# Excitation Efficiency and Limitations of the Luminescence of $Eu^{3+}$ Ions in GaN

D. Timmerman,[1,*] B. Mitchell,[2] S. Ichikawa,[1] J. Tatebayashi,[1] M. Ashida,[3] and Y. Fujiwara[1]

[1] *Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*

[2] *Department of Physics, West Chester University, West Chester, Pennsylvania 19383, USA*

[3] *Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan*

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The excitation efficiency and external luminescence quantum efficiency of trivalent $Eu^{3+}$ ions doped into gallium nitride (GaN) is studied under optical and electrical excitation. For small pump fluences, the excitation of $Eu^{3+}$ ions is limited by an efficient carrier trap that competes in energy transfer from the host material. For large pump fluences, the limited number of high-efficiency $Eu^{3+}$ centers and the small excitation cross section of the majority $Eu^{3+}$ centers limit the quantum efficiency. At low temperatures, under optimal excitation conditions, the external luminescence quantum efficiency reaches a value of 46%. These results show the high potential for this material as an efficient light emitter and demonstrate the importance of excitation conditions on the light-output efficiency.

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## I. INTRODUCTION

Eu-doped GaN shows great promise for its application as a red-light emitter with temperature-insensitive, sharp, and stable emission based on the well-developed GaN platform. Current injection is relatively easy in these materials, and high optical output powers of device structures have been shown [1,2]. However, past research has shown that the excitation mechanism of Eu-related emitting centers is diverse and their optical activity is determined by various factors [3–9]. The origin of this variation lies in the existence of multiple incorporation centers of the $Eu^{3+}$ ions in the GaN host. The variation of their local environments gives rise to small variations in the excitation and emission wavelengths, which allow the local environments to be distinguished [10]. For GaN:Eu grown by organometallic vapor epitaxy (OMVPE), the majority center, comprising about 90% of the total $Eu^{3+}$ ions, is referred to as OMVPE4 (Eu1) and shows emission at around 622 nm. Two other important centers, known as OMVPE7 (Eu2) and OMVPE8 ($Eu2^{*}$), which are related through the charge state of a local vacancy defect [11], show the most pronounced emission under current injection [12]. These two centers comprise $<10\%$ of the $Eu^{3+}$ ions. It is noted that, at room temperature, it is not possible to distinguish between OMVPE4 and OMVPE7 ($\sim$622 nm), while the peak of OMVPE8 ($\sim$618 nm) is easy to isolate. Here, we quantitatively determine the basic excitation properties of OMVPE7 and OMVPE8 (minority) and OMVPE4 (majority) centers under optical and electrical excitation. Additionally, the factors that limit the output efficiency are determined. It is shown that, while the external quantum efficiency of luminescence can reach values up to about 50%, it is strongly dependent on the excitation conditions. These results encourage the use of these materials in microlight-emitting diodes (micro-LEDs), where relatively low current densities are typically employed.

## II. MATERIALS AND METHODS

For photoluminescence (PL) experiments, a Pharos laser system (Light conversion, Vilnius, Lithuania), operating at 1 kHz with about 200 fs pulse width and about 0.2 mJ pulse energy at an output wavelength of 1030 nm, is used to pump an optical parametric amplifier (OPA), Orpheus-HP (Light Conversion, Vilnius, Lithuania), to generate excitation pulses with a wavelength of 350 nm. The excitation laser is guided through a circular pinhole to obtain a homogenous intensity throughout the excitation spot (top-hat profile) for all optical experiments. Luminescence is spectrally dispersed by a 0.5 spectrometer, SpectraPro HRS-300 (Acton Research Corporation, Acton, USA), and detected with an air-cooled CCD, PIXIS 256 (Princeton Instruments, Trenton, USA). For the determination of absolute PL quantum efficiencies, the sample is placed in an integrating sphere (LabSphere). Low-temperature measurements are performed with a nitrogen-cooled cryostat.

