Rare Earth Ions - The Vitamins of Phosphors

Thomas Jüstel

Scottsdale, AZ, March 22nd, 2012

To My Person

Thomas Juestel (43), German, married

CV

• University Bochum (1987 - 1994)	*Coordination Chemistry*
• Max-Planck Institute Mülheim (1995)	*Electrochemistry*
• Philips Research Aachen (1995 - 2004)	*Solid State Chemistry, Luminescence*
• University of Applied Sciences Münster (since 2004)	*Functional optical materials*

Teaching

- Inorganic Chemistry
  - Solid state chemistry
  - Coordination chemistry
- Material Science
  - Optical materials
  - Luminescent materials
  - Material characterisation
- Incoherent Light Sources

https://www.fh-muenster.de/juestel

Literature

- A.H. Kitai, Solid State Luminescence, Chapman & Hall, London (1993)
- G. Blasse, B.C. Grabmeier, Luminescent Materials, Springer Verlag Berlin Heidelberg (1994)
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- T. Jüstel, S. Möller, H. Winkler, Luminescent Materials in Ullmann's Encyclopedia of Technical Chemistry (2012)

Agenda

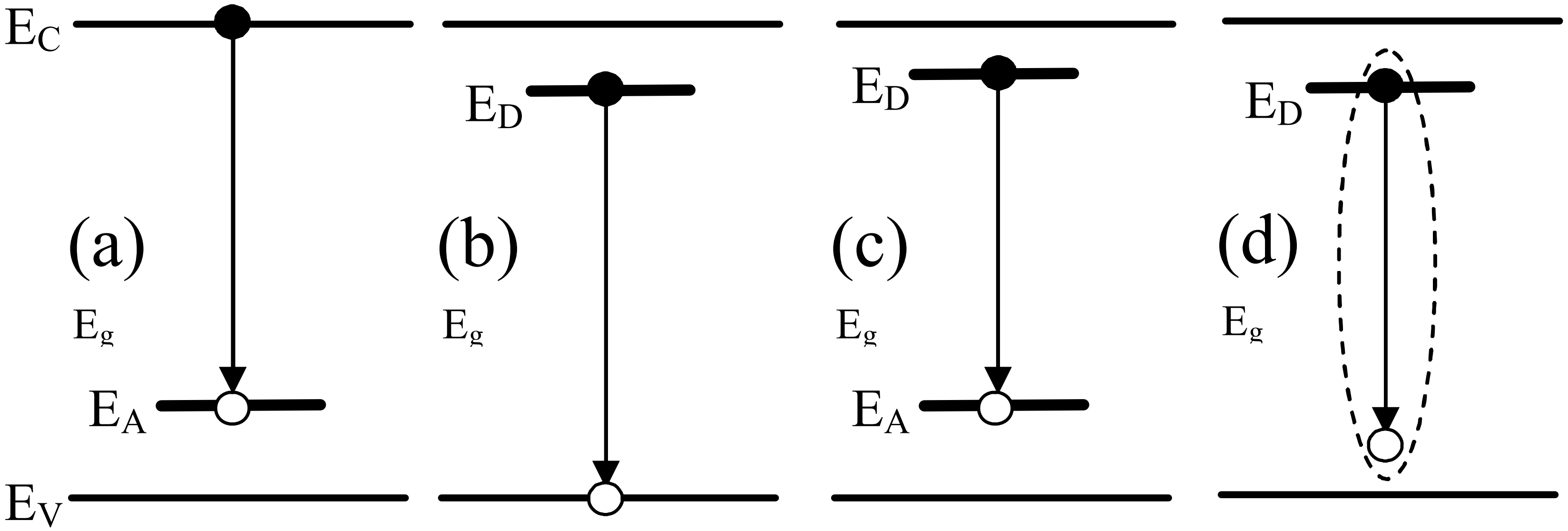
What is Luminescence?

- Definition
- Difference to incandescence
- Inorganic luminescent materials
- Role of physicists and chemists
- Application areas

Definition

Luminescence is a process that corresponds to emission of electromagnetic radiation beyond thermal equilibrium.

Inorganic materials: Radiative recombination involving impurity levels:
(a) conduction-band–acceptor-state transition
(b) donor-state–valence-band transition
(c) donor-acceptor recombination
(d) bound-exciton recombination



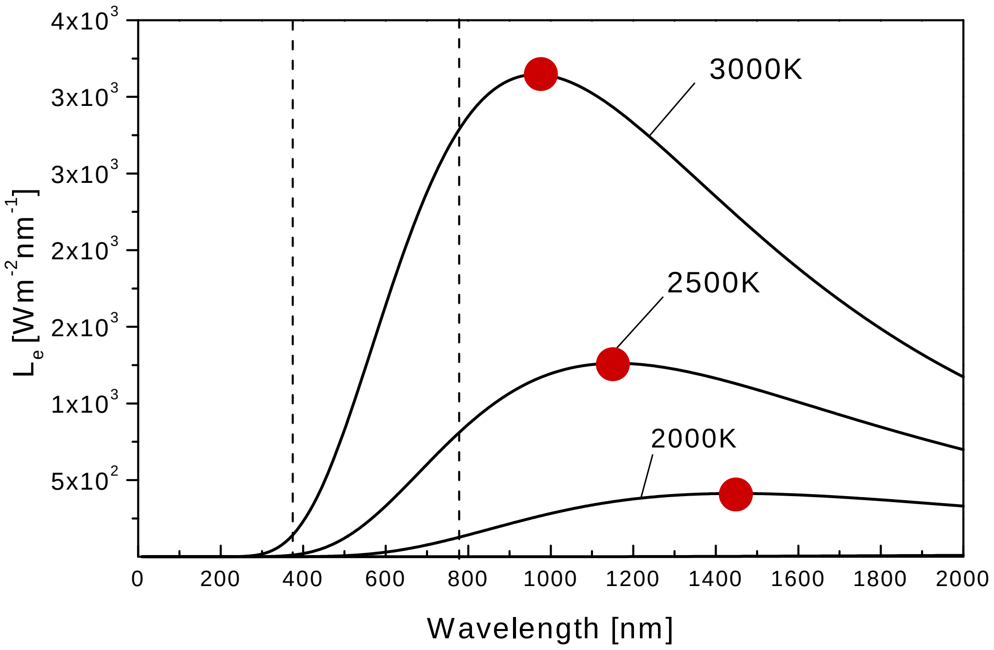
Difference to Incandescence

Incandescence corresponds to emission from solids in thermal equilibrium → „Black body radiation“, e.g. from incandescent lamps

Planck‘s law (1900)

$$\boxed{L_e = \frac{c_1}{\lambda^5} \cdot \frac{1}{e^{c_2/\lambda T} - 1}}$$

c_1 = 3.741832·10^{-16} Wm^2
c_2 = 1.438786·10^{-2} Km
λ = Wavelength [m]
L_e = Spectral irradiance
T = Temperature [K]



Wien’s law

$$\boxed{\lambda_{max} \cdot T = 2880\,[\mu m \cdot K]}$$

Inorganic Luminescent Materials

Luminescent material = Host lattice + defects (+ dopants)

Host lattice Y_2O_3, $Y_3Al_5O_{12}$, ZnS, $Sr_2Si_5N_8$, …

- Selection in accordance to requirements defined by the application: excitation energy, absorption strength, chemical environment, temperature

Defects V_K, V_A, interstitials, ...

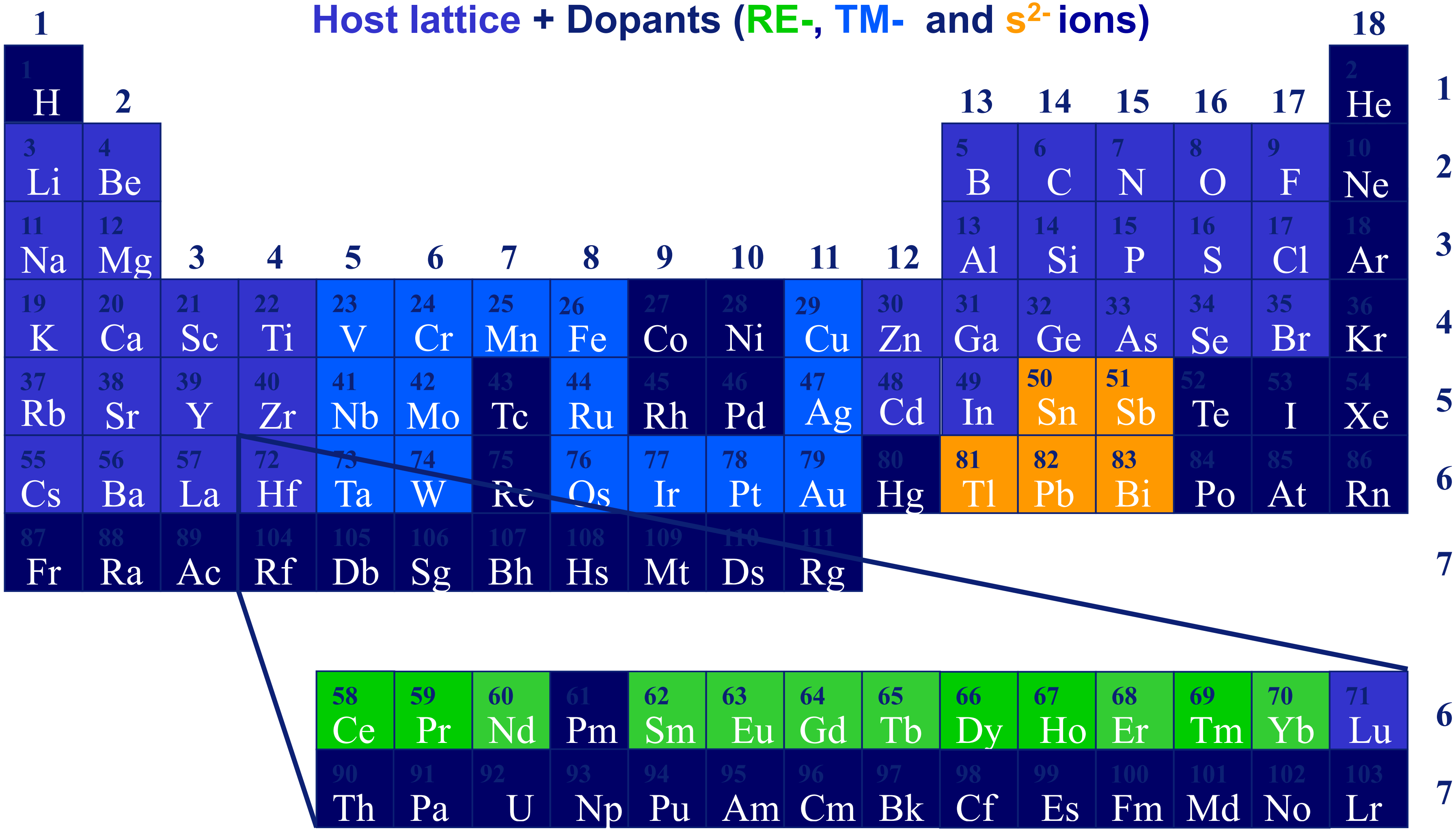
- Afterglow (persistent luminescence)
- Luminescence quenching (concentration and thermal quenching)
  - competitive absorption
  - energy transfer to defects + non-radiative relaxation
  - re-absorption of emission
- Stability reduction
  - formation of colour centres due to electron trapping

Dopants Cr^{3+}, Mn^{4+}, Sb^{3+}, Pb^{2+}, $Eu^{2+/3+}$, Ce^{3+}, ...

- Selection and concentration depends on host lattice and application: Solubility, mobility, oxidation state stability, CT state location
- Co-dopants to enhance absorption

Inorganic Luminescent Materials

Host lattice + Dopants (RE-, TM- and s^{2-} ions)



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1 H																	2 He	1
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	2
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	3
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	4
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	5
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	6
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg								7
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	6
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	7

Inorganic Luminescent Materials

Requirements on efficient phosphors

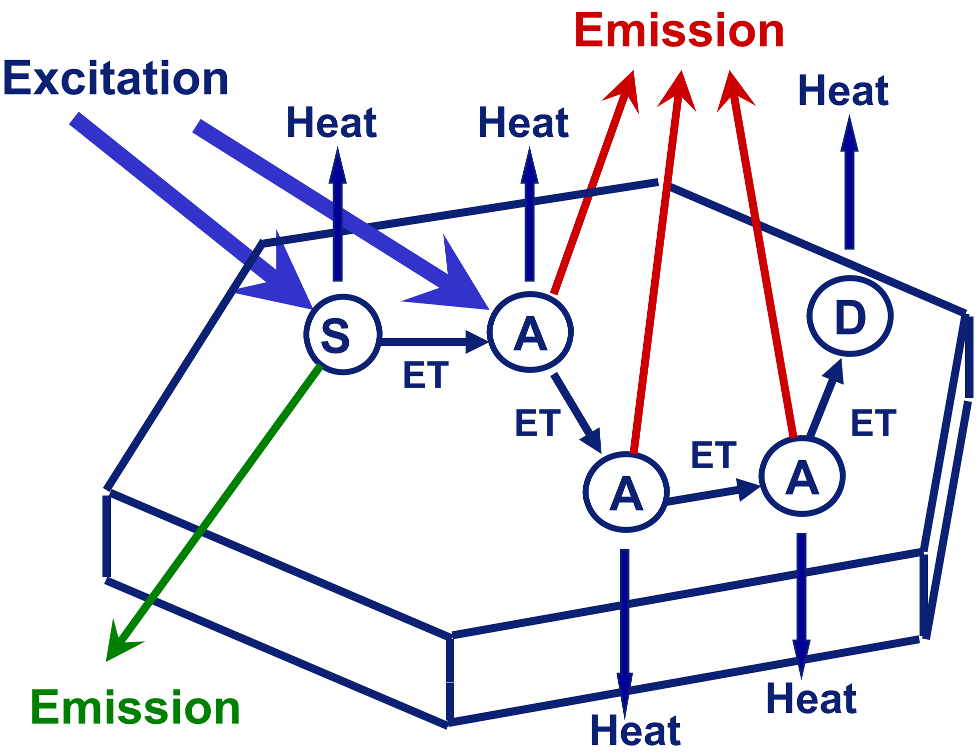
- Highly crystalline particles
- High purity (99,99% or better)
- Homogeneous distribution of activator and sensitizer ions

Absorption process related to

Optical centres (impurities)

• activators	(A)
• sensitizers	(S)
• defects	(D)
• host lattice	(band edge)

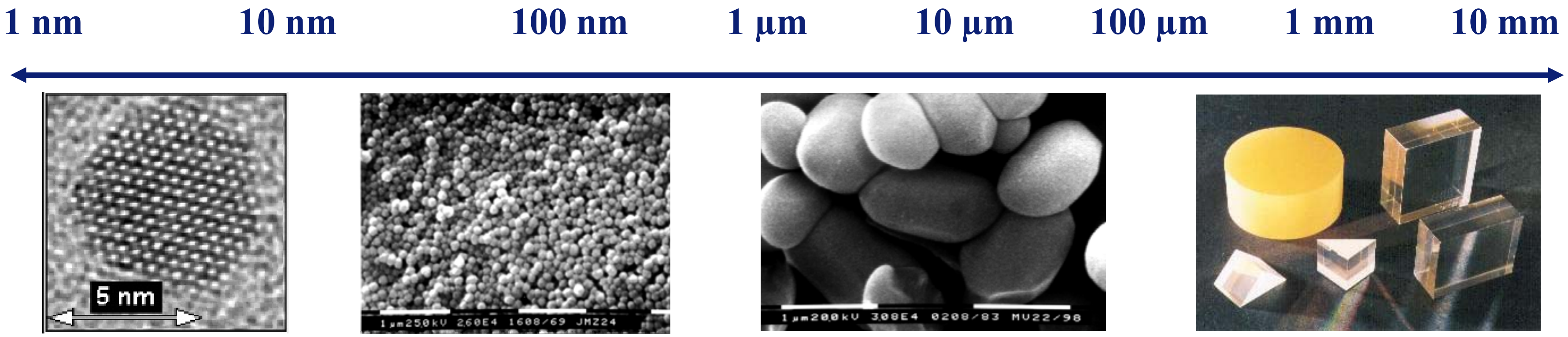
Energy transfer often occur prior to emission process!



Inorganic Luminescent Materials

Morphology

• Nanoscale particles	Molecular imaging, precursors
• µ-sized particles	Lamps, LEDs, CRTs
• Large single crystals	Scintillators, LASERs
• Ceramics (cubic materials preferred)	LEDs, scintillators, LEDs



Role of Physicists and Chemists

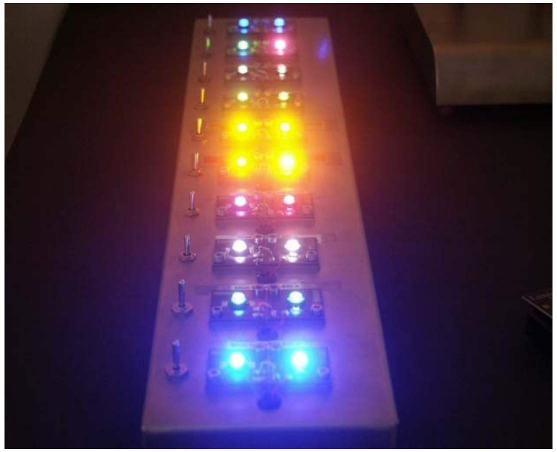
Identify needs of specific application and translate into suitable materials taking physical/chemical processes into account:

- Excitation mechanisms
- Energy transfer mechanisms
- Emission mechanisms
- Loss mechanisms
- Stability
- Saturation
- Colour point (shift)
- Material preparation
- Price and raw material access

Application Areas

CRTs

LEDs



Plasma displays

Fluorescent lamps

Tomographs

EL Displays

Application Areas

Application Area	Examples
Optical brightening	Paint, pulp and paper, washing powder
Product protection	Bills, stamps, credit cards, tickets, etc.
Emergency illumination	Emergency exits and signs, runways
Advertisement illumination	Ne discharge lamps
Medical imaging and treatment	x-ray converter films, CTs, PETs Lamps for psoriasis and jaundice treatment Dental ceramics
Astronomy	EUV/VUV-Amplifier
Biochemistry	Labels for DNA, RNA, proteins
Lithography	Photocopy machines

Luminescence Processes

Type	Excitation by	Example
X-ray luminescence	X-rays	X-ray amplifier
Cathode luminescence	Electrons (high U)	CRTs
Photo luminescence	UV/Vis photons	Fluorescent lamps
Electro luminescence	Electrical field (low U)	LEDs, EL displays
Chemo luminescence	Chemical reaction	Emergency signals
Bio luminescence	Biochemical reaction	Jelly fish, glow worms
Thermo luminescence	Heat	Afterglow phosphors
Sono luminescence	Ultra sound	-
Mechano luminescence	Mechanical energy	Peeling tape *Nature 455 (2008) 1089)* *Blue + UV + x-ray!*

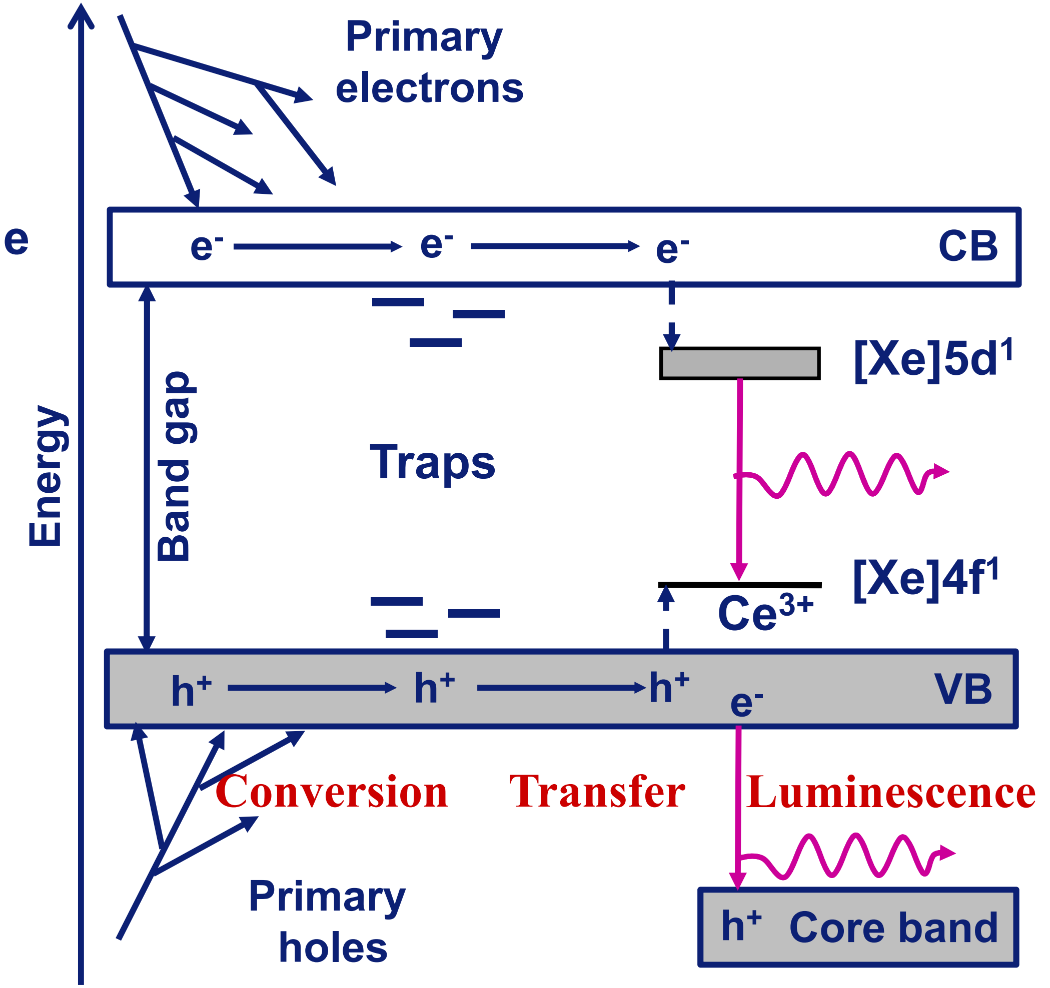
Excitation Mechanisms

X-ray and high voltage electron excitation

1. Excitation of highly energetic core states
2. Thermalization of electron-hole pairs with band gap energy
3. Energy transfer to activator ions or centers
4. (Center) Luminescence

Efficiency surprisingly well understood, but with two different models:

1. Robbins
2. Bartram-Lempicki



Excitation Mechanisms

1. Robbins

- Excitation with high energy particles
- Energy used to create electron-hole pairs with band gap energy
- Electron-hole pairs excite activators
- $\eta = \langle h\nu \rangle / (\beta E_g) \cdot \eta_t \cdot \eta_{qe} \cdot \eta_{esc}$

  - *β determined by host lattice, E_g by host lattice too*
  - *$1/(\beta E_g)$: proportional to photon yield or charge yield, also important in direct conversion*
  - *$\eta_t = \alpha N/(\alpha N + \Delta)$ (ratio capture by activator and defect centers)*
  - *η_{qe} = quantum efficiency of activator ion*
  - *η_{esc} = photon escape probability*

D.J. Robbins. On predicting the maximum efficiency of phosphor systems excited by ionizing-radiation, J. Electrochem. Soc. 127 (1980) 2694

Excitation Mechanisms

2. Bartram-Lempicki

- $\eta = \beta \cdot \eta_t \cdot \eta_{qe}$
- $\beta \approx 2.5$ independent of compounds
- Variations in scintillating efficiencies due to differences in energy transfer efficiency (< 1) and band gap values
- Important role of lattice excitation

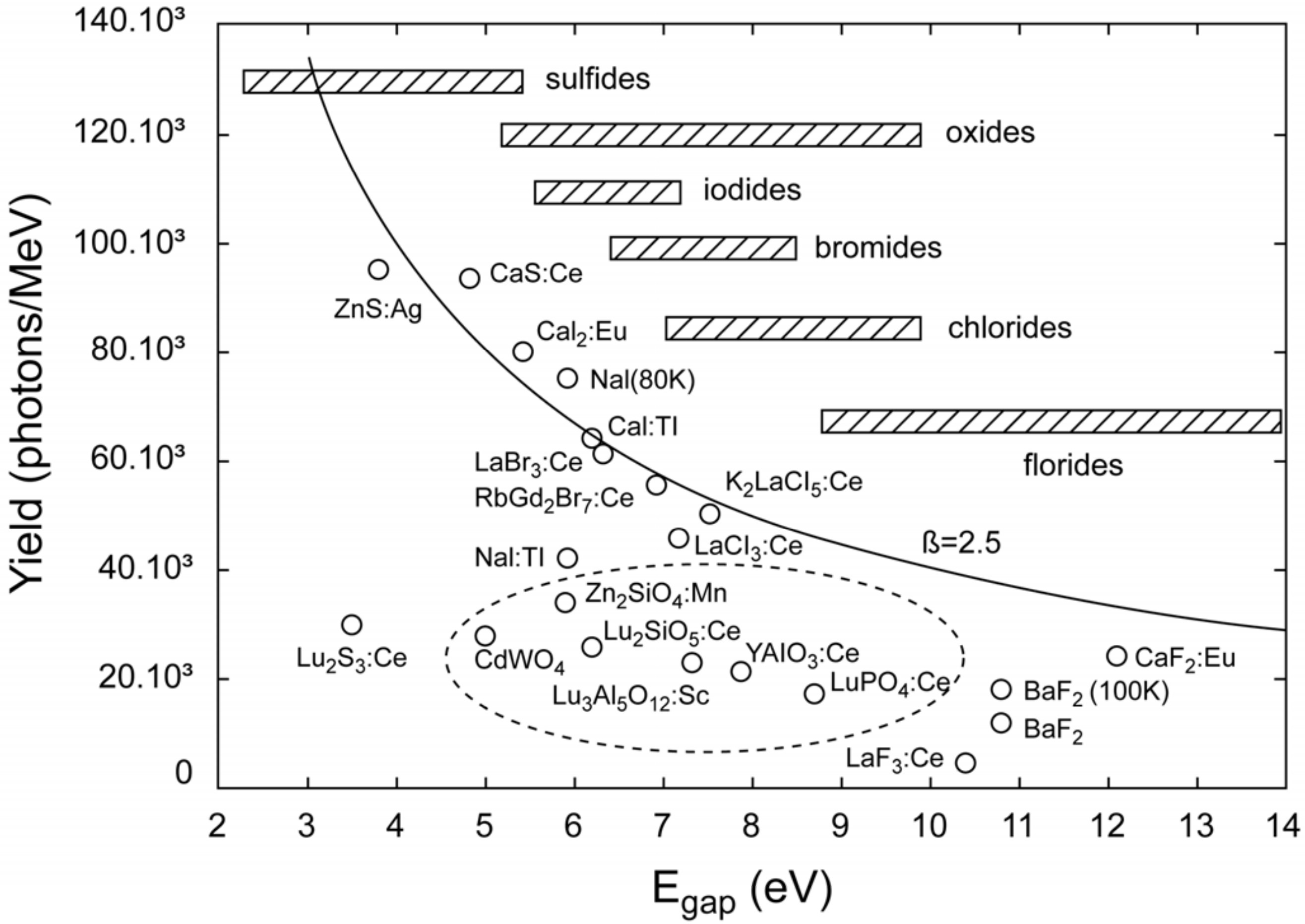
R.H. Bartram and A. Lempicki, Efficiency of electron-hole pair production in scintillators, J. Luminescence 68 (1996) 225

Excitation Mechanisms

- Robbins description implies
  - Efficiently scintillating lattices
  - Efficiency is a lattice property
  - Scintillating efficiency decreases more than proportional on increasing ionicity (oxides), expressed in β

- Bartram-Lempicki description implies
  - Energy transfer lattice to activator determines efficiency
  - β (almost) host lattice independent, generally assumed $\beta = 2.5$
  - Oxidic (ionic) materials can be much more efficient than predicted by Robbins

Excitation Mechanisms



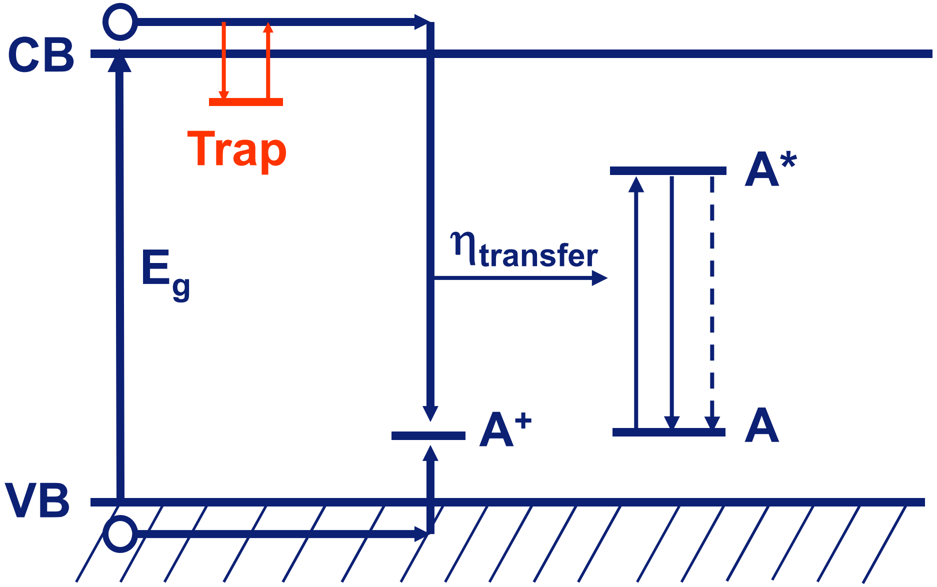
Excitation Mechanisms

- Observations on X-ray and CRT phosphors
  - Increasing covalency increases efficiency
  - Small band gap desired
  - Issues with quenching due to photoionisation
  - Lattice defects cause undesired afterglow

Excitation Mechanisms

VUV (EUV) excitation

Excitation energy > E_G of the host lattice → Band gap excitation



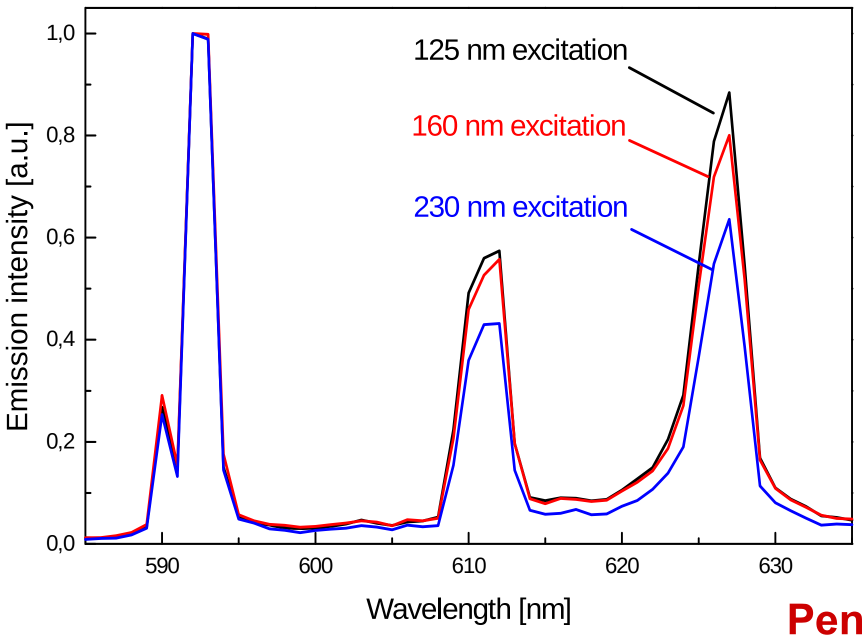
$$QE = QE_A * \eta_{transfer} = k_r/(k_r + k_{nr}) * \eta_{transfer}$$

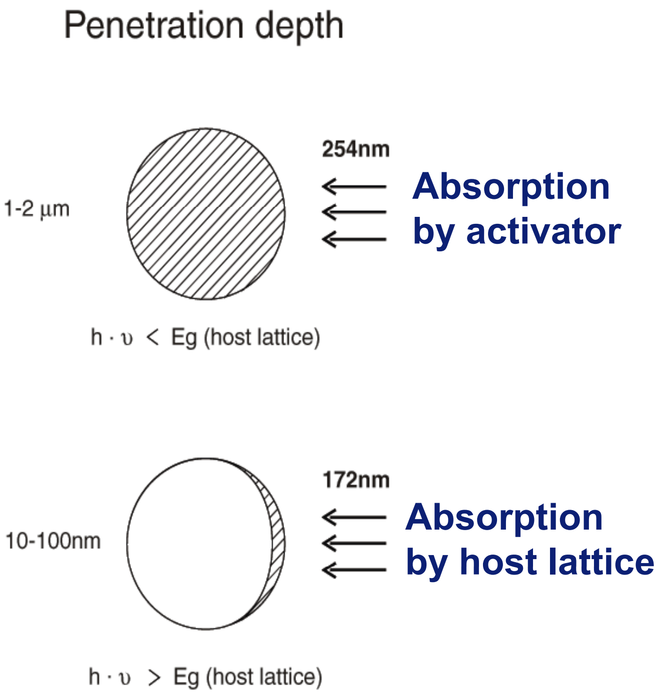
Crystallinity (defect density) has strong impact on VUV efficiency and afterglow

Excitation Mechanisms

Penetration depth of VUV radiation

Emission spectra of $(Y,Gd)BO_3:Eu$ are dependent on local symmetry





Absorption by activator

Absorption by host lattice

Penetration depth = $0.046*U^{5/3}/\rho$ [µm]

230 nm exc. x = 0.638, y = 0.360

160 nm exc. x = 0.646, y = 0.349

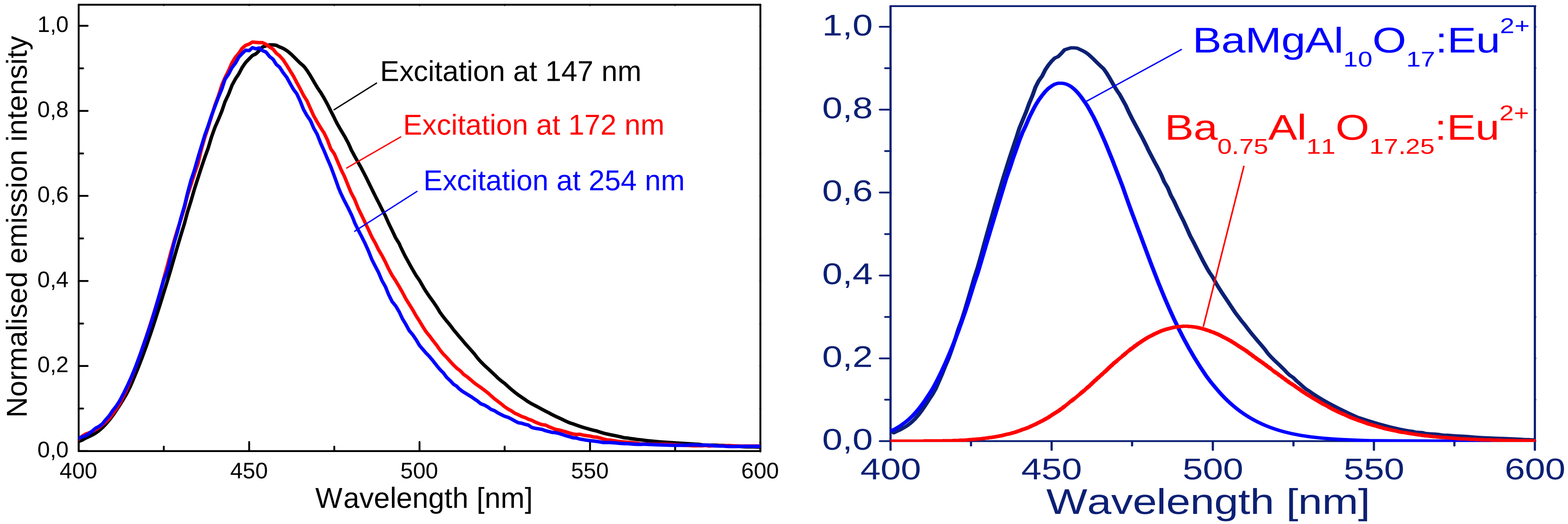
10 kV electrons (~400 nm) x = 0.637, 0.362

