



OPEN

SUBJECT AREAS:

INORGANIC LEDS

OPTICAL MATERIALS AND
STRUCTURESReceived
14 April 2014Accepted
20 May 2014Published
10 June 2014Correspondence and
requests for materials
should be addressed to
T.G. (T.
Gregorkiewicz@uva.
nl)

Optical excitation and external photoluminescence quantum efficiency of Eu^{3+} in GaN

W. D. A. M. de Boer¹, C. McGonigle¹, T. Gregorkiewicz¹, Y. Fujiwara², S. Tanabe³ & P. Stallinga⁴¹Van der Waals-Zeeman Institute, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands, ²Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, Osaka, Japan, ³Graduate School of Human and Environmental studies, Kyoto University, Kyoto, Japan, ⁴FCT-DEEI, University of The Algarve, 8005-139 Faro, Portugal.

We investigate photoluminescence of Eu-related emission in a GaN host consisting of thin layers grown by organometallic vapor-phase epitaxy. By comparing it with a reference sample of Eu-doped Y_2O_3 , we find that the fraction of Eu^{3+} ions that can emit light upon optical excitation is of the order of 1%. We also measure the quantum yield of the Eu-related photoluminescence and find this to reach ($\sim 10\%$) and ($\sim 3\%$) under continuous wave and pulsed excitation, respectively.

Wide-gap semiconductors doped with rare-earth ions are of great interest for applications in light-emitting diodes (LEDs), because of their temperature insensitive, sharp and stable emission and an ease of current injection^{1,2}. Blue and green LEDs based on galliumnitrides are already successfully commercialized. However, red emission from these materials is still lacking and monolithic full-color displays are at this moment impossible until this problem is solved. Large effort is thus spent on research of GaN materials that emit in the red. Among them, Eu-doped GaN (GaN:Eu) attracts special attention for its intense red emission around 622 nm, originating from the $^5D_0 \rightarrow ^7F_2$ transition of the Eu^{3+} ions³⁻⁷. In combination with Er^{3+} and Tm^{3+} doped GaN, GaN:Eu could be applied in monolithic full-color displays⁸. In fact, for displays with the full color gamut, a phosphor with an emission line around 610 nm is needed, and it is clear that only the Eu^{3+} ion can satisfy this requirement⁹. However, the light output power of the presently available GaN:Eu LEDs is still too low to compete with ‘conventional’ red-light LEDs based on III-V materials. To overcome this, material characteristics of GaN:Eu layers need to be optimized. For that, we have to determine the limiting factor in the optical performance.

The main concerns are the optical accessibility – the percentage of Eu^{3+} ions which contribute to the emission – and the external quantum efficiency (of both electro- and PL). Past research has revealed that a variety of Eu-related emitting centers, as well as a variety of energy transfer routes exist¹⁰⁻¹⁴. These findings imply that the potential for improvement of emission is mainly to be found in material engineering towards optimization of the energy transfer between the GaN-host and Eu^{3+} ions³⁻⁶. We present here in this work the careful analysis of Eu luminescence in GaN and come to the conclusion that the problem lies in the low percentage of Eu that is optically active. We were able to draw this conclusion by comparing our GaN:Eu sample to a well-characterized standard reference sample of $\text{Y}_2\text{O}_3:\text{Eu}$. The europium in this reference sample, by being embedded in a non-active and insulating host matrix without any defects that can act as quenching centers, has an internal quantum efficiency of over 90% with, moreover, basically all Eu is participating in emission; the reference sample can thus be used as a way to calibrate the optical accessibility of europium in other matrices.

GaN:Eu material can be prepared in various ways. In particular, samples with high crystalline quality can be produced by organometallic vapor phase epitaxy (OMVPE, the de facto standard for GaN growth). For this technique, it has been shown that samples grown under atmospheric pressure feature significant enhancement of PL compared to those grown under low pressure, while the absolute Eu^{3+} concentration is smaller. Since the effective PL lifetime is not affected, this implies that the enhancement is due to a larger number of Eu^{3+} ions contributing to emission^{3,4}. In this study we quantify this notion; we investigated the level of optical accessibility of Eu^{3+} and its temperature dependence in GaN layers grown by OMVPE and determined the fraction of Eu^{3+} dopants participating in emission to be in the order of only some percent. We also determined the external quantum yield (QY) of the Eu-related PL under different excitation conditions.



Experimental

In this study, the GaN:Eu layers were grown by the OMVPE technique on a sapphire (0001) substrate. Specific details on the sample preparation procedure can be found in Ref. 4. The particular sample used in this study has the optically active GaN:Eu layer with a thickness of approximately 400 nm and nominal concentration of Eu^{3+} ions $N_{\text{Eu}} = 3 \times 10^{19} \text{ cm}^{-3}$, as measured by secondary-ion mass-spectroscopy. The reference sample is a conventional industrial Y_2O_3 powder with a high concentration of Eu^{3+} ions, $N_{\text{Eu}} = 1.16 \times 10^{21} \text{ cm}^{-3}$, compressed to a solid pellet to facilitate handling in optical experiments. Y_2O_3 is an insulating host typically used in rare-earth-based efficient phosphors; the wide band-gap character of this host makes that the Eu^{3+} ions can only be excited resonantly and can attain near 100% optical accessibility. Therefore, the chosen material can be suitably used as a reference, allowing for the determination of the percentage of Eu^{3+} ions contributing to the photo-luminescence, i.e., being optically accessible.

