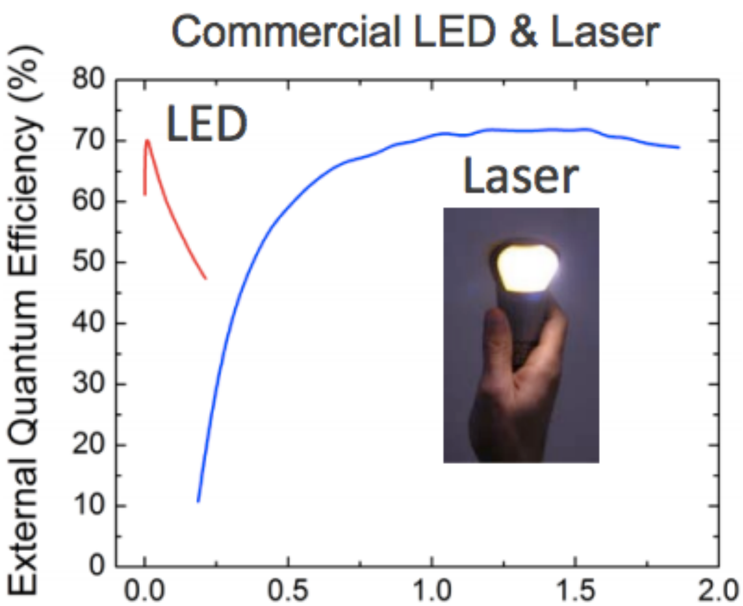
Quantum cutting phosphors

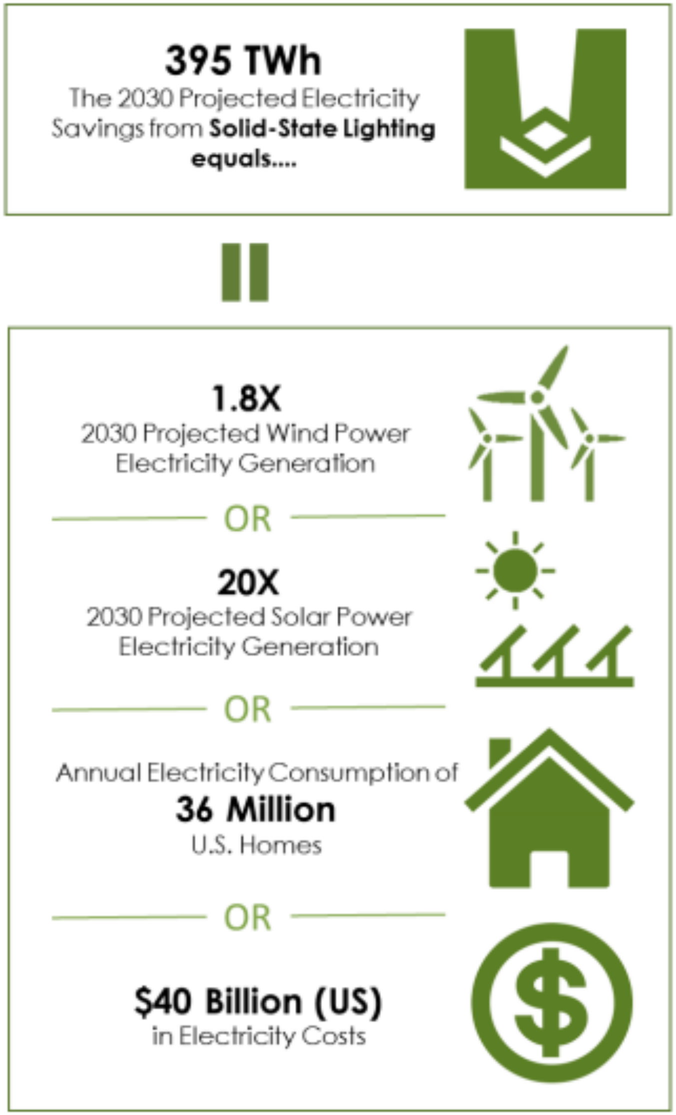
Clayton Cozzan

Solid state lighting is very efficient

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



Current Density (kA/cm²)
M .Cantore *et al.*, UCSB



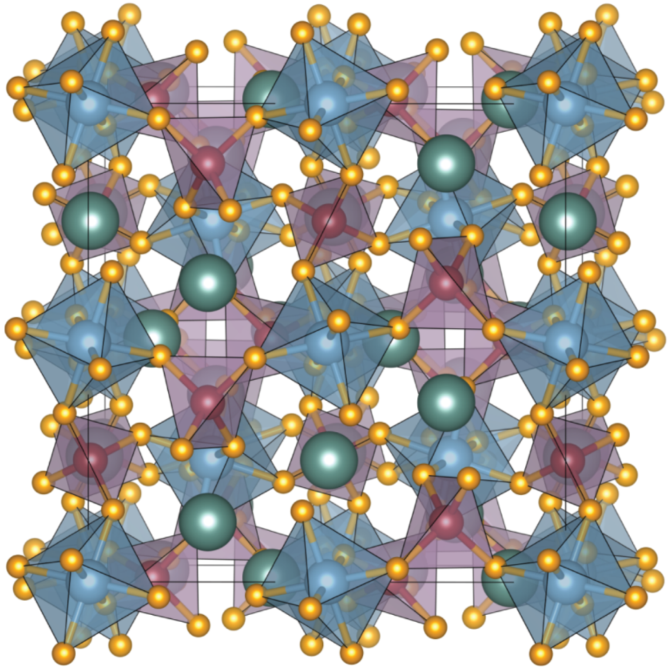
Solid state lighting research and development map, DOE, May 2015

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+}

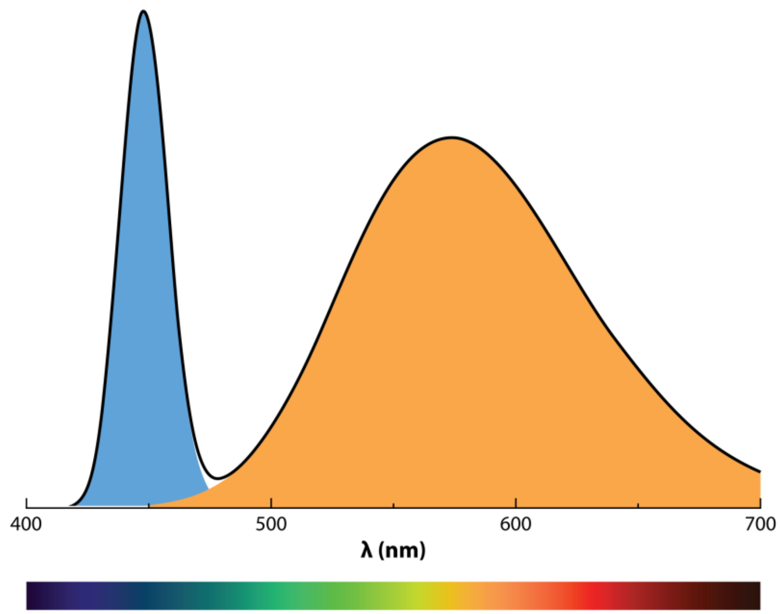
George, Denault, Seshadri, Phosphors for solid state white lighting, *Annu. Rev. Mater. Res*, **43**, 2013

Phosphors are wavelength converters for LEDs and laser diodes

Stokes shift: wavelength conversion loss

Typical phosphors: convert a short λ photon to a longer λ photon

Quantum cutting/splitting phosphors: convert short λ photon into two longer λ photons



George, Denault, Seshadri, "Phosphors for solid state white lighting," *Annu. Rev. Mater. Res*, **43**, 2013.

$$h\nu_1 = h\nu_2 + h\nu_3$$

energy absorbed ($h\nu_1$) energy emitted ($h\nu_2$, $h\nu_3$)