2 kV electrons (~30 nm) x = 0.644, 0.350

Band gap excitation ⇒ penetration depth < 100 nm

Excitation Mechanisms

Emission spectra of $BaMgAl_{10}O_{17}:Eu^{2+}$ as function of penetration depth



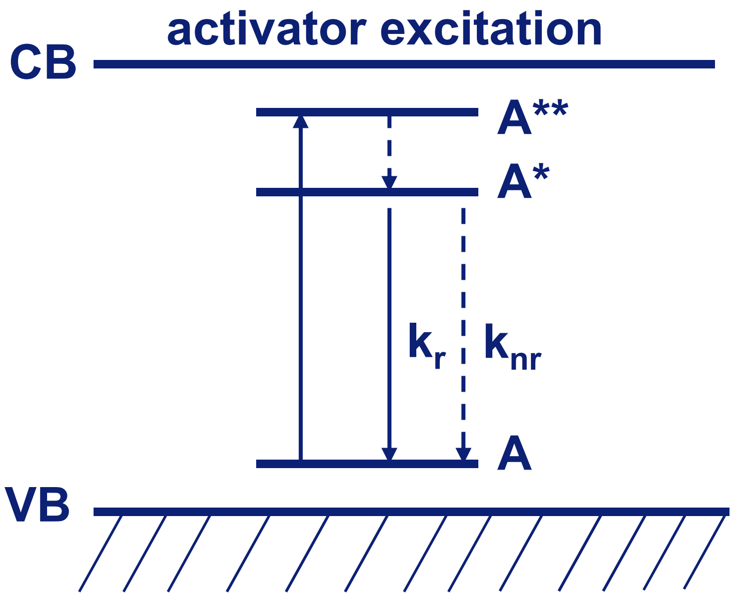
BAM:Eu surface suffers from MgO lack ⇒ formation of $Ba_{1-x}Al_{11}O_{17.5-x}:Eu$

(Improved $BaMgAl_{10}O_{17}:Eu,(Mn)$ by application of Mg^{2+} excess during synthesis, J.-P. Cuif, Rhodia, PGS 2005)

Excitation Mechanisms

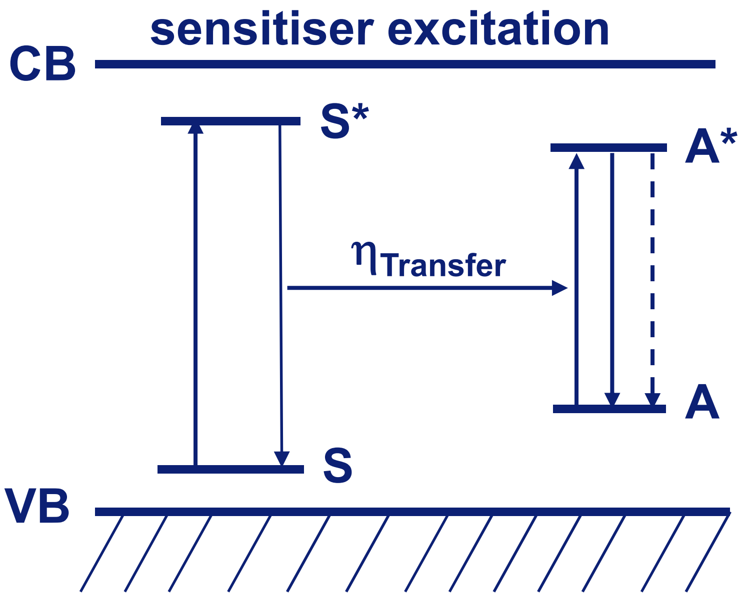
Excitation by UV or visible radiation

Excitation energy < E_G of the host lattice → Excitation of optical centres



$$QE_A = k_r/(k_r + k_{nr}) = \tau/\tau_0$$

with $k_r + k_{nr} = 1/\tau$ and $k_r = 1/\tau_0$

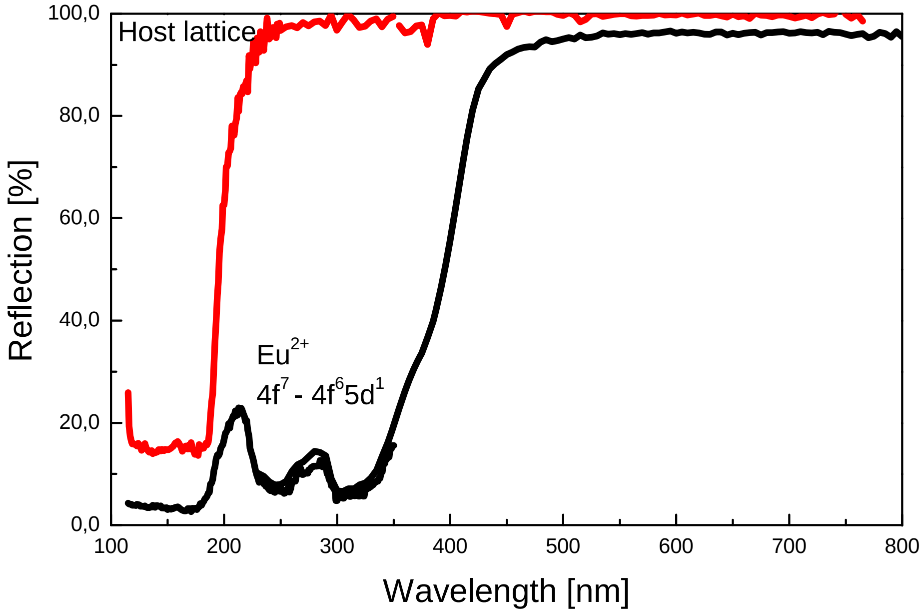


$$QE = QE_A * \eta_{Transfer}$$

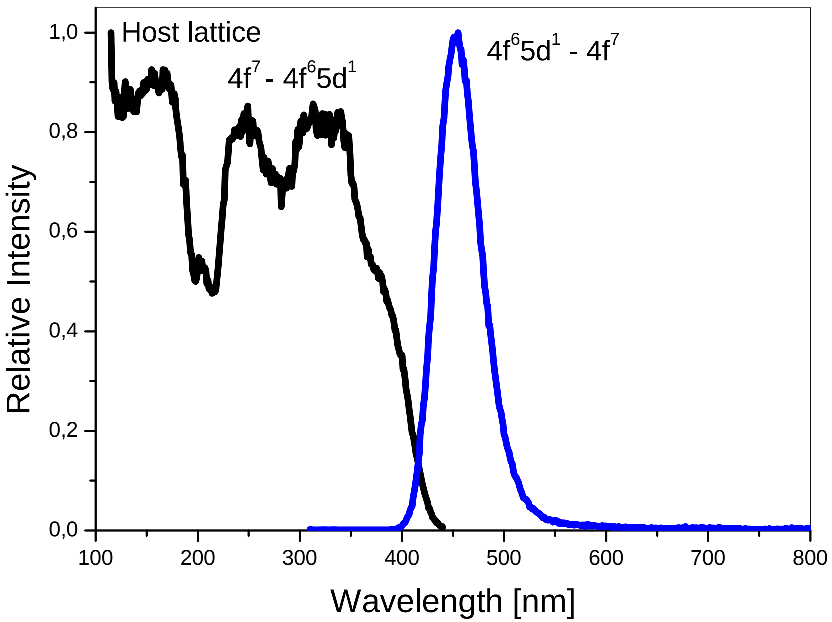
Excitation Mechanisms

Example: $BaMgAl_{10}O_{17}$ doped by 10% Eu^{2+}

Reflection spectra



Emission and excitation spectra

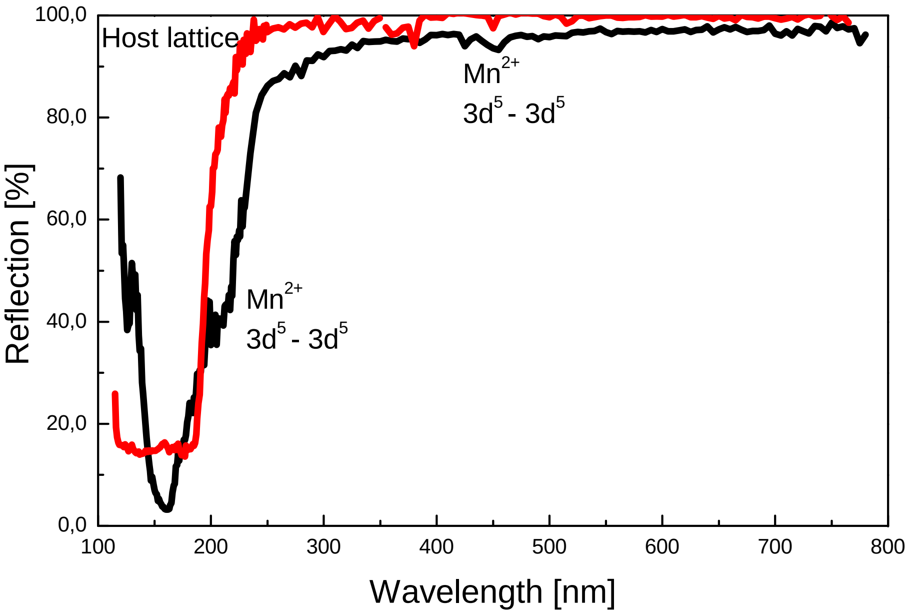


- **Host lattice** VB → CB 180 nm (7.0 eV)
- **Eu^{2+}** $[Xe]4f^7 \rightarrow [Xe]4f^65d^1$ 250 nm (5.0 eV) and 310 nm (4.0 eV)
- **Allowed transition ⇒ Intense absorption bands and fast decay (~1 µs)**

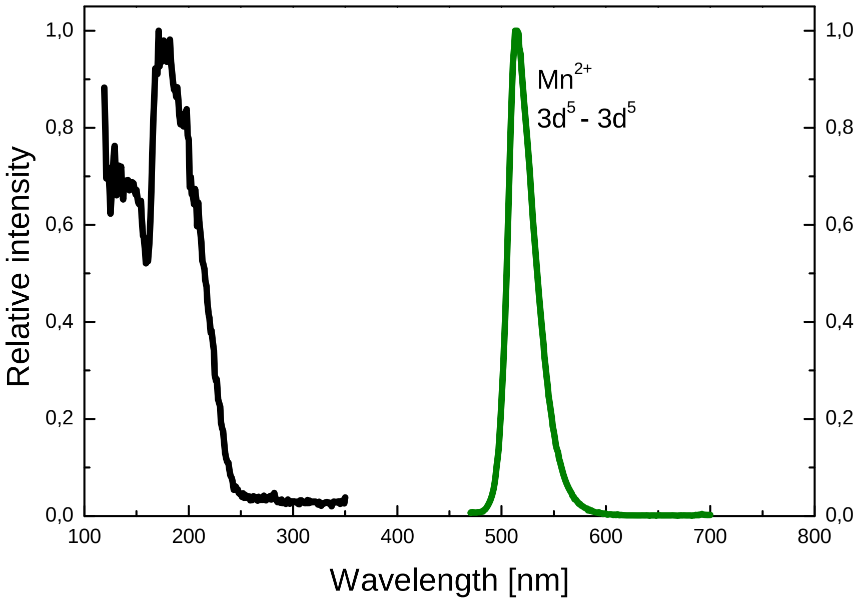
Excitation Mechanisms

Example: $BaMgAl_{10}O_{17}$ doped by 5% Mn^{2+}

Reflection spectra



Emission and excitation spectra

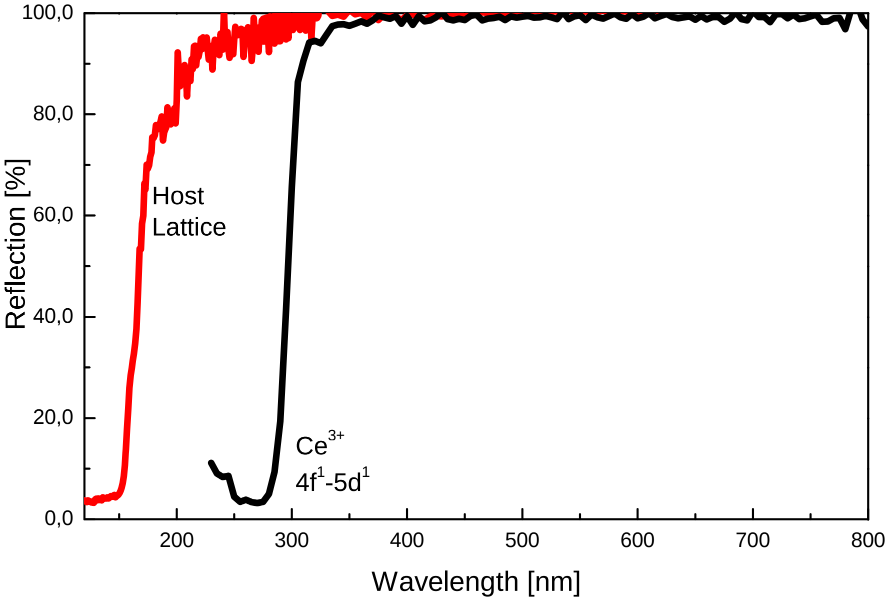


- **Host lattice VB → CB 180 nm (7.0 eV)**
- **Mn^{2+} $[Ar]3d^5 \rightarrow [Ar]3d^5$ 200 nm (6.2 eV) and 450 nm (2.8 eV)**
- **Forbidden transition ⇒ Weak absorption bands and slow decay (~10 ms)**

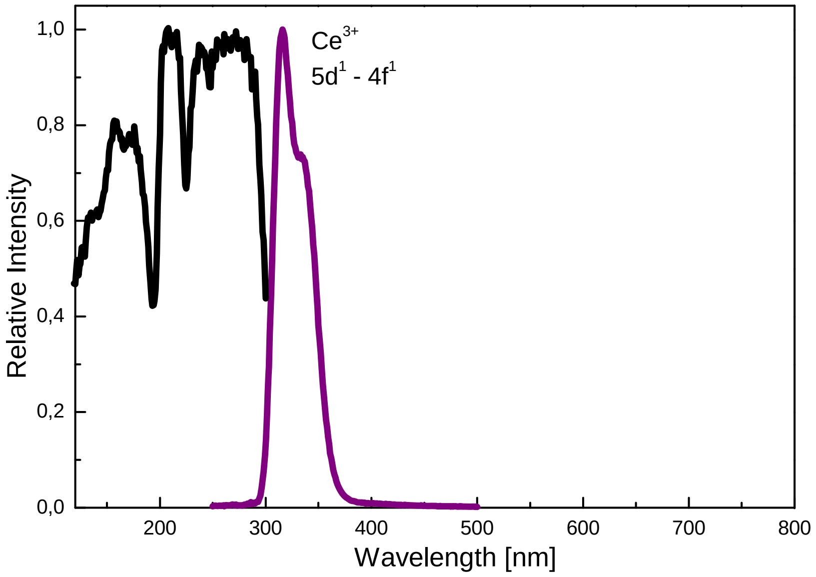
Excitation Mechanisms

Example: $LaPO_4$ doped by 20% Ce^{3+}

Reflection spectra



Emission and excitation spectra

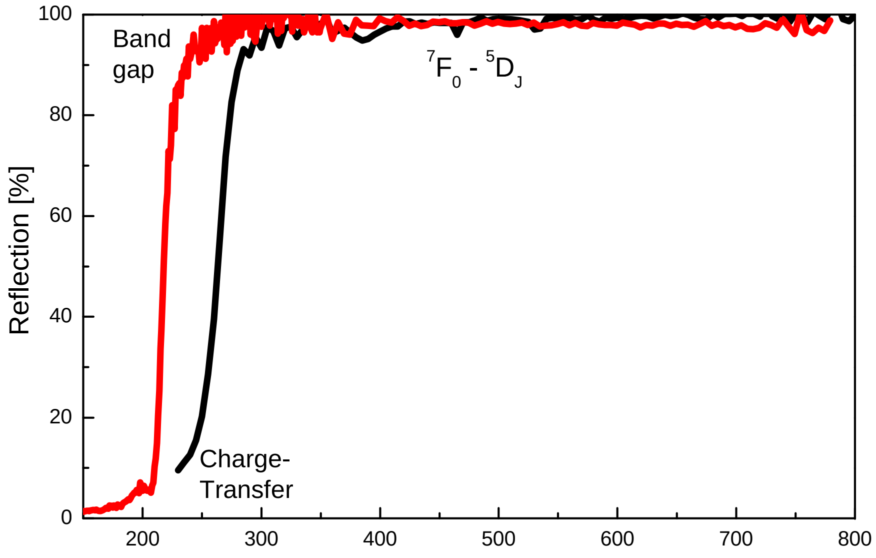


- **Host lattice VB → CB 150 nm (8.2 eV)**
- **Ce^{3+} $[Xe]4f^1 \rightarrow [Xe]5d^1$ 200 nm (6.2 eV) and 450 nm (2.8 eV)**
- **Allowed transition ⇒ Intense absorption bands and fast decay (~ 30 ns)**

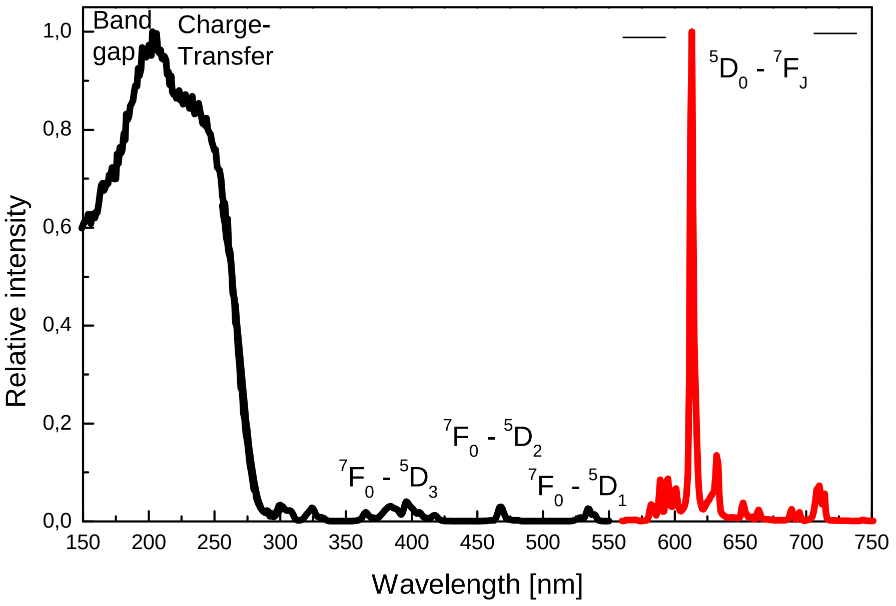
Excitation Mechanisms

Example: Y_2O_3 doped by 5% Eu^{3+}

Reflection spectra



Emission and excitation spectra



•	**Host lattice**	**VB → CB**	**210 nm (5.9 eV)**
•	**Eu^{3+}**	**Charge transfer**	**230 nm (5.4 eV)**
		$[Xe]4f^6 \rightarrow [Xe]4f^6$	**395 nm (3.1 eV) and 465 nm (2.2 eV)**

- **Forbidden transitions ⇒ Weak absorption bands and slow decay (~3 ms)**

Excitation Mechanisms

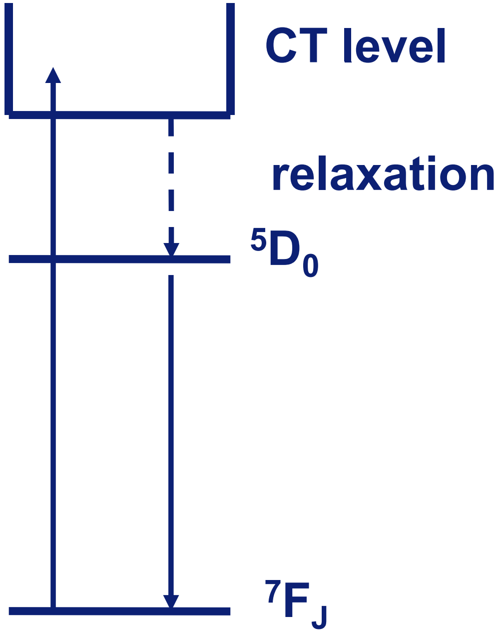
Sensitisation

→ $3d^n$ - $3d^n$ and $4f^n$ - $4f^n$ transitions of are very weak

Ways to enhance absorption

- Involvement of allowed transitions
  - Charge-transfer (CT) of Eu^{3+}
  - $4f^n$ – $4f^{n-1}5d^1$ levels (Tb^{3+}, Eu^{2+}, Ce^{3+})

- Sensitisation (Energy Transfer)
  - Ce → Tb
  - Pr → Tb
  - Nd → Gd
  - Pr → Gd
  - Bi → Eu
  - ….



Simplified energy level scheme of Eu^{3+}

Energy Transfer (ET)

Requirements

- Sensitiser ion and the activator ion have to show physical interaction:
  - Coulomb interaction
  - Exchange interaction

- Spectral overlap (conservation of energy)

Energy Transfer

The probability P_{ET} for energy transfer is given by the following term:

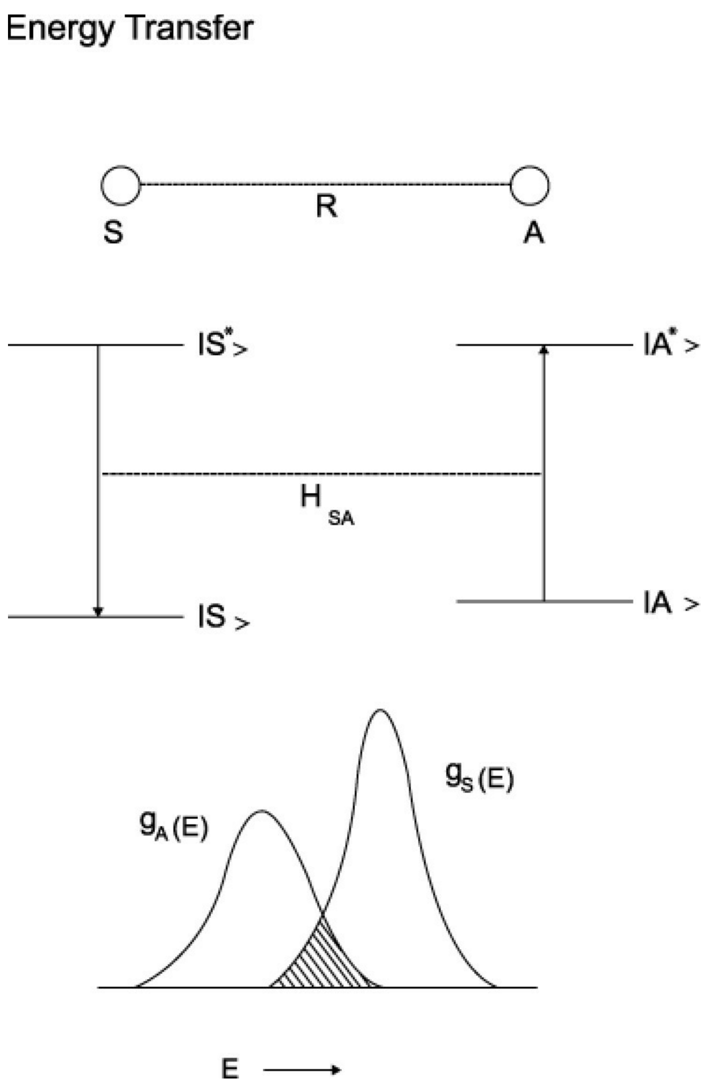
$$P_{ET} = (2\pi/\hbar)\cdot(\rho) < \varphi_i \mid H \mid \varphi_f >^2$$

φ_i: Wave function of the initial state
φ_f: Wave function of the final state
H: Operator coupling the states
ρ: Spectral overlap (energy conservation)

Spectral overlap

$$\rho = g_S(E)\cdot g_A(E)\cdot dE$$

$g_S(E)$ and $g_A(E)$: Normalised optical line shape functions for sensitiser and activator ions



Energy Transfer

Corresponds to

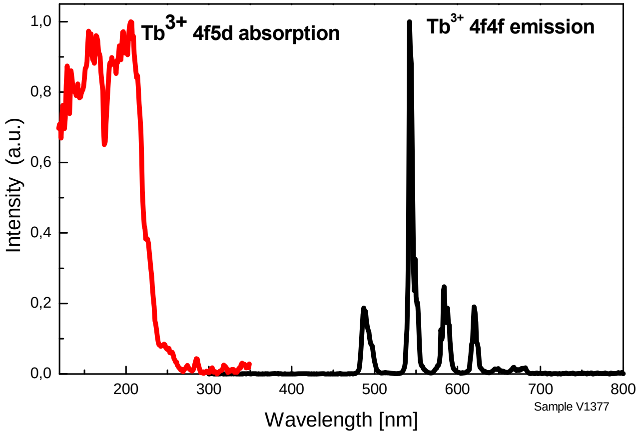
- Energy migration
- Concentration quenching
- Thermal quenching
- Cross relaxation
- Sensitization schemes

Some rules

- ET from a broad band emitter to a line emitter only possible for nearest neighbor in the host lattice (Ce^{3+} - Tb^{3+})
- ET from a line emitter to a band absorber proceeds over long distances (Gd^{3+} - Ce^{3+})
- ET strongly depends on average distance and thus concentration of luminescent centers

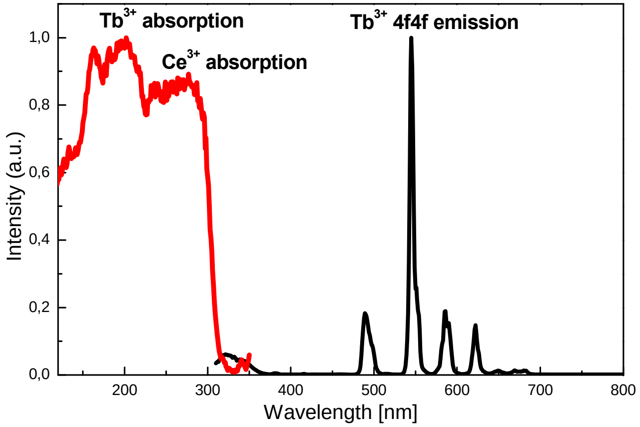
Energy Transfer

Example: Ce^{3+} and Tb^{3+} doped $LaPO_4$



$LaPO_4$:Tb

$Tb^{3+} \rightarrow (Tb^{3+})^{**}$	**Absorption 4f - 5d**
$(Tb^{3+})^{**} \rightarrow (Tb^{3+})^{*}$	**Relaxation to 4f level**
$(Tb^{3+})^{*} \rightarrow Tb^{3+}$	**Emission 4f - 4f**



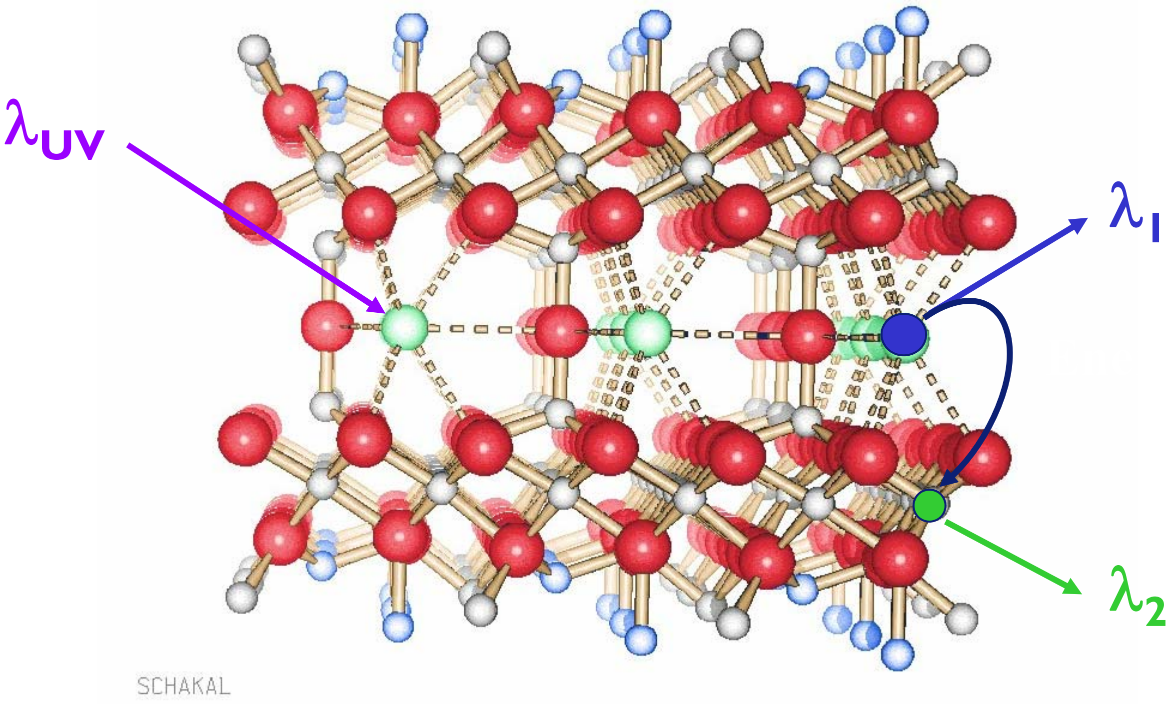
$LaPO_4$:Ce,Tb

$Ce^{3+} \rightarrow (Ce^{3+})^{*}$	**Absorption 4f - 5d**
$(Ce^{3+})^{*} + Tb^{3+} \rightarrow Ce^{3+} + (Tb^{3+})^{*}$	**ET from Ce to Tb**
$(Tb^{3+})^{*} \rightarrow Tb^{3+}$	**Emission 4f - 4f**

Efficiently excited by 254 nm radiation!

Energy Transfer

Example: $BaMgAl_{10}O_{17}$:Eu co-doped by transition metal ions

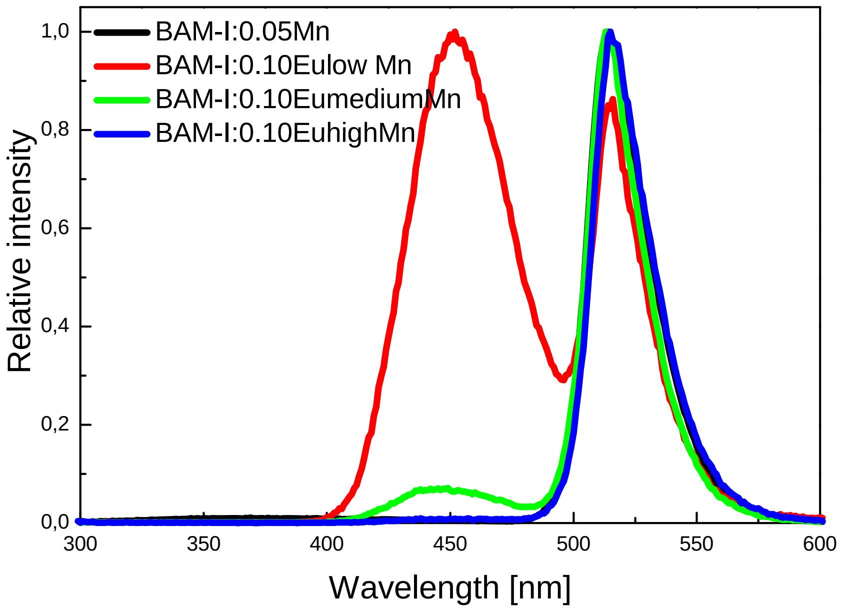


Divalent RE ions	**Ba^{2+} sites in the conduction layer**	**Eu^{2+}, Yb^{2+}**
Divalent TM ions	**tetrahedral gaps in the spinel blocks**	**Mn^{2+}, Co^{2+}**
Trivalent TM ions	**octahedral gaps in the spinel blocks**	**Cr^{3+}, Ti^{3+}**