The PL experiments were conducted under pulsed and continuous wave (CW) excitations. For the former, a Nd:YAG-pumped optical parametric oscillator with a repetition rate of $f = 100 \text{ Hz}$ and a pulse duration of $\Delta t \approx 7 \text{ ns}$ was used to obtain resonant excitation of the Eu in Y_2O_3 . For GaN-host-mediated excitation, the 3rd harmonic of the same laser pump was used, $\lambda_{\text{exc}} = 355 \text{ nm}$. The CW GaN-mediated excitation was achieved with an Ar-ion laser operating at a wavelength of $\lambda_{\text{exc}} = 364 \text{ nm}$. The spectral information was resolved by a multi-grating monochromator and detected by a CCD camera; time-resolved PL signals were registered with a water-cooled photo-multiplier tube with 1 μs resolution in the applied settings. The QY measurements were performed in both pulsed (resonant) and CW (host-mediated) excitation conditions, where for the latter a low-intensity xenon lamp was used in combination with a monochromator selecting the appropriate excitation wavelength, and recorded with a CCD camera. The sample was placed inside an integrating sphere for homogeneous distribution of the emitted and excitation light; The evaluation of the PL QY was done following the procedure of Refs. 15–17.

For the evaluation of the optical accessibility of Eu^{3+} in GaN, the integrated PL intensity was measured as a function of the applied photon fluence per pulse. The methodology is based on a comparison of the measured PL intensity with that of Eu^{3+} ions in the reference sample. In that way, the experimentally measured PL intensity can be directly related to a specific concentration of Eu^{3+} contributing to emission^{18,19}. In this experimental approach, identical excitation and detection configurations for both samples were maintained in order to ensure constant alignment, independent of the excitation settings. A pinhole placed in front of the investigated sample defines the dimensions of the excitation spot, which, in combination with the exact measurement of the energy per laser pulse after the pinhole, determines the photon fluence value (the number of photons per cm^2 per pulse, Φ).

Results

For the initial optical characterization, the sample was measured upon CW band-to-band excitation, as done in previous studies on similar materials^{3–6}. Figure 1 shows the normalized PL spectra of GaN:Eu measured at room temperature and at $T = 10 \text{ K}$ in red and blue, respectively. The peaks associated with the intra-4f shell transitions are visible⁹, with the main contribution arising from the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition at 621.5 nm, as labeled in the figure. In addition to the Eu^{3+} -related PL peaks, the spectrum measured at room temperature (red) shows a broad structure centered around $\lambda = 575 \text{ nm}$ and some 100s of nm wide, which decreases in intensity for lower temperatures. This feature appeared independently of the excitation photon flux – it has a constant relative amplitude – and can possibly be assigned to a recombination path involving defects and is not further discussed here. With the exception of this specific band,

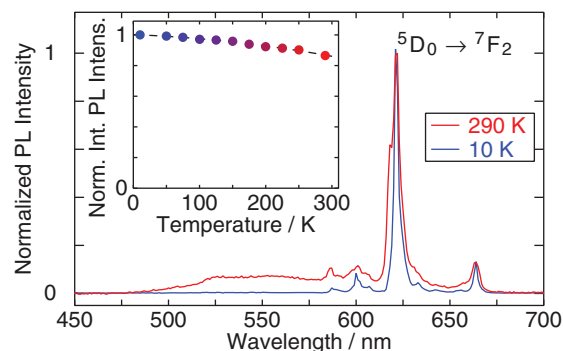


Figure 1 | PL spectra of GaN:Eu measured under CW excitation at $T = 10 \text{ K}$ (blue line) and $T = 290 \text{ K}$ (red line). The inset shows the temperature dependence of the wavelength-integrated PL intensity.

the PL spectral line positions of the investigated material are independent of temperature. The inset of Fig. 1 shows the temperature dependence of the PL intensity, obtained under a photon flux of $j_{\text{exc}} = 9.4 \times 10^{18} \text{ cm}^{-2}\text{s}^{-1}$. Saturation at low temperatures was seen, in agreement with previous reports⁴.

