ELSEVIER

Journal of Alloys and Compounds 300–301 (2000) 421–425

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Downconversion: a new route to visible quantum cutting

K.D. Oskam*, R.T. Wegh, H. Donker, E.V.D. van Loef, A. Meijerink

Debye Institute, Department of Condensed Matter, Utrecht University, P.O. Box 80 000, 3508 TA Utrecht, The Netherlands

---

Abstract

To obtain vacuum ultraviolet (VUV) phosphors with quantum efficiencies higher than 100%, the concept of downconversion is used. In a downconversion process a VUV photon is split into two visible photons by making use of energy transfer between different rare earth ions. Two examples of downconversion couples are discussed, viz. the Gd^{3+}–Eu^{3+} couple and the Er^{3+}–Gd^{3+}–Tb^{3+} system. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Quantum cutting; Vaccum ultraviolet; Phosphors; Energy transfer

---

1. Introduction

The idea that an ultraviolet photon contains enough energy to be split into two visible photons was already mentioned by Dexter in 1957 [1]. Nevertheless, it was not until 1974 that two research groups independently reported the observation of quantum cutting in YF_3:Pr^{3+} [2–4]. Upon excitation in the $4f5d$ levels of Pr^{3+}, it was observed that the relaxation of Pr^{3+} to the ground state can take place in two steps, both resulting in the emission of a visible photon. However, the photon that is released in the first step, due to the $^1S_0 \rightarrow {}^1I_6$ transition, has a wavelength of 407 nm. This is deep in the violet region of the spectrum where eye sensitivity is low. This makes quantum cutters based on solely Pr^{3+} ions unsuited as lamp phosphors [5].

For several purposes, new phosphors are needed to convert vacuum ultraviolet (VUV) radiation efficiently into visible light. VUV radiation is generated by, e.g., noble gas discharges. These discharges are used in plasma display panels (flat TV screens) and in mercury-free fluorescent tubes. The most efficient noble gas discharge is the Xe-dimer discharge, with its maximum intensity at 172 nm. Currently used phosphors do not efficiently convert VUV radiation ($\lambda < 200$ nm) into visible light: too much energy is lost by converting one VUV photon into one visible photon. Theoretical studies have been done on rare earth ions, showing that no efficient visible quantum cutter can be expected, based on one type of rare earth ion [5,6].

Starting from this point, extensive research has been carried out in our group to find phosphors with $\eta_{vis} >$ 100%. First, the $4f^n$ and $4f^{n-1}5d$ levels of the rare earth ions were studied in the VUV region. Several new levels were discovered and emission was observed from high lying levels for different ions [7–9]. From these results, however, it can be concluded that no efficient quantum cutter can be obtained from a compound doped with one single rare earth ion, because losses in the ultraviolet and the infrared regions are always present. To overcome this problem, it was attempted to use energy transfer between different rare earth ions to enhance the visible quantum efficiency: the quantum cutting ion transfers part of its energy to one or more other ions, leading to the emission of two visible photons per absorbed VUV photon. This process is opposite to ‘‘addition de photons par transfert d’energie’’ (discovered by Auzel in 1966 [10]), which is now usually called upconversion. Therefore, we have called the process of visible quantum cutting by using energy transfer between different ions downconversion [11]. The concept of downconversion will be described in more detail in Section 3.1, and in Sections 3.2 and 3.3 two examples of will be given, viz. the Gd^{3+}–Eu^{3+} couple and the Er^{3+}–Gd^{3+}–Tb^{3+} system.

2. Experimental

Powders of $LiGdF_4$ doped with different rare earth ions were synthesized according to the method described in Ref. [7]. The samples were checked to be single phase by X-ray powder diffraction. $LiGdF_4$ has the inverse scheelite

---

*Corresponding author.

E-mail address: k.d.oskam@phys.uu.nl (K.D. Oskam)

0925-8388/00/$ – see front matter
PII: S0925-8388(99)00755-0

structure, space group $I4_1/a$, in which the lanthanide ion occupies an S_4 site [12]. Luminescence spectra were recorded on a Spex 1680 spectrofluorometer, adapted to excite in the VUV by using a D_2-lamp, gratings blazed at 150 nm in the excitation monochromator and flushing the setup with dry nitrogen. The spectral resolution was approximately 0.5 nm. The setup is described in more detail in Ref. [7].