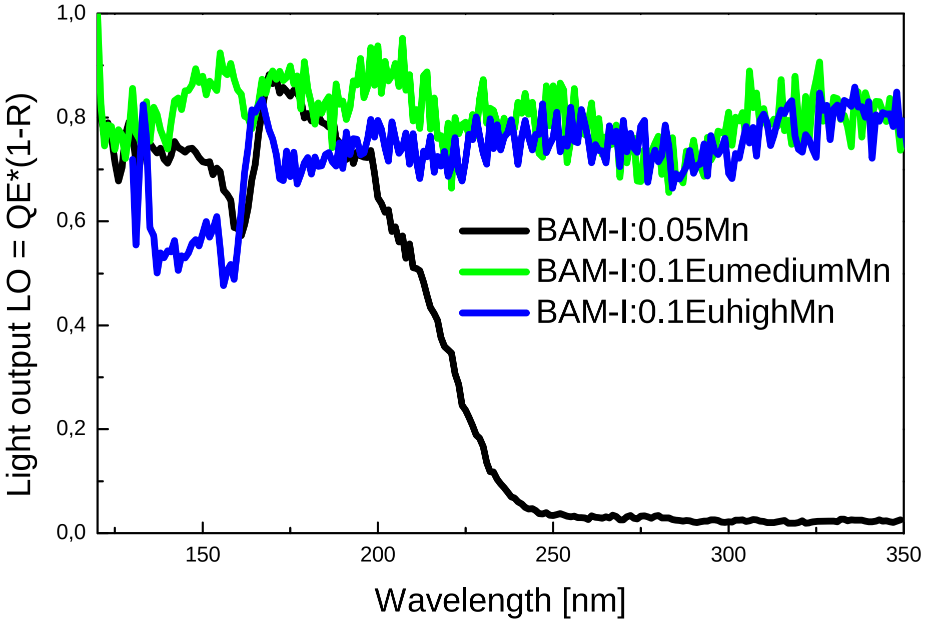
Energy Transfer

Example: $BaMgAl_{10}O_{17}:Eu^{2+}$ co-doped by Mn^{2+}

Emission spectra



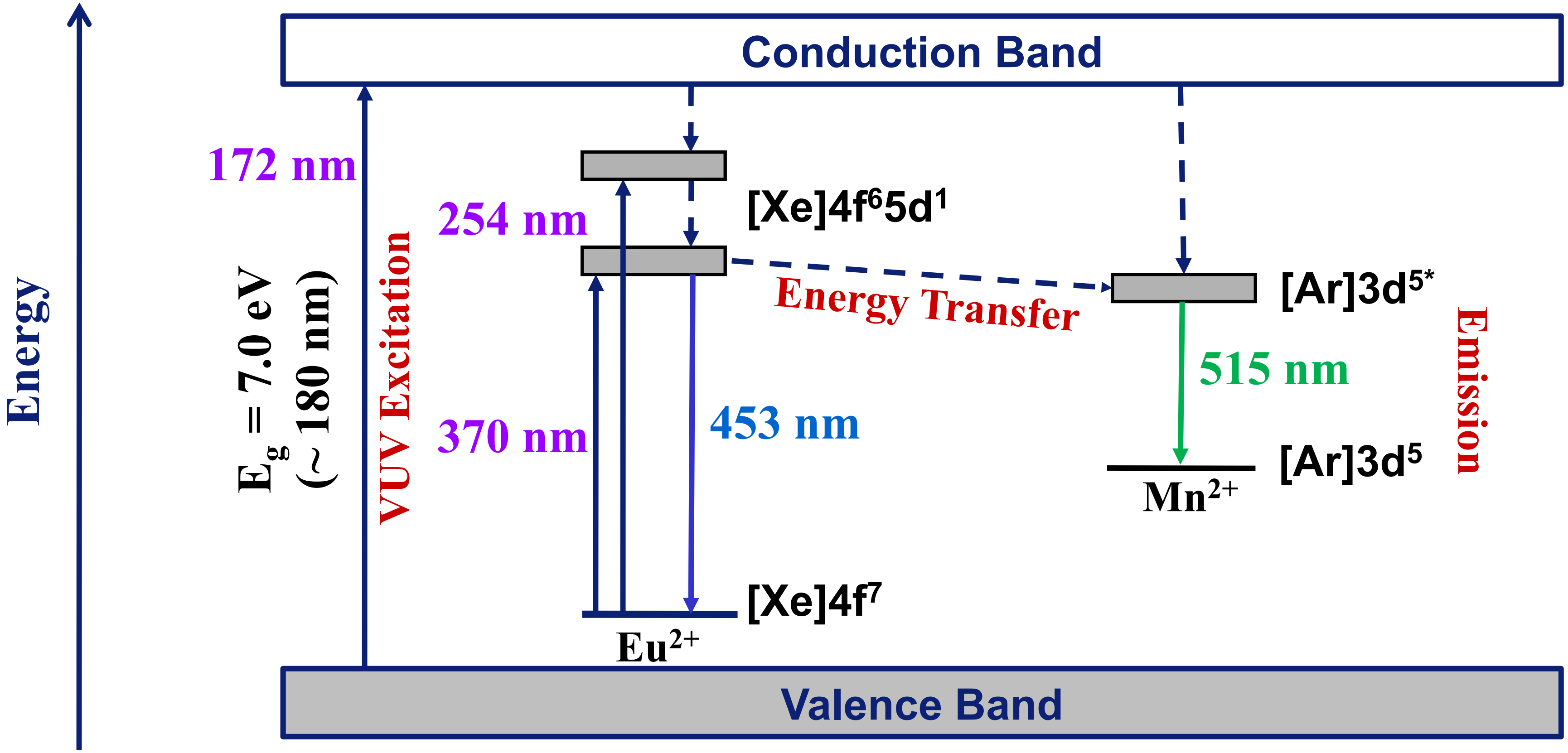
Light output



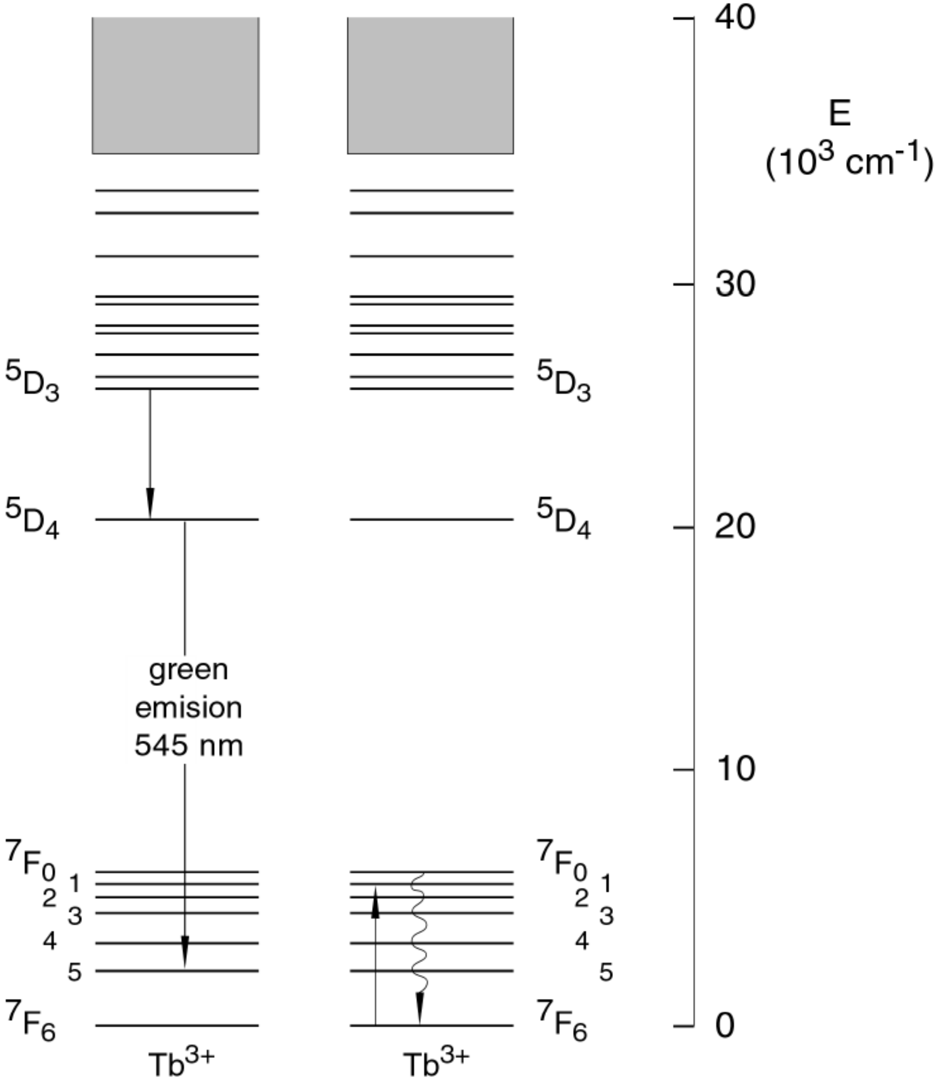
- Efficient energy transfer from Eu^{2+} to Mn^{2+}
- Eu^{2+} improves VUV efficiency of Mn^{2+} doped $BaMgAl_{10}O_{17}$
- High Mn^{2+} concentration reduces VUV efficiency of $BaMgAl_{10}O_{17}:Eu,Mn$

Energy Transfer

Energy pathways in $BaMgAl_{10}O_{17}$:Eu,Mn



Energy Transfer and Cross Relaxation



- **Cross relaxation responsible for the quenching of luminescence of higher 4f levels of Tb^{3+} at a high Tb^{3+} concentration**
- **Cross relaxation also for Eu^{3+}, Sm^{3+} , Pr^{3+}, and Dy^{3+}**
- **Relaxation to the first excited state can be promoted by high-energy photons too**

Loss Mechanisms

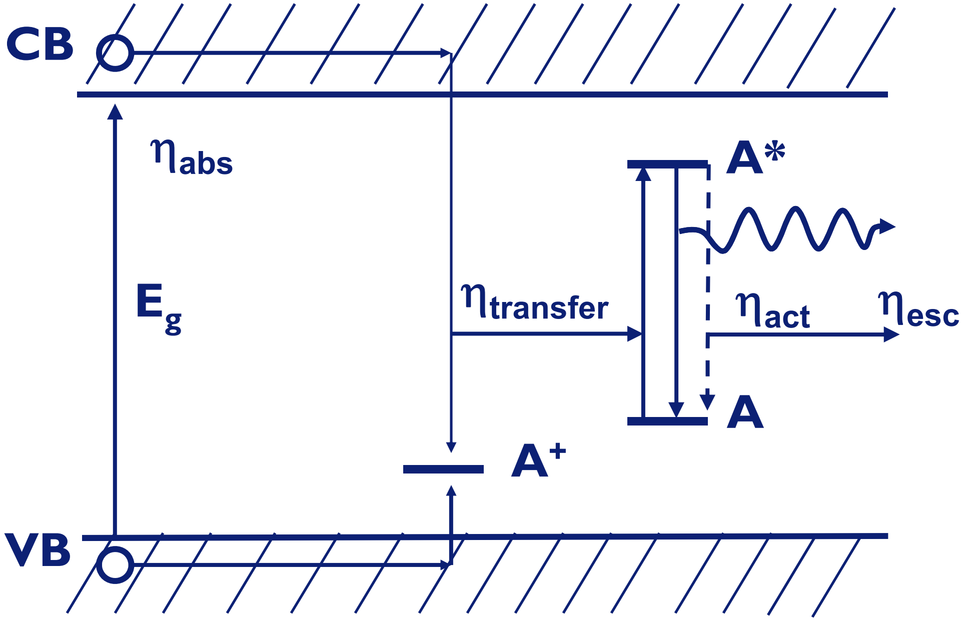
1. The absorbed energy does not reach the activator ion ($\eta_{transfer}$)
   a) Competitive absorption
   b) ET to defects or non-luminescent impurity ions
   c) Excited state absorption
   d) Auger processes

2. The absorbed energy reaches the activator ion, but non-radiative channels exists at the cost of radiative return to the ground state (η_{act})
   a) Crossing of excited and ground state parabola (tunneling)
   b) Multi-phonon relaxation
   c) Cross-relaxation
   d) Photoionisation
   e) Energy transfer to quenching sites = f(T)

3. Emitted radiation is re-absorbed by the luminescent material (η_{esc})
   a) Self-absorption due to spectral overlap between excitation and emission band
   b) Additional absorption bands due to degradation of the material, e.g. by colour centre formation

Loss Mechanisms

Related to the host lattice and host lattice activator interaction



Internal Quantum Efficiency

IQE $= \eta_{act}$
$= \eta_r/(\eta_r + \eta_{nr})$
$= \tau/\tau_0$

(Anti proportional to decay time)

External Quantum Efficiency

EQE $= N_{h\nu(emitted)}/N_{h\nu(absorbed)}$
$= \eta_{transfer} * \eta_{act} * \eta_{esc}$

(No correlation to decay time!)

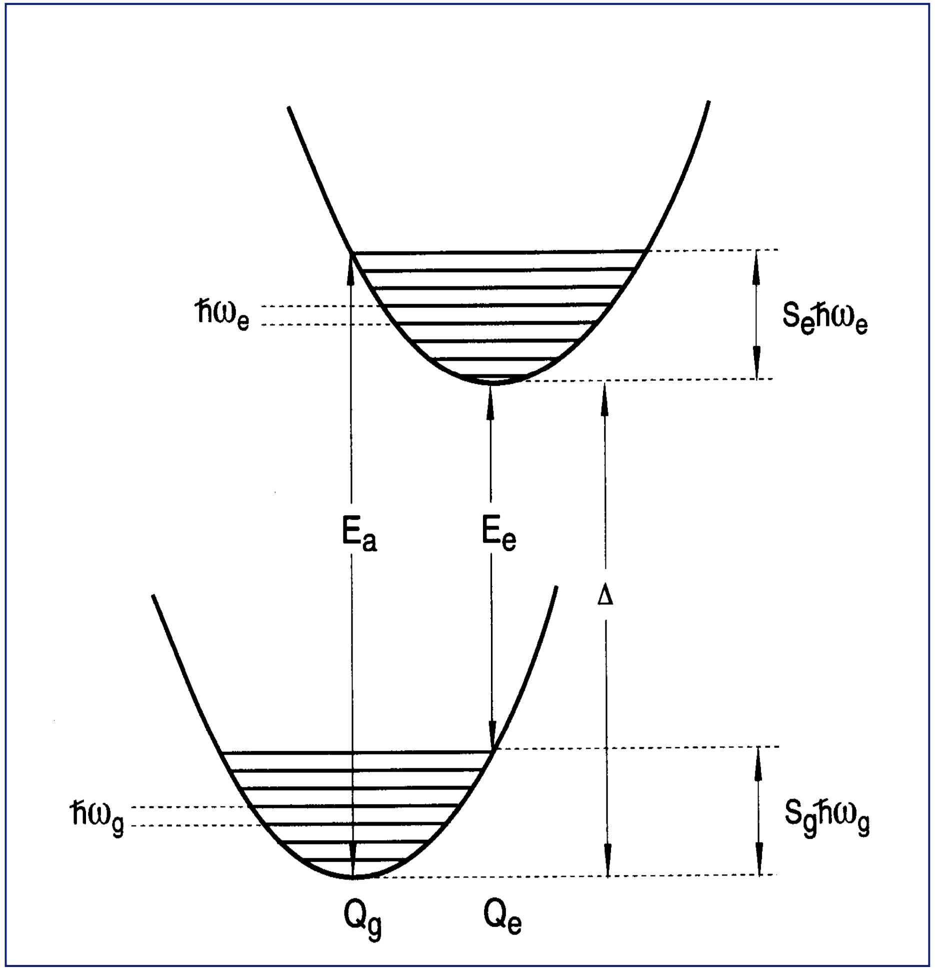
Light Yield

LY $= EQE * \eta_{abs} = EQE*(1-R)$

(No correlation to decay time!)

Loss Mechanisms

Related to the activator ions (center luminescence)



Relevant quenching mechanisms

a) Tunneling to the ground state (direct)

- Stokes Shift = Energy distance between absorption and emission band

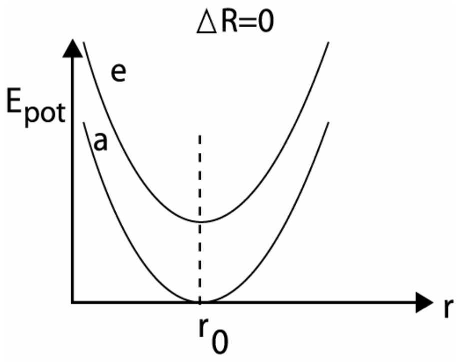
  $S = S_e hw_e + S_g hw_g$
- FWHM ~ $\sqrt{S}$
- Thermal quenching increases with increasing Dr = $r_e - r_g$ and

  Dr depends on activator-host lattice interaction

b) Tunneling to the ground state via a low-lying CT state

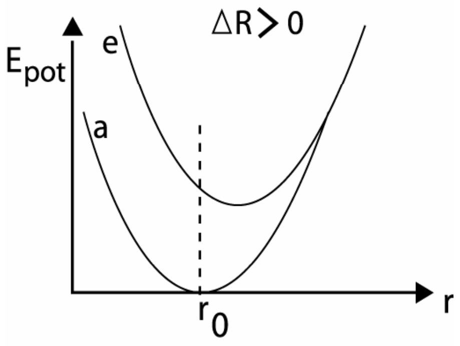
c) Photoionisation to CB

Loss Mechanisms



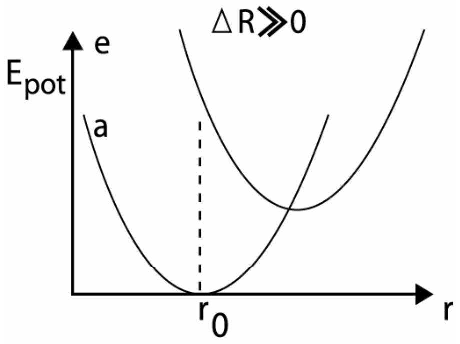
1. **Weak to no electron-phonon-coupling**

- High IQE, EQE determined by ET processes
- Thermal quenching mainly due to photoionisation
- 4f → 4f transitions (shielded 4f-shell: small CFS)
- Lines Eu^{3+}, Tb^{3+}, ….



2. **Moderate electron-phonon-coupling**

- High to moderate IQE
- Thermal quenching due to tunneling or photoionis.
- 4f → 5d transitions (large CFS)
- Narrow bands Eu^{2+}, Ce^{3+}, ….



3. **Strong electron-phonon-coupling**

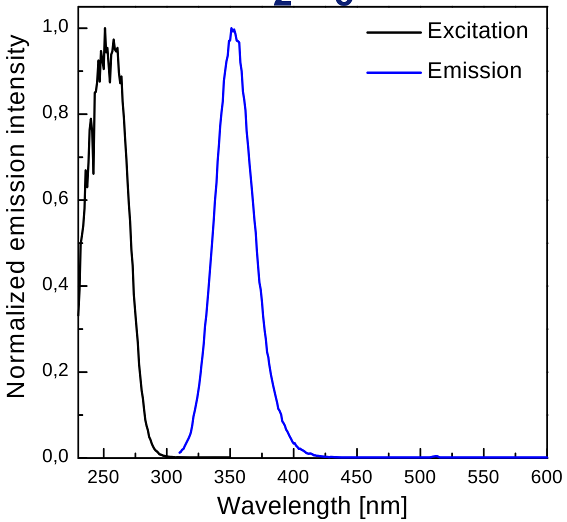
- High to low IQE at RT, strong thermal quenching
- Thermal quenching mainly due to tunneling
- $ns^2 \rightarrow ns^1np^1$ or CT transitions
- Broad bands Pb^{2+}, Bi^{3+}, ….

Loss Mechanisms

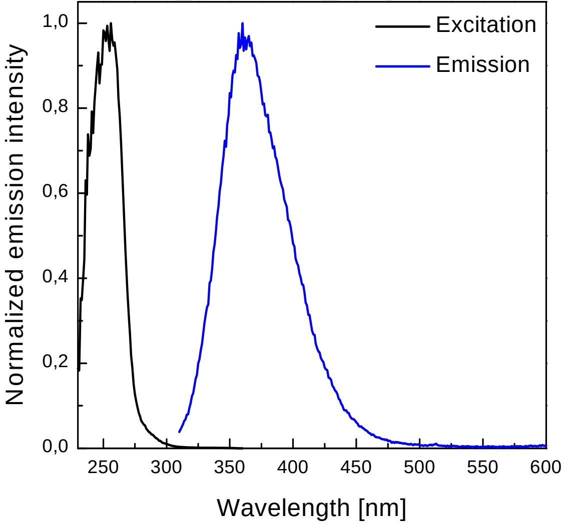
Strong electron-phonon-coupling

Example: Luminescence of Pb^{2+} - $[Xe]4f^{14}5d^{10}6s^{2} \rightarrow [Xe]4f^{14}5d^{10}6s^{1}6p^{1}$

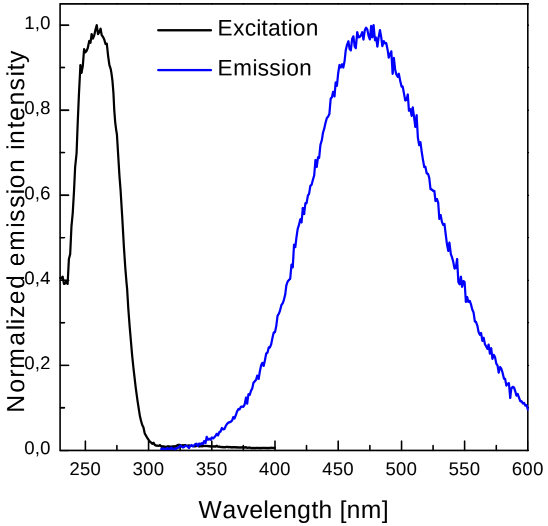
$BaSi_2O_5$:Pb



$Sr_2MgSi_2O_7$:Pb



$SrLaBO_4$:Pb

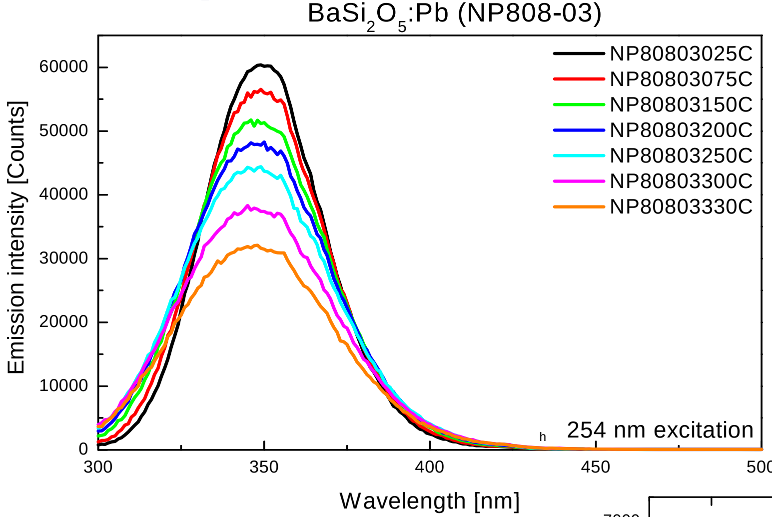


Phosphor	Stokes Shift [cm^{-1}]	FWHM [cm^{-1}]	EQE [%]
$BaSi_2O_5$:Pb	10600	2700	90
$Sr_2MgSi_2O_7$:Pb	12000	4300	75
$SrLaBO_4$:Pb	17700	5300	65

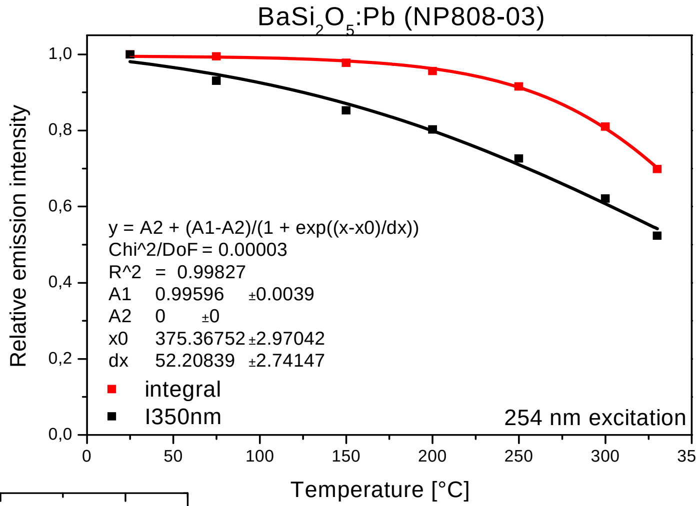
Loss Mechanisms

Strong electron-phonon-coupling

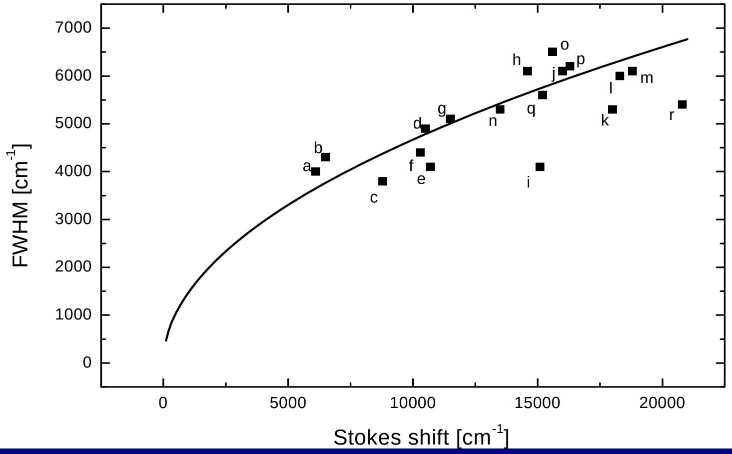
Example: Luminescence of Pb^{2+} - $[Xe]4f^{14}5d^{10}6s^2 \rightarrow [Xe]4f^{14}5d^{10}6s^16p^1$



$BaSi_2O_5$:Pb (NP808-03)



$BaSi_2O_5$:Pb (NP808-03)

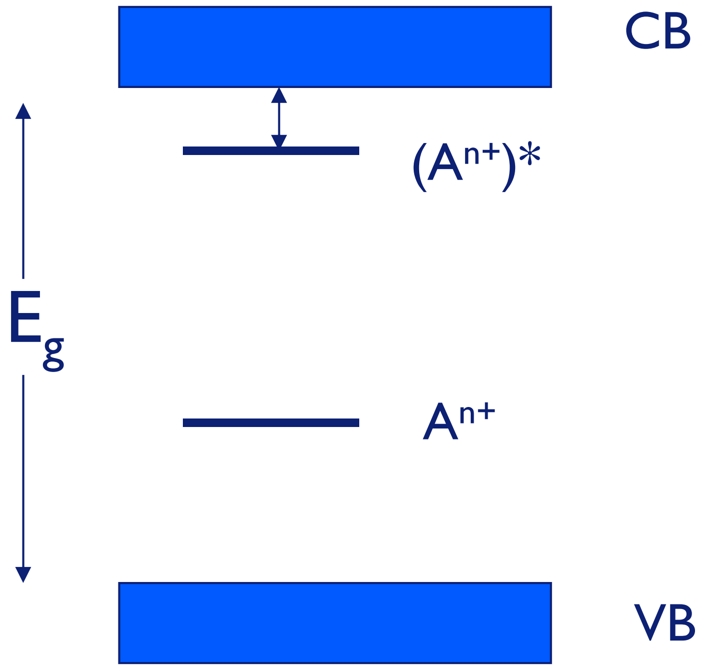


Correlation between FWHM and Stokes Shift for s^2-ion activated phosphors

Quenching due to tunneling to the ground state

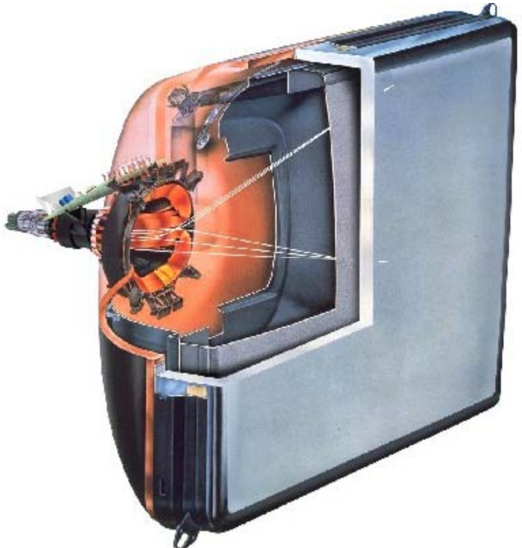
Loss Mechanisms

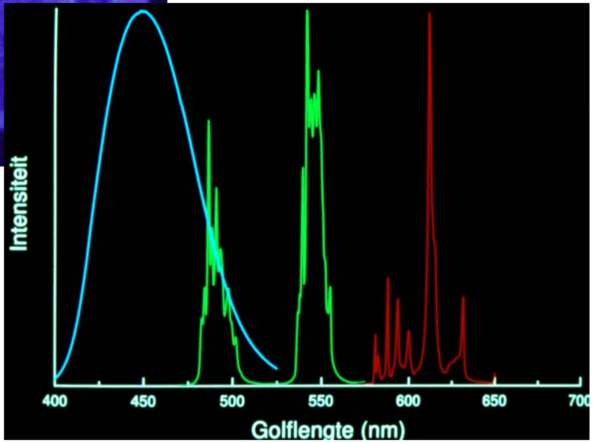
Photoionisation

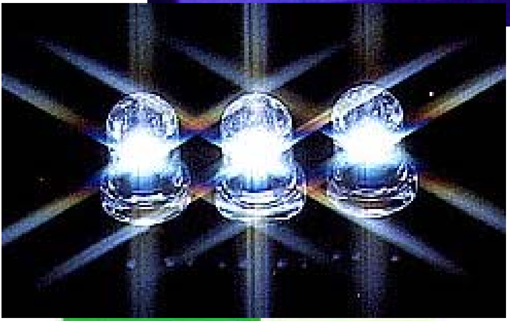


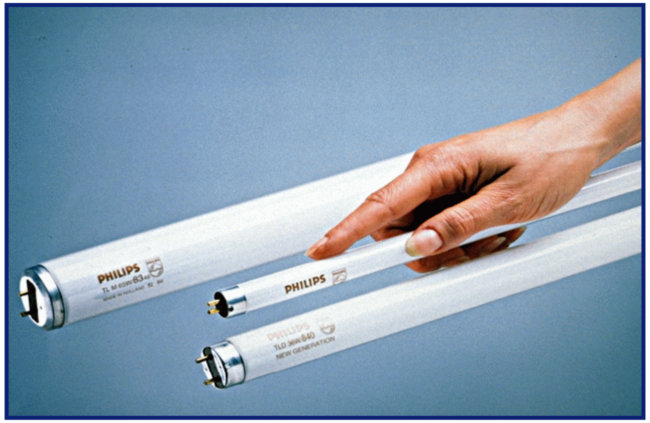
- Excited A^{n+} ion ionises
- Released electron is retrapped, e.g. by anion vacancies
- Causes afterglow
  - Scintillators
  - Persistent phosphors

Rare Earth Ions









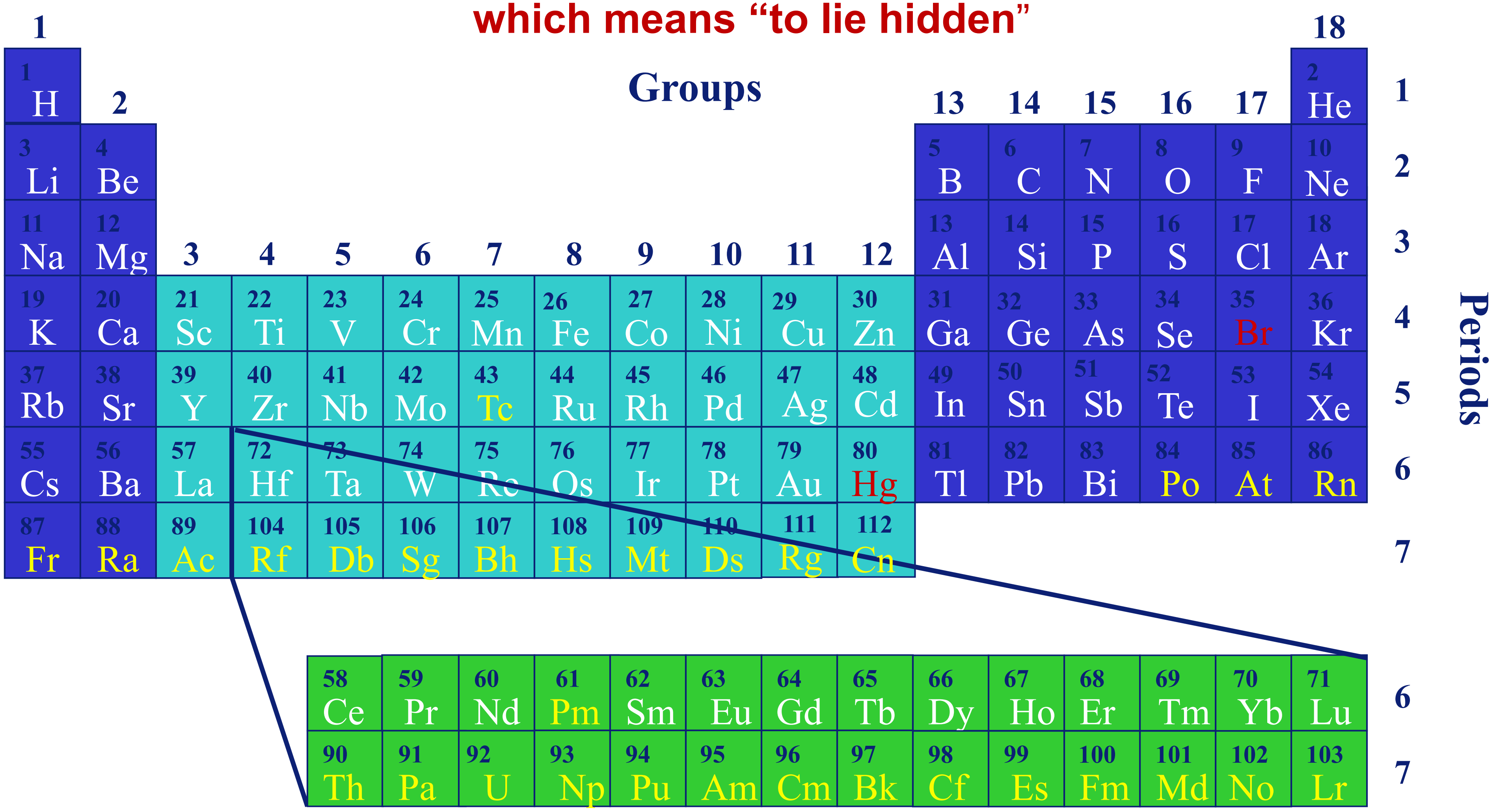
Rare Earth Ions – Vitamins?