The samples and devices in this work are grown by OMVPE on (0001) sapphire substrates, and trimethylgallium (TMGa) and ammonia ($NH_3$) are used as the

*dolfscience@gmail.com

 

gallium and nitrogen sources, respectively. The reactor pressure is maintained at 100 kPa during growth. For the GaN:Eu layers, $EuCp^{pm}_2$ (Bis(normal-propyltetramethylcyclopentadienyl)) is used as the Eu source. The Eu source and transfer lines are maintained at 125 and 135 °C, respectively. The Eu concentration is determined to be $1 \times 10^{20}$ cm$^{-3}$ by means of secondary-ion mass spectroscopy. The growth temperature of the optically active layer is 960 °C, which is the optimal growth temperature for GaN:Eu [13,14]. A LED structure is grown using the same structure as that of the active layer, which is surrounded by a LED structure similar to that in Ref. [11]. Ti/Au and Ni/Au contacts are formed by electron beam deposition on the *n*- and *p*-type layers, respectively.

## III. EXPERIMENTAL RESULTS

### A. Effective excitation cross section of photoluminescence

To quantitatively determine the efficiency of excitation of the most important centers for above band-gap pumping, power-dependent PL spectra are obtained under pulsed excitation at room temperature. A laser repetition rate of 1 kHz ensures that excited $Eu^{3+}$ ions relax to the ground state before the next pulse arrives [15]. Figure 1(a) shows the PL spectra for different pump fluences, at an excitation wavelength of 350 nm. The number of $Eu^{3+}$ ions in the excited state that contribute to PL under laser illumination, $N^*$, is governed by simple kinetics:

$$\frac{dN^*(t)}{dt} = \sigma_{ex}\varphi[N_{tot} - N^*(t)] - \frac{N^*(t)}{\tau}, \tag{1}$$

where $N_{tot}$ is the total number of excitable $Eu^{3+}$ ions, $\tau$ is the relaxation time, $\sigma_{ex}$ is the effective excitation cross section, and $\varphi$ is the flux density. If the laser pulse length is short compared with $\tau$ (~220 $\mu$s for Eu:GaN at room temperature), and the repetition rate is low enough to allow excited $Eu^{3+}$ ions to relax to the ground state, the second term describing the relaxation can be ignored and the solution becomes

$$N^* = N_{tot}(1 - e^{-\sigma_{ex} f}), \tag{2}$$

where the photon fluence is $f = \varphi\Delta t$ and $\Delta t$ is the laser pulse width. Spectral deconvolution is performed to isolate the primary peaks originating from the OMVPE8 center (~618 nm) and the primary peak originating from an overlap of the OMVPE4 and OMVPE7 centers to gain information about these two peaks, independently (see the Supplemental Material for details [16]). The pump fluence dependence of OMVPE8 is shown in Fig. 1(b), together with a fit of Eq. (2). An effective excitation cross section of $1.6 \times 10^{-15}$ cm$^2$ is found. As the PL lifetime of all peaks have similar values, it can be assumed that the emission efficiency of the different centers is similar. This allows us

