



## Study of Luminescence from GaN:Tb<sup>3+</sup> Powders and Thin Films Deposited by MOVPE and PLD Methods

Jonathan H. Tao,<sup>a</sup> Joseph Laski,<sup>d</sup> Nestor Perea-Lopez,<sup>a</sup> Steven Shimizu,<sup>b</sup>  
Joanna McKittrick,<sup>a,c</sup> Jan B. Talbot,<sup>a,b,\*z</sup> K. C. Mishra,<sup>d,\*\*</sup> David W. Hamby,<sup>d</sup>  
Madis Raukas,<sup>d,\*\*</sup> Keith Klinedinst,<sup>d</sup> and Gustavo Hirata<sup>e</sup>

<sup>a</sup>Materials Science & Engineering Program, <sup>b</sup>Department of Nanoengineering and <sup>c</sup>Department of Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, California 92093, USA

<sup>d</sup>Osram Sylvania, Central Research, Beverly, Massachusetts 01915, USA

<sup>e</sup>Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, C. P. 22800 Ensenada Baja California, México

Due to the recent commercial interest in nitride-based optoelectronics and rare-earth emission in nitride materials, the structural and optical characteristics of GaN:Tb<sup>3+</sup> powders and thin films have been investigated in this work. The powder samples were made using a three-step solution method. Pulsed laser deposition (PLD) and metallorganic vapor phase epitaxy (MOVPE) methods were utilized for depositing GaN:Tb<sup>3+</sup> films on sapphire substrates. The GaN powders with activator concentrations up to 8 atom % exhibited Tb<sup>3+</sup> luminescence due to the <sup>5</sup>D<sub>3,4</sub> → <sup>7</sup>F<sub>j</sub> transitions under cathodoluminescence (CL) as well as under 243 nm photon excitation. Both near-band-edge emission and activator emission have been observed in PLD thin films made from the corresponding GaN:Tb<sup>3+</sup> powders. X-ray diffraction revealed polycrystalline PLD thin films with a preferred growth direction along the *c* axis, while scanning electron micrographs showed rough film morphology with submicrometer particles. CL emission from Tb<sup>3+</sup> accompanied by near-band-edge emission and defect emissions from the GaN host was observed for the MOVPE films made using tris(2,2,6,6-tetramethyl-3,5-heptanedionato)terbium but not films made with tris(isopropylcyclopentadienyl)terbium. Despite visible luminescence from Tb<sup>3+</sup> in GaN powders and thin films, no energy transfer from the host to activator ions was observed. This suggests that Tb<sup>3+</sup> is unlikely to fluoresce if used in a GaN-based optoelectronic device.  
© 2009 The Electrochemical Society. [DOI: 10.1149/1.3116203] All rights reserved.

Manuscript submitted November 17, 2008; revised manuscript received February 27, 2009. Published April 23, 2009. This was Paper 3212 presented at the Honolulu, Hawaii Meeting of the Society October 12–17, 2008.

Recently, there has been considerable interest in the fluorescence of rare-earth (RE) ions in III-V nitrides. Emissions from RE ions due to transitions with energy levels originating from the 4f levels are less sensitive to the host lattice and can be predicted based on Dieke's energy-level diagram.<sup>1</sup> In the past, this aided fluorescent lamp technology to utilize RE<sup>3+</sup>-activated oxide phosphors for designing blend compositions that produce white light with a desired color rendering index (CRI) compatible with optimum efficacy.<sup>2</sup> Similar advantages are expected from the nitride hosts, which form the basis of recent developments in solid-state lighting technology. Red emission from Eu<sup>3+</sup> together with green emission from Tb<sup>3+</sup> and blue emission from InGaN could produce white light with high CRI and efficacy (in lumens per watt). The ability to incorporate these RE ions into nitride hosts and make them to fluoresce as efficiently as in oxide hosts has been the focus of recent research in this area.<sup>3-6</sup>

RE incorporation into nitride hosts has been attempted with success in various aspects. Powders of GaN activated with Eu<sup>3+</sup>, Tb<sup>3+</sup>, and Er<sup>3+</sup> have been prepared in the past using a mixture of freeze-dried nitrate precursors,<sup>7</sup> by nitridation of a mixture of gallium and activator metals with bismuth as a catalyst,<sup>8-10</sup> or by combustion synthesis followed by nitridation.<sup>11</sup> For thin films, pulsed laser deposition (PLD) of GaN:RE<sup>3+</sup> is a relatively unexplored approach. Pure GaN films<sup>12-14</sup> and Eu<sup>3+</sup>-activated GaN<sup>15</sup> have been grown using this approach, in which GaN:RE<sup>3+</sup> powder is used for deposition of thin films. Attempts have also been made to deposit RE-activated PLD films from a GaN powder source and RE metallorganic precursors.<sup>16</sup> However, the most common method for depositing GaN:RE<sup>3+</sup> films has been molecular beam epitaxy (MBE) using ion implantation to incorporate RE ions.<sup>3,4,17-22</sup> In situ incorporation of RE ions in nitride hosts using metallorganic vapor phase epitaxy (MOVPE) has been attempted with Eu<sup>3+</sup>,<sup>23</sup> Er<sup>3+</sup>,<sup>24</sup> Tb<sup>3+</sup>,<sup>25</sup> and Tm<sup>3+</sup>.<sup>26</sup> But the few available metallorganic precursors for RE ions

have low vapor pressure, long and complex organic chains, oxygen ligands in most of these compounds, and multiple valence states of RE ions; all are factors contributing to the difficulty in fabricating RE-activated nitride thin films by MOVPE. Nevertheless, direct comparison of ion-implanted MOVPE films and MBE films<sup>26</sup> showed a reduced yellow-luminescence band and higher activator cathodoluminescent (CL) emission in MOVPE films, suggesting a lower concentration of radiative defects and higher film quality for MOVPE films. Thin-film technology based on MOVPE is the industry standard for III-V semiconductor chip fabrication;<sup>27</sup> therefore, implementation of a MOVPE process for deposition of GaN:Tb<sup>3+</sup> is critical for eventual integration of this approach to white light emitting solid-state light sources.