Vitamins are organic molecules that are needed in small amounts in the diets of higher animals to maintain all metabolic functions

Higher animals	Advanced phosphors
~ 12 Vitamins	12 Rare earth ions
A, B_1, B_2, B_3, B_6, B_{12}, B_{13}, C, D, E, H, K	Ce^{3+}, Pr^{3+}, Nd^{3+}, $Sm^{2+/3+}$, $Eu^{2+/3+}$, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, $Yb^{2/3+}$
Low concentrations required mg – g / day	Low doping levels 0.1 – 5 atom-%

Rare Earth Ions

Lanthanides originates from the Greek word "λανθανειν", which means "to lie hidden"

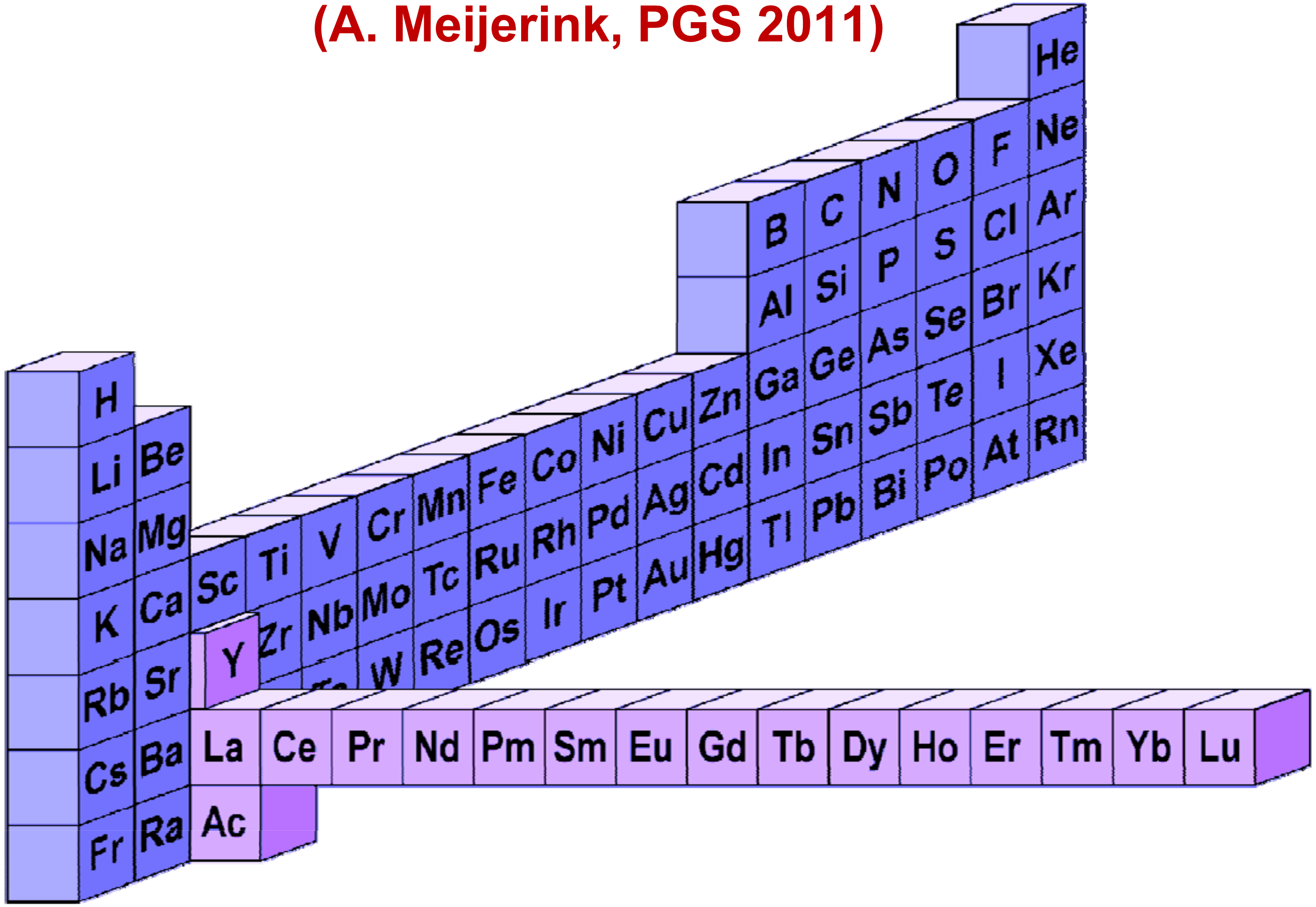


Groups

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Periods
1 H																	2 He	1
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	2
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	3
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	4
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	5
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	6
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn							7
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	6
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	7

Rare Earth Ions

Instead of "to lie hidden" λανθανειν,
a better name would be "to be outstanding" επιφανης – epifanides
(A. Meijerink, PGS 2011)



Phosphors Activated by Rare Earth Ions

Cathode-ray tubes	Early phosphors	Recent phosphors
	$ZnS:Ag$ $ZnS:Cu,Al,Au$ $(Zn,Cd)S:Ag$ $Zn_3(PO_4)_2:Mn$	$ZnS:Ag$ $ZnS:Cu,Al,Au$ $YVO_4:Eu$ $Y_2O_2S:Eu$
Fluorescent lamps		
	$MgWO_4$ $Zn_2SiO_4:Mn$ $(Zn,Be)_2SiO_4:Mn$ $Ca_5(PO_4)_3(F,Cl):Sb,Mn$	$BaMgAl_{10}O_{17}:Eu$ $LaPO_4:Ce,Tb$ $CeMgAl_{11}O_{19}:Tb$ $GdMgB_5O_{10}:Ce,Tb$ $Y_2O_3:Eu$ $GdMgB_5O_{10}:Ce,Tb,Mn$

Phosphors Activated by Rare Earth Ions

Activator	Host Lattice	Emission at [nm]	Colour	Application
Ce^{3+}	$SrAl_{12}O_{19}$ $LaPO_4$ YPO_4	300 320 335, 355	UV-B UV-B UV-A	Tanning lamps
Pr^{3+}	Gd_2O_2S $CaTiO_3$	510 610	Green Red	CT Scanner FEDs
Nd^{3+}	$Y_3Al_5O_{12}$	1064	Red	Laser
Sm^{3+}	$Y_3Al_5O_{12}$	620	Red	Laser
Eu^{2+}	SrB_4O_7 $Sr_4Al_{14}O_{25}$ CaS	368 490 655	UV-A Blue Rot	Black light lamps Afterglow LEDs
Eu^{3+}	$(Y,Gd)BO_3$ YVO_4	611 615	Red Red	Plasma displays HP Hg discharge lamps
Gd^{3+}	$(La,Bi)B_3O_6$	311	UV-B	Psoriasis lamps
Tb^{3+}	Y_2SiO_5 $(Y,Gd)BO_3$ Gd_2O_2S	544 544 544	Green Green Green	Projection TV sets Plasma displays X-ray converter screens
Yb^{3+}	$Y_3Al_5O_{12}$	620	Red	Laser

Rare Earth Ions – Fundamental Aspects

Electron configuration of rare earth metals and ions

Metals

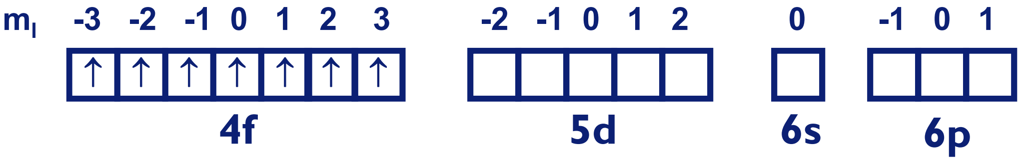
[Xe]	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
6s	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
5d	1	0	0	0	0	0	0	1	0	0	0	0	0	0	1
4f	0	2	3	4	5	6	7	7	9	10	11	12	13	14	14

Ions

[Xe]	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
	Ce^{4+}	Pr^{4+}	Nd^{4+}				Sm^{2+}	Eu^{2+}						Tm^{2+}	Yb^{2+}
4f	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

Example

Gd^{3+}/Eu^{2+}



$S = \Sigma s = 7/2$ → $2S+1 = 8$ → strongly paramagnetic ions

$L = |\Sigma l| = 0$ → „S“ → LS-Term symbol ^8S

Rare Earth Ions – Fundamental Aspects

History of distangling the energy level structure

1908 Bequerel
sharp lines in optical spectra of lanthanide ions

1937 Van Vleck
The puzzle of rare earth

1960's Judd, Wybourne, Dieke, Carnall
Theory for energy level structure and transition probabilities of 4f-4f transitions

Rare Earth Ions – Fundamental Aspects

Energy level structure of [Xe]$4f^n$ ions

Partly filled 4f-shell results in multiple electron configurations:

e.g. Tb^{3+} $4f^8$ → 8 electrons into 7 f-orbitals: 3003 different arrangements!

Free ion energy levels due to:

1. **Electrostatic interactions (comparable to $3d^n$ ions)**
2. **Spin-orbit coupling (larger than for $3d^n$ ions)**
3. **Crystal field splitting (smaller than for $3d^n$ ions)**

Ground state m_l =

-3	-2	-1	0	1	2	3
↑	↑	↑	↑	↑	↑	↑↓

4f

$^7F_6$

1^{st} excited state m_l =

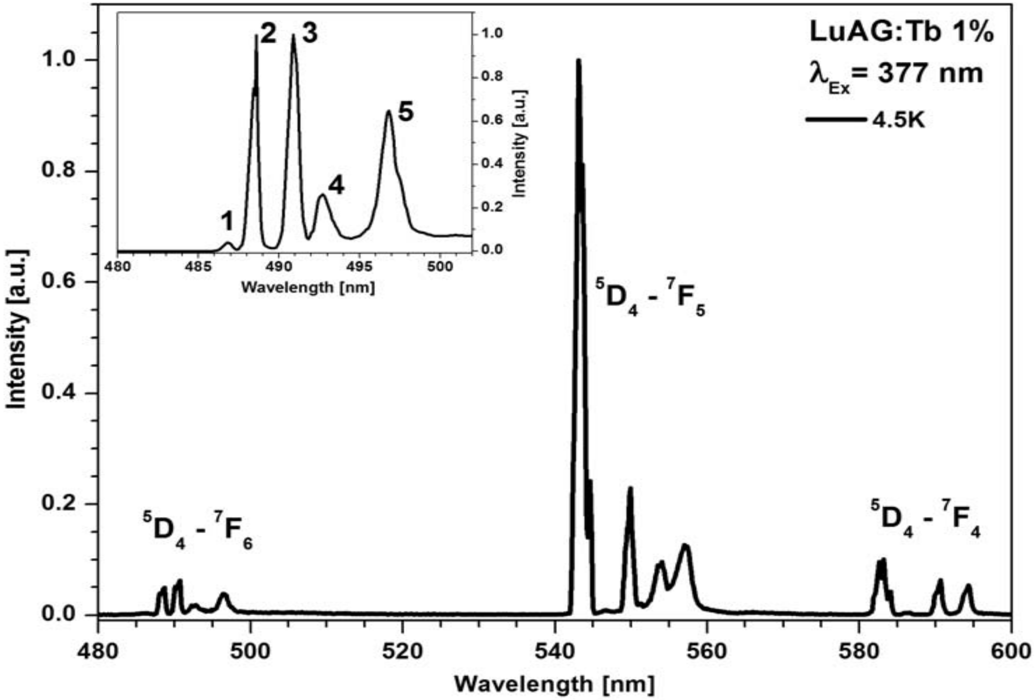
-3	-2	-1	0	1	2	3
↑	↑	↑	↑	↑	↑↓	↓

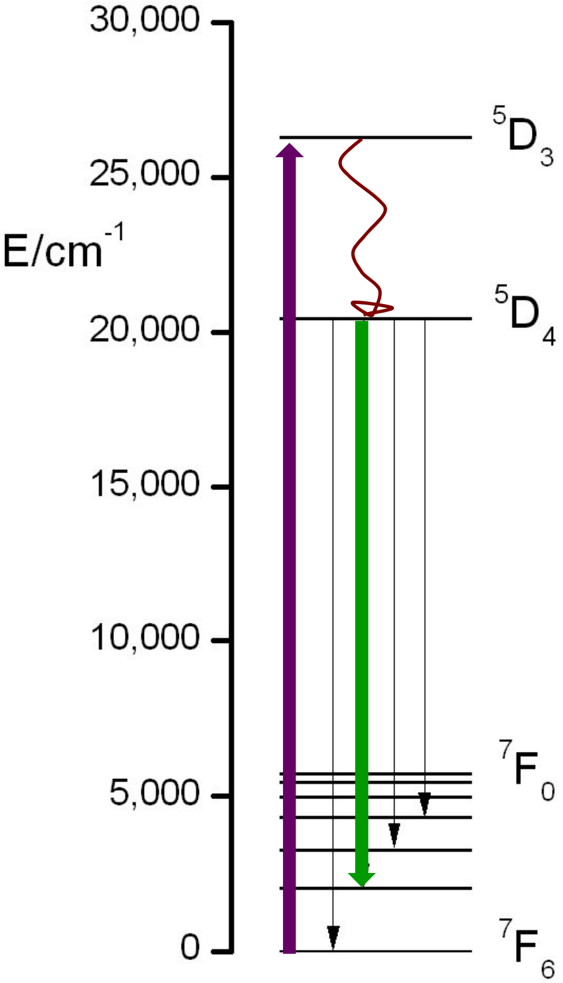
4f

$^5D_4$

Rare Earth Ions – Fundamental Aspects

Typical emission spectrum of Tb^{3+} (LuAG:Tb)



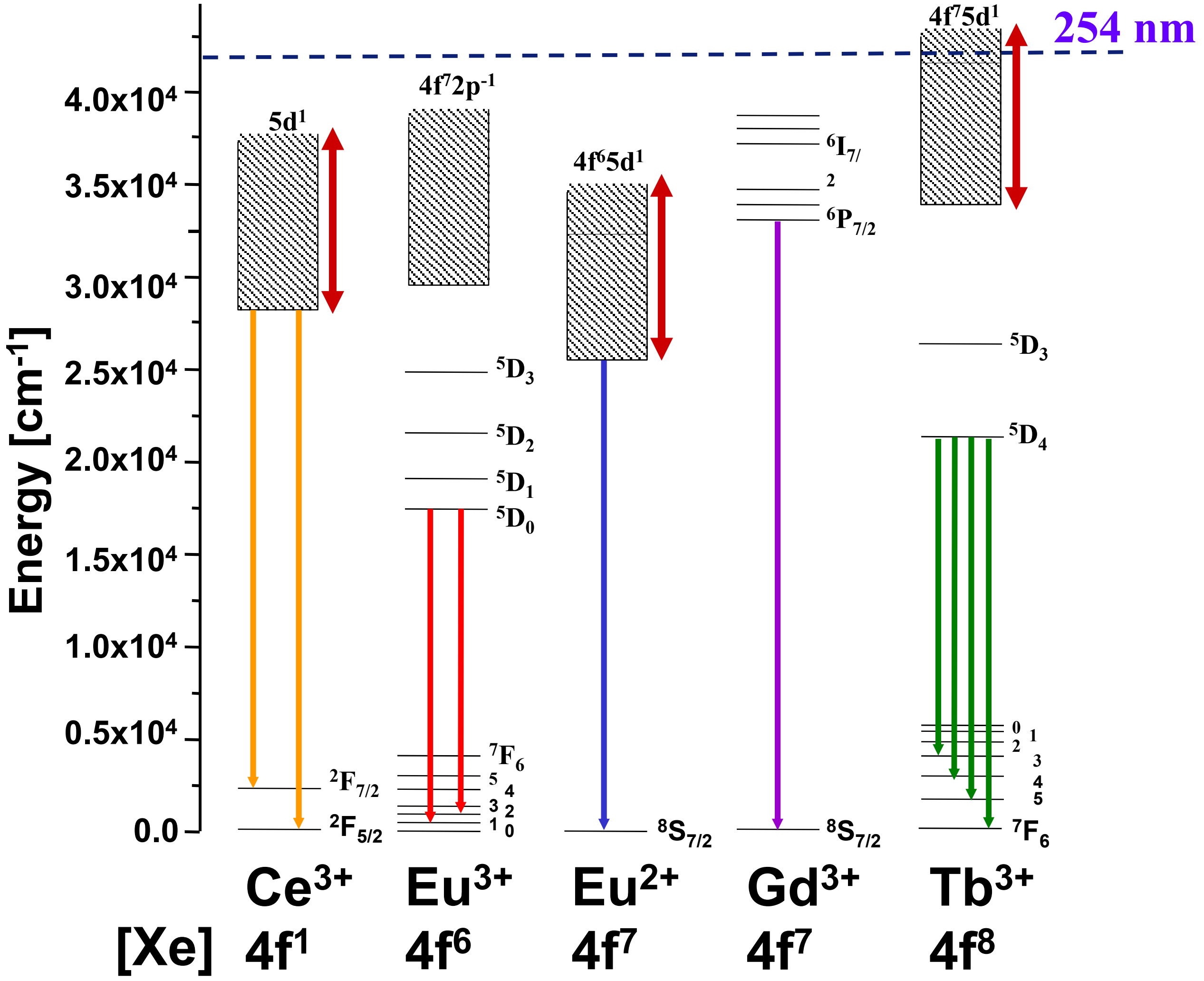


Characteristic luminescence of lanthanides

- Sharp emission lines
- Almost independent of chemical environment, e.g. green-yellow emission of Tb^{3+} phosphors
- High quantum yield (> 90%), due to small Stokes shift

Rare Earth Ions – Fundamental Aspects

Simplified energy level schemes of selected RE ions



Line emitting ions

- Pr^{3+}
- Nd^{3+}
- $Sm^{2+/3+}$
- Eu^{3+} (Eu^{2+})
- Gd^{3+}
- Tb^{3+}
- Dy^{3+}
- Ho^{3+}
- Er^{3+}
- Tm^{3+}
- Yb^{3+}

Band emitting ions

- Ce^{3+}
- Pr^{3+}
- Nd^{3+}
- Eu^{2+}
- Yb^{2+}

Rare Earth Ions – Fundamental Aspects

1. Electrostatic interactions

Shielding due to inner electrons described by the so-called Slater parameters (compare to Racah parameters)

$$F^{(k)} = \frac{e^2}{4\pi\varepsilon_0} \int_0^\infty \int_0^\infty \frac{r_<^k}{r_>^{k+1}} [R'_{4f}(r_i) R'_{4f}(r_j)]^2 r_i^2 r_j^2 \, dr_i \, dr_j$$

Electrostatic interaction increases with effective charge on the activator ion (charge density)

Therefore splitting between different terms depends on

- **Oxidation state**
- **Nucleus charge**
- **Charge flow back from ligands (polarisibility of anions)**

Rare Earth Ions – Fundamental Aspects

2. Spin-orbit coupling

Spin-orbit coupling constant ζ increases through the lanthanide series, i.e. from ζ(Ce) = 650 cm^{-1} to ζ(Yb) = 2930 cm^{-1}

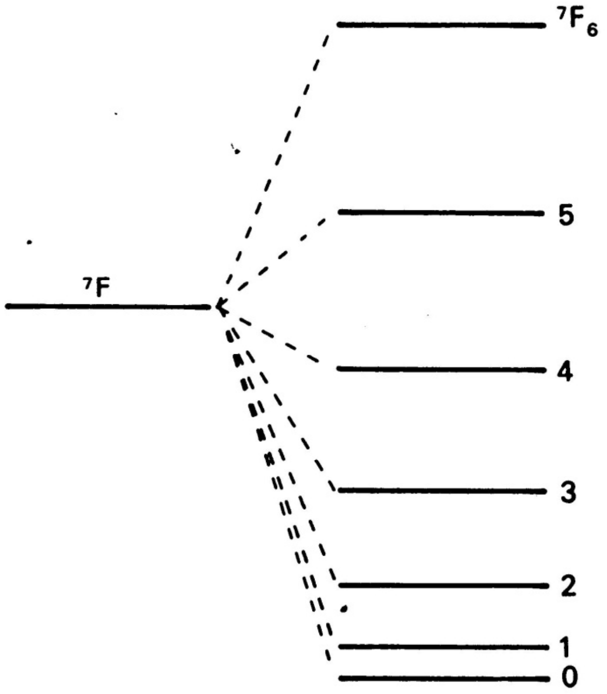
Further splitting of *LS* terms into *J*-levels by energy, assuming weak spin-orbit coupling:

→ Complete term symbol:

$^{2S+1}L_J$ with |L-S| < J < L+S

For Tb^{3+} Ground state: $^7F_{6,5,4,3,2,1,0}$

Excited state: $^5D_{4,3,2,1,0}$

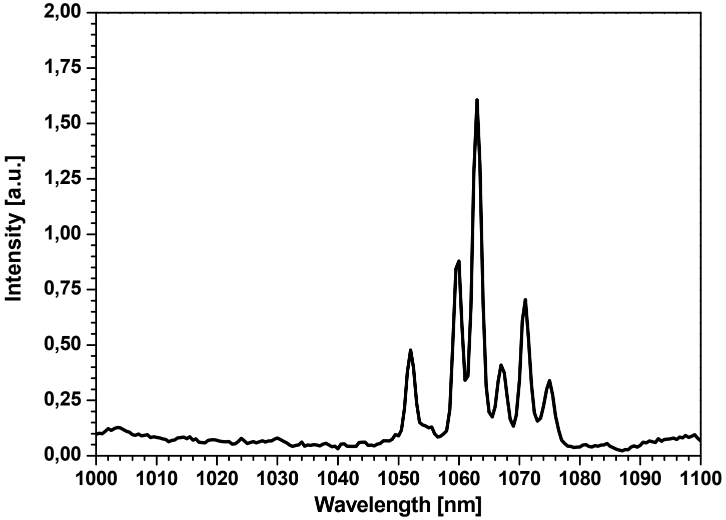


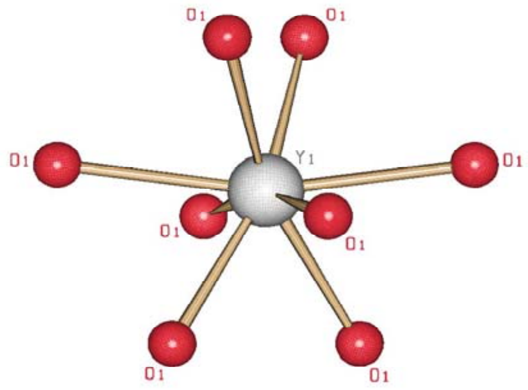
Rare Earth Ions – Fundamental Aspects

3. Crystal-field splitting

Further splitting of *J* multiplets into a maximum of 2*J*+1 levels
Crystal field splitting ~ 100 cm^{-1} + sensitive function of site symmetry

LuAG:Nd^{3+}
$^4F_{3/2} - {}^4I_{11/2}$
$\Delta E = 203$ cm^{-1}
six levels without external magnetic field





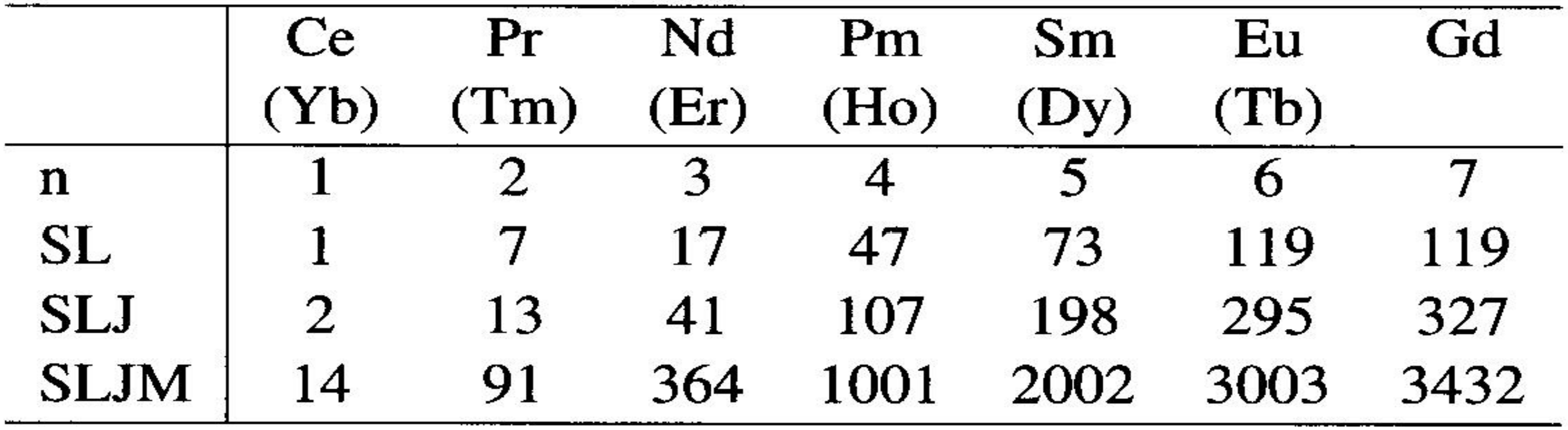
Dodecahedral coordination

Extra fitting parameters B^k_q for fit of experimentally observed levels:

$$\mathcal{H}_c^{O_h} = B_0^4\left[C_0^{(4)} + \sqrt{\frac{5}{14}}\left(C_{-4}^{(4)} + C_4^{(4)}\right)\right] + B_0^6\left[C_0^{(6)} - \sqrt{\frac{7}{2}}\left(C_{-4}^{(6)} + C_4^{(6)}\right)\right]$$

Rare Earth Ions – Fundamental Aspects

In summary: RE ions exhibit a large number of energy levels $^{2S+1}L_J$

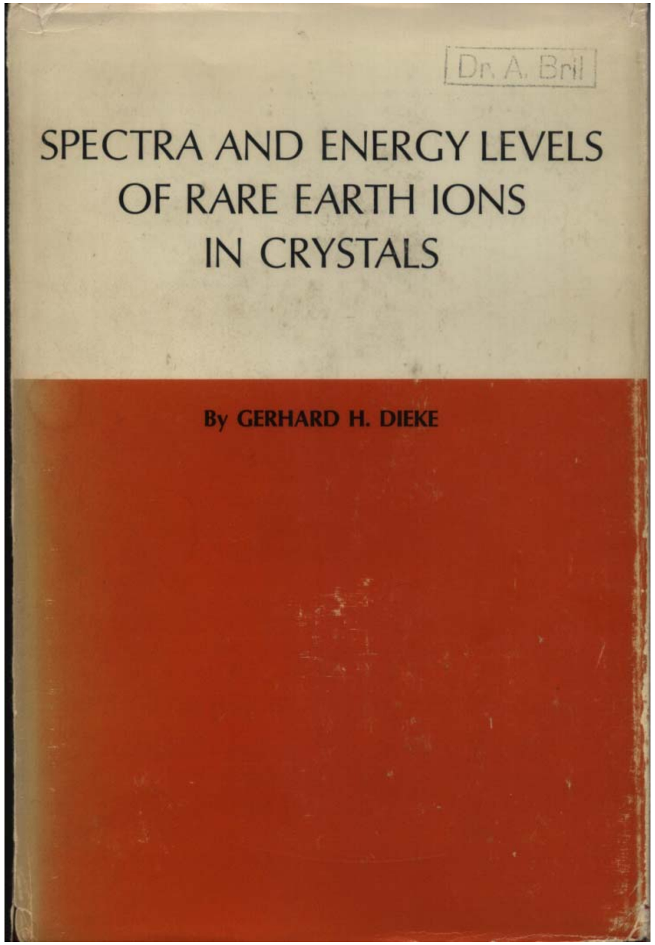


	Ce (Yb)	Pr (Tm)	Nd (Er)	Pm (Ho)	Sm (Dy)	Eu (Tb)	Gd
n	1	2	3	4	5	6	7
SL	1	7	17	47	73	119	119
SLJ	2	13	41	107	198	295	327
SLJM	14	91	364	1001	2002	3003	3432

Early experimental and theoretical work on $LaCl_3:Ln^{3+}$ and $LaF_3:Ln^{3+}$ by Dieke and Carnall (experiment) and Judd, Crosswhite, Wybourne (theory):
“Dieke diagram” and the “Blue book”

Rare Earth Ions – Fundamental Aspects

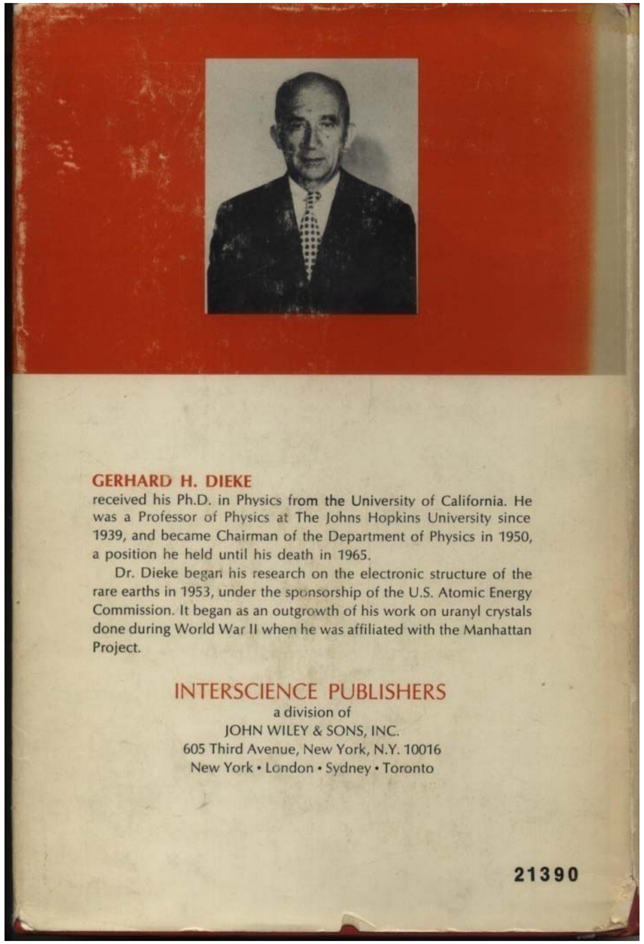
Gerhard H. Dieke 1968



Dr. A. Bril

SPECTRA AND ENERGY LEVELS
OF RARE EARTH IONS
IN CRYSTALS

By GERHARD H. DIEKE



GERHARD H. DIEKE
received his Ph.D. in Physics from the University of California. He was a Professor of Physics at The Johns Hopkins University since 1939, and became Chairman of the Department of Physics in 1950, a position he held until his death in 1965.

Dr. Dieke began his research on the electronic structure of the rare earths in 1953, under the sponsorship of the U.S. Atomic Energy Commission. It began as an outgrowth of his work on uranyl crystals done during World War II when he was affiliated with the Manhattan Project.

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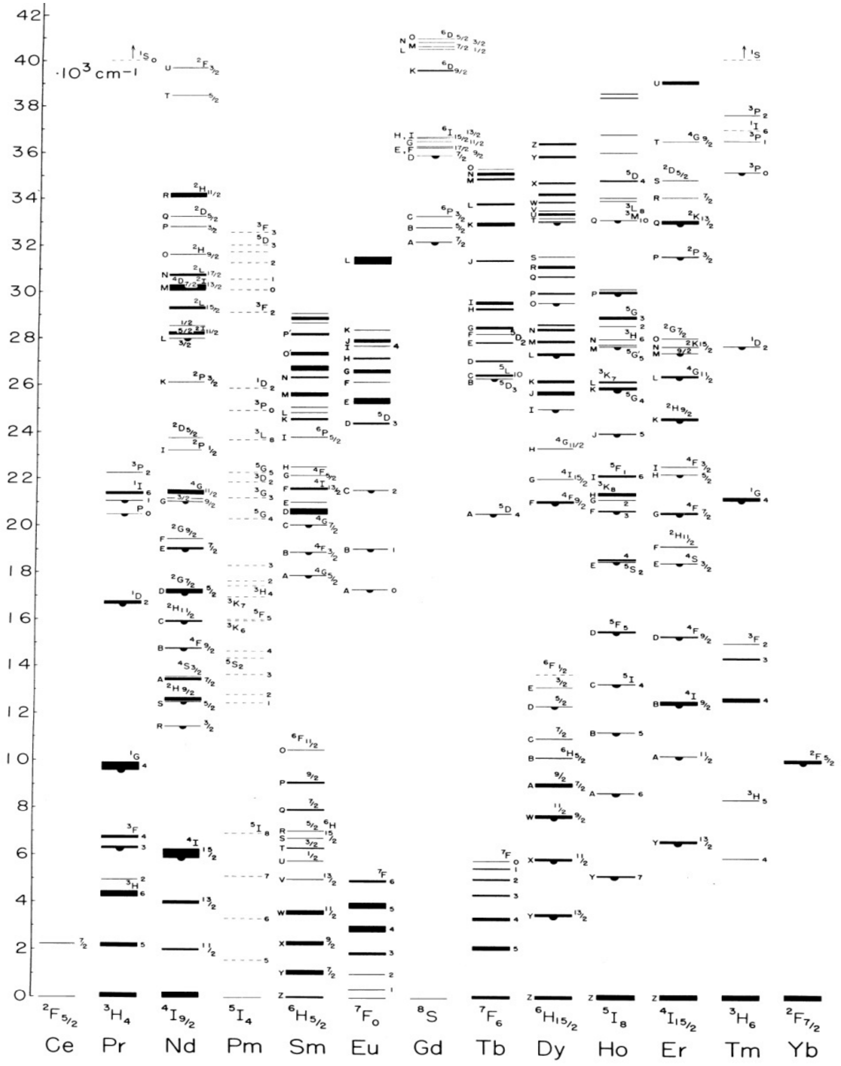
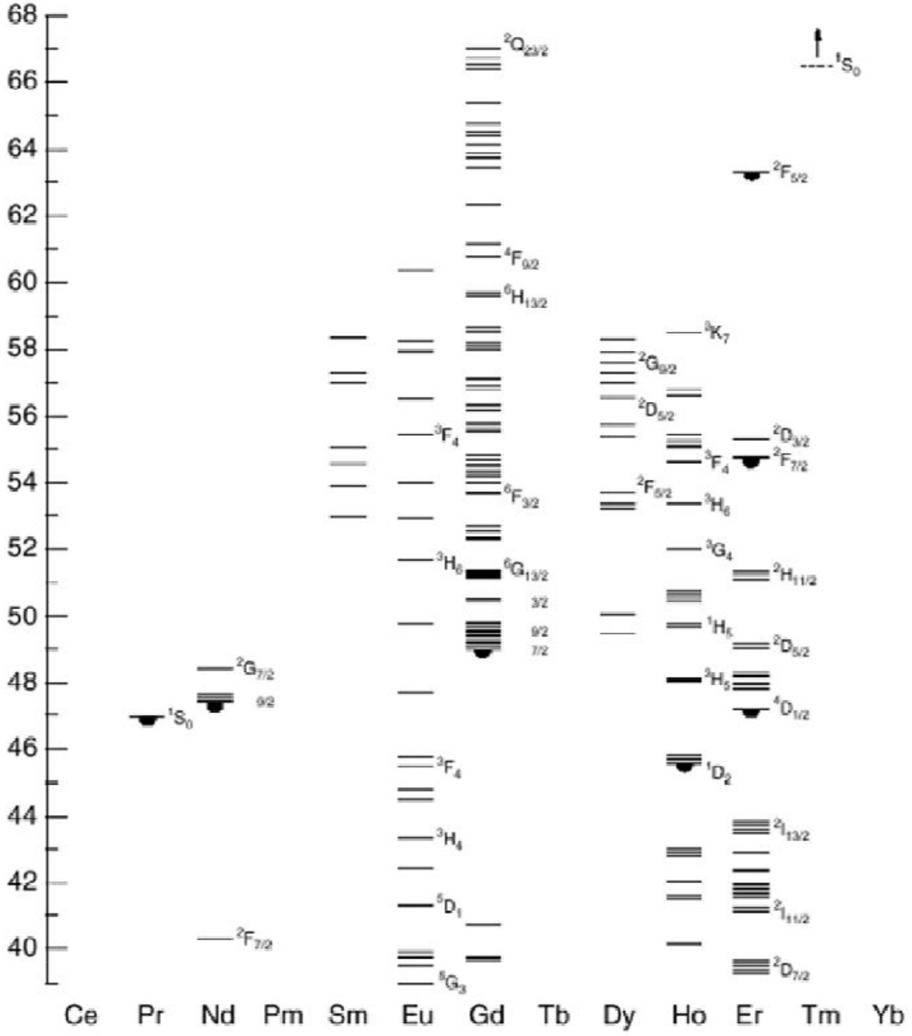
Rare Earth Ions – Fundamental Aspects

Energy levels of trivalent lanthanides: Dieke diagram



Rare Earth Ions – Fundamental Aspects

A. Meierjink: Extended Dieke diagram



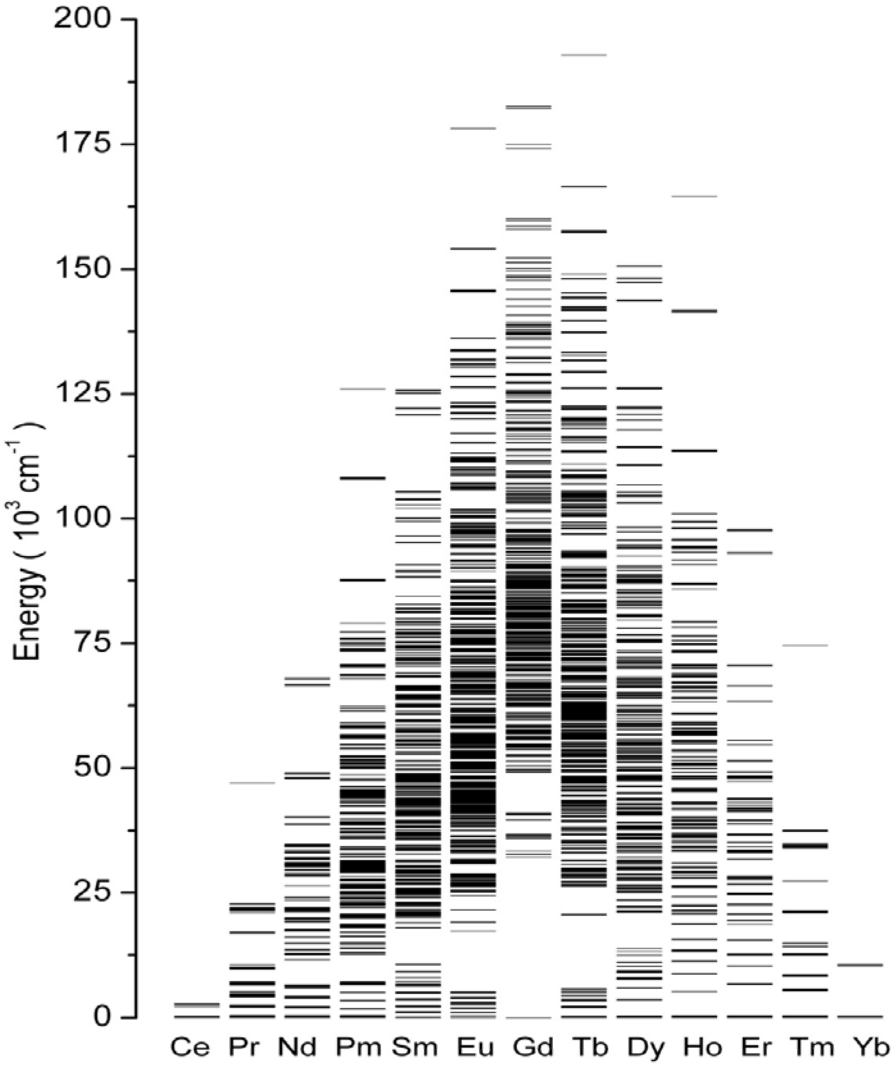
P.S. Peijzel, A. Meijerink, R.T. Wegh et al, J. Solid State Chem. **178** (2005) 448

