

SITE MULTIPLICITY OF RARE EARTH IONS IN III-NITRIDES

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ABSTRACT

This presentation reviews recent lattice location studies of rare earth (RE) ions in GaN by electron emission channelling (EC) and X-ray absorption fine structure (XAFS) techniques. These studies agree that RE ions at low concentrations (whether they are incorporated during growth or introduced later by ion implantation) predominantly occupy Ga substitutional sites, as expected from considerations of charge equivalence. We combine this result with some examples of the well-documented richness of optical spectra of GaN:RE³⁺ to suggest that the luminescence of these materials may be ascribed to a family of rather similar sites, all of which feature the RE_{Ga} defect.

INTRODUCTION

RE ions in suitable hosts offer an all-nitride route to the realisation of optoelectronic devices in visible light [1]. For example, GaN doped with Tm, Er and Eu emits spectrally pure light in the blue, green and red spectral regions, respectively, which may be additively combined to stimulate most of the possible human colour responses. In contrast, it is well known that the efficiency of the commercially successful In_xGa_{1-x}N light emission decreases drastically with increasing wavelength [2]. This fact is well illustrated by a comparison of the composition map and the spectral imaging cathodoluminescence (CL) intensity map of the graded-composition sample, InGaN336X, which are shown in Figure 1. A shift in peak wavelength from 570 nm to 700 nm (which corresponds to an increase of InN fraction from $x \sim 0.25$ to 0.4) is accompanied by a decrease of more than one order of magnitude in the photoluminescence (PL) output. As far as we are aware, no comparable study has been carried out for samples, now more widely available, with InN fractions higher than $x = 0.4$, although at very low x , the PL and EL (electroluminescence) intensities *increase* with x [3].

The study of RE luminescence in semiconductors has quite a long history, in particular concerning the 1.54 μm band emitted by erbium in several hosts [4]. Favenec et al showed that wider gap semiconductors should suffer less from the temperature quenching of luminescence that is generally found in bulk hosts [5]. Application of Favenec's principle to nitrides came with the emergence of suitable epitaxial host material in the 90's. A recent review of the application of RE-doped nitrides to light emitting devices has been provided by Steckl et al [6]. Finally, the recently accomplished incorporation of RE ions in nitride heterostructures offers considerable promise for the future [7].

