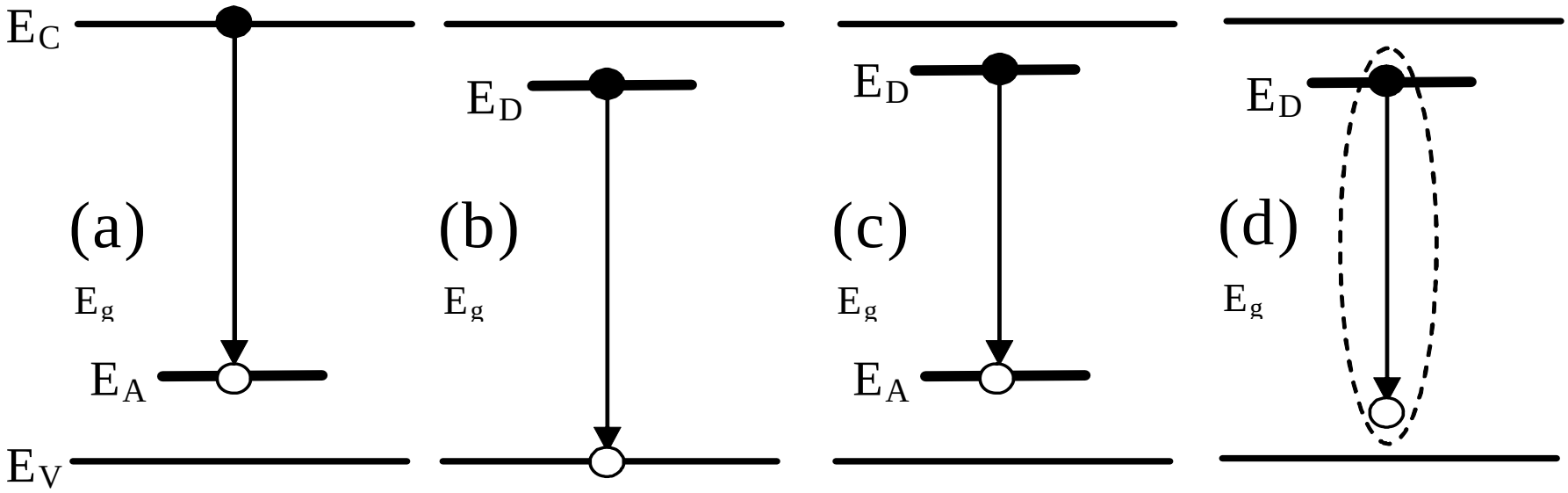
8. Luminescence Mechanisms

Content

8.1 Luminescence - 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



Thus: Luminescence requires localisation of absorbed energy by discrete states!

8.1 Luminescence - Definition

Thermal and non-thermal radiators

Thermal radiators emit a radiation spectrum that equals black body radiation at a corresponding temperature

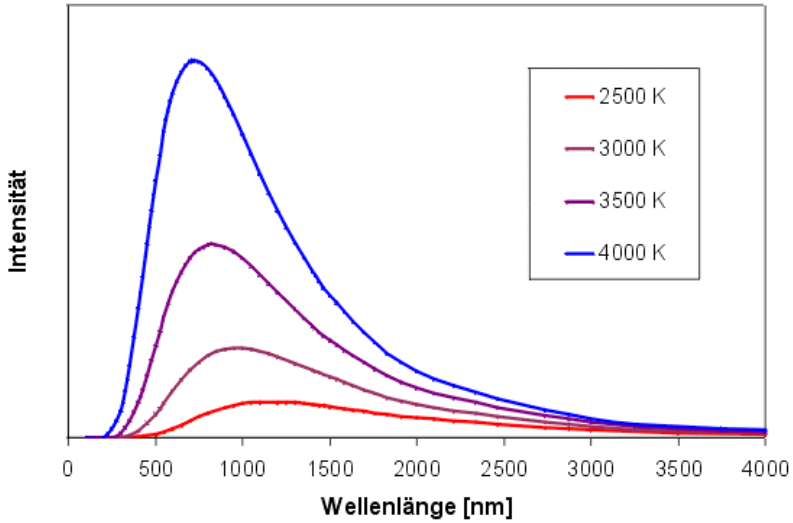
→ **Planck radiation**

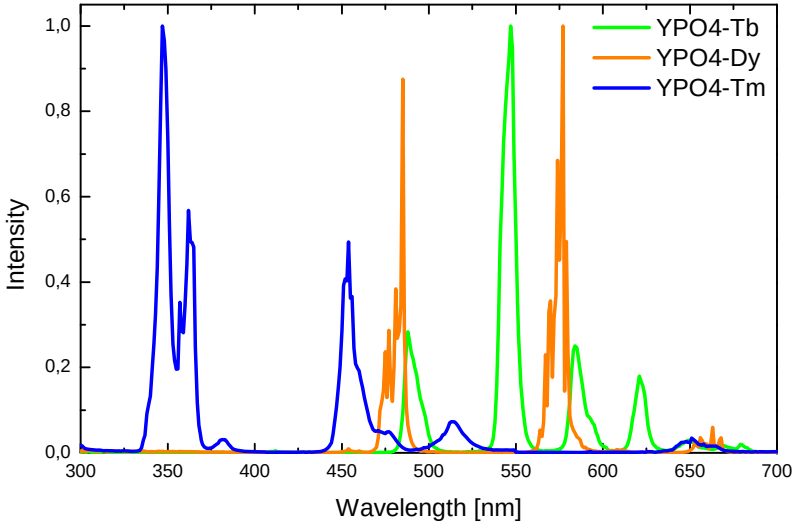
Examples: Cosmic background radiation, cosmic objects, halogen- and incandescent lamps

Non-thermal radiators emit a radiation spectrum originating from electronic transitions between discrete electronic energy levels

→ **Luminescence**

Examples: Luminescent materials, LEDs, Lasers





8.1 Luminescence – Materials

Inorganic luminescent materials = Host lattice + defects + dopants

Host lattice Y_2O_3, $Y_3Al_5O_{12}$, ZnS, $CaAlSiN_3$, $Sr_2Si_5N_8$, …

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

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

- Selection and concentration depend on host lattice and application area:
  Solubility, mobility, oxidation state stability, CT state location

Defects V_K, V_A, F, interstitials, ...

cause:

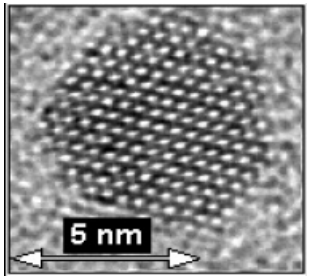
- Afterglow and charge storage
- Concentration and thermal quenching
- Reduction of stability and colour point shift

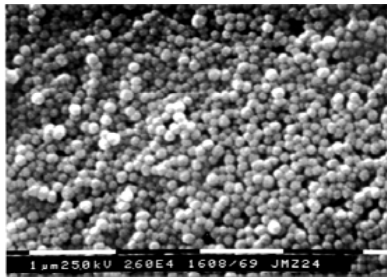
8.1 Luminescence – Materials

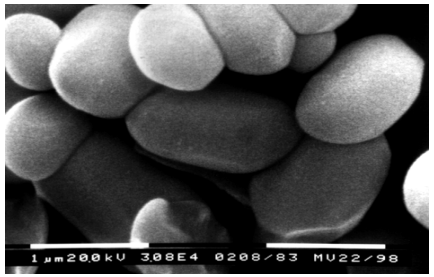
Inorganic luminescent materials - Morphology

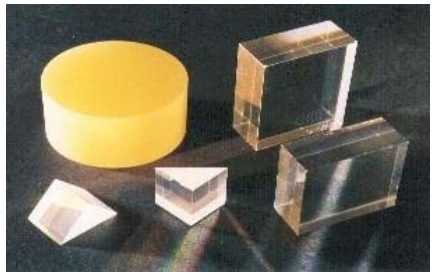
• Nanoscale particles	Molecular imaging, precursors
• µ-sized particles	Lamps, LEDs, CRTs, PDPs, EL Displays, x-ray converter films
• Large single crystals	Scintillators, Lasers
• Ceramics	LEDs, scintillators, LEDs
• Glasses	Detectors, Lasers

1 nm 10 nm 100 nm 1 µm 10 µm 100 µm 1 mm 10 mm









8.1 Luminescence – Materials

Inorganic luminescent materials – Requirements for high efficiency

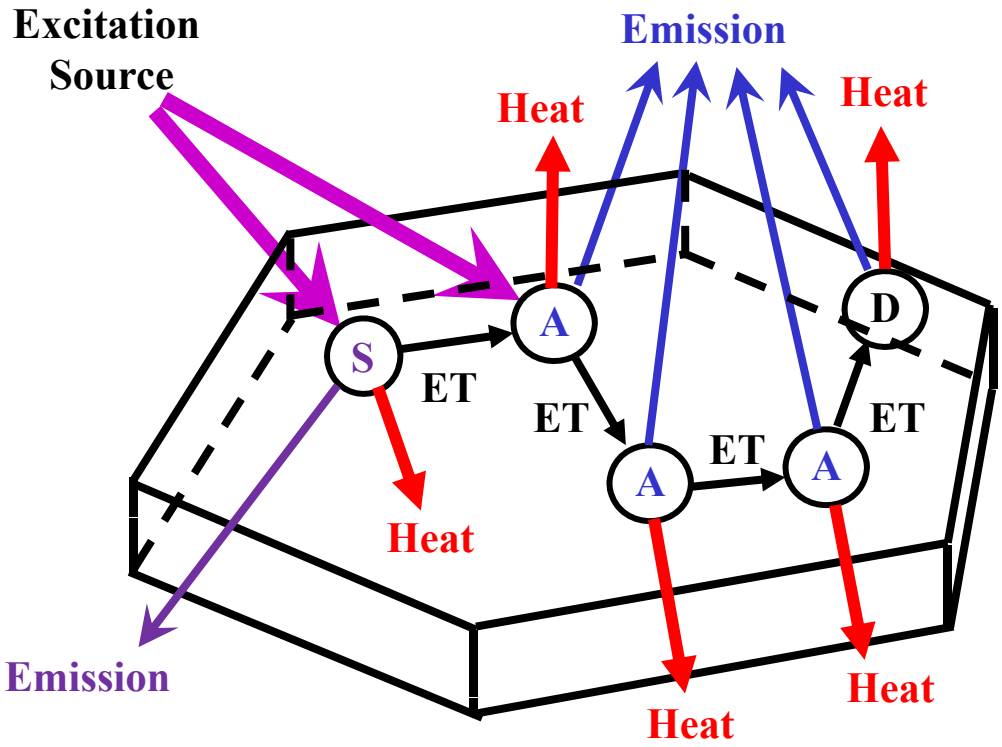
- Strong absorption
- Highly crystalline particles, low defect density
- High purity (99,99% or higher)
- Homogeneous distribution of activator and sensitizer ions
- Low phonon frequencies

Absorption process related to

Optical centres (impurities)

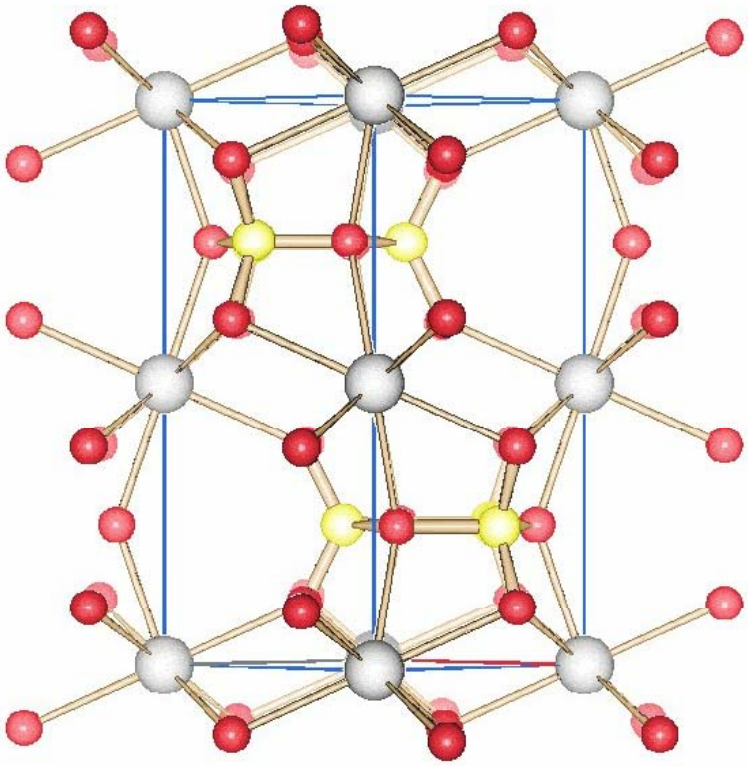
- activators (A)
- sensitizers (S)
- defects (D)
- host lattice (band edge)

Energy transfer often occurs prior to emission process!



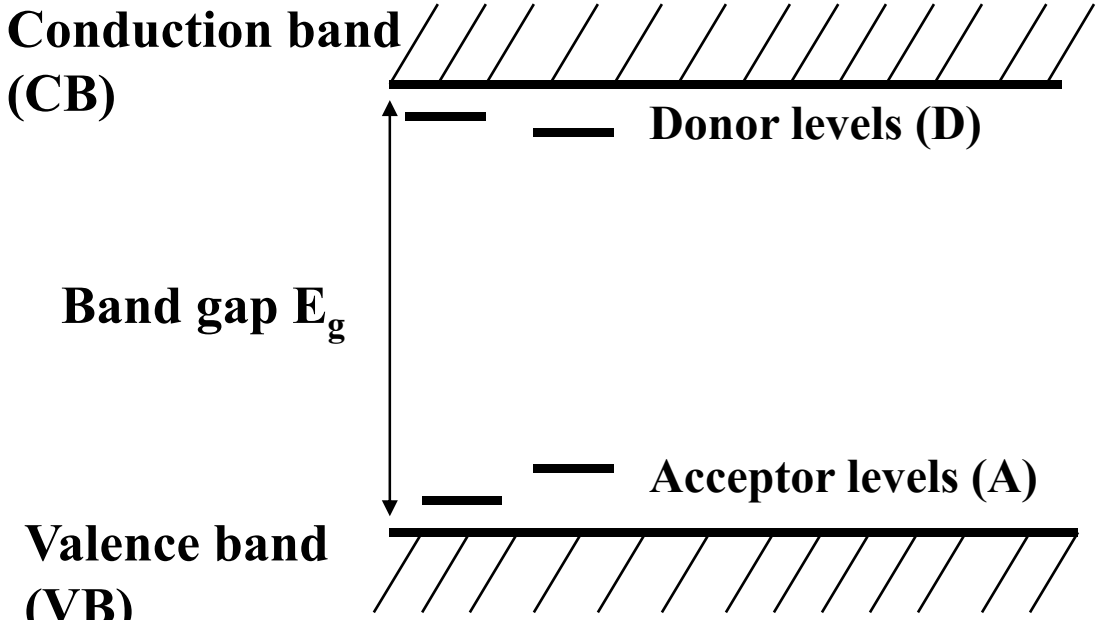
8.1 Luminescence – Materials

Inorganic luminescent materials – The role of the host lattice



YBO_3 (Vaterite)

Band gap E_g = 6.5 eV



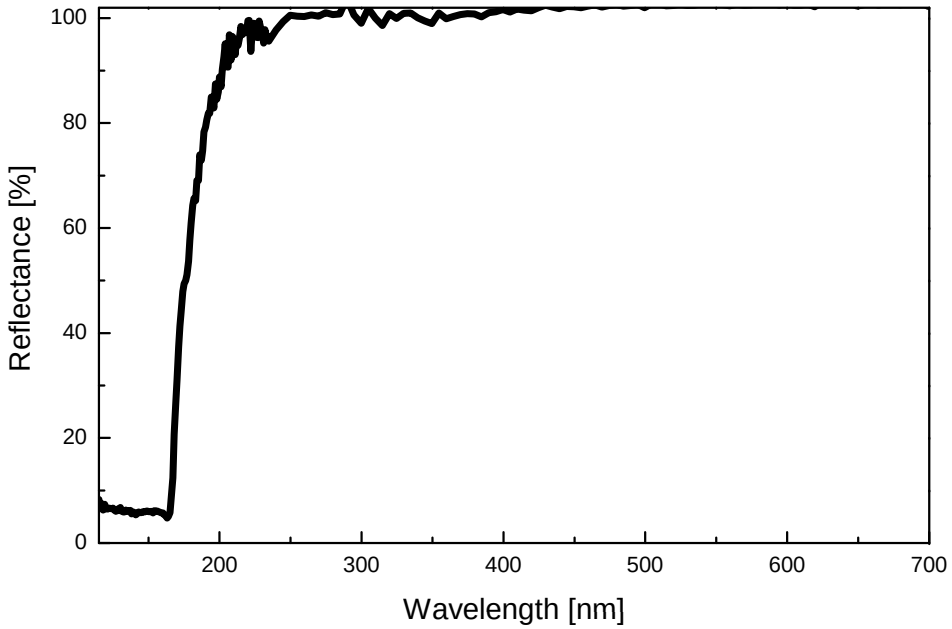
Absorption via

- Host lattice
  → Charge-Transfer or VB to CB
- Defects (colour centers)
  → Donor and acceptor levels

8.1 Luminescence – Materials

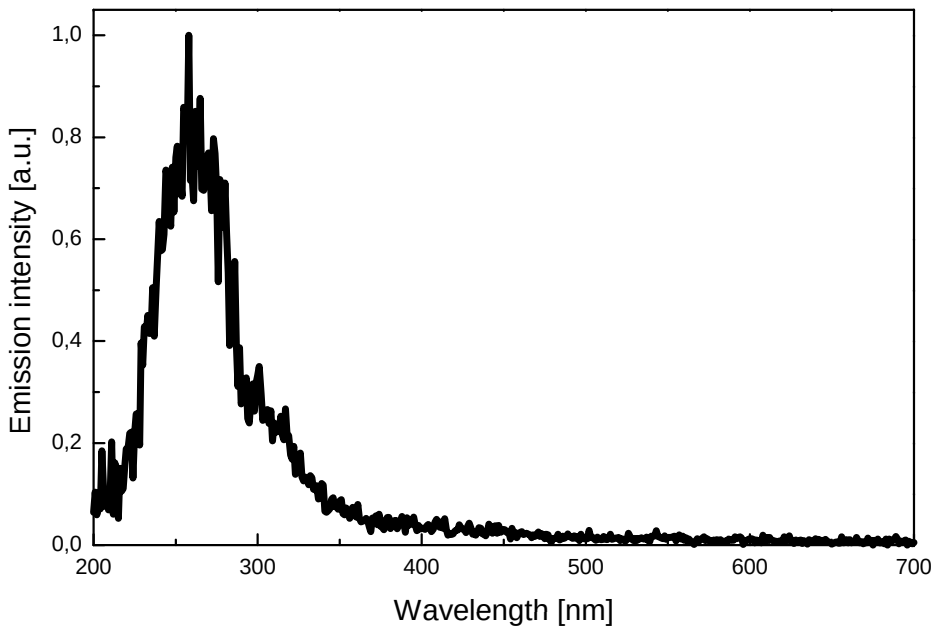
Inorganic luminescent materials – The role of the host lattice

Reflection spectrum of YBO_3



Band gap absorption at 170 nm

Emission spectrum of YBO_3 upon 160 nm excitation

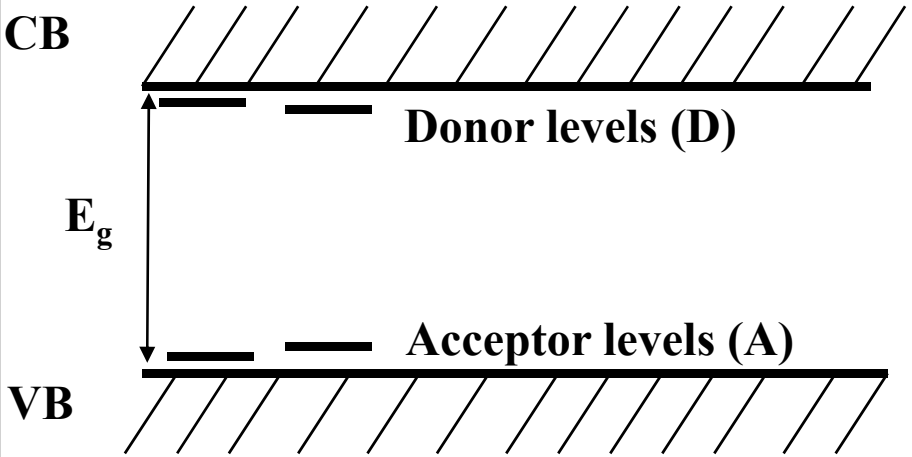


Exciton luminescence at 260 nm

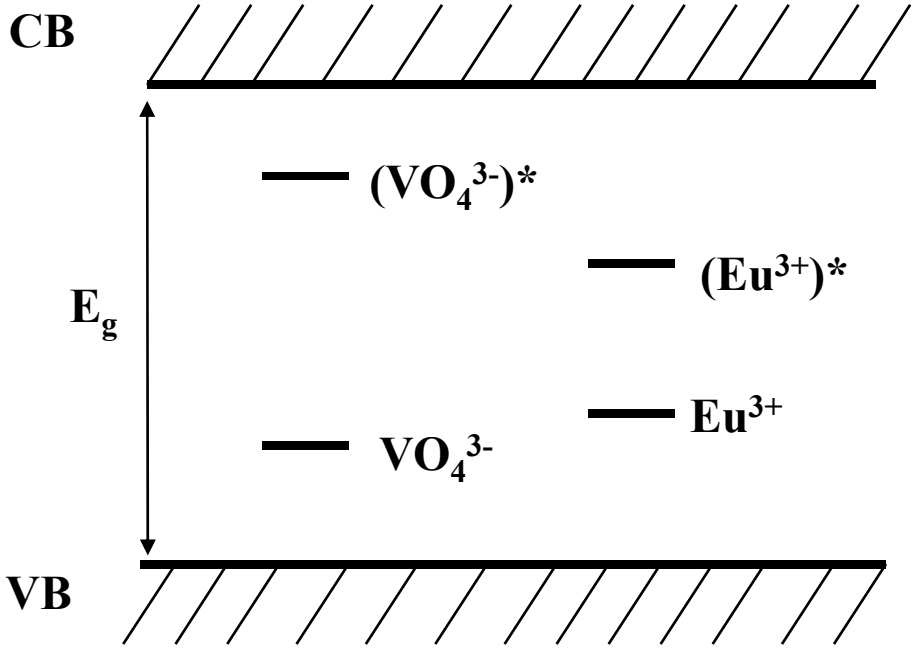
8.1 Luminescence – Materials

Inorganic luminescent materials – The role of the dopants

YVO_4 (tetragonal), E_g = 4.2 eV



YPO_4:V,Eu (tetragonal), E_g = 8.2 eV

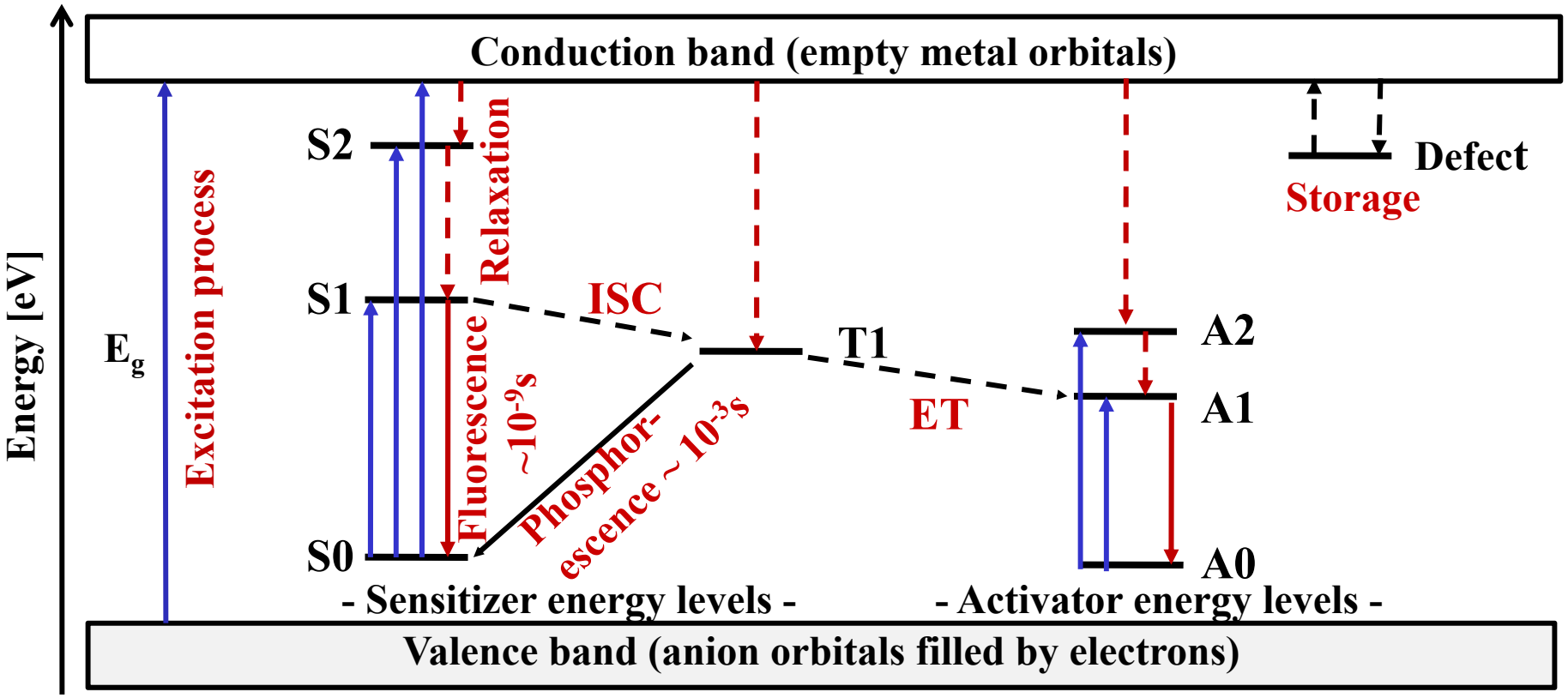


Absorption via

- Host lattice → Charge-Transfer or VB to CB
- Defects (colour centers) → Donor and acceptor levels
- Dopants (impurities) → Activators and sensitizers

8.1 Luminescence - Processes

The overall picture



E_g

S0, S1, S2, T1, A0, A1 = Energy levels of the activators and sensitizers

ISC = Intersystem Crossing "spin-forbidden singulett-triplett transition"

ET = Energy transfer

8.1 Luminescence - Processes

Electronic Ground States of Atoms and Ions (Dopants)

The electronic energy levels are defined by the spin and orbital momentum of the electrons and by the coupling of these to the total spin and total (orbital) momentum

Atom/Ion	Electron configuration	Spectroscopic term $^{2S+1}L_J$
Li^0	$1s^2\ 2s^1$	$^2S_{1/2}$
Li^+	$1s^2$	$^1S_0$
Na^0	$[Ne]3s^1$	$^2S_{1/2}$
Ti^{3+}	$[Ar]3d^1$	$^2D_{3/2}$
Cr^{3+}/Mn^{4+}	$[Ar]3d^3$	$^4F_{3/2}$
Mn^{2+}/Fe^{3+}	$[Ar]3d^5$	$^6S_{5/2}$
Zn^{2+}/Cu^+	$[Ar]3d^{10}$	$^1S_0$
Ce^{3+}	$[Xe]4f^1$	$^2F_{5/2}$
Eu^{3+}	$[Xe]4f^6$	$^7F_0$
$Eu^{2+}/Gd^{3+}/Tb^{4+}$	$[Xe]4f^7$	$^8S_{7/2}$
Tb^{3+}	$[Xe]4f^8$	$^7F_6$
Lu^{3+}	$[Xe]4f^{14}$	$^1S_0$

8.1 Luminescence - Processes

Selection rules for electric dipole radiation (transitions)

Overall requirement: Conservation of momentum of the system "atom/ion + photon"

1.	Spin selection rule	$\Delta S = 0$
2.	Angular momentum (single electron)	$\Delta l = \pm 1$
3.	Angular momentum (multi electron)	$\Delta J = 0, \pm 1$ (but not $J = 0 \rightarrow J = 0$) $\Delta L = 0, \pm 1$ (but not $L = 0 \rightarrow L = 0$)
4.	Laporte selection rule	$g \rightarrow u$ or $u \rightarrow g$ not $g \rightarrow g$ or $u \rightarrow u$

Examples:	Ce^{3+}	$[Xe]4f^1\,(^2F_{5/2}) \rightarrow [Xe]5d^1\,(^2D_{3/2})$	$\Rightarrow$ allowed	~ ns
	Eu^{3+}	$[Xe]4f^6\,(^7F_0) \rightarrow [Xe]4f^6\,(^5D_0)$	$\Rightarrow$ forbidden	~ ms

8.1 Luminescence - Processes

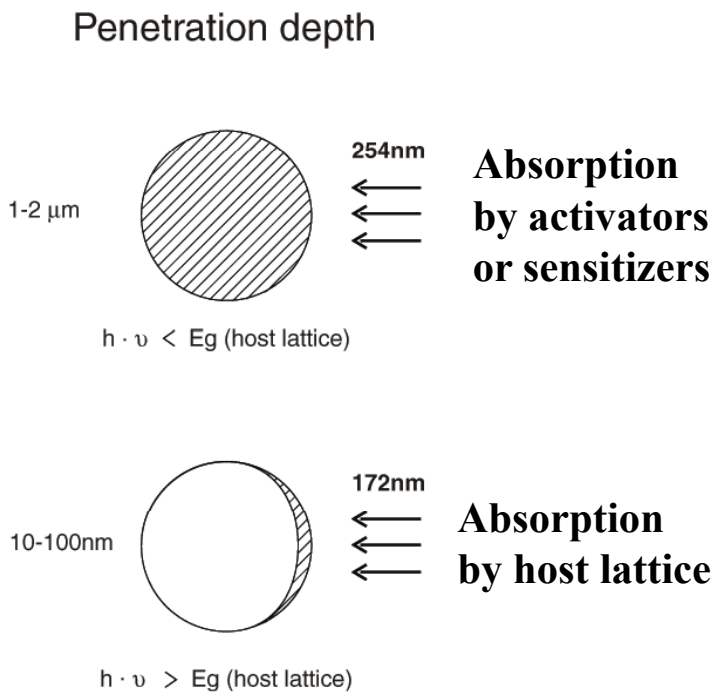
Type	Excitation by	Example
Scintillation	High energy particles	high-energy physics
	γ-rays	PET detectors
X-ray luminescence	X-rays	X-ray amplifier, CT
Cathode luminescence	Electrons (high voltage)	CRTs, oscilloscopes
Photo luminescence	UV/Vis photons	Fluorescent lamps
Electro luminescence	Electrical field (low voltage)	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 scotch tape

Nature 455 (2008) 1089, blue + UV + x-ray!