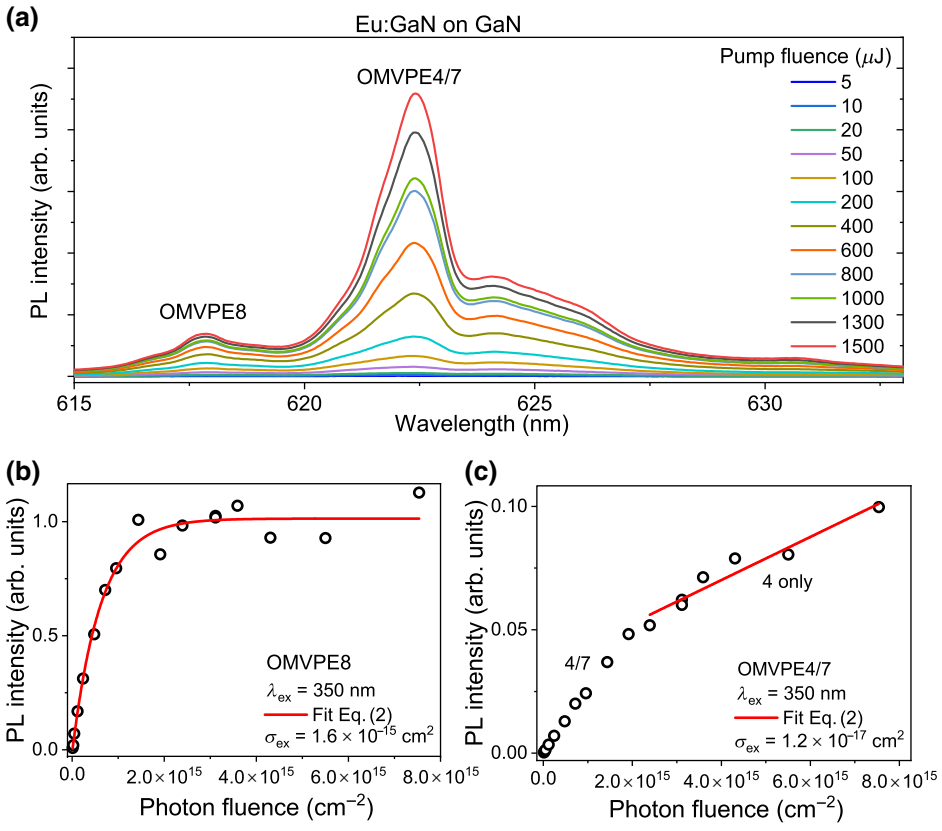


FIG. 1. (a) PL spectra for an excitation wavelength of 350 nm for various pump fluences. Intensity of the peaks related to (b) OMVPE8 and (c) OMVPE4 and OMVPE7, as obtained by spectral deconvolution of the PL spectra. The vertical axis indicates the relative fraction of excited centers. The red lines show fits of Eq. (2).

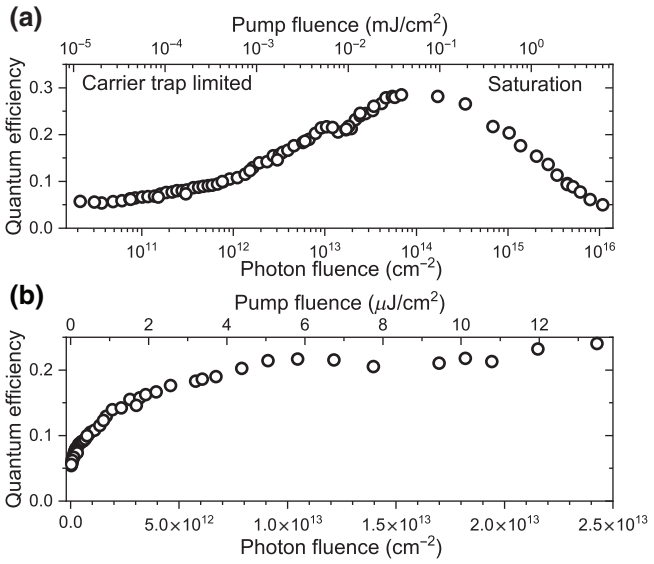


FIG. 2. (a) Dependence of the external QE of Eu-related emission on the pump fluence over six orders of magnitude. (b) Linear plot for the low pump fluence region.

to use the saturation value of OMVPE8, and the relative abundance of the centers, to scale the excited fraction of the OMVPE4 and OMVPE7 peaks. In the fluence dependence of OMVPE4 and OMVPE7, two regions can be observed [Fig. 1(c)]. In the low-fluence region, there is a contribution from both centers. However, OMVPE7 saturates at the same excitation fluence as that of OMVPE8, and a fit of Eq. (2) on the high-fluence part of the peak gives the effective excitation cross section of the OMVPE4 center, with a value of $1.2 \times 10^{-17}$ cm$^2$, which is slightly over two orders of magnitude smaller than that of the high-efficiency centers.