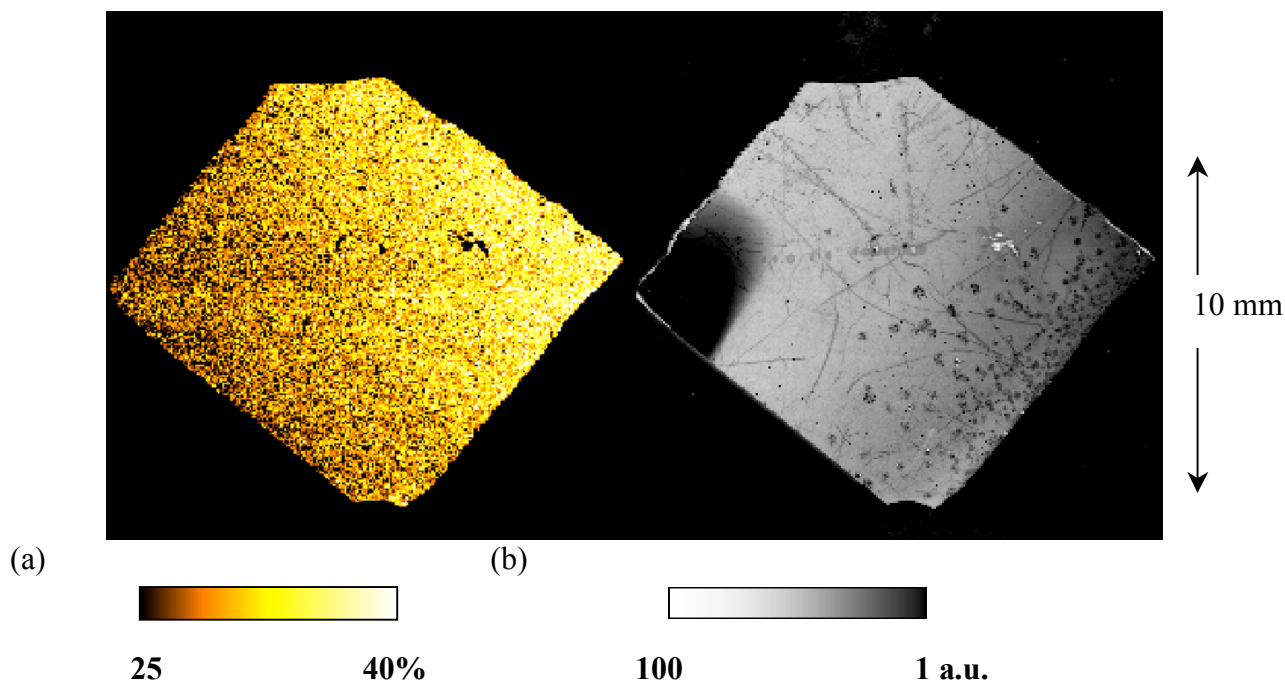


Figure 1 (a) Composition map of InGaN336X, obtained using Wavelength-Dispersive X-ray Spectroscopy in an electron probe microanalyser; (b) Integrated CL intensity map of the same sample, obtained by spectrum imaging. (Note: the shadowy area on the left in the CL intensity map is caused by previous exposure of the sample to 2 MeV He^+ ions in a Rutherford Backscattering Spectrometry experiment.)

Luminescence from RE in solid hosts involves transitions of the 4f-shell electrons that would be strictly forbidden in the free ion. It is therefore important to consider the lattice location of RE ions in nitrides, since the substitutional site RE_{Ga} expected from charge equivalence (RE^{3+} for Ga, say, in the semi-ionic material GaN) might not be the main one. If several sites are occupied, it may be possible to engineer the occupation statistics to maximise the defect emission. At the same time, we should be aware that the transfer of excitation from the host to the inner electron shells of the impurity ions is itself not well understood; it may well favour the excitation of particular sites through some as-yet undiscovered mechanism. In the absence of a clear steer from theory in these matters (but see Ref 8. for a discussion of site energetics of RE in nitrides) we focus attention on the Smakula product, Nf , for each site, given by the product of the number of defects (per unit volume) and the oscillator strength of the particular transition involved. The overall efficiency of RE emission is quite low in nitrides. In its simplest form, our problem is to find out if light emission by III-N:RE is mainly due to:

- a) a majority site with a low oscillator strength
- or
- b) a minority site of exceptional luminescence efficiency (a ‘magic’ site).

Firstly, we describe sample preparation. We then review lattice location studies of RE in suitably prepared epitaxial samples. Most of the work to be presented here was carried out by members of RENiBEL, a consortium of 8 university laboratories funded by the European Commission in a Fifth Framework Research Training Network [9]. We finally attempt to compare the results of the lattice location studies with purely spectroscopic evidences of site multiplicity.

SAMPLE DETAILS

III-N:RE samples can be prepared in one of two ways, either by ion implantation of previously grown material or by in-situ doping during growth.

Implantation of high-quality epitaxial layers by fast ions, usually along a major crystal direction coincident with the surface normal, results in a thin layer (~ 100 nm) of doped material. The crystal lattice is grossly disrupted by the implantation damage and annealing is usually required to obtain luminescence from the implant. In this work, Metallorganic Vapour Phase Epitaxy (MOVPE) at the University of Montpellier in France was used to grow GaN templates of high quality. Implantation/annealing experiments were carried out either at ITN, Lisbon in Portugal or at IKS, University of Leuven, Belgium. A few GaN:Eu layers were also obtained from the University of Toyohashi in Japan (Yoshida-Wakahara laboratory).

In-situ doping of nitride samples during Molecular Beam Epitaxy (MBE), requiring use of solid RE metallic sources, was also carried out at the University of Montpellier. MOVPE templates were employed as pseudo-substrates for the MBE growth.

MBE layers can be considerably thicker and more heavily doped than implants, which can be advantageous in some cases. For the purposes of this study, however, we do not need to distinguish the experimental results from differently prepared samples.

