dependence of n is a few percents at maximum which is small compared to the cubic contribution of v^3 to the transition probability.

Usually emission is observed from an energy level when the energy gap to the next lower level is more than four times the maximum phonon energy of the host-lattice. If the energy difference with the lower level is less, then non-radiative relaxation becomes more

probable. With the Judd–Ofelt calculations the radiative transition probability between different J -multiplets can be calculated. The crystal field splitting has to be considered in order to find the energy gaps between energy levels for a lanthanide ion incorporated in a host-lattice. For Er^{3+} we used the emitting levels that have been observed in previous investigations [7]. In $\text{LaF}_3:\text{Er}^{3+}$ the highest energy levels from which emission is observed are the ${}^2\text{F}(2)_{5/2}$ ($63\,110\text{ cm}^{-1}$), ${}^2\text{F}(2)_{7/2}$ ($54\,390\text{ cm}^{-1}$), ${}^4\text{D}_{1/2}$ ($47\,150\text{ cm}^{-1}$) and the ${}^2\text{P}_{3/2}$ level ($31\,570\text{ cm}^{-1}$). Fig. 1 depicts the schematic energy level diagram of Er^{3+} showing the free-ion levels up to the ${}^2\text{F}(2)_{5/2}$ level at $63\,100\text{ cm}^{-1}$. Levels that show visible emission in LaF_3 are indicated with a filled semi-circle, all other levels in the visible and UV region of the spectrum show multi-phonon relaxation to the next lower level.

No correction for the degeneracy of the initial level was applied, since this will not affect the calculated branching ratios. Using the calculated reduced matrix elements $U^{(\lambda)}$ and the assumptions mentioned above it is possible to calculate the visible quantum efficiencies for photon cascade emission that depend only on the values of Ω_2 , Ω_4 and Ω_6 . By setting two of the three Ω_λ values to zero, the values that are found for the maximum visible quantum efficiency can be used to determine the maximum quantum efficiency that is possible

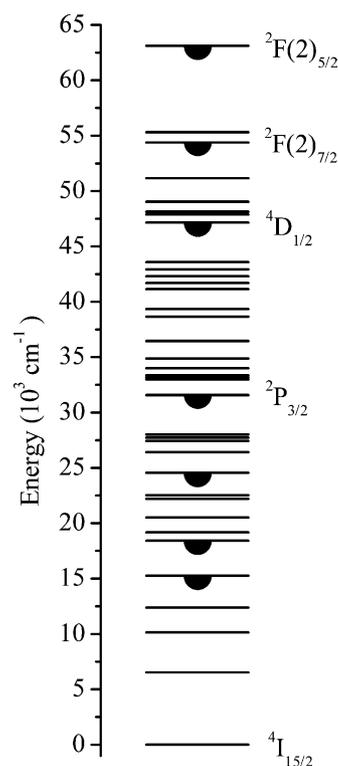


Fig. 1. Schematic energy level diagram for $\text{LaF}_3:\text{Er}^{3+}$ up to $65\,000\text{ cm}^{-1}$. Energy levels from which visible emission may be observed are indicated with a filled semi-circle.

for emission from a certain multiplet. In an actual crystal, with finite values for all three Ω_λ parameters, the visible quantum efficiency will be between ‘extreme’ values that are calculated for the (hypothetical) situation in which only one of the Judd–Ofelt parameters is non-zero.

Any energy level can be chosen as a starting level. The energy gap to the next lower level is used to decide if the level shows emission. If so, then branching ratios for all emissions originating from this level are calculated for each of the three sets of $U^{(\lambda)}$ reduced matrix elements. From the branching ratios the visible, ultraviolet and infrared quantum efficiency for the emissions of the starting level can be calculated. If the starting level is not expected to show emission, its population is added to the next lower level. This process is repeated going down one level at a time until the ground state is reached. If all branching ratios have been calculated, it is possible to evaluate the number of visible photons N_{vis} that can be emitted upon populating N ions into the starting level. The ratio N_{vis}/N yields the maximum visible quantum yield, which can be calculated independently for values of Ω_2 , Ω_4 and Ω_6 .

4. Results and discussion

To check the applicability of our calculation method, we calculated the maximum visible quantum efficiency for $\text{YF}_3:\text{Pr}^{3+}$ using Judd–Ofelt intensity parameter ratios of $\Omega_2/\Omega_6 = 0.013$ and $\Omega_4/\Omega_6 = 0.07$ as reported by Piper et al. [4]. A visible quantum efficiency of 157% was calculated, which is the same as found by Piper et al. and Pappalardo [6]. The experimentally observed visible quantum efficiency of $\text{YF}_3:\text{Pr}^{3+}$ is $140 \pm 15\%$ [4] which is lower than the calculated one, because the calculation method does not consider losses of energy due to impurities and other non-radiative processes that lower the actual quantum efficiency in a real luminescent material.

In the ‘Blue Report’ of Carnall et al. [11] the reduced matrix elements were listed for transitions on erbium up to the $^4\text{G}_{7/2}$ level at about $28\,200\text{ cm}^{-1}$. For the calculation of transitions to and from the higher energy levels of Er^{3+} , we calculated the reduced matrix elements for transitions up to the $^2\text{F}(2)_{5/2}$ energy level situated at $63\,100\text{ cm}^{-1}$ [13]. For the calculation of the reduced matrix elements we used the computer program of Reid, described in detail in [14].