### B. External photoluminescence quantum yield

By taking the ratio of excitation fluence and PL intensity, a relative quantum efficiency (QE) of the PL efficiency is determined. Simultaneously, the absolute quantum efficiency is determined by an integrating-sphere methodology to calibrate the relative values [16]. The results for a variation of the pump fluence over six orders of magnitude are shown in Fig. 2(a). For small fluences, the QE increases as a function of the pump fluence, until it reaches a maximum of around 0.05 mJ cm$^{-2}$, while for larger pump fluences the QE decreases again. From a linear plot of the low pump fluence regime, it can be observed that the QE quickly rises until about 5 $\mu$J cm$^{-2}$, after which point it increases more gradually [Fig. 2(b)]. This behavior can be explained by an efficient trapping center that competes with the Eu ions, lowering its QE, and reducing its influence when all traps are filled. The photon fluence for which this center is saturated is about $10^{13}$ cm$^{-2}$, i.e., the trapping center has an effective cross section in the order of about $10^{-13}$ cm$^2$. The most likely candidate for this center is the H1 hole-trapping center [17,18]. It is typically found in OMVPE-grown GaN and has a large carrier capture cross section of about $10^{-13}$ cm$^{-2}$, with a typical concentration of a few times $10^{16}$ cm$^{-3}$. The origin of this trap is controversial and is attributed to gallium vacancies ($V_{Ga}$) [19,20] or $C$-related defects ($C_N$) [21,22]. For completeness, it is noted that other native defects also contribute in this pump fluence region, competing with Eu excitation, but these have typically lower concentrations and/or smaller carrier capture coefficients, and thus, a limited contribution.

In the high pump fluence regime, the PL QE drops as the number of available $Eu^{3+}$ ions for excitation limits the emission after a single pulse. We note that the determination of the PL QE after a short excitation pulse gives a much "cleaner" result, when compared with continuous-wave (cw) excitation, as the dynamics of the competing carrier traps are less important. If the carrier trap lifetimes are relatively short (relative to the Eu emission), the observed PL QE will generally be lower in cw excitation, as these traps can trap multiple carriers before Eu ions relax back to the ground state. This explains why much lower values of the external QE efficiency have been found previously under low-power cw excitation [23]. Also, in that work, under pulsed excitation, a value was found for the PL QE (~0.03) for a photon fluence of $4.6 \times 10^{16}$ cm$^{-2}$; this value is actually in line with the values determined here.

Under intense cw excitation, a common experimental condition that is used for the study of these materials, thermal quenching results in a PL intensity at room temperature that is about 15% of the value observed at low

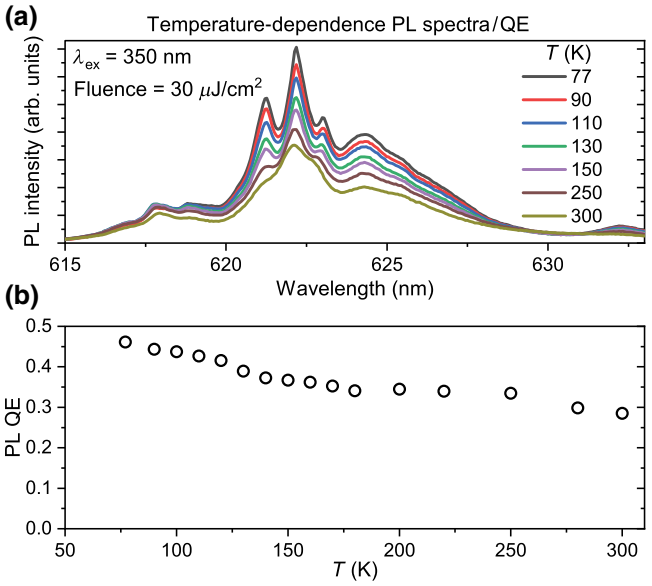


FIG. 3. (a) Temperature dependence of the PL spectrum. (b) PL QE of the Eu-related emission.