8.2 Absorption

Penetration depth of photons and electrons

Photons (Lambert-Beer law)



Electrons (Feldman equation: R in [Å])

$$R = 250\frac{A}{\rho Z^{n}/_{2}}U^{n} \quad with\, n = \frac{1,2}{1 - 0,29log_{10}Z}$$

For 5.7 keV electrons	Density [g/cm³]	R [Å]	R [nm]
SiO_2	2.20	6171	617.8
Al_2O_3	3.97	3476	347.6
$Mg_3(PO_4)_2$	2.56	5345	534.4
ZnS	4.04	4248	424.8
MgO	3.59	3799	379.8
MgF_2	3.15	4464	446.4
MgS	2.68	5603	560.4

Simplified R ~ 0.046*$U^{5/3}/\rho$ [µm]

For a material with r = 5.0 g/cm³ (Y_2O_3)
10 kV electrons R ~ 400 nm
2 kV electrons R ~ 30 nm

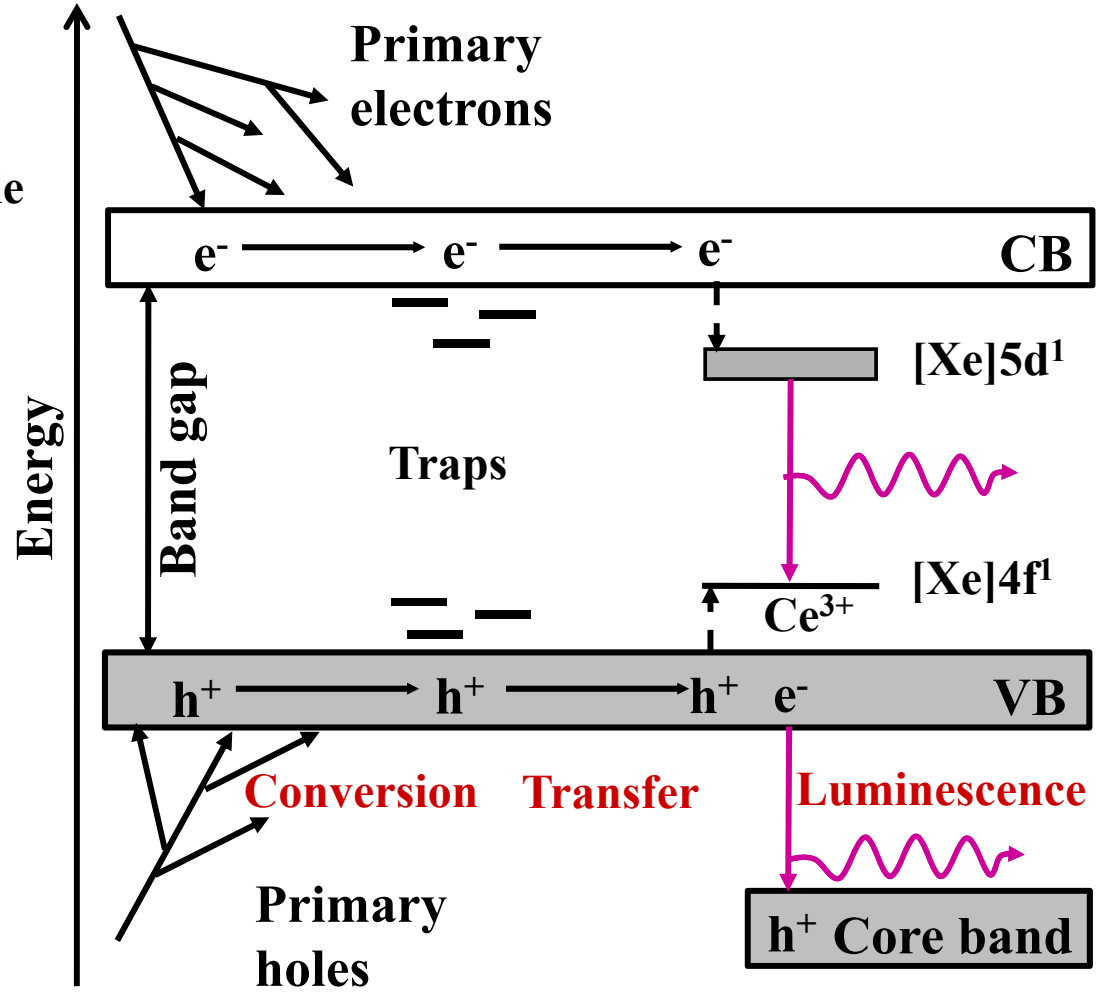
8.3 Excitation Mechanisms

High energy particles, γ- ray, 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

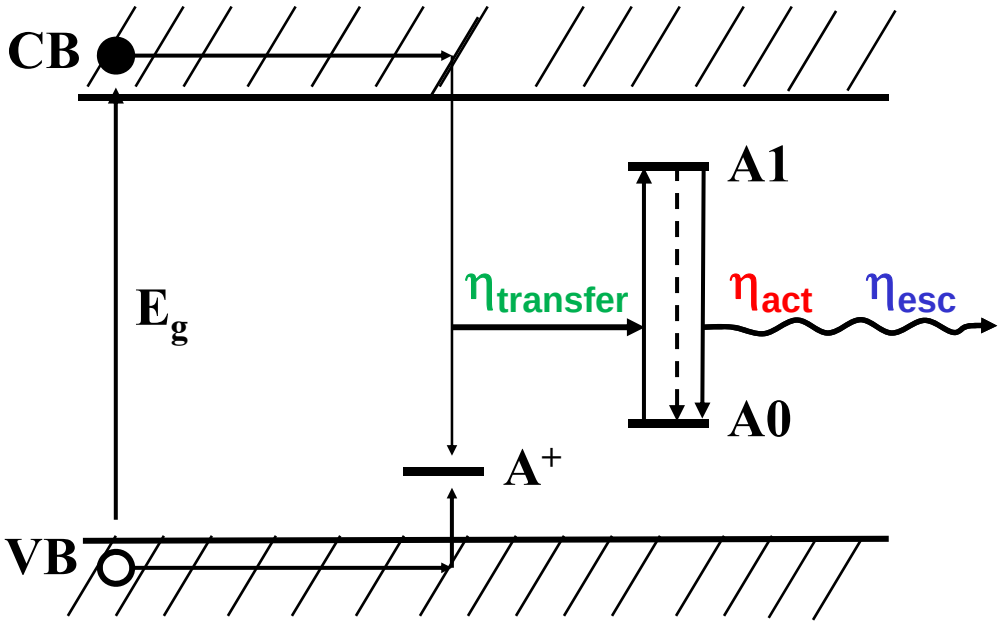
Efficiency surprisingly well understood, but with two different models:

1. Robbins
2. Bartram-Lempicki



8.3 Excitation Mechanisms

Photons with an energy > band gap of the host lattice: PDPs and Xe excimer lamps



Host lattice	Band gap E_g [eV]
MgF_2	12.2
Al_2O_3	8.0
Y_2O_3	5.6
ZnS	3.9
ZnSe	2.8
ZnTe	2.4
CdS	2.6
CdTe	1.6

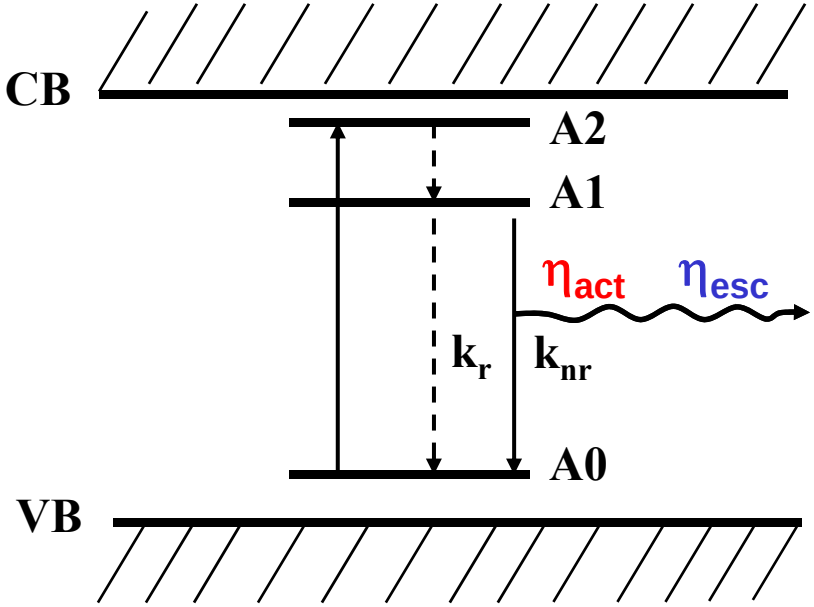
Internal quantum efficiency: $IQE = \eta_r/(\eta_r + \eta_{nr}) = \eta_{act}$

External quantum efficiency: $EQE = \eta_{act} * \eta_{transfer} * \eta_{esc}$

8.3 Excitation Mechanisms

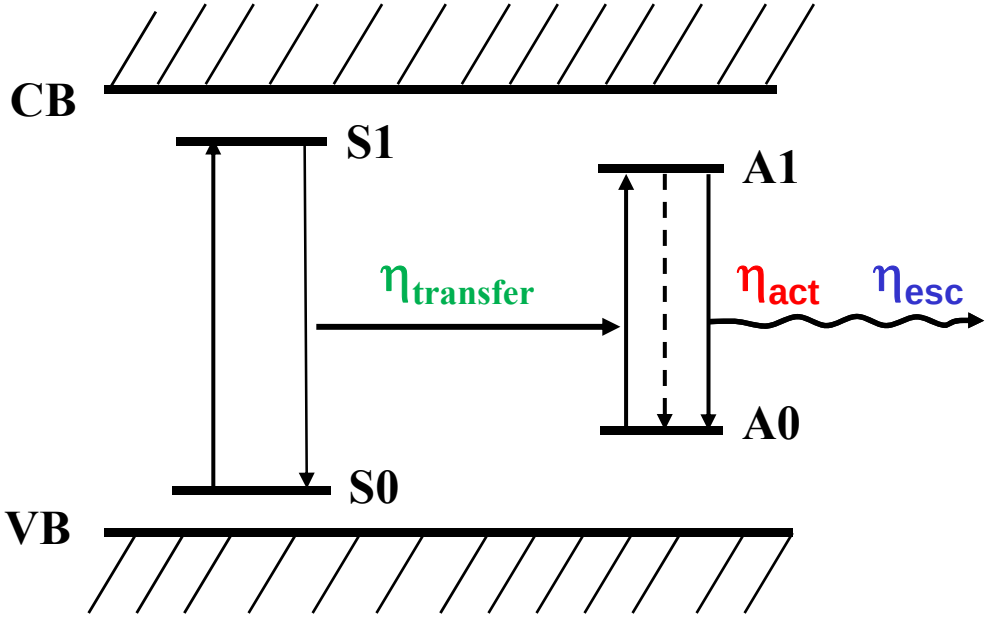
Photons with an energy < band gap of the host lattice: Fluorescent lamps and LEDs

Activator excitation



$IQE = \eta_{act} = k_r/(k_r + k_{nr}) = \tau/\tau_0$
with $k_r + k_{nr} = 1/\tau$ and $k_r = 1/\tau_0$

Sensitizer excitation

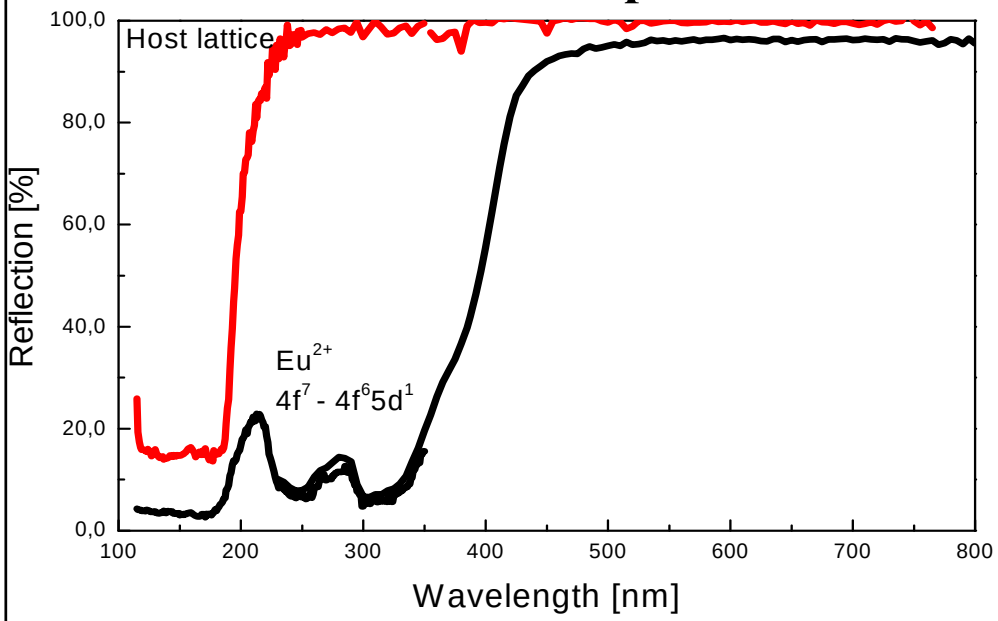


$EQE = \eta_{act} * \eta_{transfer} * \eta_{esc}$

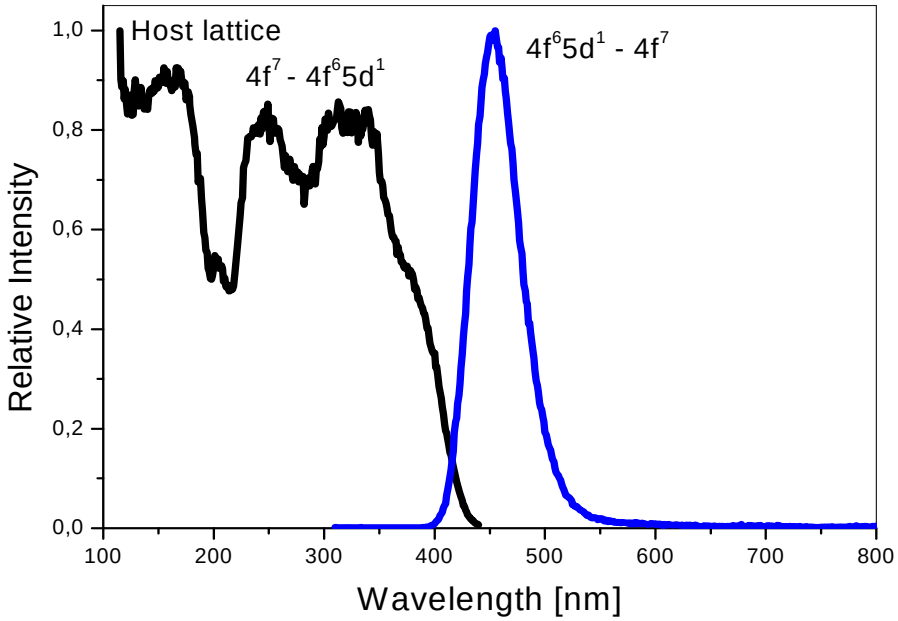
8.3 Excitation Mechanisms

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

Reflection spectra



Emission and excitation spectra

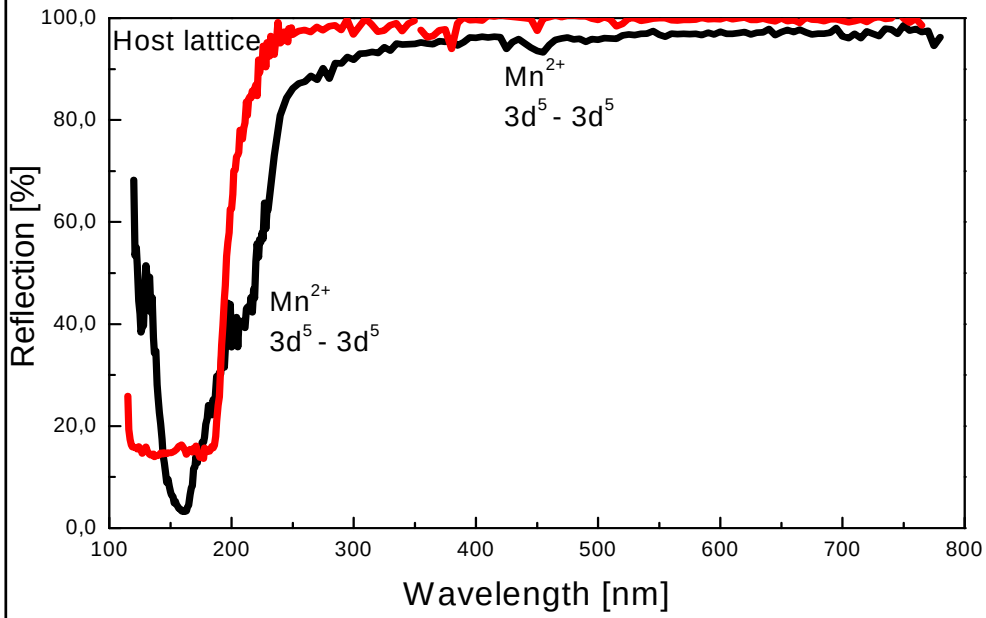


- **Host material VB → CB 180 nm (7.0 eV)**
- **Eu^{2+} $[Xe]4f^7 \rightarrow [Xe]4f^65d^1$ 250 nm (5.0 eV) and 310 nm (4.0 eV)**
- **Allowed transition ⇒ Intense absorption bands and fast decay (~1 µs)**

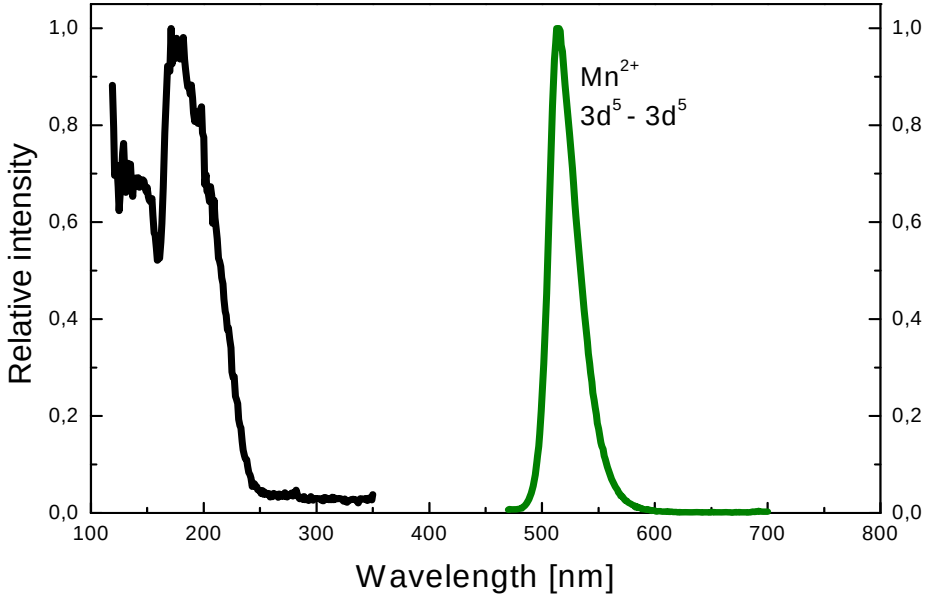
8.3 Excitation Mechanisms

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

Reflection spectra



Emission and excitation spectra

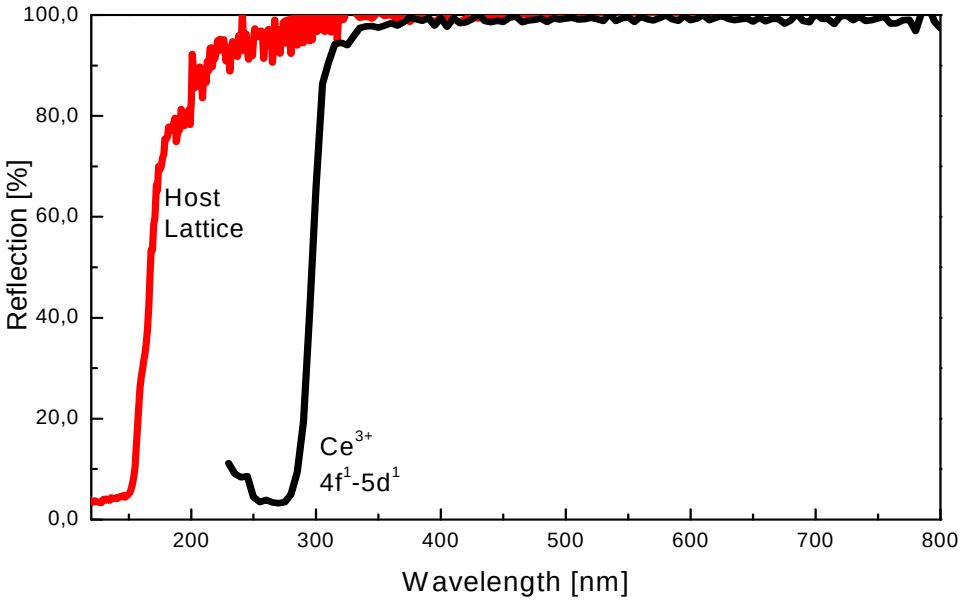


- **Host material VB → CB 180 nm (7.0 eV)**
- **Mn^{2+} $[Ar]3d^5 \rightarrow [Ar]3d^5$ 200 nm (6.2 eV) and 450 nm (2.8 eV)**
- **Forbidden transition ⇒ Weak absorption bands and slow decay (~10 ms)**

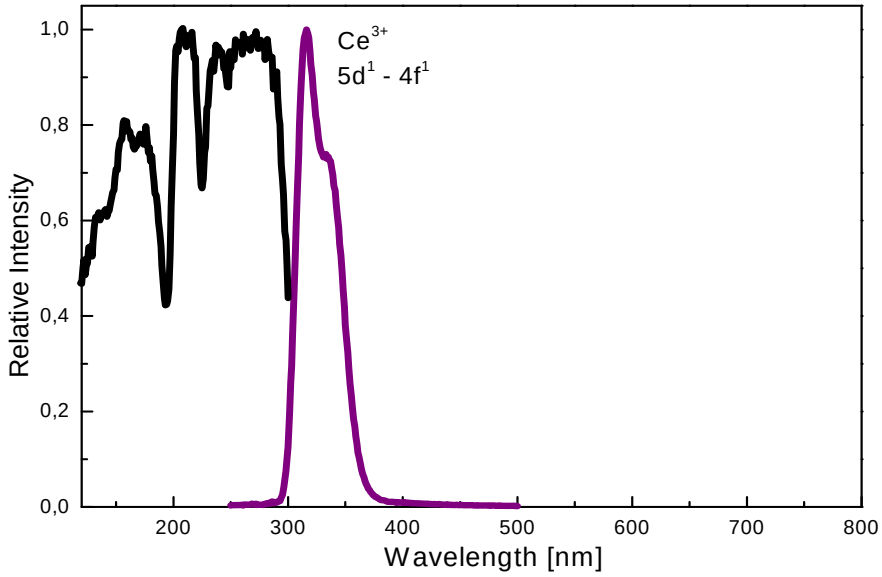
8.3 Excitation Mechanisms

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

Reflection spectra



Emission and excitation spectra

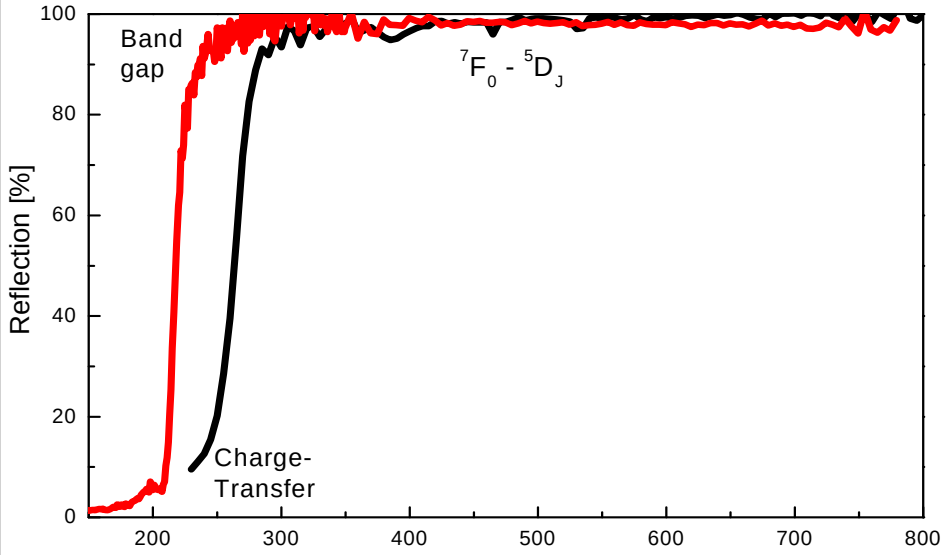


- **Host material VB → CB 150 nm (8.2 eV)**
- **Ce^{3+} $[Xe]4f^1 \rightarrow [Xe]5d^1$ 200 nm (6.2 eV) and 450 nm (2.8 eV)**
- **Allowed transition ⇒ Intense absorption bands and fast decay (~ 30 ns)**

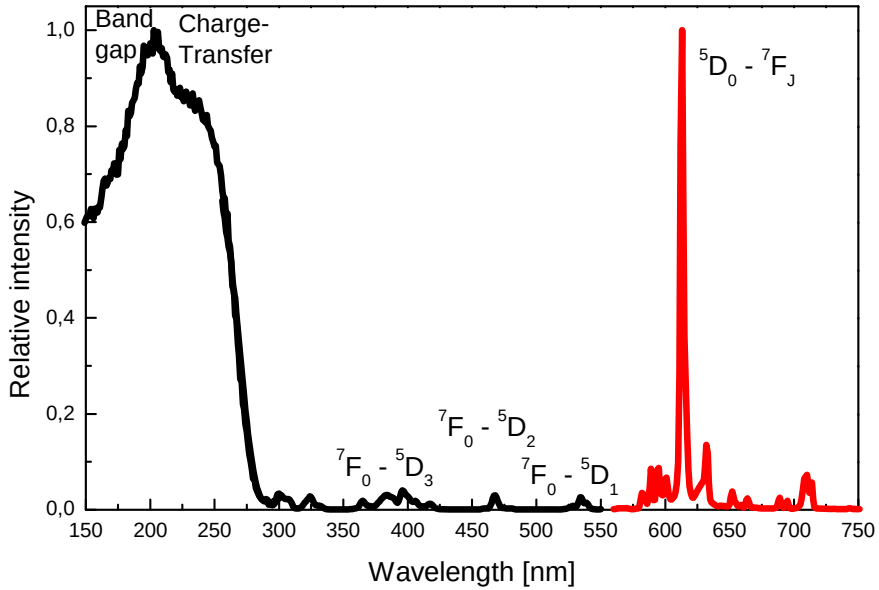
8.3 Excitation Mechanisms

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

Reflection spectra



Emission and excitation spectra



- **Host material** 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)**

8.3 Excitation Mechanisms

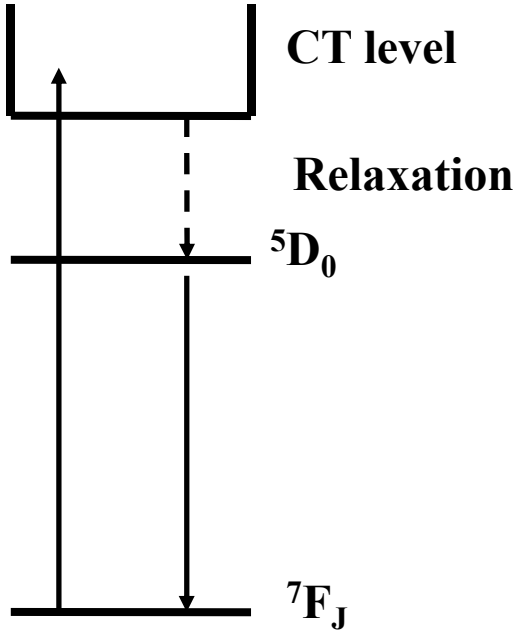
Sensitisation to enhance absorption strength

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

Ways to enhance absorption:

- Taking advantage of allowed transitions
  - Charge-Transfer (CT) states → Eu^{3+}, Yb^{3+}
  - Low-lying energy levels of the $[Xe]4f^{n-1}5d^1$ configuration → Tb^{3+}, Eu^{2+}, Ce^{3+}, Pr^{3+}

- Sensitisation (via energy transfer)
  - Ce^{3+} → Tb^{3+}
  - Pr^{3+} → Tb^{3+}
  - Nd^{3+} → Gd^{3+}
  - Pr^{3+} → Gd^{3+}
  - Bi^{3+} → Eu^{3+}
  - Sb^{3+} → Mn^{2+}



Simplified energy level scheme of Eu^{3+}

8.4 Energy Transfer

Requirements for ET ($S^* + A \rightarrow S + A^*$)

- Sensitizer S and activator A interact with each other by
  - Coulomb interaction (multipolare interaction)

    Dipole-Dipole: $P_{SA} = (1/\tau_S)(r_0/r_{SA})^6$ — Ce^{3+} - Eu^{2+}

    Dipole-Quadrupole: $P_{SA} = (1/\tau_S)(r_0/r_{SA})^8$ — Ce^{3+} - Tb^{3+}

    Quadrupole-Quadrupole: $P_{SA} = (1/\tau_S)(r_0/r_{SA})^{10}$ — unknown

  - Exchange interaction

    $P_{SA} \sim J \cdot \exp(-2\, r_{SA})$

    for $r_{SA} < 5$ Å with J = coupling constant — Mn^{2+} - Mn^{2+}

- Spectral overlap ($\rightarrow$ Energy conservation law!)