EXPERIMENTAL RESULTS 1: ELECTRON EMISSION CHANNELING

Lattice location studies by electron emission channeling (EC) aim to determine the site occupied by implanted radioactive ions. Production of such ions requires a gigavolt proton source. EC measures the angular distribution with respect to major crystal axes of β^- or conversion electrons (from daughter nuclei) that are emitted during radioactive decay. A radiative heater is incorporated in the set-up to allow annealing studies. At the present time the experimental set-up at CERN, used in our experiments, is unique in its deployment of two-dimensional electron detectors to measure the emission patterns [10].

The physical basis of EC is the guiding of the ejected electrons by lines of positive nuclei that lie along certain directions in the crystal; the electron yield increases if the emitting atom is “in line”. Simulation compares patterns calculated for emission by atoms in certain sites with the results of experiments. Some possible sites in the wurtzite lattice that should be considered in such simulations are indicated in Figure 2.

A key observation in EC studies is that the patterns produced by different sites are very easily distinguishable from one another.

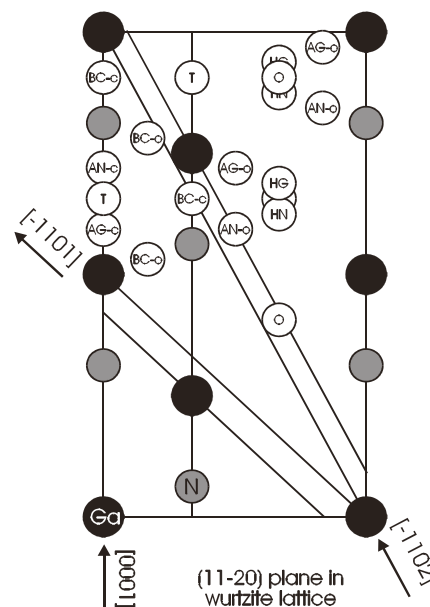


Figure 2 A projection on the [11-20] plane of the principle sites of high symmetry for impurity atom incorporation in the wurtzite lattice.

An experiment on ^{167m}Er implanted in GaN is compared in Figure 3 with a simulation of EC from the substitutional site Er_{Ga} [11].

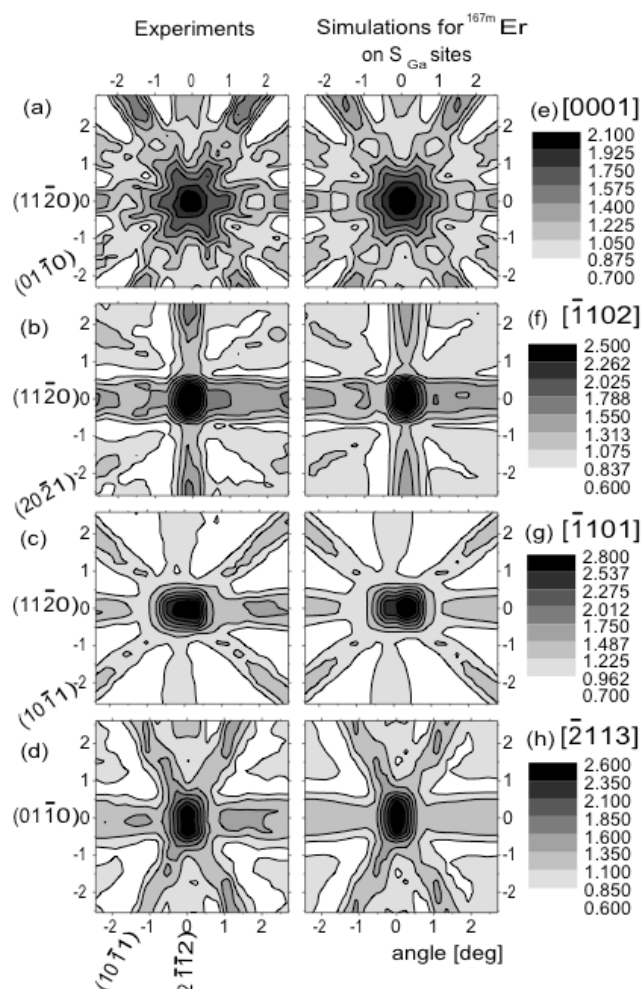


Figure 3. Comparison of experiment with simulation of EC in Er-implanted GaN.

