WHITE LIGHT-EMITTING DIODES

Stabilizing colour and intensity

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Phosphor converted white LEDs: stabilizing color and intensity

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Thermally activated defects in a blue-emitting phosphor can enhance energy transfer to the activator, and compensate for thermal quenching.

White light-emitting diodes (wLEDs) are rapidly replacing incandescent and fluorescent light sources, both in general lighting and display backlights, due to their long lifetime, small footprint, spectral tunability and most importantly their high efficiency in converting electrical to optical power [Schubert-2005][Abe-2017]. As the emission of LEDs is essentially monochromatic, wLEDs are typically composed of a blue pumping LED and one or more luminescent materials, also called *phosphors*, which convert part of the blue light to longer wavelengths, the mixture yielding white light (Fig. 1a, c).

One of the requirements [Smet-2011] that luminescent materials for LED applications need to fulfil is maintaining their emission intensity at the elevated temperatures that can be reached in the LED device. Won Bin Im and colleagues have developed a novel phosphor, the Eu^{2+} -doped phosphate $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$, which shows an extraordinary thermal stability of the emission intensity for a specific dopant concentration [Kim-2017].

Figure 1. Structure, efficiency and thermal optical characteristics of a wLED. **a)** Schematic view of a wLED, with the luminescent layer displaced from the blue LED chip in a so-called remote phosphor configuration. **b)** Power budget of a wLED assuming a luminous efficacy of 180lm/W, a phosphor quantum efficiency of 90% and the emission spectrum as shown in **c)**. EQE, external quantum efficiency. **d)** Electronic structure of dopant and defects, **e)** thermal quenching and **f)** illustration of a crystal defect near a luminescent dopant or activator.

Inorganic luminescent materials commonly consist of an optically transparent host compound doped with specific impurities, often lanthanides, such as cerium or europium, or transition metal ions (e.g. manganese). Electronic transitions within these dopants determine the absorption and emission characteristics (Fig. 1d). The role of the host surpasses the mere structural incorporation of the dopant ions as it influences transition probabilities and – very often – also the position and splitting of the relevant energy levels of the dopants [Dorenbos-2013]. Hence, variation of the host's composition allows one to obtain the desired emission colour, combined with a strong absorption of the pumping LED's blue emission. Ideally, this conversion process is lossless, as expressed by the quantum efficiency, QE (the ratio between the number of emitted and absorbed photons). Although thousands of host-dopant combinations have been investigated in the framework of LED conversion

since the invention of the efficient blue LED [Nakamura-1995], one of the key elements hampering the application of novel phosphors is their thermal behaviour.

The operating temperature of the phosphor inside a wLED is essentially determined by two major heat sources, the LED chip and the luminescent material itself. With the improvement of the conversion efficiency of the blue pumping LEDs, its heat production compared to the generated optical power has significantly decreased, rendering the heat production in the phosphor material itself the main problem. Even with a quantum efficiency of 100%, heat is generated due to the so-called Stokes losses (the energy difference between the absorbed and emitted photon). Additionally, non-radiative paths become important in the decay of the excited state of the dopant at elevated temperature (Fig. 1e). Absorption still occurs, however without the emission of a photon, leading to a decrease in the quantum efficiency; this behaviour is described as *thermal quenching* (TQ) [Xia-2017], and is typically onset between 100°C and 200°C. When such a phosphor material is embedded in an LED, not only the emission intensity will decrease, but also the emission colour of the entire wLED will change above a certain threshold temperature. With the drive to have increasingly bright wLEDs, the increased photon flux at the phosphor level aggravates the thermal effects.

Im and co-workers managed to produce a blue-emitting $\text{Na}_{3-2x}\text{Sc}_2(\text{PO}_4)_3:\text{xEu}^{2+}$ phosphor (NSPO:xEu²⁺) whose luminescence could be sustained up to 200 °C [Kim-2017]. The emission losses induced by non-radiative paths were effectively suppressed by a counter mechanism, which was associated with the increased Na⁺ disorder in the host at high temperatures. The associated structural transformation leads to the formation of defect levels that can act as electron-trapping centres, favouring an energy transfer to the activator (Eu²⁺), which can counteract the quenching behavior.

While the field of luminescent materials for solid state lighting has seen a tremendous increase in the past two decades, only a limited number of phosphors are actually commercially applied as the room temperature behavior remains a grave issue. While the quantum efficiency can often be improved by changes in the phosphor synthesis conditions, this is in general not true for the thermal quenching behavior. An improved understanding requires good models for the thermal quenching routes, which can be adjusted to the specificity of the type of dopants and the composition of the host. Over the past two decades, empirical relations have been found that relate the thermal quenching behavior to the details of the luminescence spectra [Dorenbos-2013], yet uncertainties are substantial and a profound understanding is still lacking [Joos-2015]. Resolving this ambitious scientific question will require advanced quantum mechanical techniques to model the luminescent impurities and their interaction with the inorganic matrix. While radiative processes can now be reliably described, even for these highly correlated d- or f-electron systems [Seijo-2016], the quantum mechanical models describing the temperature dependent non-radiative processes are still in their infancy. Correctly treating non-radiative processes necessitates a good knowledge of the details of electron-vibrational interactions and should moreover include the influence of other dopant ions and most importantly, crystal defects (Fig. 1d,f).

While a number of issues remain open, the work from Im and colleagues demonstrates that certain phosphors can show unconventional thermal behavior, offering the prospect of understanding and controlling the non-radiative pathways in other phosphor systems as well.

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