Luminescence and luminescent materials

- Introduction
- Part I: basic processes
- Part II: rare earth luminescence

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Luminescence: definition

'Cold light': generation of light in a non-thermal way

- Photoluminescence (PL)
- Cathodoluminescence (CL)
- Electroluminescence (EL)
- Chemoluminescence
- Bioluminescence
- Radioluminescence
- Thermoluminescence (TL): false!
- Triboluminescence
- Sonoluminescence

Types of luminescence (2)

- Atomic transitions (Hg, Xe, Na,...)
- Organic luminescences (dyes, OLEDs)
- Quantum dots (CdS, CdSe, PbS, ZnS,...)
- Doped semiconductors/insulators: localized defects

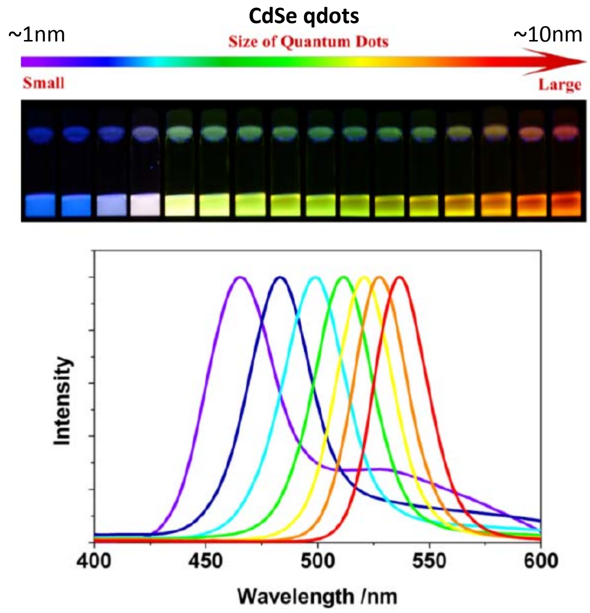
size ↓

Types of luminescence: organic LEDs

- Flexible devices
- First large area prototypes

- Issues: stability, lifetime

Types of luminescence: quantum dots

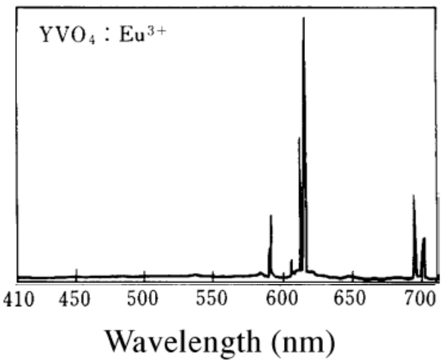


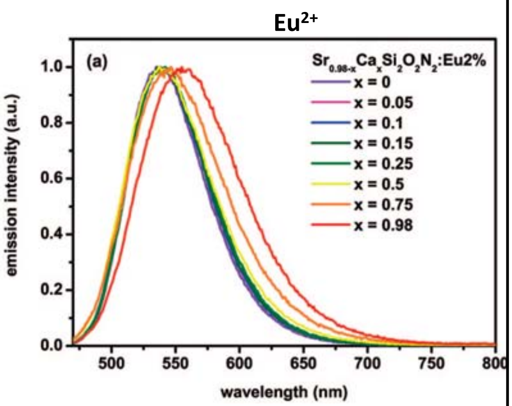
Bera et al, Materials 2010, 3, 2260-2345

Part I. Luminescence: basic processes and measurement

- Observations
- Configuration coordinate diagram
- Stokes shift
- Emission band width
- Non-radiative decay
- Characterization of luminescence

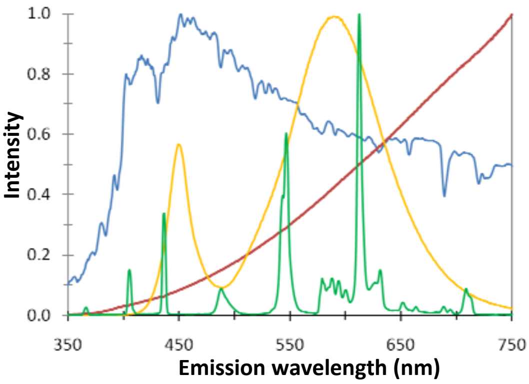
Observations: europium





Phosphor Handbook; Chem. Mater. 21 (2009)

Observations: light sources



A: Sun LED Incandescent Fluorescent

B: Sun LED Incandescent Fluorescent

C: Sun LED Incandescent Fluorescent

D: Sun LED Incandescent Fluorescent

Observations

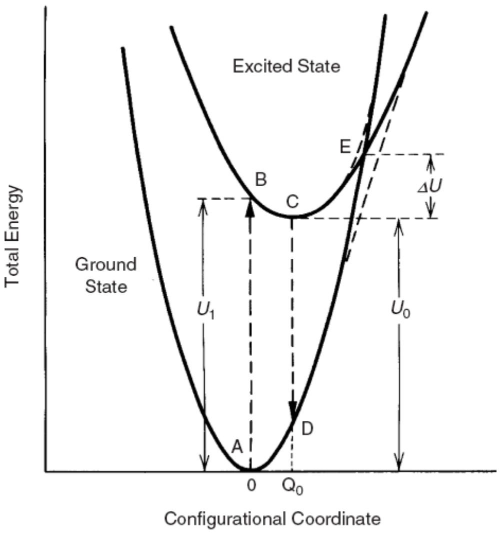
- Typical example: photoluminescence (PL)

Explanation? Model?

- Processes:
  - **Excitation** of an ion (absorption of light)
  - Desexcitation:
    - Non-radiative decay
    - Radiative decay: **emission** of 'light'

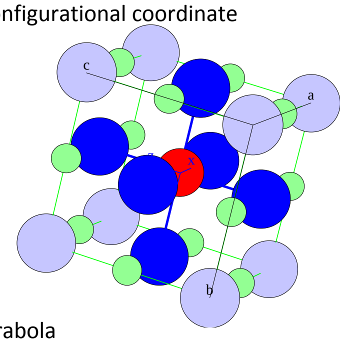
- **Difference** in energy excitation-emission: **Stokes shift**

Configuration coordinate diagram



Components

- Configurational coordinate



- Parabola
- Vertical transitions

$$U_e = K_e \frac{(Q-Q_0)^2}{2} + U_0$$

- Relaxation
- Stokes shift
  $= E_{abs} - E_{em}$
- Intersystem crossing
- Thermal quenching

Stokes shift

- Assume equal force constants for g and e:

$$\frac{1}{2}k\left(R_0^{'}-R_0\right)^2 = S\hbar\omega$$

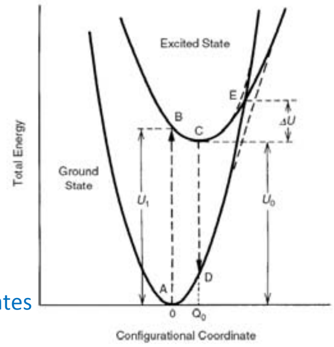
- With $\hbar\omega$ the phonon energy; S = Huang-Rys parameter.
  The Stokes shift becomes:

$$\Delta E_s = k\left(R_0^{'}-R_0\right)^2 = 2S\hbar\omega$$

- S = average number of phonons emitted.

$$S \sim (R_0'-R_0)^2$$

- **3 cases:**
  S < 1: weak coupling (4f-4f); zero-phonon dominates
  1 < S < 5: intermediate coupling
  S > 5: strong coupling; large Stokes shift



Luminescence: basic processes
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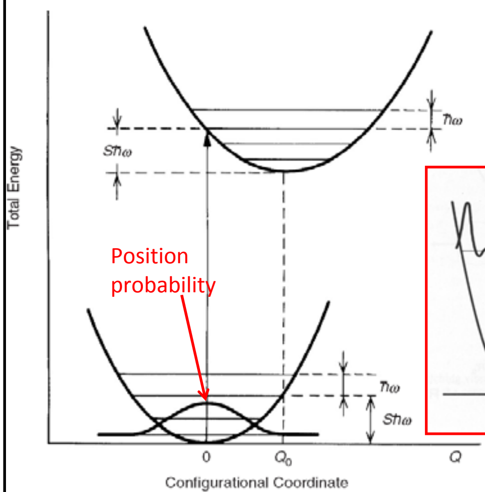
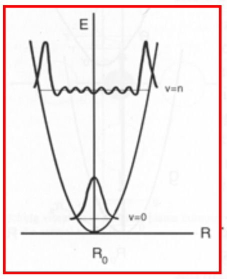
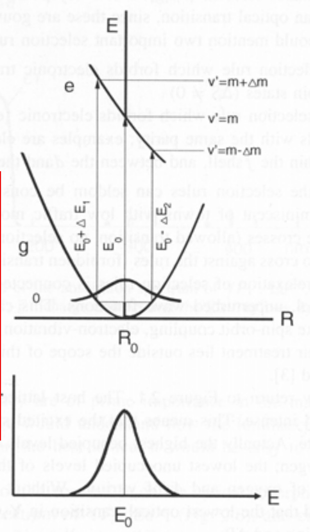
Band width

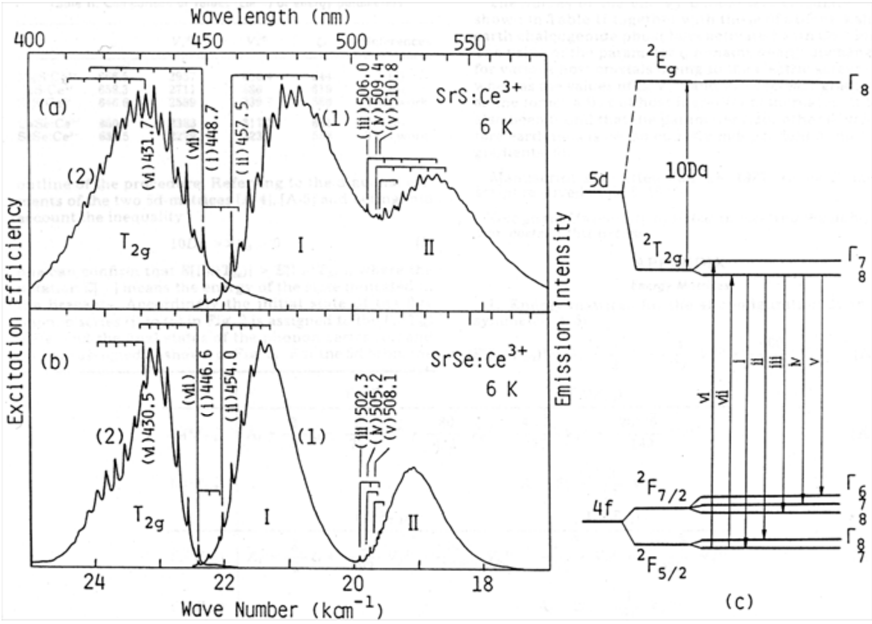




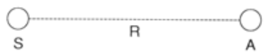


- **Gaussian** shaped (absorption) **bands**
- Width is ~ $R_0'-R_0$
  = measure of the electron – lattice coupling

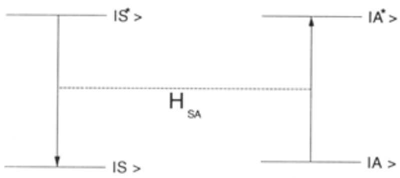
Phonon lines in SrS(e):Ce



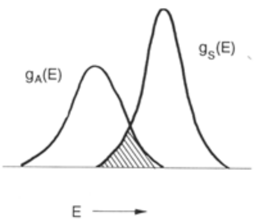
Energy transfer



S = sensitizer
A = activator



Transfer from S to A if overlap between the emission from S **$g_S(E)$** and the absorption of A **$g_A(E)$**



