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Rare earth luminescence: A way to overcome concentration quenching

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A model is developed to simulate the rare earth luminescence intensity in dependence of both the excitation rate and the dopant concentration. For low excitation rates, as in the case of photoluminescence investigations, concentration quenching is expected. In contrast for high excitation rates (as generally realized in cathodoluminescence experiments) concentration quenching can be suppressed and thus luminescence intensity increases with increasing dopant concentration. These results reconcile the recent photo- and cathodoluminescence results on GaN:Er presented by Chen *et al.* (APL **96**, 181901, 2010). Further experimental results indicate that the physical basis of the model is adequate. *Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License.* [<http://dx.doi.org/10.1063/1.4760248>]

Optically excited rare earth doped semiconductors suffer from the so-called concentration quenching effect,¹⁻⁴ *i.e.* the intensity of the rare earth luminescence decreases with increasing dopant concentration. This effect dominates if the excitation energy is transferred between many ions in the time necessary for the radiative decay (called energy transfer here, frequently also called energy migration). In such a situation the probability to reach a path of non-radiative decay is strongly enhanced. Since the energy transfer probability is increased with decreasing dopant distance (*i.e.* increasing concentration), *e.g.*,⁵ concentration quenching is a typical effect at high concentrations.

Recently Chen *et al.* reported on the green luminescence from GaN:Er⁶ that concentration quenching was absent when using cathodoluminescence, but present when using photoluminescence. This obvious contradiction can be reconciled by describing the underlying physical processes by a rate equation model. This model spans the excitation rate from the case of a few excited ions that can with high probability loose their energy to one of the many unexcited ions to the case that almost all of the ions are excited and thus practically no chance to loose their energy to a nearby ion.

Basically, an excited quantum state can either be disturbed by fluctuations causing spontaneous emission and/or by an electromagnetic field resulting in stimulated emission. The overall probability for a radiative transition equals to:⁷

$$p^{\text{rad}} = A + B \times u(\omega_0), \quad (1)$$

with A and B Einstein's coefficients and u the radiation density at the transition frequency ω_0 . An excited rare earth ion emits as an electric dipole; its radiation density in the near field can be approximated by (neglecting angular dependencies):

$$u(\omega_0) \approx \frac{P^2}{32\pi^2 \varepsilon_0 \varepsilon_r} \times \frac{1}{r^6}, \quad (2)$$

with r distance from the excited ion, ε_0 the vacuum permittivity, ε_r the relative permittivity of the surroundings and P the dipole strength. For sake of clarity we shall call this case in the following 'stimulated emission'.

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Now we can write the probability for non-radiative loss of the excitation energy in a form similar to Eq. (1):⁴

$$p^{\text{non-rad}} = C + D \times p^{\text{ET}}. \quad (3)$$

Here C accounts for concentration-independent loss mechanisms like the emission of phonons or the transfer of the excitation energy to a defect. The loss probability is enhanced if an additional energy transfer channel is present in the system, which is, in the present case, concentration dependent. p^{ET} denotes the probability for such an energy transfer. The constant D is proportional to the number density of the considered additional non-radiative decay path. We note that this energy transfer probability term can comprise any energy loss process that depends on an interesting variable, also different loss paths, *e.g.* thermal quenching, can be considered by similar structured terms acting additively. Here we focus on electrostatic dipole-dipole interaction, as proposed by Förster.⁸ In this case the probability for an energy transfer is:

$$p^{\text{ET}} = \frac{1}{\tau_0} \times \left(\frac{R_0}{r} \right)^6 \propto N^2, \quad (4)$$

with the constant τ_0 , containing basically the dielectric properties of the surroundings, and the critical distance for energy transfer R_0 . Hence the loss probability is proportional to the interspace r (between excited and ground-state atoms) to the power of minus six, which corresponds to the squared number density of centers N (see below).

The distance dependencies of both stimulated emission and concentration quenching differ as they are determined by different groups of centers. The probability for concentration quenching depends on the distance, r_{gr} , between an excited ion and an ion in the ground state. The probability for stimulated emission depends on the distance, r_{exc} , between an excited ion and another excited ion. Since the overall number density of ions N is constant (it is composed of the number density of ions in the excited state N_{exc} and in the ground state N_{gr}), these distances depend on each other and obey the equation:

$$N = N_{exc} + N_{gr} \Leftrightarrow \frac{1}{r^3} \propto \frac{1}{r_{exc}^3} + \frac{1}{r_{gr}^3}. \quad (5)$$

A rate equation is used to describe the influence of both concentration quenching and excitation rate on the luminescence intensity. We start with the equation that describes the time evolution of the number density of ions in the excited state N_{exc} as a function of the excitation rate $p^{\text{exc}} \times N_{gr}$ and the radiative and non-radiative decay rates $p^{\text{rad}} \times N_{exc}$ and $p^{\text{non-rad}} \times N_{exc}$, respectively:

$$\frac{d}{dt} N_{exc} = p^{\text{exc}} \times N_{gr} - (p^{\text{rad}} + p^{\text{non-rad}}) \times N_{exc}. \quad (6)$$

The integral of this equation can unfortunately not be obtained in a straightforward way (the probabilities themselves depend on the populations). Instead the two limiting cases low excitation rates as expected for optical excitations (photoluminescence; excitation power density typically around 1 mW/mm²) and high excitation rates as in the case of cathodoluminescence (typical excitation power density around 7 W/mm²⁶) will be discussed here.