To summarise a large number of studies performed to date, all implanted RE studied so far prefer substitutional Ga/Al/In sites [10-12 and refs therein]. There is no indication of RE on any other highly symmetric lattice site. Rms off-site displacements of RE ions, an adjustable parameter in the simulation procedure, seem to be much larger than we would expect if only thermal vibrations were present. This additional displacement is most likely to be attributable to the surrounding crystal disorder. However, in all cases the rms displacements decrease after annealing, indicating better substitutional incorporation of the RE. At the same time there is an increase in the efficiency of RE luminescence, which indicates at least a correlation between crystal perfection and luminescence output.

EXPERIMENTAL RESULTS 2: XRAY ABSORPTION FINE STRUCTURE

XAFS determines the lattice sites occupied by native or impurity ions by exploring local structure interactions [13]. What is measured is the X-ray absorption spectrum in the vicinity of characteristic ‘edges’ due to particular elements, for example the Tm L_{III} edge at 8.64 keV. The investigation of such absorption spectra requires a continuously tunable bright X-ray source, such as an electron synchrotron. The local environment of a target atom influences its X-ray absorption spectrum (XAS). Interference of emitted and reflected photoelectrons introduces a series of oscillations (Fine Structure) above the edge. An example is shown in Figure 4.

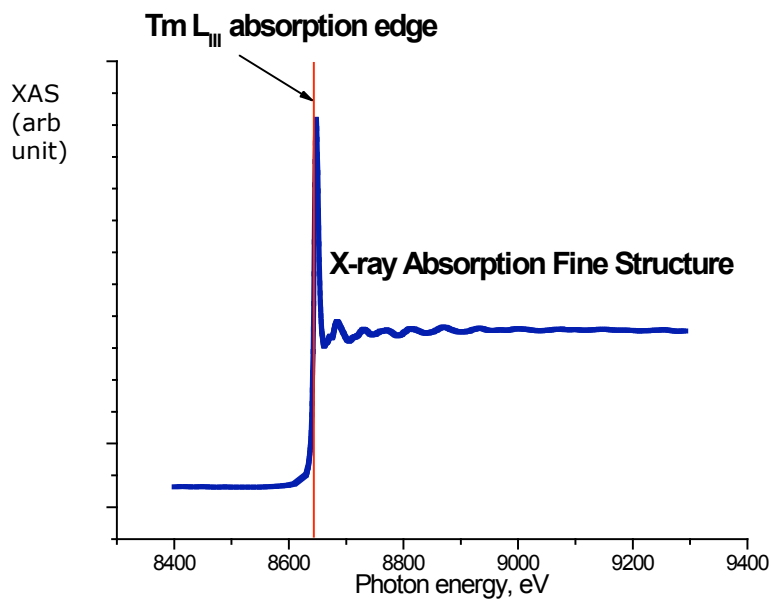


Figure 4. Showing the XAS of Tm-doped GaN in the vicinity of the Tm L_{III} edge.

A Fourier Transform of the XAFS oscillation yields the RDF (radial distribution function) of the ions neighbouring the target atom: N, Ga, etc., as shown for two different GaN:Tm samples in Figure 5.