Using the calculation method described in the Section 3 we calculated the maximum visible quantum efficiency for photon cascade emission in erbium. Table 1 shows the ultraviolet, visible and infrared quantum efficiencies upon excitation into the starting-levels indicated, assuming no non-radiative losses. Quantum efficiencies are listed in three rows, indicated with Ω_2 , Ω_4 and Ω_6 , for

Table 1
Calculated maximum visible quantum efficiencies for photon cascade emission of Er^{3+} for different high energy starting levels

Starting level	Dominant Ω_λ	η_{UV} (%)	η_{VIS} (%)	η_{IR} (%)
$^2\text{F}(2)_{5/2}$	Ω_2	89	79	17
	Ω_4	93	92	18
	Ω_6	96	98	7
$^2\text{F}(2)_{7/2}$	Ω_2	84	63	7
	Ω_4	94	53	36
	Ω_6	79	112	10
$^4\text{D}_{1/2}$	Ω_2	16	96	8
	Ω_4	96	47	83
	Ω_6	67	83	9
$^2\text{P}_{3/2}$	Ω_2	0	78	22
	Ω_4	0	107	85
	Ω_6	15	85	5

The quantum efficiencies indicated for dominant Ω_λ are determined by setting the other two Ω_λ values to zero.

the extreme cases that only one of the parameters Ω_2 , Ω_4 or Ω_6 is non-zero.

Contrary to what was suggested in [7] a visible quantum efficiency exceeding 100% is theoretically possible. For emission from the $^2\text{F}(2)_{7/2}$ level the theoretical quantum efficiency is 112% if Ω_6 dominates (is much larger than Ω_2 and Ω_4). Emission from the $^2\text{P}_{3/2}$ level can exceed 100% for a crystal in which Ω_4 is large compared to the other two Judd–Ofelt parameters. For both levels, however, the quantum efficiency is well below the values that are required for quantum cutting phosphors in a xenon discharge lamp. The extreme cases, where only one of the intensity parameters Ω_λ is non-zero do not occur in real crystals, and the actual visible quantum efficiency is always in between the efficiencies calculated. For example, the intensity parameters reported for $\text{LaF}_3:\text{Er}^{3+}$ (in 10^{-20} cm^2) are $\Omega_2 = 1.16$, $\Omega_4 = 1.38$ and $\Omega_6 = 0.88$ [15]. Using these values, the highest visible quantum efficiency calculated is 89% for the $^2\text{F}(2)_{5/2}$ level, 72% for the $^2\text{F}(2)_{7/2}$ level, 73% for the $^2\text{F}(2)_{5/2}$ level and 91% for the $^2\text{P}_{3/2}$ starting level.

In the calculations, discussed above we assumed that the UV emissions of erbium do not contribute to the visible emission. If an ion can be found that converts the UV emissions of erbium into visible light, for example, via a down-conversion process or direct energy transfer, without interfering with the photon cascade transitions on the erbium ion, visible quantum efficiencies between 150% and 190% are possible. This opens new routes to design efficient quantum cutting phosphors by combining Er^{3+} with another luminescent ion.

5. Conclusions

We calculated all reduced matrix elements for transitions involving the high energy levels of the Er^{3+} ion. A

model was used to predict the maximum visible quantum efficiency for photon cascade emission originating from several (V)UV levels of erbium. For two cases in which only one of the Judd–Ofelt intensity parameters dominates, the visible quantum efficiency may exceed 100% (for emission from the $^2F(2)_{7/2}$ or the $^2P_{3/2}$ level). The maximum visible quantum efficiency is 112% and this is not sufficient for a xenon discharge lamp phosphor. However, if an ion can be found that efficiently converts the UV emissions of erbium into visible light, visible quantum efficiencies between 150% and 190% may be achieved.

References

- [1] D.L. Dexter, *Phys. Rev.* 108 (1957) 630.
- [2] J.L. Sommerdijk, A. Bril, A.W. de Jager, *J. Lumin.* 8 (1974) 341.
- [3] J.L. Sommerdijk, A. Bril, A.W. de Jager, *J. Lumin.* 9 (1974) 288.
- [4] W.W. Piper, J.A. DeLuca, F.S. Ham, *J. Lumin.* 8 (1974) 344.
- [5] T. Jüstel, H. Nikol, C. Ronda, *Angew. Chem., Int. Ed.* 37 (1998) 3084.
- [6] F. Pappalardo, *J. Lumin.* 14 (1976) 159.
- [7] R.T. Wegh, E.V.D. van Loef, G.W. Burdick, A. Meijerink, *Mol. Phys.* 101 (2003) 1047.
- [8] B.R. Judd, *Phys. Rev.* 127 (1962) 750.
- [9] G.S. Ofelt, *J. Chem. Phys.* 37 (1962) 511.
- [10] C. Görller-Walrand, K. Binnemans *Handbook on the Physics and Chemistry of Rare Earths*, vol. 25, Elsevier, Amsterdam, 1998, p. 126.
- [11] W.T. Carnall, H. Crosswhite, H.M. Crosswhite, *Energy Level Structure and Transition Probabilities of the Trivalent Lanthanides in LaF₃*, Argonne National Laboratory, Argonne, IL, 1977.
- [12] S. Kück, I. Sokólska, M. Henke, M. Döring, T. Scheffler, *J. Lumin.* 102–103 (2003) 176.
- [13] Tables containing these reduced matrix elements can be obtained from a.meijerink@phys.uu.nl.
- [14] P.S. Peijzel, A. Meijerink, R.T. Wegh, M.F. Reid, G.W. Burdick, *J. Solid State Chem.* (accepted).
- [15] M.J. Weber, B.H. Matsinger, V.L. Donlan, G.T. Surratt, *J. Chem. Phys.* 57 (1972) 562.