E. Fred Schubert, *Light-Emitting Diodes*, Cambridge University Press, 2006

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%

Light-Emitting Diodes, E. Fred Schubert, Cambridge University Press, 2006

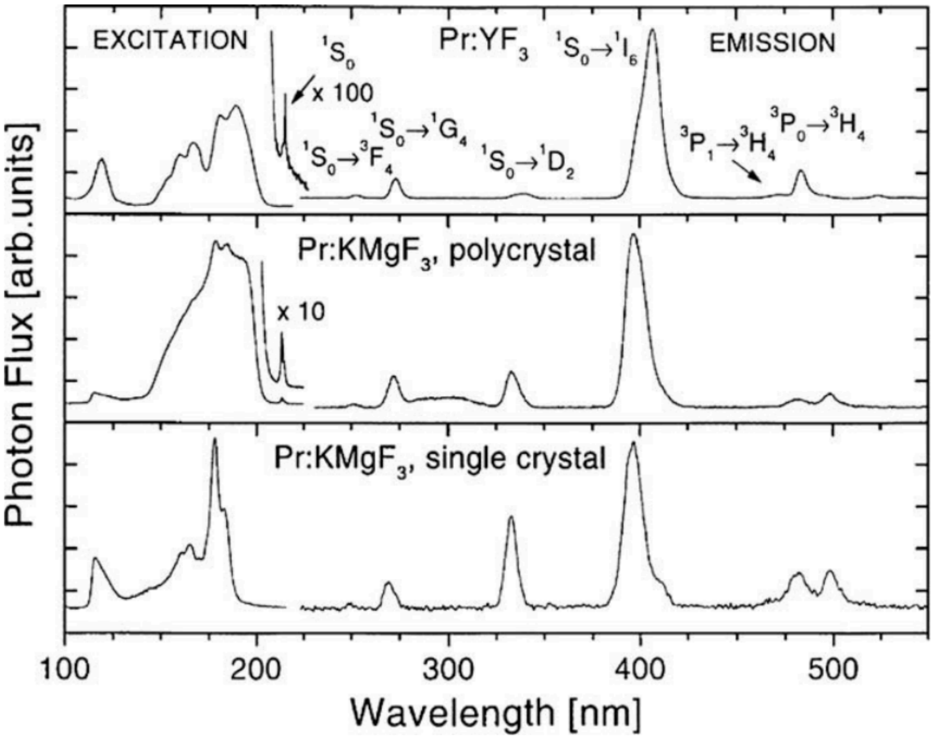
Fluorides are used for QC phosphors

Need bandgap > 3.0 eV

Excitation energy > 6 eV
(λ < 200 nm)

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

Downside: unstable



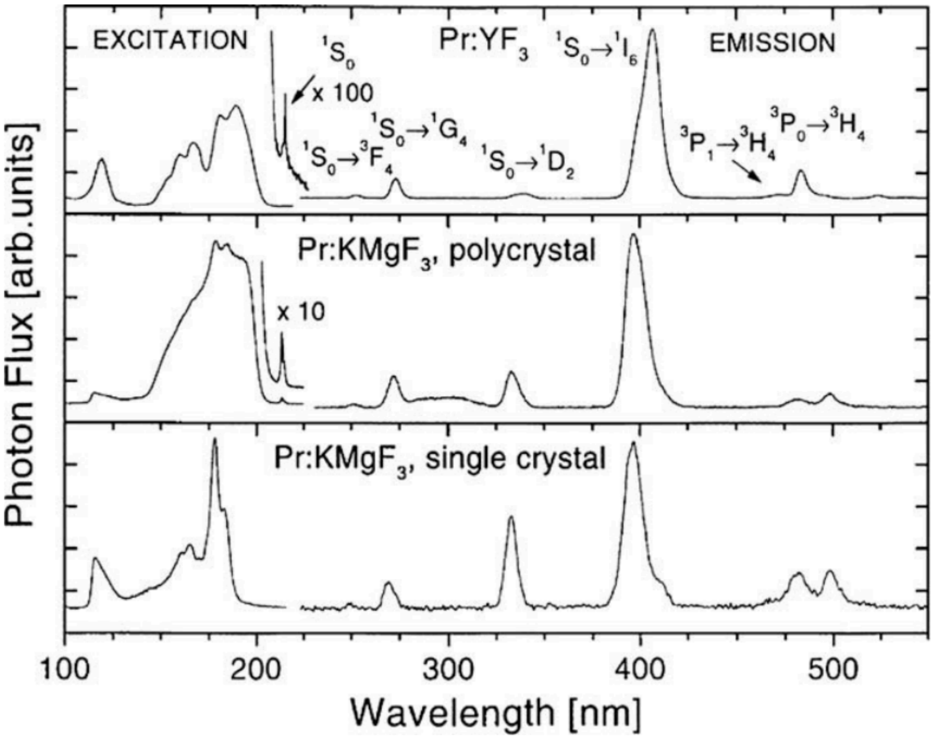
Zhang, Huang, Recent progress in quantum cutting phosphors, *Prog. Mater Sci.*, **55** 2010

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 octhedral coordination produce large CFS