The present work compared the incorporation of Tb<sup>3+</sup> in GaN hosts by powder synthesis, PLD, and MOVPE. In an earlier work, we have used a three-step solution method to synthesize AlN powders with emission from Tm<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup>, Dy<sup>3+</sup>, and Er<sup>3+</sup> ions,<sup>28,29</sup> as well as GaN powders demonstrating Tb<sup>3+</sup> emission.<sup>30</sup> In this paper, we have explored the dependence of fluorescence on the concentration of Tb<sup>3+</sup> ions varying from 0.25 to 8 atom % in GaN using powder samples prepared by the same method. These powders were also used as targets for depositing thin films by PLD. Furthermore, we continue our earlier efforts to dope GaN with RE ions using MOVPE. In a recent publication, we reported a detailed analysis of the nature and origin of fluorescence from Eu<sup>3+</sup> in GaN deposited by the MOVPE method.<sup>31</sup> In this paper, we report results of structural and luminescence measurements on MOVPE thin films of GaN:Tb<sup>3+</sup>. To the best of our knowledge, there has been only one other report of fluorescence from GaN:Tb<sup>3+</sup> deposited by MOVPE.<sup>25</sup> These three methods, used in a complementary manner, allowed us to explore the scope of GaN:Tb<sup>3+</sup> as a green emitting material for applications in solid-state lighting devices.

Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD) have been used for structural and phase characterization of the samples. Photoluminescence (PL) and PL excitation (PLE) using lamp and laser exci-

\* Electrochemical Society Fellow.

\*\* Electrochemical Society Active Member.

<sup>z</sup> E-mail: jtalbot@ucsd.edu

tation, as well as CL, were performed at room temperature for optical characterization of the powders and thin films. PLE was also performed at 23 K for MOVPE films.

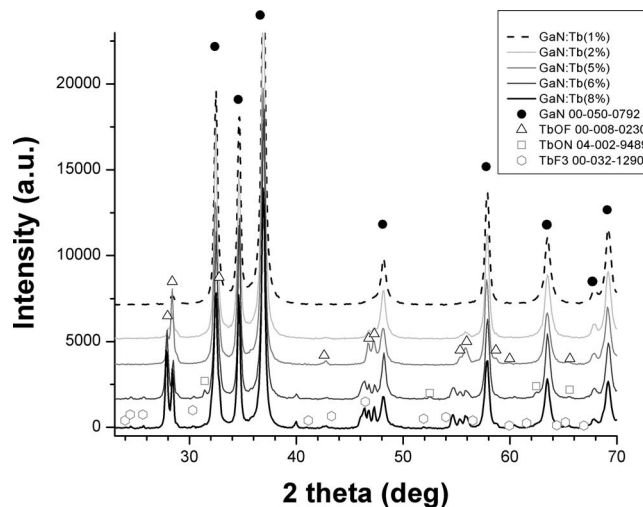
### Experimental

**Powder synthesis.**— GaN:Tb<sup>3+</sup> powders were prepared from a mixture of Ga(NO<sub>3</sub>)<sub>3</sub> and Tb(NO<sub>3</sub>)<sub>3</sub> in solution following a three-step process, with a nominal Tb concentration from 0.25 to 8 atom %. For each step, the amount of reactants was calculated and weighed based on the desired product weight and 100% conversion. First, an aqueous solution of Tb(NO<sub>3</sub>)<sub>3</sub> and Ga(NO<sub>3</sub>)<sub>3</sub> (REacton by Alfa-Aesar, 99.99%; Puratronic by Alfa-Aesar, 99.999%), was thoroughly mixed with ammonium hydroxide solution (NH<sub>4</sub>OH, Fisher Scientific, 28.50%) to react at room temperature until the hydroxide product, Ga<sub>1-x</sub>Tb<sub>x</sub>(OH)<sub>3</sub> ( $x = 0.25-8$  atom %), became a viscous gel. After filtration and drying in a desiccator, approximately three times the stoichiometric amount of ammonium fluoride (NH<sub>4</sub>F·XH<sub>2</sub>O, Alfa-Aesar, 99.9975%) was combined with the product from the previous step in deionized water and heated to react at approximately 80°C. After subsequent filtration and drying, the hexafluoride [(NH<sub>4</sub>)<sub>3</sub>Ga<sub>1-x</sub>Tb<sub>x</sub>F<sub>6</sub>] precipitate was introduced into a tube furnace to react with flowing ultrahigh-purity ammonia gas (Matheson Trigas, ULSI grade, 99.9995%) at 900°C for 150 min for the final conversion to GaN:Tb<sup>3+</sup>. The synthesis procedure has been reported in detail elsewhere.<sup>32</sup>

**PLD thin-film deposition.**— GaN:Tb<sup>3+</sup> thin films by PLD were fabricated with a source target made from GaN:Tb<sup>3+</sup> (1 atom %) and GaN:Tb<sup>3+</sup> (2 atom %) powders synthesized by the solution method. Once the powders were thoroughly mixed, they were pressed into a pellet and annealed at 1200°C in NH<sub>3</sub>. The films were deposited on GaN buffer layers grown by PLD from a pressed GaN target made from pure GaN powder (Alfa Aesar, 99.99%) on sapphire substrates. A neodymium-doped yttrium aluminum garnet (Nd:YAG) laser at 532 nm was used for the deposition process in an ultrahigh-vacuum chamber. The GaN:Tb<sup>3+</sup> target was rotated at 20 rpm, while the substrate, which was mounted on a heating stage, was rotated at 5 rpm. During deposition, the chamber was maintained at 100 mTorr N<sub>2</sub> pressure for a deposition time of 2 min for the Tb<sup>3+</sup>-doped film. Substrates were heated to 650°C. Following deposition, all films were annealed again at 1000°C in NH<sub>3</sub> in order to activate the luminescent centers and improve the emission intensity.<sup>33,34</sup> For this study, two films were fabricated at a laser power of 250 and 300 mW, corresponding to a surface fluence of 0.20 and 0.24 J/cm<sup>2</sup>.