8.4 Energy Transfer

Probability P_{ET}

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

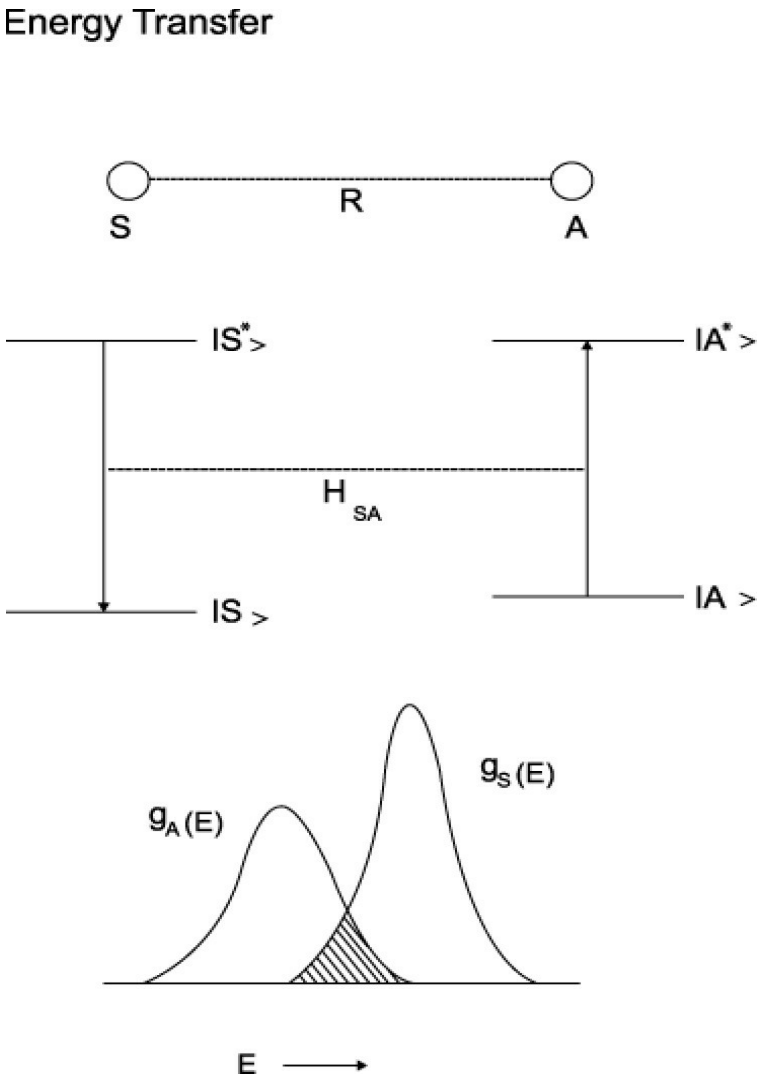
$$P_{ET} = (2\pi/\hbar)\cdot(\rho) < \varphi_i \mid H \mid \varphi_f >^2$$

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 sensitizer and activator ions



8.4 Energy Transfer

Consequences for luminescence processes

ET causes

- **Energy migration**
- **Concentration quenching**
- **Thermal quenching**
- **Cross-relaxation**
- **Possibility of sensitization**

Some rules

- **ET from a broad band emitter to a line emitter only possible for nearest neighbors 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**

8.4 Energy Transfer

Example: ET in $LaPO_4$:Ce,Tb

$LaPO_4$:Ce

$Ce^{3+} \rightarrow (Ce^{3+})^*$ Excitation 4f - 5d

$(Ce^{3+})^* \rightarrow Ce^{3+}$ Emission 5d - 4f

$LaPO_4$:Tb

$Tb^{3+} \rightarrow (Tb^{3+})^{**}$ Excitation 4f - 5d

$(Tb^{3+})^{**} \rightarrow (Tb^{3+})^*$ Relaxation

$(Tb^{3+})^* \rightarrow Tb^{3+}$ Emission 4f - 4f

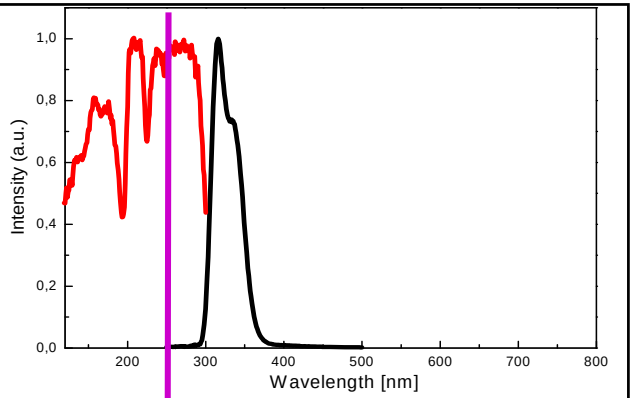
$LaPO_4$:Ce,Tb

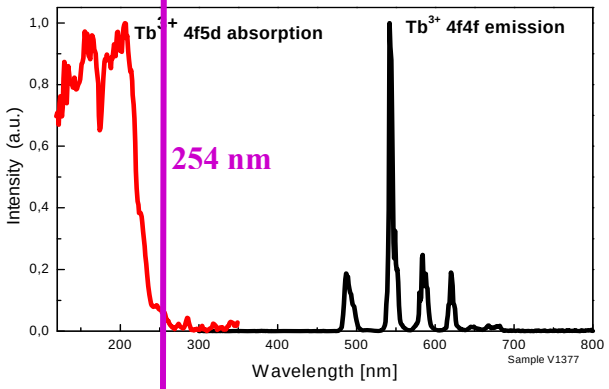
$Ce^{3+} \rightarrow (Ce^{3+})^*$ Excitation 4f - 5d

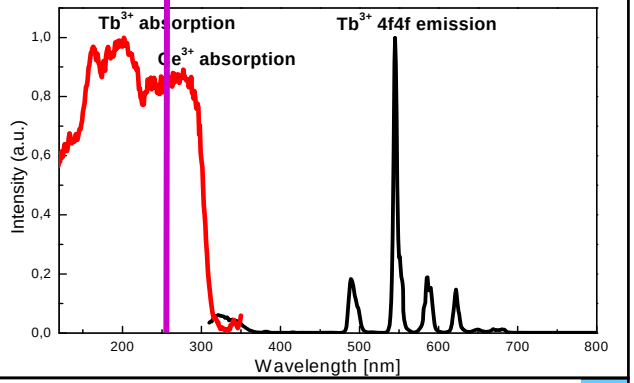
$(Ce^{3+})^* + Tb^{3+} \rightarrow Ce^{3+} + (Tb^{3+})^*$ ET from Ce^{3+} to Tb^{3+}

$(Tb^{3+})^* \rightarrow Tb^{3+}$ Emission 4f - 4f

Fluorescent lamps $\Rightarrow$ Excitation at 254 nm

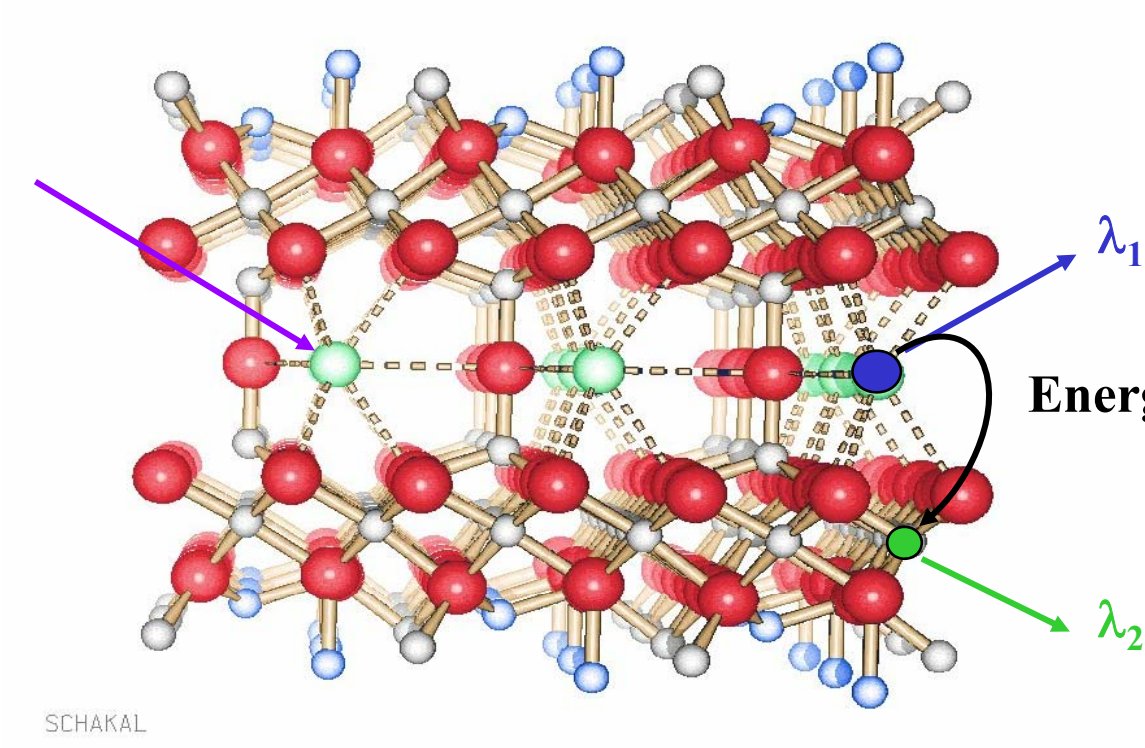






8.4 Energy Transfer

Example: ET in $BaMgAl_{10}O_{17}$: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+}**

8.4 Energy Transfer

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

$BaMgAl_{10}O_{17}$:Eu

$Eu^{2+} \rightarrow (Eu^{2+})^*$ Absorption 4f - 5d

$(Eu^{2+})^* \rightarrow Eu^{3+}$ Emission 5d - 4f

$BaMgAl_{10}O_{17}$:Mn

$Mn^{2+} \rightarrow (Mn^{2+})^*$ Absorption 3d - 3d

$(Mn^{2+})^* \rightarrow Mn^{2+}$ Emission 3d – 3d

$BaMgAl_{10}O_{17}$:Eu,Mn

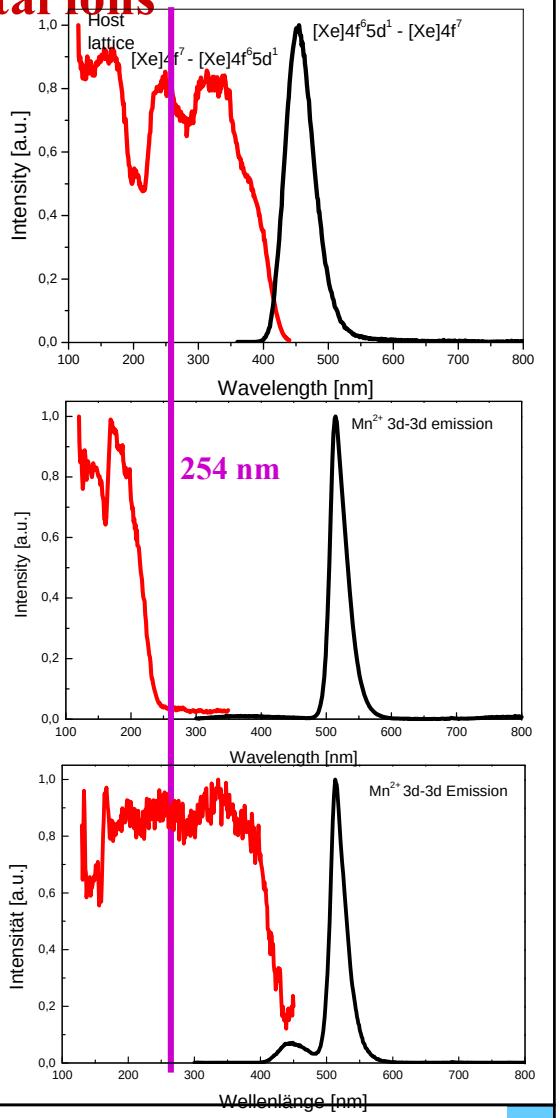
$Eu^{2+} \rightarrow (Eu^{2+})^*$ Absorption 3d - 3d

$(Eu^{2+})^* + Mn^{2+} \rightarrow Eu^{2+} + (Mn^{2+})^*$ ET from Eu to Mn

$(Mn^{2+})^* \rightarrow Mn^{2+}$ Emission 3d – 3d

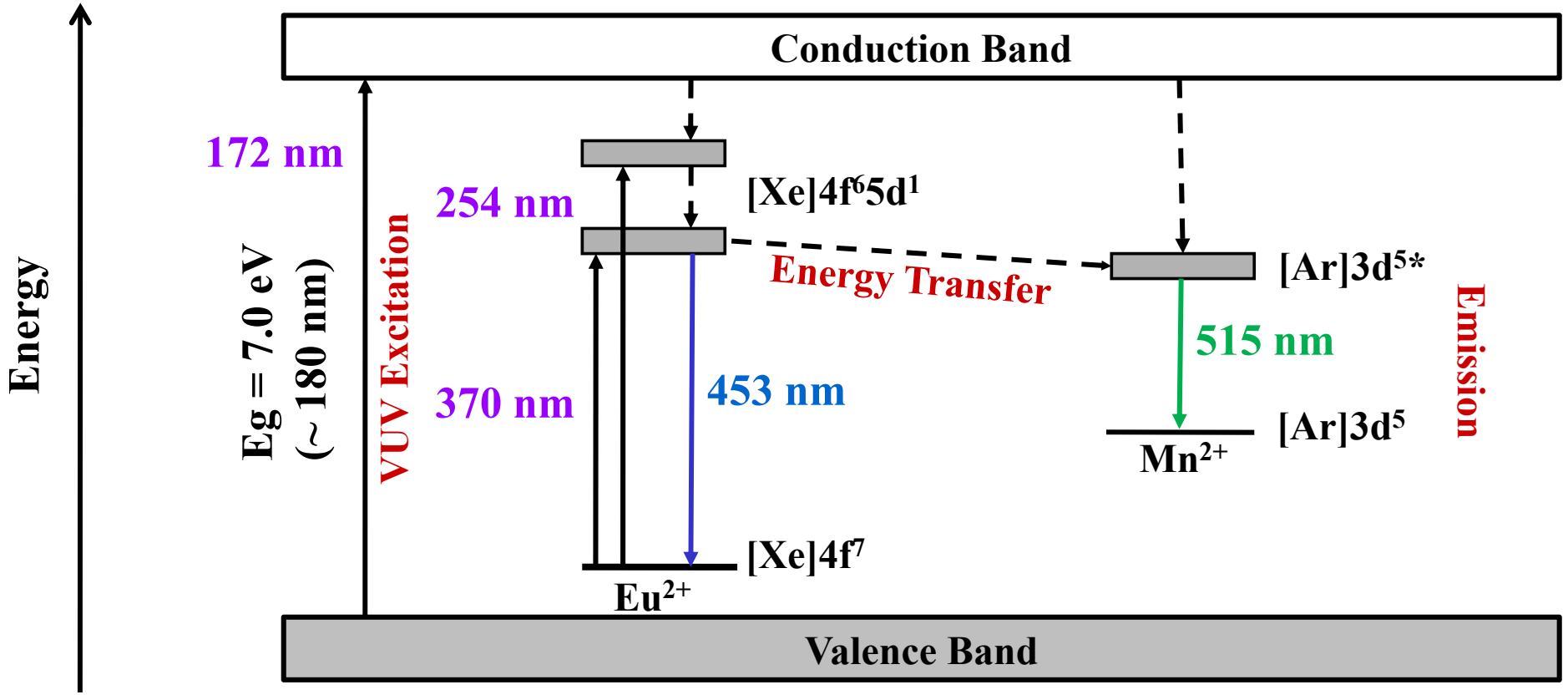
$BaMgAl_{10}O_{17}$:Eu(Mn) can be excited at 172 nm, 254 and 370 nm

⇒ Application in PDPs, FLs (and near UV emitting LEDs)

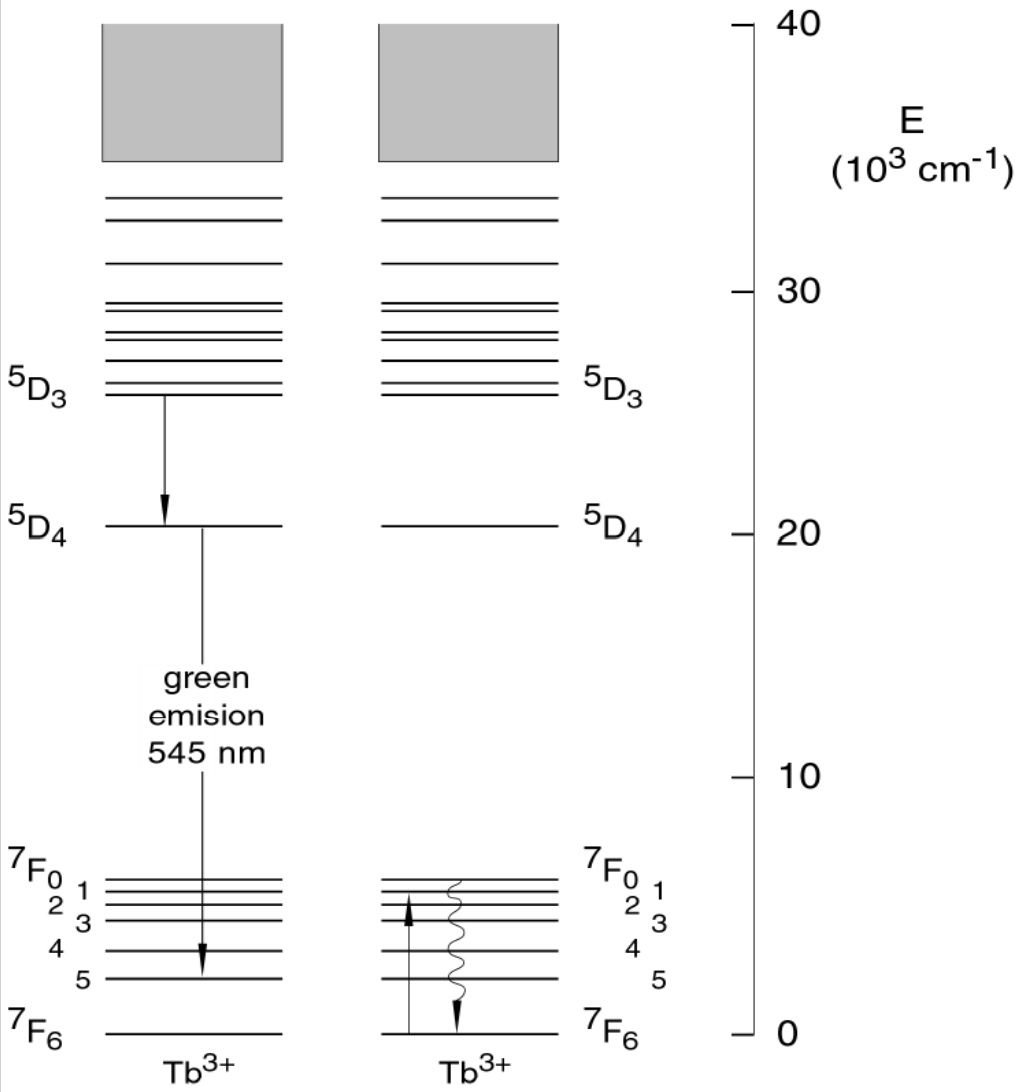


8.4 Energy Transfer

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



8.5 Cross-Relaxation



- **Cross-relaxation processes are responsible for the quenching of luminescence of higher 4f levels of Tb^{3+} at a high Tb^{3+} concentration**
- **Cross-relaxation also occurs in Eu^{3+}, Sm^{3+}, Pr^{3+}, and Dy^{3+} doped materials**
- **Concentration quenching for Sm^{3+} or Dy^{3+} activated materials by cross-relaxation and not by energy migration**
- **Relaxation to the first excited state can also be triggered by high-energy photons**

8.6 Loss Processes

Overview of the most relevant processes leading to luminescence quenching

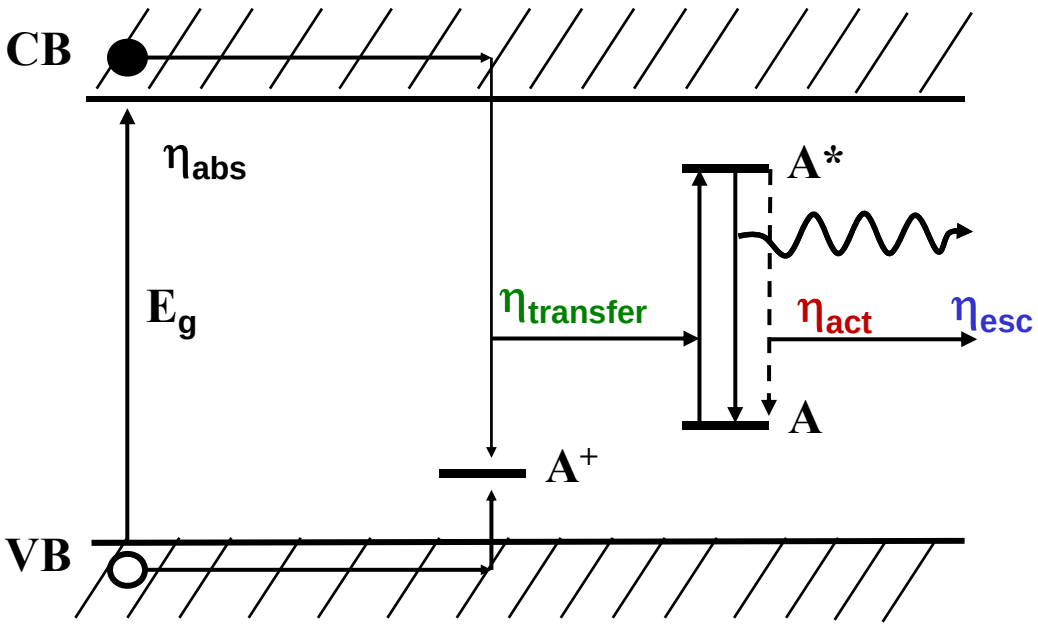
1. **The absorbed energy does not reach the activator ion** ($\eta_{transfer}$)
   - a) Competitive absorption
   - b) ET to defects or non-luminescent impurity ions
   - c) Excited state absorption (ESA)
   - d) Auger processes

2. **The absorbed energy reaches the activator ion, but non-radiative channels dominate the radiative return to the ground state** (η_{act})
   - a) Crossing of excited and ground state parabola
   - b) Multi-phonon relaxation
   - c) Cross-relaxation
   - d) Photoionization
   - 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

8.6 Loss Processes

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!)

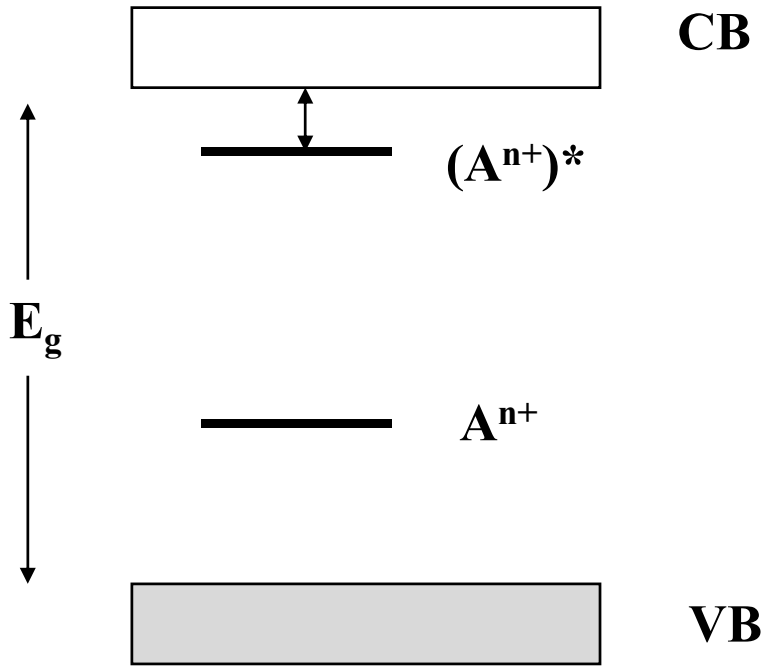
Light Yield

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

(No correlation to decay time!)

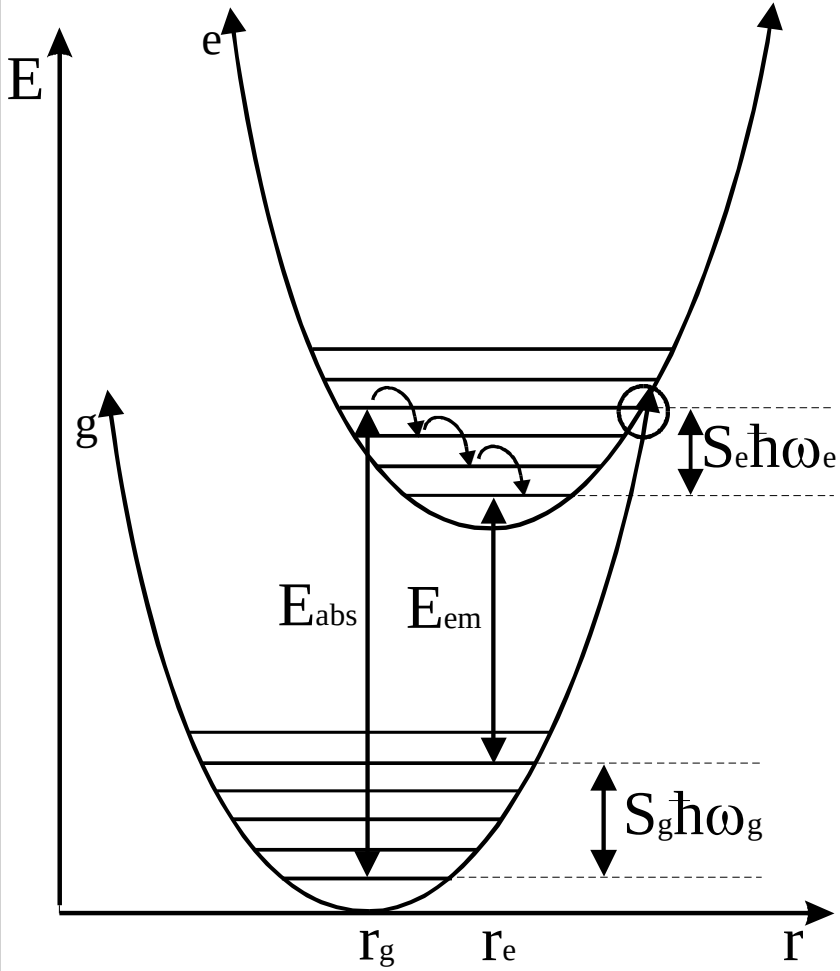
8.6 Loss Processes

Photoionization



- Excited A^{n+} ion gets ionised
- Released electron is re-trapped, e.g. by anion vacancies
- Causes afterglow in
  - scintillators
  - persistent phosphors

8.7 Configuration Coordinate Diagram



- **Stokes shift**

  Energy gap between absorption and emission band

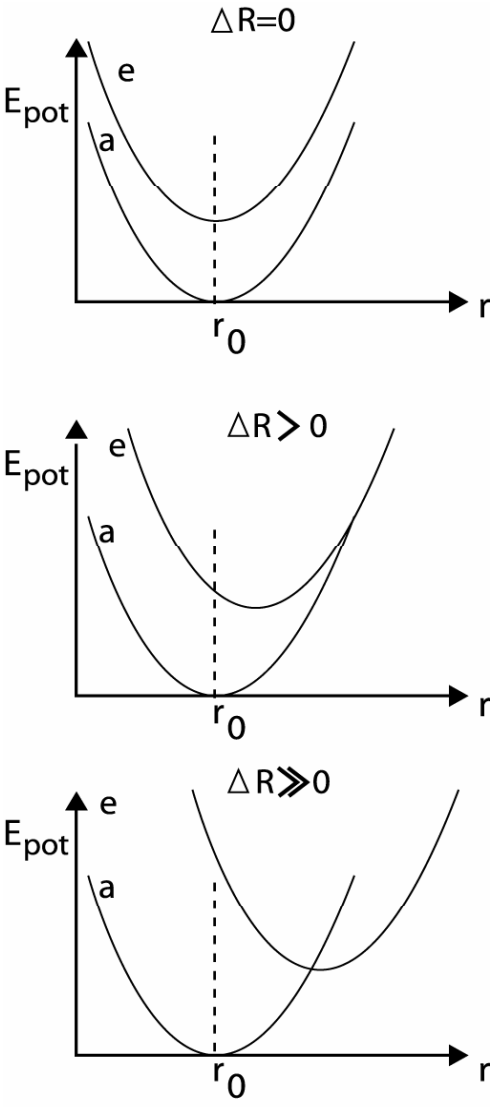
  $S = S_e h\omega_e + S_g h\omega_g$

- **Full width at half maximum of the emission band**

  FWHM ~ √S

- **Thermal quenching decreases with increasing $\Delta R = r_e - r_g$**

8.7 Configuration Coordinate Diagram



1. **Weak to no electron-phonon-coupling**
- High IQE, EQE determined by ET processes
- Thermal quenching mainly due to photoionization
- 4f → 4f transitions (shielded 4f-shell: small crystal field splitting [CFS])
- Lines Eu^{3+}, Tb^{3+}, ….

2. **Moderate electron-phonon-coupling**
- High to moderate IQE
- Thermal quenching due to tunnelling or photoioniz.
- 4f → 5d transitions (large CFS)
- Narrow bands Eu^{2+}, Ce^{3+}, ….