Rare Earth Ions – Fundamental Aspects

Complete energy level diagram

Ce^{3+}	~	Yb^{3+}
Pr^{3+}	~	Tm^{3+}
Nd^{3+}	~	Er^{3+}
Pm^{3+}	~	Ho^{3+}
Sm^{3+}	~	Dy^{3+}
Eu^{3+}	~	Tb^{3+}
Gd^{3+}		

Energy level splitting increases from Ce^{3+} to Yb^{3+} due to increasing nucleaus charge



Fundamental Aspects – 4f-4f Transitions

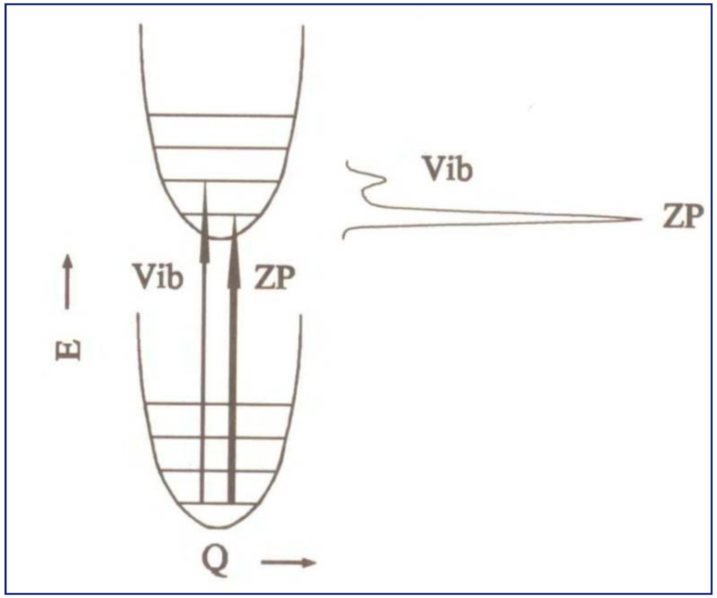
Characteristic optical properties

1) Sharp lines (atomic like), Stokes shift ~ 0 cm^{-1}

2) Little influence of environment on energy level scheme

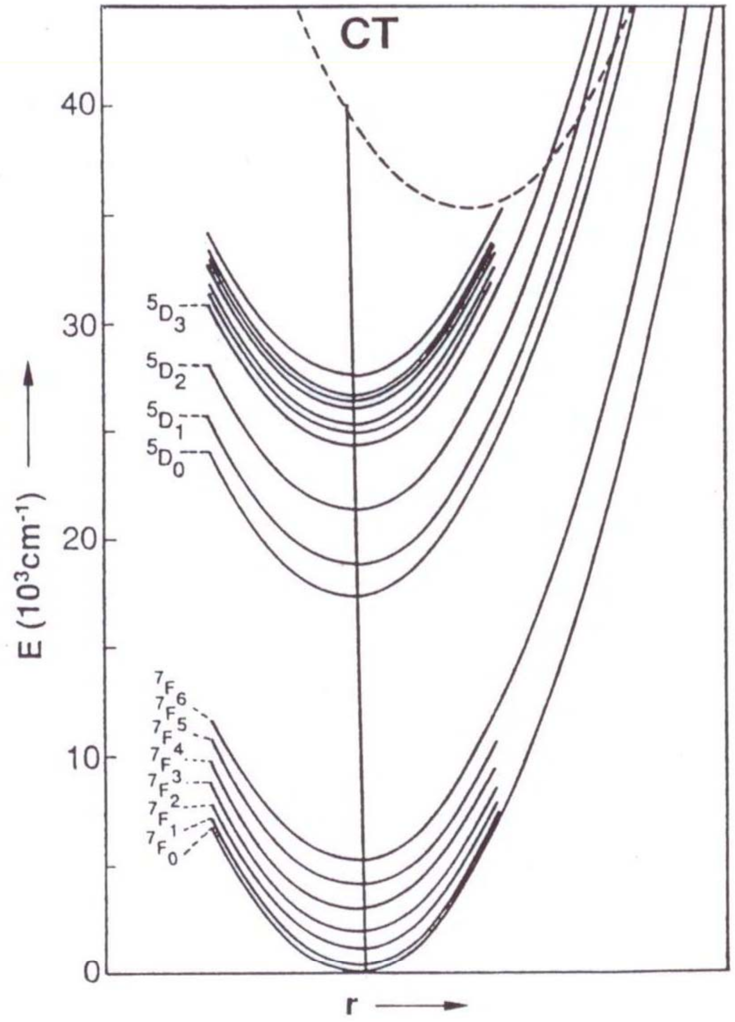
3) Parity forbidden transitions (~ms life time, f ~10^{-5})

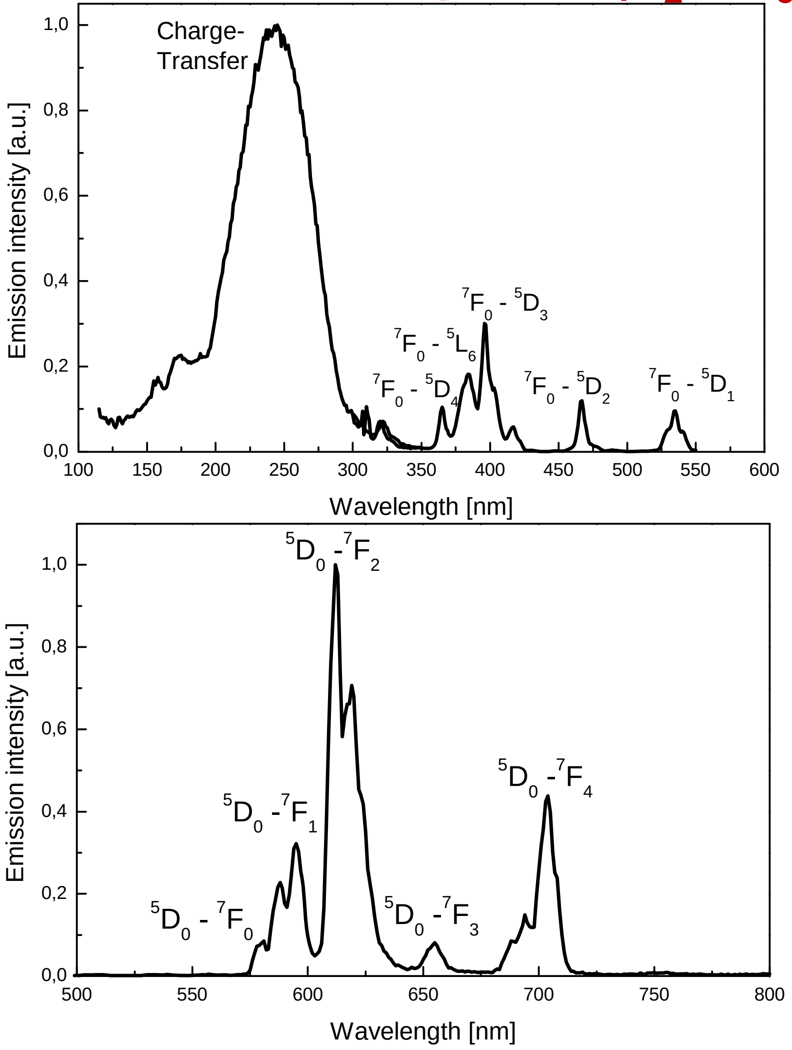
Origin: Shielding of $4f^n$ electrons
by outer filled 5s and 5p shells
→ no shift of excited state parabola
and strong zero-phonon lines (ZP)



Fundamental Aspects – 4f-4f Transitions

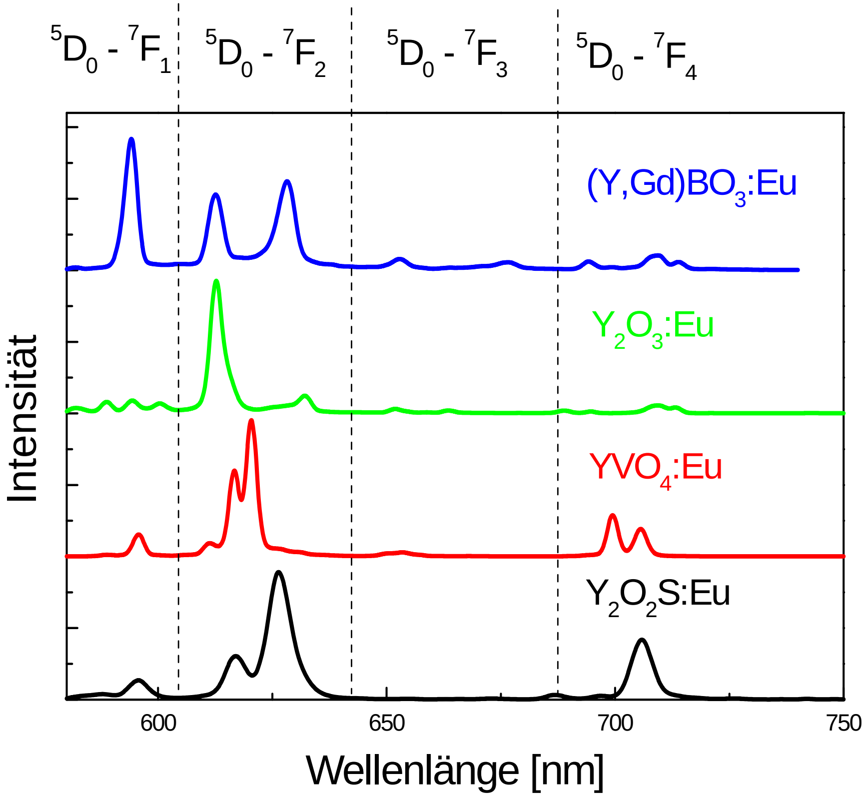
Example: Eu^{3+} - Typical excitation and emission spectra (Y_2SiO_5:Eu)





Fundamental Aspects – 4f-4f Transitions

Emission spectra and colour points of Eu^{3+} activated phosphors

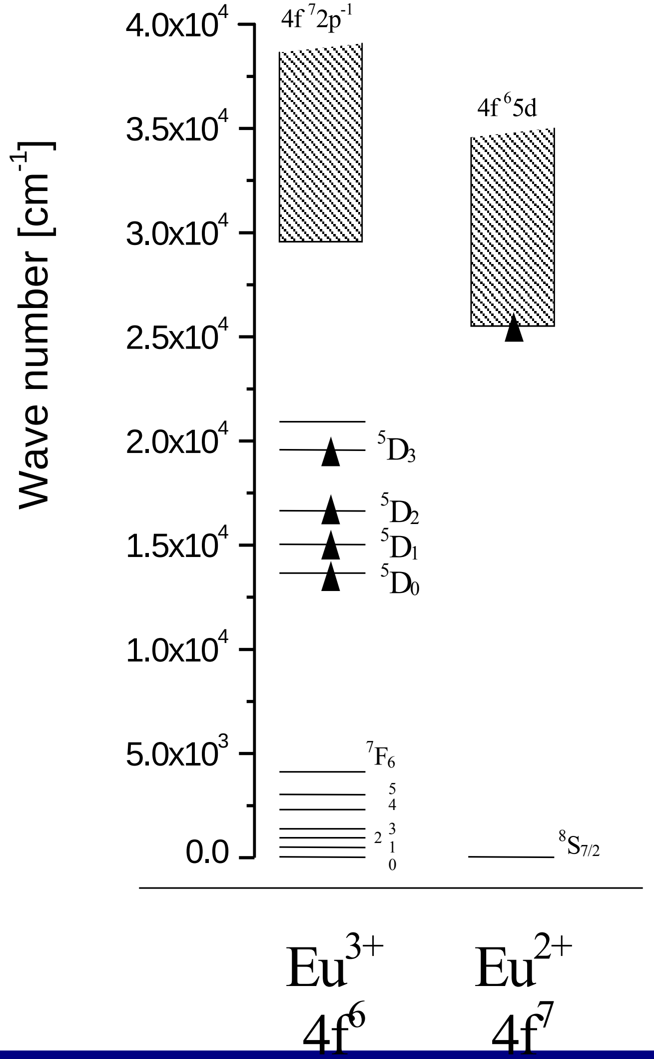


Phosphor	CIE1931 colour point x	CIE1931 colour point y
$(Y,Gd)BO_3$:Eu	0.640	0.360
Y_2O_3:Eu	0.641	0.344
YVO_4:Eu	0.645	0.343
Y_2O_2S:Eu	0.650	0.342

Colour saturation: Y_2O_2S:Eu > YVO_4:Eu > Y_2O_3:Eu > $(Y,Gd)BO_3$:Eu

Fundamental Aspects – 4f-4f Transitions

Emission spectra and colour points of Eu^{3+} activated phosphors

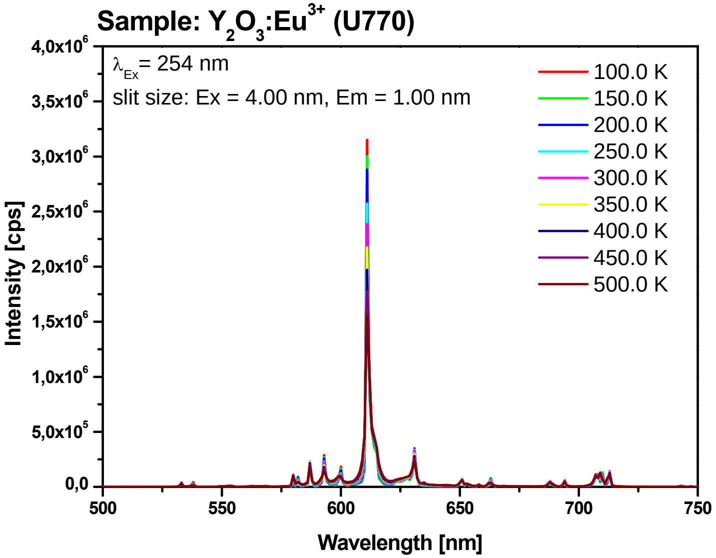


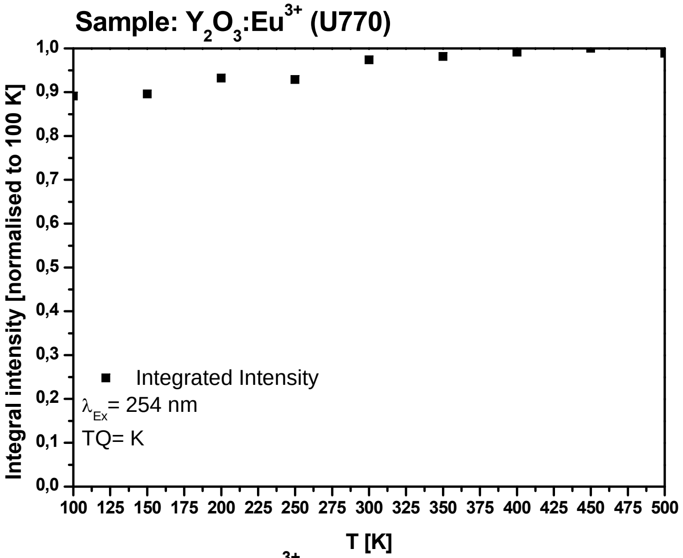
Observed emission spectrum due to $^5D_0 \rightarrow {}^7F_J$ transitions (lines)

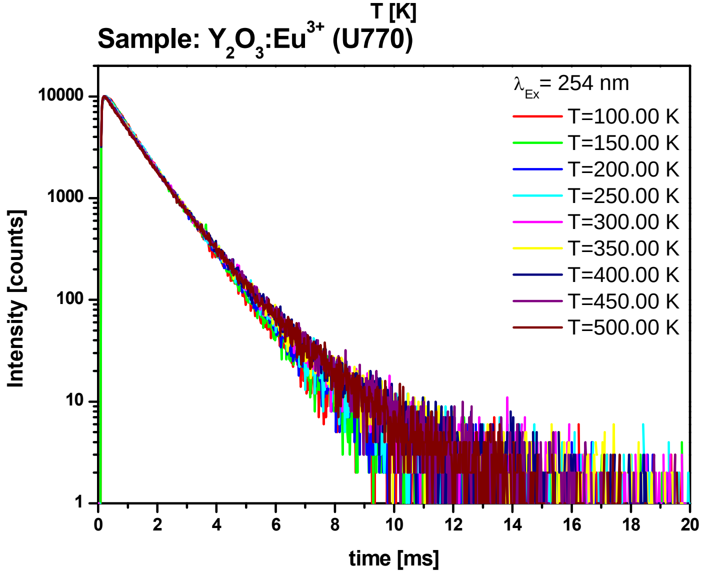
a) Inversion symmetry (S_6, D_{3d})
Magnetic dipole transitions, e.g. $^5D_0$ - $^7F_1$
$\Delta J = 0, \pm 1$ ($J = 0 \rightarrow J = 0$ forbidden)
$MeBO_3$:Eu (Calcite, Vaterite)
$\tau \sim 8 - 16$ ms

b) No inversion symmetry
Electric dipole transitions $^5D_0$ -$^7F_{2,4}$
$\Delta J \leq 6$ ($J_i = 0 \rightarrow J_f = 2, 4, 6$)
Y_2O_3:Eu (Bixbyite), $Y(V,P)O_4$:Eu (Xenotime)
$\tau \sim 2 - 5$ ms

Fundamental Aspects – 4f-4f Transitions







Y_2O_3:Eu(5%)

λ_{exc} = 254 nm

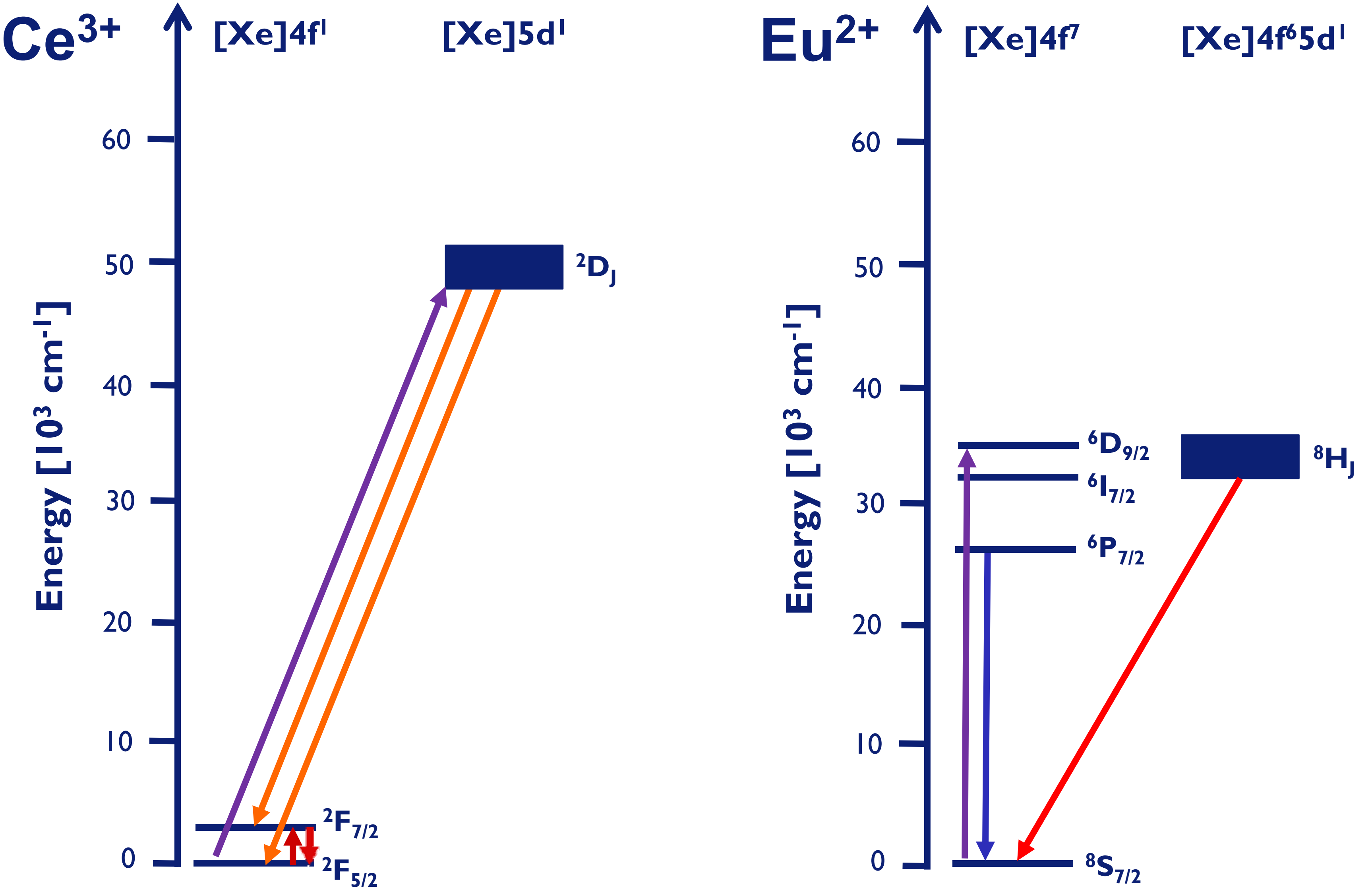
λ_{em} = 611 nm

QE ~ 95%

$\tau_{1/e}$ = 1.1 ms, $\tau_{1/10}$ = 2.5 ms

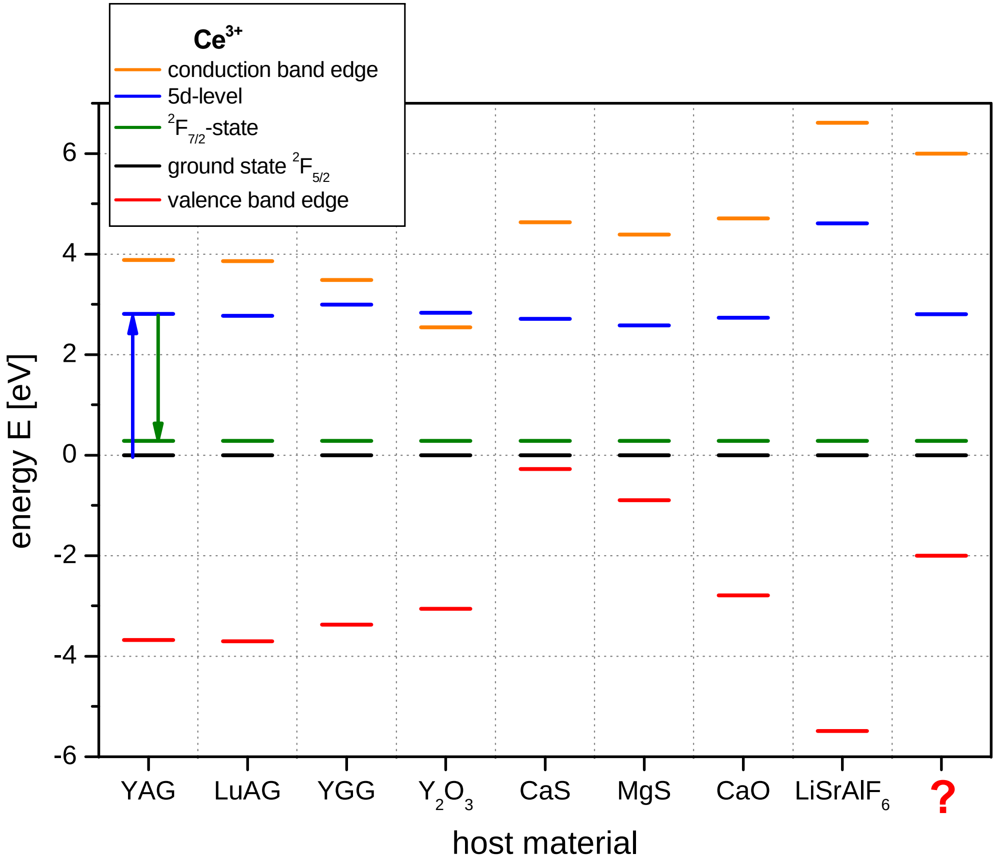
$TQ_{1/2}$ > 500 °C

Fundamental Aspects $4f^n \rightarrow 4f^{n-1}5d^1$ Transitions



Fundamental Aspects $4f^n \rightarrow 4f^{n-1}5d^1$ Transitions

Example: Ce^{3+} luminescence in different inorganic host lattices



Some observations

YAG:Ce and LuAG:Ce are efficient phosphors with a high thermal quenching temperature

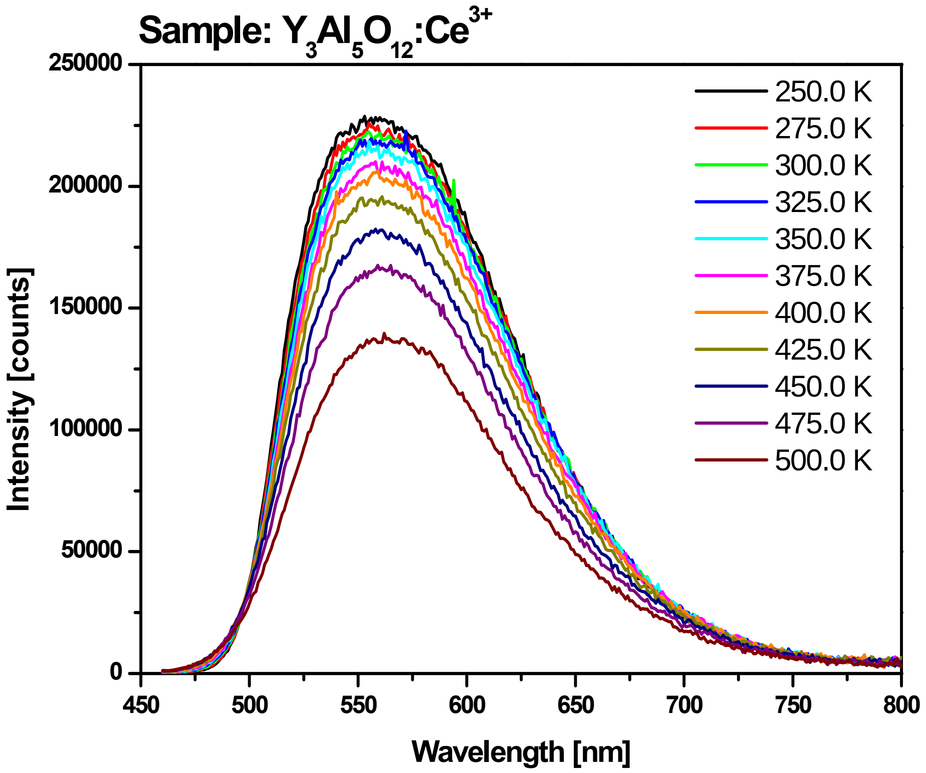
YGG:Ce and LGG:Ce suffer from thermal quenching

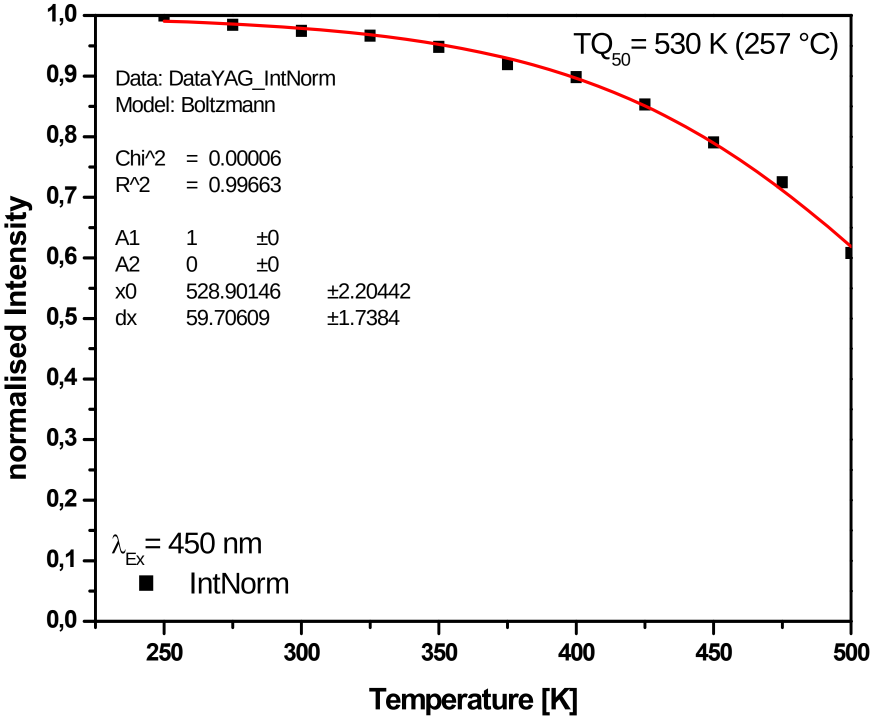
Y_2O_3:Ce does not luminesce at all

MgS:Ce and CaS:Ce are efficient EL phosphors

Quenching by		
	multiphonon relaxation?	No
	cross-relaxation?	No
	tunneling?	Yes for a large S.S.: $Gd_3Al_5O_{12}$:Ce
	photoionisation?	Yes for small $[Xe]4f^65d^1$ to CB distance

Fundamental Aspects $4f^n \rightarrow 4f^{n-1}5d^1$ Transitions





Thermal quenching of YAG:Ce(2%)

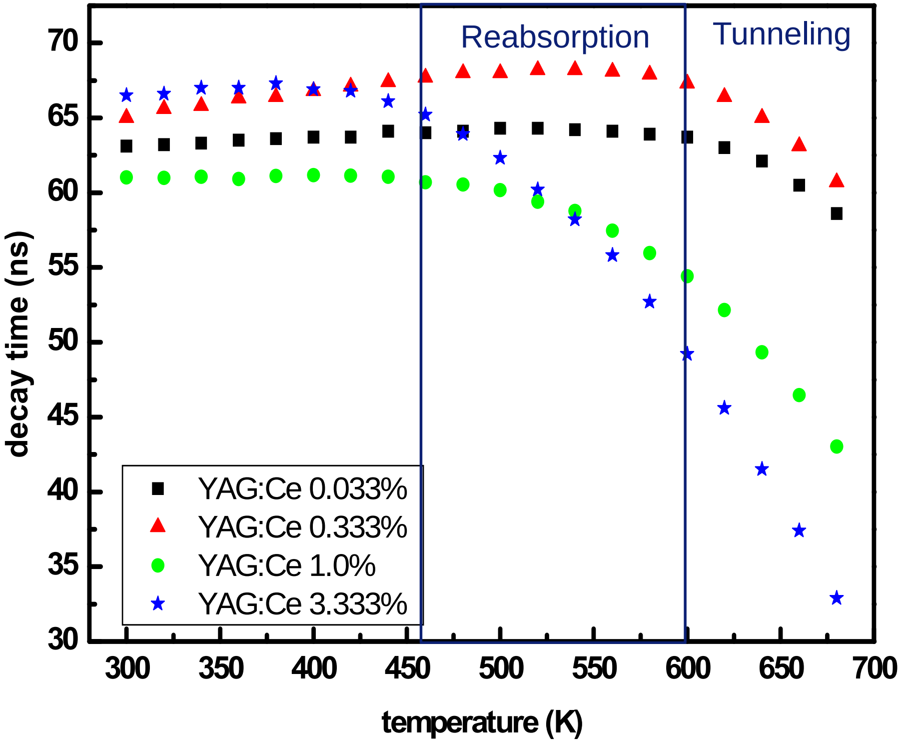
λ_{exc} = 450 nm

λ_{em} = 560 nm

$TQ_{1/2}$ = 260 °C

Fundamental Aspects $4f^n \rightarrow 4f^{n-1}5d^1$ Transitions

A closer look into the thermal quenching of YAG:Ce



a) At low Ce^{3+} concentration < 1%
Quenching due to tunneling
$TQ_{1/2}$ > 300 °C

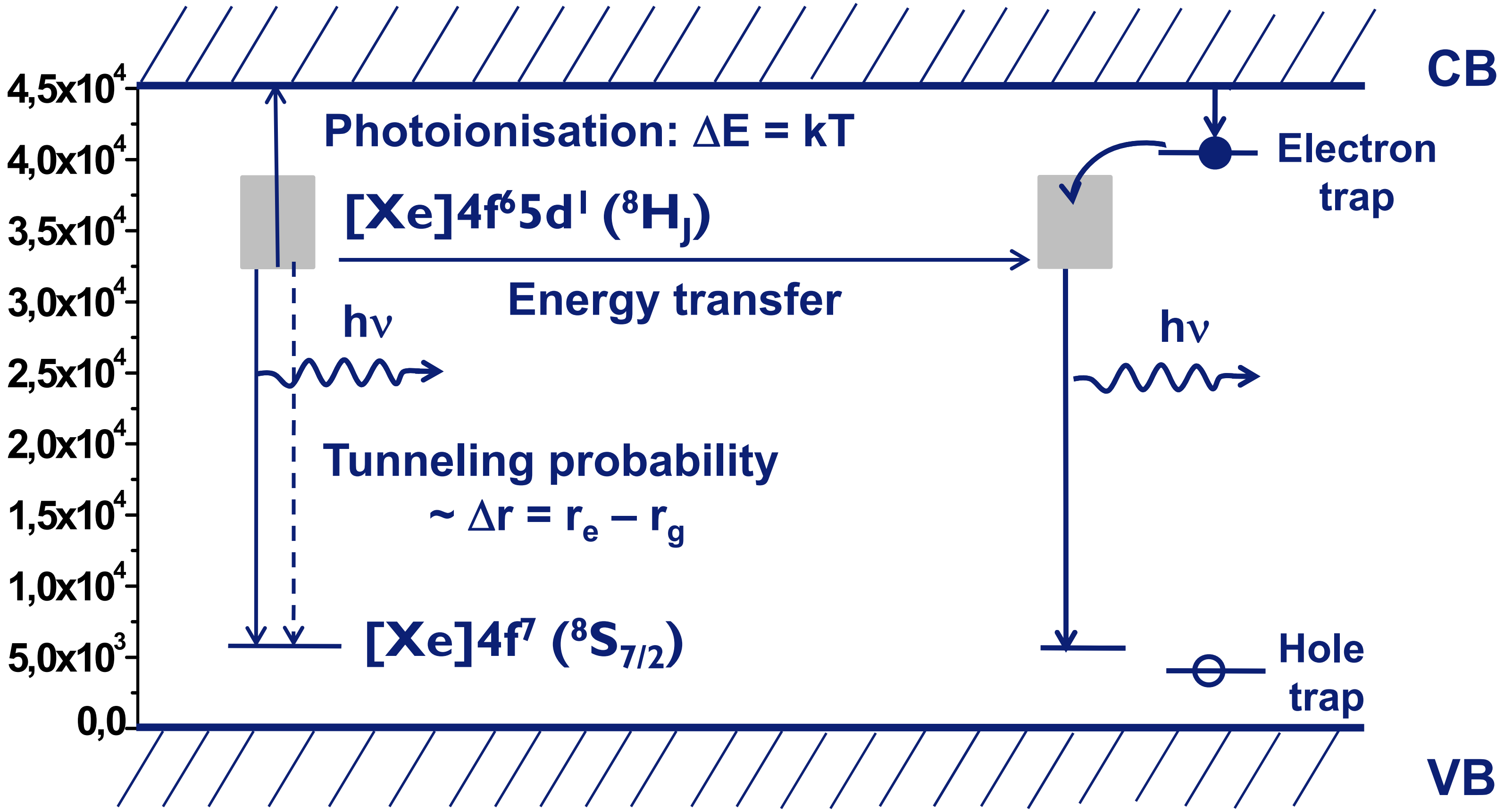
b) At high Ce^{3+} concentration > 1%
Quenching due to re-absorption
$TQ_{1/2}$ < 300 °C

Conclusion

A high activator concentration results in strong re-absorption and thus in pronounced thermal quenching.