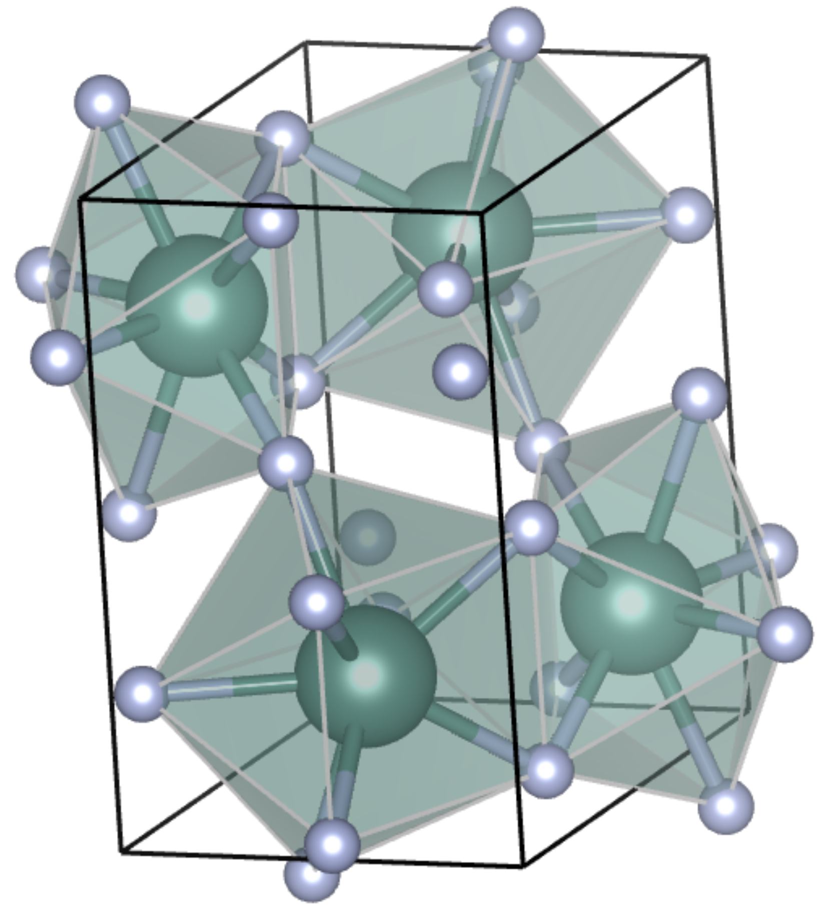
Zhang, Huang, Recent progress in quantum cutting phosphors, *Prog. Mater Sci.*, **55** 2010