The experiments for the evaluation of the percentage optical accessibility have been performed under pulsed excitation. The reference $\text{Y}_2\text{O}_3:\text{Eu}$ sample was excited resonantly ($\lambda_{\text{exc}} = 470 \text{ nm}$, coinciding with the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transition^{9,20,21}), while the GaN:Eu sample was pumped with over-bandgap-energy photons. Figure 2(a) shows the normalized PL spectra of both GaN:Eu and $\text{Y}_2\text{O}_3:\text{Eu}$ at room temperature in black and blue, respectively, with the corresponding excitation mechanisms schematically illustrated in the insets. In both samples, multiple peaks due to the intra-4f shell transitions are observed (labeled in the figure), with the whole emission band being clearly blue-shifted for $\text{Y}_2\text{O}_3:\text{Eu}$ in comparison to GaN:Eu. The dominant PL feature in both cases can be associated with the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition⁹, and is observed at $\lambda_{\text{max}} = 612 \text{ nm}$ for $\text{Y}_2\text{O}_3:\text{Eu}$ and $\lambda_{\text{max}} = 621.5 \text{ nm}$ for GaN:Eu. Apart from the blue-shift of the main PL line, the influence of the host matrix can also be observed in the effective PL lifetime of the dominant peak, shown in Fig. 2(b). While in both materials a mono-exponential decay is measured – as indicated by dashed lines – the time constants differ by almost an order of magnitude, being $\tau_{\text{eff}} \approx 250 \mu\text{s}$ (GaN, upper panel) and $\tau_{\text{eff}} \approx 1.2 \text{ ms}$ (Y_2O_3 , lower panel).

The PL intensity measurements were conducted from room temperature cooling down. Figure 3(a) shows the temperature dependence of the integrated PL intensity at a photon fluence of $\Phi = 4.6 \times 10^{16} \text{ cm}^{-2}$. As can be seen, upon cooling, the PL intensity initially increases – down to $T = 150 \text{ K}$ – and then quenches somewhat. A similar dependence has been reported before for a Mg^{2+} co-doped GaN:Eu sample upon CW over-bandgap excitation^{22–24}. Such behavior might be due to thermal activation of specific defect centers participating in excitation and de-excitation paths, which can then either enhance or quench the PL. At the same time, the lowering of temperature results in a moderate increase of PL effective lifetime from 220 μs to 265 μs , as shown in Figs. 3(b) and 3(c). This lack of correlation between PL intensity and lifetime temperature dependencies indicates that the effect of temperature is stronger on the excitation than on the recombination, as argued by Lee et al.²². The difference between the temperature dependence of the integrated PL intensity of GaN:Eu observed in our research and the research reported by Fujiwara et al. is most likely due to the difference between pulsed and CW excitation^{3–6}. The differences are consistent with the concept of a variety of different Eu^{3+} centers, and site-selective excitation paths with individual thermal characteristics, as concluded in the past on basis of high-resolution PL and PL excitation investigations^{10–14}.

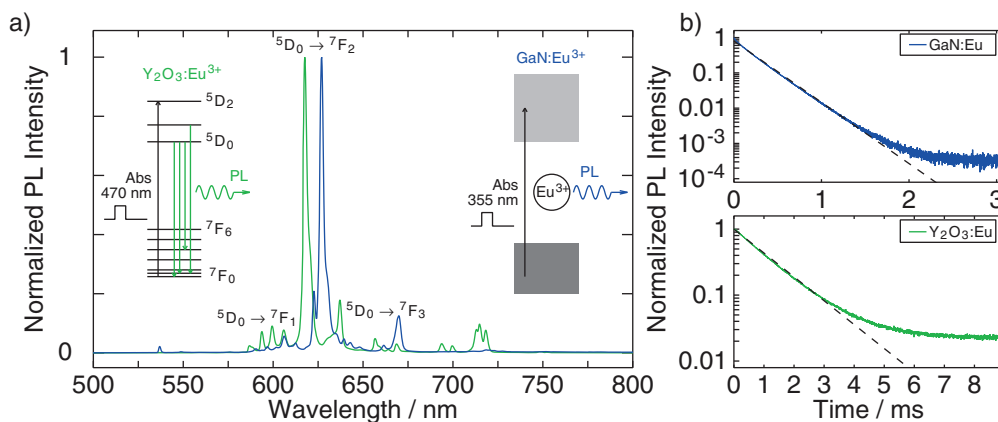


Figure 2 | (a) PL spectra of GaN:Eu and $\text{Y}_2\text{O}_3:\text{Eu}$ at room temperature under pulsed excitation, with the peaks labeled according to convention⁹ and consistent with measurements by Tallant et al.²¹. The insets show the respective excitation paths: the Eu^{3+} ions in GaN are excited by means of an indirect excitation mechanism, where photons are initially absorbed by the host, with the subsequent energy transfer to Eu^{3+} ions. In case of $\text{Y}_2\text{O}_3:\text{Eu}$, excitation is accomplished via direct resonant pumping of the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transition. (b) Decay profiles of PL from GaN:Eu (upper panel) and $\text{Y}_2\text{O}_3:\text{Eu}$ (lower panel), measured at a wavelength of the maximum PL intensity, corresponding to recombination through the ${}^3\text{D}_0 \rightarrow {}^7\text{F}_2$ transition.