**MOVPE thin-film deposition.**— Deposition of GaN:Tb<sup>3+</sup> epitaxial films was performed at atmospheric pressure in a horizontal research MOVPE reactor developed specifically for this purpose. The reactor had a 1 × 1 in. square cross section, with the sapphire substrate mounted on an inclined-plane shaped susceptor, which was heated externally using infrared lamps. Trimethylgallium (TMGa) and ammonia gases were used as the source for Ga and N, respectively. In situ terbium doping was performed using two types of precursor molecules: tris(2,2,6,6-tetramethyl-3,5-heptanedionato)terbium, abbreviated as Tb(TMHD)<sub>3</sub>, and tris(isopropylcyclopentadienyl)terbium, abbreviated as Tb(i-PrCp)<sub>3</sub> (Strem Chemicals, Inc.). TMGa was maintained in a bubbler at -15°C. Tb(TMHD)<sub>3</sub> was sublimated in a standard bubbler at 150°C. The RE precursor delivery lines were heated to at least 15°C higher than the bubbler temperature to avoid condensation en route to the reaction chamber. The reactor was configured in order to have the Tb precursor carrier gas mixed with the other process gases (NH<sub>3</sub>, TMGa, and H<sub>2</sub> push gas) at the final stage, just before entering the reactor chamber. The thin-film growth was carried out at atmospheric pressure on the basal (0001) plane of sapphire substrates.

The approximate growth rate of undoped GaN layers in the reactor was 1.5 μm/h. The growth rate of the GaN:Tb<sup>3+</sup> layer was



**Figure 1.** XRD pattern of GaN:Tb<sup>3+</sup> powder samples with  $\geq 1$  atom % Tb ion concentration. Additional phases including TbOF, TbF<sub>3</sub>, and TbON have been observed.

presumed to be proportional to the TMGa flow rate, which was at times lowered to increase the relative concentration of terbium. The entire deposition process consisted of the following steps: (i) treatment of the sapphire substrate with 1000 sccm of H<sub>2</sub> at 1050°C for 10 min, (ii) nitridation of the sapphire substrate with a mixture of 1000 sccm H<sub>2</sub> and 1200 sccm NH<sub>3</sub> at 600°C for 90 s, (iii) deposition of an approximately 22 nm GaN buffer layer at 600°C (using the above H<sub>2</sub>/NH<sub>3</sub> mixture plus 2.4 sccm of H<sub>2</sub> carrier gas through the TMGa bubbler for 75 s), (iv) deposition of approximately 1 μm of undoped GaN at 1040°C (using a mixture of 840 sccm H<sub>2</sub> push gas, 1400 sccm NH<sub>3</sub>, and 4 sccm of H<sub>2</sub> carrier gas through the TMGa bubbler) for typically 40 min, and (v) deposition of GaN:Tb<sup>3+</sup> layer at 1040°C with a TMGa flow rate of 0.5 sccm to increase the relative concentration of Tb. Flow rate through the Tb(TMHD)<sub>3</sub> bubbler was 150 sccm. NH<sub>3</sub> and H<sub>2</sub> push gas were the same as in the undoped GaN layer. GaN:Tb<sup>3+</sup> layer thickness is estimated at approximately 700 nm, assuming a proportional growth rate based on TMGa availability.

**Material characterization.**— A Rigaku X-ray diffractometer model Miniflex II was used to perform phase characterization for both powder samples and thin films. SEM imaging and EDX measurements were done with an FEI Quanta 600 scanning electron microscope. All powder and thin-film samples were sputter-coated with gold and palladium and analyzed under 20 kV accelerating voltage. The elemental compositions of each sample along with the standard deviation were averaged from eight points, 1 μm<sup>2</sup> in size, on each sample.

CL measurements were performed on all powders and films with a Kimball Physics electron gun model EGPS-14B at room temperature, with the data collected by a Jobin-Yvon Triax 180 monochromator and SpectrumOne charge-coupled device detection system, which was shared with the PL system that uses a 450 W Xe lamp as the excitation source. Additional PL and PLE measurements were measured with a SPEX spectro-fluorometer using a pulsed laser as the excitation source, with the data collected by a cooled Hamamatsu R928 photomultiplier tube.

### Results

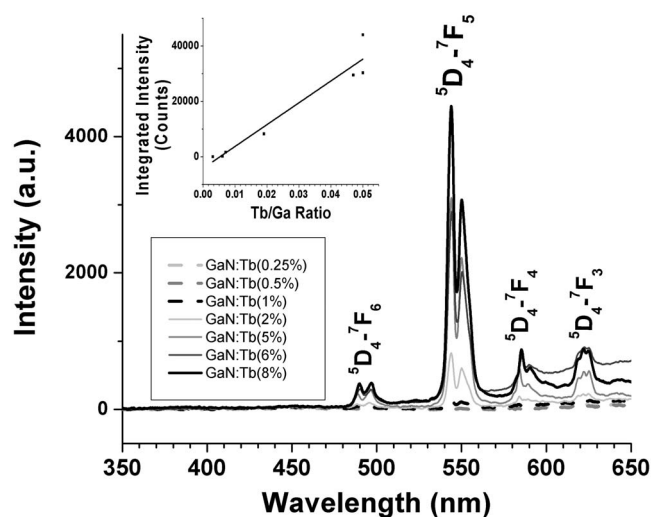
**Powders.**— XRD measurements of the GaN:Tb<sup>3+</sup> powders at various compositions show GaN in a wurtzite structure as the major phase. Minor peaks from an additional phase are observed for samples with a nominal 1 atom % Tb concentration or higher (Fig. 1), which has been assigned as TbOF (JCPDS card 00-008-0230).

**Table I. Tb:Ga ratio for GaN:Tb powders.**

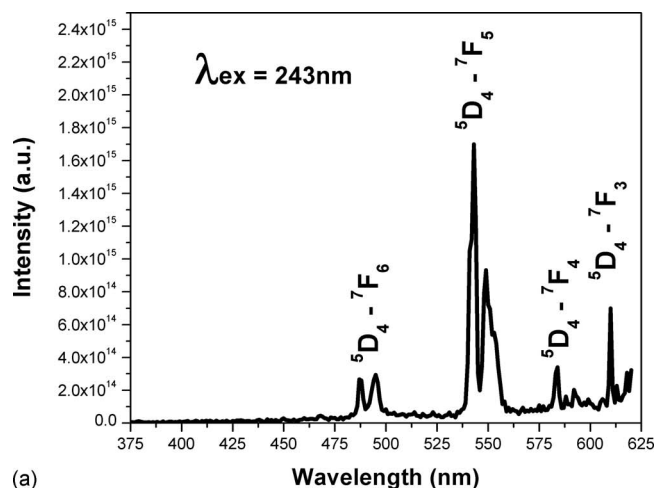
Nominal Tb (atom % Tb)	Tb/Ga ratio (from atom % of Tb and Ga measured by EDX)
0.25	0.003
0.5	0.006
1	0.007
2	0.019
5	0.047
6	0.050
8	0.050