QC phosphors rely on *f* electron transitions

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

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

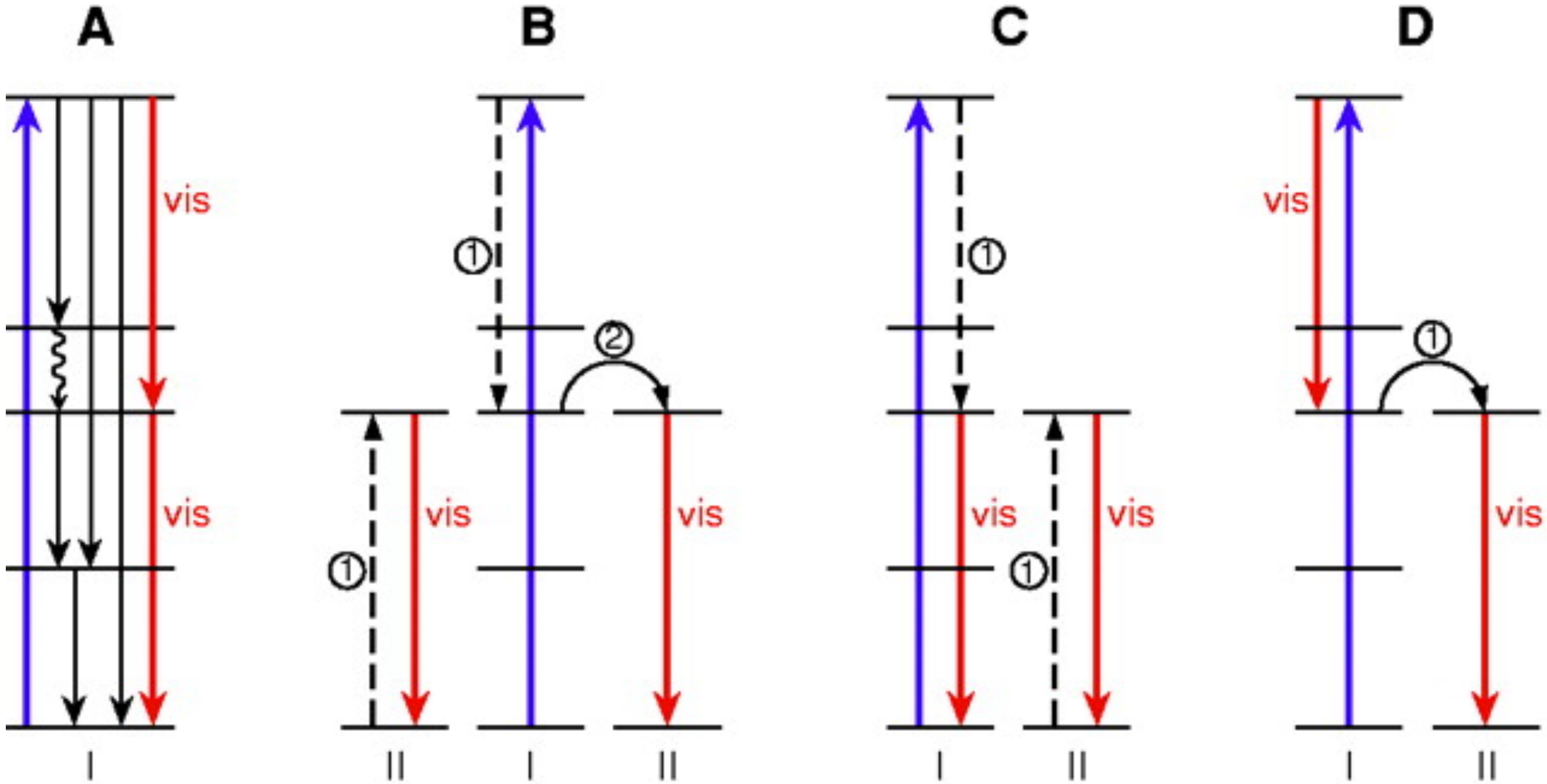
Gd^{3+}/Eu^{3+} pair, cascade emission



$YF_3:Pr^{3+}$, *Pnma*

Structure: Cheetham, Norman, The Structures of Yttrium and Bismuth Trifluorides by Neutron Diffraction, *Acta Chem. Scand. A* **28** 1974

QC can happen via multiple pathways



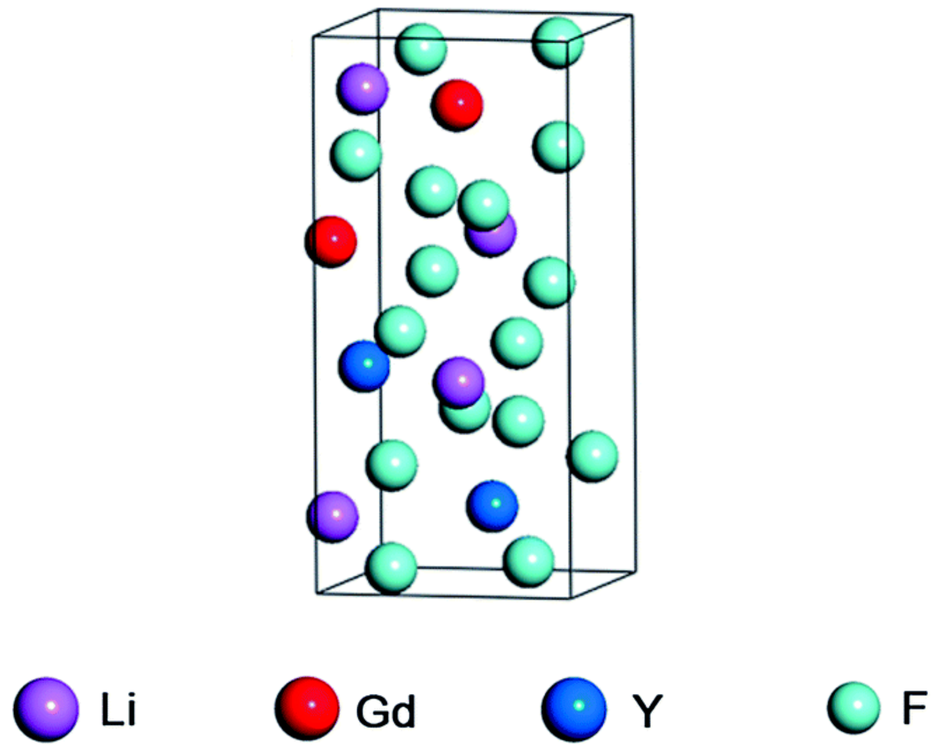
Wegh, Donker, Oskam, Meijerink, Visible Quantum Cutting in $LiGdF_4$:Eu^{3+} through downconversion, *Science* **283** 1999

