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Thulium as a sensitizer for the Gd³⁺/Eu³⁺ quantum cutting couple

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The increasing knowledge of the energy level structure of the lanthanides has led to new applications for these ions. The Gd³⁺/Eu³⁺ quantum cutting couple was discovered a few years ago and may be applied in phosphors for fluorescent tubes based on a VUV xenon discharge. The VUV absorption of the phosphor LiGdF₄:Eu³⁺ is poor and therefore a sensitizer is needed. This contribution describes an investigation of the use of the strong $4f^{12} \rightarrow 4f^{11}5d$ VUV absorption bands of thulium ions as a sensitizer for the Gd³⁺/Eu³⁺ quantum cutting couple. The incorporation of thulium in the quantum cutting phosphor LiGdF₄ does result in sensitization of Gd³⁺ but not in downconversion in the Gd³⁺/Eu³⁺ couple. A competing downconversion process between gadolinium and thulium occurs resulting in infrared emission of thulium, which is not suitable for lighting applications.

1. Introduction

During the twentieth century, knowledge on the spectroscopic properties of lanthanides expanded vastly and was based on both experimentally obtained and calculated energy level diagrams. Wybourne described a method for the calculation of the energy level diagrams of lanthanide ions [1, 2]. Dieke constructed an energy level diagram based on experimentally observed energy levels up to $40\,000\,\mathrm{cm}^{-1}$ in LaCl₃ and is still referred to nowadays as the Dieke diagram [3, 4].

In the 1980s Carnall and coworkers [5] performed an extensive study of the energy levels of lanthanides in LaF₃. Carnall combined experimentally observed levels with calculations and extended the energy level diagram up to $50\,000\,\mathrm{cm}^{-1}$.

The vacuum ultraviolet (VUV) region of the electromagnetic spectrum is situated between 50 and 200 nm ($200\,000$ to $50\,000\,\mathrm{cm}^{-1}$). Research on the VUV energy levels of lanthanide ions has been very limited until recently. Two decades ago, VUV absorption spectra were reported for Ho³⁺ [6] and Er³⁺ [7]. A few f–f transitions in the VUV were observed, but at that time no further research investigating $4f^n$–$4f^n$ transitions of other lanthanide ions was performed. One reason for this was the absence of good experimental facilities for VUV spectroscopy. VUV spectroscopy requires special setups, with intense tunable sources of VUV radiation, such as deuterium lamps or synchrotrons and VUV monochromators.

Another reason for the low number of reports on VUV spectroscopy was the absence of applications that require knowledge of VUV levels of these ions.

This has changed with the need for new phosphors in, for instance, plasma display panels and mercury-free fluorescent tubes.

The efficiency of the phosphors currently applied in mercury-based fluorescent tubes is close to 100%. For environmental reasons, however, an alternative to the mercury discharge is being investigated. Xenon discharge seems to be a promising candidate, having emissions at 147 and 172 nm with a ratio depending on the xenon pressure. The phosphors applied in mercury-based fluorescent tubes have been optimized for absorption at the main mercury emission line at 254 nm. These phosphors do not all perform well under excitation by a xenon discharge since VUV absorption and stability are low, and consequently new phosphors have to be found. Another issue is the energy loss involved in the conversion of a photon in the ultraviolet to a visible photon (65% loss for a 172 nm photon compared to 50% for a 254 nm photon). Moreover, the efficiency of the mercury plasma is 75% whereas the highest xenon discharge efficiency reported is 65% [8].

In order to obtain a higher energy efficiency than a mercury-based discharge lamp, a xenon-based fluorescent tube needs phosphors with a visible quantum efficiency higher than 100%. This is possible with a so-called quantum cutting phosphor which upon VUV excitation emits two (visible) photons, for each VUV photon absorbed. Already in 1957 the possibility for quantum cutting was discussed by Dexter [9] and in the 1970s it was shown that Pr³⁺ can emit two visible photons upon VUV excitation [10–12]. More recently Wegh et al. reported on the quantum cutting phosphor LiGdF₄:Eu³⁺ [13]. Upon VUV excitation this phosphor emits two visible photons via a two-step energy transfer

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process. After VUV excitation of the gadolinium ions and energy migration over the gadolinium sublattice, part of the excitation energy is transferred via cross relaxation to a neighbouring europium ion, which becomes excited into the $^5D_0$ state. Next, the europium emits a visible photon. A second europium ion is excited by direct energy transfer of the remaining energy of the excited gadolinium ion. This europium ion also emits a visible photon. The estimated quantum yield that can be achieved for this system is 190%.