The presence of TbOF was also confirmed via EDX in subsequent samples, with oxygen and fluorine impurities of up to 4.77 and 2.44 atom %, respectively, in the sample with a nominal 8 atom % Tb concentration. Other minor phases including TbF<sub>3</sub> (JCPDS card 00-032-1290) and TbON (JCPDS card 04-002-9489) were observed in that sample. As shown in Table I, EDX measurements revealed an increasing Tb:Ga ratio from 0.003 to 0.050 as the nominal Tb concentration increased from 0.25 to 5 atom %. This indicates that the amount of activator incorporated was consistent with the amount intended, up to approximately 5 atom %. As the nominal Tb concentration continued to increase to 8 atom %, the Tb:Ga ratio remained around 0.050. At concentrations higher than 5 atom %, Tb-rich phases such as TbOF may have separated from the main GaN:Tb<sup>3+</sup> phase. In addition, some parts of the powder had a metallic gray appearance. This was likely due to the dissociation of Ga ions from the GaN host, as the reaction was carried out in a reducing atmosphere that can cause Ga ions to exist on the surface of the powder as Ga metal.<sup>32</sup>

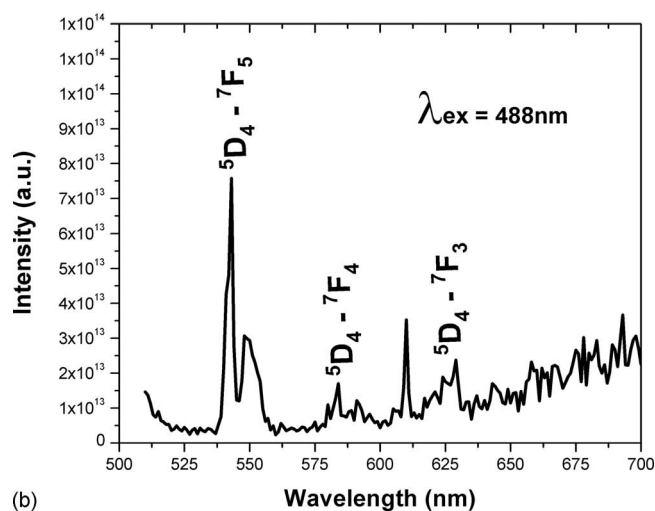
CL measurements of the GaN:Tb<sup>3+</sup> powders excited at 4 keV and 400  $\mu$ A, shown in Fig. 2, consistently yielded emission peaks associated with <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>J</sub> transitions, with the most intense transition being <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub>. The latter transition leads to a Stark-split doublet with the most intense peak at 543 nm for all the powder samples, starting with the 1 atom % Tb sample. In comparison, Nyk et al.<sup>35</sup> observed the strongest emission around 543 nm in their nano-grained GaN:Tb<sup>3+</sup> powders excited with a 90 keV electron beam at 60  $\mu$ A. Our GaN:Tb<sup>3+</sup> powders have a grain size of ~30 nm as calculated by the Scherrer formula,<sup>36</sup> which is only slightly larger



**Figure 2.** Room-temperature CL measurements of GaN:Tb<sup>3+</sup> powder samples with increasing Tb<sup>3+</sup> concentration. All samples are measured with 4 keV excitation at 400  $\mu$ A current. (Inset) Integrated CL emission intensity of the <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> transition with increasing Tb/Ga ratio.



(a)

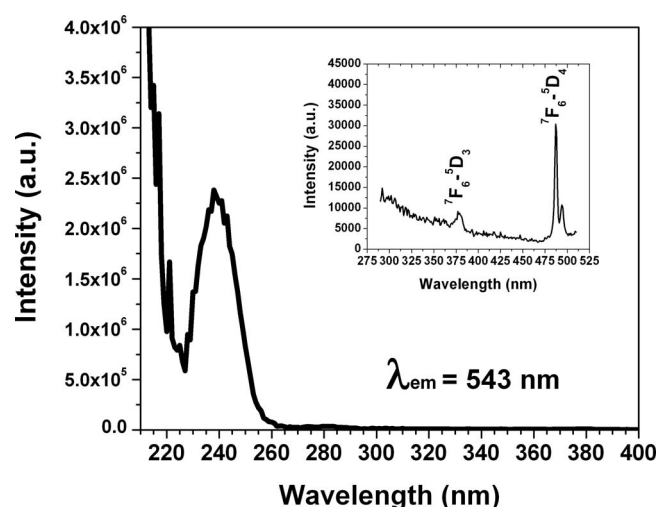


(b)

**Figure 3.** (a) PL emission spectra of the <sup>5</sup>D<sub>4</sub>-<sup>7</sup>F<sub>5</sub> transition for the GaN:Tb<sup>3+</sup> (5 atom %) powder with 243 nm excitation and acquired using the cooled photomultiplier tube. (b) PL emission spectra of the <sup>5</sup>D<sub>4</sub>-<sup>7</sup>F<sub>5,4,3</sub> transition for the GaN:Tb<sup>3+</sup> (5 atom %) powder with 488 nm excitation and acquired using the cooled photomultiplier tube.

than that reported in Ref. 35, ~20 nm. This accounted for the identical Tb<sup>3+</sup> emission peaks despite the different excitation parameters. The integrated CL emission intensity of the dominant peak in Fig. 2 increased with Tb/Ga ratio, as illustrated in the inset, up to 0.050. Interestingly, concentration quenching was not observed at high Tb/Ga ratios. Samples with lower Tb/Ga ratios did not show any Tb emission in CL, despite the presence of Tb as measured by EDX. Near-band-edge (NBE) emission, expected around 360 nm (3.44 eV),<sup>37</sup> was not observed in any of the powders.