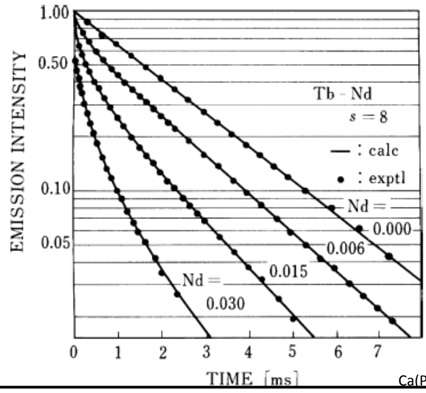
$$P_{SA} = \frac{2\pi}{\hbar} \left| \langle S, A^* | H_{SA} | S^*, A \rangle \right|^2 \int g_S(E) g_A(E) dE$$

Energy transfer

$$P_{SA} = \frac{2\pi}{\hbar} \left| \left\langle S, A^* \middle| H_{SA} \middle| S^*, A \right\rangle \right|^2 \int g_S(E) g_A(E) dE$$

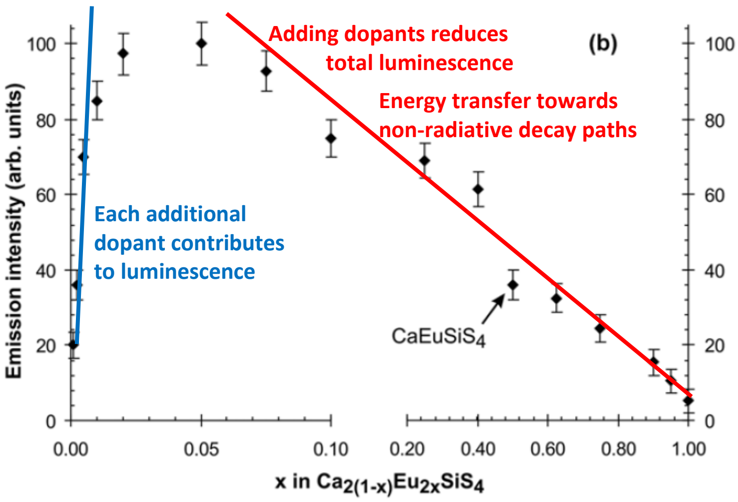
3 types of interactions:

- Exchange interaction (wave function overlap): distance $R_{S-A} < 0{,}8$ nm
- Multipole interactions: $P_{SA} \sim R_{S-A}^{-n}$
  For dipole interactions: $n = 6$; $R_{S-A} < 5$ to 10 nm
- Radiative transition: emission from S is absorbed by A: usually less important



Ca(PO3)2:Tb,Nd, Phosphor Handbook

Concentration quenching

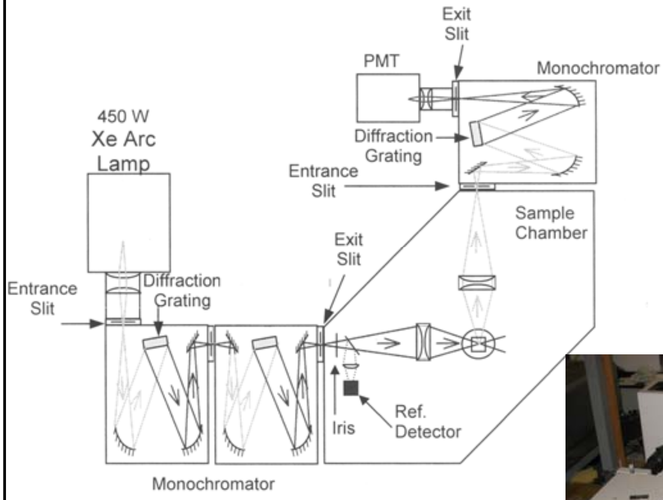


Ideal dopant concentration:

- Depends on type of host and dopant
- Ranges from 0.1% to 10% substitution

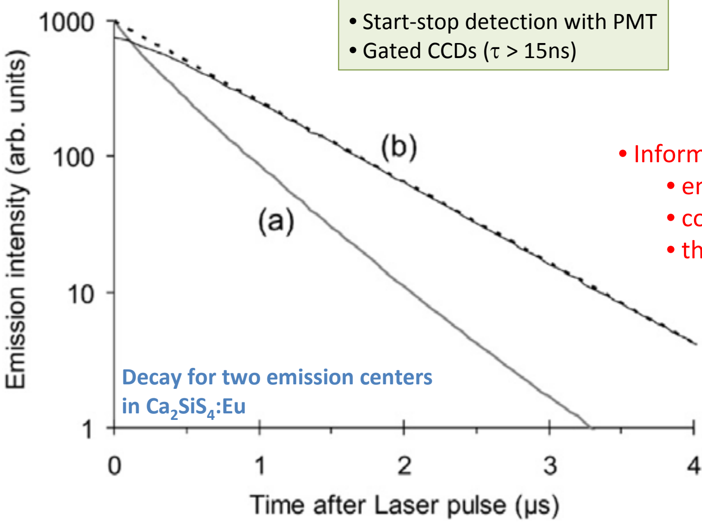
J. Phys.: Condens. Matter **19** (2007) 246223

Photoluminescence: emission-excitation



Photoluminescence: decay spectroscopy

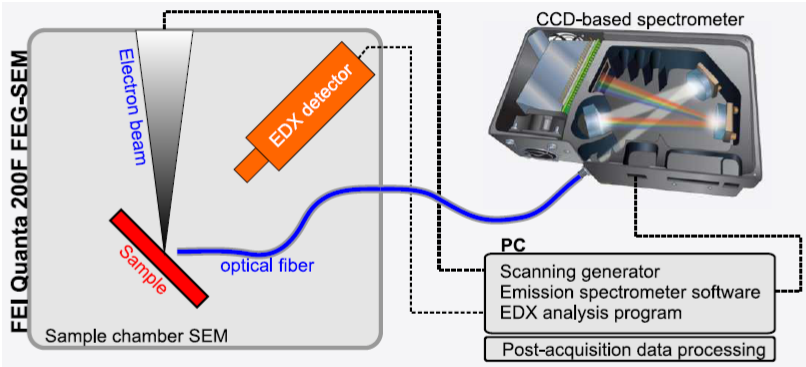
- Pulsed excitation source
  (laser (<1ns), LEDs (~5ns))
- Start-stop detection with PMT
- Gated CCDs (τ > 15ns)



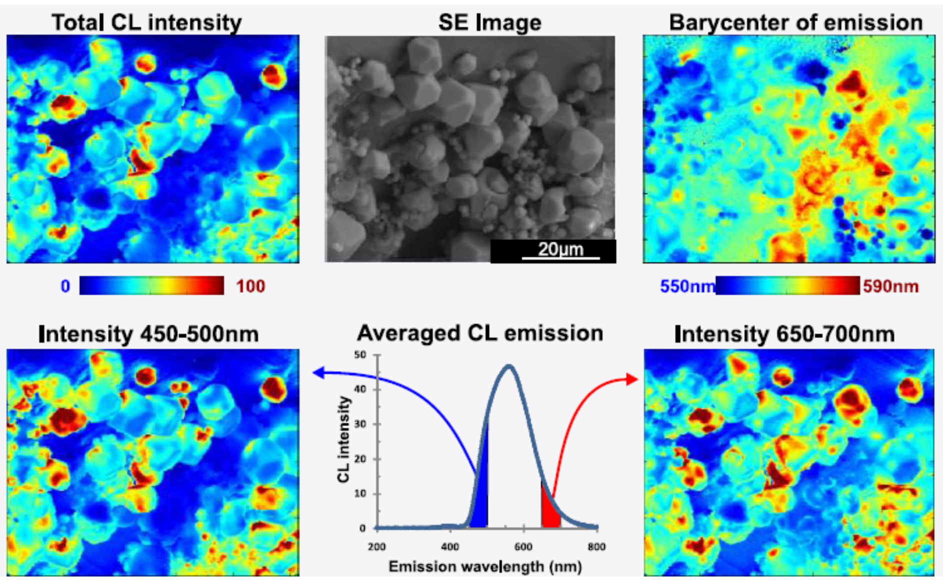
- Information:
  - energy transfer
  - concentration quenching
  - thermal quenching

Luminescence at microscopic level

- Fluorescence microscopy
- Cathodoluminescence in electron microscopy

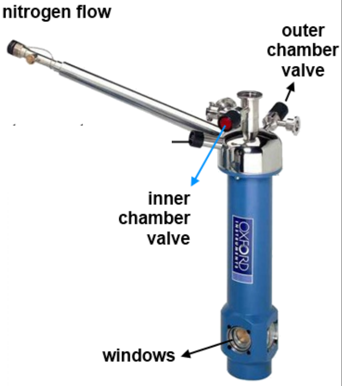


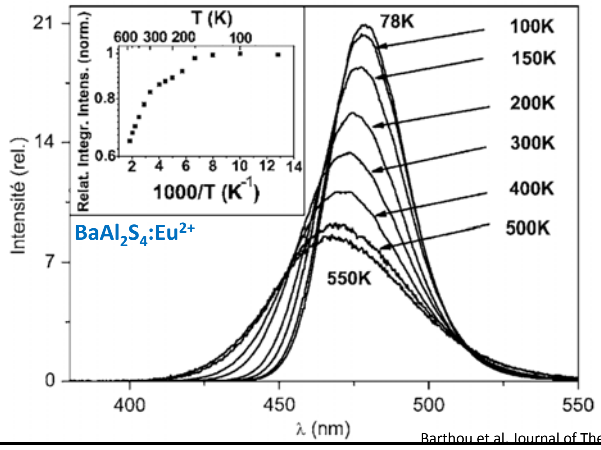
- Cathodoluminescence in electron microscopy
  Example: SrS:Eu|SrS:Ce core shell particles



Temperature dependency

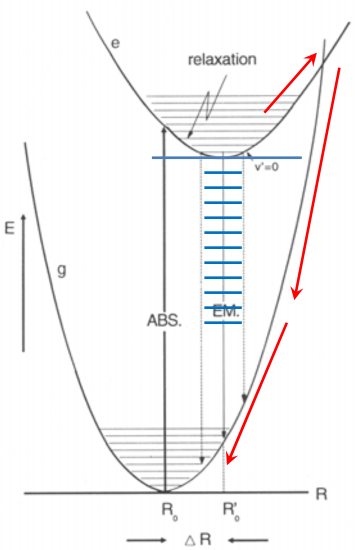
- **Temperature quenching**
- Spectral shifts
- Broadening (phonon coupling strength)
- Low temperature: phonon energies
- Energy transfer
- Thermoluminescence



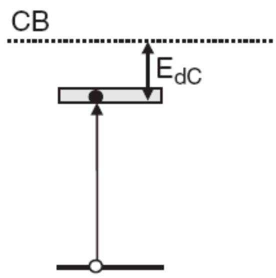


Barthou et al, Journal of The Electrochemical Society, 153, G253-G258 (2006)

Temperature quenching



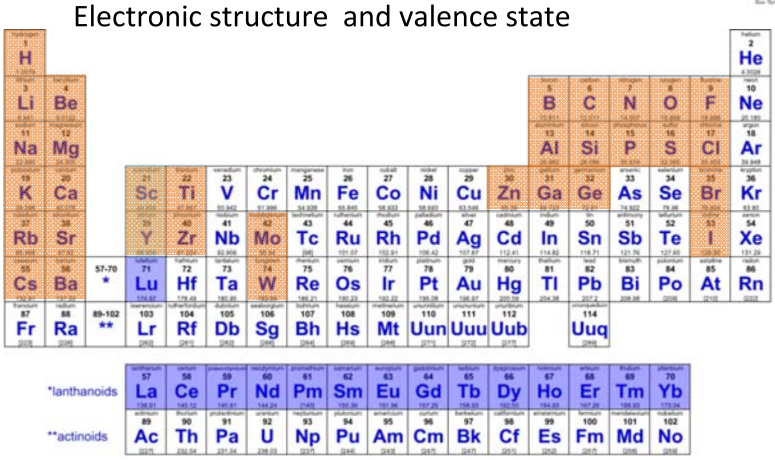
- **Crossing g-e intersection by thermal energy**
- **Multiple phonon emission**
- **Interaction with host conduction bands**



Blasse, Phosphor Handbook

Part II. Luminescence in rare-earth compounds. Physics and applications.