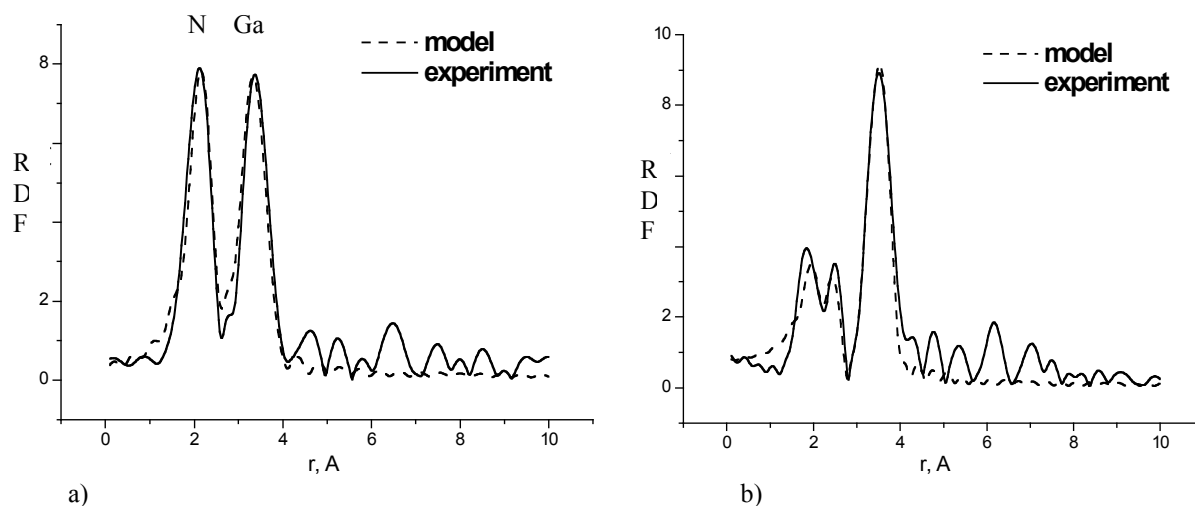


Figure 5. RDF for Tm-doped samples of GaN, containing (a) 0.5% and (b) 3.4% of Tm, respectively.

In the more strongly doped sample, the split nitrogen shell clearly indicates the presence of phase decomposition: a sizeable proportion of the Tm ions find themselves in a pure TmN environment in this sample [14].

To summarise our XAFS results to date, all RE ions studied have been found to reside on Ga substitutional sites. When the RE concentration increases, REGaN clusters form with locally high RE content. A further increase of RE concentration results in the formation of REN (Rare-Earth Nitride) phases. The concentration threshold for formation of the REN phase depends on the species of RE atom and the sample growth conditions.

EXPERIMENTAL RESULTS 3: OPTICAL STUDIES

It is not surprising that most previously reported work on RE-doped semiconductors has focused on their optical properties. In all cases, luminescence spectroscopy offers clear evidence for the co-existence of a number of different sites with distinct excitation and emission signatures. Dierolf et al. [15] have provided a recent example of such *site-selective spectroscopy* for MBE-doped GaN:Er by using wavelength-stepped laser excitation with CCD-spectrograph detection of luminescence to produce Combined Excitation-Emission Spectra (CEES). Different sites are resolved by the coincidence of excitation and emission lines in particular groupings. Dierolf et al find two ‘majority’ and up to four ‘minority’ groupings in CEES spectra of GaN:Er, in broad agreement with previous results [16, 17].

Here we present some recent work on GaN:Eu, which emits predominately in the red near 622 nm in a transition identified as $^5D_0 \rightarrow ^7F_2$. High resolution PL spectroscopy shows that this line is in fact a multiplet [18]. Figure 6 shows the remarkable consistency found in the optical spectra taken from 10 different positions on the surface of one sample placed in a confocal microscope at 140 K.

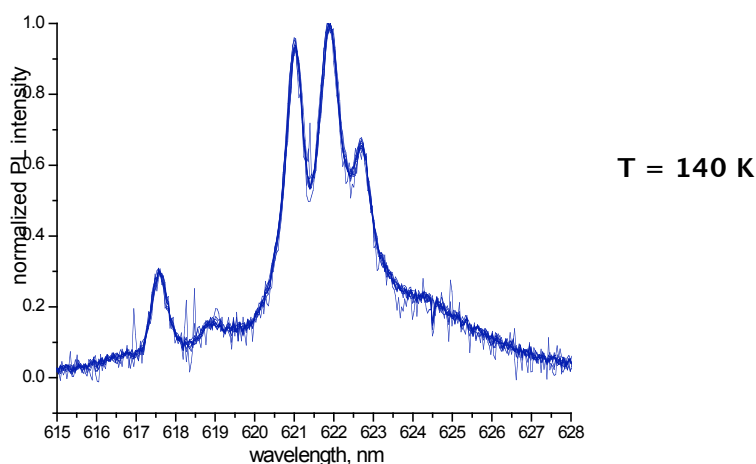


Figure 6. The red emission of GaN:Eu is in fact a multiplet of at least 6 lines. This measurement maximises the component at 617.5 nm which is very temperature-sensitive (see later).

Depth resolving cathodoluminescence (CL) spectroscopy reveals differences in the response of different components of the 622 nm multiplet (Figure 7). For example, the line at 621 nm shifts to higher energy with increasing electron beam energy in the more deeply implanted sample. These differences reflect a depth dependence of the transition energy.