$LiGdF_4:Eu^{3+}$ is one of the highest performing QC phosphors

Process:
Gd is excited by high-energy photon

Two step energy transfer to Eu^{3+}

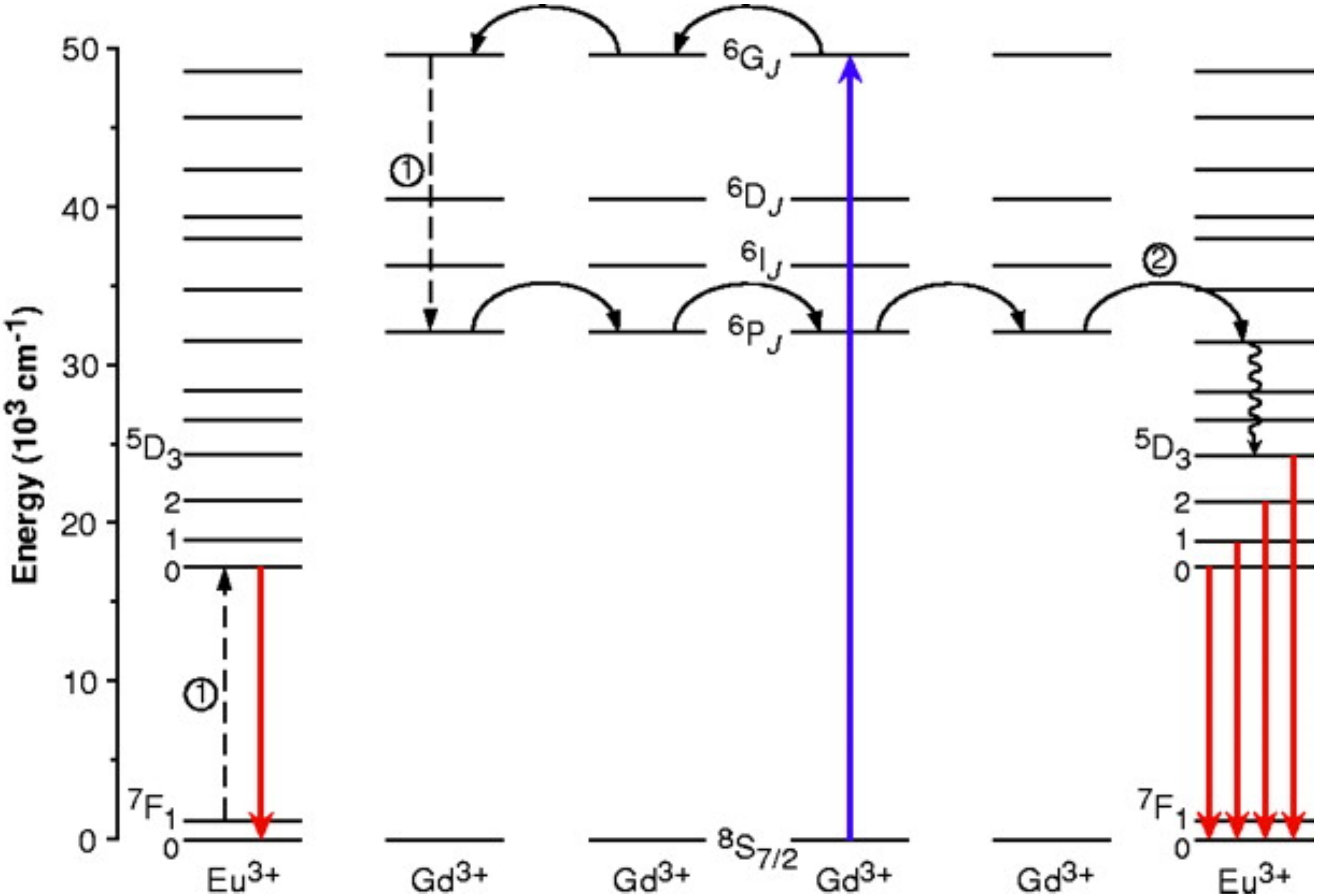
two visible photons emitted by Eu^{3+} (downconversion)



$Li(Gd_{0.5}Y_{0.5})F_4$, $I4_1/a$ (88)

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