Figure 3(d) shows the integrated PL spectra of $\text{Y}_2\text{O}_3:\text{Eu}$ and GaN:Eu as a function of the applied photon fluence. The red, purple and blue squares correspond to the integrated PL intensity of GaN:Eu at $T = 290$ K, $T = 150$ K and $T = 20$ K, respectively. Initially, in the low photon fluence regime, a linear dependence can be observed for the sample, after which saturation sets in; a stretched exponential was fit to the data and shown as solid lines in the figure. It has to be noted that the PL spectrum remained unaltered within the investigated excitation flux range. The black circles depict the integrated PL intensity of the $\text{Y}_2\text{O}_3:\text{Eu}$ reference sample measured at room temperature, and the solid black line is a linear fit to the data.

Discussion

Based on this, an estimation of the optical accessibility of Eu^{3+} in GaN can be made by comparing the time-integrated PL intensity of the investigated sample with that of the $\text{Y}_2\text{O}_3:\text{Eu}$ reference. The instantaneous PL intensities of both samples are proportional to $N_{\text{Eu}}^*(t)/\tau_{\text{rad}}$, where N_{Eu}^* and τ_{rad} correspond to the density of excited Eu^{3+} ions and their radiative lifetimes, respectively. From here on, omitting the time (t) signifies the number at $t = 0$. Since the PL signals are integrated over time, the result will be proportional to $N_{\text{Eu}}^* \times \tau_{\text{eff}}/\tau_{\text{rad}}$, where τ_{eff} is the effective PL lifetime, as measured in the experiment, and N_{Eu}^* the initial number of excited Eu ions. (Note:

The ratio of effective and radiative lifetimes is the internal quantum efficiency – number of photons created divided by the number of photons absorbed – $\text{IQE} = \tau_{\text{eff}}/\tau_{\text{rad}}$). To find the number of photons coming out of the sample and the external quantum efficiency (EQE), this value has to be multiplied by the extraction efficiency η that is determined by the refractive index of the material for that specific wavelength; ($\text{EQE} = \eta \times \text{IQE}$; We ignore in this definition other effects such as photon reabsorption, as well as light-insertion efficiencies, the latter not entering the calculation anyway). Therefore, the total equation for the ratio of the number of photons emitted by GaN:Eu and $\text{Y}_2\text{O}_3:\text{Eu}$ is given by

$$\frac{I_{\text{GaN}}}{I_{\text{Y}_2\text{O}_3}} = \frac{N_{\text{Eu}(\text{GaN})}^* \cdot \text{EQE}_{\text{GaN}}}{N_{\text{Eu}(\text{Y}_2\text{O}_3)}^* \cdot \text{EQE}_{\text{Y}_2\text{O}_3}} \quad (1)$$

$$= \frac{N_{\text{Eu}(\text{GaN})}^*}{N_{\text{Eu}(\text{Y}_2\text{O}_3)}^*} \cdot \frac{\eta_{\text{GaN}}}{\eta_{\text{Y}_2\text{O}_3}} \cdot \frac{\tau_{\text{eff}}^{\text{Eu}(\text{GaN})}}{\tau_{\text{eff}}^{\text{Eu}(\text{Y}_2\text{O}_3)}} \cdot \frac{\tau_{\text{rad}}^{\text{Eu}(\text{Y}_2\text{O}_3)}}{\tau_{\text{rad}}^{\text{Eu}(\text{GaN})}}$$

On basis of this, we can calculate the number of excited europium ions in our GaN sample, $N_{\text{Eu}(\text{GaN})}^*$, from the measured PL intensities I_{GaN} and $I_{\text{Y}_2\text{O}_3}$. This goes as follows.

In the first step, we calculate the extraction efficiencies, knowing that these are determined by the refractive index of that particular