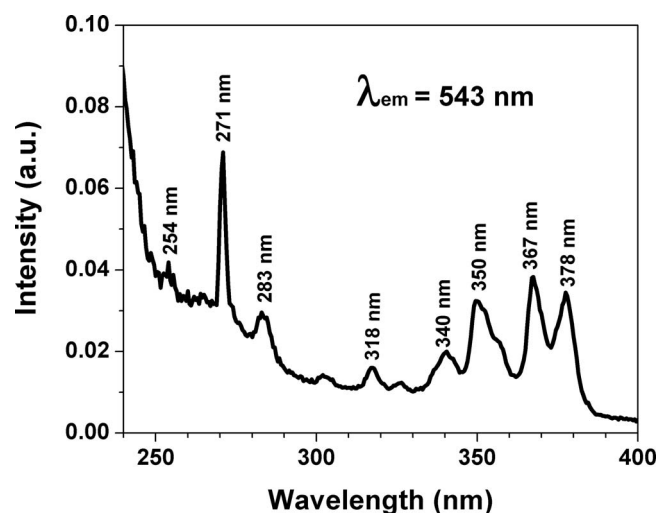
PL and PLE measurements were performed on GaN powder samples with 5 atom % Tb. Using a cooled photomultiplier tube as the detector and above gap excitation at 243 nm, no bandgap emission was observed, but there was emission due to <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>J</sub> transitions from Tb<sup>3+</sup> (Fig. 3a). Direct excitation at 488 nm was also able to produce <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> transition at 542 nm (Fig. 3b). However, excitation at 360 nm did not produce any emission. PLE measurements (Fig. 4 and inset), when monitored at 543 nm emission, show excitation peaks at 243, 378, and 488 nm. In Fig. 4 inset, the doublet around 488 nm is associated with the <sup>7</sup>F<sub>6</sub> → <sup>5</sup>D<sub>4</sub> transition, and the unresolved peak near 378 nm is associated with the <sup>7</sup>F<sub>6</sub> → <sup>5</sup>D<sub>3</sub> transition. These two bands are superimposed on a broad-band with much lower intensity relative to the peak at 243 nm. Because excitation near the bandedge did not produce any emission from Tb<sup>3+</sup>,



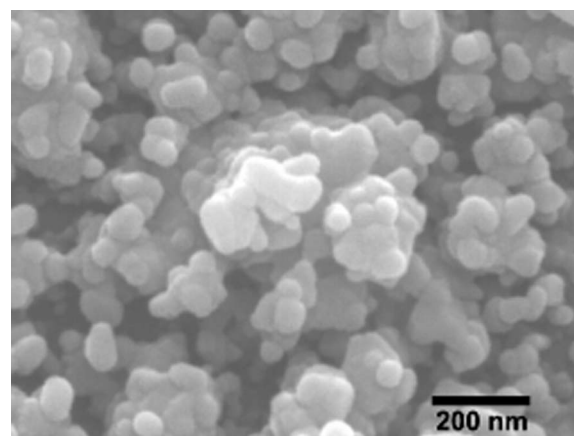
**Figure 4.** Excitation spectrum for GaN:Tb<sup>3+</sup> (5 atom %) powder at 543 nm emission, showing excitation peaks at 243, 378 (inset), and 488 nm (inset), as measured by cooled photomultiplier tube.

the broad-band may be associated with the defect emission from the host material which always accompanies emission near 543 nm due to the  $^5D_4 \rightarrow ^7F_5$  transition of Tb<sup>3+</sup>. The nature of excitation near 243 nm is unclear. Because TbOF was found to be a secondary phase in all the samples, we considered the possibility that the 243 nm excitation peak was due to Tb<sup>3+</sup> ions in this phase. In contrast, the room-temperature PLE spectrum of commercial TbOF powder (Alfa-Aesar) (Fig. 5) shows a weak peak around 254 nm. After correcting for system response at lower wavelengths, no distinct peaks were observed below 240 nm; all other prominent peaks above 250 nm appear to be due to intra- $4f^n$  configurational transitions, with the peak at 271 nm being a second-order artifact from the diffraction grating. This rules out the possibility that the observed emission in our GaN:Tb<sup>3+</sup> powder is due to Tb<sup>3+</sup> in the secondary phase of TbOF.

**PLD thin films.**— PLD thin films were fabricated from a mixture of GaN:Tb<sup>3+</sup> source powders with nominal 1 and 2 atom % Tb. As seen in Fig. 6, the fabricated films show a rough morphology with particle sizes in the range of ~100 nm. The average Tb concentration in the films was approximately 0.10 atom % as measured by



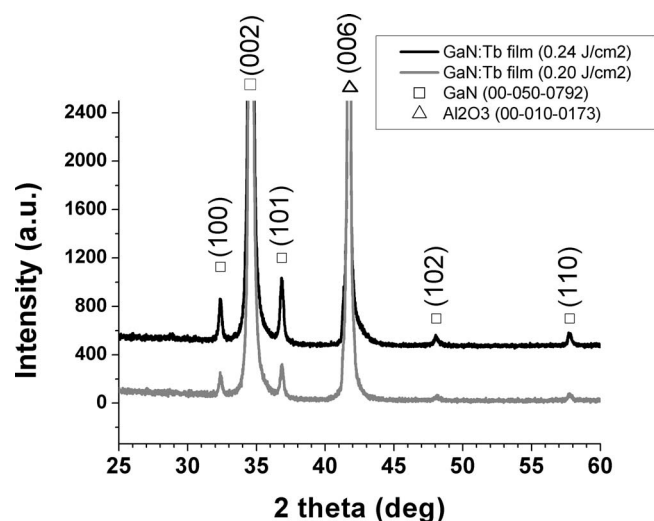
**Figure 5.** Excitation spectrum of commercial TbOF powder at 543 nm emission, showing a weak excitation peak at 254 nm and above.



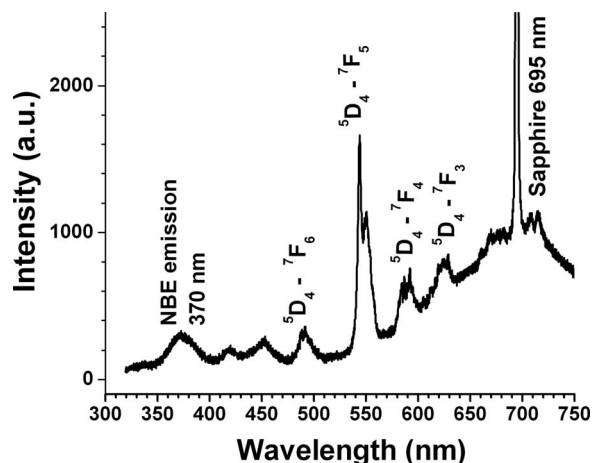
**Figure 6.** SEM micrograph showing GaN:Tb<sup>3+</sup> PLD films consisting of ~100 nm particles.