Low excitation rates means almost all ions are in the ground state, thus $N_{gr} \approx N$. In such a case the distance between two excited ions is generally very large, thus stimulated emission is practically zero. On the other hand the distance between an excited ion and an ion in the ground state is practically equal to the average distance between the ions (*cf.* Eq. (5)). Solving Eq. (6) with these approximations (boundary condition $N_{exc}(0) = 0$) renders:

$$N_{exc}(t) = \frac{p^{\text{exc}} \times N}{p^{\text{exc}} + A + C + D \times p^{\text{ET}}} \times (1 - \exp[-t \{p^{\text{exc}} + A + C + D \times p^{\text{ET}}\}]). \quad (7)$$

The luminescence intensity, I , in the steady state ($t \rightarrow \infty$) is equal to the number density of ions in the excited state multiplied with the probability for a radiative decay (here $p^{\text{rad}} \approx A$):

$$I = \frac{A \times p^{\text{exc}} \times N}{p^{\text{exc}} + A + C + D \times p^{\text{ET}}}. \quad (8)$$

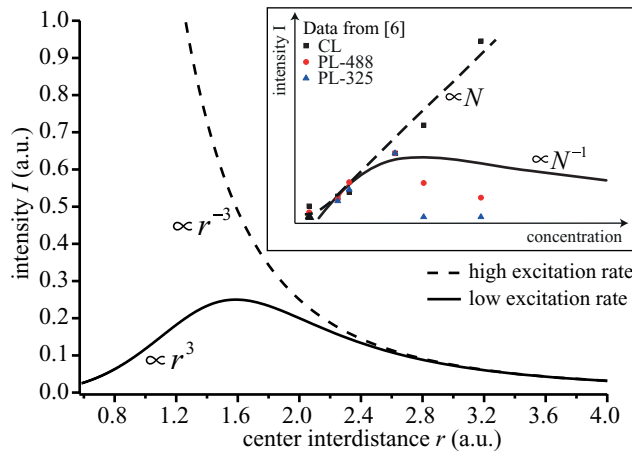


FIG. 1. Calculated intensity *versus* distance curves for high (dashed line) and low (bold line) excitation. The inset shows Chen *et al.*'s experimental data⁶ in comparison with our calculated curves (note, the abscissa has inverted character to main abscissa, see eq. (5)). In parts reprinted with permission from Appl. Phys. Lett. **96**, 181901 (2010). Copyright 2010 American Institute of Physics.

The numerator increases linearly with the number density and the denominator, or more specifically the probability for energy transfer to another ion, p^{ET} , increases, under the conditions of the approach, as the number density squared (*cf.* Eq. (4)). The intensity thus decreases inversely with concentration as $I \propto 1/N \propto r^3$ (see Fig. 1).

At very large excitation rates nearly all ions can be found in the excited state. Therefore the approximation $N \approx N_{\text{exc}}$ is used. By evaluating Eq. (6) with the above-mentioned boundary conditions the intensity in the steady state region becomes:

$$I = \frac{[A + B \times u(\omega_0)] \times p^{\text{exc}} \times N}{p^{\text{exc}} + A + B \times u(\omega_0) + C}. \quad (9)$$

We may summarize this result. This limiting high excitation rate case is represented by an excessively large number of excited ions with only a few ions in the ground state dispersed among them. The rather large distance between these ground state ions then makes energy transfer practically impossible, $p^{\text{ET}} \approx 0$, (*cf.* Eq. (4)). The numerator essentially increases with the number density to the power of three (here is $u \propto N_{\text{exc}}^2$) and the denominator with the number density to the power of two. Consequently the luminescence intensity increases linearly with the concentration, $I \propto N \propto r^{-3}$, which result is in accordance with the intuitive expectation for no concentration quenching.

Fig. 1 shows the discussed two limiting cases; both curves can be regarded as boundaries that localize all possible curves of intermediate behavior in between. The experimental cathodoluminescence data obtained by Chen *et al.*⁶ are consistent with this predicted linear increase for high excitation (*cf.* inset Fig. 1). However, Chen *et al.*'s photoluminescence data in the quenching region lie distinctly below our theoretical curve. The reason is most probably that only dipole-dipole interaction is included in our calculations. Exchange interaction and multipole interaction in addition can lead to a much steeper decrease in intensity with increasing concentration.