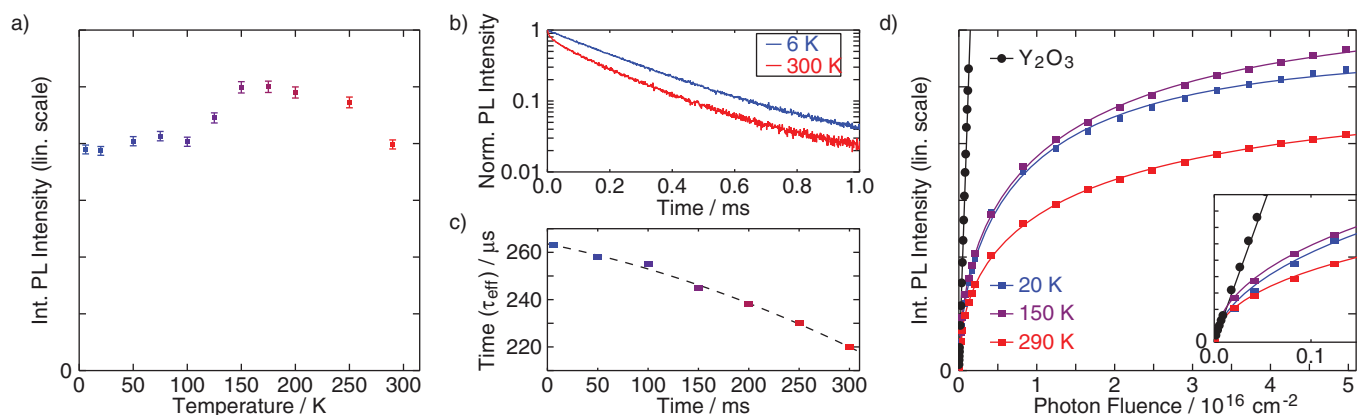


Figure 3 | (a) Temperature dependence of the integrated PL of GaN:Eu for the temperature range of $T = 6$ – 300 K upon pulsed excitation with the photon fluence $\Phi = 4.6 \times 10^{16} \text{ cm}^{-2}$. (b) Decay profile of PL in GaN:Eu at $T = 6$ and $T = 300$ K. (c) Temperature dependence of the PL decay time of GaN:Eu. (d) Time-integrated PL intensity of GaN:Eu at $T = 20$ K, $T = 150$ K and $T = 290$ K and $\text{Y}_2\text{O}_3:\text{Eu}$ at $T = 290$ K as a function of the applied photon fluence. The solid lines show linear (Y_2O_3) and stretched exponential (GaN) fits to the data. Parameters of the fits are given in Table 1.



material and wavelength. By Snell's law, light will not manage to come out at an angle greater than the critical angle that depends on the ratio of refractive indexes. For isotropic emission into air, it can be shown that the (double sided) extraction efficiency of a planar device is equal to

$$\eta(\lambda) = 1 - \cos \left[\sin^{-1} \left(\frac{n_{\text{air}}}{n(\lambda)} \right) \right]. \quad (2)$$

In our case, for GaN at $\lambda = 621.5$ nm, $n = 2.39$, and for Y_2O_3 at $\lambda = 612$ nm, $n = 1.93^{25}$. With n_{air} assumed unity, the extraction coefficients can be calculated as: $\eta_{\text{GaN}} = 0.091$ and $\eta_{\text{Y}_2\text{O}_3} = 0.144$.

The measured EQE of the $\text{Y}_2\text{O}_3:\text{Eu}$ sample was 29.5% and this is much larger than the above implied maximum possible EQE of 14.4%. This shows that the above calculation for $\eta_{\text{Y}_2\text{O}_3}$ is incorrect, possibly due to a different geometry (a pellet rather than a planar device) and surface roughness. However, it does indicate that the internal quantum efficiency must be close to 100%. We continue, therefore, with a best guess of the extraction efficiency of $\eta_{\text{Y}_2\text{O}_3} = 0.295$ and an internal quantum efficiency of

$$\text{IQE}_{\text{Y}_2\text{O}_3} = \tau_{\text{eff}}^{\text{Eu}(\text{Y}_2\text{O}_3)} / \tau_{\text{rad}}^{\text{Eu}(\text{Y}_2\text{O}_3)} = 1. \quad (3)$$

This introduces a substantial uncertainty in the following calculation. Continuing, the ratio of extraction efficiencies is then

$$\frac{\eta_{\text{GaN}}}{\eta_{\text{Y}_2\text{O}_3}} = 0.31. \quad (4)$$

These values were used in our calculations.

Next, the effective lifetime of GaN:Eu PL, $\tau_{\text{eff}}^{\text{Eu}(\text{GaN})}$, is measured via PL transients, as in Fig. 3(b). The radiative lifetime, $\tau_{\text{rad}}^{\text{Eu}(\text{GaN})}$, can be found from the radiative lifetime of $\text{Y}_2\text{O}_3:\text{Eu}$ using Fermi's golden rule for spontaneous emissions that states that radiative lifetimes scale with the refractive index of the host material, $\tau_{\text{rad}} \propto 1/n$. With for Y_2O_3 the radiative and effective lifetimes equal (as discussed above) and the effective lifetime Y_2O_3 , again, measured in transients, the radiative lifetime in GaN can be found as

$$\tau_{\text{rad}}^{\text{Eu}(\text{GaN})} = \frac{n_{\text{Y}_2\text{O}_3}}{n_{\text{GaN}}} \times \tau_{\text{eff}}^{\text{Eu}(\text{Y}_2\text{O}_3)}. \quad (5)$$

Finally, for this comparison we assume that all Eu^{3+} -ions in $\text{Y}_2\text{O}_3:\text{Eu}$ are equivalent and all contribute to the PL (in contrast to those in GaN:Eu). We can then calculate the number of excited europium atoms in $\text{Y}_2\text{O}_3:\text{Eu}$. Because the pulse duration in this experiment is much shorter than the effective lifetime τ_{eff} of Eu^{3+} , it can be assumed that recombination does not take place during an excitation pulse and that $N_{\text{Eu}(\text{Y}_2\text{O}_3)}^*$ follows the equation²⁶

$$N_{\text{Eu}(\text{Y}_2\text{O}_3)}^* = 100\% \times N_{\text{Eu}(\text{Y}_2\text{O}_3)} [1 - \exp(-\sigma_{\text{abs}(\text{Y}_2\text{O}_3)} \Phi)], \quad (6)$$