Fundamental Aspects $4f^n \rightarrow 4f^{n-1}5d^1$ Transitions

Example: Eu^{2+} luminescence in an oxidic host lattice



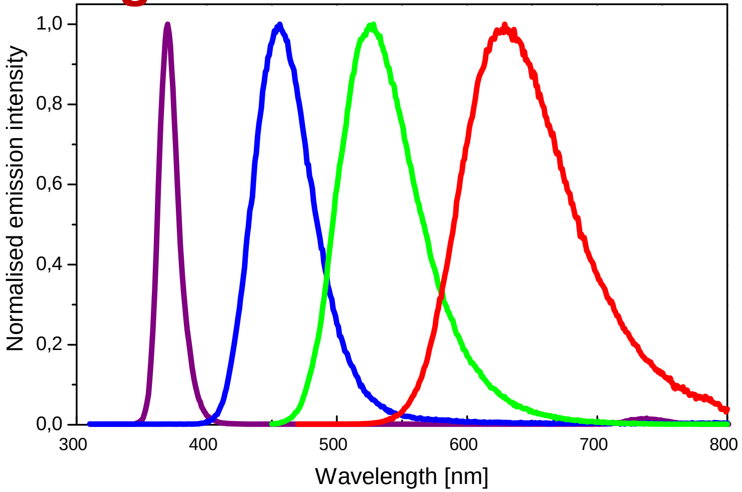
Quenching by		
	multiphonon relaxation?	No
	cross-relaxation?	No
	tunneling?	Yes for a large Stokes Shift: Sr_2SiO_4:Eu
	photoionisation?	Yes for a small $[Xe]4f^65d^1$ to CB distance

Fundamental Aspects $4f^n \rightarrow 4f^{n-1}5d^1$ Transitions

Example: Eu^{2+} luminescence in inorganic host lattices

The Stokes Shift is roughly correlated to the width of the emission band.

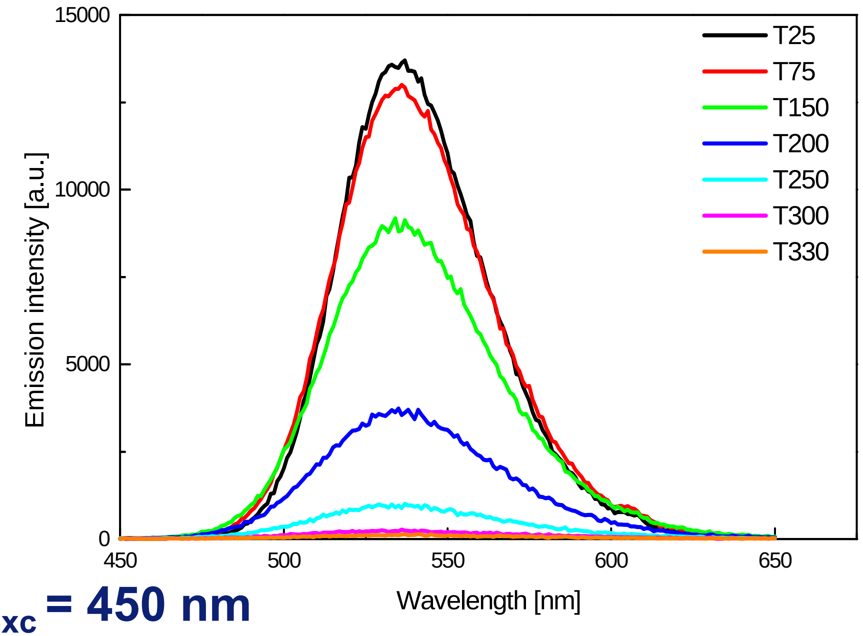
SrO:Eu is violet-black and not luminescent at ambient temperature due to the very large Stokes Shift.

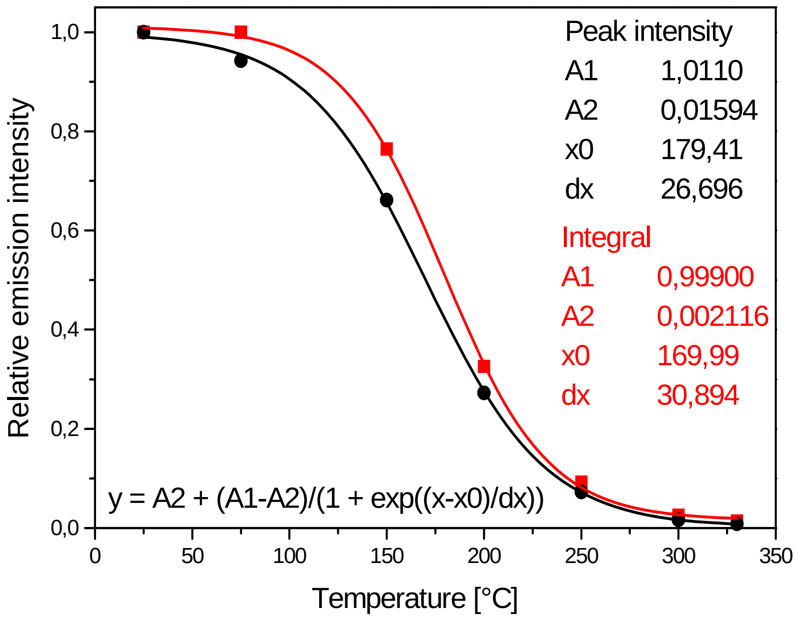


Phosphor	λ_{exc} [nm]	λ_{em} [nm]	Stokes Shift [cm^{-1}]	FWHM [cm^{-1}]	
SrB_4O_7:Eu	356	367	1030	1420	
$BaMgAl_{10}O_{17}$:Eu	408	453	2440	2400	
$BaSi_2N_2O_2$:Eu	460	490	1300	1200	1 site
Ba_2SiO_4:Eu	434	505	3240	2360	
Sr_2SiO_4:Eu	440	570	5200	3200	
MgS:Eu	562	592	900	1120	1 site
$CaAlSiN_3$:Eu	530	650	3500	2300	
CaS:Eu	600	654	1330	1460	1 site

Fundamental Aspects $4f^n \rightarrow 4f^{n-1}5d^1$ Transitions

Thermal quenching of $AEGa_2S_4$:Eu with AE = Ca, Sr, Ba





λ_{exc} = 450 nm

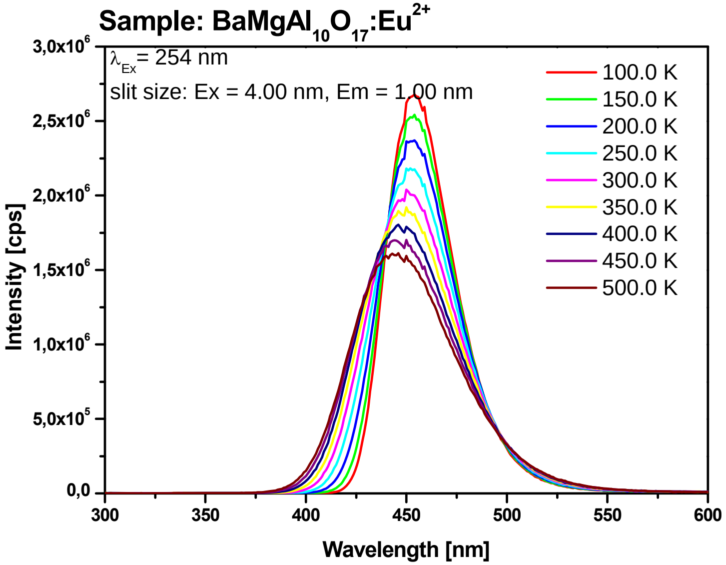
λ_{em} = 525 nm

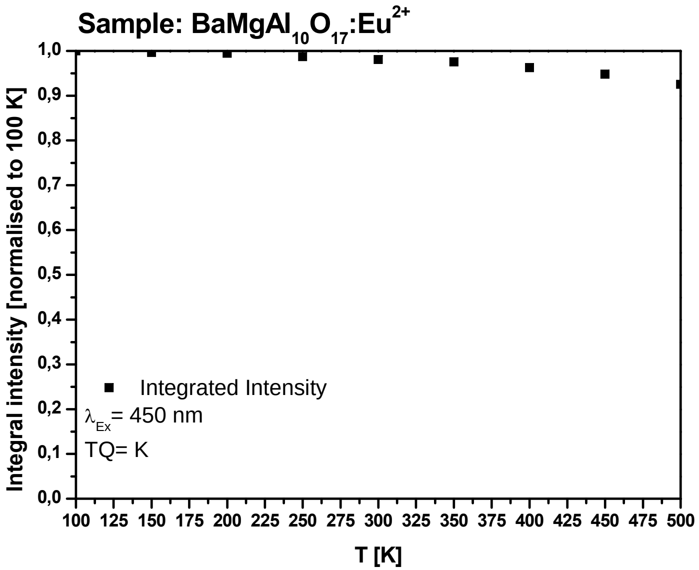
$BaGa_2S_4$:Eu	**Lit.:**	**$TQ_{1/2}$ = 210 °C**
$SrGa_2S_4$:Eu	**Lit.:**	**$TQ_{1/2}$ = 200 °C**
$CaGa_2S_4$:Eu	**Lit.:**	**$TQ_{1/2}$ = 170 °C**

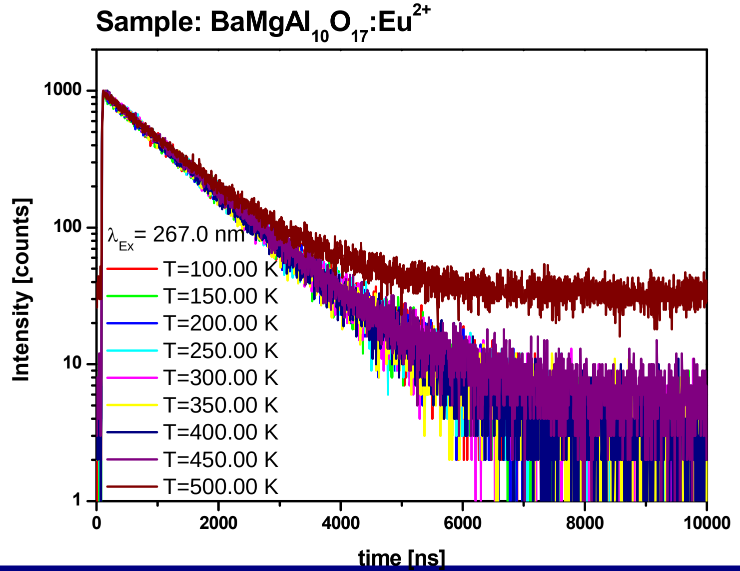
Quenching mechanism is photoionisation

Fundamental Aspects $4f^n \rightarrow 4f^{n-1}5d^1$ Transitions

Thermal quenching of $AEMgAl_{10}O_{17}$:Eu







λ_{exc} = 254 nm

λ_{em} = 453 nm

$\tau_{1/e}$ = 1.1 µs, $\tau_{1/10}$ = 2.5 µs

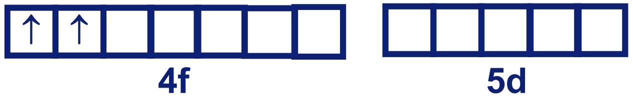
BAM $TQ_{1/2}$ = 340 °C

SAM $TQ_{1/2}$ = 300 °C

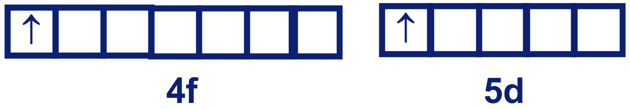
CAM $TQ_{1/2}$ = 80 °C

Fundamental Aspects - Pr^{3+} Luminescence

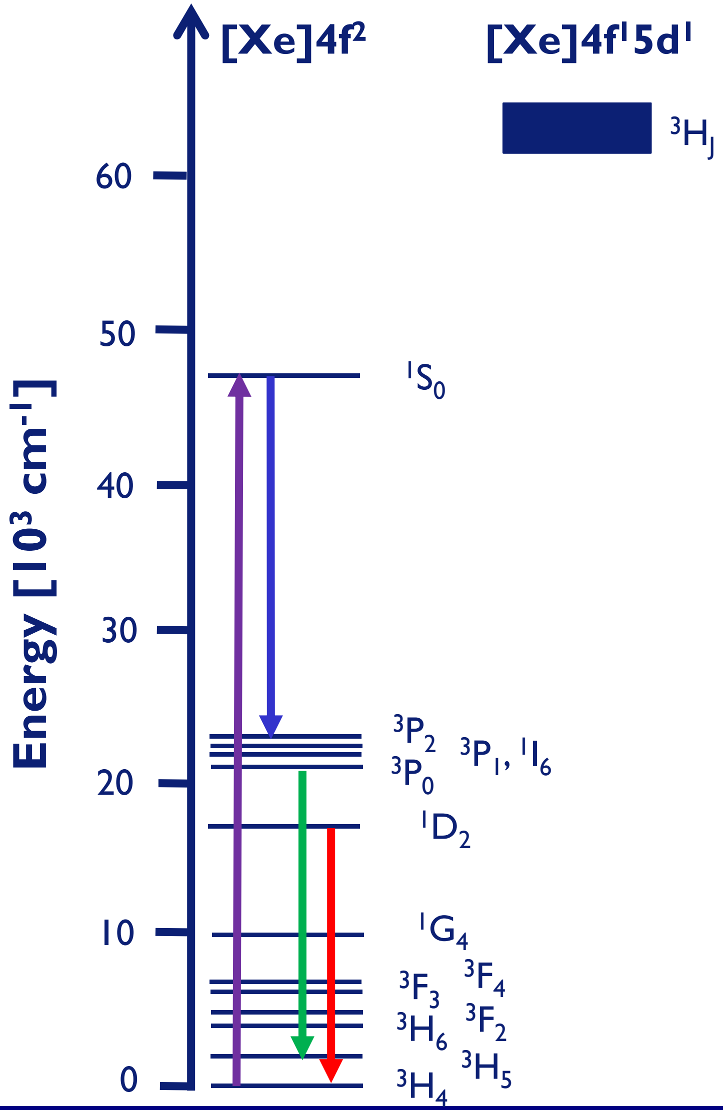
Pr^{3+} ground state configuration
$[Xe]4f^2$ → 13 SLJ-States



Pr^{3+} excited state configuration
$[Xe]4f^15d^1$

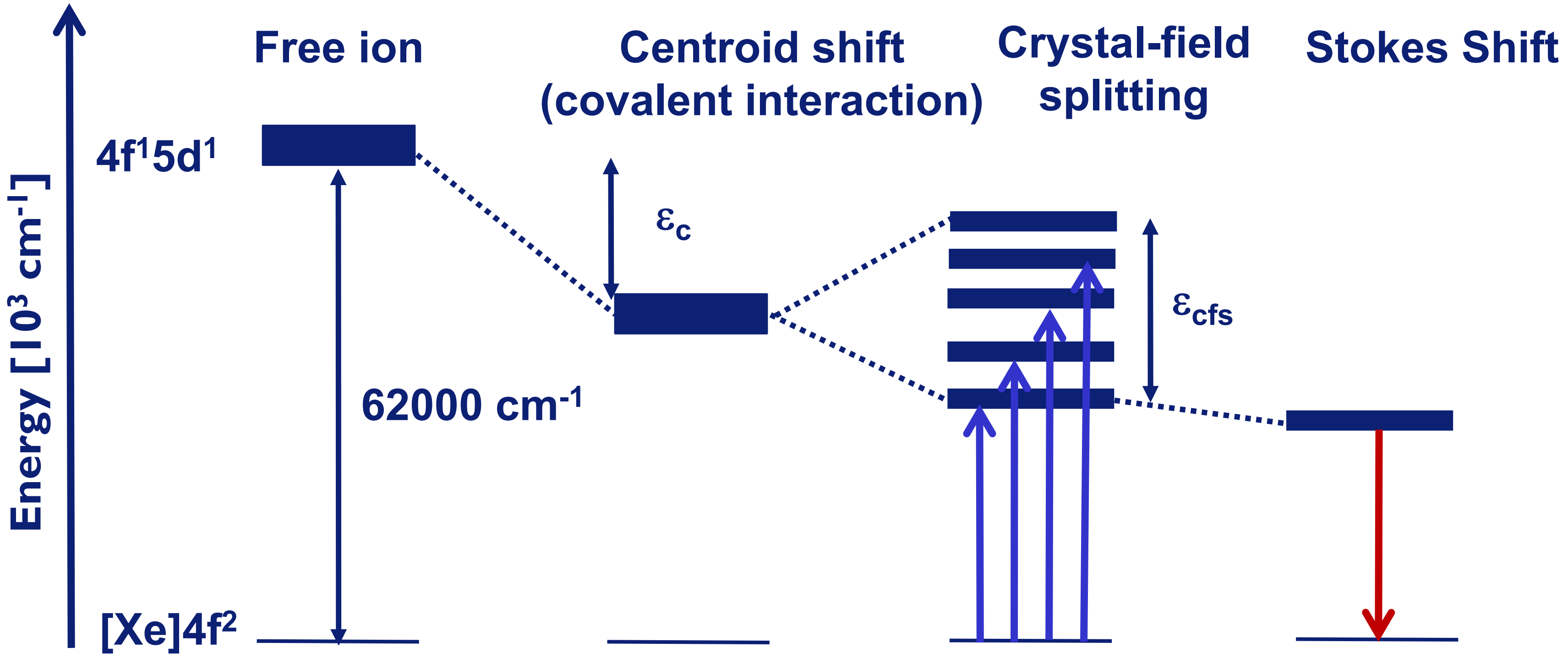


Energy distance between the $[Xe]4f^2$ and $[Xe]4f^15d^1$ configuration is 62000 cm^{-1} (for free Pr^{3+} ions)
$E^0(Pr^{3+/4+})$ = 3.2 V in $[Pr(H_2O)_9]^{3+}(aq)$
$IE(Pr^{3+/4+})$ = 7.8 eV in $CaF_2(s)$



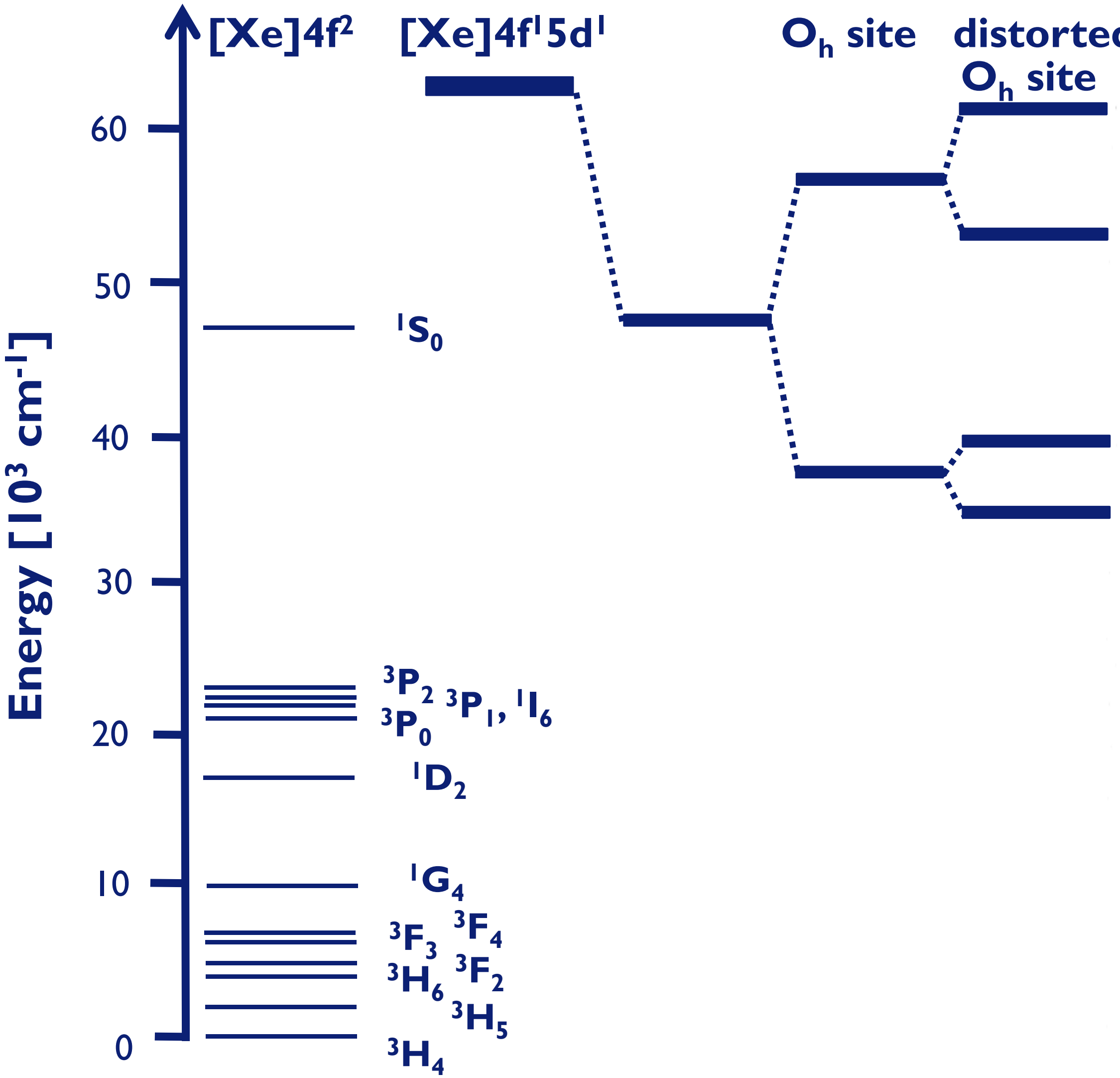
Fundamental Aspects - Pr^{3+} Luminescence

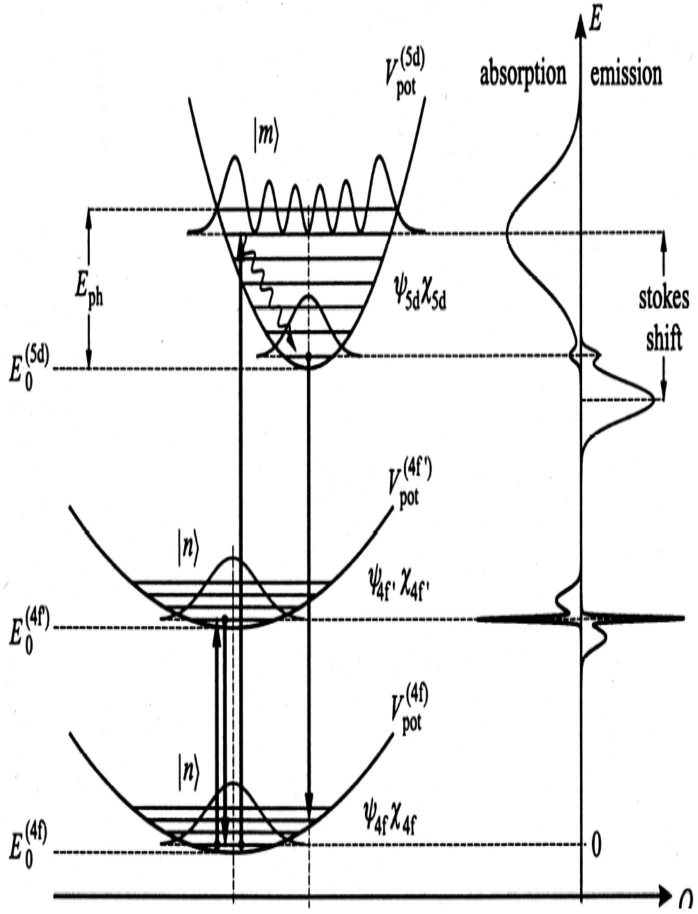
Tuning the distance between the $[Xe]4f^2$ and $[Xe]4f^15d^1$ configuration



Determining factors: (Spectroscopic) Polarisibility, ion charge density, site symmetry, coordination number, metal-ligand distance

Fundamental Aspects - Pr^{3+} Luminescence





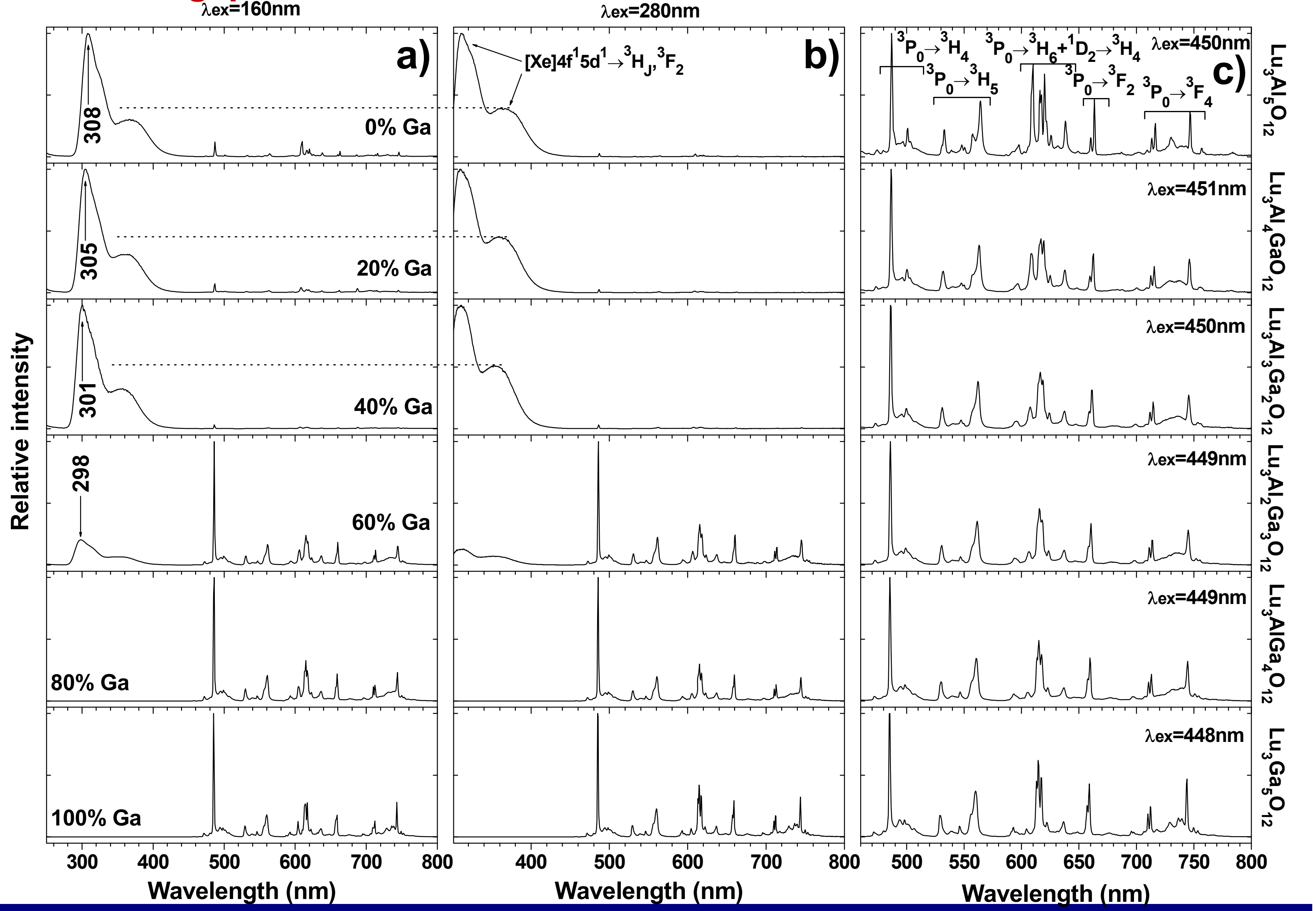
Fundamental Aspects - Pr^{3+} Luminescence

Band gap exc. **4f-5d exc.** **4f-4f exc.**

LuAG

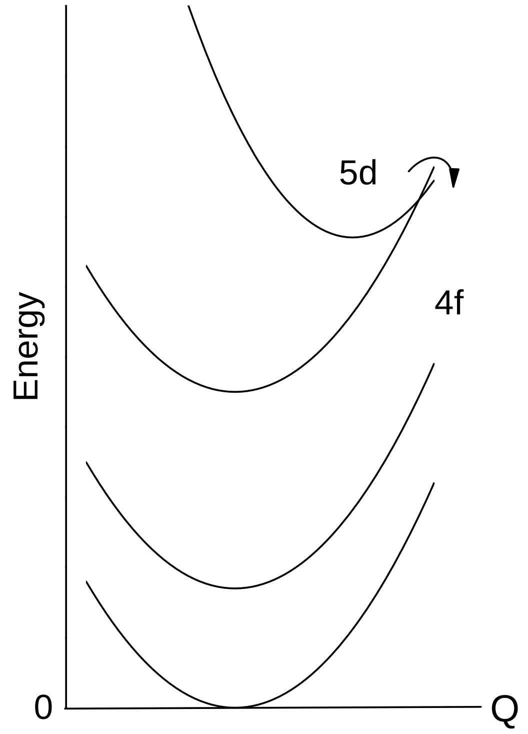
LuAGG

LGG

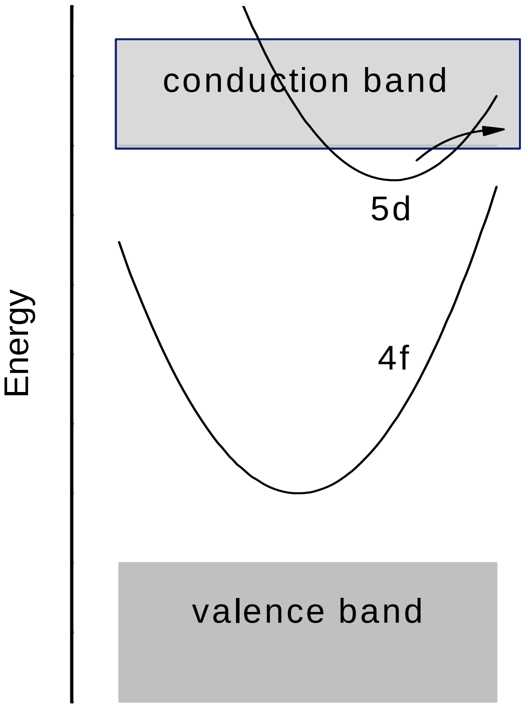


Fundamental Aspects - Pr^{3+} Luminescence

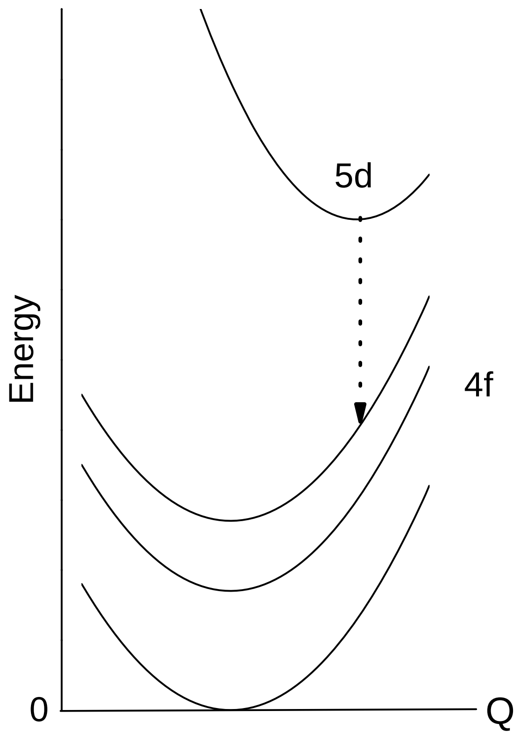
Quenching mechanisms of $[Xe]4f^{n-1}5d^1$ to $[Xe]4f^2$ transitions



Thermally activated intersystem crossing (IC)



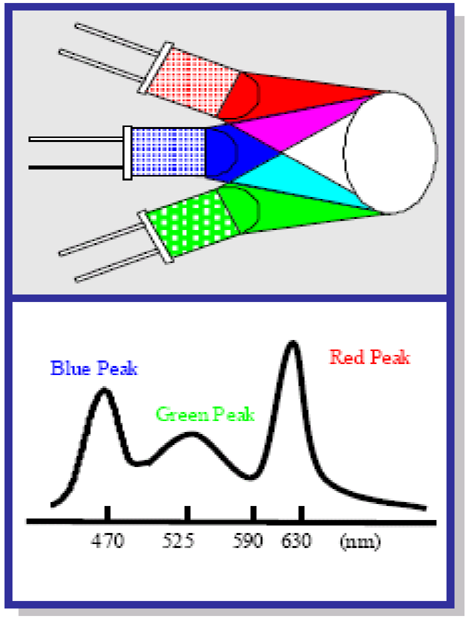
Thermally activated ionization to conduction band (PI)



Multi-phonon relaxation (issue for Pr^{3+})