EDX, with a Tb:Ga ratio of approximately 0.012. In addition, regions of the film show a higher Tb concentration than the rest of the film of up to 0.85 atom %. XRD indicated a polycrystalline film despite the preferential  $c$ -axis growth of the GaN buffer layer underneath. However, as the surface fluence increased with the laser power, the film became more polycrystalline as evidenced by higher (100) and (101) reflection intensity, shown in Fig. 7. CL measurements of the film made with lower surface fluence, as shown in Fig. 8, displayed all the Tb<sup>3+</sup> transitions in the film that were originally observed in the source powder, along with NBE emission at 370 nm. While it is possible that NBE emission could come from the GaN buffer layer, earlier CL measurements of both commercial GaN powder used to make the GaN buffer layer as well as the source GaN:Tb<sup>3+</sup> powder did not show NBE emission. Therefore, the presence of NBE emission suggests a reduction in the overall defect level from the powder to the film regardless of the polycrystalline nature of both.

**MOVPE thin films.**— For the films grown by MOVPE with Tb(TMHD)<sub>3</sub>, XRD measurements revealed a strong (002) GaN  $2\theta$  peak with additional small peaks attributed to a secondary phase of Tb<sub>2</sub>O<sub>3</sub>. EDX analysis indicated a Tb:Ga ratio in the range of 0.09–

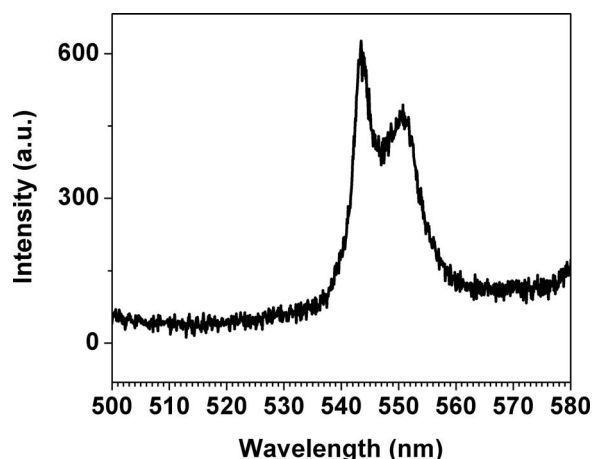


**Figure 7.** XRD patterns of GaN:Tb<sup>3+</sup> PLD films fabricated at a surface fluence of 0.20 and 0.24 J/cm<sup>2</sup>, showing a more oriented film with lower intensity peaks in the (100) and (101) direction for the film made with lower surface fluence.



**Figure 8.** Room-temperature CL measurement of GaN:Tb<sup>3+</sup> PLD film made at 0.20 J/cm<sup>2</sup> surface fluence. Measured with 5 keV and 500  $\mu$ A electron beam excitation, the film shows NBE emission, not previously observed in the source powder, along with Tb<sup>3+</sup> transitions.

0.15, with O:Tb ratios typically about 4:1. This was likely related to the fact that each Tb precursor molecule arrives with six oxygen atoms as part of the ligand. The increased O:Tb ratio may also be due to the formation of the Tb<sub>2</sub>O<sub>3</sub> phase. The CL spectrum presented in Fig. 9 indicated NBE emission (not shown) along with characteristic terbium emission peaks at 543 and 550 nm, consistent with those observed in our GaN:Tb<sup>3+</sup> powders and PLD thin films. The terbium emission peaks were more prominent at the center of the film than the edges. Also present was a 612 nm peak, tentatively identified as europium, presumably a residual contaminant from previous work with this element. While some previous characterizations of powders showed similar Tb<sup>3+</sup> emission,<sup>35,38</sup> other thin-film measurements made by Lozykowski et al. showed the strongest emission at 558 nm with CL excitation from AlN:Tb<sup>3+</sup> as well as GaN:Tb<sup>3+</sup> films where Tb<sup>3+</sup> was incorporated by ion implantation.<sup>39-41</sup> We made an additional MOVPE film with a lower terbium concentration (typical Tb:Ga ratio of 0.016) that showed similar results to our higher concentration film but with weaker terbium CL emission peaks (data not shown). In both cases, the amount of terbium that formed the oxide phase or substituted into the GaN lattice was unknown. In contrast to Hara et al.,<sup>25</sup> no terbium emission was observed with PL under either lamp or laser excitation at the bandedge (350–360 nm) or direct excitation of Tb<sup>3+</sup> ions



**Figure 9.** Room-temperature CL emission from GaN:Tb<sup>3+</sup> film made by MOVPE; excited with 3 keV, 280  $\mu$ A electron beam.

(480–490 nm). Pulsed laser excitation was performed at both room temperature and 23 K at 360, 320, 250, and 230 nm; no PL emission was observed.

Alternatively, films were grown using a Tb(i-PrCp)<sub>3</sub> precursor under similar conditions except with a lower bubbler temperature (between 115 and 125°C, depending on dopant concentration) as required by this precursor molecule. XRD measurements did not show a secondary phase of Tb<sub>2</sub>O<sub>3</sub> due to the lack of oxygen ligands of the  $\beta$ -diketonate from the Tb(TMHD)<sub>3</sub> precursor. However, no CL from Tb<sup>3+</sup> was observed. Torvik et al.<sup>42</sup> showed that the presence of oxygen can enhance the optical emission of Er<sup>3+</sup> ions; Hara et al.<sup>25</sup> have also suggested a similar effect of oxygen on the luminescent process of GaN:Tb<sup>3+</sup>. Therefore, the presence of oxygen ligands in Tb(TMHD)<sub>3</sub> could contribute to the ease of Tb<sup>3+</sup> ion incorporation and luminescence as opposed to films made from oxygen-free Tb(i-PrCp)<sub>3</sub> precursors.

### Conclusions

In this paper, we have investigated the fluorescence properties of GaN:Tb<sup>3+</sup> in powder samples and thin films deposited by PLD and MOVPE methods. This study on Tb<sup>3+</sup> in GaN provides several meaningful insights about the incorporation of Tb<sup>3+</sup> into a nitride host and luminescence processes associated with Tb<sup>3+</sup>.