For application in a xenon-based fluorescent tube, the quantum cutting phosphors must have good absorption in the VUV. For LiGdF$_4$:Eu^{3+} this is not the case since the gadolinium absorptions at 172 nm are parity and spin-forbidden 4f^n–4f^n transitions. A so called sensitizer is needed that shows good absorption in the VUV and can transfer the energy efficiently to the gadolinium ions. Wegh [14] reported on the energy transfer from thulium to gadolinium ions. Thulium absorbs efficiently in the VUV, where the 4f^{12} →4f^{11}5d absorption bands are situated. The energy transfer for LiGdF$_4$:Tm^{3+} is depicted schematically in figure 1. The thulium f–d emission has a good overlap with the high energy levels of gadolinium. Since efficient transfer to the ^6G_J and higher states of gadolinium has been found, thulium may be used as a sensitizer for the Gd^{3+}/Eu^{3+} quantum cutting couple. In this paper we investigate whether Tm^{3+} can be used as an efficient sensitizer for the Gd^{3+}/Eu^{3+} quantum cutting system in LiGdF$_4$:Eu^{3+}.

2. Experimental

Powder samples of LiGdF$_4$:Tm^{3+} 1% and LiGdF$_4$:Tm^{3+} 1%,Eu^{3+} 0.3% were prepared by firing stoichiometric amounts of GdF$_3$, LiF (10% excess), TmF$_3$ and EuF$_3$ in a furnace. The samples were heated at 200°C for 3 hours to remove water adsorbed in the starting materials. The fluoride mixture was then heated to 675°C for 8 hours. The furnace was flushed with nitrogen and NH$_4$F was added to the crucibles to create a fluoride atmosphere. X-ray diffraction patterns were recorded to confirm the structure and phase purity of the sample using a Philips PW1729 X-ray diffractometer.

Low resolution excitation and emission measurements were performed on a SPEX 1680 spectrofluorometer equipped with 0.22 m double monochromators. The spectral resolution of these spectrofluorometers is about 0.5 nm. For VUV/UV excitation a D2-lamp (Hamamatsu L1835, 150W) fitted with a MgF$_2$ window was used. The excitation monochromator contains VUV gratings blazed at 150 nm (1200 lines/mm) and Al mirrors coated with MgF$_2$. Excitation spectra were recorded in the range 140–350 nm and were corrected for lamp
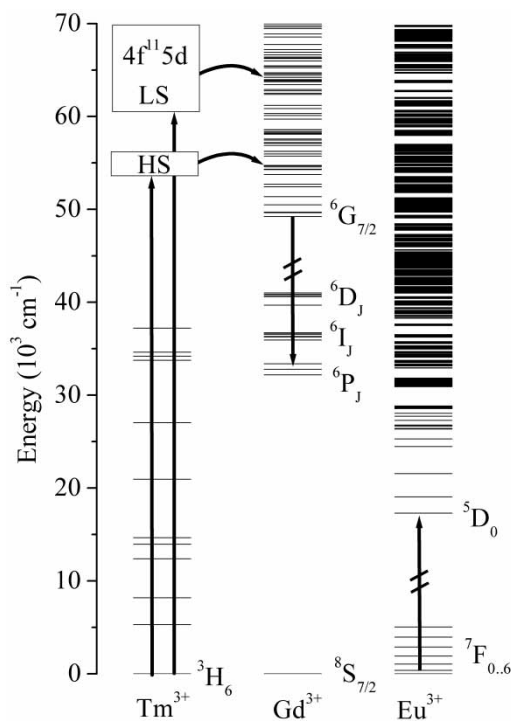

Figure 1. Schematic energy level diagram for LiGdF$_4$:Tm^{3+}, Eu^{3+} showing energy transfer upon 4f^{11}5d excitation of Tm^{3+}.

intensity using sodium salicylate excitation spectra as reference. To avoid absorption of VUV radiation by oxygen the lamp housing, excitation monochromator and sample chamber were flushed with nitrogen for at least 2 hours prior to measurements. The emission monochromator is equipped with gratings blazed at 500 nm (1200 lines/mm). The signal was detected with a cooled Hamamatsu R928 photomultiplier tube, with which emission in the range of 250–800 nm could be measured. Emission spectra recorded with the R928 photomultiplier tube were corrected for monochromator and detector response using correction spectra provided by the manufacturer.