Electronic structure and valence state



- **Rare earths (RE)** = **lanthanides (La-Lu)** + **Sc** + **Y**
- Stable valence states: 2+ (some) , 3+ (all), 4+(a few)
- Trivalent lanthanides: Ln^{3+} : $[Xe]4f^n$
- Ce^{3+} ($4f^1$), Nd^{3+} ($4f^3$),...
- Host materials

Transitions in RE ions

- Transitions in RE ions favorable for luminescence
- Emission from **UV** to **near-IR**

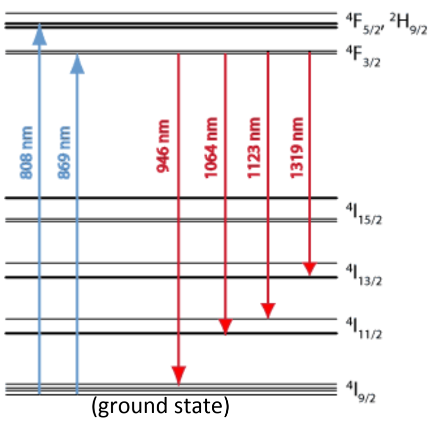
- Used in many light-applications based on luminescence
  (lasers, LEDs, lamps, displays, dosimeters...)

- Two types of RE-emission:

  - ground state $4f^n$ – excited state $4f^n$ ***(f-f emittors)***
    - **Emission lines** (FWHM < 10nm)
    - Largely independent of host
    - 4f-electrons shielded by outer s and p orbitals

  - ground state $4f^n$ – excited state $4f^{n-1}5d$ ***(d-f emittors)***
    - **Emission bands** (FWHM: 30-100nm)
    - Strongly dependent on host
    - Spatially extended 5d electron orbitals

4f-4f emittor: Nd^{3+} as example



Nd:YAG laser ($Y_3Al_5O_{12}$:Nd^{3+})
- 1064nm emission
- 532nm/355nm with frequency doubling/tripling

- **Nd^{3+}: $4f^3$**
- 4f-electron: s = ½, ℓ = 3
  (14 possible states)

- 364 different electron configurations
  (Pauli principle!)

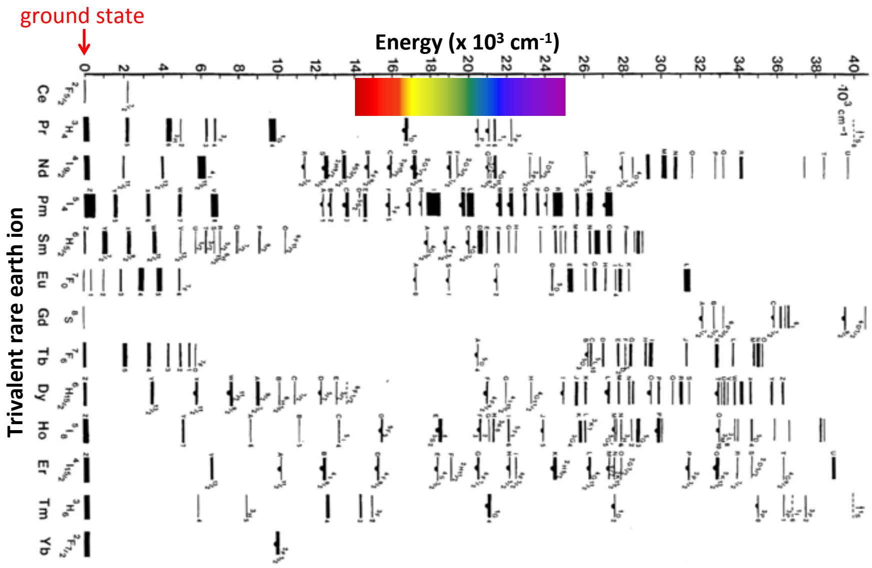
- Ordered in 'terms' $^{2S+1}L_J$
  (Russell-Saunders notation)

- Each term split along M_J (M_J = -J,... , J-1, J)
  - Stark levels
  - Depends on host compound

- Selection rules (ΔS, ΔL, ΔJ)
  - Transition probability
  - Decay rates

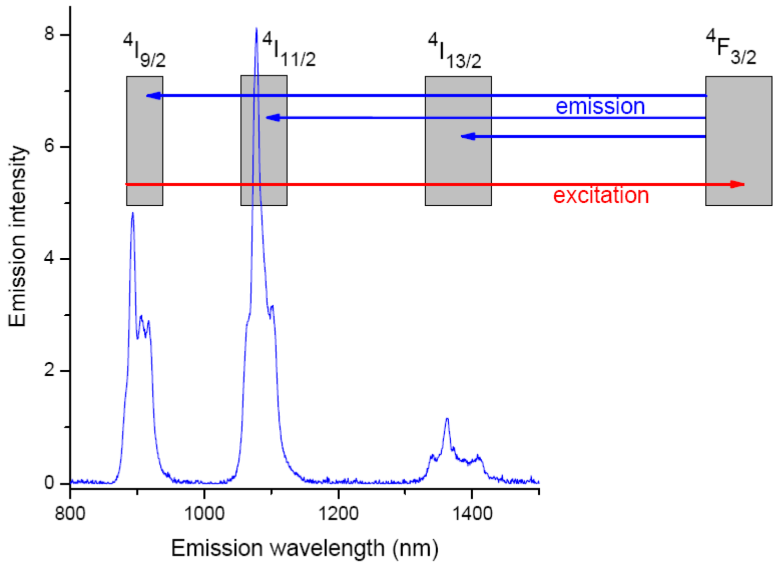
www.rp-photonics.com/img/ndyag_levels.png

4f^n energy levels of trivalent RE ions: Dieke's diagram



G. H. Dieke and H. M. Crosswhite, Appl. Opt., 1963, 2, 675–686

4f-4f emittor: Nd^{3+} as example



Emission spectrum $Ca_2SiS_4:Nd^{3+}$. Smet PF et al., J. Electrochem. Soc. 156 , H243-H248 (2009)

Luminescence in rare earth (RE) ions

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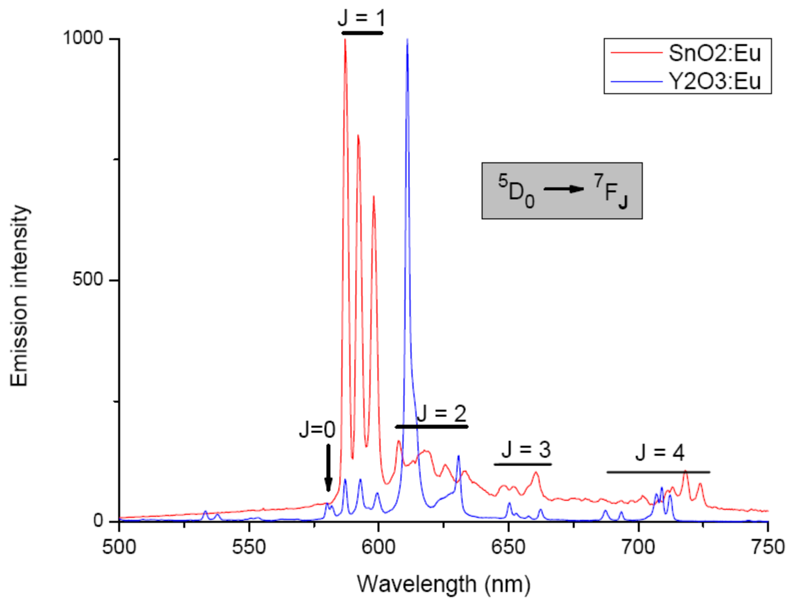
4f-4f emittor: Eu^{3+} emission



Luminescence in rare earth (RE) ions

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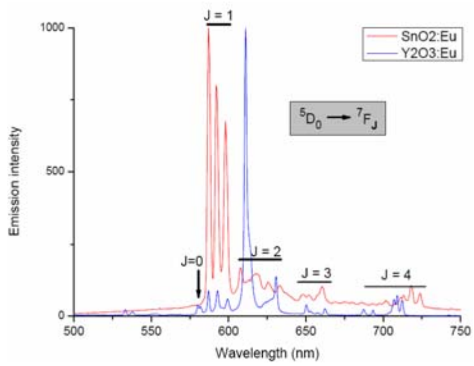
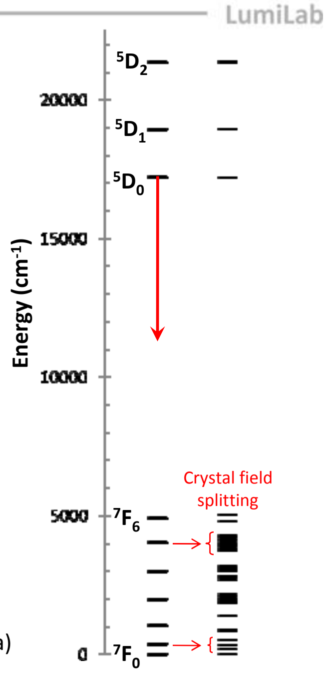
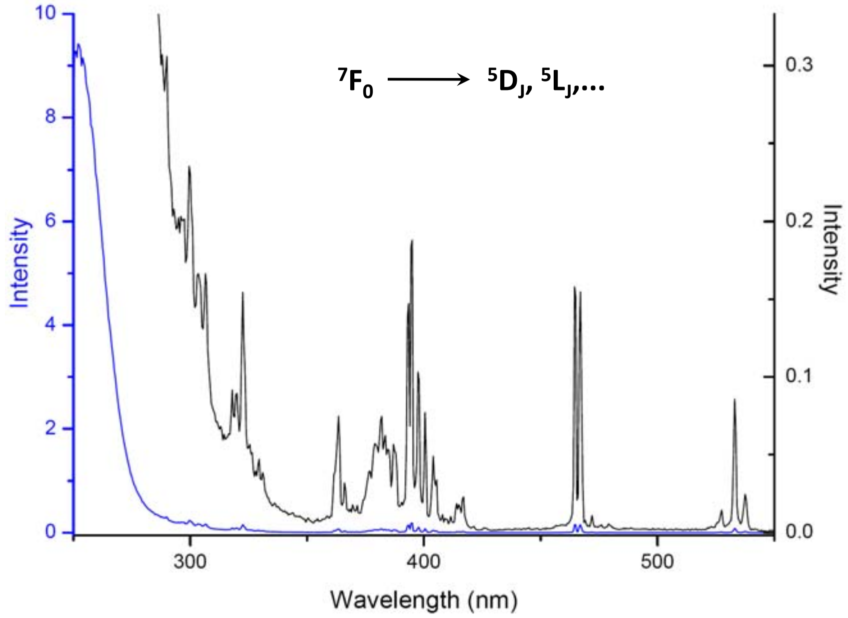
4f-4f emittor: Eu^{3+} emission



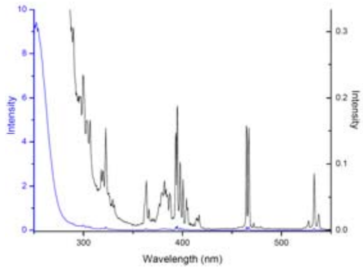


- **Stark splitting** (M_J): depends on host
- Transition probabilities: hypersensitivity to symmetry
- Decay time: typ. 1-2ms ('forbidden' transition)
- Small stokes shift (little displacement in energy parabola)