3. Results

3.1. Downconversion

The concept of downconversion is described with the aid of Fig. 1, in which imaginary energy level schemes are given for ion I and II. In Fig. 1(a), the situation for quantum cutting on one ion is drawn. Upon excitation in a high energy level, different processes can occur. Visible quantum cutting is indicated by the bold arrows. The other arrows indicate processes that lead to emission in the ultraviolet and/or infrared part of the spectrum. To avoid these unfavorable emissions, we make use of energy transfer between different rare earth ions (downconversion). Three possibilities for downconversion can be discerned. Fig. 1(b) depicts the possibility of downconversion by two-step energy transfer. After excitation of ion I, part of the energy is transferred to ion II by cross relaxation (indicated by ①). Ion II returns to the ground state by emitting a visible photon. Ion I can transfer the remaining excitation energy to another ion II (step ② in Fig. 1b), which also emits a photon in the visible part of the spectrum. If the ion of type I is able to emit a visible photon itself, only one energy transfer step is needed. Fig. 1(c) illustrates the possibility of cross relaxation between ions I and II: ion I relaxes from the high lying energy level to an intermediate state while exciting ion II from the ground state to a higher state. Both ions emit visible photons from these excited states, or relax nonradiatively to an emitting state. In the third case (Fig. 1d), the first visible photon is emitted by a transition from a high lying energy level of ion I to an intermediate level on this ion. This step is followed by energy transfer to ion II, which relaxes to the ground state by emitting a visible photon. In all three cases, a quantum efficiency of 200% can be obtained if all processes described here are efficient.

3.2. The Gd^{3+}–Eu^{3+} system

The energy level scheme for the Gd^{3+}–Eu^{3+} downconversion couple is given in Fig. 2. Upon excitation in the ^6G_J levels of Gd^{3+} (positioned at about 50.000 cm^{-1}), the energy migrates over the Gd^{3+} sublattice until it reaches a Eu^{3+} ion. Energy transfer from Gd^{3+} to Eu^{3+} can take place via cross relaxation. Hereby, Gd^{3+} relaxes from the ^6G_J state to one of the ^6P_J states, exciting Eu^{3+} from the $^7F_1$ state to the $^5D_0$ state. The cross relaxation step can take place because there is a good spectral overlap between the $^6G_J \rightarrow {}^6P_J$ transition on Gd^{3+} and the $^7F_1 \rightarrow {}^5D_0$ transitions on Eu^{3+} (both situated at about 590 nm [11]). Thus, this process can only occur if the Eu^{3+} $^7F_1$ level is populated. Indeed, no cross relaxation is observed at low temperatures [13]. After the cross relaxation step, the Eu^{3+} ion in the $^5D_0$ state relaxes to one of the ^7F_J states under emission of a visible photon. The remaining excitation energy is transferred via the ^6P_J levels of the Gd^{3+} sublattice to another Eu^{3+} ion (② in Fig. 2). The excited Eu^{3+} ion relaxes fast to one of the ^5D_J states. From one of these states, emission of a visible photon can occur due to a $^5D_J \rightarrow {}^7F_J$ transition.