Higher resolution excitation spectra and low resolution VUV/UV/Vis emission spectra and luminescence decay times were measured at the HIGITI setup of the HASYLAB Synchrotron-Strahlungslabor at DESY in Hamburg. For a detailed description of this setup, see [15]. The excitation monochromator consists of a Wadsworth 1m monochromator with a holographic MgF$_2$-coated Al grating blazed at 150 nm (1200 lines/mm), providing an ultimate resolution of 0.3 Å. Excitation was possible in the range 80–400 nm. Emission spectra in the range of 250–1080 nm were recorded using a Tektronix CCD array attached to

a monochromator with a 150 lines/mm and 1200 lines/mm grating. The temperature of the sample could be varied between 10 K and room temperature. The pressure in the sample chamber was maintained below 10^{-8} mbar.

3. Results and discussion

Figure 2 shows the excitation spectrum of $LiGdF_4$:Tm^{3+} (1%) monitoring gadolinium $^6P_{7/2}$ emission (311 nm) measured at the synchrotron setup. The low-spin and high-spin $4f^{11}5d$ bands of thulium are observed between 120 and 160 and 160 and 165 nm, respectively. The observation that the Tm^{3+} excitation bands are present in the excitation spectrum of Gd^{3+} emission indicates that energy transfer from thulium to gadolinium occurs. In the region 165–205 nm excitation lines corresponding to the $4f^7$ levels of gadolinium are observed. This region of the spectrum is similar to the excitation spectrum for Gd^{3+} in $LiYF_4$ [15].

In order to serve as an efficient sensitizer for the Gd^{3+}/Eu^{3+} couple, the absorption of VUV radiation should be followed by energy transfer to one of the high energy (VUV) energy levels of Gd^{3+}. From the high energy levels fast relaxation to the $^6G_{7/2}$ level occurs and this level serves as the starting level for the quantum cutting process. The strongest f–d emission bands of Tm^{3+} in $LiYF_4$ are situated in the VUV region and have good spectral overlap with the VUV energy levels of Gd^{3+} [16]. As a result, energy transfer to the high energy levels of Gd^{3+} is expected, resulting in population of the $^6G_{7/2}$ level.

The excitation spectrum in figure 2 shows that the Tm fd absorption bands can efficiently absorb the VUV emission from a Xe discharge in the spectral region below 160 nm. To test if absorption of the VUV radiation is followed by quantum cutting through the down-conversion process in the Gd/Eu couple, emission spectra have been recorded. By comparison of the emission spectra recorded upon VUV excitation and lower energy excitation, for example in the ^6I_J levels (272 nm), the occurrence of quantum cutting can be observed by an increase in the $^5D_0$ emission of europium relative to the emissions from the $^5D_1$ and higher levels. The first step of the quantum cutting process (cross-relaxation from the $^6G_{7/2}$ level of Gd^{3+}) only populates the $^5D_0$ level of europium, while the second energy transfer populates all ^5D_J levels.