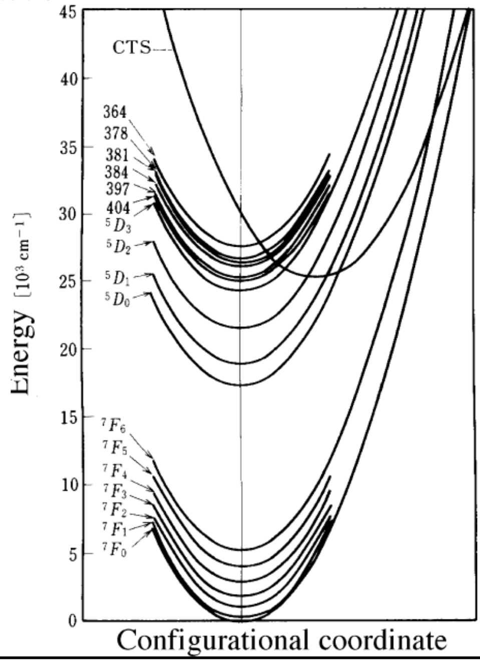
4f-4f emittor: Eu^{3+} excitation



4f-4f emittor: Eu^{3+} excitation



- **CTS: charge transfer state**
  e^- (VB) to Eu^{3+}
  recombination and Eu^{3+*}
- Efficient transition < 300nm
  (large cross-section)
- **In Yb^{3+} CT luminescence**
- **Sensitizes Eu^{3+} 4f-4f emission**
- CTS energy depends on host and
  electronegativity of anion



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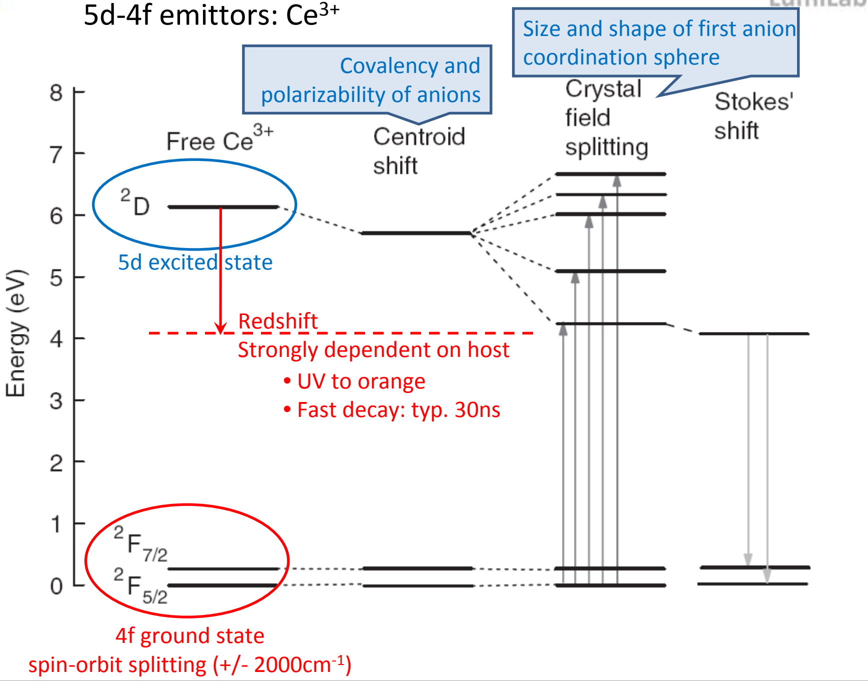
5d-4f emittors: Ce^{3+}



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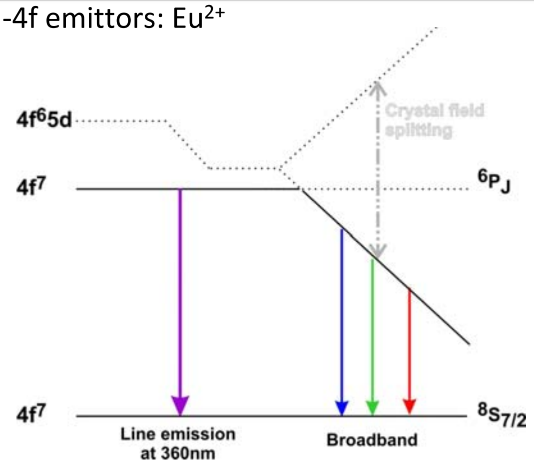
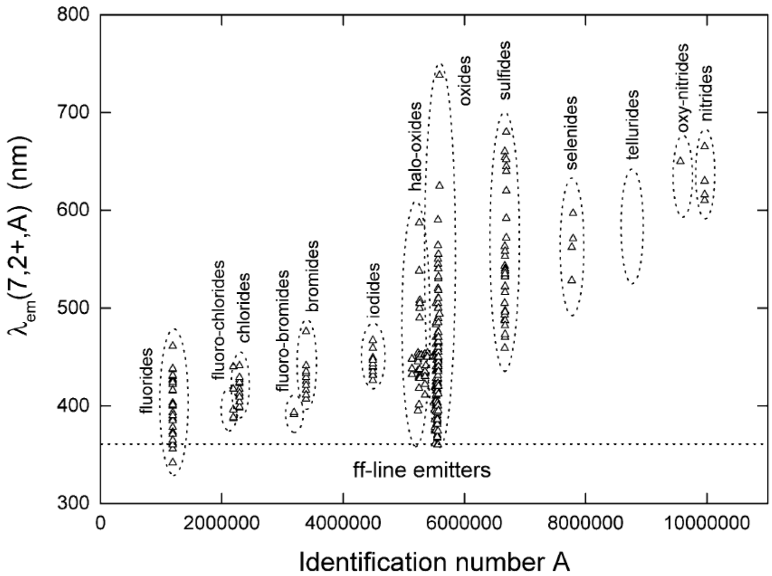
5d-4f emittors: Eu^{2+}



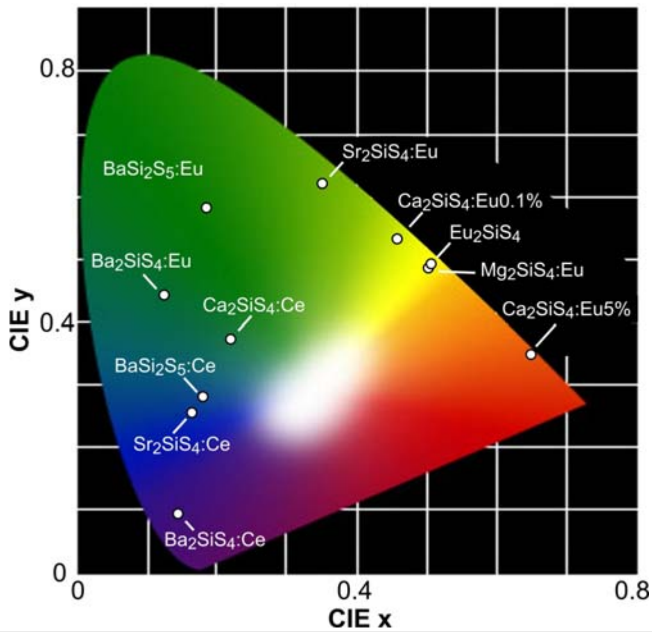
- Fluorides

- Most other compounds
- Decay time: 300-900ns
- Blue to red (tunable)
- FWHM: typ. 30-80nm

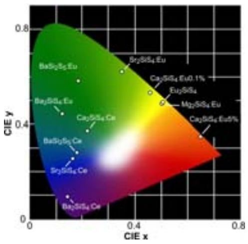
5d-4f emittors: Eu^{2+}

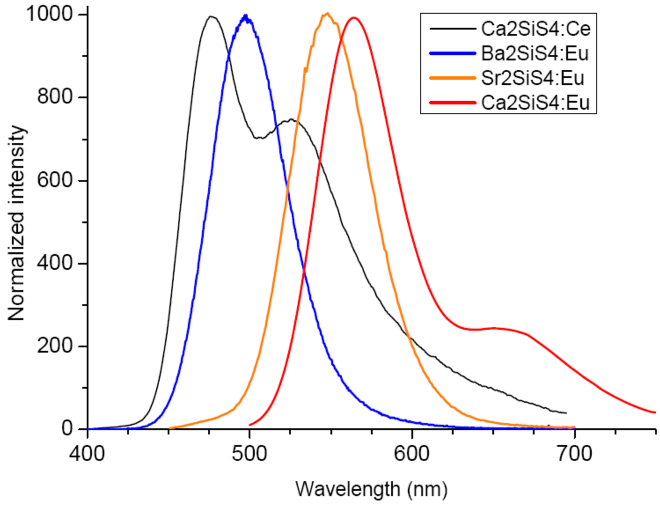


5d-4f emittors: influence of host



5d-4f emittors: influence of host

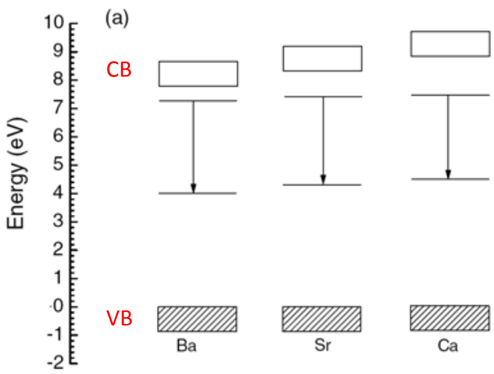




Energy level positions in semiconductors

Modelling of RE energy levels with respect to host's band structure

- Emission spectrum (influence of host composition)
- Identification of **'anomalous' emission**
- Thermal quenching (interaction 5d-CB)



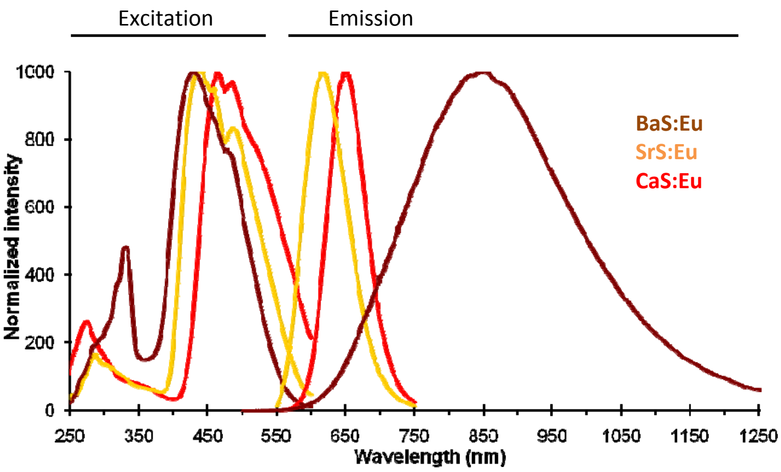
- Bottom CB determined by M cation
- Eg: Ba < Sr < Ca
- CTS: Ba < Sr < Ca
- E(5d-4f): Ba > Sr > Ca
- $T_{0.5}$: Ba < Sr < Ca

Type I compounds (MO, MS, MF_2, with M= Ca, Sr or Ba), doped with Eu^{2+}

Energy level positions in semiconductors

Modelling of RE energy levels with respect to host's band structure

- Identification of **'anomalous' emission** (e.g. in BaS:Eu)



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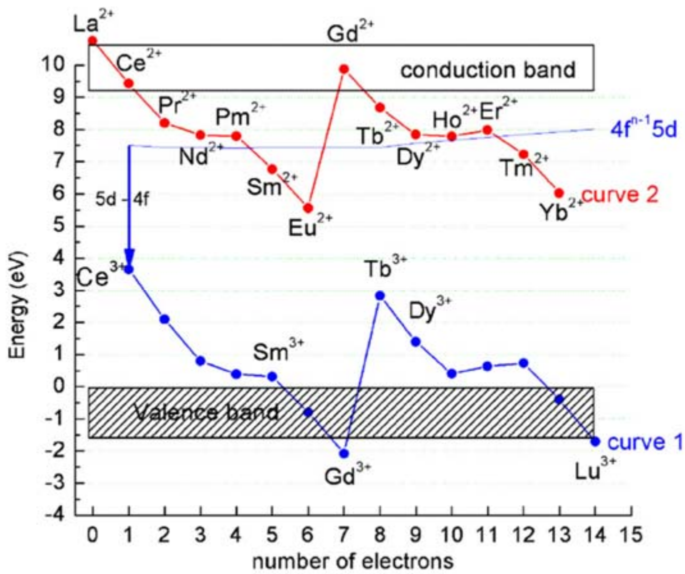
Energy level positions in semiconductors



Overview

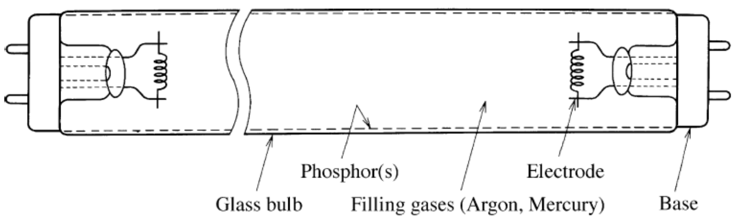
Applications of rare earth luminescence

- Lamp and display phosphors.
- LED conversion phosphors.
- Afterglow (persistent) and storage phosphors.
- Quantum cutting phosphors.
- Upconversion phosphors.