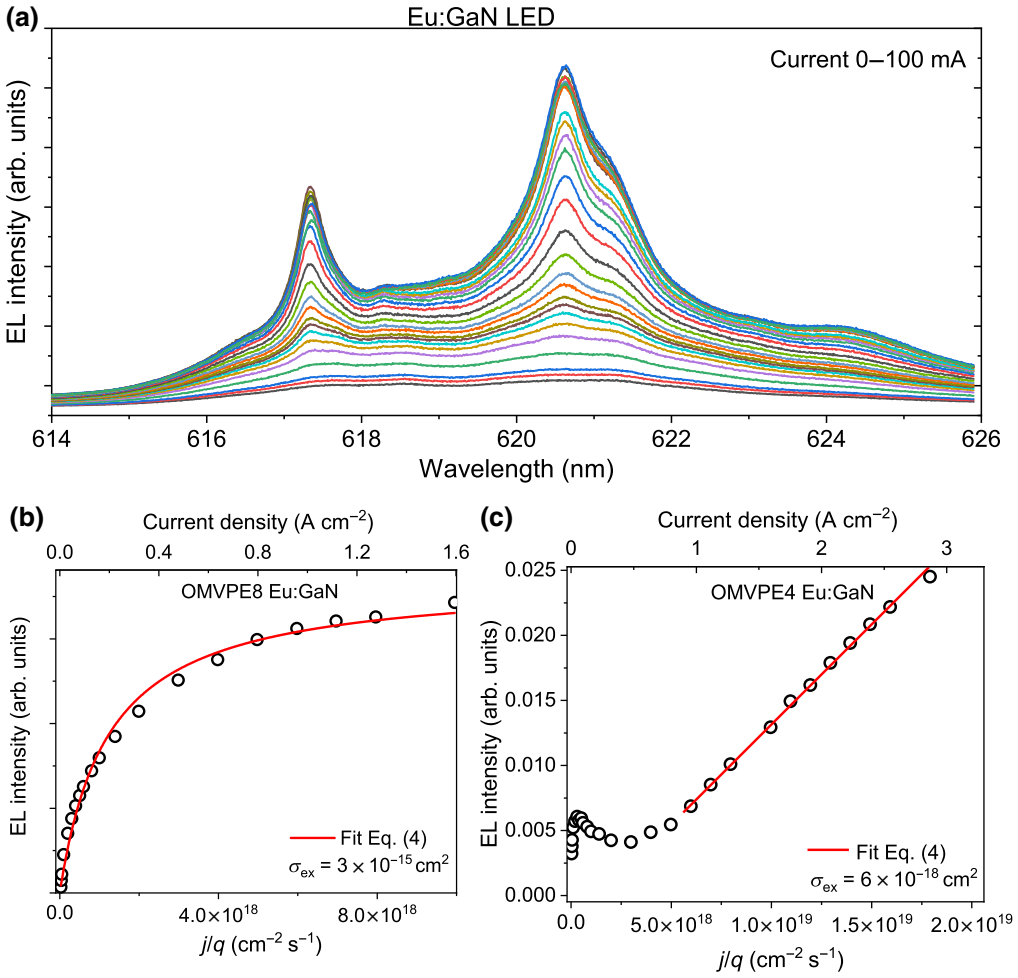


FIG. 4. (a) EL spectra for various injection currents up to 100 mA. Intensity of the peak related to (b) OMVPE8 and (c) OMVPE4, as obtained by spectral deconvolution of the EL spectra and following the procedure described in the main text. The vertical axis indicates the relative fraction of excited centers. The red lines show fits of Eq. (4).

temperature [24]. However, this is different under the pulsed excitation conditions used in this study. Figure 3 shows the PL spectrum and PL QE as a function of temperature in the range of 77–300 K under excitation conditions where the QE has its maximum. It can be seen that the QE increases relatively continuously, up to a value of 0.46. The OMVPE8 center is hardly quenched and shows only a small increase in intensity, when going to lower temperature, while the intensity from the OMVPE4 center nearly doubles.

