8. Luminescence Mechanisms

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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! No metals!
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
Inorganic luminescent materials = Host lattice + defects + dopants

**Host lattices**

- $Y_2O_3$, $Y_3Al_5O_{12}$, ZnS, CaAlSiN$_3$, Sr$_2$Si$_5$N$_8$, …

  - 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, …

  - Afterglow and charge storage
  - Concentration and thermal quenching
  - Reduction of stability and colour point shift
Inorganic luminescent materials - Morphology

- **Nanoscale particles**: Molecular imaging, precursors, bio and product labeling, anticounter feiting
- **μ-sized particles**: Lamps, LEDs, CRTs, PDPs, EL Displays, x-ray converter films, Field Emission Displays
- **Large single crystals**: Scintillators, Lasers
- **Ceramics**: LEDs, scintillators, Lasers
- **Glasses**: Detectors, Lasers
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!

Excitation Source

Energy transfer (ET)

Emission

Heat
8.1 Luminescence – Materials

Inorganic luminescent materials – The role of the host lattice

YBO$_3$ (Vaterite)

Band gap $E_g = 6.5$ eV

Conduction band (CB)

Band gap $E_g$

Valence band (VB)

Absorption via
- Host lattice
  → Charge-Transfer or VB to CB
- Defects (colour centers)
  → Donor and acceptor levels
Inorganic luminescent materials – The role of the host lattice

Reflection spectrum of YBO$_3$  
Emission spectrum of YBO$_3$ upon 160 nm excitation

Band gap absorption at 170 nm  
Exciton luminescence at 260 nm
8.1 Luminescence – Materials

Inorganic luminescent materials – The role of the dopants

YVO₄ (tetragonal), \( E_g = 4.2 \) eV

\[ \begin{array}{c}
\text{CB} \\
\text{Donor levels (D)} \\
\text{E}_g \\
\text{Accepter levels (A)} \\
\text{VB}
\end{array} \]

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

YPO₄:V,Eu (tetragonal), \( E_g = 8.2 \) eV

\[ \begin{array}{c}
\text{CB} \\
\text{(VO}_4^{3-})^* \\
\text{E}_g \\
\text{(Eu}^{3+})^* \\
\text{VO}_4^{3-} \\
\text{Eu}^{3+} \\
\text{VB}
\end{array} \]
8.1 Luminescence - Processes

The overall picture

- Sensitizer energy levels -

- Activator energy levels -

Valence band (anion orbitals filled by electrons)

Conduction band (empty metal orbitals)

Eg

Excitation

Fluorescence ~ 10^{-9}s

Phosphorescence ~ 10^{-3}s

Relaxation

ISC

ET

Excitation

S0, S1, S2, T1, A0, A1 = Energy levels of activator and sensitizer ions

ISC = Intersystem Crossing “spin-forbidden singulett-triplett transition”

ET = Energy transfer
8.1 Luminescence - Processes

Photonic or thermal stimulated luminescence (PSL or TSL)

Charging  Stimulated luminescence

CB  

Electron trap  Stimulation  Tunneling

VB

X-ray or UV

E > E_g

Hole trap

E_g
### 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.

<table>
<thead>
<tr>
<th>Atom/Ion</th>
<th>Electron configuration</th>
<th>Spectroscopic term $^2S^+^1L_J$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^0$</td>
<td>1s$^2$ 2s$^1$</td>
<td>$^2S_{1/2}$</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>1s$^2$</td>
<td>$^1S_0$</td>
</tr>
<tr>
<td>Na$^0$</td>
<td>[Ne]3s$^1$</td>
<td>$^2S_{1/2}$</td>
</tr>
<tr>
<td>Ti$^{3+}$</td>
<td>[Ar]3d$^1$</td>
<td>$^2D_{3/2}$</td>
</tr>
<tr>
<td>Cr$^{3+}$/Mn$^{4+}$</td>
<td>[Ar]3d$^3$</td>
<td>$^4F_{3/2}$</td>
</tr>
<tr>
<td>Mn$^{2+}$/Fe$^{3+}$</td>
<td>[Ar]3d$^5$</td>
<td>$^6S_{5/2}$</td>
</tr>
<tr>
<td>Zn$^{2+}$/Cu$^+$</td>
<td>[Ar]3d$^{10}$</td>
<td>$^1S_0$</td>
</tr>
<tr>
<td>Ce$^{3+}$</td>
<td>[Xe]4f$^1$</td>
<td>$^2F_{5/2}$</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>[Xe]4f$^6$</td>
<td>$^7F_0$</td>
</tr>
<tr>
<td>Eu$^{2+}$/Gd$^{3+}$/Tb$^{4+}$</td>
<td>[Xe]4f$^7$</td>
<td>$^8S_{7/2}$</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>[Xe]4f$^8$</td>
<td>$^7F_6$</td>
</tr>
<tr>
<td>Lu$^{3+}$</td>
<td>[Xe]4f$^{14}$</td>
<td>$^1S_0$</td>
</tr>
</tbody>
</table>
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\(^{3+}\)**: \([\text{Xe}]4f^1 (2F_{5/2}) \rightarrow [\text{Xe}]5d^1 (2D_{3/2})\) \(\Rightarrow\) allowed \(\sim\) ns
- **Eu\(^{3+}\)**: \([\text{Xe}]4f^6 (7F_0) \rightarrow [\text{Xe}]4f^6 (5D_0)\) \(\Rightarrow\) forbidden \(\sim\) ms
<table>
<thead>
<tr>
<th>Type</th>
<th>Excitation by</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scintillation</td>
<td>High energy particles</td>
<td>high-energy physics</td>
</tr>
<tr>
<td></td>
<td>$\gamma$-rays</td>
<td>PET detectors</td>
</tr>
<tr>
<td>X-ray luminescence</td>
<td>X-rays</td>
<td>X-ray amplifier, CT</td>
</tr>
<tr>
<td>Cathode luminescence</td>
<td>Electrons (high voltage)</td>
<td>CRTs, oscilloscopes</td>
</tr>
<tr>
<td>Photo luminescence</td>
<td>UV/Vis photons</td>
<td>Fluorescent lamps</td>
</tr>
<tr>
<td>Electro luminescence</td>
<td>Electrical field (low voltage)</td>
<td>LEDs, EL displays</td>
</tr>
<tr>
<td>Chemo luminescence</td>
<td>Chemical reaction</td>
<td>Emergency signals</td>
</tr>
<tr>
<td>Bio luminescence</td>
<td>Biochemical reaction</td>
<td>Jelly fish, glow worms</td>
</tr>
<tr>
<td>Thermo luminescence</td>
<td>Heat</td>
<td>Afterglow phosphors</td>
</tr>
<tr>
<td>Sono luminescence</td>
<td>Ultra sound</td>
<td>-</td>
</tr>
<tr>
<td>Mechano luminescence</td>
<td>Mechanical energy</td>
<td>Peeling scotch tape</td>
</tr>
</tbody>
</table>