Lamp phosphors

- Fluorescent tubes
- Energy saving bulbs

- Working principle:



- Discharge and excitation of mercury atoms
- Hg emits UV (254nm, 365nm) and visible light
- **Phosphor coating converts UV to visible light**
- Colour and colour rendering determined by phosphor composition

Applications of rare earth luminescence

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Lamp phosphors

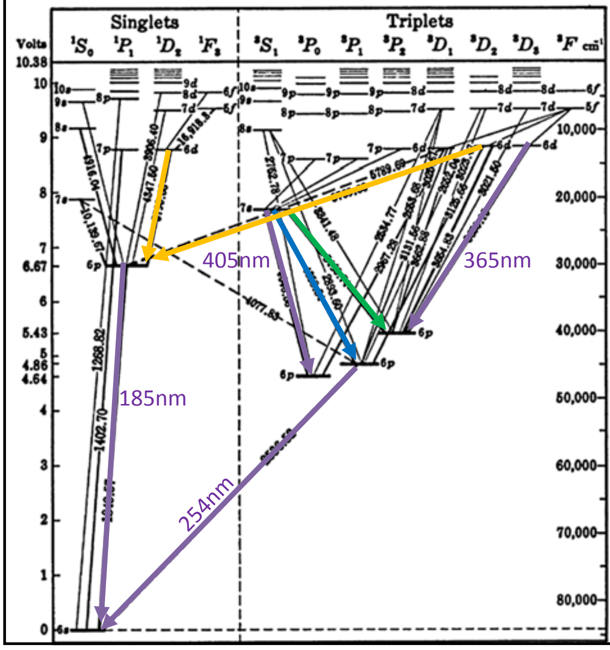

Table 2 Energy Conversion Ratio in Positive Column of Fluorescent Lamp

Discrimination		Rate (%)
Radiation	185 nm	5
	254 nm	60
	others	6
Elastic collision loss		28
Recombination loss		1
Total		100

Phosphor: QE ~ 0.90 – 0.95
Stokes Loss: ~ 50%

Total energy efficiency: 20-25%
(~ 70 lum/W)

Applications of rare earth luminescence

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Lamp phosphors

Luminescence center	Chemical composition	Peak wavelength (nm)	Luminescence color
Tl^{+}	$(Ca,Zn)_3(PO_4)_2$:Tl^{+}	310	Ultraviolet
	$Ca_3(PO_4)_2$:Tl^{+}	328	Ultraviolet
Mn^{2+}	$MgGa_2O_4$:Mn^{2+}	510	Green
	$BaMg_2Al_{16}O_{27}$:Eu^{2+},Mn^{2+}	(450), 515	Green
	Zn_2SiO_4:Mn^{2+}	525	Green
	$3Ca_3(PO_4)_2$·$Ca(F,Cl)_2$:Sb^{3+},Mn^{2+}	(480), 575	Warm white
	$CaSiO_3$:Pb^{2+},Mn^{2+}	610	Orange
	$Cd_2B_2O_5$:Mn^{2+}	620	Pink
	$GdMgB_5O_{10}$:Ce^{3+},Mn^{2+}	630	Orange
	$GdMgB_5O_{10}$:Ce^{3+},Tb^{3+},Mn^{2+}	(543), 630	Orange
Sn^{2+}	$Sr_2P_2O_7$:Sn^{2+}	464	Blue
	$(Sr,Mg)_3(PO_4)_2$:Sn^{2+}	620	Orange
Eu^{2+}	SrB_4O_7F:Eu^{2+}	360	Ultraviolet
	$SrMgP_2O_7$:Eu^{2+}	394	Blue
	$(Sr,Ba)Al_2Si_2O_8$:Eu^{2+}	400	Blue
	$Sr_3(PO_4)_2$:Eu^{2+}	408	Blue
	$Sr_2P_2O_7$:Eu^{2+}	420	Blue
	$Ba_3MgSi_2O_8$:Eu^{2+}	435	Blue
	$Sr_{10}(PO_4)_6Cl_2$:Eu^{2+}	447	Blue
	$BaMg_2Al_{16}O_{27}$:Eu^{2+},Mn^{2+}	450, (515)	Blue
	$(Sr,Ca)_{10}(PO_4)_6Cl_2$:Eu^{2+}	452	Blue
	$(Sr,Ca)_{10}(PO_4)_6$·nB_2O_3:Eu^{2+}	452	Blue
	$BaMg_2Al_{16}O_{27}$:Eu^{2+}	452	Blue
	$SrMgAl_{10}O_{17}$:Eu^{2+}	465	Blue
	$BaAl_8O_{13}$:Eu^{2+}	480	Blue-green
	$2SrO$·$0.84P_2O_5$·$0.16B_2O_3$:Eu^{2+}	480	Blue-green
	$(Sr,Ca,Mg)_{10}(PO_4)_6Cl_2$:$Eu^{2+}$	483	Blue-green
	$Sr_2Si_3O_8$·$2SrCl_2$:Eu^{2+}	490	Blue-green
	$Sr_4Al_{14}O_{25}$:Eu^{2+}	493	Blue-green
Pb^{2+}	$(Ba,Mg,Zn)_3Si_2O_7$:Pb^{2+}	295	Ultraviolet
	$BaSi_2O_5$:Pb^{2+}	350	Ultraviolet
	$(Ba,Sr,Mg)_3Si_2O_7$:Pb^{2+}	370	Ultraviolet
Sb^{3+}	$3Ca_3(PO_4)_2$·$Ca(F,Cl)_2$:Sb^{3+}	480	Blue-white
	$3Ca_3(PO_4)_2$·$Ca(F,Cl)_2$:Sb^{3+},Mn^{2+}	480, (575)	Blue-white
Tb^{3+}	$CeMgAl_{11}O_{19}$:Ce^{3+},Tb^{3+}	543	Green
	$LaPO_4$:Ce^{3+},Tb^{3+}	543	Green
	La_2O_3·$0.2SiO_2$·$0.9P_2O_5$:Ce^{3+},Tb^{3+}	543	Green
	Y_2SiO_5:Ce^{3+},Tb^{3+}	543	Green
	$GdMgB_5O_{10}$:Ce^{3+},Tb^{3+}	543	Green
	$GdMgB_5O_{10}$:Ce^{3+},Tb^{3+},Mn^{2+}	543, (630)	Green
Eu^{3+}	Y_2O_3:Eu^{3+}	611	Red
	$Y(V,P)O_4$:Eu^{3+}	619	Red
Dy^{3+}	YVO_4:Dy^{3+}	(480), 570	White
Fe^{3+}	$LiAlO_2$:Fe^{3+}	735	Infrared
Mn^{4+}	$6MgO$·As_2O_5:Mn^{4+}	655	Deep red
	$3.5MgO$·$0.5MgF_2$·GeO_2:	655	Deep red
WO_4^{2-}	$CaWO_4$	415	Blue
	$(Ca,Pb)WO_4$	435	Blue
	$MgWO_4$	480	Blue-white
TiO_4^{4-}	BaO·TiO_2·P_2O_5	483	Blue-white

Eu^{2+}

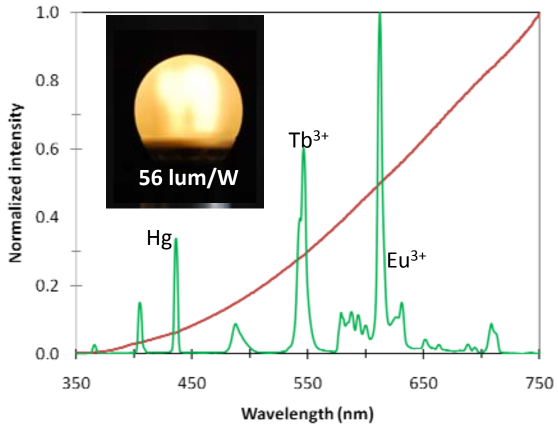
Tb^{3+}

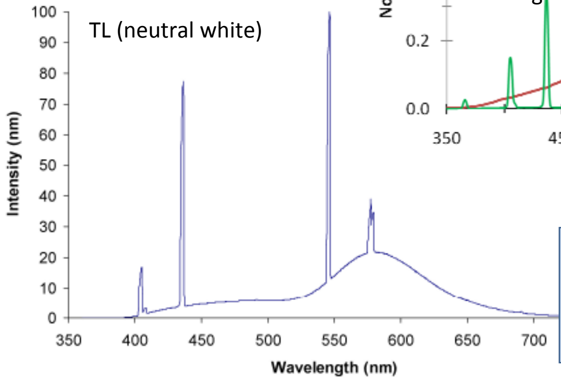
Eu^{3+}

Ce^{3+} as sensitizer for Tb^{3+} !

Phosphor Handbook, 2nd Edition, CRC Press, p. 455

Lamp phosphors





<u>Note for the Spectroscopist</u>

Fluorescent lamps are ideal wavelength calibration sources!

Applications of rare earth luminescence
LumiLab

Display phosphors

- **RE luminescence used in all display types...**
  - Cathode Ray Tube (**CRT**) : cathodoluminescence
  - Plasma Display Panel (**PDP**): Xe excitation (172nm)
  - Field emission display (FED)
  - Thin film electroluminescent displays (EL)
  - Liquid Crystal Display (**LCD**)
    - CCFL backlight (cold cathode fluorescent lamp)
    - LED-based backlight (= LED television)

Lighting technologies

Motivation for research in lighting technology

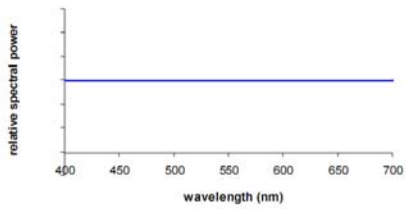
- **Lighting consumes large fraction of total energy production**
- Different technologies:
  - Incandescent lights (also tungsten halogen)
  - Fluorescent light tubes
  - Light emitting diodes (LEDs)

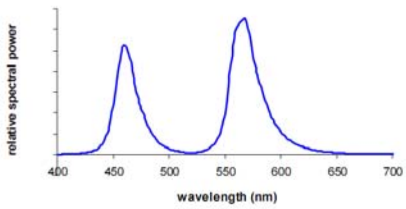
Evaluation criteria

determines overall cost {
- Efficiency (lum/W): theoretical limit for white light: ~400 lum/W
- Production cost (€/lum)
- Lifetime
}
- Environmental impact
- Temperature operating range
- Colour temperature (CCT, comparison to black body radiator)
- Colour rendering index (CRI, Ra)

Lighting technologies: CRI

Two white light sources...