### C. Excitation cross section of electroluminescence

Under current injection of GaN:Eu LEDs, the situation changes due to differences introduced by the device design [25]. The spectrum changes slightly [Fig. 4(a)], and the ratio of the peaks for high current does not change as much as that under optical excitation. The number of $Eu^{3+}$ ions in the excited state that contribute to electroluminescence (EL) under current injection, $N^*$, is governed by the following kinetics:

$$\frac{dN^*(t)}{dt} = \sigma_{ex}\frac{j}{q}[N_{tot} - N^*(t)] - \frac{N^*(t)}{\tau}, \qquad (3)$$

where $N_{tot}$ is the total number of excitable Eu ions, $\tau$ is the relaxation time, $\sigma_{ex}$ is the excitation cross section, $j$ is the current density, and $q$ is the elementary charge. Under equilibrium conditions, the solution to Eq. (3) is given by

$$N^* = N_{tot}\frac{\sigma_{ex}\tau(j/q)}{1 + \sigma_{ex}\tau(j/q)}. \qquad (4)$$

As with the optical excitation, the peaks are spectrally deconvoluted to determine their relative intensities. The current density dependence of OMVPE8 is depicted in Fig. 4(b), together with a fit of Eq. (4). A value for the excitation cross section of $3.0 \times 10^{-15}$ cm$^2$ is found; this value is about twice as large as that under optical excitation. We exploit the relationship between OMVPE7 and OMVPE8 to subtract a rescaled intensity dependence from the OMVPE4 and OMVPE7 peaks to isolate the OMVPE4 contribution. For a current density over 1 A/cm$^2$, this gives a linear dependence. Following the same rescaling procedure as that under optical excitation, the relative fraction of excited majority centers is determined. Subsequently, the high current density dependence is fitted with Eq. (4) and results in an excitation cross section of $6 \times 10^{-18}$ cm$^2$.

## IV. DISCUSSION

Multiple processes compete with radiative relaxation of the $Eu^{3+}$ ions and decrease the efficiency of the emission originating from transitions within its $4f$ shell, most prominently at elevated temperatures [26]. The two most important types in the GaN:Eu system under study are energy transfer to an impurity state outside of the $4f$ shell and an Auger-type relaxation with free carriers. The PL lifetimes of GaN:Eu at room and low temperature indicate that there is only minor quenching at room temperature under pulsed conditions; about 80% of the excited $Eu^{3+}$ ions can decay radiatively at room temperature [10,23]. In this case, only the available thermally excited free carriers at elevated temperatures, and possibly nearby thermally excited states, contribute to the nonradiative deexcitation of $Eu^{3+}$ ions. During cw optical or electrical excitation, the concentration of free carriers and nearby excited states increases and enhances back-transfer, giving rise to stronger quenching. In particular, an Auger-type energy transfer is shown to effectively deexcite the $Eu^{3+}$ ions at high carrier densities [13,15].