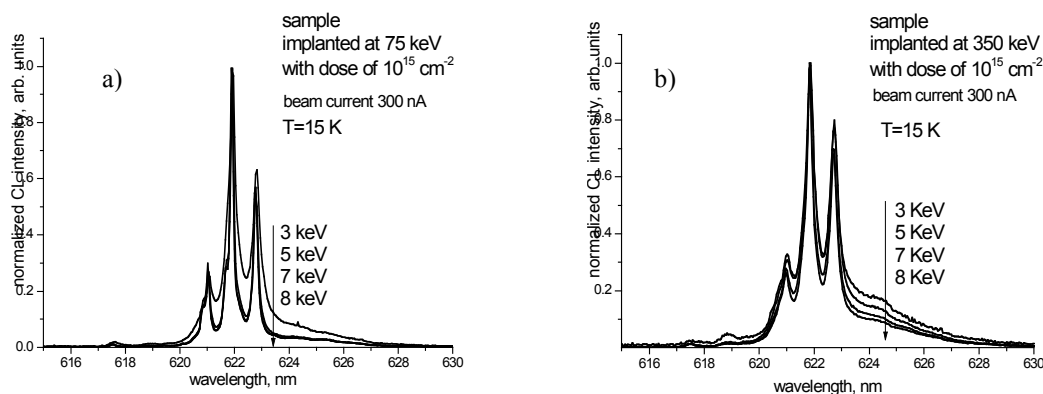


Figure 7. CL spectra of GaN samples with a) shallow, 75 keV and b) deep, 350 keV Eu implants.

In addition, the relative intensities of the various lines show a clear variation with depth and there is some indication of an unresolved background contribution to the luminescence. Very clear evidence of site multiplicity is found by comparing PL spectra of a number of different samples taken under the same conditions of excitation (5 mW, 325 nm) at the same temperature (15 K). A selection of such spectra is shown in Figure 8.

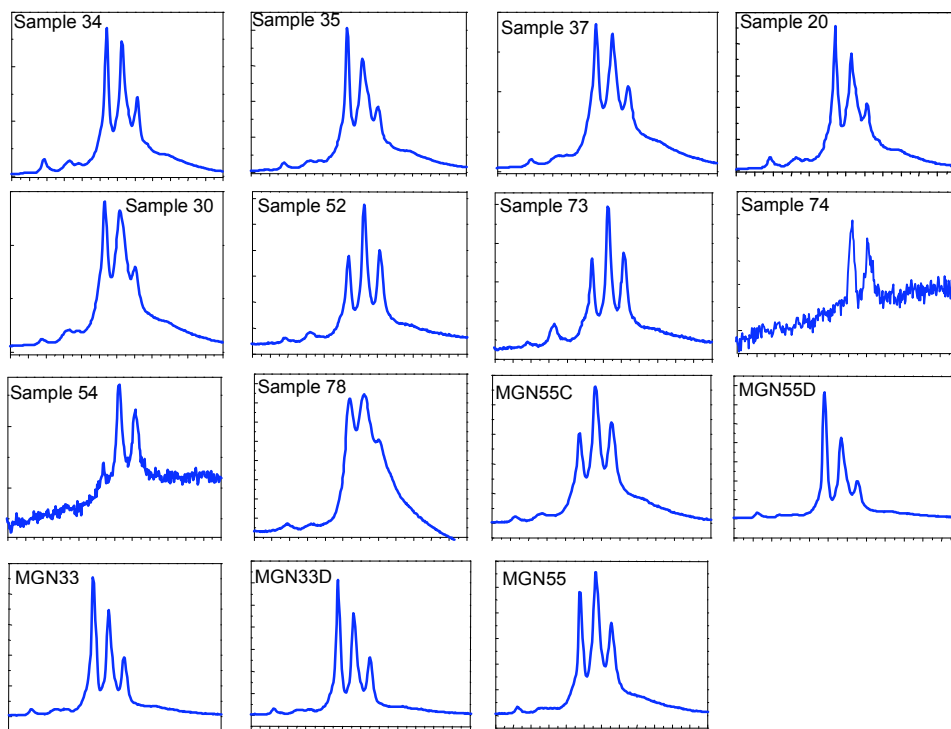


Figure 8. Different multiplet patterns for the 622 nm complex of lines in various GaN:Eu samples.

