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Indirect excitation of Eu^{3+} in GaN codoped with Mg and Eu

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Abstract. Temperature-dependent Eu^{3+} luminescence spectra in GaN(Mg):Eu can be assigned to, at least, two distinct Eu^{3+} centres, denoted by Eu0 and Eu1. The splitting energy levels of the ^7F_J (J=1,2) multiplets for the Eu0 and Eu1 centres have been calculated using the equivalent operator Hamiltonian for C$_{3v}$ crystal field with the addition of an odd parity distortion.

1. Introduction

Europium doped GaN is a candidate material of red light-emitting diodes and laser diodes [1-3]. Quantum efficiency at room temperature of the Eu^{3+} injection luminescence was less than 0.6 % [2], much lower than that of commercial blue InGaN devices (>30%); however, there are no commercial red InGaN diodes. In order to improve the quantum efficiency, that is, obtain sufficiently bright Eu^{3+} luminescence, it is very important to examine and optimize the energy transfer from the optical band-to-band excitation to the Eu^{3+} excited state [4,5]. The band-to-band excitation below 360 nm at low temperatures in GaN(Mg):Eu produces fairly strong $^5D_0 \rightarrow {}^7F_2$ luminescence lines of Eu^{3+} around 620 nm, suggesting that there are, at least, two different relaxation processes to Eu^{3+} as described in previous literature; one involves prompt relaxation from excitons produced by the band-to-band excitation immediately into the Eu^{3+} excited states [6-9]; the other involves slow relaxation to Eu^{3+} via the Auger process following donor-acceptor recombination, where V$_N$ or Mg ions play the role of donors or acceptors, respectively [10,11].

Recent optical spectroscopy of Eu^{3+} in GaN doped with Mg (GaN(Mg):Eu) has revealed temperature-dependent hysteresis of the Eu^{3+} luminescence [5]. In this paper, we propose a structural model of Eu^{3+} luminescence centres in GaN(Mg):Eu, which are associated with Mg ions as acceptors..

2. Experimental procedure

GaN films, grown by hydride vapor phase epitaxy (HVPE) on (0001) sapphire substrates and doped with Mg (p-type) were implanted with 300 keV Eu ions [5]. The concentration of Mg was 6.4×10^{17} cm^{-3}. GaN has the Wurtzite crystal structure with the space group of $P6_3mc$. Eu and Mg ions substitute
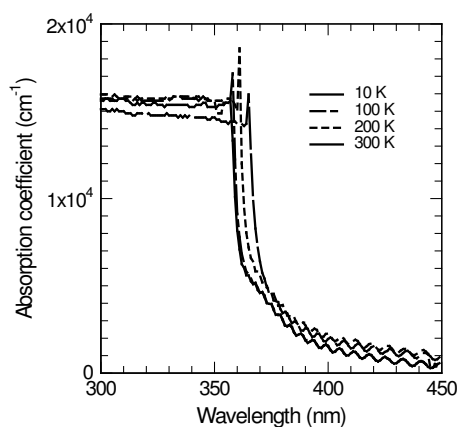
Figure 1. Temperature dependence of the absorption spectra for the GaN(Mg):Eu film.
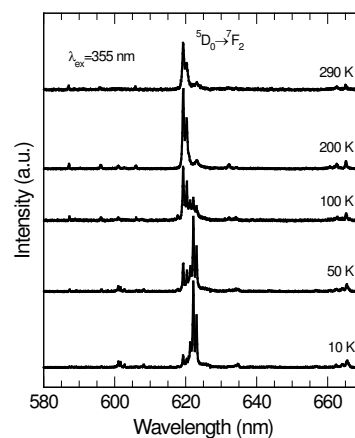
Figure 2. Eu^{3+} luminescence spectra for GaN (Mg):Eu in the temperature range from 10 up to 290 K.

for Ga ions where a Mg ion has a possibility to be located at one of six first nearest neighbour Ga sites of a central Eu ion.

Optical absorption, excitation and emission spectra in the ultraviolet and visible regions were measured using the BL3B beam of the UVSOR facility in the Institute for Molecular Science at Okazaki in Japan. A sample was attached to a cold copper finger in a liquid helium cryostat with a temperature control system. Emission spectra in the temperature range of 10-300 K were measured using an Acton SpectraPro-300i monochromator combined with a Roper Spec-10 Si-CCD detector cooled by liquid nitrogen.