The MOVPE deposition of GaN:Tb<sup>3+</sup> thin films proved to be significantly more difficult than that of GaN:Eu<sup>3+</sup>. The conditions of the epitaxial deposition process were similar to that of Hara et al.<sup>25</sup> It was done at a high Tb:Ga ratio and also higher ammonia flux in contrast to that of GaN:Eu<sup>3+</sup>.<sup>31</sup> Because some trivalent RE ions like Eu have a tendency to become divalent, while others like Tb could be tetravalent,<sup>43</sup> the incorporation of Eu<sup>3+</sup> requires an oxidizing environment as opposed to the reducing environment needed for Tb<sup>3+</sup>. The desired oxidation state is usually achieved in the solid-state synthesis of oxide phosphors by imposing a reducing or oxidizing environment. A way to achieve this with an MOVPE reactor where ammonia flow is relatively high for nitridation of Ga has not yet been fully explored.

We also observed that when cyclopentadienyl is used as the precursor, the oxide impurity phase is significantly reduced, with no residual oxygen detected in the form of a secondary oxide phase by XRD measurements. But the Tb<sup>3+</sup> concentration in GaN is also significantly reduced when this precursor is used. It is possible that oxygen is needed to incorporate Tb<sup>3+</sup> into the GaN lattice, as noted by Hara et al.<sup>25</sup>

The study of Tb concentration in powder samples revealed that concentration quenching may not be an issue in GaN activated by Tb<sup>3+</sup>. The secondary phase TbOF was observed in the powders starting with 1 atom % Tb<sup>3+</sup> and higher Tb concentrations. With similar spectral features up to 8 atom %, the emission spectra suggest that most of the emission may originate from the Tb<sup>3+</sup> ions in the secondary phase of TbOF. A critical examination of the PLE spectrum of TbOF rules out this possibility.

In the GaN:Tb<sup>3+</sup> powder samples, the 543 nm emission from Tb<sup>3+</sup> was observed at an excitation wavelength of 243 nm. When the host was directly excited with 320 or 360 nm, no PL emission was observed at wavelengths shorter than 543 nm. This suggests that the 243 nm excitation process is associated with direct excitation of Tb<sup>3+</sup>. In this connection, it is interesting to compare this excitation peak with that predicted for 4f  $\rightarrow$  5d transition for Tb<sup>3+</sup> in YSiO<sub>2</sub>N based on the crystal-field depression energy and free-ion energy by Dorenbos.<sup>44</sup> In this material, the first coordination sphere contains two oxygen atoms and two nitrogen atoms, and the second coordination sphere contains an additional four oxygen atoms.<sup>45</sup> Using the reported crystal-field depression energy of 22,313 cm<sup>-1</sup> and 4f-5d energy difference of 62,520 cm<sup>-1</sup>, the predicted energy for 4f-5d excitation energy is calculated to be 249 nm, which is comparable to that observed in the present material. Similarly, with the oxynitride Y<sub>4</sub>(SiO<sub>4</sub>)<sub>3</sub>N, the crystal-field depression energy is 21,171 cm<sup>-1</sup> at one of the Y sites, which yields a 4f  $\rightarrow$  5d transition energy of

241 nm. These estimates of  $4f \rightarrow 5d$  transition energies raise the possibility of Tb ions emitting in an oxynitride environment of GaN instead of TbOF.

However, the absence of any concentration quenching also suggests that emission of  $Tb^{3+}$  activated samples do not saturate under normal operating conditions of a typical light emitting diode. In order to avoid saturation, a typical chip operating at 350 mA would require approximately 3 atom % RE ions with a radiative lifetime of  $\sim 100 \mu s$ . Our results show that this concentration can be achieved without any accompanying concentration quenching.

In general, we observed weak PL in all our samples, even when the Tb ions were excited directly. The powders and thin films both fluoresced under CL. Because no PL emission was observed upon excitation at energies higher than the bandgap except at 243 nm, most likely the Tb ions are excited directly by energetic electrons in CL rather than electron and hole pairs generated by high-energy electrons.

Our PLE measurements indicate the absence of any energy transfer from the host to  $Tb^{3+}$  near the band-edge excitation. Unlike  $Eu^{3+}$ ,<sup>31</sup> no excitation peak developed near the bandedge that indicated transfer of energy from the host to the activator ions. The lack of any emission upon band-edge excitation, and also at energies higher than bandgap, is unfortunate from the perspective of using this material for green emission. Because excitation at energies higher than the bandgap creates electron-hole pairs, the lack of  $Tb^{3+}$  emission upon excitation of the host lattice indicates that this material is unlikely to fluoresce upon injection of electron-hole pairs into the active layer.

#### Acknowledgments

J.H.T. gratefully acknowledges the many insightful conversations with Dr. Gustaf Arrhenius as well as the assistance of Evelyn York of the Scripps Institute of Oceanography at UCSD. This research was supported by Department of Energy grant no. DE-FC26-04NT42274 and the Blasker-Rose-Miah Fund, grant no. C-2007-0024.

University of California, San Diego assisted in meeting the publication costs of this article.