Issues in Phosphor Converted LEDs

Red + Green + Blue LEDs

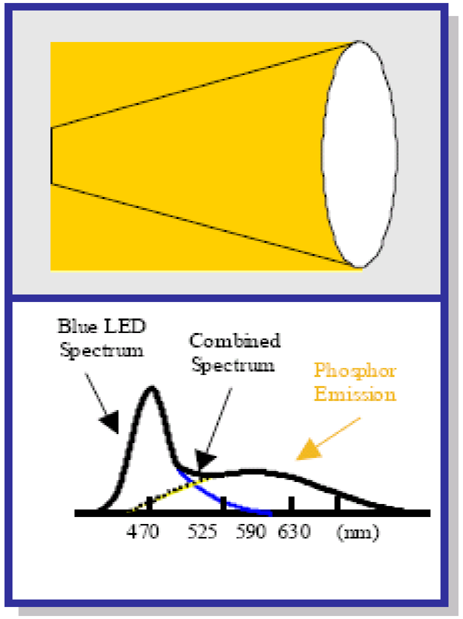


Inherently most efficient

Tunable white point

Bad colour rendering

Blue LED + yellow phosphor

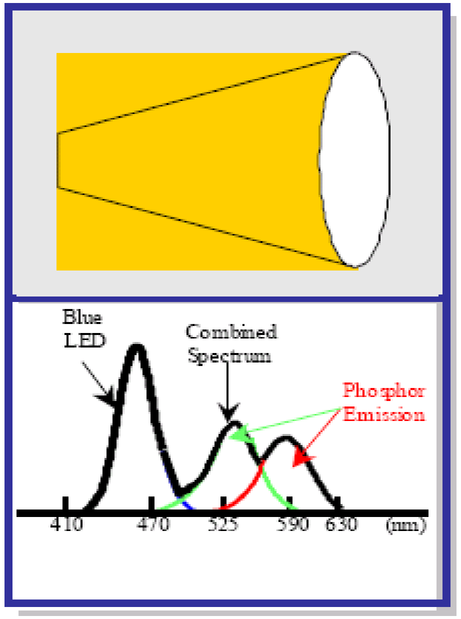


Fixed white point

Good color rendering at high T_C

Excellent stability and reliability

Blue LED + multiple phosphors



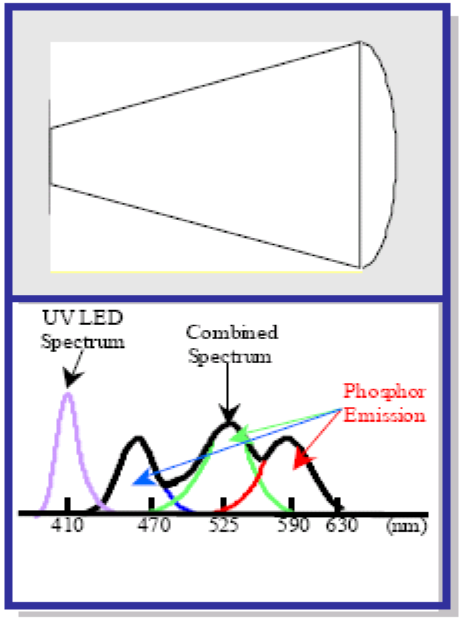
Fixed white point

Very good color rendering

Good stability and reliability

Spectral interaction

UV LED + RGB phosphors



Fixed white point

High color rendering

Degradation

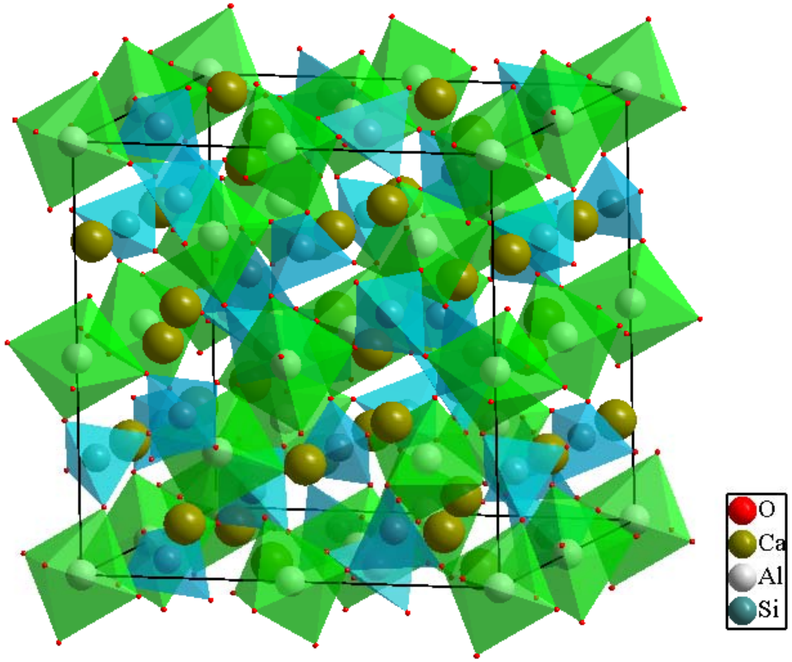
Red line emission possible

Issues in Phosphor Converted LEDs

Natural garnets: $C_3A_2D_3O_{12}$ or $C_3A_2(SiO_4)_3$

Artificial garnets: $Ln_3(Al,Ga,Fe,Sc)_5O_{12}$

C – dodecahedral site (CN = 8)
A – octahedral site (CN = 6)
D – tetrahedral site (CN = 4)



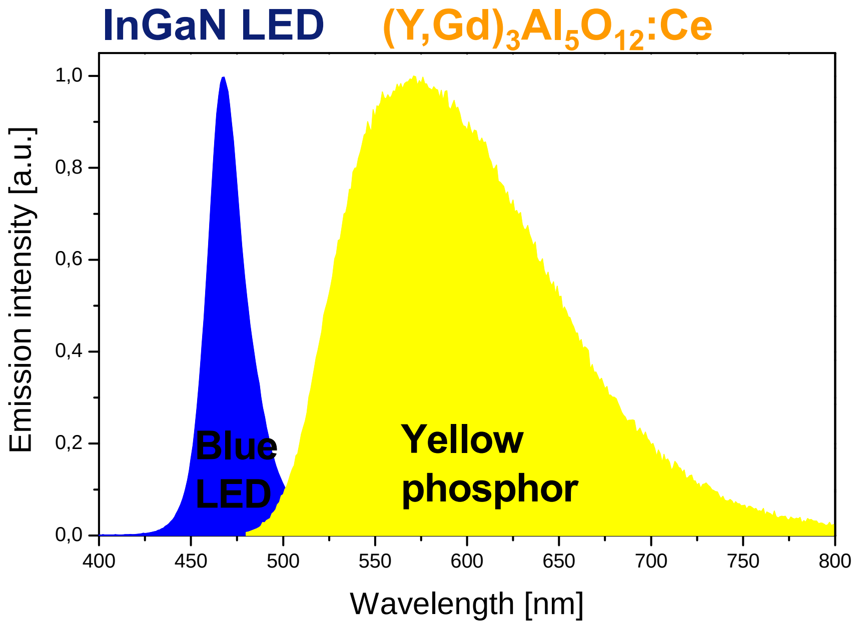
Unit cell of Grossular

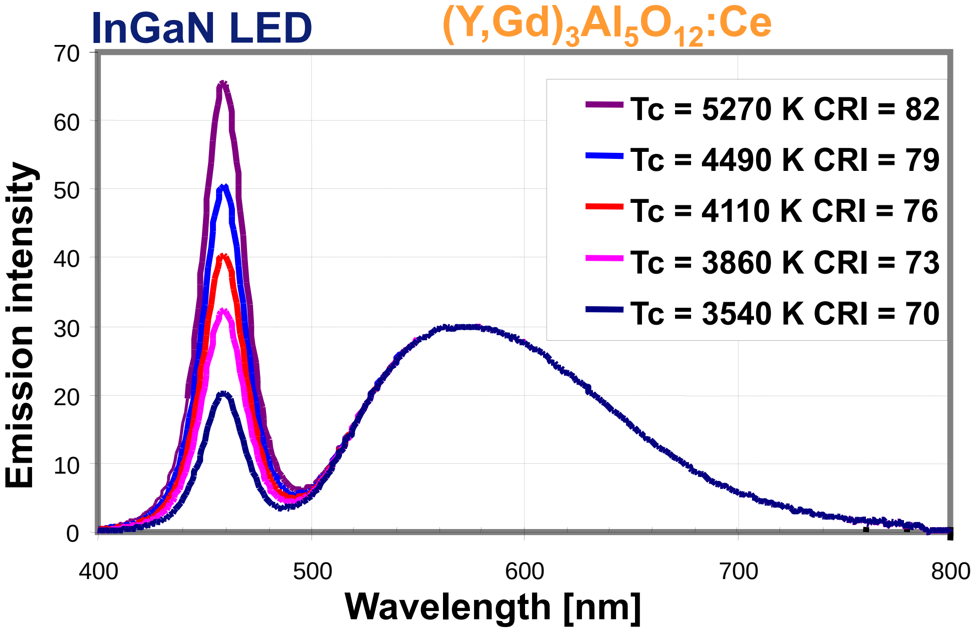
Space group *Ia-3d* (#230)

Pyrope	$Mg_3Al_2Si_3O_{12}$
Almandine	$Fe_3Al_2Si_3O_{12}$
Spessartite	$Mn_3Al_2Si_3O_{12}$
Andradite	$Ca_3Fe_2Si_3O_{12}$
Grossular	$Ca_3Al_2Si_3O_{12}$
Uvarovite	$Ca_3Cr_2Si_3O_{12}$

Issues in Phosphor Converted LEDs

First white LED → (Nichia 1996)

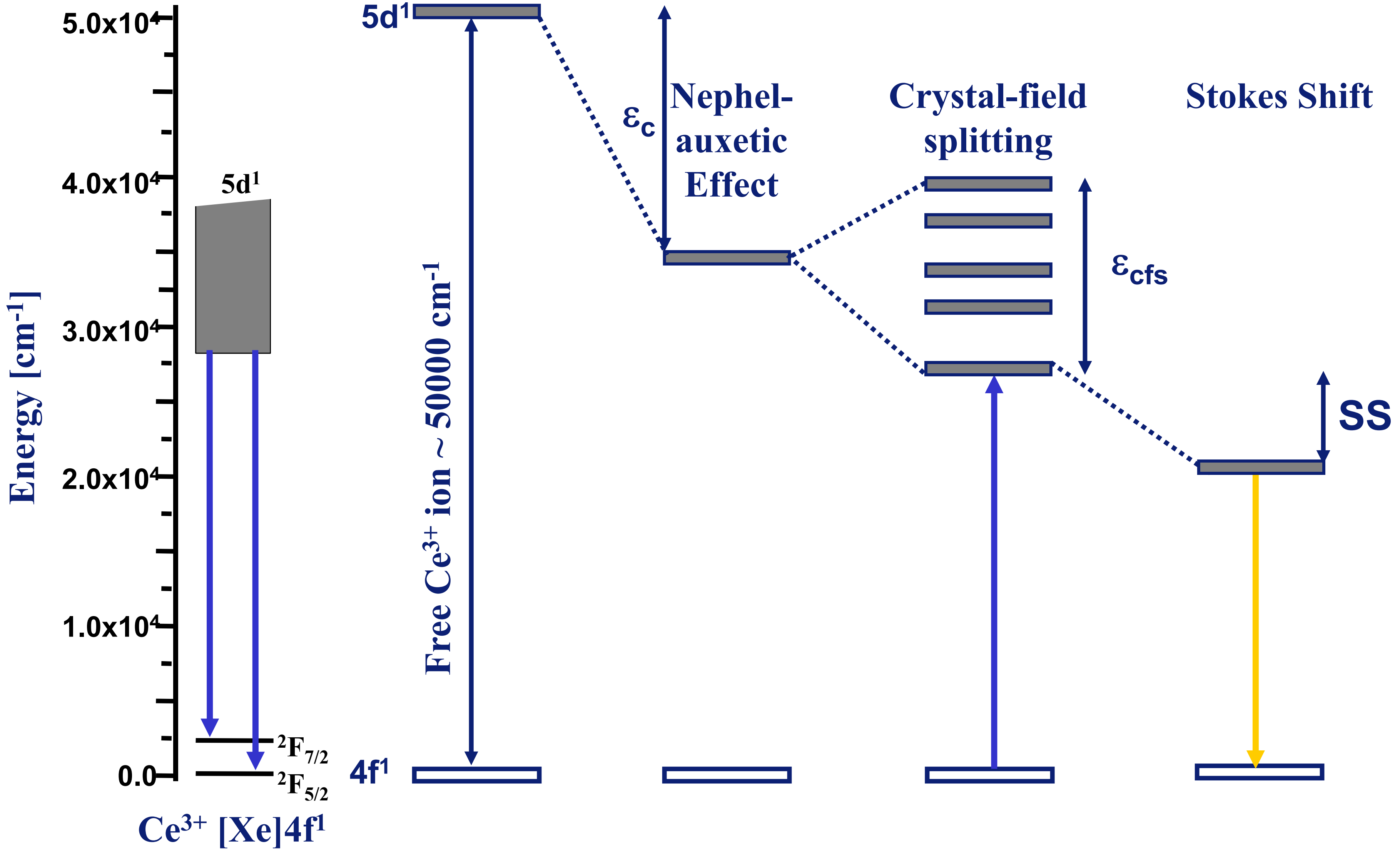




Status quo cool white pcLEDs @2012

- CRI ~70 – 80
- Color temperature typically 5000 K

Issues in Phosphor Converted LEDs – Ce^{3+}

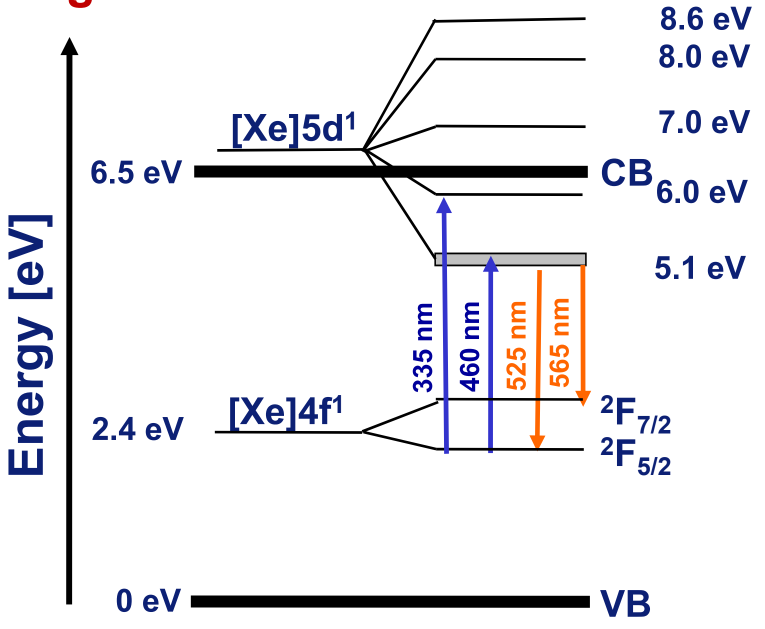


Issues in Phosphor Converted LEDs

Ce^{3+} doped Garnets $[Xe]4f^1$ ground state configuration

Emission spectrum is dominated by two $[Xe]4f^15d^1$ – $[Xe]4f^2$ emission bands separated by 2000 cm^{-1}

$LiYF_4$:Ce	300, 315 nm
YPO_4:Ce	335, 355 nm
YBO_3:Ce	390, 415 nm
$Y_3Al_5O_{12}$:Ce	525, 565 nm

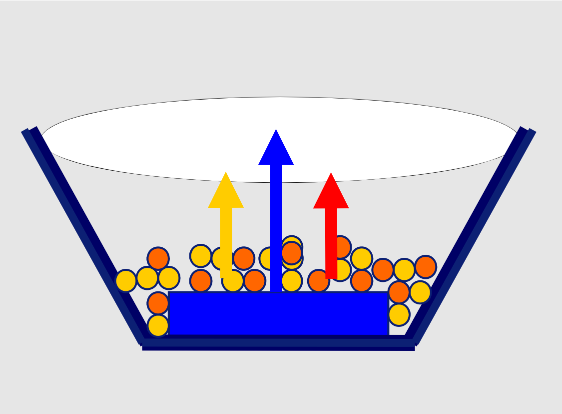


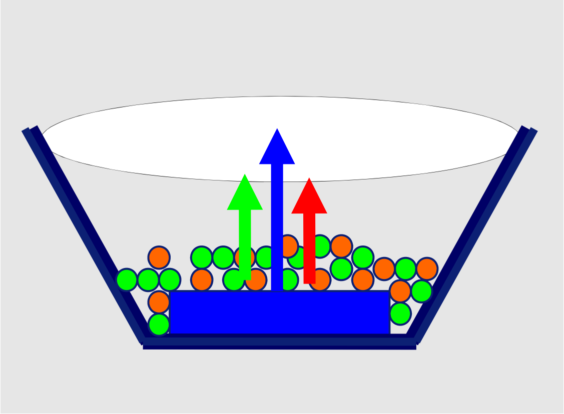
Red-shift of YAG:Ce PL due to	
• Enhancement of c(Ce^{3+})	Quenching due to re-absorption
• Replacement of Y^{3+} by Gd^{3+} or Tb^{3+}	Quenching due to thermally activated IC
• Replacement of Al^{3+} by Mg^{2+} and Si^{4+}	Quenching due to thermally activated PI
• Replacement of O^{2-} by N^{3-}	Quenching due to thermally activated PI
Blue-shift of YAG:Ce PL due to	
• Replacement of Y^{3+} by Lu^{3+}	Quenching is reduced
• Replacement of Al^{3+} by Ga^{3+} or Sc^{3+}	Quenching due to thermally activated PI

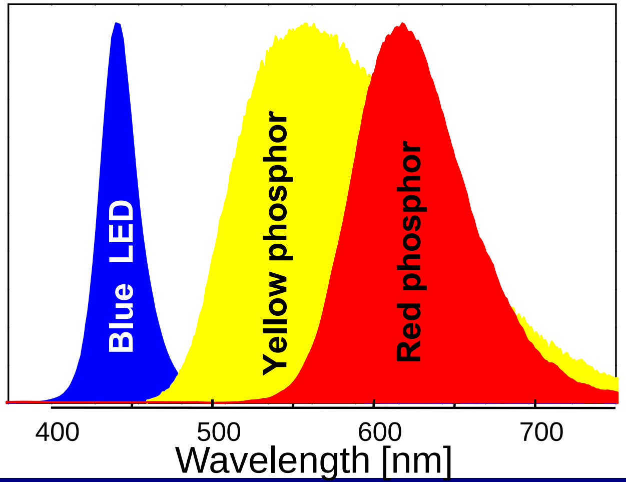
Issues in Phosphor Converted LEDs

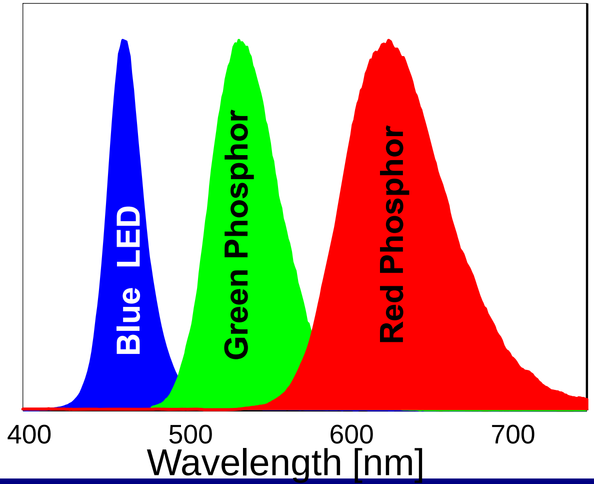
Blue LED + yellow + red phosphor

Blue LED + green + red phosphor

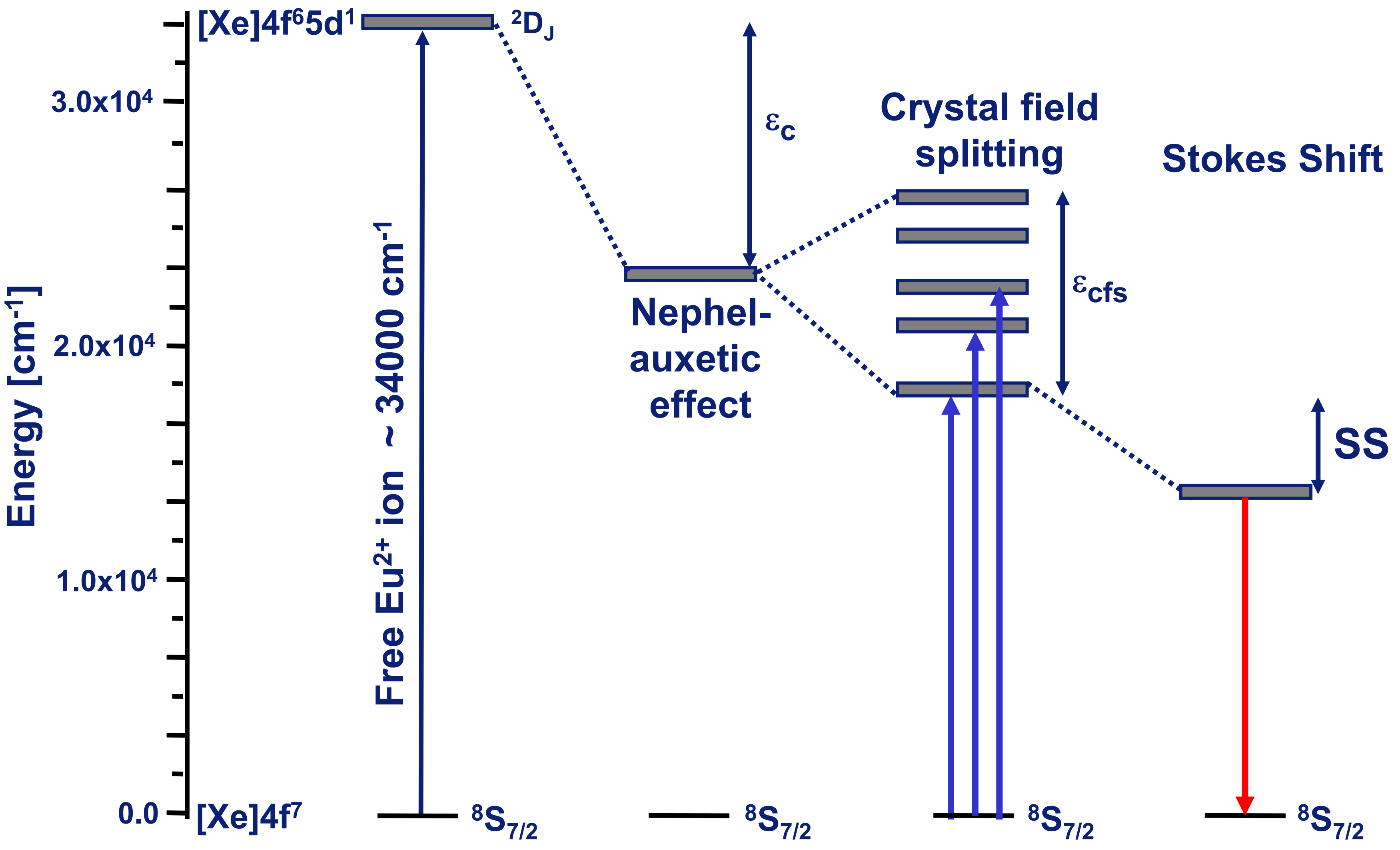








Issues in Phosphor Converted LEDs – Eu^{2+}



Issues in Phosphor Converted LEDs

Eu^{2+} Luminescent materials: Colour and colour points

Chemical composition	λ_{max}	x	y
$CaS:Eu$	655 nm	0.70	0.30
$CaAlSiN_3:Eu$	650 nm	0.66	0.34
$Sr_2Si_5N_8:Eu$	625 nm	0.62	0.38
$SrS:Eu$	610 nm	0.63	0.37
$Ba_2Si_5N_8:Eu$	580 nm	0.52	0.48
$Sr_2SiO_4:Eu$	575 nm	0.44	0.50
$SrSi_2N_2O_2:Eu$	540 nm	0.36	0.61
$SrGa_2S_4:Eu$	535 nm	0.27	0.69
$SrAl_2O_4:Eu$	520 nm	0.26	0.55
$Ba_2SiO_4:Eu$	505 nm	0.16	0.57
$Sr_4Al_{14}O_{25}:Eu$	490 nm	0.14	0.35
$SrSiAl_2O_3N:Eu$	480 nm	0.14	0.30
$BaMgAl_{10}O_{17}:Eu$	450 nm	0.15	0.06
$Sr_2P_2O_7:Eu$	420 nm	0.17	0.01
$BaSO_4:Eu$	374 nm	0.17	0.00
$SrB_4O_7:Eu$	368 nm	0.17	0.00

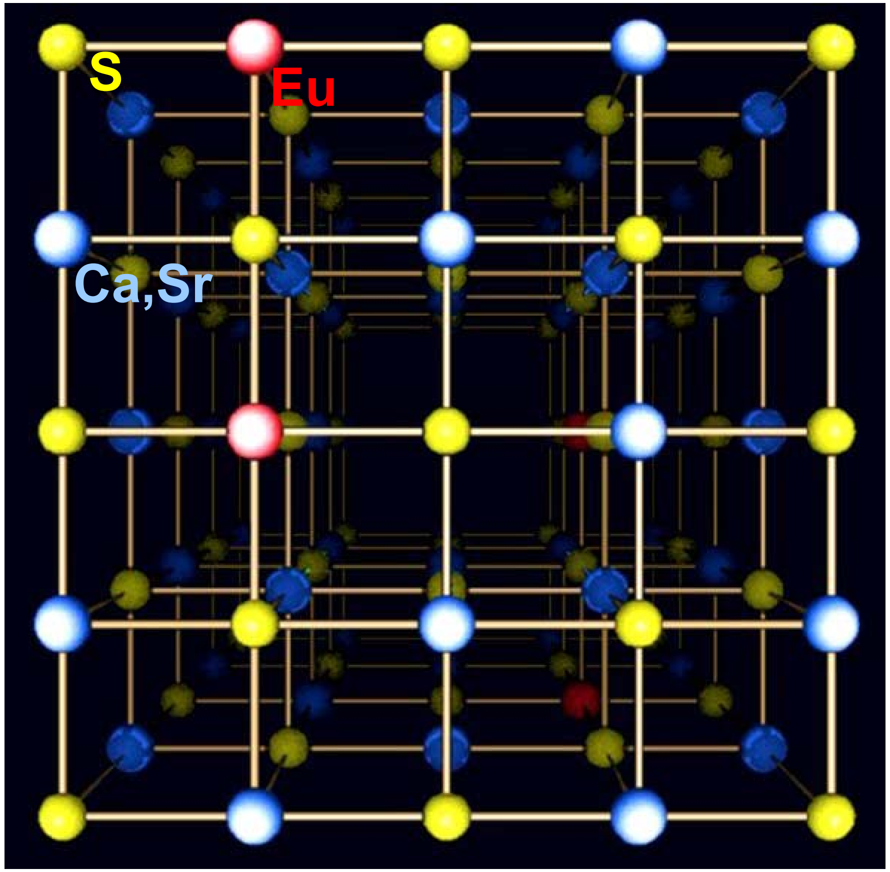
Increase of covalency and/or crystal-field strength

Nitrides +
Sulfides

Oxynitrides
+ Oxides

Issues in Phosphor Converted LEDs

Structure and luminescence of (Ca,Sr)S:Eu



- Rock salt structure
- High sensitivity towards O_2, H_2O, diluted acids, etc.
- Activator: Eu^{2+}
  - on octahedral AE^{2+} sites
  - strong 4f-5d absorption bands below 550 nm
  - quantum efficiency > 90%
  - red emission tunable by adjustment of Sr/Ca content

Issues in Phosphor Converted LEDs

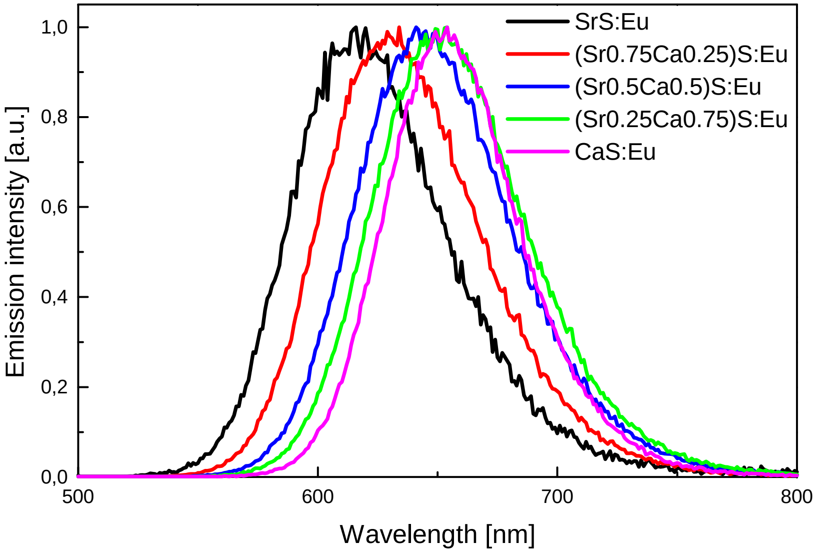
Body colour and spectra of $(Ca_{1-x}Sr_x)S:Eu$

SrS:Eu **CaS:Eu**

stability →

Crystal field strength →

← Centroid shift



Composition	QE [%]	Abs. [%]	LE [lm/W]	x	y
CaS:Eu	> 95	> 80	90	0.697	0.303
SrS:Eu	> 95	> 80	260	0.629	0.370

Issues in Phosphor Converted LEDs

Lumen equivalent (LE) of red and broad band emitting Eu2+ phosphors with a high quantum yield (90 – 100%)

Phosphor	Peak at [nm]	FWHM [nm]	LE [lm/W_{opt}]
$CaS:Eu^{2+}$	654	65	85
$CaAlSiN_3:Eu^{2+}$	650	90	125
$SrS:Eu^{2+}$	615	60	200
$Sr_2Si_5N_8:Eu^{2+}$	615	80	200
$MgS:Eu^{2+}$	591	40	350
$Ba_2Si_5N_8:Eu^{2+}$	580	60	470

↑ Colour Rendering

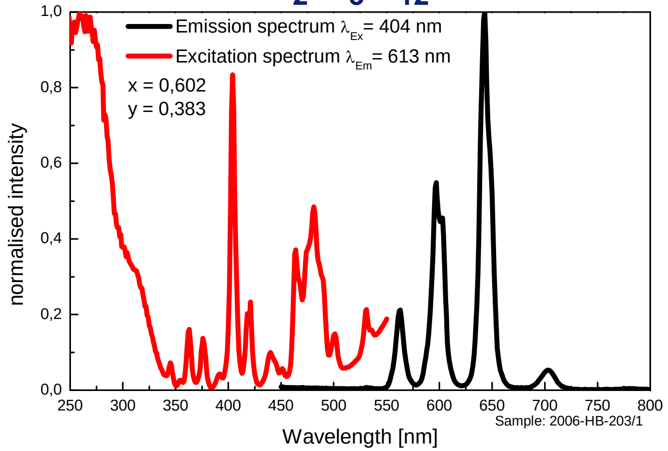
↓ Luminous Efficacy

Issues in Phosphor Converted LEDs

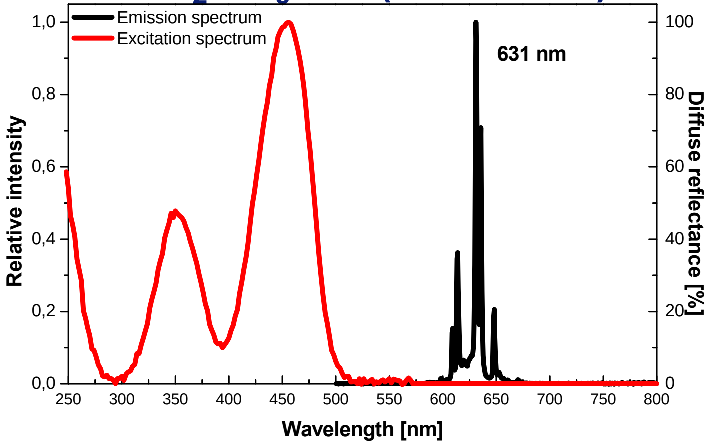
Activator ions showing red line emission are RE or Mn^{4+}

Activator ion	λ_{max} [nm]	LE [lm/W_{opt}]
Eu^{3+}	590 - 620	220 – 360
Sm^{3+}	598, 643	240 – 260
Pr^{3+}	590 - 680	100 – 220
Mn^{4+}	620 - 680	80 – 250

$La_2W_3O_{12}$:Sm



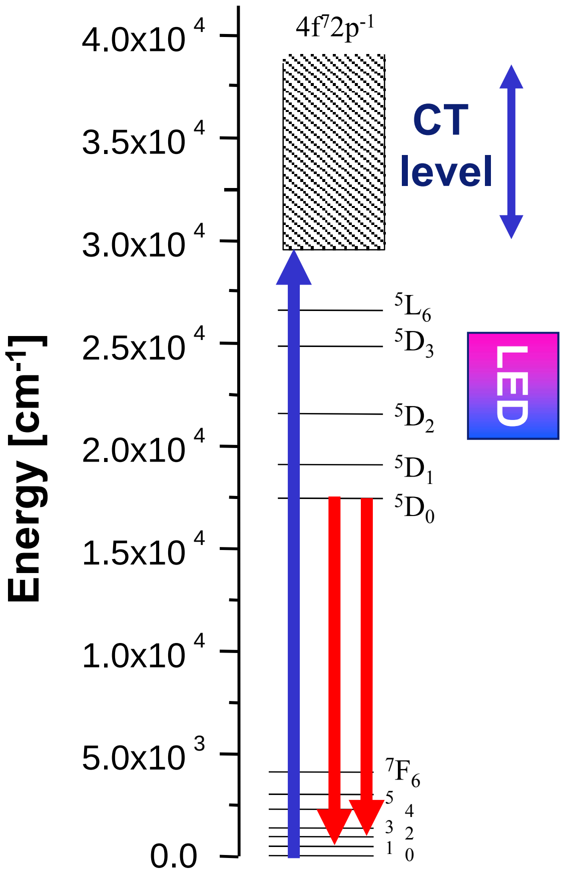
K_2SiF_6:Mn (GE Patent)



Issues in Phosphor Converted LEDs

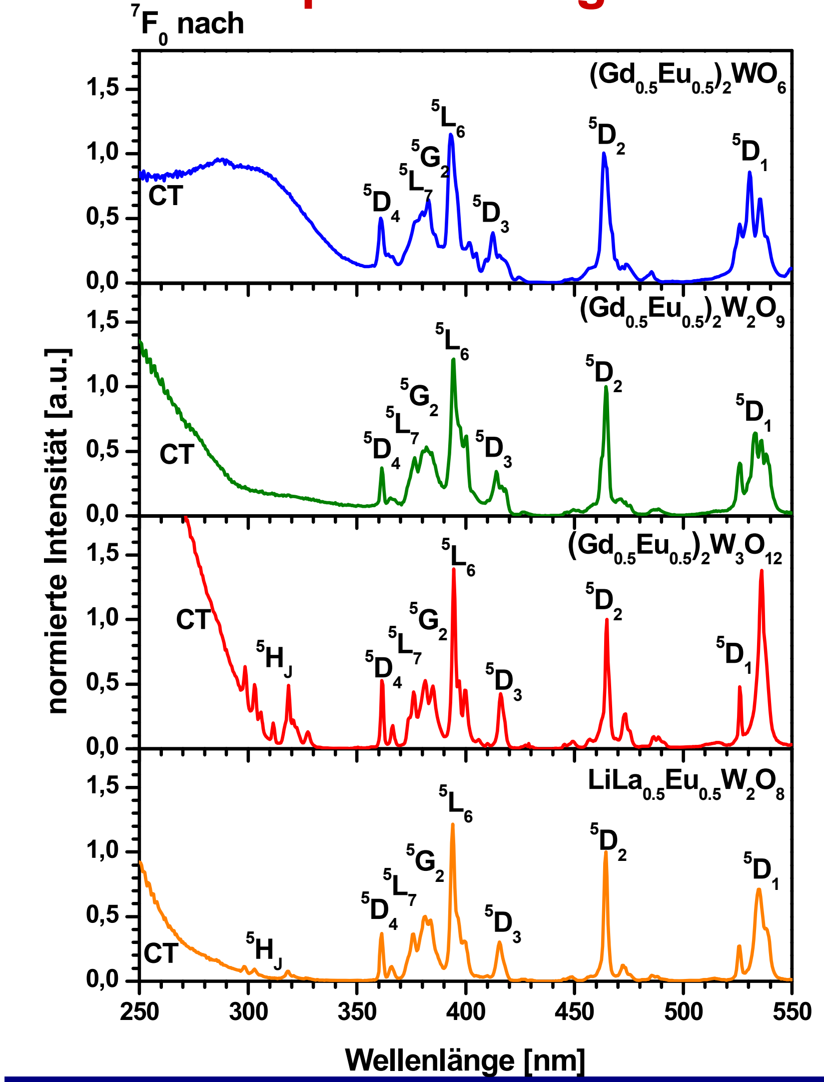
Phosphor composition	LE [lm/W_{opt}]
(Zn,Cd)S:Ag	84
$Zn_3(PO_4)_2$:Mn	157
Y_2O_2S:Eu	215
$Y(V,P)O_4$:Eu	225
$(Y,Gd)BO_3$:Eu	270
Y_2O_3:Eu	285
$Y_2W_3O_{12}$:Eu	300
Ba_2GdTaO_6:Eu	320
$BaYB_9O_{16}$:Eu	340
$InBO_3$:Eu	360