Excitation in the lower energy levels of Gd^{3+} or in the UV levels of Eu^{3+} results in a fast relaxation to the various ^5D_J levels and emission from the different ^5D_J levels in a ratio that is determined by the relaxation rates to the lower ^5D levels. As a result of the direct feeding of the $^5D_0$ level from the $^6G_{7/2}$ level a significant increase of the relative intensity of the $^5D_0$ emission is expected upon VUV excitation and serves as a signature for the occurrence of quantum cutting [17]. In figure 3 the emission spectra are shown for $LiGdF_4$:Eu^{3+},Tm^{3+} upon excitation in the f–d band of Tm^{3+} (at 156 nm), excitation in the $^6G_{7/2}$ level of Gd^{3+} (202 nm) and excitation in the ^6I_J level of Gd^{3+} (272 nm). For excitation at 202 nm (in the $^6G_{7/2}$ level of Gd^{3+}) and 156 nm (in the fd level of Tm^{3+}) quantum cutting is expected to occur. Comparison of the spectra in figure 3 shows, however, that the intensity of the $^5D_0$ emission does not increase relative to the emission from the higher energy ^5D_J levels. This indicates that the desired quantum cutting process is not sensitized by Tm^{3+} and that the incorporation
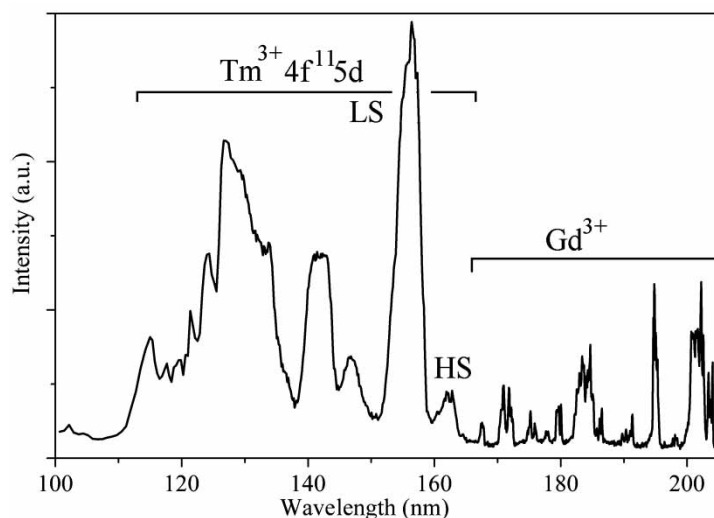

Figure 2.   Excitation spectrum of $LiGdF_4$:Tm^{3+} (1%) monitoring gadolinium $^6P_{7/2}$ emission (311 nm) at 10 K.
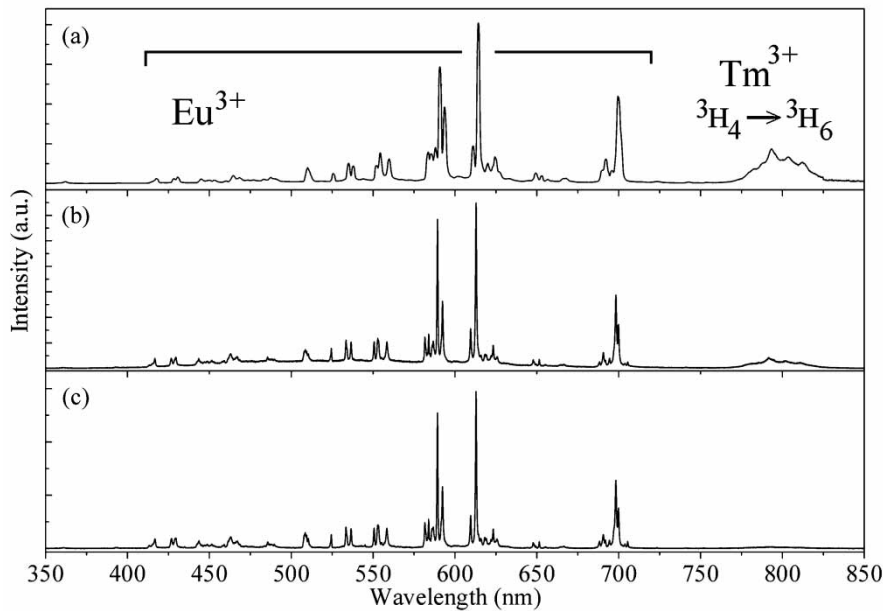
Figure 3.   Emission spectra of LiGdF$_4$:Tm^{3+} 1%,Eu^{3+} 0.3% upon excitation (a) in the f–d band of Tm^{3+} at 156 nm, (b) ^{6}G$_{7/2}$ excitation at 202 nm, and (c) upon ^{6}I$_J$ excitation at 272 nm. All spectra are recorded at room temperature.

of Tm^{3+} even eliminates the Gd^{3+}/Eu^{3+} downconversion process upon direct excitation in the ^{6}G$_{7/2}$ level of Gd^{3+}.