where $N_{\text{Eu}(\text{Y}_2\text{O}_3)} = 1.16 \times 10^{21} \text{ cm}^{-3}$ is the density of Eu-atoms, $\sigma_{\text{abs}(\text{Y}_2\text{O}_3)} = 3.9 \times 10^{-20} \text{ cm}^2$ is the absorption cross-section of Eu^{3+} for the excitation wavelength $\lambda_{\text{exc}} = 470$ nm. It is based on a value given by Wakamatsu et al.²⁷ for GaN scaled to Y_2O_3 . As shown in Fig. 3(d) $\text{Y}_2\text{O}_3:\text{Eu}$ was measured within the linear regime for low excitation density, where $\sigma_{\text{abs}(\text{Y}_2\text{O}_3)} \Phi \ll 1$. Therefore, the absorption for $\text{Y}_2\text{O}_3:\text{Eu}$ is well described by the approximation $N_{\text{Eu}(\text{Y}_2\text{O}_3)}^* = N_{\text{Eu}(\text{Y}_2\text{O}_3)} \times \sigma_{\text{abs}(\text{Y}_2\text{O}_3)} \times \Phi$. The PL intensity is proportional to this number and is thus a linear function of fluence, $I_{\text{Y}_2\text{O}_3} = A_{\text{Y}_2\text{O}_3} \Phi$. A fit to the data was made resulting in the value of the proportionality parameter $A_{\text{Y}_2\text{O}_3}$ given in Table 1. The value given indicates that, for example, at a fluence of $\Phi = 10^{16} / \text{cm}^2$ the $\text{Y}_2\text{O}_3:\text{Eu}$ PL intensity is 8.254 times the saturation PL of GaN:Eu at 290 K.

For the PL of GaN:Eu, however, a stretched exponential behavior is observed, and the excitation of Eu atoms in GaN through absorption therefore follows the equation

Table 1 | Parameter values found by fitting

Parameter	20 K	150 K	290 K
$\tau_{\text{eff}}^{\text{Eu}(\text{GaN})} / \mu\text{s}$	260	245	220
$\sigma_{\text{abs}(\text{GaN})} / 10^{-16} \text{ cm}^2$	0.891	1.258	1.570
β	0.583	0.530	0.506
A_{GaN}	1.128	1.292	1
$A_{\text{Y}_2\text{O}_3} / 10^{-16} \text{ cm}^2$			8.254
$\tau_{\text{eff}}^{\text{Eu}(\text{Y}_2\text{O}_3)} / \mu\text{s}$			1200

$$N_{\text{Eu}(\text{GaN})}^* = \alpha N_{\text{Eu}(\text{GaN})} \left[1 - \exp \left\{ - \left(\sigma_{\text{abs}(\text{GaN})} \Phi \right)^\beta \right\} \right], \quad (7)$$

with $N_{\text{Eu}(\text{GaN})} = 3 \times 10^{19} \text{ cm}^{-3}$, and α the fraction (between 0 and 1) of ions that do take part in optical processes, i.e., the parameter we are trying to establish in this work. The PL is proportional to this number and follows a stretched exponential too. Fig. 3(d) shows that it fits the data quite well at all temperatures. The parameters of the fits are given in Table 1, with A_{GaN} the amplitude of the curves normalized to saturation PL at 290 K.

With this, the ratio of excited ions thus becomes

$$\frac{N_{\text{Eu}(\text{GaN})}^*}{N_{\text{Eu}(\text{Y}_2\text{O}_3)}^*} = \frac{\alpha N_{\text{Eu}(\text{GaN})} \left[1 - \exp \left\{ - \left(\sigma_{\text{abs}(\text{GaN})} \Phi \right)^\beta \right\} \right]}{N_{\text{Eu}(\text{Y}_2\text{O}_3)} \sigma_{\text{abs}(\text{Y}_2\text{O}_3)} \Phi}, \quad (8)$$

where $\sigma_{\text{abs}(\text{GaN})}$ and β are found from fitting a curve to the data. Note that, to get a rough idea, $\sigma_{\text{abs}(\text{GaN})}$ is basically the reciprocal fluence at which the PL intensity reaches 63% ($1 - e$) of its saturation value.

With the PL behavior known (I_{GaN} and $I_{\text{Y}_2\text{O}_3}$, see Fig. 3(d)) – the geometric photon collection efficiencies are equal and thus cancel in the ratio, i.e., no integrating sphere needs to be used – the only remaining unknown in the starting equation (Eq. 1) is the fraction of active europium centers in GaN:Eu, α , which can thus be derived. As an example, for a fluence of $\Phi = 10^{16} \text{ cm}^{-2}$, a ratio of $I_{\text{GaN}}/I_{\text{Y}_2\text{O}_3} = 0.0665$ can be found from Fig. 3(d) or Table 1 for $T = 290$ K. When we substitute this into Eq. 1, with the parameters of Table 2 we get a value of 2.6%. In the same way, we find values of 2.9% and 3.3% for 20 K and 150 K, respectively.