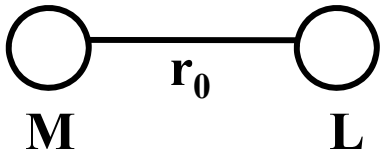
3. **Strong electron-phonon-coupling**
- High to low IQE at RT, strong thermal quenching
- Thermal quenching mainly due to tunnelling
- $ns^2 \rightarrow ns^1np^1$ or CT transitions
- Broad bands Pb^{2+}, Bi^{3+}, ….

8.7 Configuration Coordinate Diagram

Width of the transitions can be explained by the model "harmonic oscillator"

$F = -k*(r - r_0)$: Integration

$\Rightarrow E = -1/2*k*(r - r_0)^2$



Quantum mechanics provides: $E_v = (v + 1/2)*h\nu$

Franck-Condon principle: Electrons motion is much faster than nuclear motion → "vertical transitions"

Transitions: $E_g(v_g = 0) \rightarrow E_e(v_e = x)$ for $v_e = 0$ "zero-phonon line"

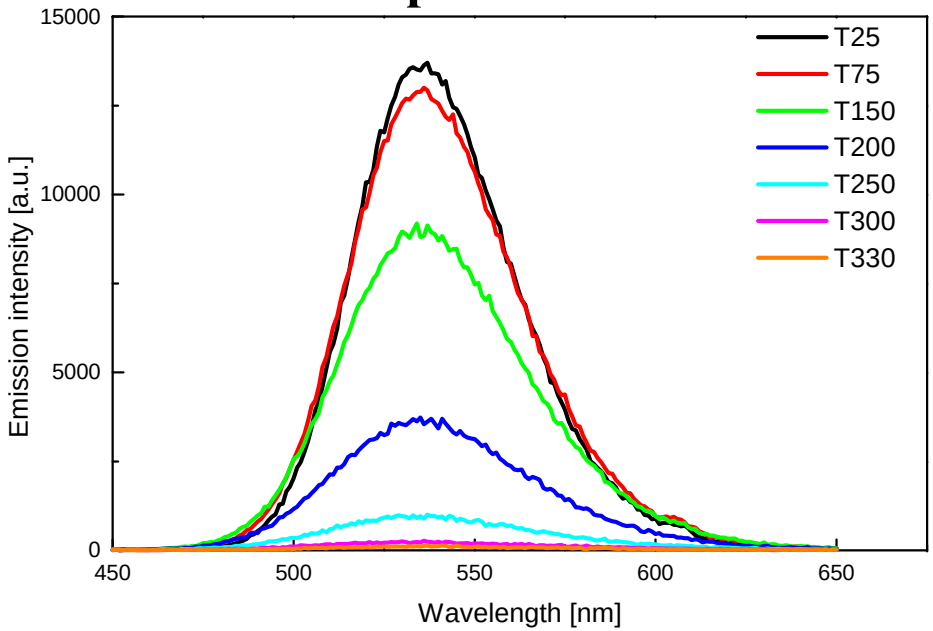
$r_{0g} = r_{0e} \Rightarrow$ narrow bands or lines ($4f \rightarrow 4f$ absorption lines)

$r_{0g} < r_{0e} \Rightarrow$ broad bands ($4f^n \rightarrow 4f^{n+1}L^{-1}$, $4f^n \rightarrow 4f^{n-1}5d$, $6s^2 \rightarrow 6s6p$)

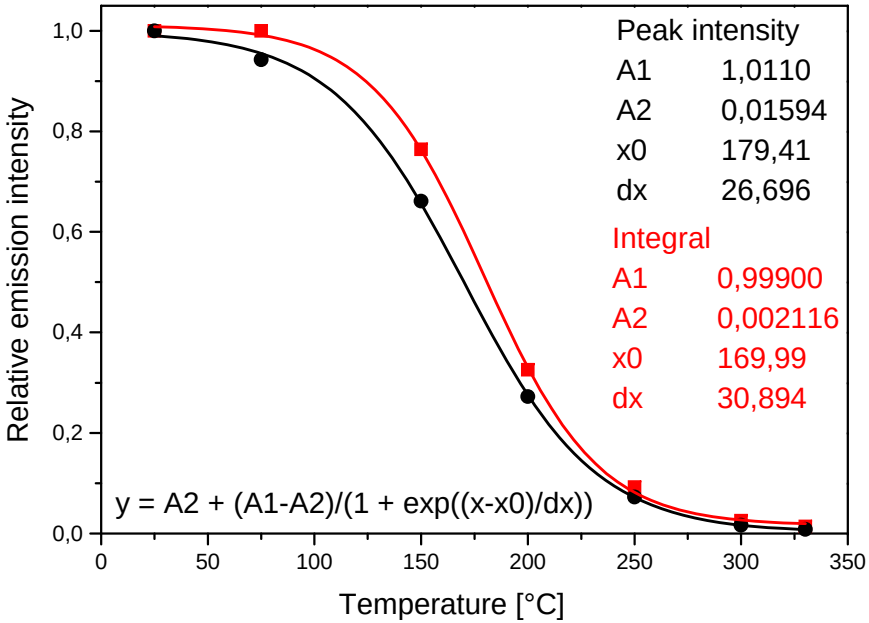
8.8 Thermal Quenching

Example: $SrGa_2S_4:Eu^{2+}$

Emission spectrum



Emission intensity

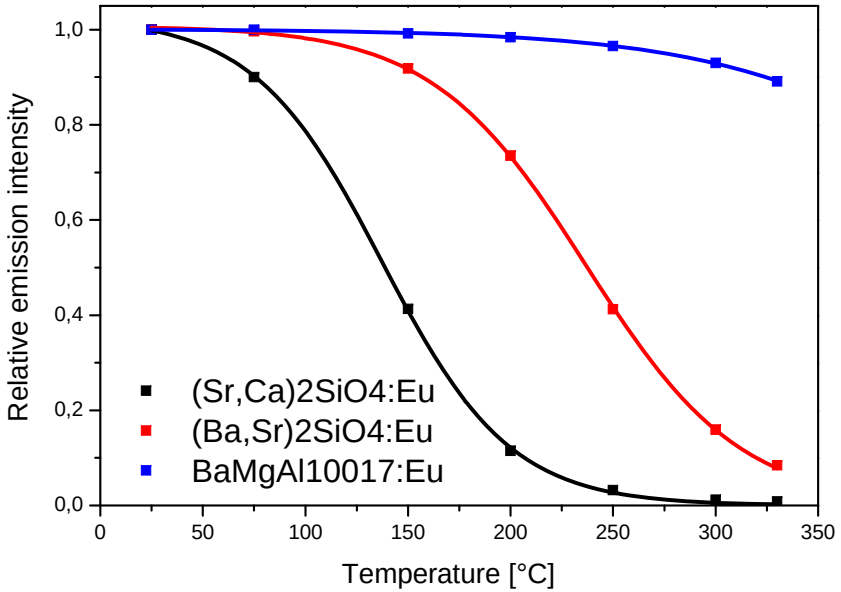


- **$T_{1/2}$ = Temperature at which the phosphor loses 50% of its initial emission intensity (here ~ 170 °C)**
- **$T_{1/2}$ depends on the extent of the activator-host lattice interaction**
- **In many industrially important phosphors the quantum yield starts increasing distinctly between 100 – 150 °C**

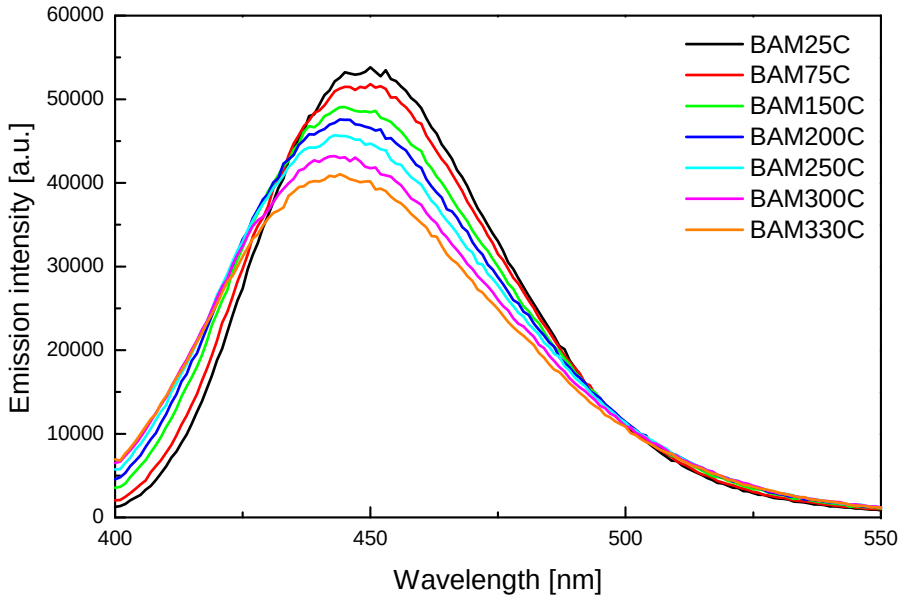
8.8 Thermal Quenching

Example: Other Eu^{2+} activated phosphors

Light yield as a function of the temperature



Spectral width of the emission band of $BaMgAl_{10}O_{17}$:Eu as a function of the temperature



Stokes shift $BaMgAl_{10}O_{17}:Eu < (Ba,Sr)_2SiO_4:Eu < (Sr,Ca)_2SiO_4:Eu$

Thermal quenching $BaMgAl_{10}O_{17}:Eu < (Ba,Sr)_2SiO_4:Eu < (Sr,Ca)_2SiO_4:Eu$

Blue shift due to thermal expansion of the host lattice and thus reduction in crystal field splitting

8.8 Thermal Quenching

Some Rules

- Increases with increasing energy separation of the ground and excited state

- Increases with increasing phonon frequencies (thus most organic compounds exhibit luminescence only at low temperatures)

- Increases with $\Delta r = r_e - r_g$

- Thermal quenching due to photoionization concerns luminescent materials, where the excited state is located close to the conduction band

8.9 Lifetime of the Excited State

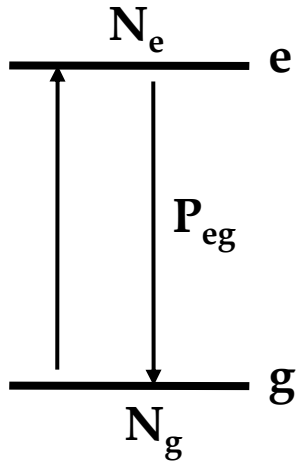
Description equal to 1st order kinetics (no energy transfer!)

$dN_e/dt = - N_e*P_{eg}$

$\Rightarrow dN_e/N_e = -P_{eg}*dt$: Integration

$\Rightarrow \ln(dN_e(t)/N_e(0)) = -P_{eg}*t$

$\Rightarrow N_e(t) = N_e(0)*\exp(-P_{eg}/\tau)$ with $\tau = 1/P_{eg}$

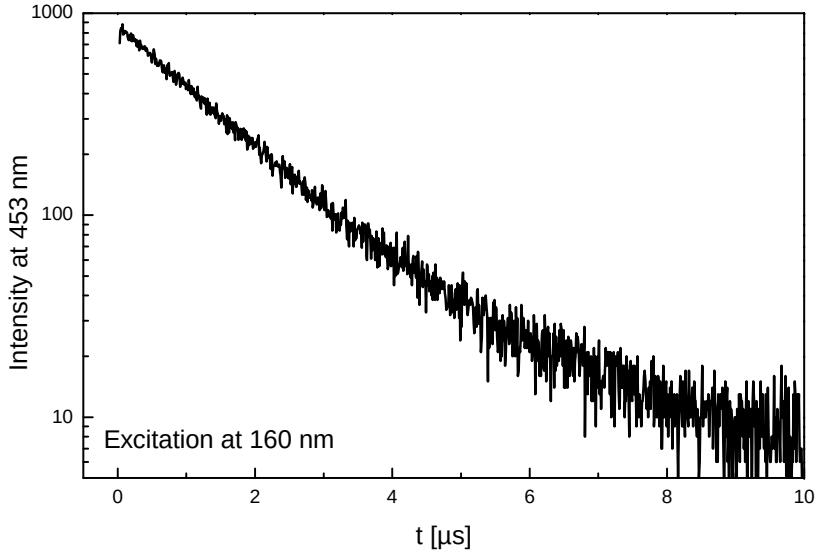


Transition	Time scale	Oscillator strength	Activators
"allowed"	~ 10^{-9} s	f ~ 0.1	Eu^{2+}, Ce^{3+}
"weak"	~ 10^{-6} s	f ~ 0.001	Pr^{3+}, Nd^{3+}
"forbidden"	~ 10^{-3} s	f ~ 10^{-5}	Eu^{3+}, Mn^{2+}

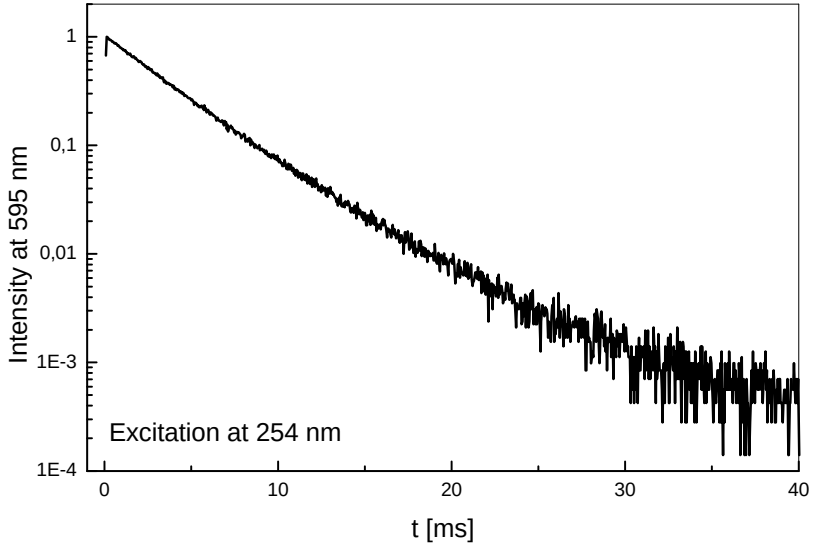
8.9 Lifetime of the Excited State

Typical decay curves

$BaMgAl_{10}O_{17}:Eu^{2+}$ (τ = 1 µs)



$(Y,Gd)BO_3:Eu^{3+}$ (τ = 3.5 ms)



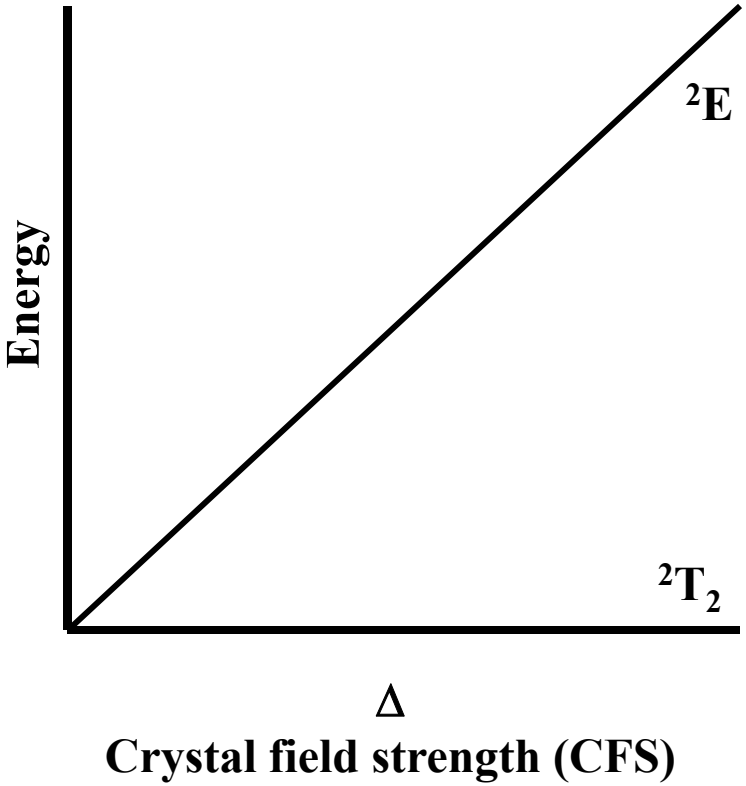
Mono-exponential decay ⇒ No energy transfer e.g. to impurities such as Fe^{3+} or Cr^{3+}

Deviation from mono-exponential decay ⇒ quenching, energy transfer, afterglow, ….

8.10 Luminescence of Transition Metal Ions

Absorption processes of d^n-ions → Tanabe-Sugano diagram

Energy level diagram of a d^1-ion (Ti^{3+}, V^{4+}, Cr^{5+}, Mn^{6+}): CFS ⇒ $^2D_{3/2}$ → $^2T_2$ + ^2E



Ion	Configuration	Example
Ti^{3+}	$[Ar]d^1$	Al_2O_3:Ti (Sapphire)
Cr^{3+}	$[Ar]d^3$	Al_2O_3:Cr (Ruby)
Mn^{4+}	$[Ar]d^3$	$Mg_4GeO_{5.5}F$:Mn
Mn^{2+}	$[Ar]d^5$	Zn_2SiO_4:Mn (Willemite)
Fe^{3+}	$[Ar]d^5$	$LiAlO_2$:Fe

d-d transitions are parity-forbidden

⇒ low absorption coefficient

⇒ high concentration needed

8.10 Luminescence of Transition Metal Ions

Absorption in glasses, laser crystals and phosphors

Ion	Configuration	Colour	Pigment	Structure type
Ti^{3+}	d^1	violet, brown		
V^{3+}	d^2	green		
V^{4+}	d^1	green, blue	$(Zr,V)SiO_4$	Zircon
Cr^{3+}	d^3	green, yellow	Cr_2O_3	Corundum
Mn^{2+}	d^5	light pink	MnO	NaCl
Mn^{3+}	d^4	violet	Mn_2O_3	Corundum
Mn^{4+}	d^3	red, brown	MnO_2	Rutile
Fe^{3+}	d^5	yellow, brown	Fe_2O_3	Corundum
Fe^{2+}	d^6	blue, green	$Fe(C_2O_4)\cdot 2H_2O$	
Co^{2+}	d^7	blue, violet	$CoAl_2O_4$	Spinel
Ni^{2+}	d^8	green	NiO	NaCl
Cu^{2+}	d^9	blue, green	CuO	

8.10 Luminescence of Transition Metal Ions

Absorption processes of transition metal ions with d^0-configuration

Examples: VO_4^{3-}, NbO_4^{3-}, TaO_4^{3-}, CrO_4^{2-}, MoO_4^{2-}, WO_4^{2-} , MnO_4^-

Absorption due to ligand to metal charge-transfer (LMCT)

$O^{2-} \rightarrow Me^{n+}$ or p(non-bonding) $\rightarrow$ d(e_g: anti-bonding)
Bond is weakened $\Rightarrow$ $\Delta R >> 0$ $\Rightarrow$ broad absorption band

Phosphor	Absorption [cm^{-1}]	CN	Polyhedron
$CaWO_4$	40000	4	Tetrahedron
Ca_3WO_6	35000	6	Octahedron

$\Rightarrow$ Position of the CT state decreases with increasing CN and effective charge of the metal center

8.11 Luminescence of Ions with s^2-Configuration

Examples: Ga^+, In^+, Tl^+, Ge^{2+}, Sn^{2+}, Pb^{2+}, As^{3+}, Sb^{3+}, Bi^{3+}

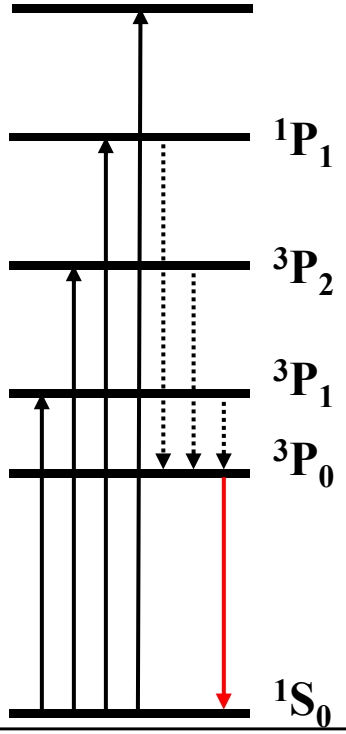
Electron configuration of s^2-ions

Ga^+, Ge^{2+} and As^{3+}: **$[Ar]3d^{10}4s^2$**

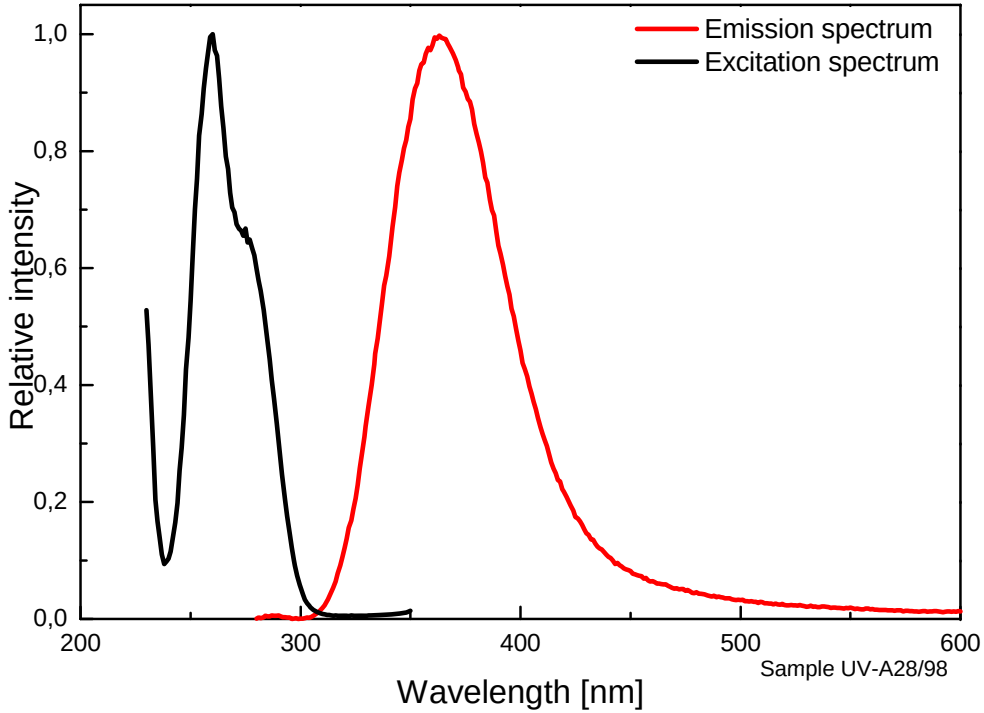
In^+, Sn^{2+} and Sb^{3+}: **$[Kr]4d^{10}5s^2$**

Tl^+, Pb^{2+} and Bi^{3+}: **$[Xe]4f^{14}5d^{10}6s^2$**

Energy level diagram of s^2-ions



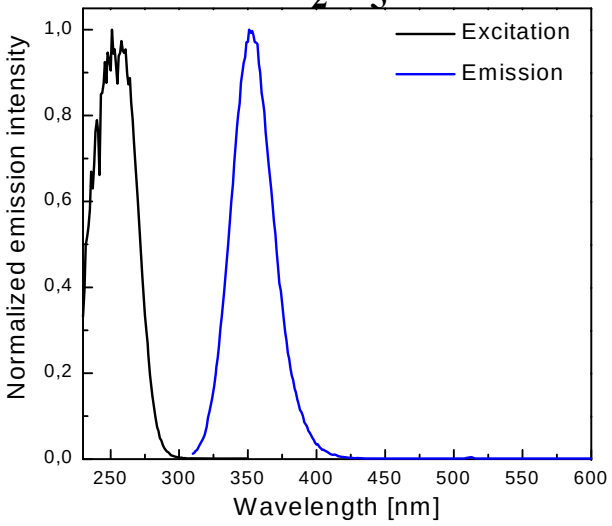
Excitation and emission spectra of $BaYB_9O_{16}:Sb^{3+}$



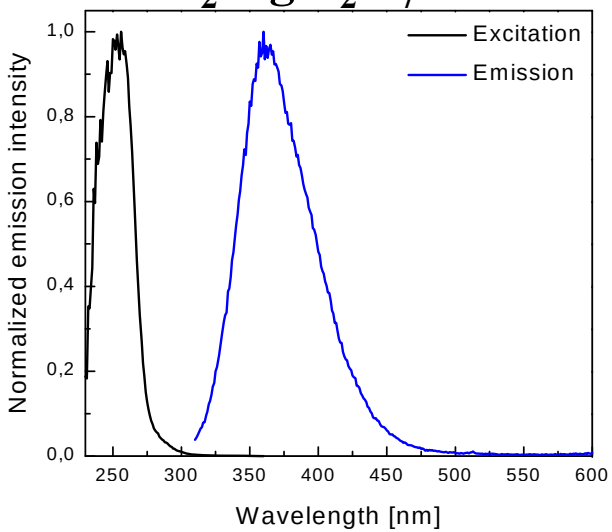
8.11 Luminescence of Ions with s^2-Configuration

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

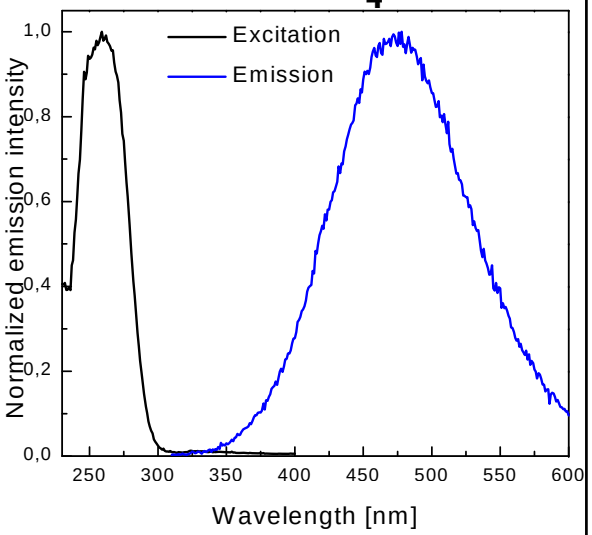
$BaSi_2O_5$:Pb



$Sr_2MgSi_2O_7$:Pb



$SrLaBO_4$:Pb

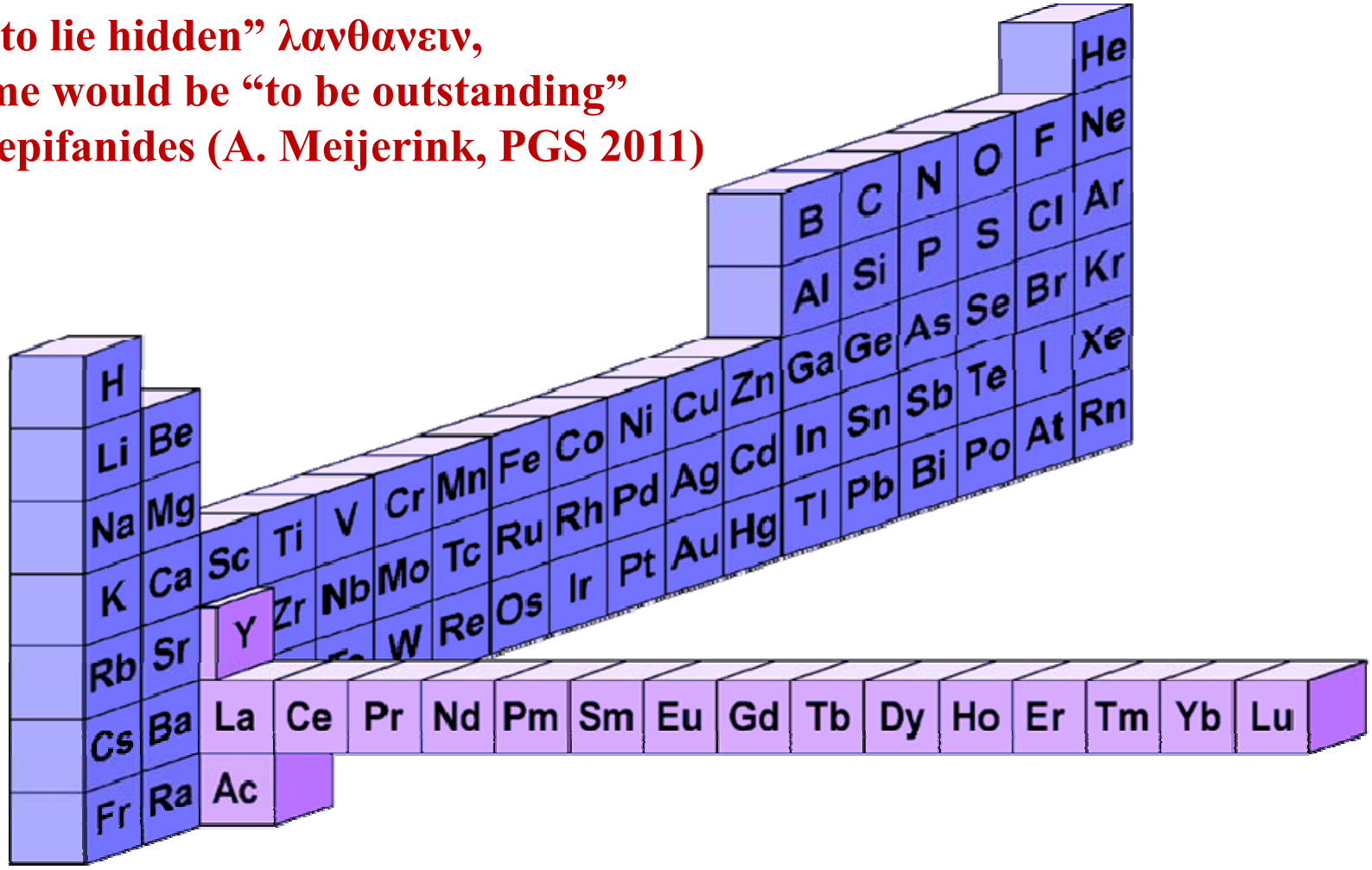


Phosphor	Structure type	Stokes shift [cm^{-1}]	Half width [cm^{-1}]	QA [%]
$BaSi_2O_5$:Pb	Sanbornite	10600	2700	90
$Sr_2MgSi_2O_7$:Pb	Akermanite	12000	4300	75
$SrLaBO_4$:Pb		17700	5300	65

8.12 Luminescence of Rare Earth Ions

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

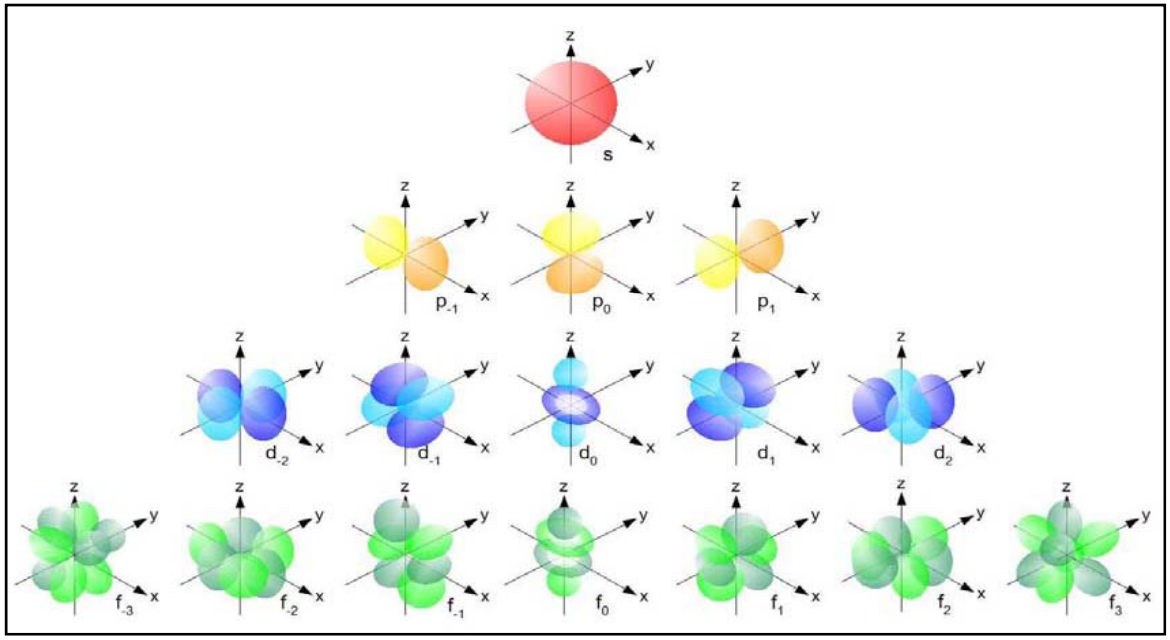
Instead of “to lie hidden” λανθανειν,
a better name would be “to be outstanding”
επιφανης – epifanides (A. Meijerink, PGS 2011)



8.12 Luminescence of Rare Earth Ions

Properties of electronic orbitals

Shape and orientation



Orbital	Parity	l	m_l
s	g	0	0
p	u	1	-1, 0, 1
d	g	2	-2, ..., 2
f	u	3	-3, ..., 3

8.12 Luminescence of Rare Earth Ions

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 m_l -3 -2 -1 0 1 2 3 | -2 -1 0 1 2 | 0 | -1 0 1

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

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

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

Spectroscopic Terms

$^{2S+1}L_J$

8.12 Luminescence of Rare Earth Ions

History of distangling the energy level structure

1908 Becquerel

Sharp lines in optical spectra of lanthanide ions

1937 Van Vleck

The Puzzle of Rare-Earth Spectra in Solids

1960s Judd, Wybourne, Dieke, Carnall

Theory for energy level structure and transition probabilities of 4f-4f transitions

8.12 Luminescence of Rare Earth Ions

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

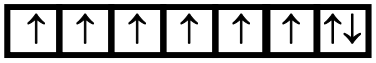
Partly filled 4f-shell results in multiple electron configurations

Example: Tb^{3+} [Xe]$4f^8$ → 8 electrons in 7 f-orbitals: 3003 different arrangements!