To understand what is causing the apparent absence of quantum cutting, a careful inspection of the emission spectra is required. Even though the ratio of the ^{5}D$_0$ to ^{5}D$_J$ emission is the same in figures 3(*a*)–(*c*), there is a significant difference in the near-infrared part of the spectrum. Only under VUV excitation (156 nm or 202 nm) as an emission observed in the infrared spectral region around 800 nm. This emission is assigned to ^{3}H$_4$→^{3}H$_6$ emission from Tm^{3+}. The fact that the ^{3}H$_4$ emission is much stronger upon VUV excitation indicates that there is direct feeding of the ^{3}H$_4$ level of Tm^{3+} from the ^{6}G$_{7/2}$ level of Gd^{3+}. This increase can be explained by a cross relaxation process between gadolinium and thulium (see figure 4).

The energies of the emissions from the ^{6}G$_{7/2}$ level to the ^{6}D$_J$ and ^{6}I$_J$ levels match the excitation energies from the thulium ^{3}H$_6$ ground state to the ^{3}H$_5$ and ^{3}H$_4$ levels. In the spectrum of figure 3 the increase in emission from the ^{3}H$_4$ level at 800 nm indicates energy transfer from gadolinium to thulium. Since no energy transfer by cross relaxation to the europium ^{5}D$_0$ level is observed, energy transfer to thulium is probably more efficient than energy transfer to europium. To understand why the cross-relaxation process from the ^{6}G$_{7/2}$ level of Gd^{3+} shown in figure 4 is more efficient than the (desired) cross-relaxation process Gd^{3+} (^{6}G$_{7/2}$→^{6}P$_{7/2}$) Eu^{3+}(^{7}F$_1$→^{5}D$_0$), we calculated
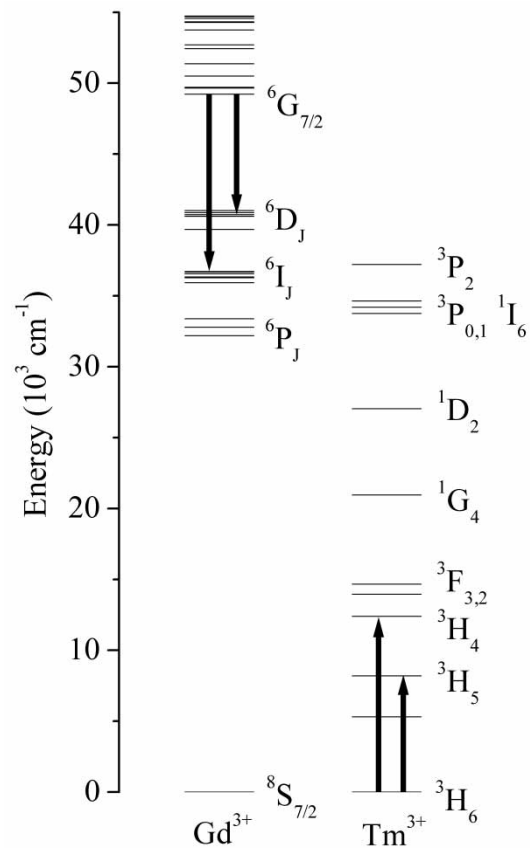

Figure 4.   Energy level diagrams of gadolinium and thulium showing the possibility for cross-relaxation.

Table 1. Squares of the reduced matrix elements for gadolinium $^6G_{7/2}$ emission and thulium $^3H_6$ absorptions. Transitions relevant for (resonant) cross-relaxation are typeset in bold.