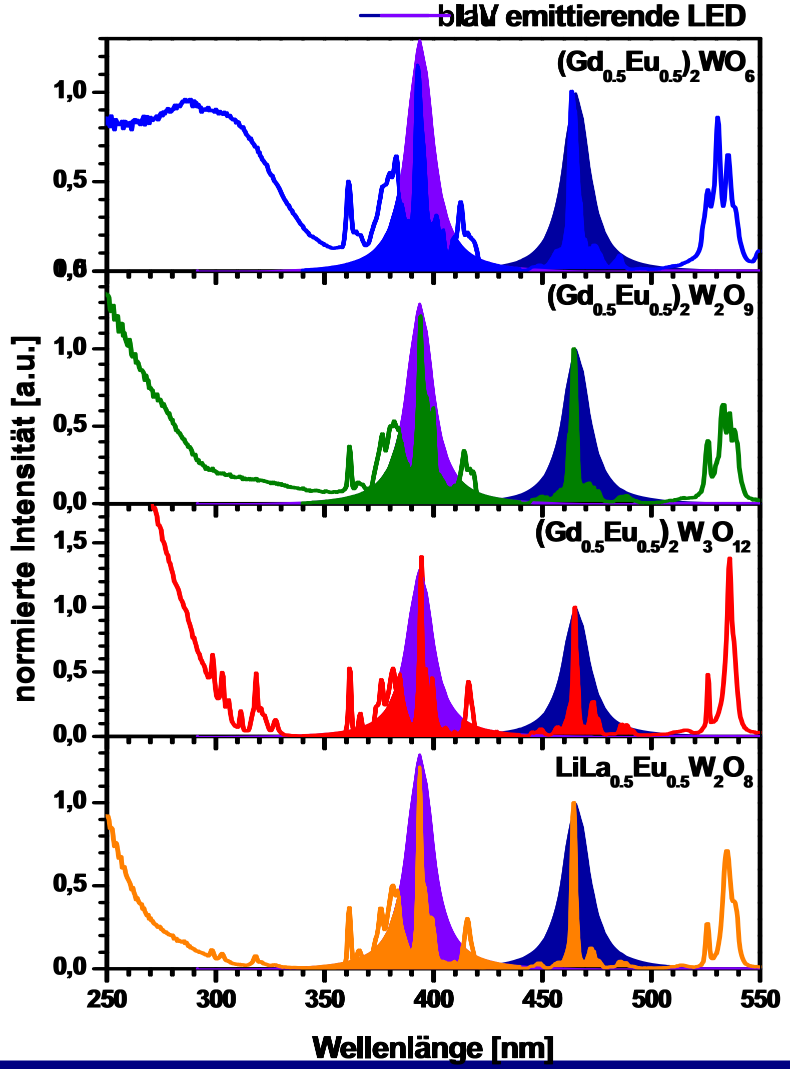
Monochrome line at	LE [lm/W_{opt}]
585 nm	558
595 nm	475
611 nm	335
700 nm	3


Simplified energy level scheme of Eu^{3+}

Issues in Phosphor Converted LEDs

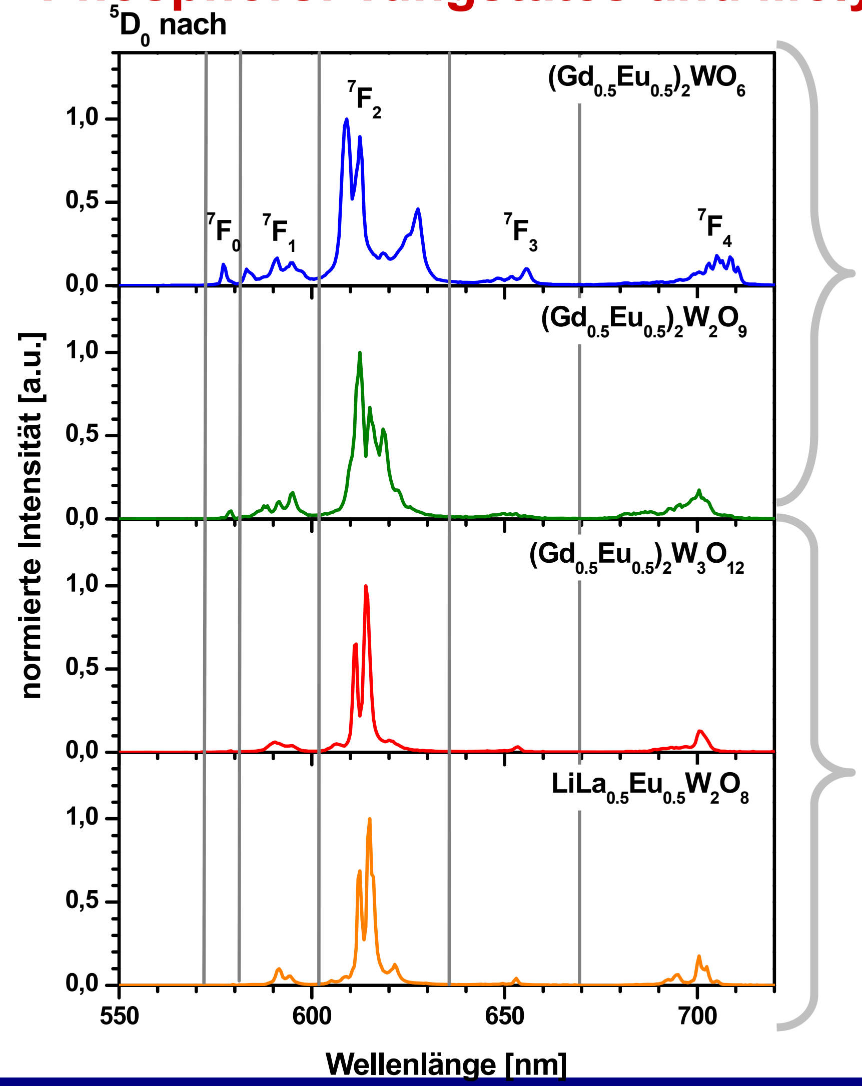
Eu^{3+} Phosphors: Tungstates and Molybdates – Excitation spectra





Issues in Phosphor Converted LEDs

Eu^{3+} Phosphors: Tungstates and Molybdates – Emission spectra



Building unit: $\{WO_6\}$-Octahedra

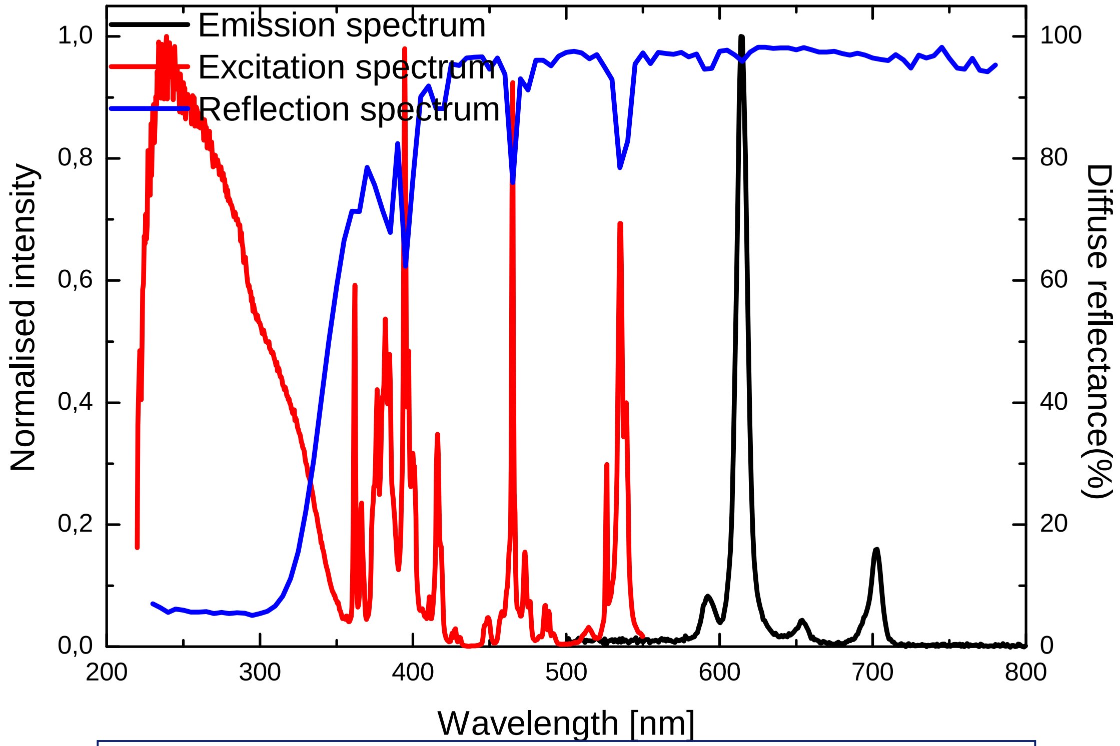
Gd_2WO_6	3 sites for Ln^{3+} CN = Gd1 = Gd2 = Gd3 = 8
$Gd_2W_2O_9$	2 sites for Ln^{3+} CN = Gd1 – 8; Gd2 – 9

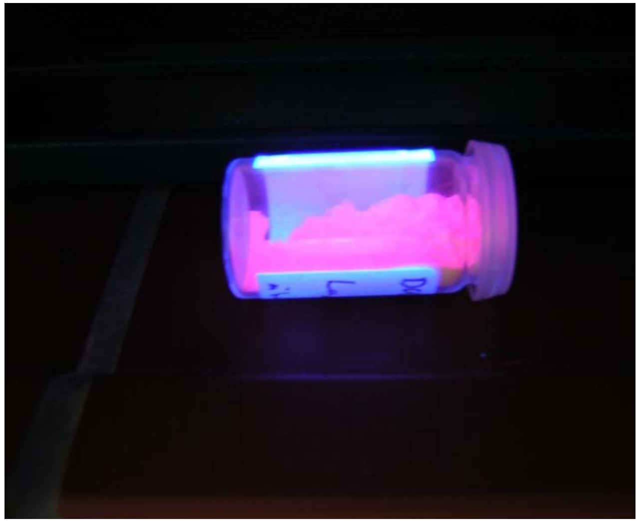
Building unit: $\{WO_4\}$-Tetrahedra

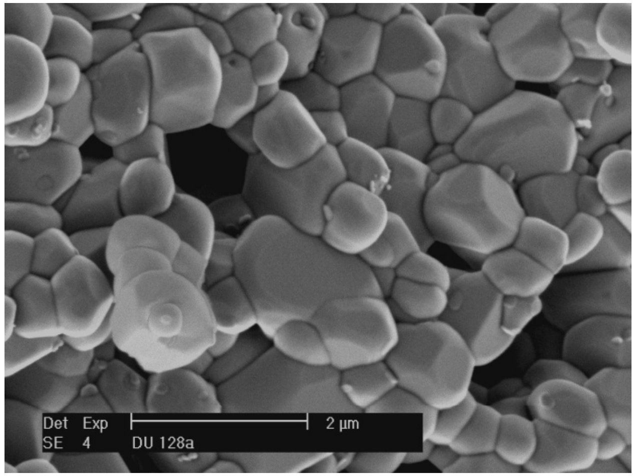
$Gd_2W_3O_{12}$	1 site for Ln^{3+} CN = 8
$LiLaW_2O_8$	1 site for Ln^{3+} CN = 8

Issues in Phosphor Converted LEDs

Spectroscopic properties of $LiEuMo_2O_8$







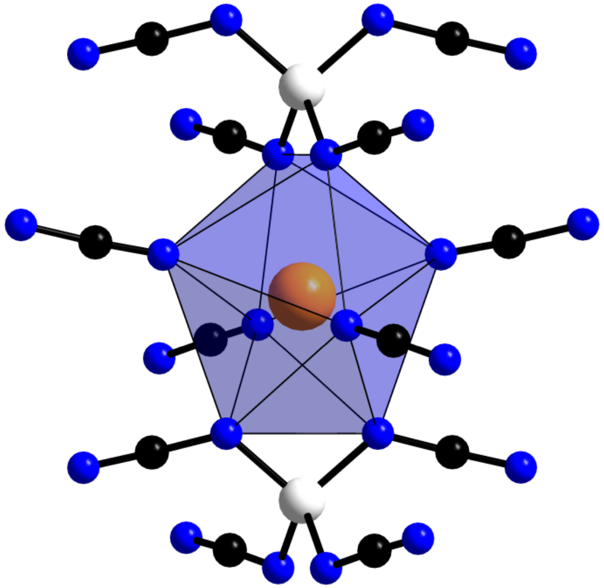
QE_{465} = 100%	LE = 269 lm/W_{opt}
RQ_{465} = 75%	λ_{max} = 614 nm
x = 0.665	$\lambda_{centroid}$ = 623 nm
y = 0.333	$\tau_{1/e}$ = 0.39 ms
d_{50} = 4.2 µm	

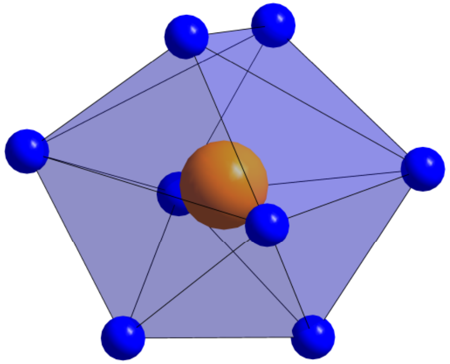
Issues in Phosphor Converted LEDs

$CsLnSi(CN_2)_4$:Eu (Ln = Y, La, Gd) - tetragonal, space group I4

Trigonal-dodecahedral environment of the rare earth ions in

$MLn[Si(CN_2)_4]$ **$Ln_3Al_5O_{12}$**

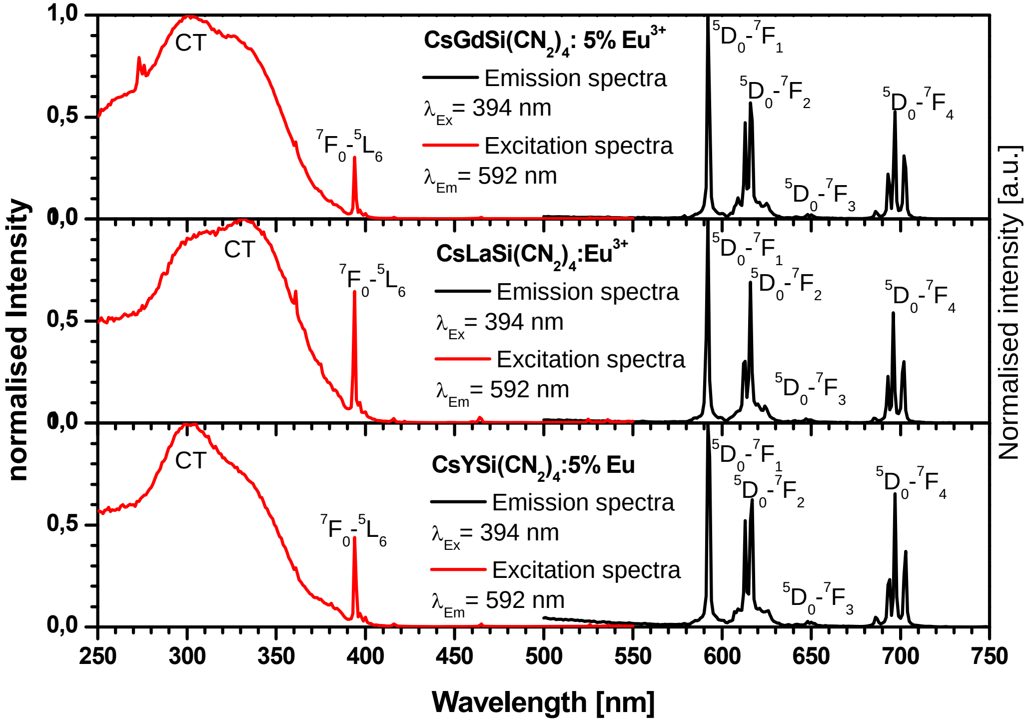


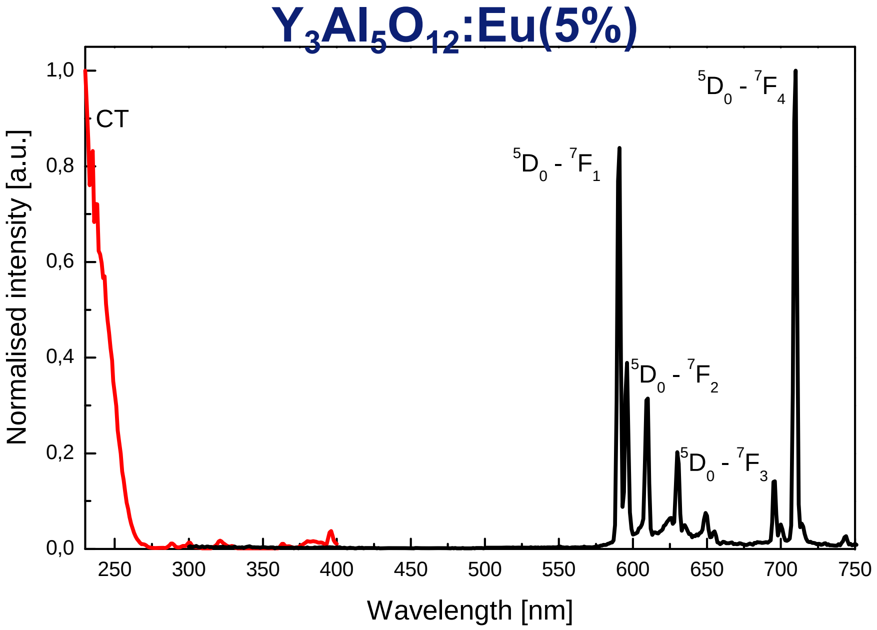


4 x O(1)
4 x O(2)

Issues in Phosphor Converted LEDs

$CsLnSi(CN_2)_4$:Eu (tetragonal) Ln = Y, La, Gd





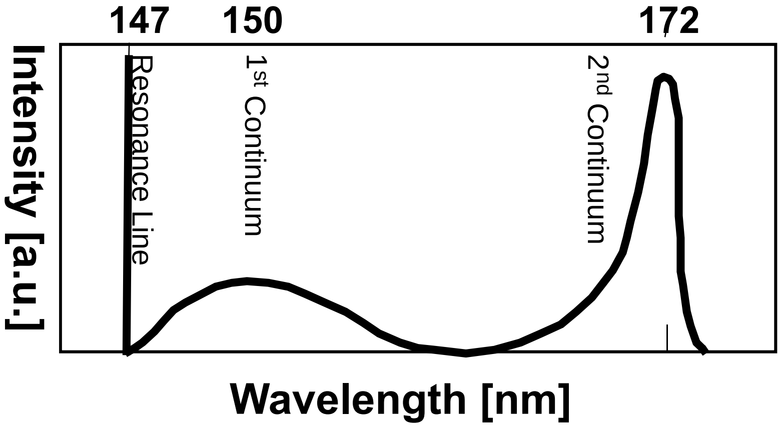
CT-Level at about 28000 cm^{-1}

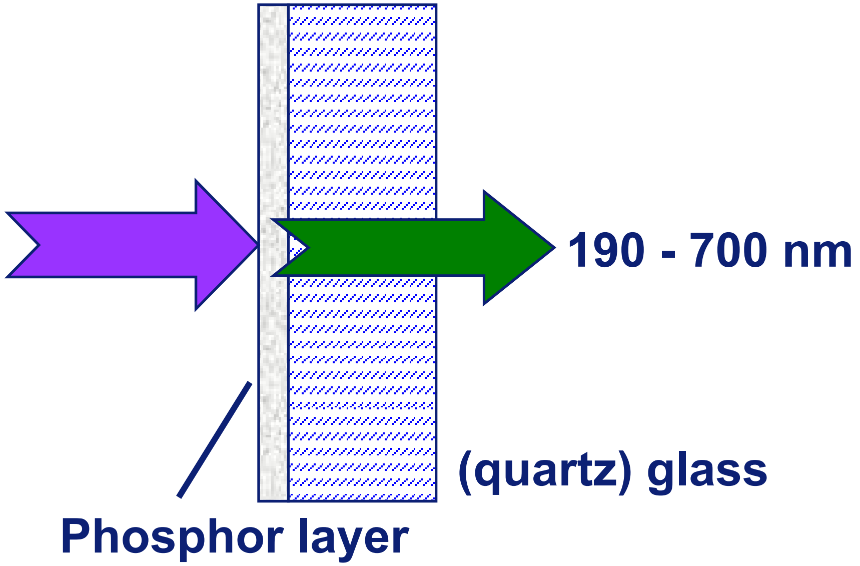
LE = 280 - 303 lm/W_{opt}

(J. Glaser, H. Bettentrup, T. Jüstel, H.-J. Meyer, Inorg. Chem. 48 (2010) 2954)

VUV Phosphors

For Xe excimer lamps





Features of Xe excimer lamps

- Discharge efficiency ~ 65%
- Hg free
- Fast switching cycles
- Temp. independent
- Dimmable
- High lifetime
- Solely VUV emission

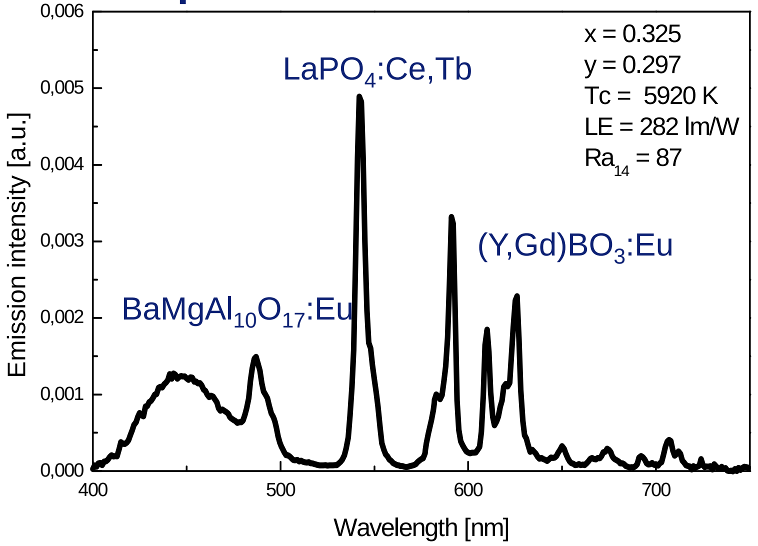
Potential application areas	Phosphor layer
– Photocopier lamps	RGB or B/W
– LCD Backlighting	RGB
– Medical skin treatment	UV-A/B
– Photochemistry	UV-A/B/C
– Disinfection	UV-C
– Ultra pure water	-
– Surface/wafer cleaning	-

VUV Phosphors

Presently applied VUV phosphors

Plasma displays	Excimer lamps
$BaMgAl_{10}O_{17}:Eu$	$BaMgAl_{10}O_{17}:Eu$
$Y(V,P)O_4$	
$Zn_2SiO_4:Mn$	$LaPO_4:Ce,Tb$
$BaAl_{12}O_{19}:Mn$	$(Y,Gd)BO_3:Tb$
$BaMgAl_{10}O_{17}:Eu,Mn$	
$(Y,Gd)BO_3:Eu$	$(Y,Gd)BO_3:Eu$
$Y_2O_3:Eu$	
$(Y,Gd)(V,P)O_4:Eu$	
5 – 10 lm/W	< 50 lm/W

Spectrum of Osram Planon



Problem areas

Efficiency → Down conversion phosphors

VUV Stability → Particle coatings (MgO or Al_2O_3)

Color point → Improved red x, y ~ $Y_2O_2S:Eu$

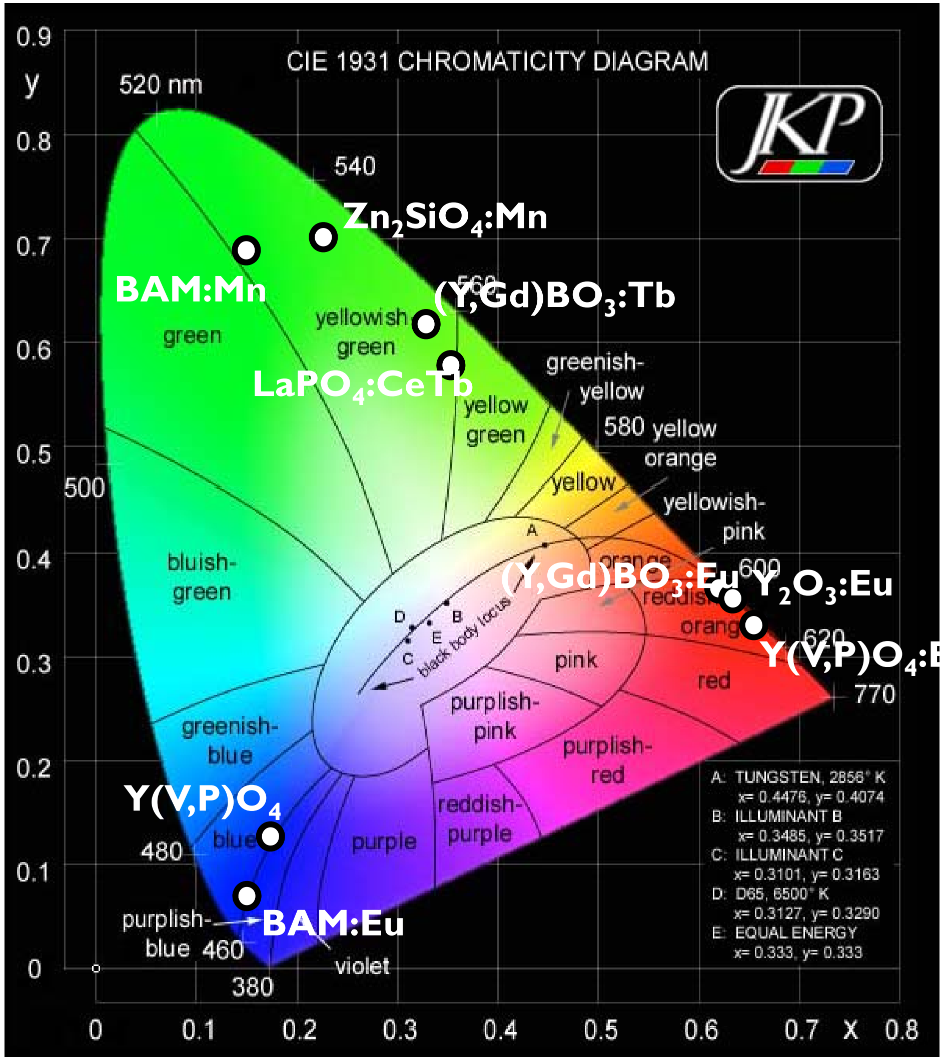
Novel application areas → UV phosphors

VUV Phosphors

For PDPs

Colour points and decay times

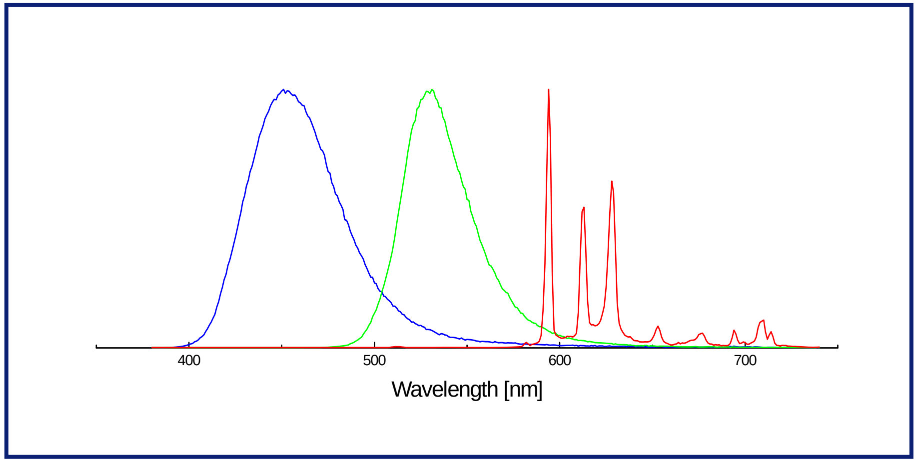
Phosphor	x	y	τ [ms]
$BaMgAl_{10}O_{17}$:Eu	0.148	0.068	< 1
$Y(V,P)O_4$	0.161	0.133	< 1
Zn_2SiO_4:Mn	0.233	0.702	10
$BaMgAl_{10}O_{17}$:Mn	0.140	0.695	12
$(Y,Gd)BO_3$:Tb	0.324	0.615	8
$LaPO_4$:Ce,Tb	0.350	0.582	3
$(Y,Gd)BO_3$:Eu	0.636	0.357	8
Y_2O_3:Eu	0.640	0.346	2.5
$Y(Y,P)O_4$:Eu	0.657	0.330	1



VUV Phosphors

For PDPs

Presently applied	shortcoming	Novel materials based on host lattices with suitable band edge
$BaMgAl_{10}O_{17}$:Eu	stability	$BaMg_3Al_{14}O_{25}$:Eu $Sr_6BP_5O_{20}$:Eu $BaAl_2Si_2O_8$:Eu $CaAl_2O_4$:Eu $LaPO_4$:Tm
Zn_2SiO_4:Mn	decay time	$BaAl_{12}O_{19}$:Mn $BaMg_3Al_{14}O_{25}$:Mn
(Y,Gd)BO_3:Eu	color point	$(Y,Gd)_2SiO_5$:Eu



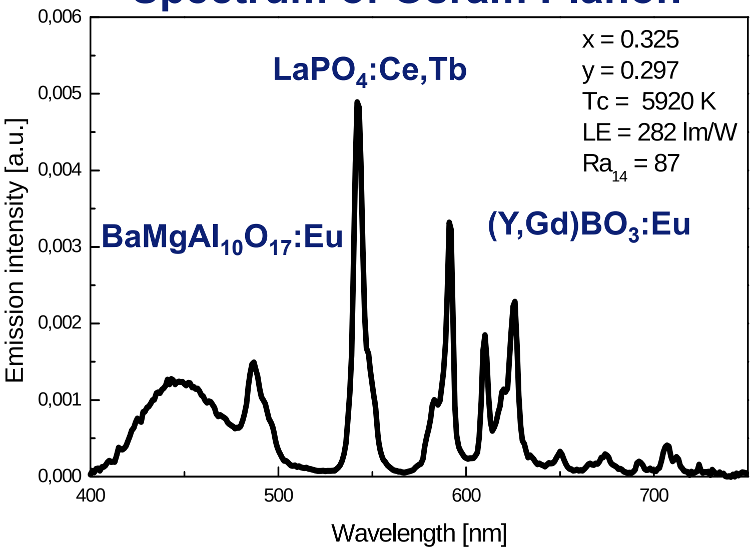
VUV Phosphors

VUV phosphors for white Xe_2^* discharge lamps

$BaMgAl_{10}O_{17}:Eu$	80 $lm/W_{opt.}$
$LaPO_4:Ce,Tb$	500 $lm/W_{opt.}$
$(Y,Gd)BO_3:Tb$	530 lm/W_{opt}.
$(Y,Gd)BO_3:Eu$	275 $lm/W_{opt.}$
$(Y,Gd)_2O_3:Eu$	290 $lm/W_{opt.}$

Efficacy < 50 $lm/W_{el.}$

Spectrum of Osram Planon



Challenges related to VUV phosphors for Xe_2^* discharge lamps

a) Lamp efficacy → Down conversion phosphors
b) VUV Stability → Particle coatings (MgO or Al_2O_3)
c) Color point stability → Optimized blue phosphor
d) Novel application areas → UV phosphors

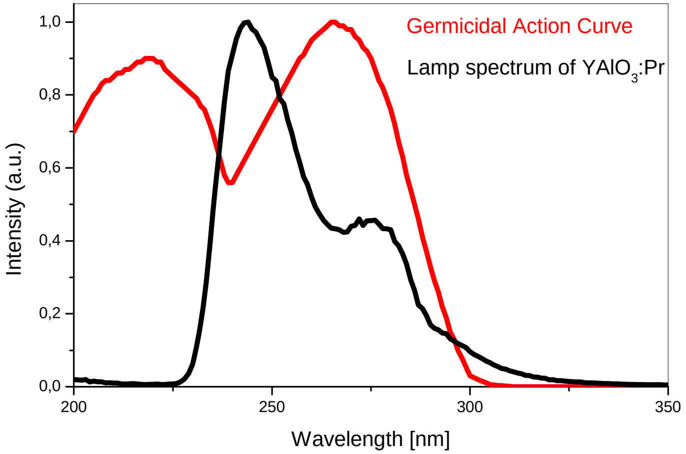
Future of Rare Earth Phosphors

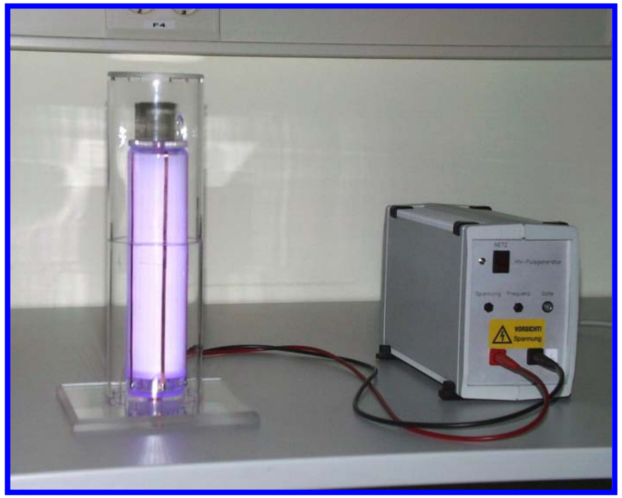
Application in UV emitting fluorescent Xe_2^* excimer lamps

→ Requires development and optimization of phosphors with strong UV emission upon 172 nm excitation

→ e.g. Ce^{3+}, Pr^{3+} , Nd^{3+} activated phosphates

YPO_4:Nd	190 nm
$LaPO_4$:Pr	225 nm
YPO_4:Pr	233 nm
$YAlO_3$:Pr	245 nm
$LuBO_3$:Pr	257 nm
YBO_3:Pr	261 nm
Y_2SiO_5:Pr	270 nm
$Lu_3Al_5O_{12}$:Pr	310 nm
$LaPO_4$:Ce	320 nm



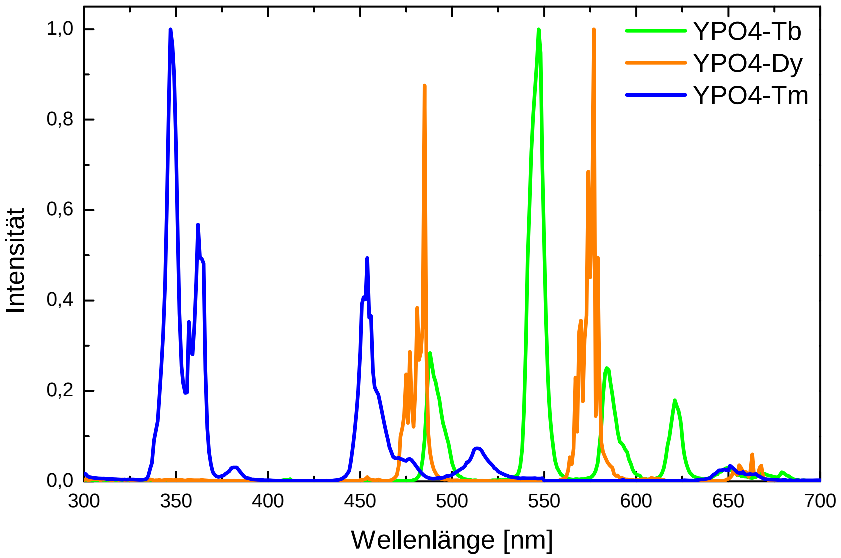


Future of Rare Earth Phosphors

Application in phosphor converted LEDs with NIR emission
→ Broad band NIR emission for sensors and spectroscopy

Near UV excitable phosphors for laser displays
→ excitation at 407 nm (blue-ray laser diode)

As a marker in
- **biolabels**
- **product protection**
- **medical imaging**



Rare earth ions enable phosphors with all kind of optical spectra in the visible, UV and NIR range

Acknowledgement

Thanks for your kind attention!

Questions?