3. Experimental results

Figure 1 shows the absorption spectra of the GaN(Mg):Eu film in a temperature range from 10 to 300 K. The total film thickness is estimated to be ~4.2 μ m from the interference fringes in the absorption spectrum at 300 K, while the implanted layer is only ~150 nm thick. The step near 360 nm corresponds to the band edge of GaN, whereas the sharp line around 360 nm is ascribed to excitons created in GaN. The absorption coefficient of such band-to-band transition is fairly large, >10^4 cm^{-1}. With increasing temperatures from 10 up to 300 K, the band gap shifts toward lower energy. Absorption lines due to Eu^{3+} could not be observed in these runs because of the weakness of the *4f-4f* transitions of Eu^{3+} and the low total Eu^{3+} content of the film.

Figure 2 shows Eu^{3+} luminescence spectra under 355 nm excitation for GaN(Mg):Eu in a temperature range from 10 up to 290 K. The luminescence spectrum is normalized to the maximum intensity of the $^5D_0 \rightarrow {}^7F_2$ line and the baseline of each spectrum is shifted for clarity. The luminescence spectra change markedly around 100 K on warming. The 622 nm lines (Eu1), dominant below 100 K, are replaced by 619 nm lines (Eu0) above 100 K. The Eu0 and Eu1 lines were first identified by O'Donnell [5]. The four groups around ~588, 596-608, 618-634 and 657-666 nm are assigned to the $^5D_0 \rightarrow {}^7F_J$ (J=0,1,2,3) intra-$4f^6$ transitions of Eu^{3+} [3,7,8].

In order to assign the luminescence lines to Eu0 and Eu1, the spectra around 600 and 620 nm in the regions of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions were observed at high resolution (not shown). The two distinct Eu^{3+} luminescence lines with notation of Eu0 and Eu1 were best observed at 200 K and 10 K, respectively. The $^5D_0 \rightarrow {}^7F_0$ 'sensitive' line of Eu0 was visible, but that of Eu1 was too weak to observe. The $^5D_0 \rightarrow {}^7F_1$ transition of Eu0 is clearly split into three, while Eu1 lines comprise a doublet and a singlet. The $^5D_0 \rightarrow {}^7F_2$ lines of both Eu0 and Eu1 clearly split into five components. Line splittings for Eu0 are larger than for Eu1. This result suggests that the symmetry of the Eu0 centre is

lower than that of the Eu1 centre, in agreement with the non-observation of the Eu1 $^5D_0 \rightarrow ^7F_0$ transition.

4. Discussion

It is reasonable to assume that substitution of Eu^{3+} on a Ga^{3+} site provides a C_{3v} symmetry electrostatic potential and that substitution of Mg on a Ga site (Mg_{Ga}) is a perturbation upon Eu^{3+}. Such an odd-parity crystal field mixes opposite parity wavefunctions into the $^5D_0$ and ^7F_J (J=0-6) multiplets of the less symmetric Eu0 centre, resulting in breakdown of the parity selection rule. We consider the energy splitting of the ^7F_J (J=1,2) multiplets of both Eu0 and Eu1 centres. The equivalent operator Hamiltonian for C_{3v} crystal field [12,13] is given by

$$H_{c.f.} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 (O_4^{-3} - O_4^3) + B_6^0 O_6^0 + B_6^3 (O_6^{-3} - O_6^3) + B_6^6 (O_6^{-6} + O_6^6) . \qquad (1)$$

The crystal field operator induced by the substitution of Mg is included in equation (1) as a perturbation term in a form of,

$$H_1 = B_2^2 O_2^2 . \qquad (2)$$

When the energy splitting of only ^7F_J (J=1,2) multiplets for the Eu0 and Eu1 centres is calculated, the sixth order terms in equation (1) can be omitted. The splitting energy levels of the $^7F_1$ and $^7F_2$ multiplets estimated from figure 2 are recalculated with the centre of gravity set equal to zero and summarized in Table 1.

Table 1. Experimental and calculated energy levels for $^7F_1$ and $^7F_2$ multiplets and optimized crystal field parameters in equations (1) and (2) for Eu0 and Eu1 with the energy unit (cm^{-1}).