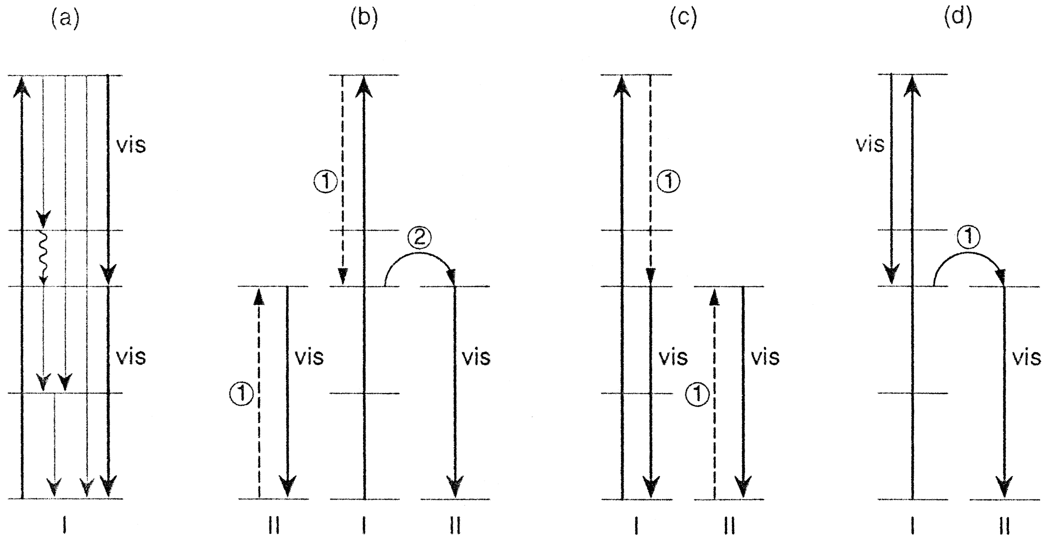

Fig. 1. Imaginary energy level schemes of rare earth ions I and II to illustrate the concept of downconversion (described in Section 3.1). Ion I is the ion at which quantum cutting takes place, ion II is the ion to which part of the excitation energy is transferred. ① and ② denote energy transfer steps.

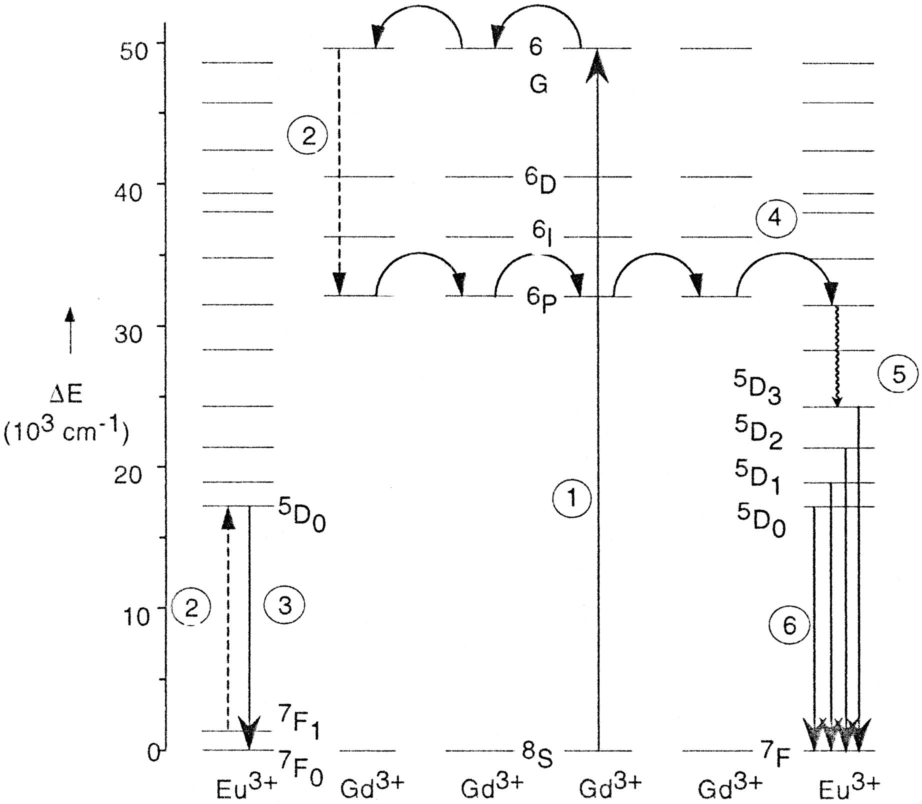

Fig. 2. Energy level scheme of the Gd^{3+}–Eu^{3+} downconversion couple (see Section 3.2).