Transition	Energy (cm^{-1})	$(U^{(2)})^2$	$(U^{(4)})^2$	$(U^{(6)})^2$
Gadolinium emissions				
$^6G_{7/2} \to {}^6P_{7/2}$	17033	9.9715E-03	1.8458E-01	8.5570E-04
$^6G_{7/2} \to {}^6P_{5/2}$	16433	3.3504E-03	1.3204E-01	3.1071E-05
$^6G_{7/2} \to {}^6P_{3/2}$	15836	6.6171E-04	1.2743E-01	0
$^6G_{7/2} \to {}^6I_{7/2}$	13295	3.5304E-02	9.0484E-02	1.5802E-01
$^6G_{7/2} \to {}^6I_{9/2}$	12948	5.4468E-02	4.8707E-02	2.2478E-02
$^6G_{7/2} \to {}^6I_{17/2}$	12893	0	0	1.0171E-01
$^6G_{7/2} \to {}^6I_{11/2}$	12669	3.1283E-02	3.3279E-04	1.4364E-02
$^6G_{7/2} \to {}^6I_{15/2}$	12550	0	**8.2359E-02**	**7.1557E-02**
$^6G_{7/2} \to {}^6I_{13/2}$	**12515**	0	**5.2193E-02**	**6.3881E-02**
$^6G_{7/2} \to {}^6D_{9/2}$	9541	4.4318E-02	8.4008E-02	2.1074E-02
$^6G_{7/2} \to {}^6D_{1/2}$	8620	0	7.4730E-04	0
$^6G_{7/2} \to {}^6D_{7/2}$	8505	1.4829E-01	5.7148E-06	1.5910E-02
$^6G_{7/2} \to {}^6D_{3/2}$	8360	9.9989E-02	6.0116E-03	0
$^6G_{7/2} \to {}^6D_{5/2}$	**8214**	**7.5861E-03**	**3.6992E-02**	**2.3796E-02**
Thulium absorptions				
$^3H_6 \to {}^3H_6$	0	1.2527E + 00	6.9030E-01	7.7510E-01
$^3H_6 \to {}^3F_4$	5308	5.5282E-01	7.3859E-01	2.5407E-01
$^3H_6 \to {}^3H_5$	**8192**	**1.0738E-01**	**2.3140E-01**	**6.3830E-01**
$^3H_6 \to {}^3H_4$	**12390**	**2.2556E-01**	**1.0006E-01**	**5.8149E-01**
$^3H_6 \to {}^3F_3$	13961	0	3.1637E-01	8.4105E-01
$^3H_6 \to {}^3F_2$	14659	0	5.5957E-06	2.5544E-01
$^3H_6 \to {}^1G_4$	20957	4.4598E-02	7.1409E-02	9.8739E-03
$^3H_6 \to {}^1D_2$	27041	0	3.6236E-01	1.0085E-01
$^3H_6 \to {}^3P_0$	33755	0	0	7.5778E-02
$^3H_6 \to {}^1I_6$	34201	1.0690E-02	3.9162E-02	1.3522E-02
$^3H_6 \to {}^3P_1$	34636	0	0	1.2390E-01
$^3H_6 \to {}^3P_2$	37213	0	2.1778E-01	1.6996E-02
$^3H_6 \to {}^1S_0$	74344	0	0	3.0686E-05

the reduced matrix elements that determine the oscillator strengths of the transitions involved. The theory for the calculation of oscillator strengths for intraconfigurational $4f^n$. transitions was developed in the early 1960s by Wybourne, Judd and Ofelt and allows one to predict the oscillator strengths with good accuracy [1, 2, 18, 19]. In table 1 the squares of reduced matrix elements for the various emissions originating from the $^6G_{7/2}$ level are collected together with the squares of the reduced matrix elements for absorptions of Tm^{3+} ions.

In this table the transitions originating from the gadolinium $^6G_{7/2}$ level that have approximately the same energy as thulium absorptions are displayed in bold. The energies show a mismatch of some tens of cm^{-1}, but the energies given are for the free ion levels. The energy mismatch for the free ion levels is so small that crystal field splitting and phonon assistance will allow for resonant energy transfer in the LiGdF$_4$ crystallites. The transition probabilities P depend on the

squares of the reduced matrix elements $(U^{(\lambda)})^2$ as follows:

$$P \propto \nu^x \sum_{\lambda=2,4,6} \Omega_\lambda (U^{(\lambda)})^2 \qquad (1)$$

with ν being the frequency of the photon being emitted or absorbed for this transition. For absorption x is 1, for emission x is 3. The Judd–Ofelt parameters Ω_λ are lattice dependent and can be obtained from absorption and emission spectra. For Gd^{3+} in LiYF$_4$ the values $\Omega_2 = 0.32 \times 32 \times 10^{-20}$ cm^2, $\Omega_4 = 0$ and $\Omega_6 = 1.8 \times 10^{-20}$ cm^2 were reported by Ellens [20]. The high value of Ω_6 implies that for Gd^{3+} in LiYF$_4$ the transition intensities are dominated by the $U^{(6)}$ reduced matrix elements. We expect the Judd–Ofelt parameters to be similar for LiGdF$_4$ and as a result the numbers for the $(U^{(6)})^2$ matrix elements in table 1 will give the dominant contribution to the dipole strengths of the transitions involved in the downconversion processes. If the energy