While the particular experimental measurements leading to these numbers are quite accurate (PL intensity vs. photon fluence), the overall accuracy of the optical accessibility determination depends on the method itself and the assumptions which have been made. The errorbar on the final value is estimated to be about a factor 2, which is mainly due to the poor knowledge of the extraction efficiency as discussed before. Other factors that might influence it are the concentration on Eu^{3+} ions in the reference sample and the assumption that all of them contribute to PL. Finally, (multiple) internal reflections might play a role. Using Fresnel's equation (for perpendicular rays), light is reflected off the interfaces of air-GaN, GaN-sapphire, and sapphire-air. Using the refractive indexes of these materials (2.4, 1.77), we estimate that effectively 83% of the incident light is in the GaN layer under study. The absorption cross section found by us is then 17% under-estimated. This further increases the error bar. Yet, undoubtedly, a lot of europium ions are in the GaN host that never participate in any way in luminescence and this is the main conclusion of this work.

In addition, the PL QY of GaN:Eu was measured upon low flux CW (Xe lamp) and pulsed indirect excitation at $\lambda = 355$ nm. This method provides information on the efficiency of the energy transfer, as it gives directly the ratio of the number of emitted and absorbed photons, without consideration of the concentration of the available optically active centers. Under CW excitation, the PL QY was $\approx 3.2\%$, while under pulsed excitation it was found to be about a factor 2.5 higher, QY $\approx 8\%$. This difference is in agreement with the results



Table 2 | Parameter values used in this work

Parameter	value
$N_{\text{Eu}(\text{Y}_2\text{O}_3)}$	$1.16 \cdot 10^{21} \text{ cm}^{-3}$
$\sigma_{\text{abs}}(\text{Y}_2\text{O}_3)$	$3.9 \cdot 10^{-20} \text{ cm}^2$
$\tau_{\text{rad}}^{\text{Eu}(\text{Y}_2\text{O}_3)}$	$\tau_{\text{eff}}^{\text{Eu}(\text{Y}_2\text{O}_3)}$
$n_{\text{Y}_2\text{O}_3} 612 \text{ nm}$	1.93
$\eta_{\text{GaN}}/\eta_{\text{Y}_2\text{O}_3}$	0.31
$N_{\text{Eu}(\text{GaN})}$	$3 \cdot 10^{19} \text{ cm}^{-3}$
$n_{\text{GaN}} 621.5 \text{ nm}$	2.39

observed in the PL spectra, since the defect-related emission shoulder, as revealed for CW excitation, is likely to lower the overall QY.

Conclusions

The current work showed that the problem of low yield in GaN:Eu LEDs lies in the relatively low levels of optical accessibility of Eu dopants, in the order of a few percent. Here thus lies the opportunity for improvement, basically in material preparation.

The temperature-dependent percentage of optically active Eu^{3+} ions – the ‘optical accessibility’ – has been determined for state-of-the-art GaN:Eu layers grown by OMVPE. The values between 2.6% and 3.3% have been found depending on the temperature ($T = 20\text{--}300 \text{ K}$). This has been achieved by comparison of the integrated PL intensity of Eu-related emission in the investigated materials and a reference sample. Also the external quantum yield of the host-mediated Eu PL in GaN has been determined as $\text{QY} \approx 10\%$ and $\text{QY} \approx 3\%$, for pulsed and CW band-to-band excitation modes, respectively.

- Steckl, A. J. *et al.* Rare-Earth-Doped GaN: Growth, Properties, and Fabrication of Electroluminescent Devices. *IEEE J. Sel. Top. Quant.* **8**, 749 (2002).
- Steckl, A. J., Park, J. H. & Zavada, J. M. Prospects for rare earth doped GaN lasers on Si. *Mater. Today* **10**, 20–27 (2007).
- Nishikawa, A., Kawasaki, T., Furukawa, N., Terai, Y. & Fujiwara, Y. Room-Temperature Red Emission from a p-Type/Europium-Doped/n-Type Gallium Nitride Light-Emitting Diode under Current Injection. *Appl. Phys. Express* **2**, 071004 (2009).
- Nishikawa, A., Furukawa, N., Kawasaki, T., Terai, Y. & Fujiwara, Y. Improved luminescence properties of Eu-doped GaN light-emitting diodes grown by atmospheric-pressure organometallic vapor phase epitaxy. *Appl. Phys. Lett.* **97**, 051113 (2010).
- Nishikawa, A., Kawasaki, T., Furukawa, N., Terai, Y. & Fujiwara, Y. Electroluminescence properties of Eu-doped GaN-based red light-emitting diode by OMVPE. *Phys Status Solidi A* **207**, 1397–1399 (2010).
- Furukawa, N., Nishikawa, A., Kawasaki, T., Terai, Y. & Fujiwara, Y. Atmospheric pressure growth of Eu-doped GaN by organometallic vapor phase epitaxy. *Phys. Status Solidi A* **208**, 445–448 (2011).
- Roqan, I. S. *et al.* Identification of the prime optical center in GaN:Eu³⁺. *Phys. Rev. B* **81**, 085209 (2010).
- Wang, Y. Q. & Steckl, A. J. Three-color integration on rare-earth-doped GaN electroluminescent thin films. *Appl. Phys. Lett.* **82**, 502 (2003).
- Luminescence. From Theory to Applications* (ed Ronda, C. R.) ISBN: 978-3-527-31402-7 (Wiley-VCH, 2007).
- Woodward, N., Nishikawa, A., Fujiwara, Y. & Dierolf, V. Site and sample dependent electron-phonon coupling of Eu ions in epitaxial-grown GaG layers. *Opt. Mater.* **33**, 1050–1054 (2011).
- Fleischman, Z. *et al.* Excitation pathways and efficiency of Eu ions in GaN by site-selective spectroscopy. *Appl. Phys. B* **97**, 607–618 (2009).
- Penn, S. T., Fleischman, Z. & Dierolf, V. Site-specific excitation of Eu ions in GaN. *Phys. Status Solidi a* **205**, 30–33 (2008).