In view of the presented model we may also look at measured lifetimes or relaxation times in rare earth luminescence. For photoluminescence a shorter lifetime is expected than in cathodoluminescence since concentration quenching takes place; in the case of cathodoluminescence mostly radiative emission (both stimulated and spontaneous) control the overall lifetime hence a longer lifetime can be anticipated. Appropriate experimentally observed lifetimes are available for the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of trivalent terbium ions (green luminescence) and confirm this notion. Aldabergenova *et al.* reported a lifetime of 1.1 ms (at 300 K, *a*-AlN) for the case of photoluminescence,⁹ Lozykowski *et al.* using cathodoluminescence (at 310 K, GaN, 5 keV, 75 μA) obtained approximately 1.7 ms,¹⁰ *i.e.* a by around 50 % larger lifetime (note, because of the shielded 4f electrons of

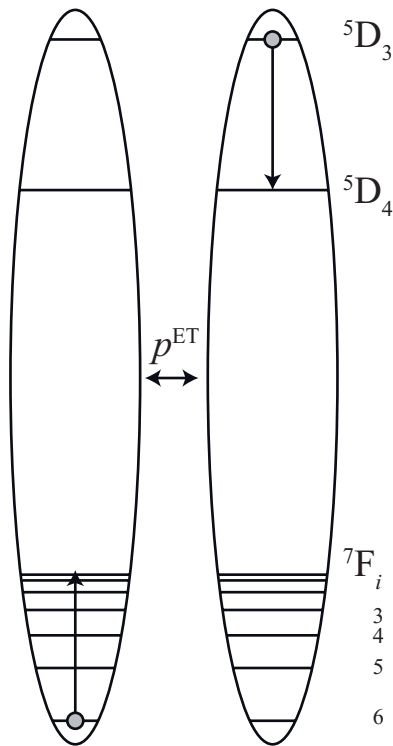


FIG. 2. The process of cross-relaxation in the case of terbium ions. The quantum energy liberated by the decay of the 5D_3 level to 5D_4 can be transferred non-radiatively to a nearby terbium ion being in the ground state and excite a transition in the 7F family there.

rare earth ions, the matrix type is of negligible influence on the luminescence properties, for details see e.g.).¹¹

Terbium luminescence supports also the validity of the physical basis chosen for the present model. We refer to the deep blue luminescence of terbium, which arises by a transition from the energy level 5D_3 (energetically above 5D_4) into the ground state 7F_6 . The characteristics of this transition is that the level 5D_3 can be depopulated in addition to the luminescent decay by the resonant non-radiative cross-relaxation process.¹² The process is illustrated in Fig. 2, it consists in a transition into 5D_4 with transfer of the respective energy into a nearby terbium ion that is correspondingly resonantly excited within the 7F level family.

Figure 3 shows a comparison between a terbium spectrum obtained by photoluminescence (low excitation rate, dashed line) and one obtained by cathodoluminescence (high excitation rate, solid line). It is clear that at low excitation rates (PL with approximately 1 mW/mm^2) practically no blue emission is observed, since many ions in the ground state can depopulate the blue level of excited ions by cross correlation. On the other hand, at high excitation rate (CL) one observes blue luminescence in addition since ions in the ground state are practically absent and the competing cross correlation cannot occur anymore.

In conclusion the calculations show that a rate equation model can solely describe the observed absence of concentration quenching at high excitation rates. In essence it is the fraction of excited ions in the steady state that determines whether concentration quenching (low population in the excited state) or practically no concentration quenching (high population in the excited state, inversion state) occurs. Chen *et al.*'s⁶ results on the quenching behaviour of Er in GaN matrix are in accord with this model. This effect appears to be of general validity. Indications are taken from lifetimes of rare-earth ions and, in the case of terbium ions, from the ratio between luminescence from 5D_4 and 5D_3 levels (cross-relaxation process).

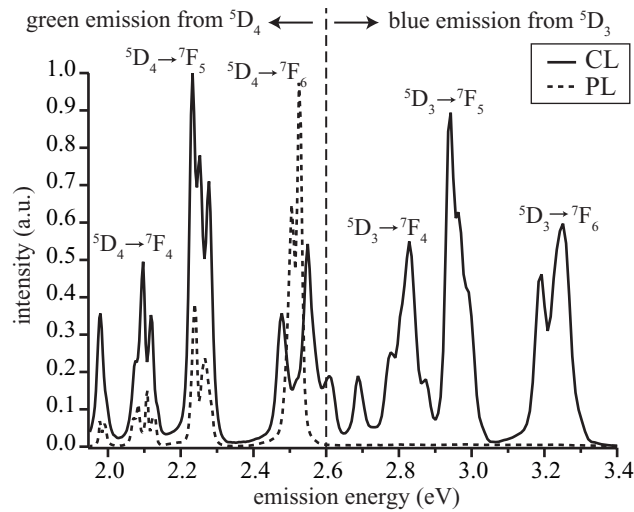


FIG. 3. Emission spectra of GaN:Tb obtained by CL (beam current $75 \mu\text{A}$, 5 kV, solid line)¹⁰ and AlN:Tb obtained by PL (250 nm excitation wavelength, solid line). In the case of PL almost no luminescence from $^5\text{D}_3$ is present, indicating the depopulation of this state by cross-relaxation.

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