Experimentally, the quantum efficiency of this system can be estimated as follows. As is seen from Fig. 2, only the Eu^{3+} $^5D_0$ state is populated via the cross relaxation step (①). As a consequence, only emission from this level (to one of the ^7F_J states) is to be expected. In the second energy migration step, however, all ^5D_J levels can become populated by multiphonon relaxation from higher levels. Thus, this second step will lead to emissions from all $^5D_0$, $^5D_1$, $^5D_2$ and $^5D_3$ levels to the ^7F_J states. The ratio of the $^5D_0$, $^5D_1$, $^5D_2$ and $^5D_3$ emissions resulting from the second step is called the ''normal'' branching ratio of the ^5D_J emissions. This ratio is determined by the competition between multiphonon relaxation and radiative decay from the ^5D_J levels. The normal branching ratio can be determined from an emission spectrum of $LiGdF_4$:Eu^{3+} upon excitation in the ^6I_J levels of Gd^{3+} (Fig. 3, lower spectrum). If we compare this emission spectrum with the spectrum obtained upon Gd^{3+} ^6G_J excitation (Fig. 3, upper spectrum), an increase of the $^5D_0$ emission intensity is observed in the latter spectrum. This is expected, because now the cross relaxation step can take place. Formulas and data by which the quantum efficiency of the system can be derived are given elsewhere [11,13]. Here, we limit ourselves with mentioning that from the increase of the $^5D_0$ emission intensity upon VUV excitation, the quantum efficiency for the $LiGdF_4$:Eu^{3+} system upon irradiation at 202 nm is estimated to be ~190%, assuming that nonradiative losses are absent.

3.3. The Er^{3+}–Gd^{3+}–Tb^{3+} system

In Fig. 4, the energy level scheme of the Er^{3+}–Gd^{3+}–Tb^{3+} downconversion system is given. Here, Er^{3+} is the quantum cutting ion. It can be calculated that several transitions from the $4f^{10}5d$ state of Er^{3+} to different ^4F_J and ^4G_J states overlap Gd^{3+} transitions from the ground state to respectively the ^6D_J, ^6I_J or ^6P_J states. Thus, upon excitation in the $4f^{10}5d$ levels of Er^{3+}, cross relaxation can take place between Er^{3+} and Gd^{3+}. After cross relaxation, Er^{3+} relaxes nonradiatively from the aforementioned ^4F and ^4G energy levels to the $^4S_{3/2}$ state, from where the emission of a green photon can occur. The excitation energy of Gd^{3+} migrates over the Gd^{3+} sublattice, until it reaches a Tb^{3+} (or Er^{3+}) ion. Then, energy transfer can take place and a second visible photon is emitted.

To investigate if this process indeed takes place, a comparative method as with the Gd^{3+}–Eu^{3+} couple is used. Upon excitation into the $4f$ levels of Gd^{3+}, no cross relaxation from Er^{3+} to Gd^{3+} can take place: only the second step of the mechanism described above can occur. If we excite in the $4f^{10}5d$ levels of Er^{3+}, a relative increase of the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ emission intensity with respect to the other emissions is expected, due to the cross relaxation step. To see if this is true, emission spectra of $LiGdF_4$ doped with 1.5% Er^{3+} and 0.3% Tb^{3+} were recorded upon excitation in the Gd^{3+} ^6I_J and in the Er^{3+}

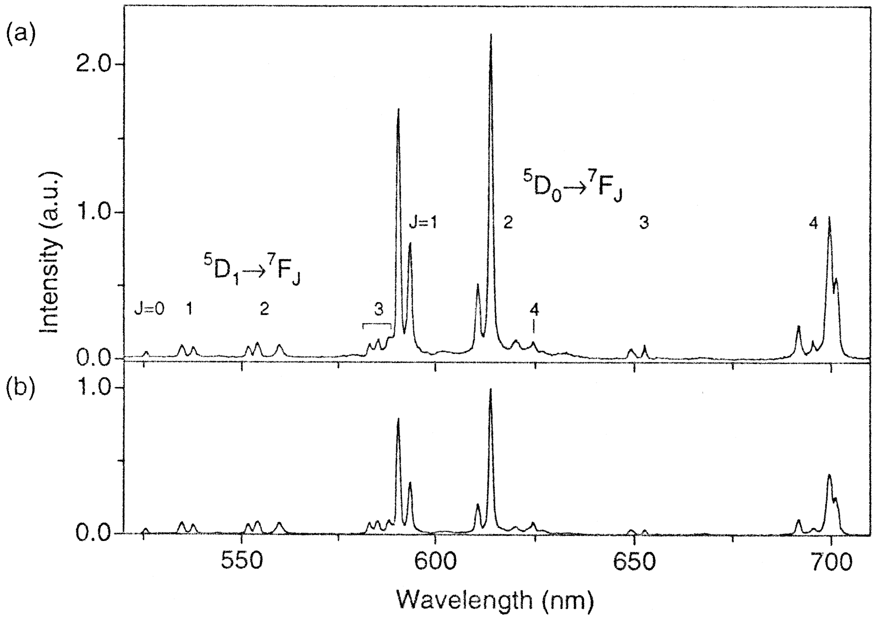

Fig. 3. Emission spectra of LiGdF$_4$:Eu^{3+} (0.5%) upon (a) $^8S_{7/2} \rightarrow {}^6G_J$ excitation on Gd^{3+} (202 nm) and (b) $^8S_{7/2} \rightarrow {}^6I_J$ excitation on Gd^{3+} (273 nm), both at 300 K. Spectra are scaled on the $^5D_1 \rightarrow {}^7F_J$ emission intensity.

