Quantum cutting phosphors

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Solid state lighting is very efficient

“The laser, we believe, is the next generation of lighting, even for general applications”
– Nakamura

![Graph showing the efficiency of Commercial LED & Laser by M. Cantore et al., UCSB](image)

![Graph showing the projected electricity savings from Solid-State Lighting](image)

Solid state lighting research and development map, DOE, May 2015
Phosphors are typically oxides or nitrides

Phosphors luminesce when excited by a given energy

Oxides and nitrides doped with optically active rare earth compounds

Optical properties depend on host structure and local environment ion

Prototypical phosphor: $Y_3Al_5O_{12}$ doped with $Ce^{3+}$

Phosphors are wavelength converters for LEDs and laser diodes

Stokes shift: wavelength conversion loss

Typical phosphors: convert a short $\lambda$ photon to a longer $\lambda$ photon

Quantum cutting/splitting phosphors: convert short $\lambda$ photon into two longer $\lambda$ photons

$\hbar \nu_1 = \hbar \nu_2 + \hbar \nu_3$

energy absorbed $\Rightarrow$ energy emitted


External quantum efficiency (EQE) describes performance

EQE is number of photons emitted by phosphor (s$^{-1}$) over number of photons absorbed (s$^{-1}$)

$$EQE = IQE * \eta_{transfer} * \eta_{outcoupling}$$

Excitation wavelengths vacuum ultraviolet (VUV) (<200 nm); xenon discharge lamps

Normal phosphors (max): ~100%
QC phosphors (max): ~200%

Fluorides are used for QC phosphors

Need bandgap > 3.0 eV

Excitation energy > 6 eV ($\lambda < 200$ nm)

Energy of phonons low to reduce multiphonon relaxations (oxides are high, show no emission)

Downside: unstable

Fluorides are used for QC phosphors

High centroid energy (occurs for compounds with high EN of anions)

Small crystal field splitting (CFS); depends on anion coordination polyhedron

Cube and octahedral coordination produce large CFS

Zhang, Huang, Recent progress in quantum cutting phosphors, Prog. Mater Sci., 55 2010
QC phosphors rely on $f$ electron transitions

Focus in on fluorides doped with $\text{Pr}^{3+}, \text{Tm}^{3+}, \text{Er}^{3+},$ and $\text{Gd}^{3+}$

For $\text{Gd}^{3+}$, donor transfers stepwise to two acceptors via downconversion

$\text{Gd}^{3+}/\text{Eu}^{3+}$ pair, cascade emission

$\text{YF}_3:\text{Pr}^{3+}, \text{Pnma}$

QC can happen via multiple pathways

Wegh, Donker, Oskam, Meijerink, Visible Quantum Cutting in LiGdF$_4$:Eu$^{3+}$ through downconversion, Science 283 1999
LiGdF$_4$:Eu$^{3+}$ is one of the highest performing QC phosphors

**Process:**
Gd is excited by high-energy photon

Two step energy transfer to Eu$^{3+}$

two visible photons emitted by Eu$^{3+}$ (downconversion)

Wegh, Donker, Oskam, Meijerink, Visible Quantum Cutting in LiGdF$_4$:Eu$^{3+}$ through downconversion, *Science* **283** 1999
Na, Jeong, Chang, Kim, Woo, Lim, Mkhoyan, Jang, Facile synthesis of intense green light emitting LiGdY$_4$:Yb,Er-based upconversion bipyramidal nanocrystals and their polymer composites, *Nanoscale*, **6** 2014
Downconversion

Wegh, Donker, Oskam, Meijerink, Visible Quantum Cutting in LiGdF$_4$:Eu$^{3+}$ through downconversion, Science 283 1999