In Figure 9, we show the temperature dependence in the range from 13 K to room temperature of the emission from a sample with a well-resolved line structure.

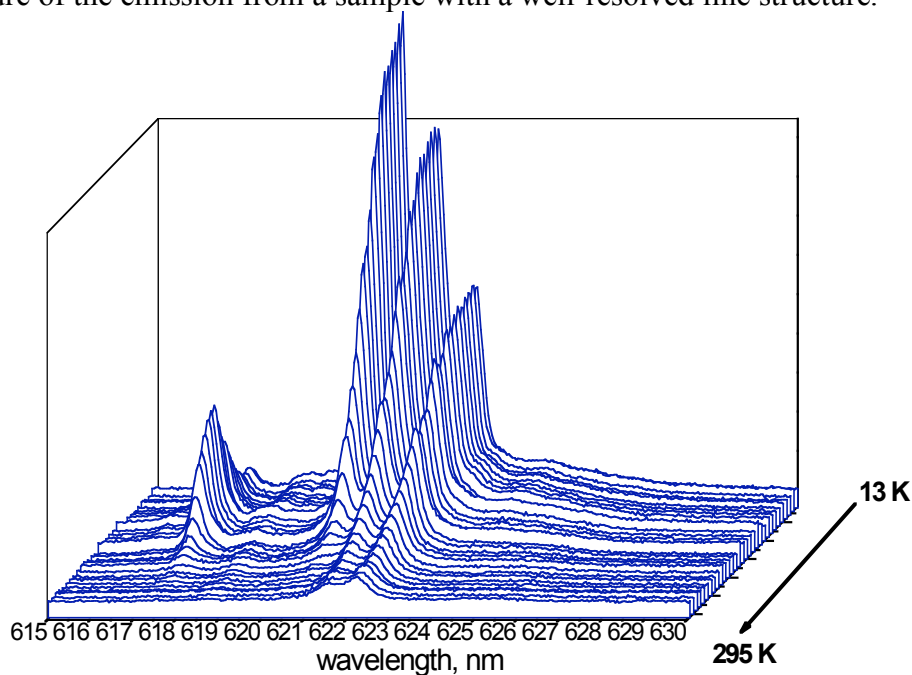


Figure 9. Temperature dependence of 622 nm luminescence from GaN:Eu.

A comparison of the spectra at high and low temperatures shows the very different temperature dependences of the central triplet. The line at highest energy, dominant at low temperature, vanishes near 250 K, while the other two lines of the triplet reverse the ordering of their relative intensities. In fact the activation energies for temperature quenching are different for the three lines. At the same time, a line at 617 nm increases in intensity between 13 K and 140 K and seems to “borrow” intensity from the other lines before it quenches at higher temperature. The behaviour of the minor lines near 620 nm is even more complicated.

Finally, we show the dependence of the line pattern on the excitation wavelength. In Figure 10a) the line pattern changes dramatically when the excitation wavelength crosses the band edge of GaN (about 356 nm at low temperatures). Excitation below the band edge appears also to sharpen the lines. In the excitation spectrum of Figure 10b) we see a bandedge feature and a below-gap plateau. Additional lines in the PL spectrum of GaN appear in the plateau region, as seen in Figure 10c): there seem to be at least 6 different components.