Applications of rare earth luminescence

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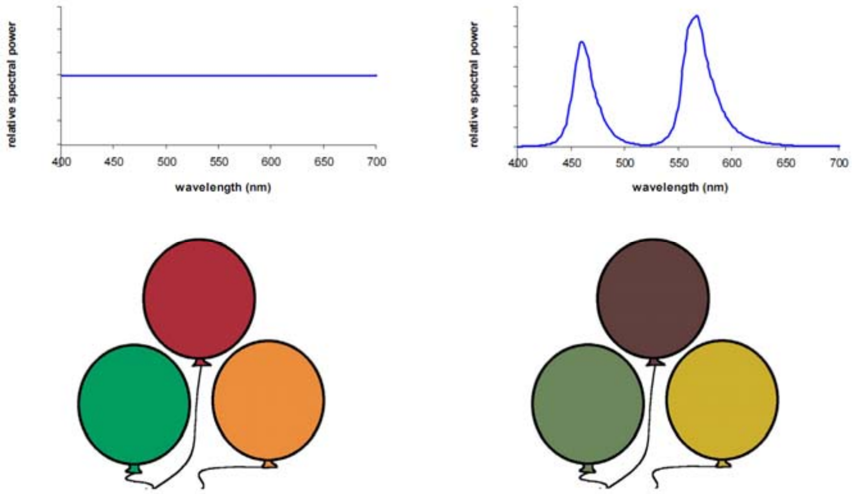
Lighting technologies: CRI

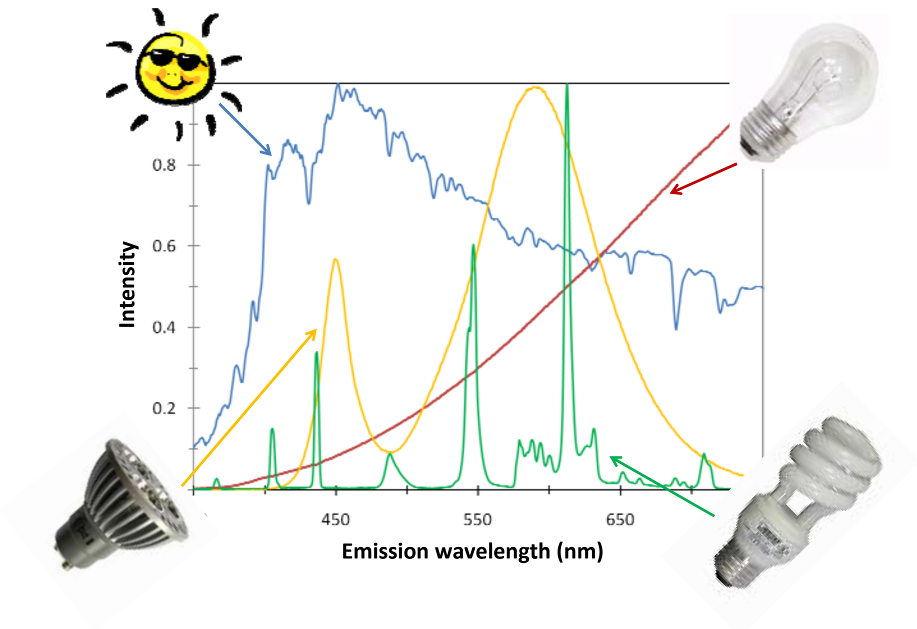
... reproduce colours in a different way!



Applications of rare earth luminescence

LumiLab

Lighting technologies



Applications of rare earth luminescence

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Lighting technologies

Criterion	Incandescent	Fluorescent	LED
Efficiency (lum/W)	10-15	50-70	60
Light output (lum)	>1000	>1000	<300
Lifetime (h)	1.5k	5k-10k	15k
Production cost (€/lum)	Low	Moderate	High
Temperature range	wide	narrow	wide
Size	large	large	small
Colour rendering	100	70-90	typ. 70
Colour temperature	<3000K	all	"all"

Applications of rare earth luminescence

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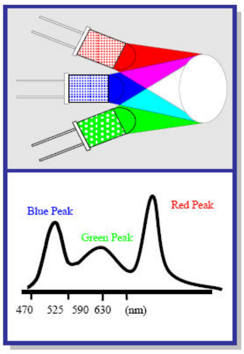
White LED approaches

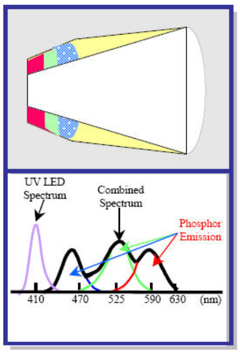
Red + Green + Blue LEDs



RGB LEDs

- Different ageing
- Dimming problems
- Colour mixing: -
- **Smart light sources**

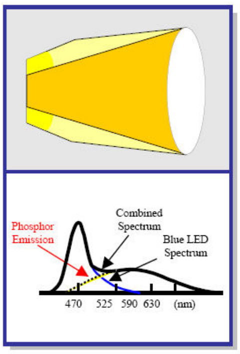
UV LED + RGB Phosphor



UV LED + RGB phosphor

- **Full phosphor approach**
- Inspired by fluorescent lamps
- No colour differences

Binary Complimentary

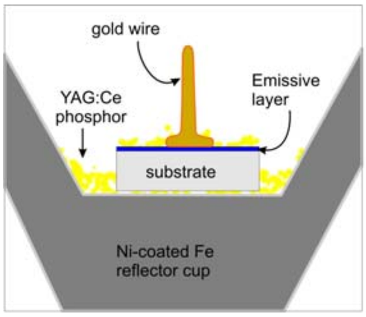


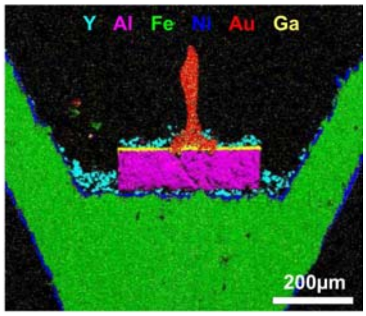
Blue LED + Yellow phosphor

- **Current favorite**
- Yellow or Green+Red
- Halo to be avoided

LED conversion phosphors

- LED chip has strong edge emission
- Placed in reflective cup
- Topped with phosphor (“YAG:Ce”)
- Loading determines converted fraction (colour temperature)
- White light is created
- Packaging determines light cone





LED conversion phosphors

Requirements for LEDs.

A good phosphor satisfies ALL requirements

- Emission spectrum
  - Phosphor(s)+LED must yield white light
  - Spectrum determines efficiency (lum/W) and colour rendering
- Excitation spectrum
  - Good overlap with pumping LED
  - Sufficiently flat around LED emission (high current: shift of LED peak)
- Thermal behaviour
  - No thermal quenching up to 150°C
  - No colour shifts
- Quantum efficiency
  - As high as possible (90-100%)
- No saturation
  - High flux devices (Mn^{2+} less suited)
- Stability (lifetime)
  - Chemically and thermally stable materials

Applications of rare earth luminescence

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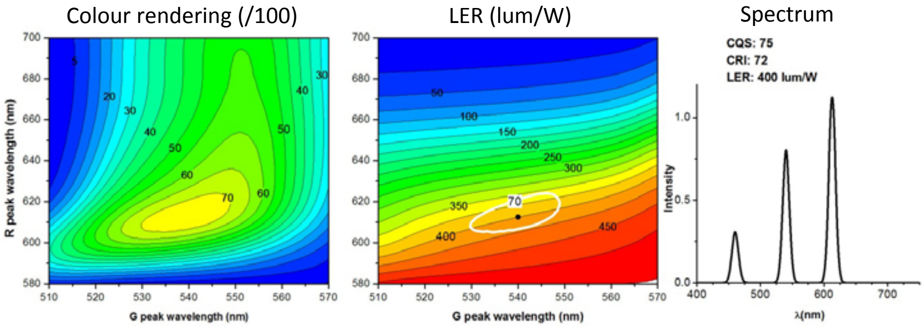
LED conversion phosphors: emission spectrum

- Narrow emittors or broad band emittors?
  - 3 Narrow light sources (FWHM = 10nm)
    - High efficiency
    - Poor colour rendering



Simulates use of Tb^{3+} (green) and Eu^{3+} (red)... if they could be excited...

Applications of rare earth luminescence

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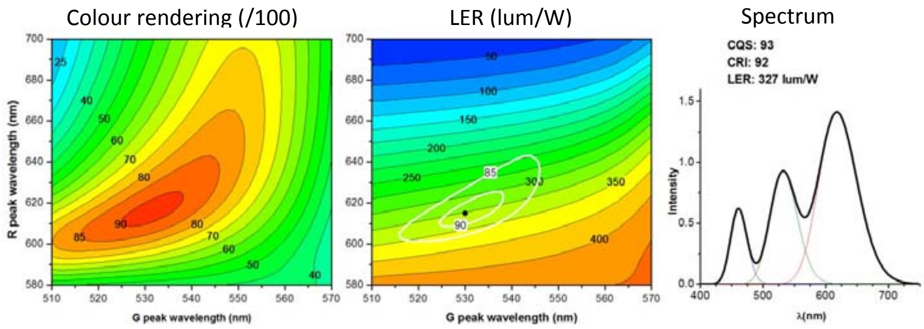
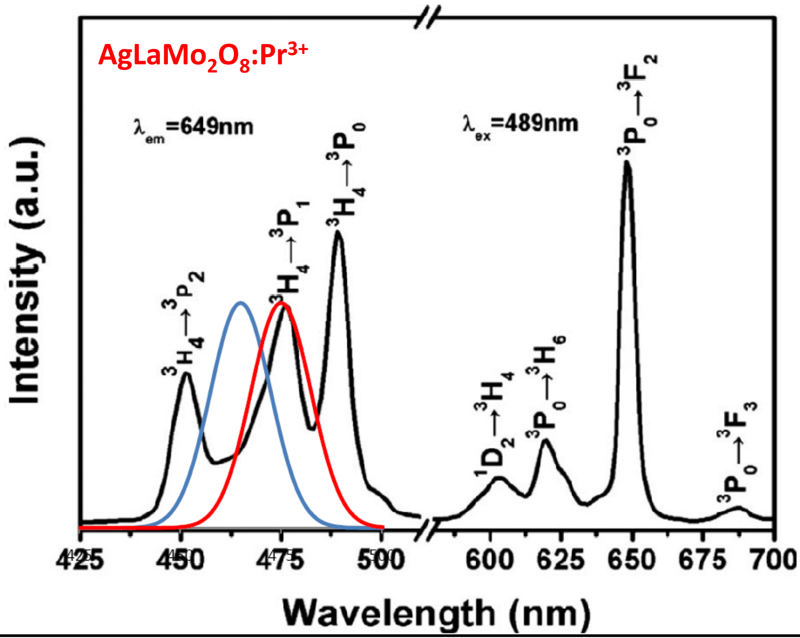
LED conversion phosphors: emission spectrum

- Narrow emittors or broad band emittors?
  - 3 Narrow light sources (FWHM = 10nm)
    - High efficiency
    - Poor colour rendering
  - 3 Broad light sources (FWHM = 30nm (B) – 50nm (G) – 70nm (R))
    - Lower efficiency
    - Good colour rendering