Since the back-transfer rate is too small to explain the observed thermal quenching under pulsed excitation, an explanation must be sought in differences in the excitation efficiency of the $Eu^{3+}$ ions. There are several deactivation channels available for optically excited carriers. Among nonradiative recombination processes is the trapping of carriers by Eu-related traps. These can then subsequently transfer their energy to the $Eu^{3+}$ ion or otherwise deexcite by different processes, for example, radiative or nonradiative energy transfer to free or trapped carriers. For the minority centers (OMVPE7 and OMVPE8), the small thermal quenching and similarity between optical and electrical excitation indicate efficient energy transfer from a bound exciton state [27]. The thermal quenching for these centers can be fully explained by the lifetime shortening of the Eu-related PL, i.e., the energy-transfer efficiency from the trap state to the $Eu^{3+}$ ions is about 100%. Contrarily, the OMVPE4 center shows a much stronger quenching, indicating that the energy-transfer efficiency from its associated state is much lower and improves at low temperatures. Furthermore, OMVPE4 shows large differences between optical and electrical excitation. From earlier work, it is known that excitation of the OMVPE4 center is likely to be related to donor-acceptor pair (DAP) transitions [28]. The DAP is excited primarily by optical excitation. A similar mechanism is also observed for intentionally codoped samples [29].

The PL quantum efficiency has a maximum value of 0.285 for a photon fluence of $7 \times 10^{13}$ $cm^{-2}$. From the concentration and excitation cross sections of the centers, we can estimate a total concentration of excited $Eu^{3+}$ ions of $1.7 \times 10^{17}$ $cm^{-3}$ at room temperature, which increases to $2.4 \times 10^{17}$ $cm^{-3}$ at 77 K. For this fluence, all of the efficient trapping centers will be occupied, which, together with the QE of 0.46, sets an upper limit to the trap concentration, $N_T = 2.0 \times 10^{17}$ $cm^{-3}$. Since the carbon concentration is determined to be $1.2 \times 10^{16}$ $cm^{-3}$, we conclude it is more likely that the competing trap is related to $V_{Ga}$.

A summary of the concentrations and effective excitation cross sections found in this study is given in Table I.

Under a simple trapping-energy-transfer mechanism, the ratio of the cross sections for a single center should not be dependent on the excitation conditions. In this case, however, the OMVPE7 and OMVPE8 centers show a larger cross section under optical excitation, while the OMVPE4 center shows a larger cross section for electrical excitation. This is because the majority site has an associated energy-transferring defect that can be excited optically as well, as observed by the possibility of subband-gap excitation [9]. Under above band-gap excitation, there is a contribution of nonequilibrium carrier trapping and direct optical excitation in the energy transfer to the majority site center.

TABLE I. Concentrations and excitation cross sections of the centers considered in this study.

| | OMVPE7 and OMVPE8 ($N = 10^{18}$ $cm^{-3}$) | OMVPE4 ($N = 5 \times 10^{19}$ $cm^{-3}$) |
|---|---|---|
| PL | $1.6 \times 10^{-15}$ $cm^2$ | $1.2 \times 10^{-17}$ $cm^2$ |
| EL | $3.0 \times 10^{-15}$ $cm^2$ | $6.0 \times 10^{-18}$ $cm^2$ |

## V. CONCLUSIONS

The excitation efficiency of the majority center (OMVPE4) and two important "minority" centers (OMVPE7 and OMVPE8) of Eu-doped GaN are studied under optical and electrical excitation. By evaluating the excitation cross sections under both excitation conditions, it is found that the OMVPE7 and OMVPE8 centers have an excitation cross section that is two orders of magnitude larger than that of the majority center (OMVPE4) and dominate the luminescence properties at low excitation fluences. Under these conditions, competition from an efficient carrier trap, likely related to a Ga vacancy, limits the external QE of Eu-related luminescence, however, it still reaches about 29% at room temperature and about 48% at 77 K. For large pump fluences, the limited number of OMVPE7 and OMVPE8 centers, and the small excitation cross section of the OMVPE4 center, limit the quantum efficiency, as other nonradiative recombination channels will be more effective in decreasing the excited carrier concentration. These results show the potential of GaN:Eu as an efficient light emitter, especially in devices operating with low current densities.

## ACKNOWLEDGMENTS

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