- O'Donnell, K. P., Roqana, I. S., Wanga, K., Lorenz, K. & E. Alves, M. B. The photoluminescence/excitation (PL/E) spectroscopy of Eu-implanted GaN. *Opt. Mater.* **33**, 1063–1065 (2011).
- Lorenz, K. *et al.* Lattice site location of optical centers in GaN:Eu light emitting diode material grown by organometallic vapor phase epitaxy. *Appl. Phys. Lett.* **97**, 111911 (2010).
- De Mello, J. C., Wittmann, H. F. & Friend, R. H. An Improved Experimental Determination of External Photoluminescence Quantum Efficiency. *Adv. Mater.* **9**, 230–232 (1997).
- Mangolini, L., Jurbergs, D., Rogojina, E. & Kortshagen, U. Plasma synthesis and liquid-phase surface passivation of brightly luminescent Si nanocrystals. *J. Lumin.* **121**, 327–334 (2006).
- Timmerman, D., Valenta, J., Dohnalová, K., de Boer, W. D. A. M. & Gregorkiewicz, T. Step-like enhancement of luminescence quantum yield of silicon nanocrystals. *Nat. Nanotechnol.* **6**, 710–713 (2011).
- Vinh, N. Q., Minissale, S., Vrielinck, H. & Gregorkiewicz, T. Concentration of Er³⁺ ions contributing to 1.5- μm emission in Si/Si:Er nanolayers. *Phys. Rev. B* **76**, 085339 (2007).
- Wojdak, M. *et al.* Sensitization of Er luminescence by Si nanoclusters. *Phys. Rev. B* **69**, 233315 (2004).
- Elmanharawy, M. S., Eid, A. H. & Kader, A. A. Spectra of europium-doped yttrium oxide and yttrium vanadate phosphors. *Czech. J. Phys. B* **28**, 1164 (1978).
- Tallant, D. R., Seager, C. H. & Simpson, R. L. Energy transfer and relaxation in europium-activated Y₂O₃ after excitation by ultraviolet photons. *J. Appl. Phys.* **91**, 4053 (2002).
- Lee, D., Nishikawa, A., Terai, Y. & Fujiwara, Y. *Appl. Phys. Lett.* **100**, 171904 (2012).
- Lee, D.-G. *et al.* Effect of thermal annealing on luminescence properties of Eu,Mg-codoped GaN grown by organometallic vapor phase epitaxy. *Appl. Phys. Lett.* **102**, 141904 (2013).
- Wakahara, A., Sekiguchi, H., Okada, H. & Takagi, Y. Current status for light-emitting diode with Eu-doped GaN active layer grown by MBE. *J. of Lumin.* **132**, 3113–3117 (2012).
- This uses Sellmeier's equation. <<http://refractiveindex.info/>> (visited on 04/11/2014).
- Fernández, M. F. *Two-color spectroscopy of energy transfers in Si:Er* PhD thesis (University of Amsterdam, 2004), 110.
- Wakamatsu, R., Lee, D.-G., Koizumi, A., Dierolf, V. & Fujiwara, Y. Luminescence properties of Eu-doped GaN under resonant excitation and quantitative evaluation of luminescent sites. *J. Appl. Phys.* **114**, 043501 (2013).

Acknowledgments

This work was financially supported by Stichting voor de Technologische Wetenschappen (STW), and, in part, by a Grant-in-Aid for Creative Scientific Research (Grant No. 19GS1209) and a Grant-in-Aid for Scientific Research (S) (Grant No. 24226009) from the Japan Society for the Promotion of Science, and by the Global Centre of Excellence Program ‘Advanced Structural and Functional Materials Design’ from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Author contributions

Wd.B. and T.G. conceived the project and designed the experiments, Ch.Mc.G. and Wd.B. performed the experiments, Y.F. and S.T. supplied the GaN structure and the Y₂O₃ reference, Wd.B., Ch.Mc.G. and P.S. analyzed the data, Wd.B., P.S. and T.G. wrote the manuscript, T.G. facilitated and supervised the project. All the authors contributed to the analysis and data interpretation, and discussed the manuscript.

Additional information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: de Boer, W.D.A.M. *et al.* Optical excitation and external photoluminescence quantum efficiency of Eu³⁺ in GaN. *Sci. Rep.* **4**, 5235; DOI:10.1038/srep05235 (2014).



This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder in order to reproduce the material. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>