Free ion energy levels due to:

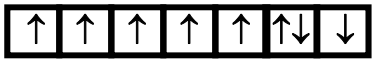
1. **Electrostatic interactions (comparable to $3d^n$ ions)**
2. **Spin-orbit coupling (larger than for $3d^n$ ions)**
3. **Crystal field splitting (smaller than for $3d^n$ ions)**

Ground state m_l = -3 -2 -1 0 1 2 3 $^7F_6$



4f

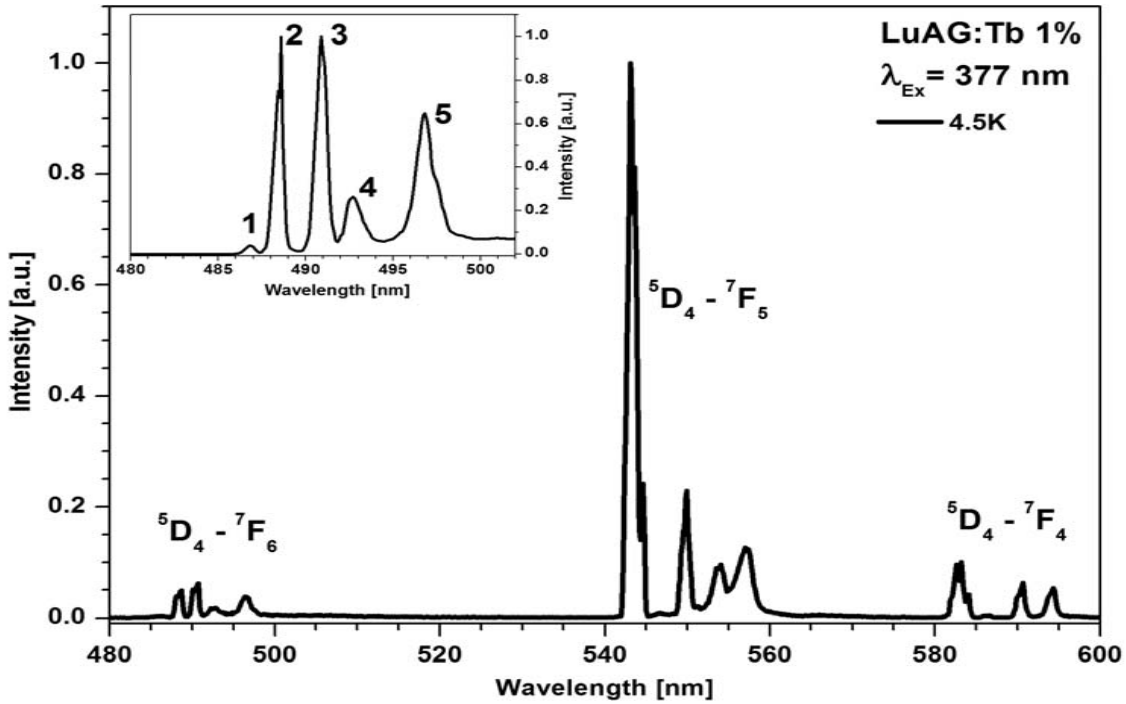
1st excited state m_l = -3 -2 -1 0 1 2 3 $^5D_4$

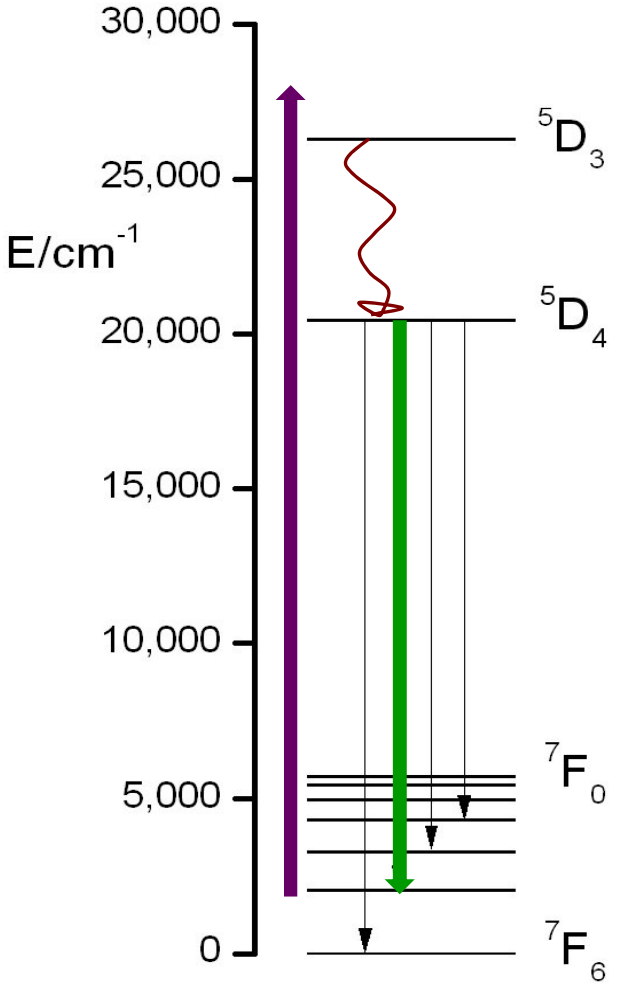


4f

8.12 Luminescence of Rare Earth Ions

Typical emission spectrum of Tb^{3+} (Example: $Lu_3Al_5O_{12}$:Tb)



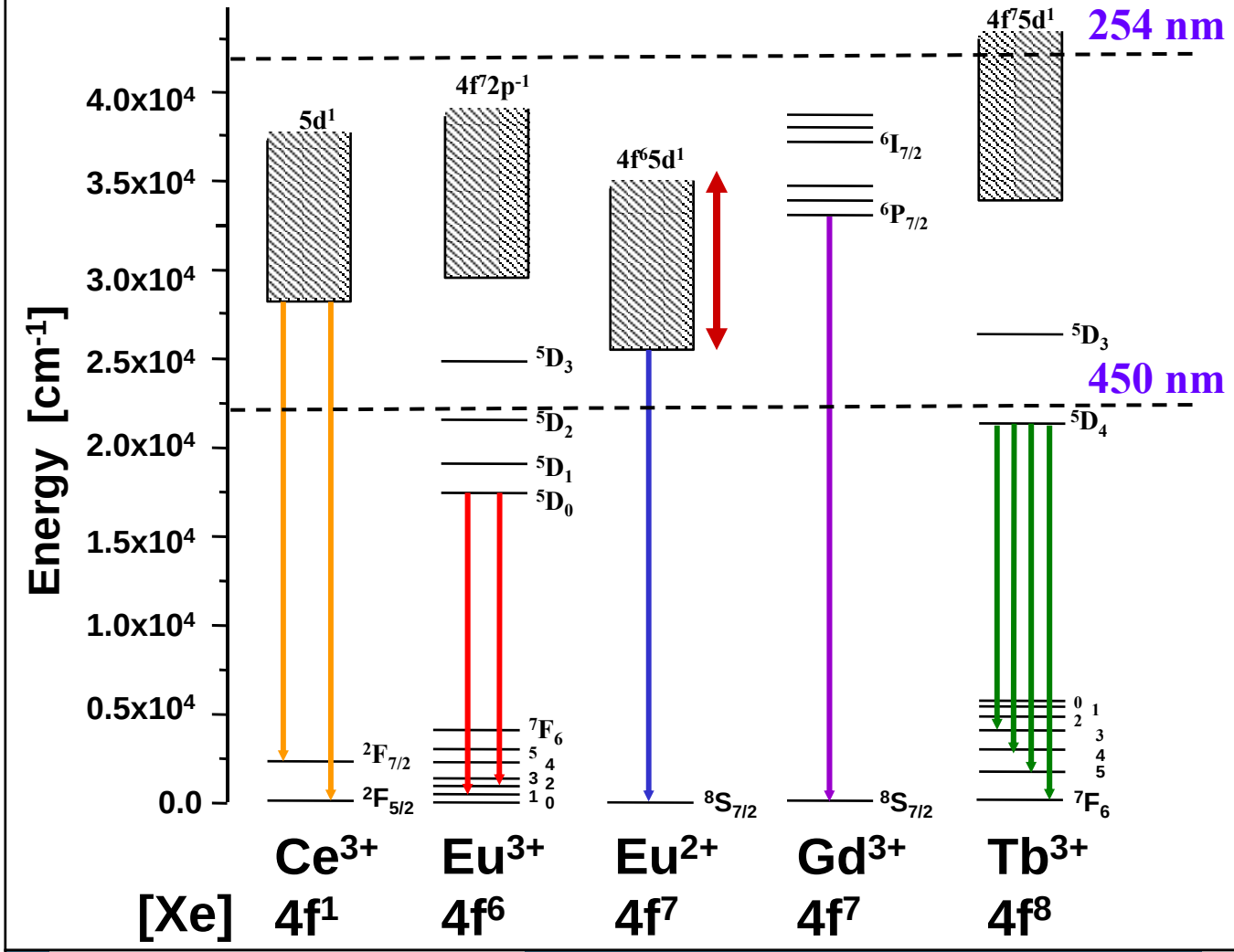


Characteristic luminescence of lanthanides

- 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

8.12 Luminescence of Rare Earth Ions

Simplified energy level diagram of selected Ln^{3+} 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+}

8.12 Luminescence of Rare Earth Ions

1. Electrostatic interactions

Shielding due to inner electrons described by the so-called Slater parameters (comparable 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 (ion charge density)

Therefore splitting between different terms depends on

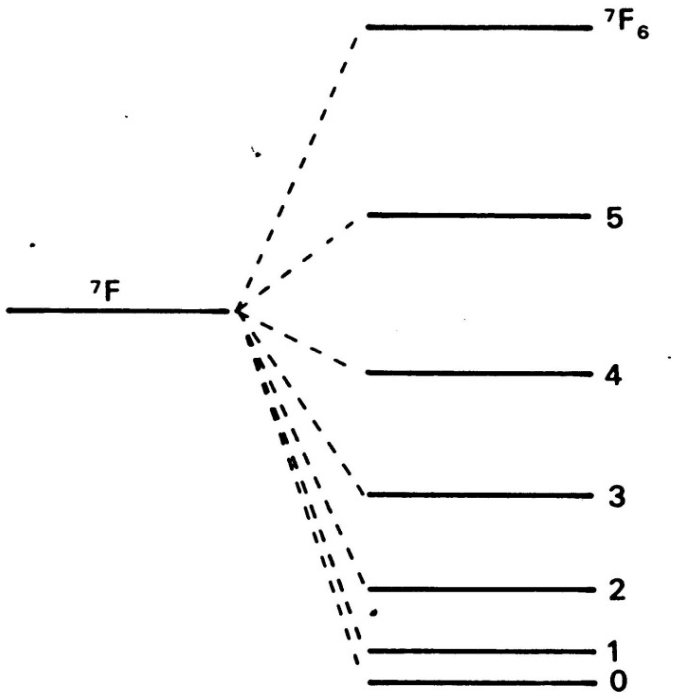
- **Oxidation state**
- **Nucleus charge**
- **Charge flow back from ligands (polarizibility of surrounding anions)**

8.12 Luminescence of Rare Earth Ions

2. Spin-orbit coupling

Spin-orbit coupling constant ζ increases throughout 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: $^7F_{6,5,4,3,2,1,0}$

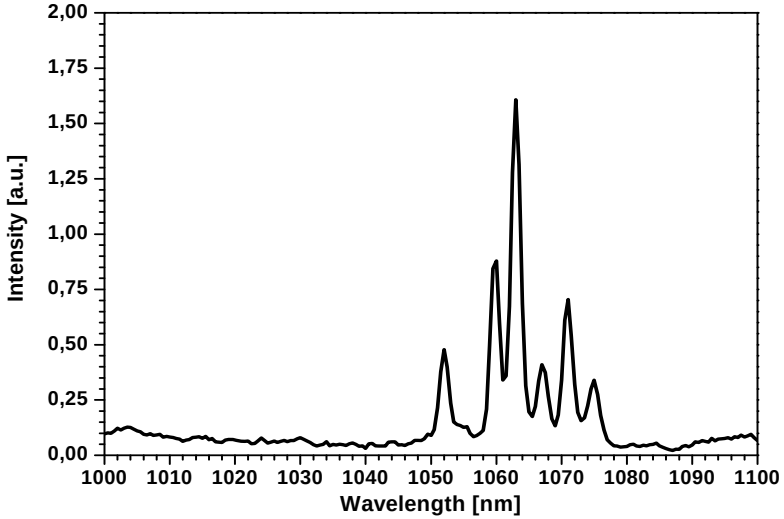
Excited state: $^5D_{4,3,2,1,0}$

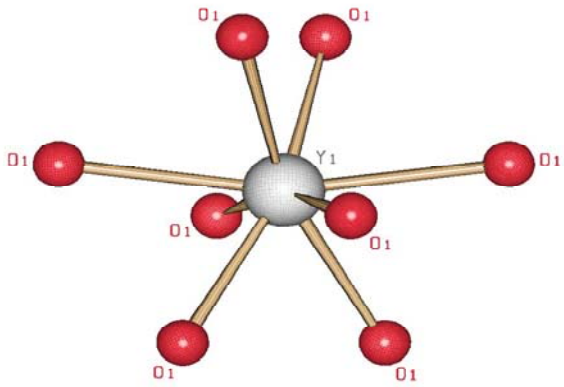
8.12 Luminescence of Rare Earth Ions

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

$Lu_3Al_5O_{12}:Nd^{3+}$
$^4F_{3/2} - {}^4I_{11/2}$
$\Delta E = 203\ cm^{-1}$
six levels without external magnetic field





Dodecahedral coordination

Extra fitting parameters *Bkq* to graphically fit experimentally observed levels:

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

8.12 Luminescence of Rare Earth Ions

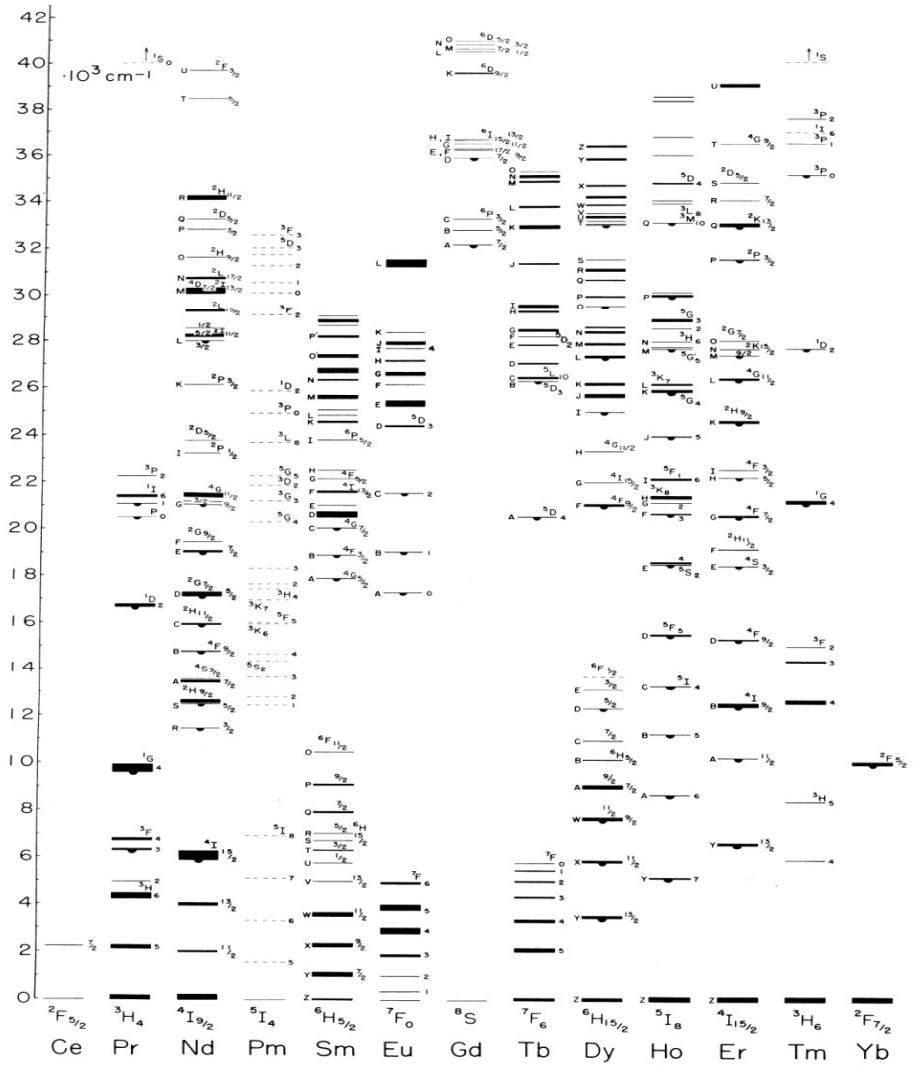
In summary: RE ions exhibit a great number of energy levels $^{2S+1}L_J$

	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	4	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 and Wybourne (theory): "Dieke diagram" and the "Blue book"

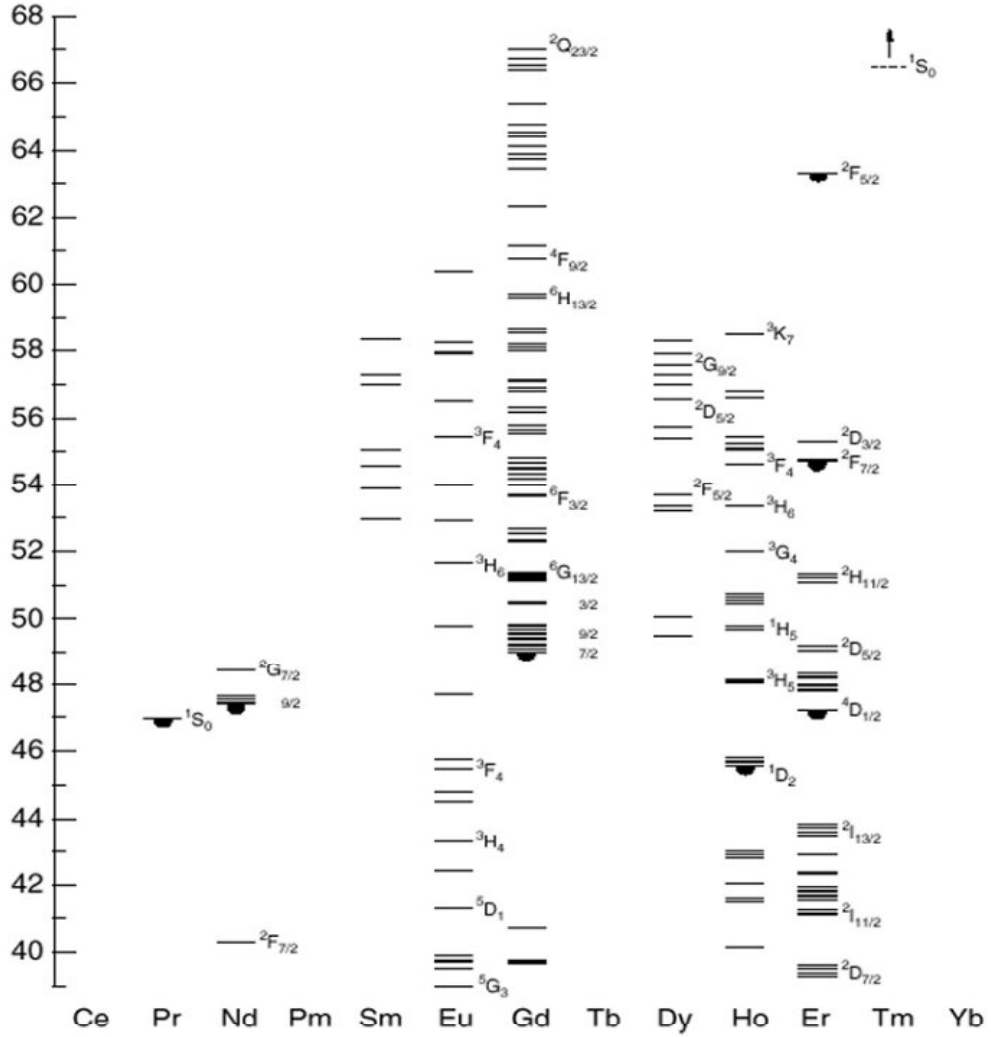
8.12 Luminescence of Rare Earth Ions

Dieke diagram (1968): Energy levels of trivalent RE ions



8.12 Luminescence of Rare Earth Ions

Extended Dieke diagram (2005): Energy levels of trivalent RE ions up to the VUV



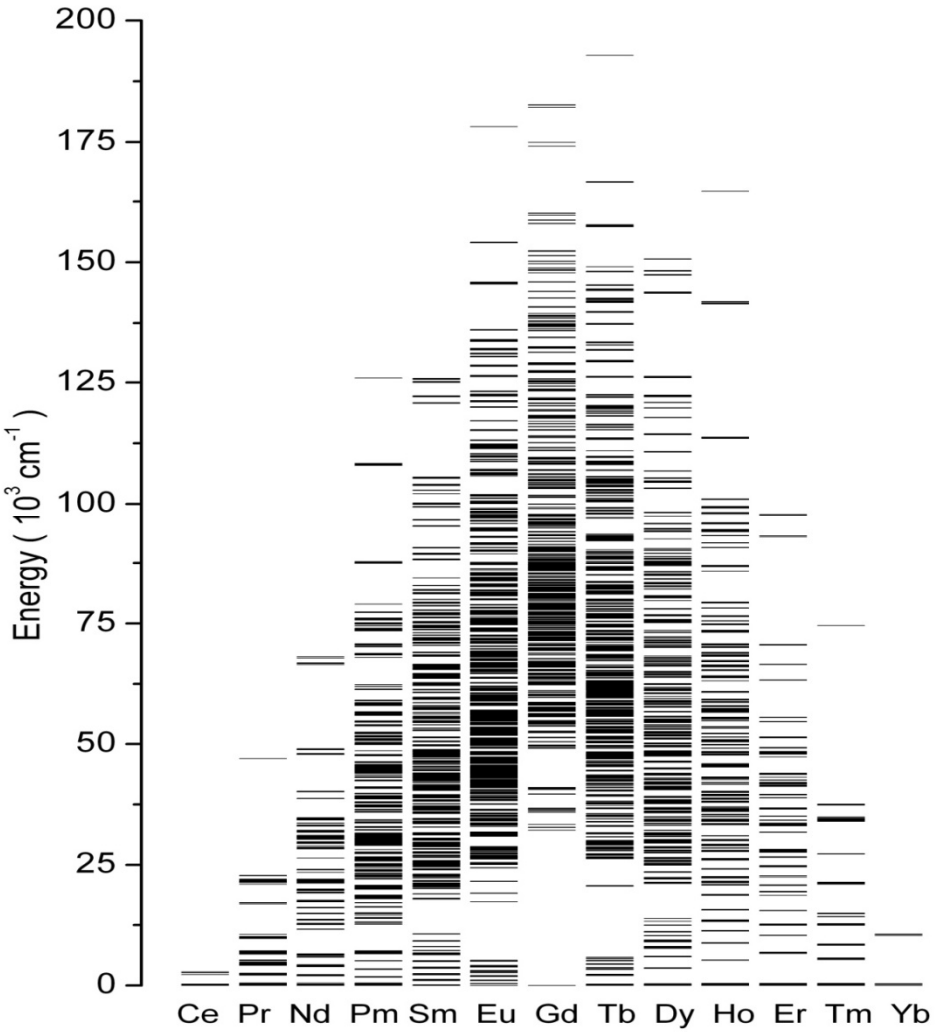
P.S. Peijzel, A. Meijerink, R.T. Wegh et al, J. Solid State Chem. 178 (2005) 448

8.12 Luminescence of Rare Earth Ions

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 nucleus charge



8.12 Luminescence of Rare Earth Ions

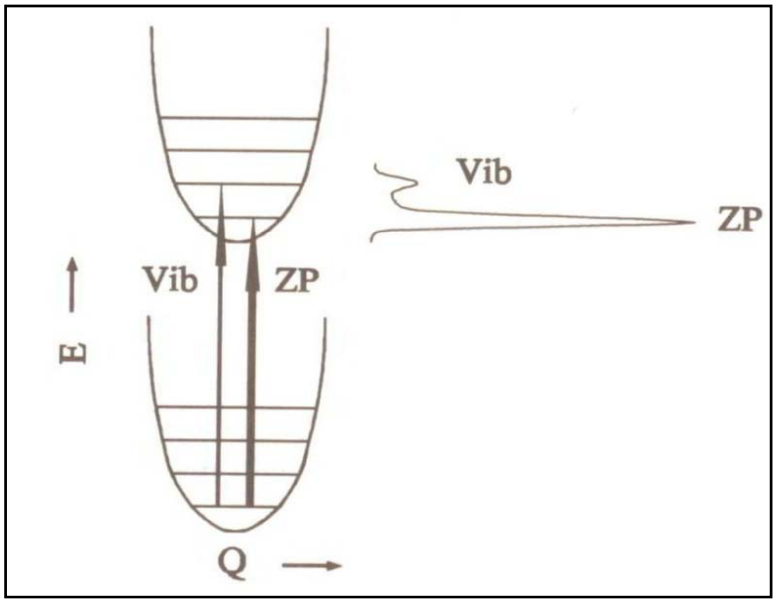
Characteristic optical properties

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

2) Little influence of environment on energy level scheme

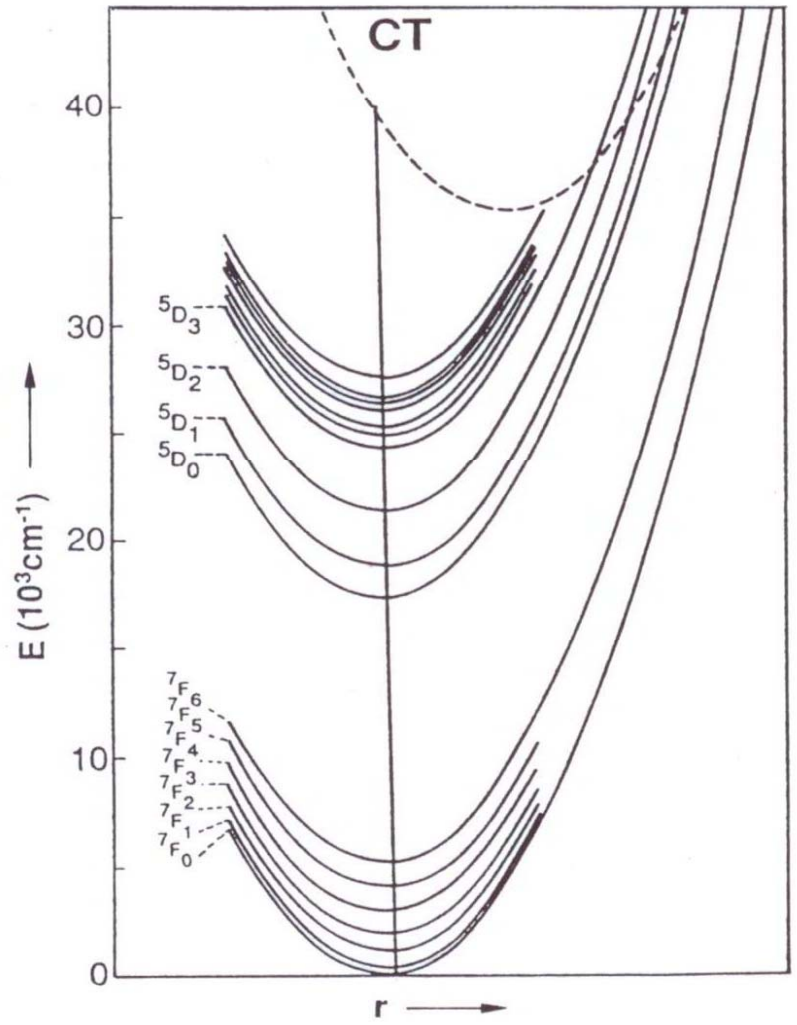
3) Parity forbidden transitions (~ms life time, f ~10^{-5})