#### References

- G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals*, Wiley Interscience, New York (1968).
- K. H. Butler, *Fluorescent Lamp Phosphors*, Pennsylvania State University Press, University Park, PA (1980).
- A. J. Steckl and R. Birkhan, *Appl. Phys. Lett.*, **73**, 2143 (1998).
- J. Heikenfeld and A. J. Steckl, *IEEE Trans. Electron Devices*, **49**, 557 (2002).
- K. P. O'Donnell and B. Hourahine, *Eur. Phys. J.: Appl. Phys.*, **36**, 91 (2006).
- R. J. Xie and N. Hirotsaki, *Sci. Technol. Adv. Mater.*, **8**, 588 (2007).
- A. El-Himri, D. Pérez-Coll, P. Núñez, I. R. Martín, V. Lavín, and V. D. Rodríguez, *J. Solid State Chem.*, **177**, 4213 (2004).
- H. Wu, C. B. Poitras, M. Lipson, M. G. Spencer, J. Hunting, and F. J. DiSalvo, *Appl. Phys. Lett.*, **86**, 191918 (2005).
- H. Wu, C. B. Poitras, M. Lipson, M. G. Spencer, J. Hunting, and F. J. DiSalvo, *Appl. Phys. Lett.*, **88**, 011921 (2006).
- J. Shi, M. V. S. Chandrashekar, J. Reiherzer, W. J. Schaff, J. Lu, F. J. DiSalvo, and M. G. Spencer, *J. Cryst. Growth*, **310**, 452 (2008).
- G. Hirata, F. Ramos, R. Garcia, E. J. Bosze, J. McKittrick, O. Contreras, and F. A. Ponce, *Phys. Status Solidi A*, **188**, 179 (2001).
- R. D. Vispute, V. Talyansky, R. P. Sharma, S. Choopun, M. Downes, T. Venkatesan, K. A. Jones, A. A. Iliadis, M. Asif Khan, and J. W. Yang, *Appl. Phys. Lett.*, **71**, 102 (1997).
- T. F. Huang, A. Marshall, S. Spruytte, and J. S. Harris, Jr., *J. Cryst. Growth*, **200**, 362 (1999).
- K. W. Mah, E. McGlynn, J. Castro, J. G. Lunney, J.-P. Mosnier, D. O'Mahony, and M. O. Henry, *J. Cryst. Growth*, **222**, 497 (2001).
- N. Perea-Lopez, J. H. Tao, J. McKittrick, J. B. Talbot, M. Raukas, J. Laski, K. C. Mishra, and G. Hirata, *Phys. Status Solidi C*, **5**, 1756 (2008).
- N. Perea-Lopez, J. Tao, J. B. Talbot, J. McKittrick, G. A. Hirata, and S. P. DenBaars, *J. Phys. D: Appl. Phys.*, **41**, 122001 (2008).
- H. J. Lozykowski, W. M. Jadwisieniczak, and I. Brown, *Appl. Phys. Lett.*, **74**, 1129 (1999).
- S. Morishima, T. Maruyama, and K. Akimoto, *J. Cryst. Growth*, **209**, 378 (2000).
- H. Bang, S. Morishima, Z. Li, K. Akimoto, M. Nomura, and E. Yagi, *Phys. Status Solidi B*, **228**, 319 (2001).
- T. Monteiro, C. Noemare, M. J. Soares, R. A. Sá Ferreira, L. D. Carlos, K. Lorenz, R. Vianden, and E. Alves, *Physica B*, **308-310**, 22 (2001).
- E. E. Nyein, U. Hömmerich, J. Heikenfeld, D. S. Lee, A. J. Steckl, and J. M. Zavada, *Appl. Phys. Lett.*, **82**, 1655 (2003).
- H. Peng, C. W. Lee, H. O. Everitt, C. Munasinghe, D. S. Lee, and A. J. Steckl, *J. Appl. Phys.*, **102**, 073520 (2007).
- M. Pan and A. J. Steckl, *Appl. Phys. Lett.*, **83**, 9 (2003).
- C. Ugolini, N. Nepal, J. Y. Lin, H. X. Jiang, and J. M. Zavada, *Appl. Phys. Lett.*, **89**, 151903 (2006).
- K. Hara, N. Ohtake, and K. Ishii, *Phys. Status Solidi B*, **216**, 625 (1999).
- S. Hernández, R. Cuscó, L. Artús, E. Nogales, R. W. Martin, K. P. O'Donnell, G. Halambalakis, O. Briot, K. Lorenz, and E. Alves, *Opt. Mater.*, **28**, 771 (2006).
- B. Gil, *Group III Nitride Semiconductor Compounds: Physics and Applications*, p. 125, Oxford University Press, New York (1998).
- B. Han, K. C. Mishra, M. Raukas, K. Klinedinst, J. Tao, and J. B. Talbot, *J. Electrochem. Soc.*, **154**, J44 (2007).
- B. Han, K. C. Mishra, M. Raukas, K. Klinedinst, J. Tao, and J. B. Talbot, *J. Electrochem. Soc.*, **154**, J262 (2007).
- J. H. Tao, N. Perea-Lopez, J. McKittrick, J. B. Talbot, K. Klinedinst, M. Raukas, J. Laski, K. C. Mishra, and G. Hirata, *Phys. Status Solidi C*, **5**, 1889 (2008).
- J. Laski, K. Klinedinst, M. Raukas, K. C. Mishra, J. Tao, J. McKittrick, and J. B. Talbot, *J. Electrochem. Soc.*, **155**, J315 (2008).
- J. H. Tao, N. Perea-Lopez, J. McKittrick, J. B. Talbot, B. Han, M. Raukas, K. Klinedinst, and K. C. Mishra, *J. Electrochem. Soc.*, **155**, J137 (2008).
- E. Silkowski, G. S. Pomrenke, Y. K. Yeo, and R. L. Hengehold, *Phys. Scr.*, **T69**, 276 (1997).
- R. Weingärtner, O. Erlenbach, A. Winnacker, A. Welte, I. Brauer, H. Mendel, H. P. Strunk, C. T. M. Ribeiro, and A. R. Zanatta, *Opt. Mater.*, **28**, 790 (2006).
- M. Nyk, R. Kudrawiec, W. Strek, and J. Misiewicz, *Opt. Mater.*, **28**, 767 (2006).
- E. F. Kaelble, *Handbook of X-Rays*, McGraw-Hill, New York (1967).
- M. Leroux and B. Gil, in *Processing and Applications of Gallium Nitride and Related Semiconductors*, J. H. Edgar, Editor, p. 47, Institution of Engineering and Technology (1999).
- A. Podhorodecki, M. Nyk, J. Misiewicz, and W. Strek, *J. Lumin.*, **126**, 219 (2007).
- W. M. Jadwisieniczak, H. J. Lozykowski, I. Berishev, A. Bensaoula, and I. G. Brown, *J. Appl. Phys.*, **89**, 4384 (2001).
- H. J. Lozykowski, W. M. Jadwisieniczak, and I. Brown, *Appl. Phys. Lett.*, **76**, 861 (2000).
- H. J. Lozykowski, W. M. Jadwisieniczak, and I. Brown, *Mater. Sci. Eng., B*, **81**, 140 (2001).
- J. T. Torvik, C. H. Qiu, R. J. Feuerstein, J. I. Pankove, and F. Namavar, *J. Appl. Phys.*, **81**, 6343 (1997).
- G. Blasse and B. C. Grabmaier, in *Luminescent Materials*, p. 28, Springer-Verlag, Berlin (1994).
- P. Dorenbos, *J. Lumin.*, **91**, 155 (2000).
- L. Ouyang, H. Yao, S. Richey, Y. N. Xu, and W. Y. Ching, *Phys. Rev. B*, **69**, 094112 (2004).