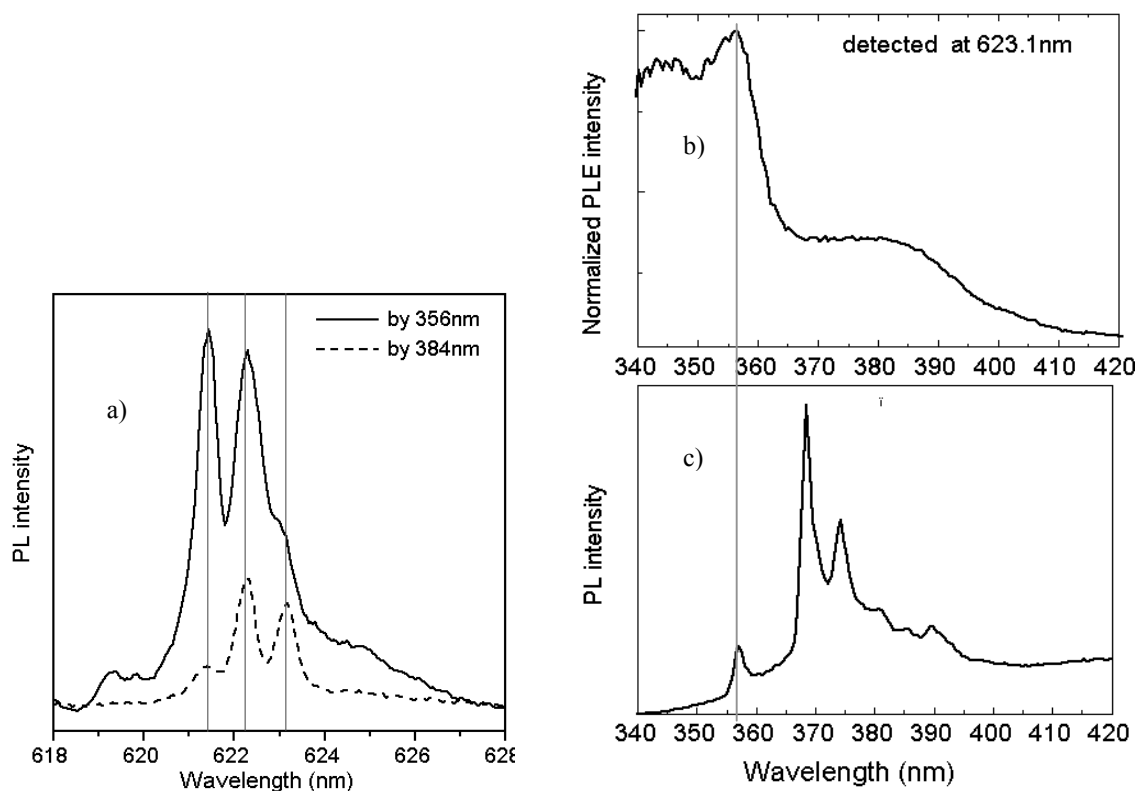


Figure 10. (a) PL spectra excited above and below the GaN bandedge; (b) PL excitation spectrum of the 623 nm line; (c) PL spectrum in the near-bandedge region, excited at 325 nm.

DISCUSSION AND CONCLUSIONS

The lattice location studies of RE-doped GaN by EC and EXAFS show that the majority of RE atoms occupy the Ga substitutional site. Theory concurs with this finding, and adds that an interstitial RE atom is less stable than an interstitial Ga. However, optical studies suggest that site-multiplicity of RE atoms in GaN is the rule rather than the exception. This

contradiction raises questions about the lattice location of optically active centres (lumophores) in GaN and their emission efficiency, yet to be answered both by theory and experiment.

It seems unlikely that the unperturbed RE ion can be responsible for any of the observed luminescence. Since there appear to be a number of subtly different centres which are active in each example, with approximately equal excitation probabilities and Nf products, it is difficult to see how *any one* of these (and *which one?*) could be RE_{Ga}. If we choose any one to be the isolated defect, we must conclude that any other active centre, necessarily in a lower symmetry site, is to be compensated for its lower numbers by a luminescence efficiency that is higher in almost perfect proportion. And so on down the chain of multiple sites. This is hard to believe.

If the unperturbed RE ion does not emit light, and there is no “magic site”, it seems likely that the observed multiple luminescence spectra are due to centres which have more or less the same basic structure. A prime candidate for such a *family* of defects is the RE_{Ga}-Ga_i pair, where Ga_i represents an interstitial Ga atom displaced by the RE substitution reaction, RE_i + Ga_s → RE_{Ga} + Ga_i. A large number of sites can accommodate the Ga_i, as shown in Figure 2.

Because the spectra of RE ions are rather insensitive to their environment, it is difficult to associate particular emission lines with particular defect configurations. On the other hand, the influence of the defects on the intrinsic emission of the host should not be underestimated. The additional luminescence lines seen in the near band-edge of RE-doped crystals (Figure 10c) may be associated with excitons bound to RE defects. This matter requires further study.

It remains true that there has been to date no definitive assignment of any luminescence band in RE-doped nitrides to a particular defect structure. Hence it seems clear that there is still a lot to do in both experiment and theory.

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