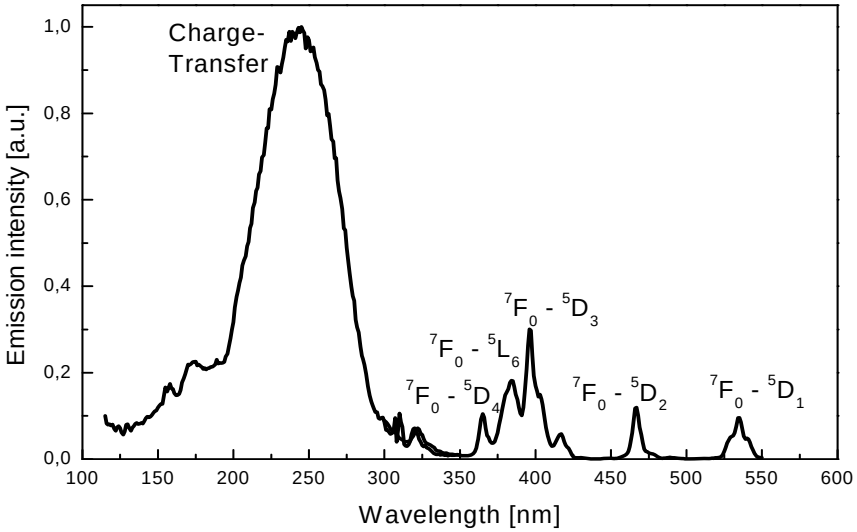
Origin: Shielding of $4f^n$ electrons
by outer filled 5s and 5p shells
→ no shift of excited state parabola
and strong zero-phonon lines (ZPL)

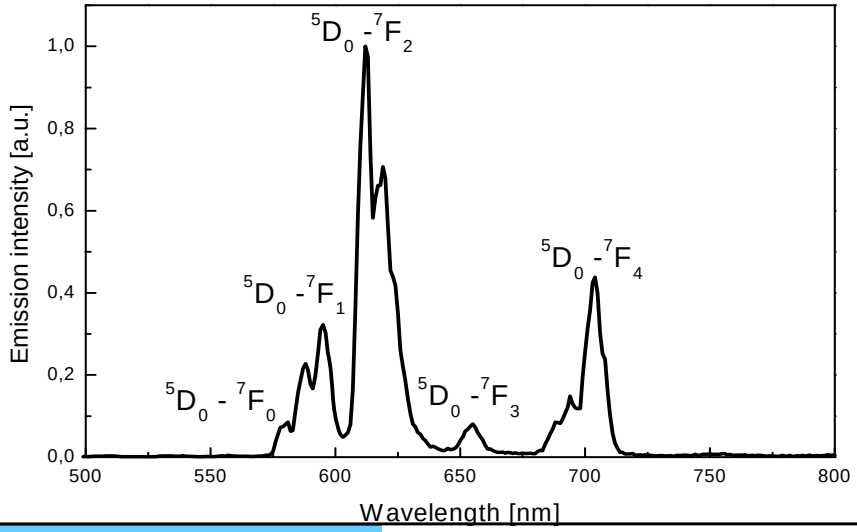


8.12 Luminescence of Rare Earth Ions

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

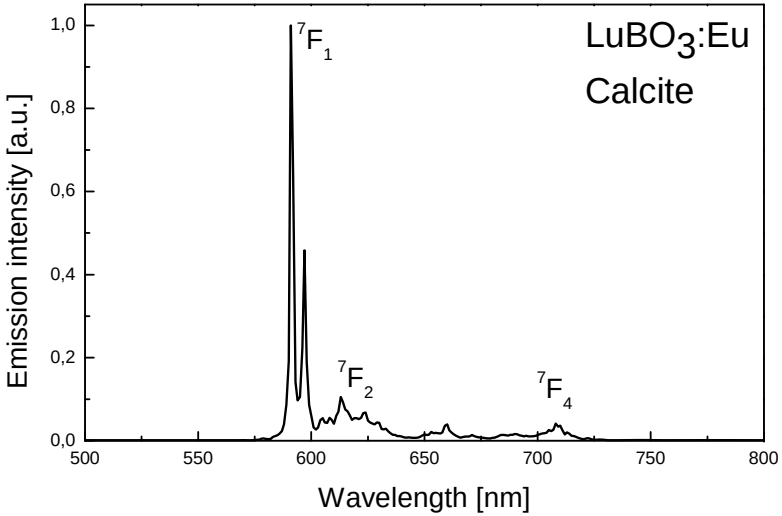


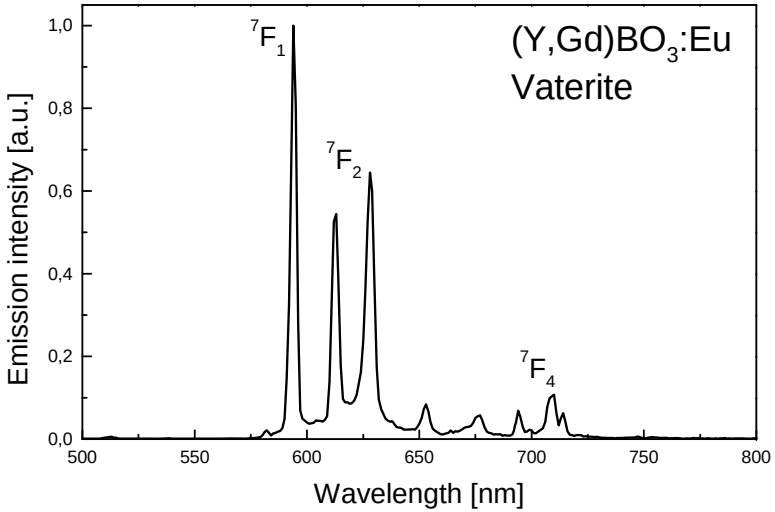


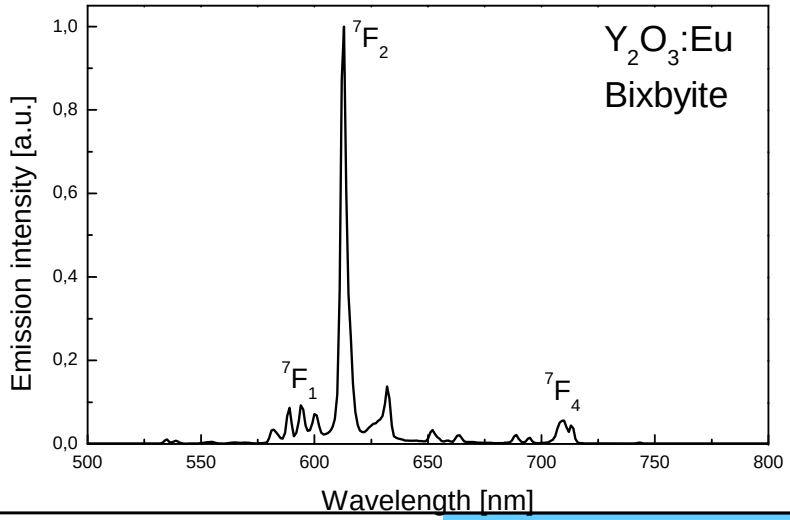


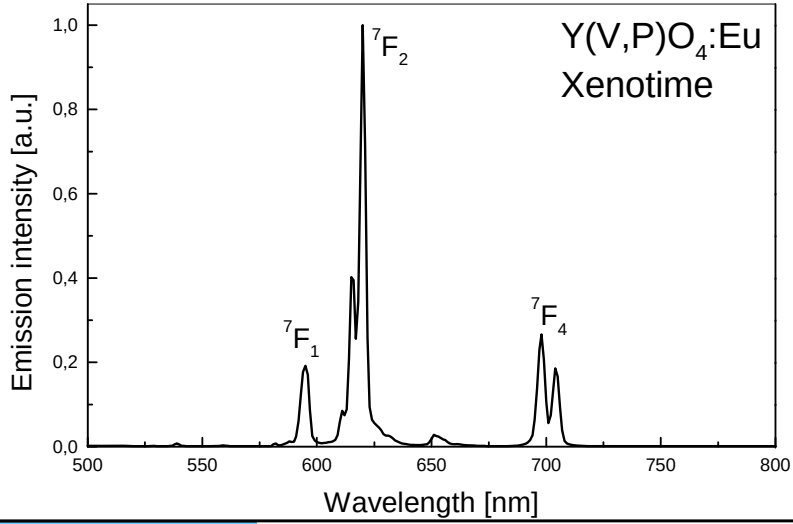
8.12 Luminescence of Rare Earth Ions

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



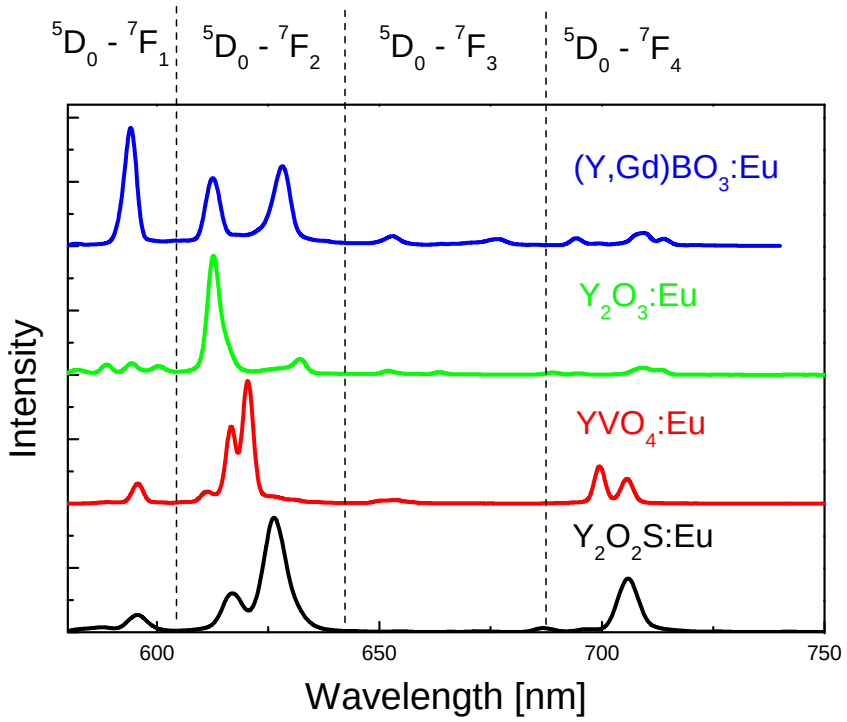






8.12 Luminescence of Rare Earth Ions

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

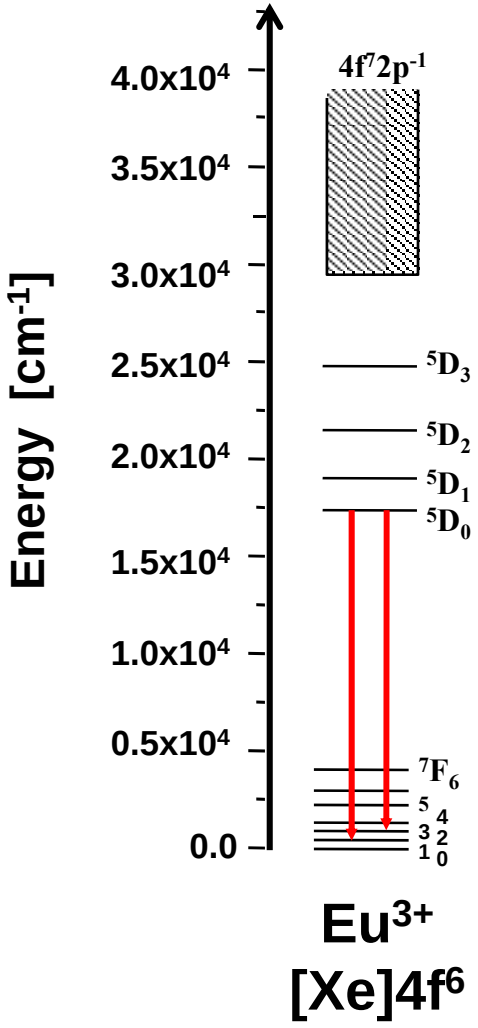


Phosphor	CIE(1931) colour point x	y
(Y,Gd)BO_3:Eu	0.640	0.360
Y_2O_3:Eu	0.641	0.344
YVO_4:Eu	0.645	0.343
Y_2O_2S:Eu	0.650	0.342

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

8.12 Luminescence of Rare Earth Ions

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



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

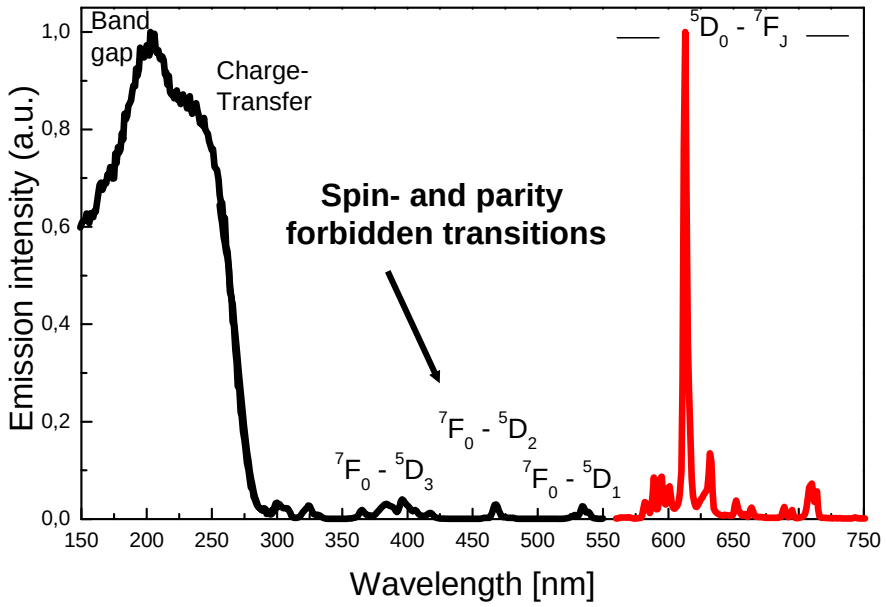
a) Inversion symmetry (S_6, D_{3d})
Magnetic dipole transitions, e.g. $^5D_0$ - $^7F_1$
$\Delta J = 0, \pm 1$ ($J = 0 \rightarrow J = 0$ forbidden)
$MeBO_3$:Eu (Calcite, Vaterite)
$\tau \sim 8$ - 16 ms

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

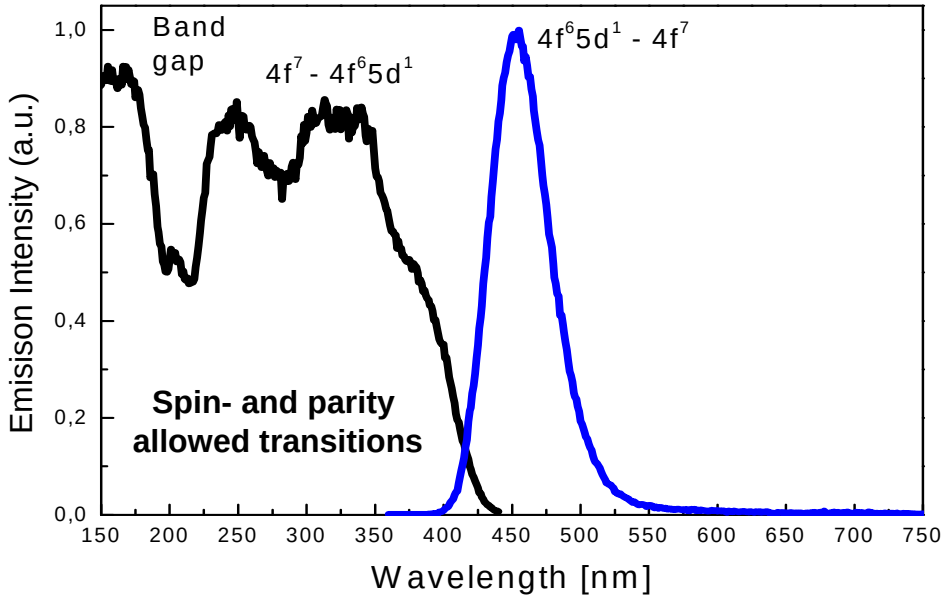
8.12 Luminescence of Rare Earth Ions

Excitation and emission spectra of Eu^{3+} and Eu^{2+} activated phosphors

$Y_2O_3:Eu^{3+}$



$BaMgAl_{10}O_{17}:Eu^{2+}$

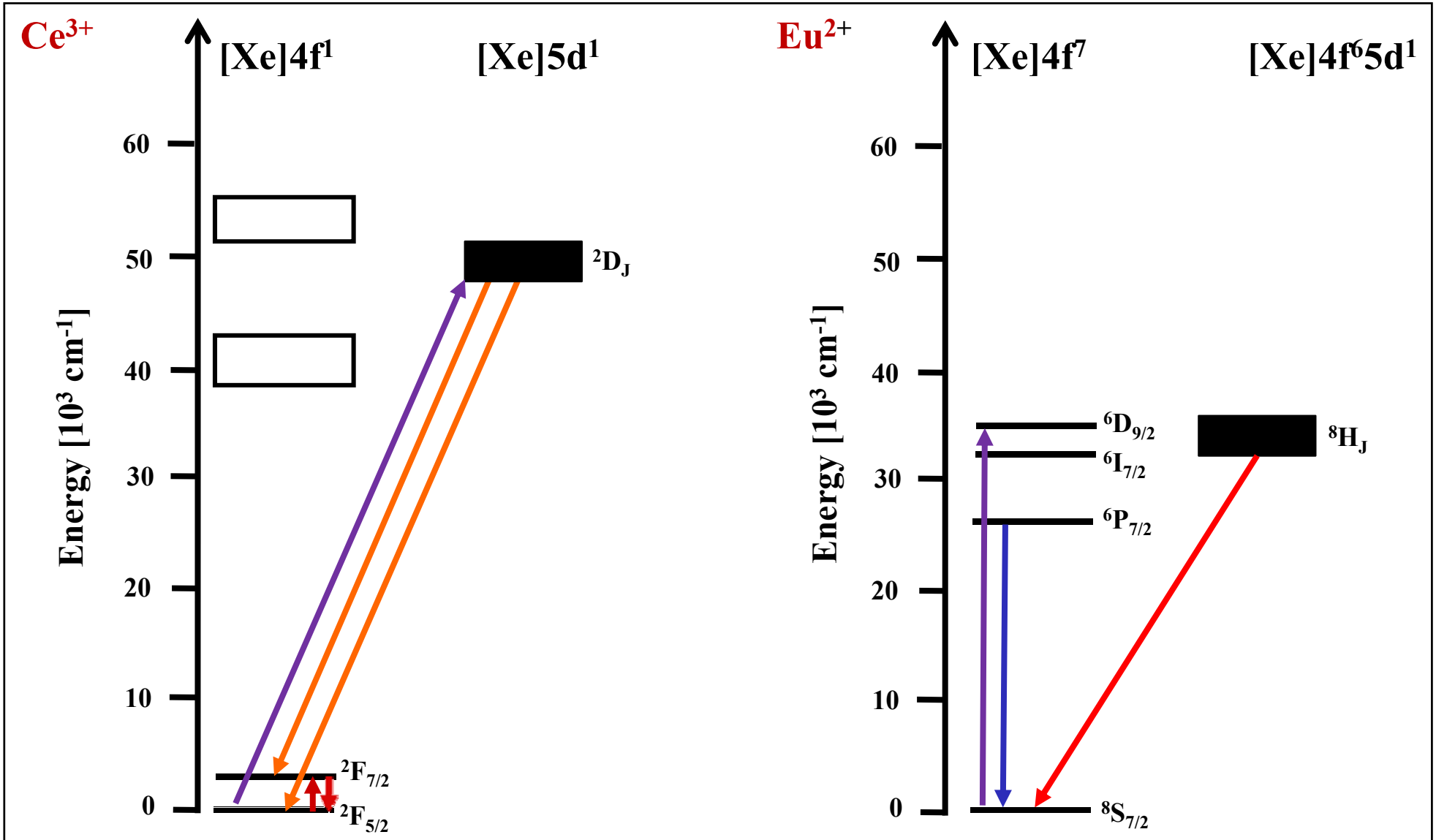


$Eu^{3+} \rightarrow (Eu^{3+})^{**}$	CT	$Eu^{2+} \rightarrow (Eu^{2+})^{**}$	4f-5d
$(Eu^{3+})^{**} \rightarrow (Eu^{3+})^{*}$	Relaxation	$(Eu^{2+})^{**} \rightarrow (Eu^{2+})^{*}$	Relaxation
$(Eu^{3+})^{*} \rightarrow Eu^{3+}$	4f-4f	$(Eu^{2+})^{*} \rightarrow Eu^{2+}$	5d-4f

Strong CT absorption band (broad)
Weak 4f-4f absorption lines (narrow)

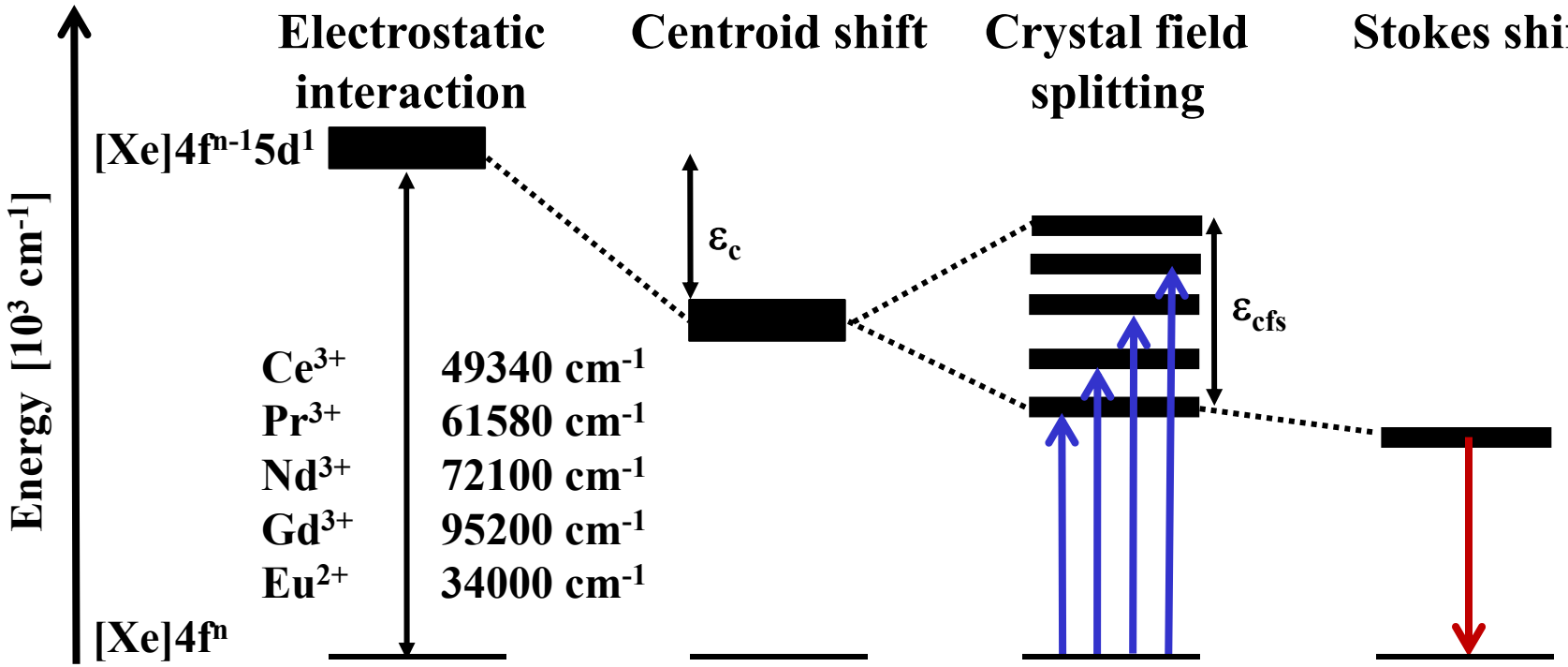
Strong 4f-5d absorption bands (broad)

8.12 Luminescence of Rare Earth Ions



8.12 Luminescence of Rare Earth Ions

Energy gap between the $[Xe]4f^n$ and $[Xe]4f^{n-1}5d^1$ states



ε_c: Centroid energy proportional to the spectroscopic polarizability α_{sp} (3000 – 20000 cm^{-1})

ε_{cfs}: Crystal field splitting (< 23000 cm^{-1})

8.12 Luminescence of Rare Earth Ions

Centroid shift ~ electron density between activator and ligands

Polarizability of the anions

- **selenides > sulfides > nitrides > oxides > fluorides**

Charge density of the surrounding anions

- **Type of network former:**

oxides	aluminates	silicates	borates	phosphates	sulfates
O^{2-}	AlO_4^{5-}	SiO_4^{4-}	BO_3^{3-}	PO_4^{3-}	SO_4^{2-}

- **Degree of networking**

neso-silicate	soro-silicate	cyclo-silicate	phyllo-silicate
$[SiO_4]^{4-}$	$[Si_2O_7]^{6-}$	$[Si_3O_9]^{6-}$	$[Si_4O_{10}]^{4-}$
garnet			
zircon			
olivine			

8.12 Luminescence of Rare Earth Ions

Crystal field splitting

Crystal field theory ⇒ ionic interaction between metal center and point charges

Energy splitting of the d-orbitals depends on:

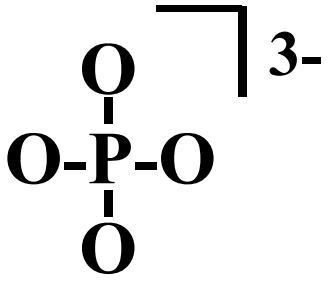
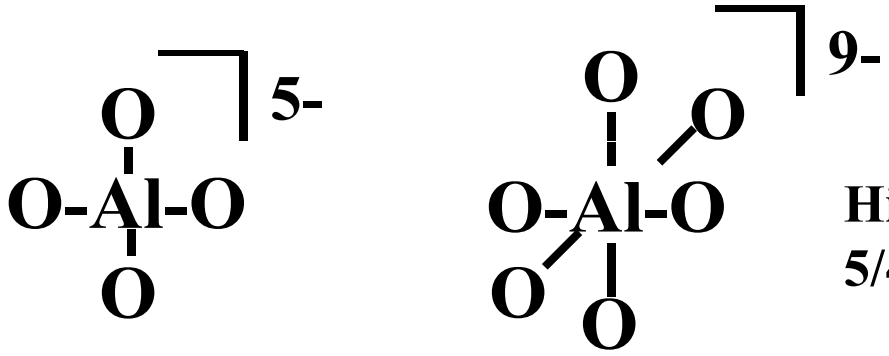
- **Anionic charge / anionic radius (spectrochemical series)**
  $I^- < Br^- < Cl^- < S^{2-} < F^- < O^{2-} < N^{3-} < C^{4-}$

- **Symmetry (coordination number and symmetry)**
  octahedral > cubic, dodecahedral, square-antiprismatic > tetrahedral

- **Metal-ligand distance (strong distance dependence)**
  $D = 35Ze/4R^5$ **R = Cation-anion distance**
  Z = Valence of the anion
  e = Electron charge

8.12 Luminescence of Rare Earth Ions

Covalent character of ionic bonds

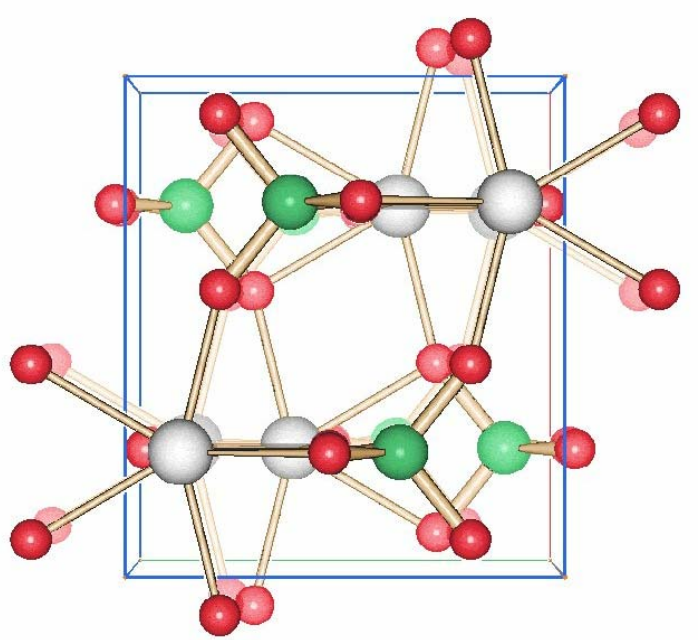
Host lattice	Cation	Type of network former	
YPO_4	Y^{3+}		Low charge density $3/4^-$ per oxygen
		tetrahedral PO_4^{3-}	
$Y_3Al_5O_{12}$	Y^{3+}		High charge density $5/4^-$ or $9/4^-$ per oxygen
		tetrahedral AlO_4^{5-} + octahedral AlO_6^{9-}	