transfer occurs through dipole–dipole interaction, the efficiency of the downconversion process will be proportional to the product of the dipole strengths of transitions involved on the donor and acceptor ions. For the Gd^{3+}/Tm^{3+} couple the transitions involved are the $^6G_{7/2} \rightarrow {}^6I_J$ and $^6G_{7/2} \rightarrow {}^6D_J$ transitions on Gd^{3+} and the $^3H_6 \rightarrow {}^3H_4$ and $^3H_6 \rightarrow {}^3H_5$ transitions on Tm^{3+}, respectively. For the Gd^{3+}/Eu^{3+} couple the transitions involved are $^6G_{7/2} \rightarrow +{}^6P_{7/2}$ on Gd^{3+} and $^7F_1 \rightarrow +{}^5D_0$ on Eu^{3+}. Inspection of table 1 shows that the $\left(U^{(6)}\right)^2$ matrix elements for the $^6G_{7/2} \rightarrow {}^6I_J$ transitions are almost two orders of magnitude higher than for the $^6G_{7/2} \rightarrow {}^6P_{7/2}$ transitions. This explains the higher efficiency of the downconversion between Gd^{3+} and Tm^{3+} in comparison with Gd^{3+} and Eu^{3+}. The dipole strengths of the transitions on Tm^{3+} $(^3H_6 \rightarrow {}^3H_4)$ and Eu^{3+} $(^7F_1 \rightarrow {}^5D_0$, the magnetic dipole strength calculated for this transition is $4.13 \times 10^{-23} \, cm^2)$ also favour cross-relaxation between Gd^{3+} and Tm^{3+} over cross-relaxation between Gd^{3+} and Eu^{3+}. This analysis shows that even though Tm^{3+} can efficiently sensitize the $^6G_{7/2}$ level of Gd^{3+} upon excitation in the $4f^{11}5d$ absorption band, the desired Gd^{3+}/Eu^{3+} downconversion process does not occur due to competition by Gd^{3+}/Tm^{3+} downconversion. As a solution for this problem one may suggest increasing the Eu^{3+} concentration. This will favour Gd^{3+}/Eu^{3+} downconversion due to a higher number of Eu^{3+} ions compared to Tm^{3+}. There is little hope, however, that this will work. Eu^{3+} has a strong charge transfer (F^- to Eu^{3+}) absorption band around 160 nm [21]. Excitation in this band is followed by fast relaxation to the various $4f^6$ excited states and results in the emission of only one visible photon from a ^5D_J level. If the Eu^{3+} concentration exceeds the Tm^{3+} concentration this competing VUV absorption will prevent sensitization of the $^6G_{7/2}$ level of Gd^{3+}. The fact that in the $LiGdF_4:Tm^{3+}1\%$, $Eu^{3+}0.3\%$ sample there is no sign of quantum cutting through the Gd^{3+}/Eu^{3+} couple indicates that the downconversion rate for the Gd^{3+}/Eu^{3+} couple is very much smaller than for the Gd^{3+}/Tm^{3+} couple. This is supported by the analysis of the dipole strengths of the transitions involved and indicates that only for very high Eu^{3+} concentrations (in comparison to the Tm^{3+} concentration) will quantum cutting through the Gd^{3+}/Eu^{3+} couple be favoured. For the high Eu^{3+} concentrations the VUV absorption due to the Eu–F charge transfer transition will be much stronger than the f–d absorption by Tm^{3+} ions and sensitization of the $^6G_{7/2}$ level of Gd^{3+} will not occur.

4. Conclusions

Thulium was investigated as a sensitizer for the gadolinium/europium quantum cutting couple.

Excitation into the strong f–d absorption bands of Tm^{3+} does result in sensitization of the Gd^{3+} $^6G_{7/2}$ level but is not followed by quantum cutting through downconversion by the Gd^{3+}/Eu^{3+} couple. Instead, a cross-relaxation process was found to occur between gadolinium and thulium ions. The higher efficiency of this (competing) downconversion process could be explained by combining the energy level schemes of the ions with calculated reduced matrix elements for the transitions involved. The results show that thulium is not a suitable candidate for sensitizing the gadolinium/ europium quantum cutting couple. The infrared emission of thulium generated by the quantum cutting process cannot be used in lighting applications. Our current research investigates other ions for their application as a sensitizer for the $LiGdF_4:Eu^{3+}$ phosphor.

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