$4f^{10}5d$ levels (Fig. 5, lower and upper part respectively). Indeed an increase in the relative intensity of the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ emission is observed. From the integrated peak intensities, it follows that this increase is about 30% with respect to the sum of all emission intensities belonging to the second step. This means that 30% of the Er^{3+} ions transfer a part of their energy so that the $^4S_{3/2}$ state is reached, and consequently, the quantum efficiency is

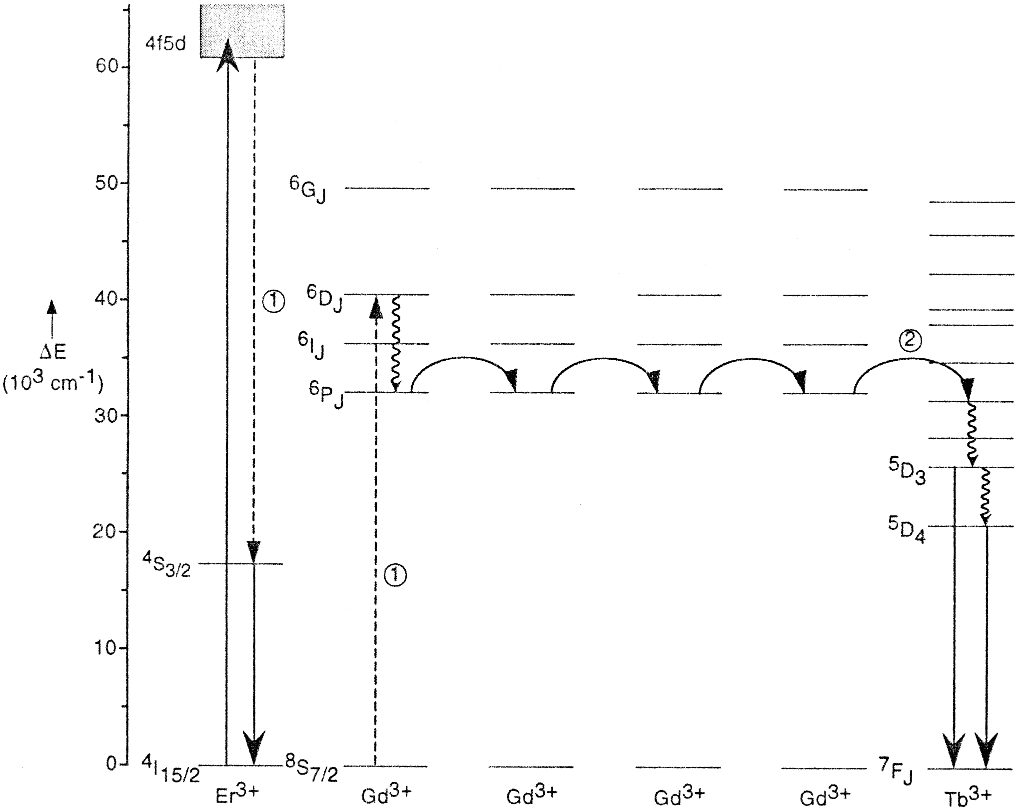

Fig. 4. Energy level scheme of the Er^{3+}–Gd^{3+}–Tb^{3+} downconversion system (explained in Section 3.3).