P^{5+} attracts more charge density of the O^{2-} anions than Al^{3+}

8.12 Luminescence of Rare Earth Ions

Electron density on the anions

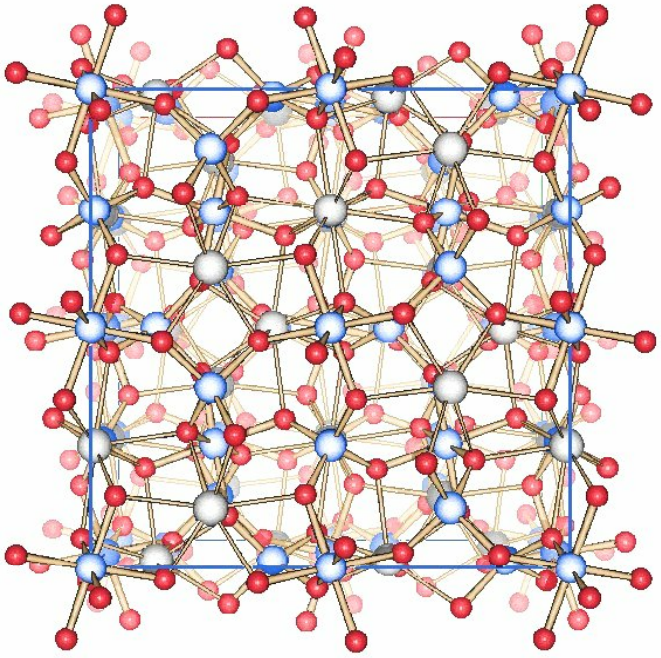
YPO_4



4 x O(1)	7.248
4 x O(2)	7.193

Low charge density on oxygen

$Y_3Al_5O_{12}$

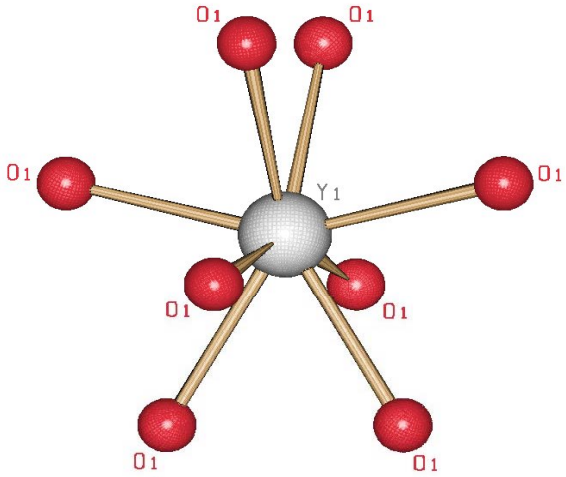


4 x O(1)	7.528
4 x O(2)	7.504

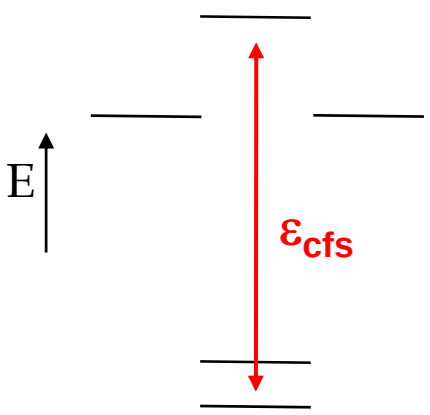
High charge density on oxygen

8.12 Luminescence of Rare Earth Ions

Luminescence of YPO_4:Ce

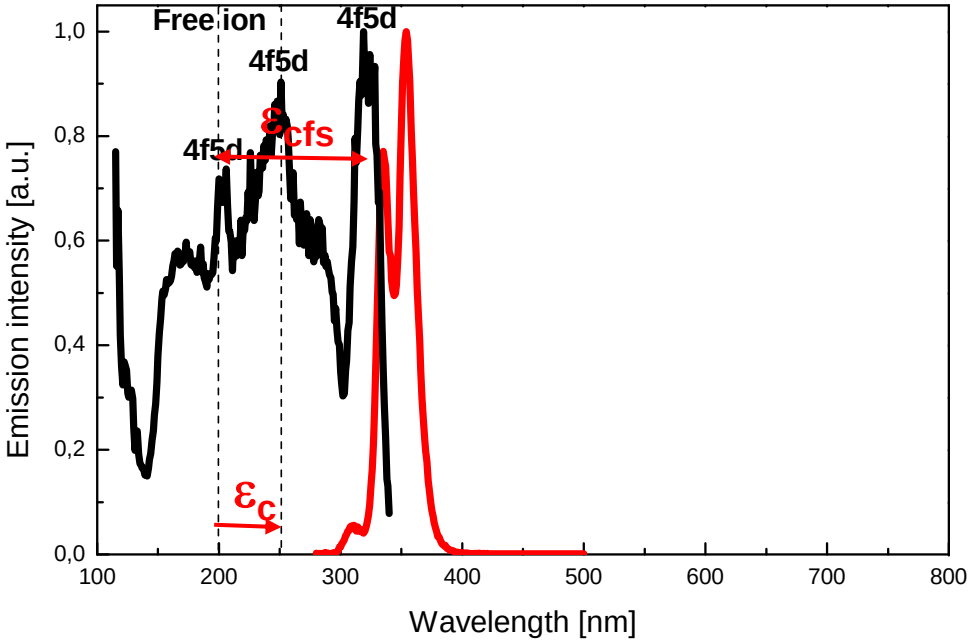


Distorted dodecahedral



Y-O distances

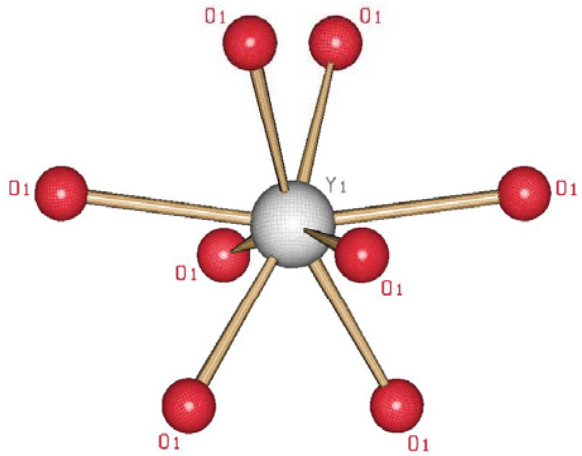
4x 2.24 Å
4x 2.24 Å
1



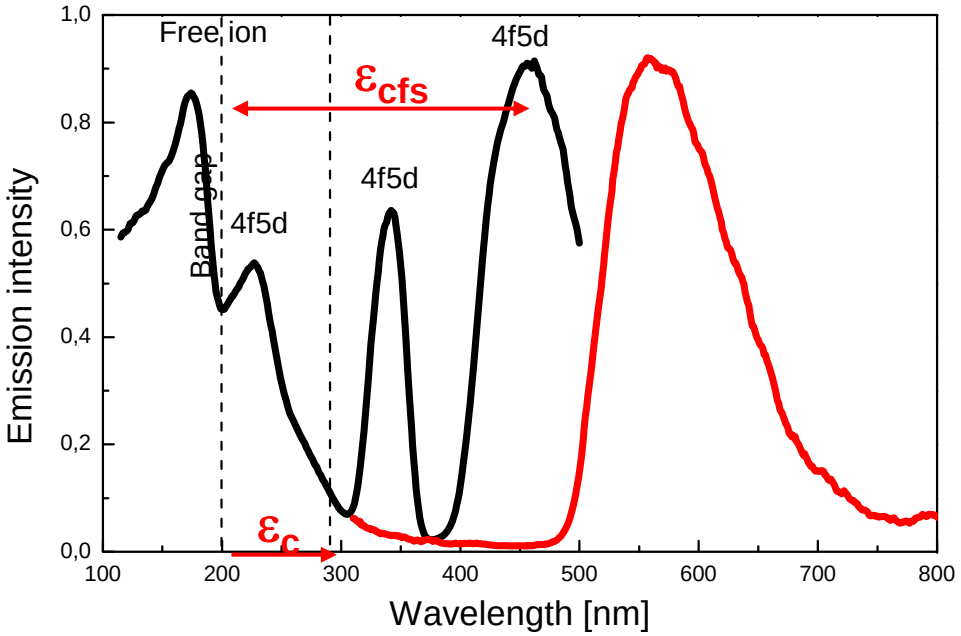
Crystal field splitting ~ 18000 cm^{-1}
Centroid shift ~ 9600 cm^{-1}
(P. Dorenbos, Phys. Rev. B, 64, 2001, 1251)
⇒ Large 4f-5d energy gap
⇒ Emission bands at 335 and 355 nm

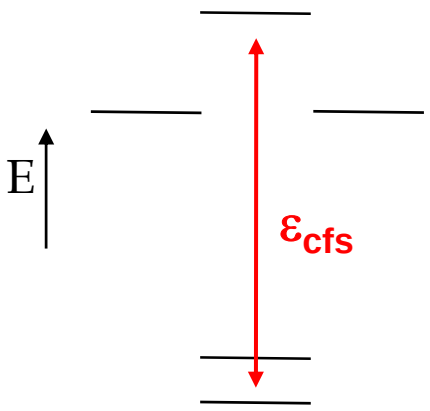
8.12 Luminescence of Rare Earth Ions

Luminescence of $Y_3Al_5O_{12}$:Ce



Distorted dodecahedral





Y-O distances

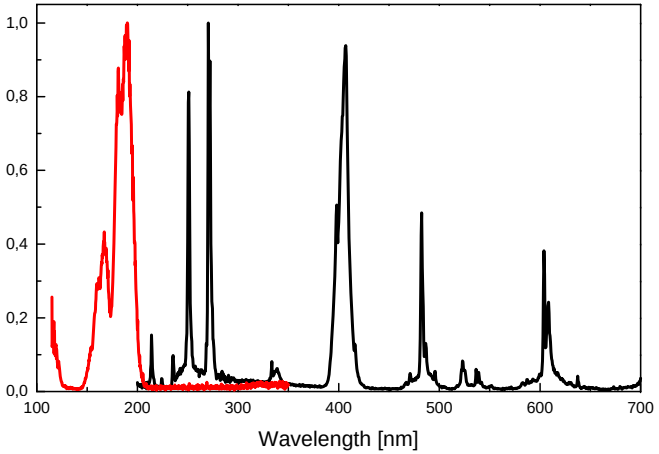
4x 2.30 Å
4x 2.44 Å

Crystal field splitting ~ 27000 cm^{-1}
Centroid shift ~ 14700 cm^{-1}
(P. Dorenbos, Phys. Rev. B, 65, 2002, 2351)
⇒ Small 4f-5d energy gap
⇒ Emission bands at 560 nm

8.12 Luminescence of Rare Earth Ions

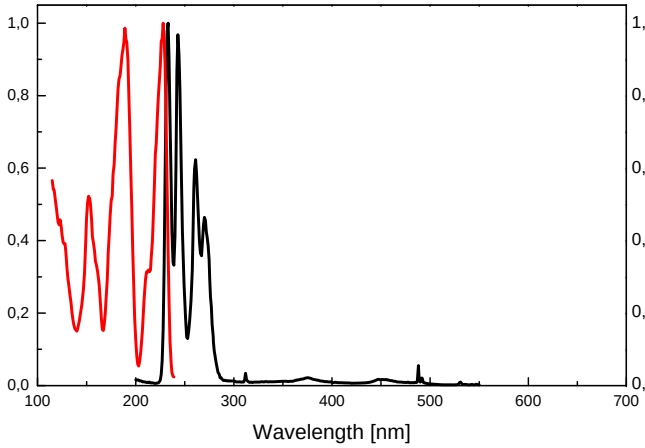
Excitation and emission spectra of Pr^{3+} activated phosphors

YF_3:Pr



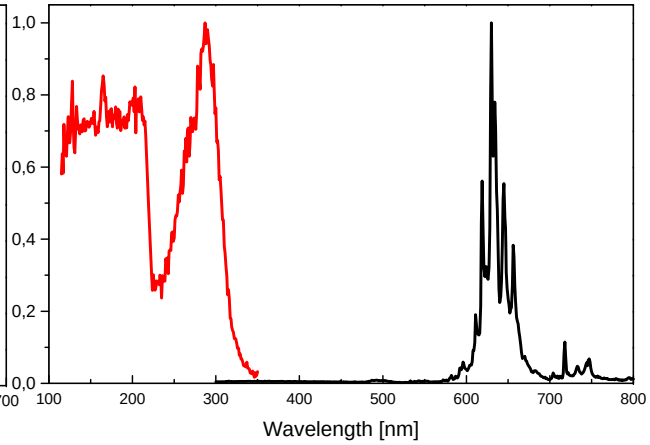
$4f^2$-$4f^2$ line emission

YPO_4:Pr



$4f^15d^1$-$4f^2$ band emission

Y_2O_3:Pr



$4f^2$-$4f^2$ line emission

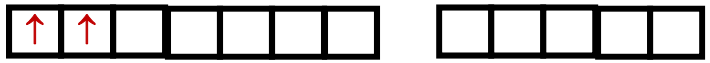
The nature of the luminescence spectrum of Pr^{3+} is strongly determined by the host lattice!

8.12 Luminescence of Rare Earth Ions

Fundamentals of Pr^{3+} luminescence

Pr^{3+} ground state configuration

$[Xe]4f^2$ → 13 SLJ-States



4f 5d

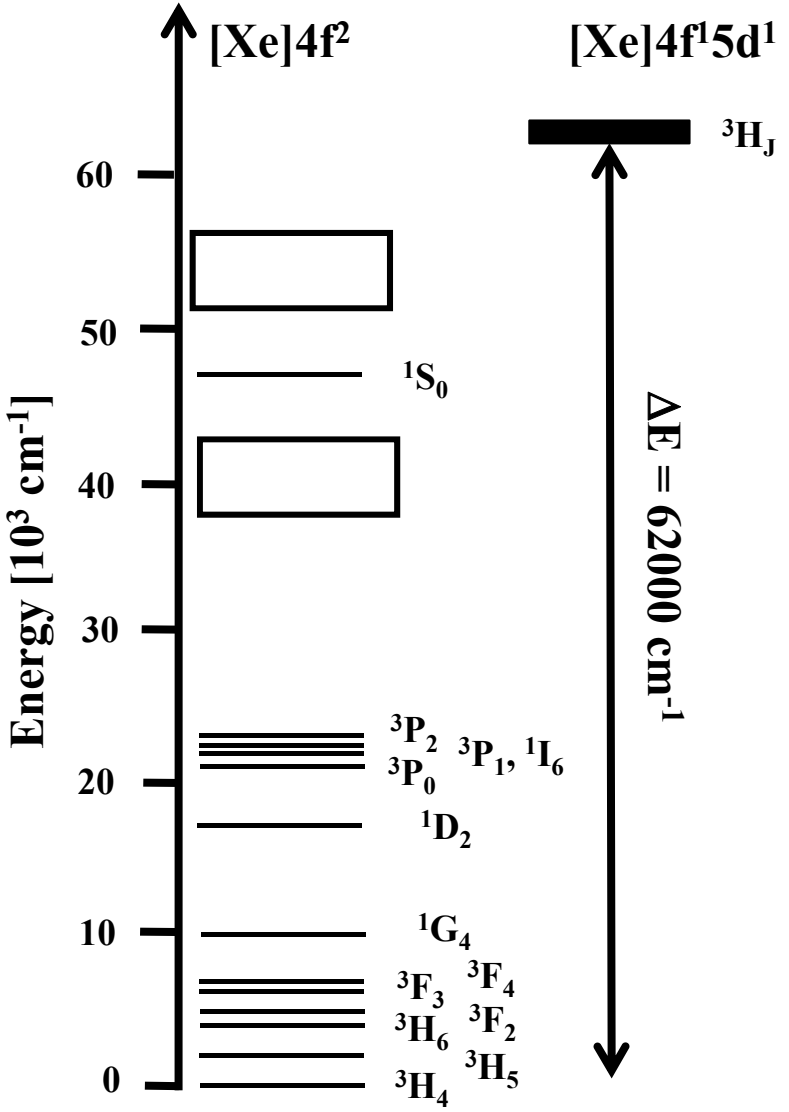
Pr^{3+} excited state configuration

$[Xe]4f^15d^1$ → 2 SLJ-States

4f 5d

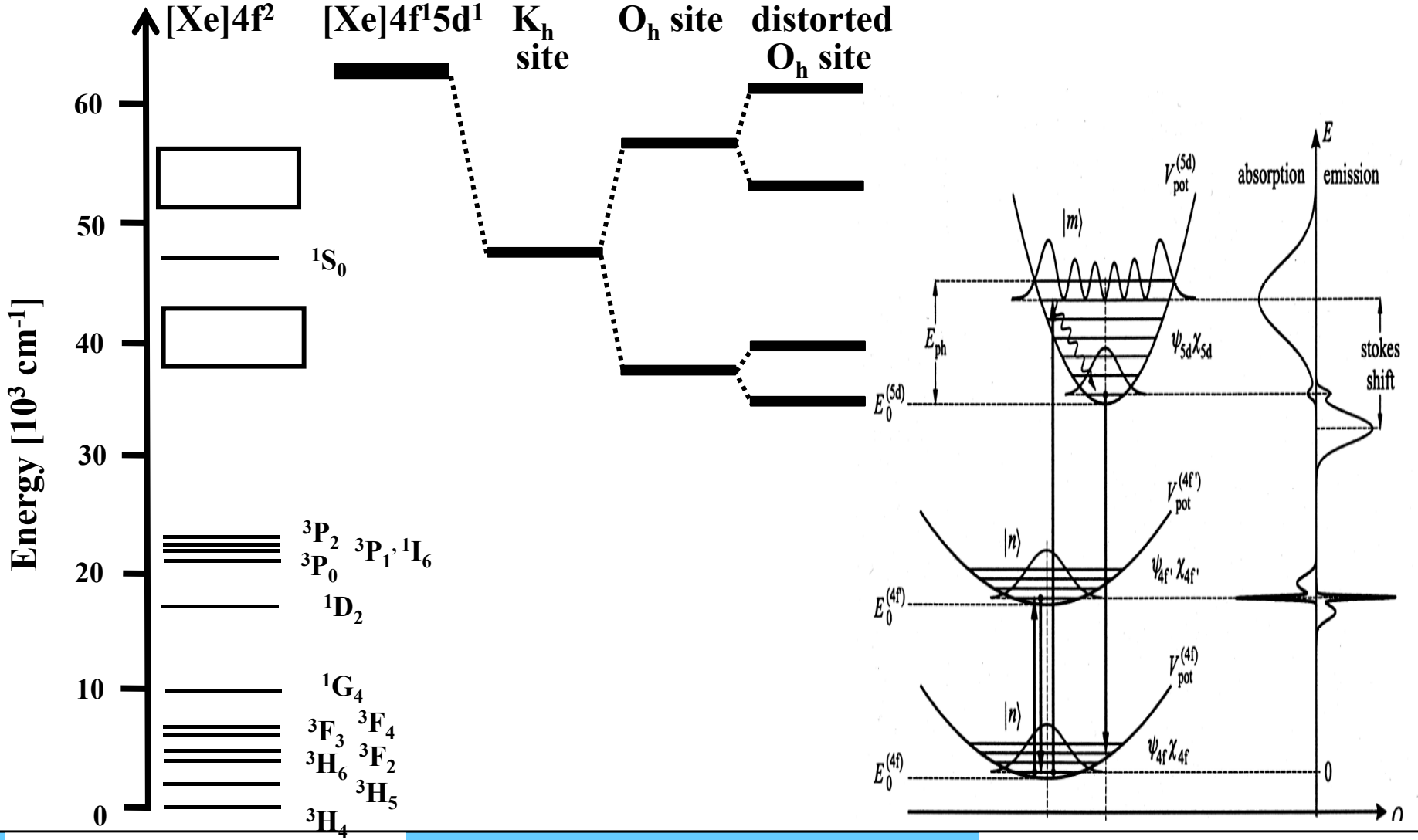
⇒ **$[Xe]4f^2$ – $[Xe]4f^2$ transitions**

⇒ **$[Xe]4f^2$ – $[Xe]4f^15d^1$ transitions**



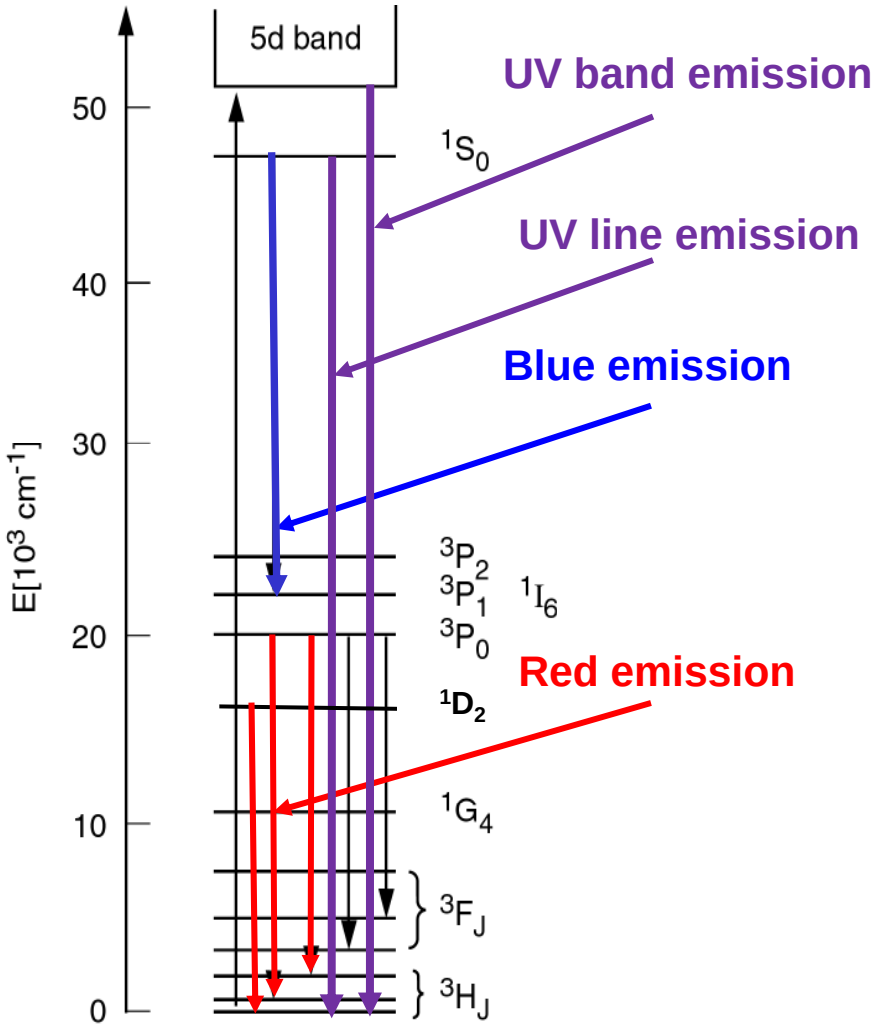
8.12 Luminescence of Rare Earth Ions

Fundamentals of Pr^{3+} luminescence



8.12 Luminescence of Rare Earth Ions

Emission spectra of Pr^{3+} phosphors



$^1S_0$ – $^{2S+1}L_J$ line emission

YF_3:Pr	213, 236
$NaYF_4$:Pr	252, 271
$SrAl_{12}O_{19}$:Pr	407 nm
$LaMgB_5O_{10}$:Pr	
LaB_3O_6:Pr	

$^1S_0$ – $^{2S+1}L_J$ lines and $4f^15d^1$ – $4f^2$ band emission

KY_3F_{10}:Pr	240, 250, 271 nm

$4f^15d^1$ – $4f^2$ band emission

$LiYF_4$:Pr	218 nm
YPO_4:Pr	232 nm
KYF_4:Pr	235 nm
$YAlO_3$:Pr	245 nm
YBO_3:Pr	263 nm
$Lu_2Si_2O_7$:Pr	273 nm
$Lu_3Al_5O_{12}$:Pr	310 nm
$Y_3Al_5O_{12}$:Pr	320 nm + line emission

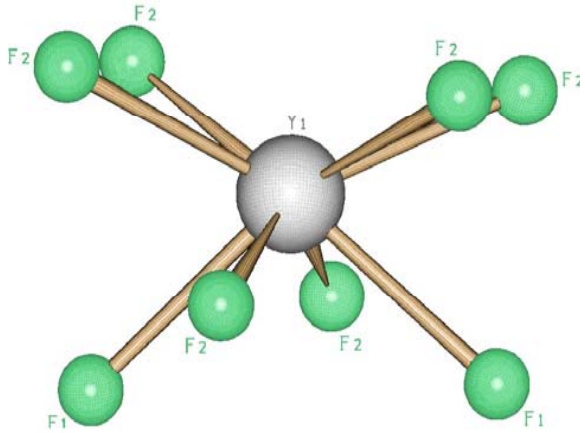
$^1D_2$- ^3H_J line emission

Y_2O_3:Pr	615 nm
$CaTlO_3$:Pr,Na	615 nm

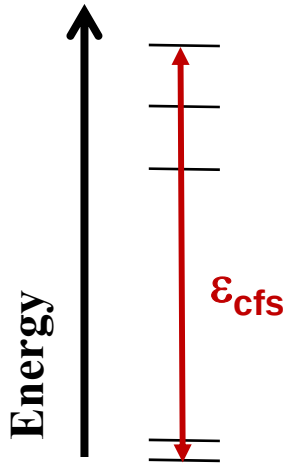
Energy of the lowest crystal field component of [Xe]$4f^15d^1$ config.