Centre	Eu0		Eu1	
	(exp.)	(calc.)	(exp.)	(calc.)
$^7F_1$	137	138	122	122
	0	0	-53	-52
	-138	-138	-70	-70
B_2^0		-68		-62
$\lvert B_2^2 \rvert$		68		8
$^7F_2$	216	236	261	261
	169	162	-34	-38
	-89	-93	-57	-53
	-135	-143	-79	-80
	-161	-165	-90	-90
B_2^0		-34		-30
B_4^0		0.1		1.13
$\lvert B_4^3 \rvert$		39		33
$\lvert B_2^2 \rvert$		34		0.8

The observed energy splitting of the $^7F_1$ multiplet for Eu0 and Eu1 can directly estimate B_2^0 and B_2^2, since the energy separation between the doublet and the singlet is equal to $3 B_2^0$ and the splitting

energy of the doublet is equal to $2B_2^2$. The values of (B_2^0, B_2^2) and the calculated energy levels of the $^7F_1$ multiplet for the Eu0 and Eu1 centres are summarized in Table 1.

The splitting energy levels of the $^7F_2$ multiplet are obtained to solve the 5×5 determinant of equation (1) including equation (2). The splitting energy levels calculated using the values of B_2^0 and B_2^2 estimated from the $^7F_1$ multiplets of Eu0 and Eu1 are too large to fit the observed energy levels. The calculated energy levels of the $^7F_2$ multiplets of Eu0 and Eu1 and their optimized fitting parameters of the crystal field are summarized in Table 1. However, the values of B_2^0 and B_2^2 estimated from the $^7F_2$ multiplets are roughly half of those for the $^7F_1$ multiplet. At present, the origin of this difference is not clear.

The values of B_2^0, and B_4^3 for the Eu0 centre are a little larger than those for the Eu1 centre, but the B_2^2 value for Eu0 is much larger than that for Eu1. This calculation suggests that the Eu0 centre is strongly perturbed by the Mg substitution, whereas the Eu1 centre has close to C_{3v} symmetry and is assigned to a Eu^{3+} ion with Mg_{Ga} and/or V_N at a relatively long distance.

5. Conclusions

The luminescence of GaN(Mg):Eu features two main centres, Eu0 and Eu1, linked by photochromic hysteresis. Crystal field analysis suggests that Eu0 is less symmetric than Eu1, which is approximately C_{3v}.

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References

[1] Sekiguchi H, Takagi Y, Otani T, Matsumura R, Okada H and Wakahara A 2013 Jpn. J. Appl. Phys. **52** 08JH01

[2] Nishikawa A, Furukawa N, Kawasaki T, Terai Y and Fujiwara Y 2010 Appl. Phys. Lett. **97** 051113

[3] Park J H and Stekl A J 2006 Opt. Mater. **28** 859

[4] Wang K, Martin R W, Nogales E, Katchkanov V, O'Donnell K P, Hernandez S, Lorenz K, Alves E, Ruffenach S and Briot O 2006 Opt. Mater. **28** 797

[5] O'Donnell K P, Edwards P R, Kappers M J, Lorenz K, Alves E and Bockowski M 2013 Phys. Status Solidi **C 11** 662

[6] Roqan I S, O'Donnell K P, Martin R W, Edwards P R, Song S F, Vantomme A, Lorenz K, Alves A and Bockowski M 2010 Phys. Rev. **B 81** 085209

[7] Poplawsky J D, Nishikawa A, Fujiwara Y and Dierolf V 2013 Optics Express **21** 30633

[8] Wisniewski K, Jadwisienczak W, Thomas T and Spencer M 2009 J. Rare Earths **27** 667

[9] Li Z, Bang H, Piao G, Sawahata J and Akimoto K 2002 J. Crystal Growth **240** 382.

[10] Fleischman Z, Munasinghe C, Steckl A J, Wakahara A, Zavada J and Dierolf V 2009 Appl. Phys. **B 97** 607

[11] Mezdrogina M M, Danilovskii E Yu and Kuz'min R V 2011 Inorg. Mater. **47** 1450

[12] Henderson B and Imbush G F 1989 *Optical Spectroscopy of Inorganic Solids* (Oxford:Clarendon Press) chapter 8

[13] Abragam A and Bleaney B 1970 *Electron Paramagnetic Resonance of Transition Ions* (Oxford : Clarendon Press) p209 and p338