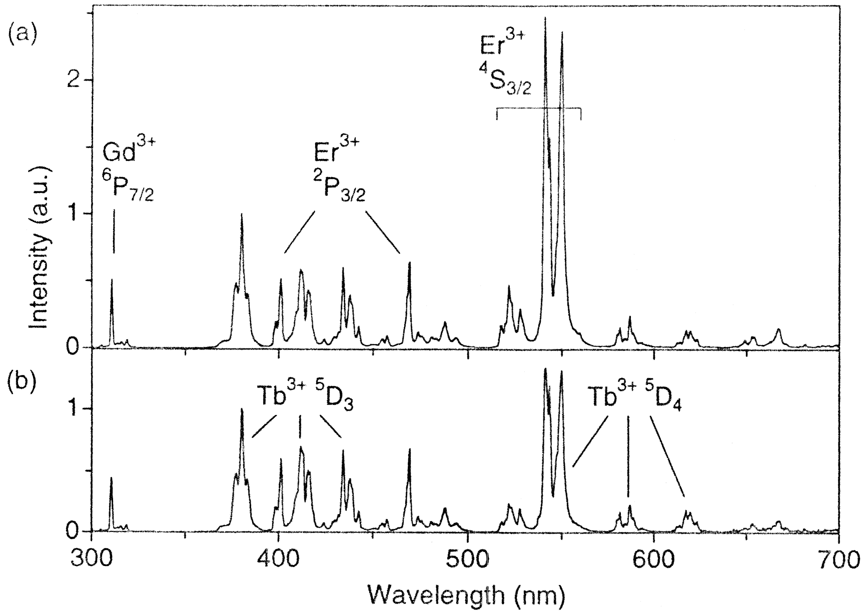

Fig. 5. Emission spectra of $LiGdF_4$:Er^{3+}, Tb^{3+} (1.5%, 0.3%) upon (a) $4f^{11}$ [$^4I_{15/2} \rightarrow 4f^{10}5d$ excitation on Er^{3+} (145 nm)] and (b) $^8S_{7/2} \rightarrow {}^6I_J$ excitation on Gd^{3+} (273 nm), both at 300 K. Spectra are scaled on the Tb^{3+} $^5D_3 \rightarrow {}^7F_J$ emission intensity.

130%. This value represents the upper limit to the quantum efficiency of the system (see Ref. [14] for a more detailed discussion). However, a part of the Tb^{3+} emission is situated in the ultraviolet part of the spectrum. This lowers the upper limit for the visible quantum efficiency to ±110%.

4. Conclusions

Visible quantum efficiencies higher than 100% can be obtained by using energy transfer between different rare earth ions. This is called downconversion. Two examples of downconversion systems are given. The first is the Gd^{3+}–Eu^{3+} couple, in which energy from the ^6G_J levels of Gd^{3+} is transferred in two steps to Eu^{3+} ions. The second system consists of Er^{3+}, Gd^{3+} and Tb^{3+} ions. Here, Er^{3+} is the quantum cutting ion and Gd^{3+} serves as a bridge to transport part of the excitation energy to Tb^{3+}.

Acknowledgements

The work described here was supported by the Council for Chemical Sciences (CW), with financial aid from the Netherlands Organisation for Scientific Research (NWO) and the Netherlands Foundation for Technical Research (STW). Financial support from Philips Lighting and Philips Research Laboratories Aachen is gratefully acknowledged.

References

[1] D.L. Dexter, Phys. Rev. 108 (3) (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] C.R. Ronda, J. Alloys Comps. 225 (1995) 534.
[6] R. Pappalardo, J. Lumin. 14 (1976) 159.
[7] R.T. Wegh, H. Donker, A. Meijerink, R.J. Lamminmäki, J. Hölsä, Phys. Rev. B 56 (1997) 13841.
[8] R.T. Wegh, H. Donker, A. Meijerink, Phys. Rev. B 57 (1998) R2025.
[9] A. Meijerink, R.T. Wegh, in: Proceedings of the International Rare Earth Conference, Fremantle, 1998, (in press).
[10] F. Auzel, C.R. Acad. Sci. (Paris) 262 (1966) 1016.
[11] R.T. Wegh, H. Donker, K.D. Oskam, A. Meijerink, Science 283 (5402) (1999) 663.
[12] R.E. Thoma, C.F. Weaver, H.A. Friedman, H. Insley, L.A. Harris, H.A. Yakel, J. Phys. Chem. 65 (1961) 1096.
[13] R.T. Wegh, H. Donker, K.D. Oskam, A. Meijerink, J. Lumin (accepted).
[14] R.T. Wegh, E.V.D. van Loef, A. Meijerink, J. Lumin (submitted).