8.12 Luminescence of Rare Earth Ions

Luminescence of YF_3:Pr

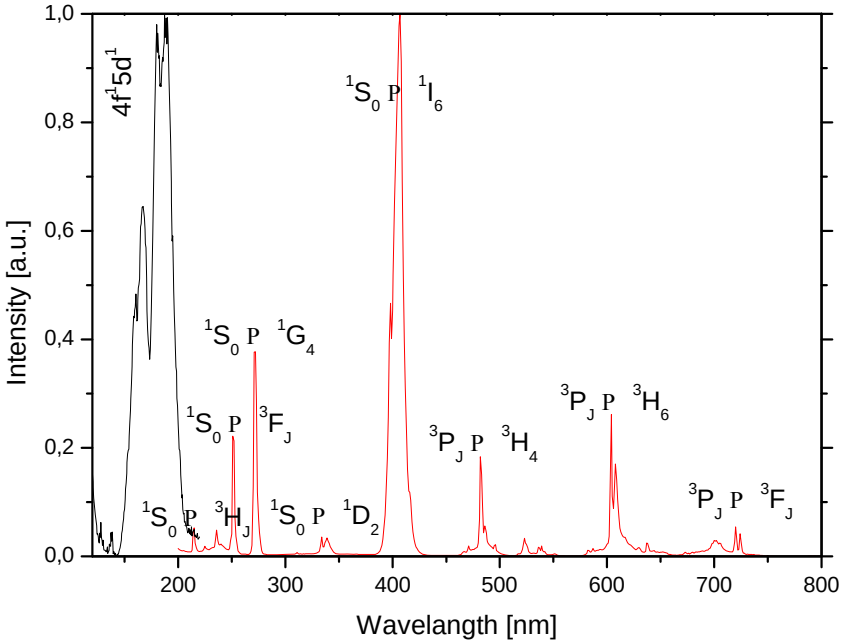


Distorted square-antiprismatic



Y-F distances
4x 2.28 Å
2x 2.30 Å
2x 2.31 Å

CF splitting
~ 8000 cm^{-1}
Centroid shift
~ 5600 cm^{-1}

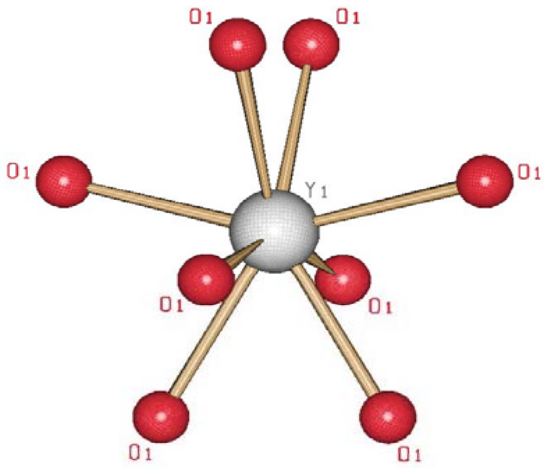


CFS + centroid shift reduces energy of lowest crystal field component of the [Xe]$4f^15d^1$ configuration by ~ 10000 cm^{-1}

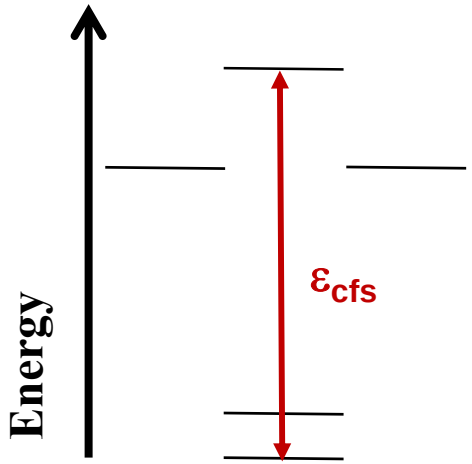
$\Rightarrow$ $E(4f^15d^1) > E(^1S_0)$
$\Rightarrow$ $^1S_0 - {}^{2S+1}L_J$ line emission

8.12 Luminescence of Rare Earth Ions

Luminescence of YPO_4:Pr

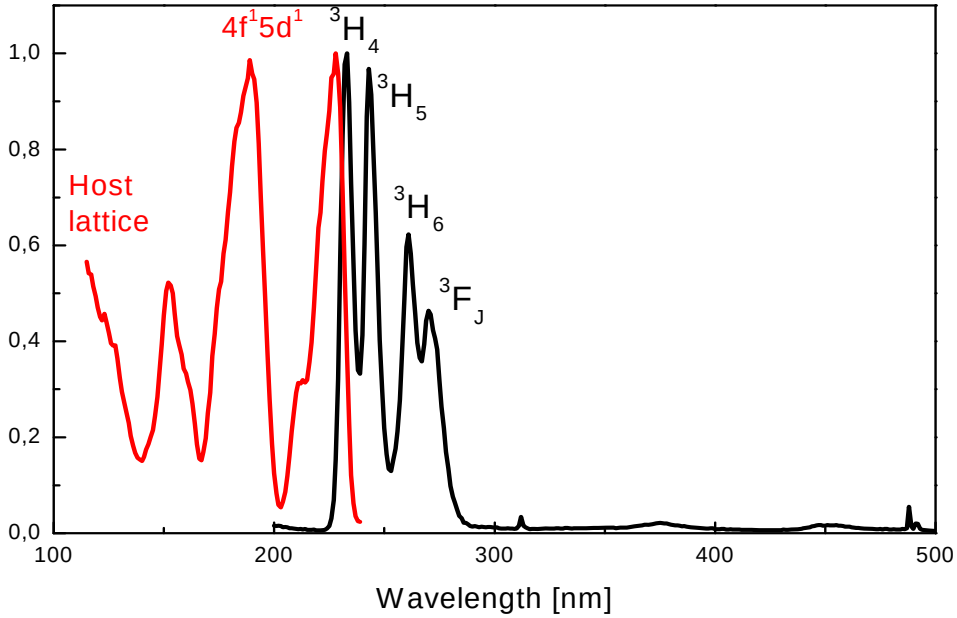


Distorted dodecahedral



Y-O distances
4x 2.24 Å
4x 2.24 Å

CF splitting
~ 12000 cm^{-1}
Centroid shift
~ 9600 cm^{-1}



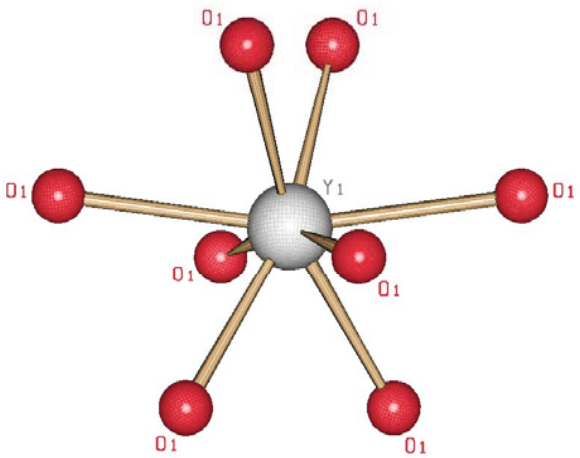
CFS + centroid shift reduces energy of lowest crystal field component of the $[Xe]4f^15d^1$ configuration by ~ 16000 cm^{-1}

$\Rightarrow$ $E(4f^15d^1) < E(^1S_0)$

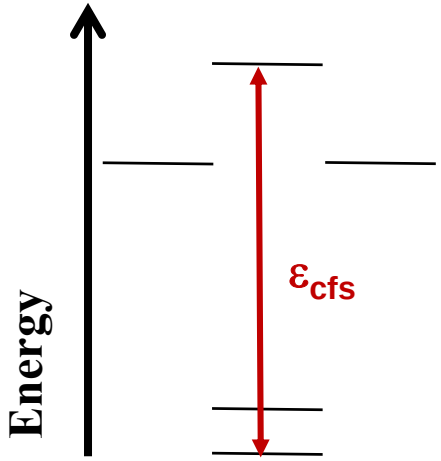
$\Rightarrow$ $[Xe]4f^15d^1$ - $[Xe]4f^2$ band emission

8.12 Luminescence of Rare Earth Ions

Luminescence of $Y_3Al_5O_{12}$:Pr

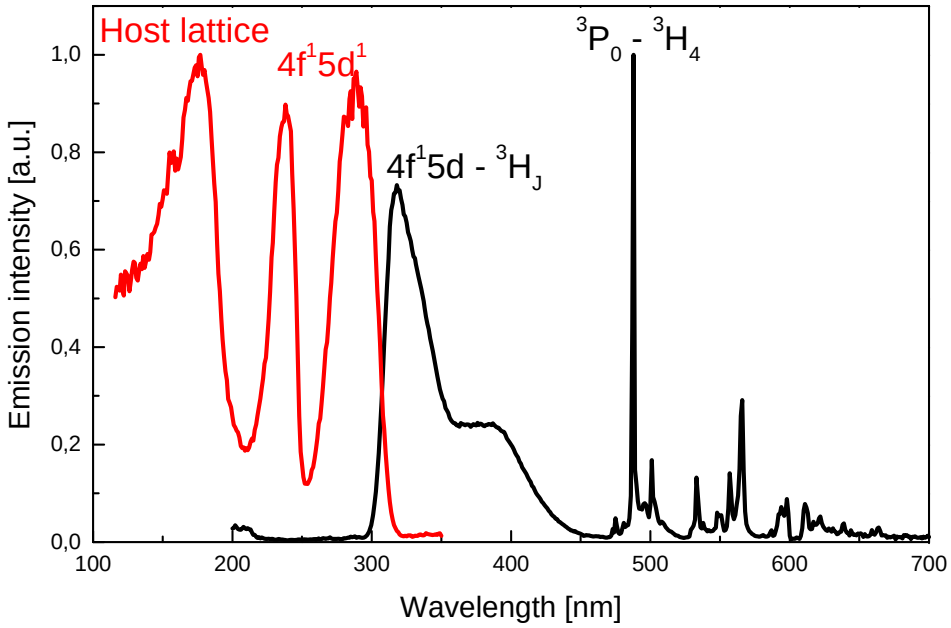


Distorted dodecahedral



Y-O distances
4x 2.30 Å
4x 2.44 Å

CF splitting
~ 22500 cm^{-1}
Centroid shift
~ 14700 cm^{-1}



CFS + centroid shift reduces energy of lowest crystal field component of the $[Xe]4f^15d^1$ configuration by ~ 26000 cm^{-1}

$\Rightarrow E(4f^15d^1) << E(^1S_0)$

$\Rightarrow$ UV band emission (320 nm) and visible line emission (> 450 nm)

8.13 Down-Conversion

First examples (1974)

Sommerdijk et al., J. Lumin. 8 (1974) 288 (Philips)

Sommerdijk et al., J. Lumin. 8 (1974) 341 (Philips)

Piper et al., J. Lumin. 8 (1974) 344 (GE)

YF_3:Pr(0.1%) and $NaYF_4$:Pr(0.1%)

$^1S_0$ - $^3P_1$, $^1I_6$ transition @ 407 nm

$^3P_0$ - ^3H_J, $^3F_2$ transitions in the red

Internal QY = 166% (total) @ 214 nm exc.

Derived from line ratio UV to blue to green/red

Oxidic luminescent materials showing PCE

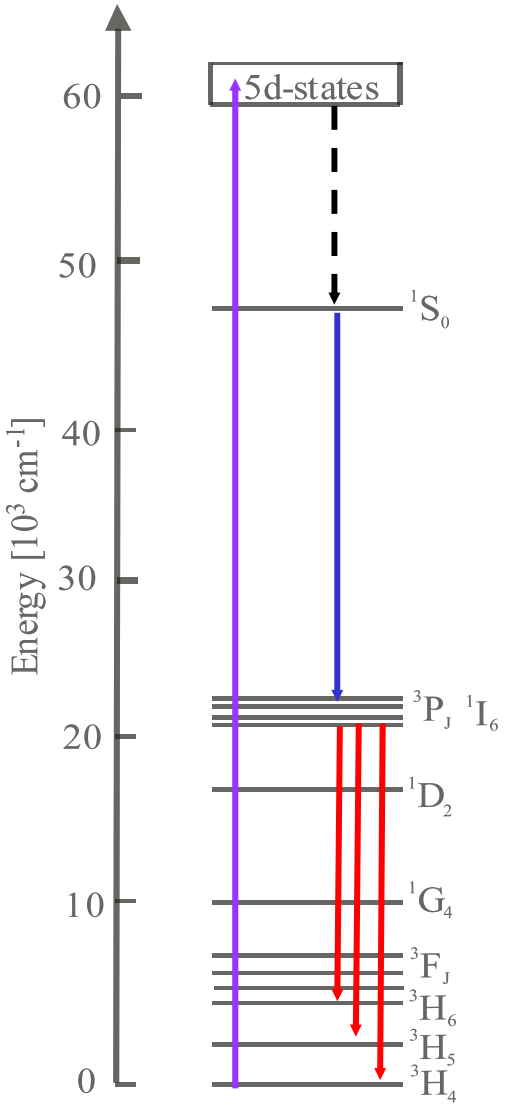
A.M. Srivastava, D.A. Doughty, W.W. Beers (GE)

Pr^{3+} on host lattice sites with high CN (> 8)

$SrAl_{12}O_{19}$:Pr,Mg

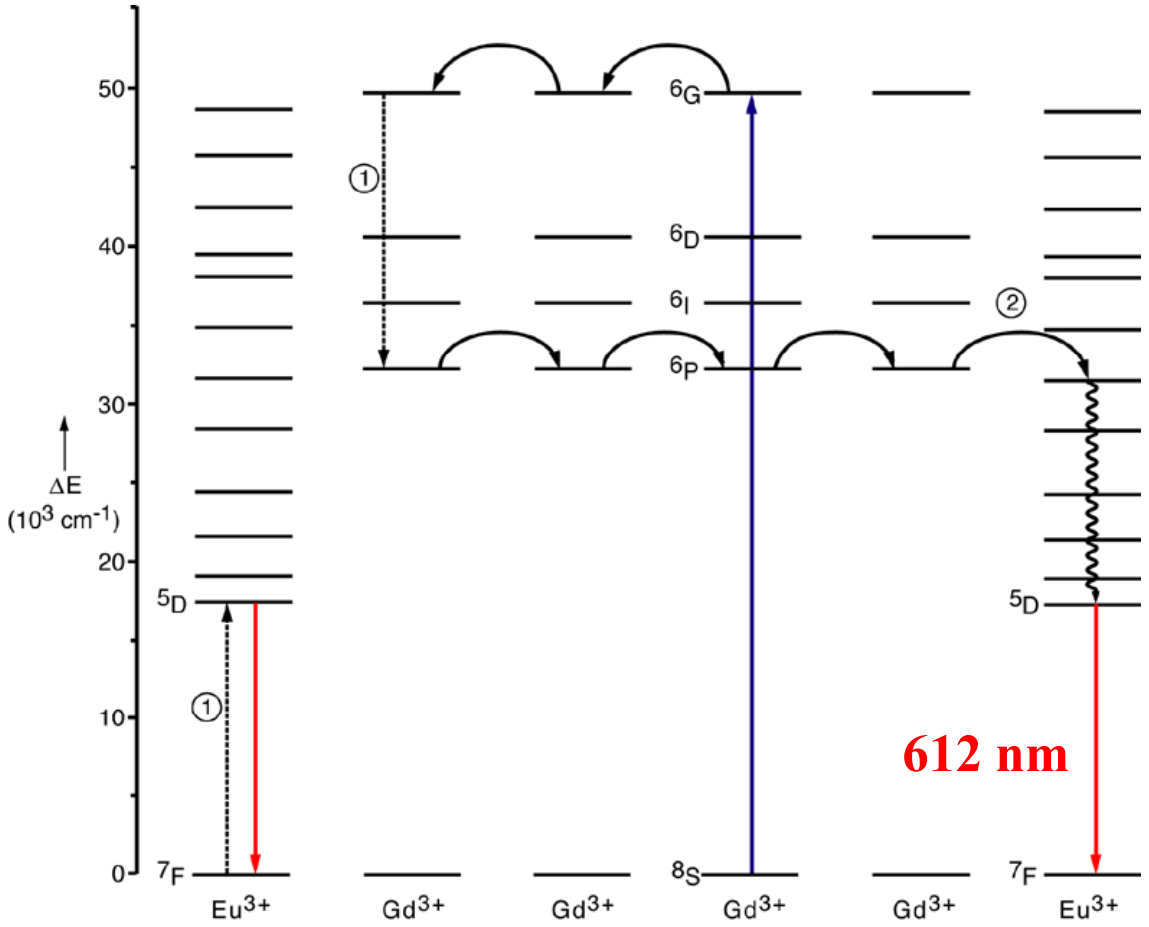
$LaMgB_5O_{10}$:Pr

LaB_3O_6:Pr



8.13 Down-Conversion

Example: $LiGdF_4$:Eu



$$Gd \xrightarrow{202\ nm} Gd^{**}$$

$$Gd^{**} + Eu \xrightarrow{CR} Eu^{*} + Gd^{*}$$

$$Eu^{*} \longrightarrow Eu + h\nu$$

$$Gd^{*} + Eu \xrightarrow{ET} Gd + Eu^{*}$$

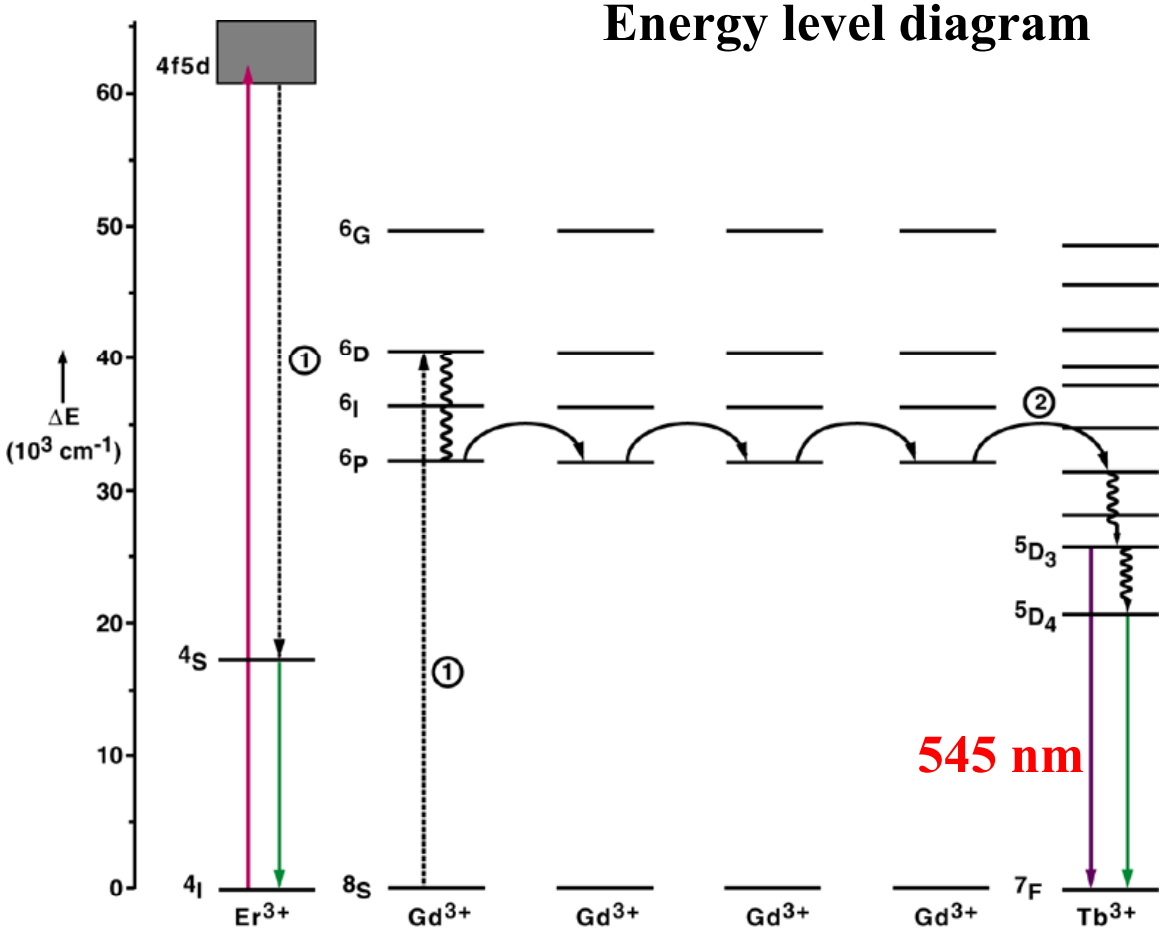
$$Eu^{*} \longrightarrow Eu + h\nu$$

612 nm

$$QY_A = 195\%$$

8.13 Down-Conversion

Example: $LiGdF_4$:Er,Tb



$$Er \xrightarrow{> 210\ nm} Er^{**}$$

$$Er^{**} + Gd \xrightarrow{CR} Er^{*} + Gd^{*}$$

$$Er^{*} \longrightarrow Er + h\nu$$

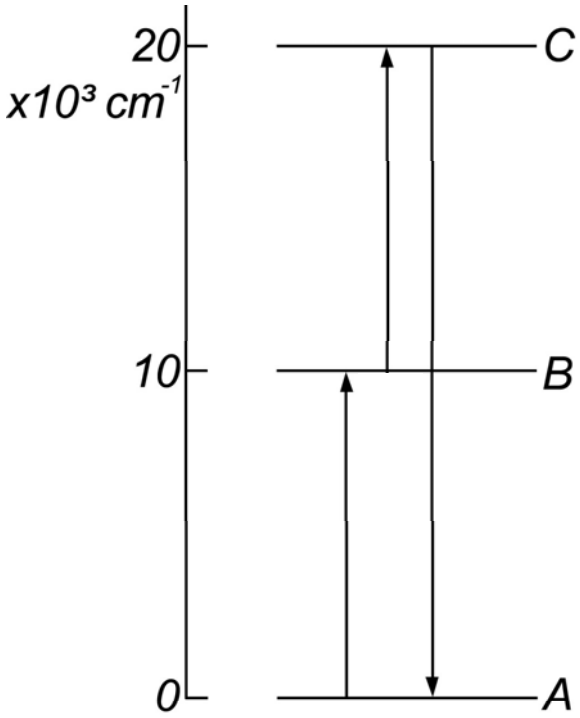
$$Gd^{*} + Tb \xrightarrow{ET} Gd + Tb^{*}$$

$$Tb^{*} \longrightarrow Tb + h\nu$$

$$QY_A = 130\%$$

8.14 Up-Conversion

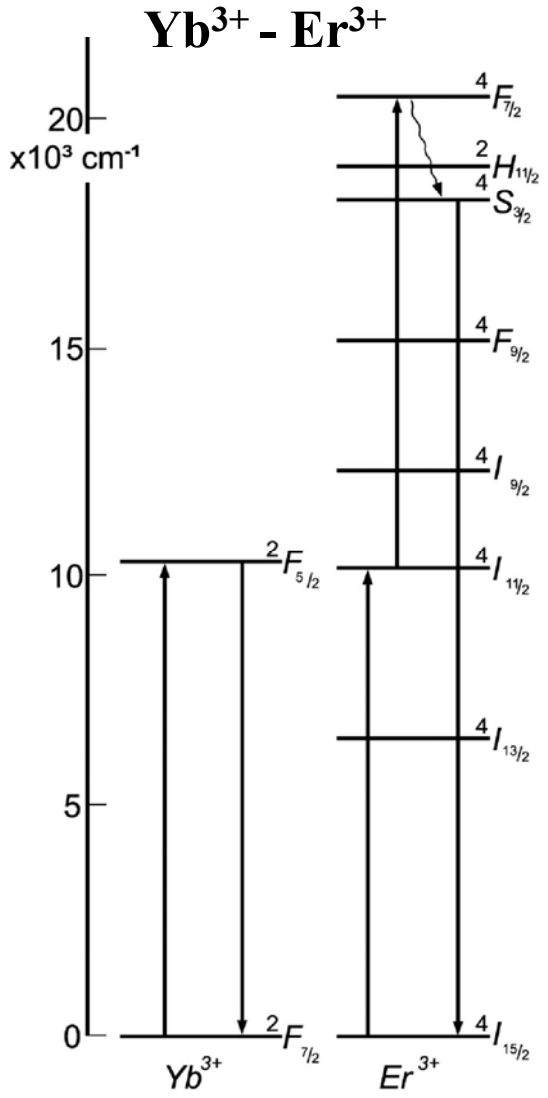
Principle



Examples

YF_3:Yb,Tm
YF_3:Yb,Er
$NaYF_4$:Yb,Er
BaY_2F_8:Yb,Er
YOCl:Yb,Er

20-35% Yb^{3+}
1-5% Er^{3+} or Tm^{3+}

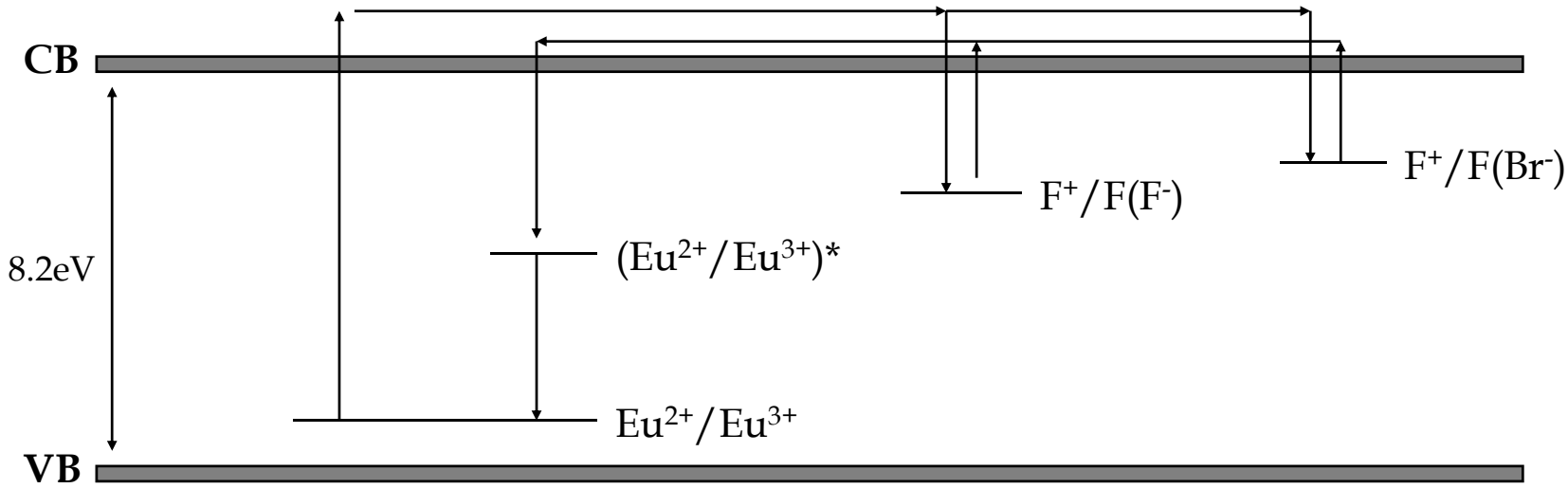


Implementation of IR radiation into visible
(in frequency multipliers, laser diodes, night vision goggles)

8.15 Afterglow

Cause: Storage of electrons / holes in certain sites in the lattice (vacancies, impurities)

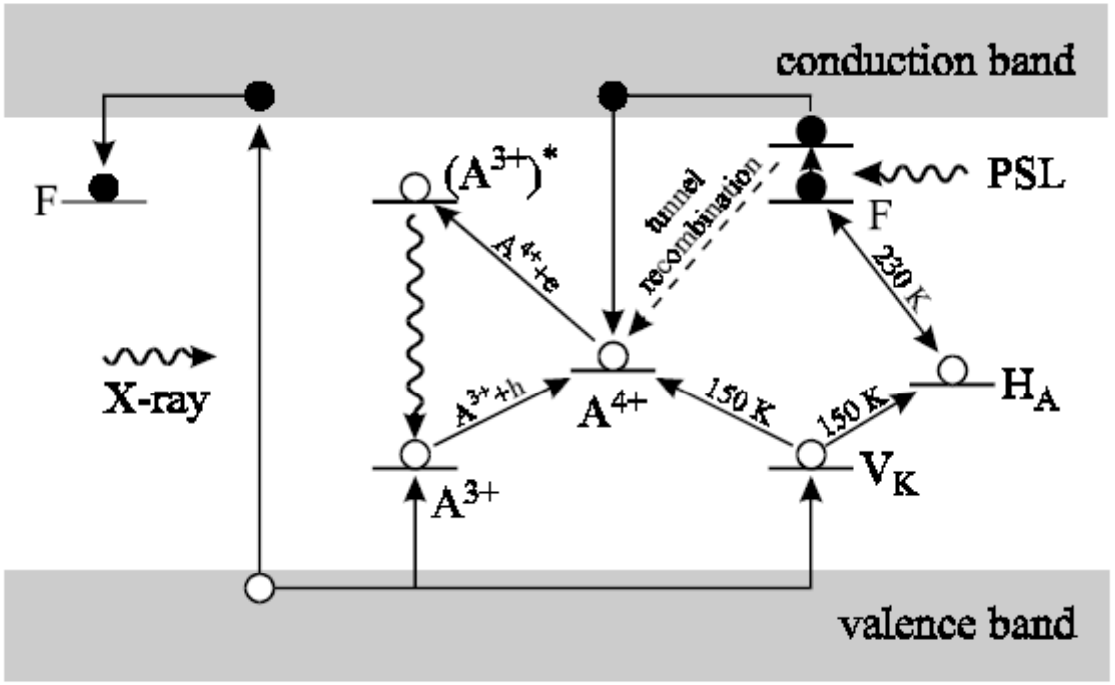
Deep traps: Emptying of the traps is done by activation (LASER)



Example: BaFBr:Eu Storage phosphor for imaging plates (detection of x-rays)
(Y. Iwabuchi et al., J. Appl. Phys. 33 (1994) 178)

8.15 Afterglow

Example: Cs_2NaYF_6:Ce and Cs_2NaYF_6:Pr (elpasolite)

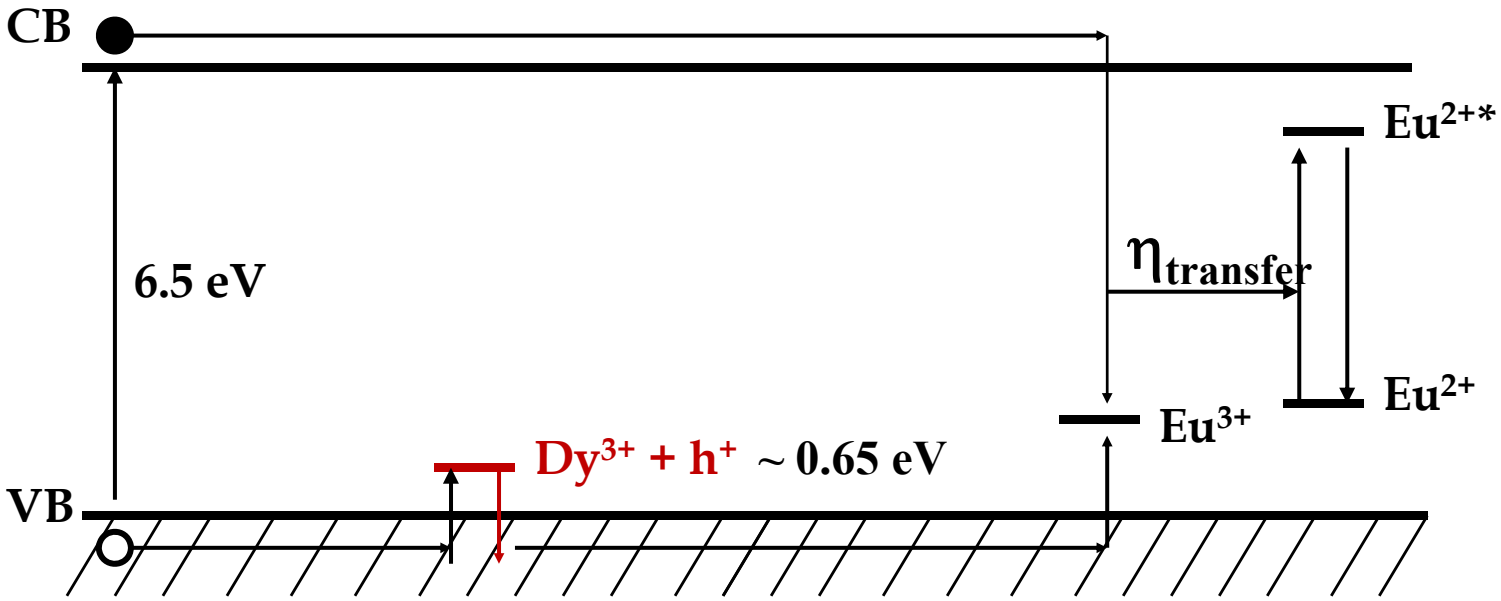


A = Ce, Pr

According to: Th. Pawlik and J.-M. Spaeth, J. Appl. Phys. 82 (9), 4236 (1997)

8.15 Afterglow

Shallow traps: Thermal emptying of the traps at room temperature



Example

$SrAl_2O_4$:Eu,Dy (*Nemoto Ltd., JECS 143 (1996) 2670)*

8.15 Afterglow

Afterglow phosphors

Composition	colour	λ_{max} [nm]
• $CaAl_2O_4$:Eu,Nd	blue	440 nm
• $Sr_2MgSi_2O_7$:Eu,Dy	blue	469 nm
• $Sr_4Al_{14}O_{25}$:Eu,Dy	cyan	490 nm
• $Mg_2SnO_4:Mn^{2+}$	cyan	499 nm
• $SrAl_2O_4$:Eu,Dy	green	520 nm
• ZnS:Cu,Co	green	530 nm
• Sr_2SiO_4:Eu,Dy	yellow	570 nm
• Y_2O_2S:Eu,Ti,Mg	red	620 nm
• $CaZnGe_2O_6$:Mn	red	648 nm
• CaS:Eu,Tm	red	655 nm
• $MgSiO_3$:Eu,Dy,Mn	red	660 nm

$Sr_4Al_{14}O_{25}:Eu^{2+},Ln^{3+}$