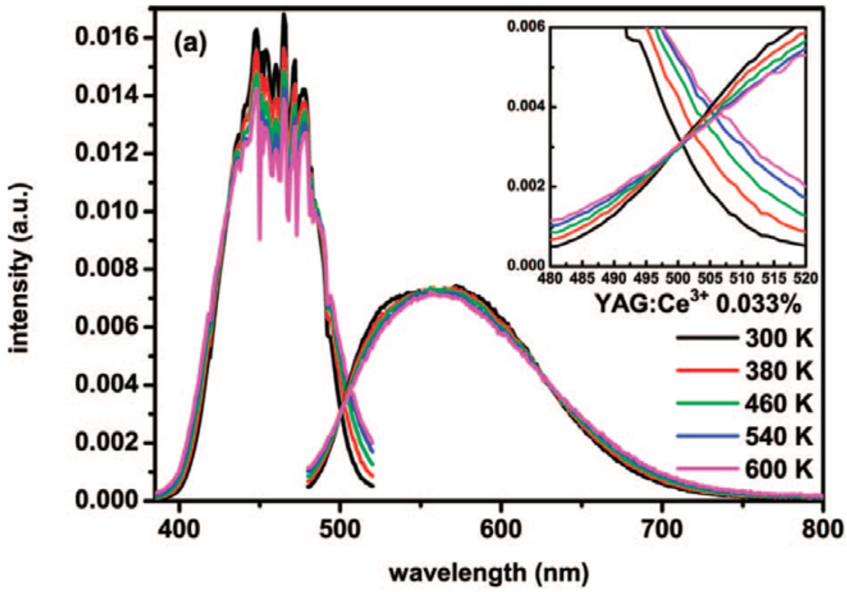


Simulates use of Ce^{3+} and Eu^{2+} (and Mn^{2+})

LED conversion phosphors: excitation spectrum (f-f)



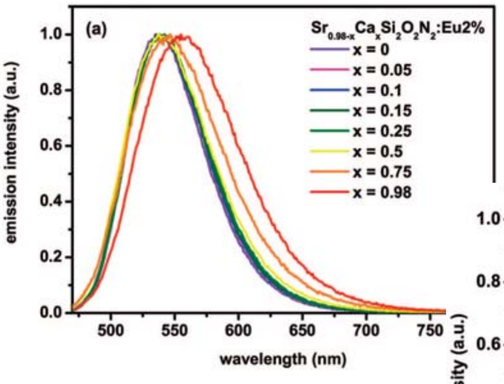
LED conversion phosphors: excitation spectrum (d-f)



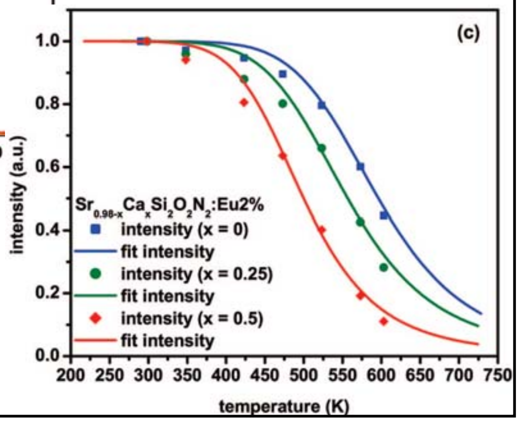
Chem. Mater. **2009,** *21,* 2077–2084

LED conversion phosphors: thermal quenching

$Sr_{0.98-x}Ca_xSi_2O_2N_2:Eu_{0.02}$



$$I(T) = \frac{I_0}{1 + De^{\frac{-E_A}{kT}}}$$



Chem. Mater., Vol. 21, No. 2, 2009

LED conversion phosphors: (quantum) efficiency

Fraction absorbed by each phosphor

$$\sum_i f_i = 1$$

Quantum efficiency of each phosphor

Efficiency of entire device (electrical P in / optical P out)

$$\eta_{e-o} = \frac{P_{el}}{P_{opt}} = \eta_L \sum_i f_i Q_{P,i} \frac{\overline{\lambda}_L}{\overline{\lambda}_{P,i}}$$

Stokes loss of conversion

$$\eta_L = \frac{P_{el,L}}{P_{opt,L}}$$

Electrical to optical power conversion efficiency of LED

$$\overline{\lambda} = \frac{\int I(\lambda)\lambda d\lambda}{\int I(\lambda) d\lambda}$$

LED conversion phosphors: (quantum) efficiency

Blue LED (typ. 460nm) and one phosphor (e.g. YAG:Ce):

$$\eta_{e-o,B} = \eta_{L,B}\left[f + (1-f)Q_P\frac{\overline{\lambda}_{L,B}}{\overline{\lambda}_P}\right]$$

UV LED and two phosphors :

$$\eta_{e-o,UV} = \eta_{L,UV}\left[fQ_{P_1}\frac{\overline{\lambda}_{L,UV}}{\overline{\lambda}_{P_1}} + (1-f)Q_{P_2}\frac{\overline{\lambda}_{L,UV}}{\overline{\lambda}_{P_2}}\right]$$

$$\eta_{e-o,B} = 0.81\eta_{L,B}$$ (460nm LED, f = 0.33, Q = 0.9, CCT = 5600K)

Considerable loss if UV LEDs are used!
... although there are some advantages...

$$\eta_{e-o,UV} = 0.61\eta_{L,UV}$$ (365nm LED, Q_i = 0.9, CCT = 5600K)

LED conversion phosphors: materials

Criterion	YAG:Ce^{3+}	4f-4f	(oxy)nitride Ce3+/Eu2+	sulfides Ce3+/Eu2+
Emission CCT	low CRI > 4000K	mod CRI full range	high CRI full range	high CRI full range
Excitation	blue	(deep) UV	blue/UV	blue/UV
Thermal	mod/good	good	moderate	poor/mod
Q.E.	>0.9	>0.9	>0.8	>0.6-7
Saturation	no	+/-	no	no
Stability	perfect	good	perfect	poor

YAG:Ce^{3+} → Low CRI, general lighting purposes with high CCT

4f-4f → requires good UV LEDs

(oxy)nitride → for low CCT and high CRI

sulfides → disappearing

Persistent phosphors

What?

- Excitation by day light or fluorescent light
- Energy storage
- Afterglow: slow emission of light

1602: Bolognian Stone (presumably BaS)


IL FOSFORO
O' VERO LA
PIETRA BOLOGNESE
Preparata per rilucere frà l'ombre.
FATICA DI
MARC' ANTONIO CELLIO
Dell' Accademia Fisicomattematica di Roma,
E dal medemo consecrata
All' Eccellentissimo Prencipe
SIGNOR D.
MARC' ANTONIO
BORGHESE.
IN ROMA. Per il Vannacci. 1680.
Con Licenza de' Superiori.

All'Eccellentissimo Signor D.
MARC' ANTONIO BORGHESE
per il libro, che gli consacra il
Sig. Marc'Antonio Cellio
intitolato il Fosforo
ò vero la Pietra
Bolognese.

SONETTO.

Del Sig. Gioseppe Paolucci
Accademico infecondo.

Phosphor Handbook

Applications of rare earth luminescence

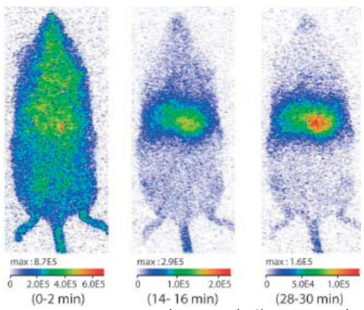
Persistent phosphors

Materials

- ZnS:Cu,Co (1960) (green, 1h)
- $SrAl_2O_4$:Eu^{2+},Dy^{3+} (1995) (green, > 24h)
- Eu^{2+}-based aluminates and silicates

Applications

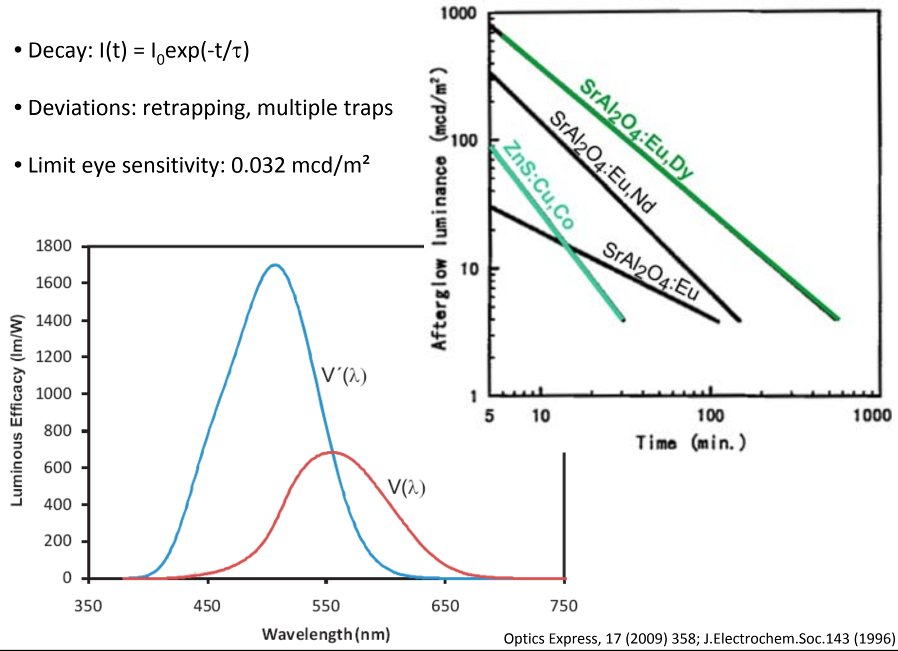
- Emergency signage
- Luminous paint
- Medical imaging
- Thermal and pressure sensor



le Masne de Chermont et al, Proc Natl Acad Sci U S A. 2007 May 29; 104(22): 9266–9271

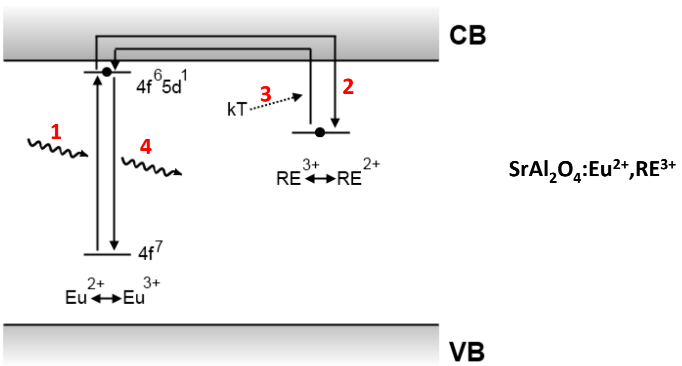
Persistent phosphors

- Decay: $I(t) = I_0 \exp(-t/\tau)$
- Deviations: retrapping, multiple traps
- Limit eye sensitivity: 0.032 mcd/m²



Optics Express, 17 (2009) 358; J.Electrochem.Soc.143 (1996) 2670

Persistent phosphors: Dorenbos' model

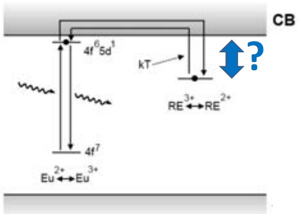


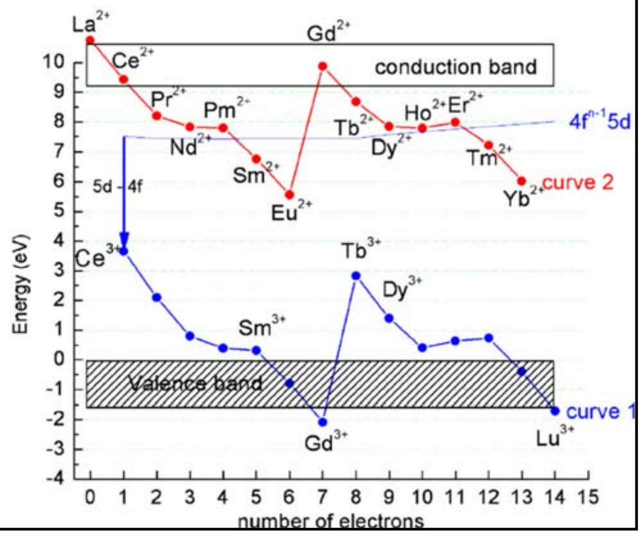
Two regimes:

- Excitation of Eu^{2+} (**1**), followed by emission (**4**): fluorescence (t ~ 500ns)
- Excitation of Eu^{2+} (**1**), ionization to Eu^{3+} , electron via CB to trap (**2**),
  Trapped charged thermally released (**3**),
  followed by recombination at Eu^{3+} and emission (**4**) (t ~ seconds to hours)

LumiLab

Persistent phosphors: prediction of trap depth





Radiation Measurements 43 (2008) 222 – 226

LumiLab

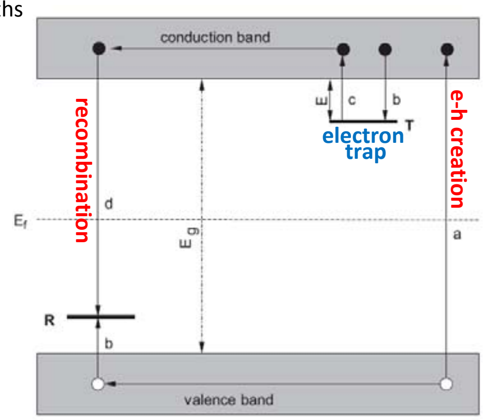
Thermoluminescence (TL)

- Thermal release of trapped carriers, followed by emission (no “luminescence” according to definition)
- Determination of trap depths
- Kinetics

probability, trap depth

$$p = s \exp\left\{-\frac{E}{kT}\right\}$$

escape frequency, temperature



First order kinetics (no retrapping):

$$I(t) = -\frac{dn}{dt} = n_0 s \exp\left\{-\frac{E}{kT(t)}\right\} \times \exp\left\{-s\int_0^t \exp\left\{-\frac{E}{kT(t')}\right\} dt'\right\}$$

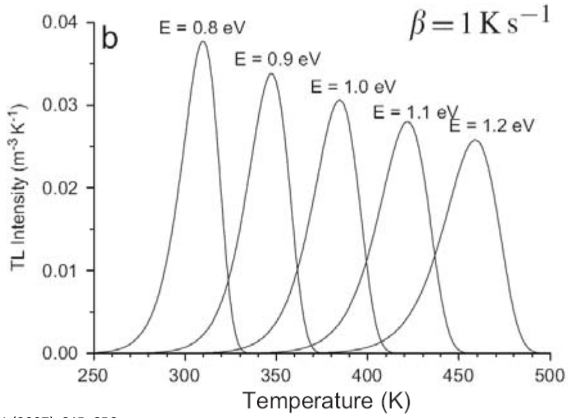
Radiation Measurements 41 (2007) S45–S56

Thermoluminescence (TL)

- Linear increase in temperature

$$T(t) = T_0 + \beta t$$

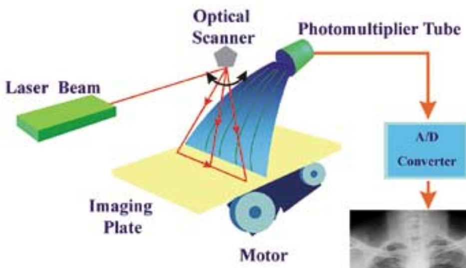
- Monitor light output (= recombination) as function of T(K): **glow curve**
- Asymmetric peak shape
- Area under glow peak is constant



Radiation Measurements 41 (2007) S45–S56

Thermoluminescence (TL): application

- Research tool for persistent luminescent materials
- Geological **dating** method (quartz, feldspar,...)
- **Dosimetry** (α, β, x-rays,...)
  - Sensitive
  - Linear dose-signal relation mGy to kGy



- Deep and stable traps: optical read-out instead of thermally
  - **OSL**: optically stimulated luminescence
  - Medical imaging (BaFBr:Eu^{2+}, CsBr:Eu^{2+})
  - Dating method

http://www.imagingeconomics.com/issues/articles/2001-04_02

Scintillator phosphors

- **Detection of high-energy radiation (α, β, γ, x-rays, neutrons)**
- Ionizing radiation creates e-h pairs
- Excite RE ions, followed by light emission detected by PMT

- **Requirements:** fast response, high light output, linearity

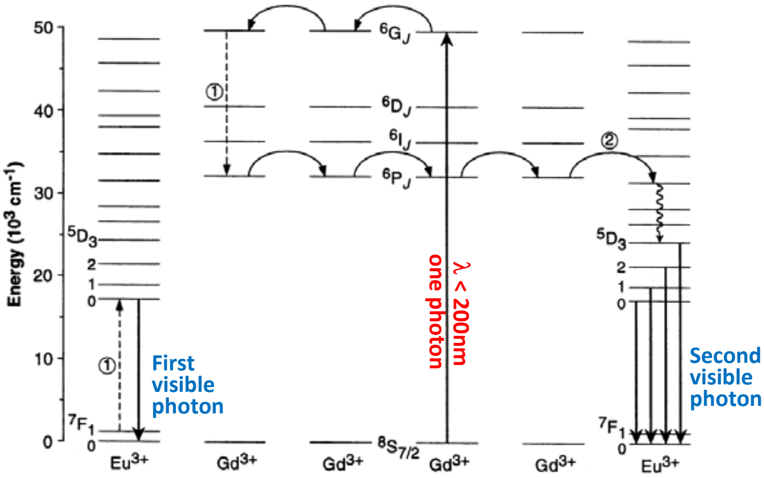
- Recent advances:
  - $LaBr_3:Ce^{3+}$ (τ = 35ns, 61000photons/MeV, 3% energy resolution)
  - $LaCl_3:Ce^{3+}$
  - $Lu_{1.8}Y_{0.2}SiO_5:Ce^{3+}$

www.detectors.saint-gobain.com/Brillance380.aspx

Applications of rare earth luminescence
LumiLab

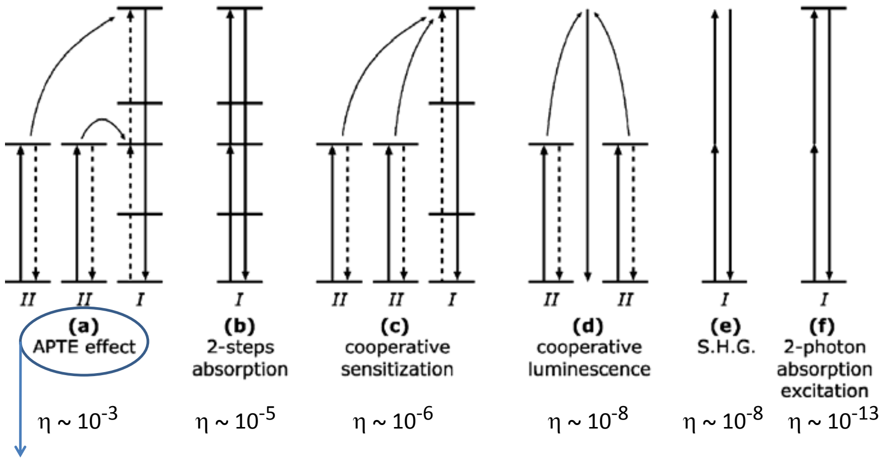
Quantum-cutting phosphors

- Replacement of mercury (254nm) by xenon (172nm) in fluorescent tubes
  - High quantum efficiency >< high energy efficiency (Stokes losses)
  - Enough energy for two visible photons **(two-for-one)**
- Solar cells: two infrared photons for one visible
- Example: **$LiGdF_4:Eu^{3+}$**



Journal of Luminescence 87-9 (2000) 1017

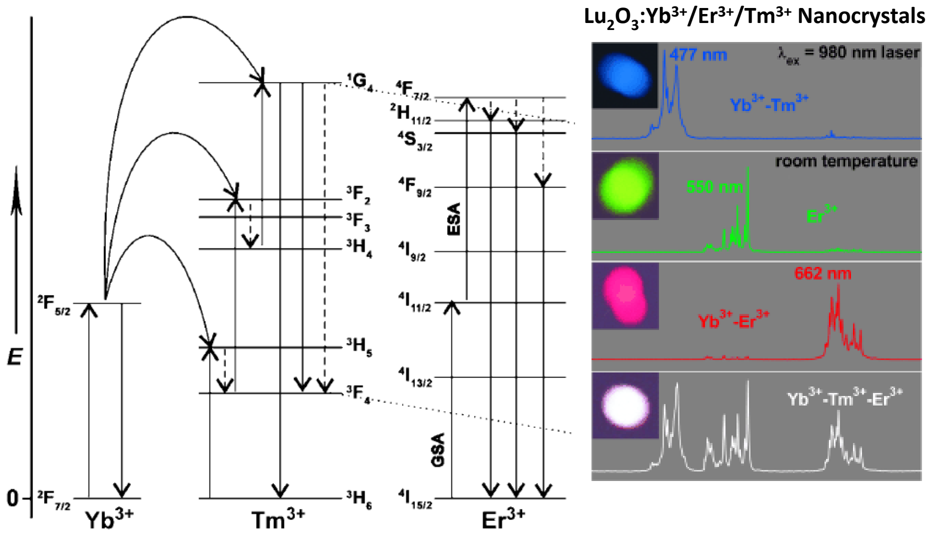
Up-conversion phosphors



Addition de photon par transfert d'energie

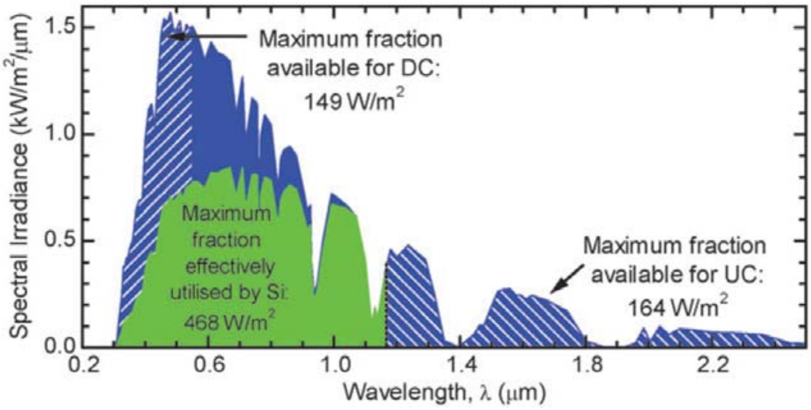
F. Auzel, *J. Lumin.*, 1990, **45**, 341–345.

Up-conversion phosphors



Chem. Eur. J. **2009**, *15*, 4649 – 4655

Spectral conversion for solar cells



- Development of upconversion (**UC**) and downconversion (**DC**) materials
- **RE**-based up to now
- Problem: excitation cross-section
- **Device incorporation... it's easier to decrease the performance!**

Bryan M. van der Ende, Linda Aarts, Andries Meijerink, *Phys. Chem. Chem. Phys.*, 2009, 11081

Conclusions

- Basic processes in luminescence
- Characterization techniques
- Luminescence in rare earth ions: ubiquitous
- Applications

Want to read more?

- Phosphor Handbook, 2nd Ed., edited by William M. Yen, Shigeo Shionoya, Hajime Yamamoto, CRC Press (ISBN 0-8493-3564-7)
- Luminescent Materials, G. Blasse, B.C. Grabmaier, Springer-Verlag (ISBN 0-3875-8019-7)

Thanks for your attention!