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

Penetration depth of photons and electrons

Photons (Lambert-Beer law)

Penetration depth

Absorption by activators or sensitizers

Absorption by host lattice

Electrons (Feldman equation: \( R \) in [Å])

\[
R = 250 \frac{A}{\rho Z^{n/2}} U^n \text{ with } n = \frac{1.2}{1 - 0.29 \log_{10} Z}
\]

<table>
<thead>
<tr>
<th>Density [g/cm³]</th>
<th>R [Å]</th>
<th>R [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>2.20</td>
<td>6171</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.97</td>
<td>3476</td>
</tr>
<tr>
<td>Mg₃(PO₄)₂</td>
<td>2.56</td>
<td>5345</td>
</tr>
<tr>
<td>ZnS</td>
<td>4.04</td>
<td>4248</td>
</tr>
<tr>
<td>MgO</td>
<td>3.59</td>
<td>3799</td>
</tr>
<tr>
<td>MgF₂</td>
<td>3.15</td>
<td>4464</td>
</tr>
<tr>
<td>MgS</td>
<td>2.68</td>
<td>5603</td>
</tr>
</tbody>
</table>

Simplified \( R \sim 0.046*U^{5/3}/\rho \) [μm]

For 5.7 keV electrons

For a material with \( r = 5.0 \text{ g/cm}³ \) (Y₂O₃)

10 kV electrons \( R \sim 400 \text{ nm} \)

2 kV electrons \( R \sim 30 \text{ nm} \)
8.3 Excitation Mechanisms

High energy particles, $\gamma$-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

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

External quantum efficiency: \( \text{EQE} = \eta_{act} * \eta_{transfer} * \eta_{esc} \)

<table>
<thead>
<tr>
<th>Host lattice</th>
<th>Band gap ( E_g ) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgF(_2)</td>
<td>12.2</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>8.0</td>
</tr>
<tr>
<td>Y(_2)O(_3)</td>
<td>5.6</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.9</td>
</tr>
<tr>
<td>ZnSe</td>
<td>2.8</td>
</tr>
<tr>
<td>ZnTe</td>
<td>2.4</td>
</tr>
<tr>
<td>CdS</td>
<td>2.6</td>
</tr>
<tr>
<td>CdTe</td>
<td>1.6</td>
</tr>
</tbody>
</table>
8.3 Excitation Mechanisms

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

**Activator excitation**

CB

\[ \begin{array}{c}
    \text{A2} \\
    \text{A1} \\
    \eta_{\text{act}} \\
    k_r \\
    k_{\text{nr}} \\
    \text{A0} \\
  \end{array} \]

VB

**Sensitizer excitation**

CB

\[ \begin{array}{c}
    \text{S1} \\
    \eta_{\text{transfer}} \\
    \text{A1} \\
  \end{array} \]

VB

\[ \begin{array}{c}
    \text{S0} \\
    \eta_{\text{esc}} \\
    \text{A0} \\
  \end{array} \]

IQE = \eta_{\text{act}} = k_r/(k_r + k_{\text{nr}}) = \tau/\tau_0

with \( k_r + k_{\text{nr}} = 1/\tau \) and \( k_r = 1/\tau_0 \)

EQE = \eta_{\text{act}} \ast \eta_{\text{transfer}} \ast \eta_{\text{esc}}
8.3 Excitation Mechanisms

Example: BaMgAl$_{10}$O$_{17}$ doped by 10% Eu$^{2+}$

- Host material  VB $\rightarrow$ CB  180 nm (7.0 eV)
- Eu$^{2+}$  [Xe]4f$^7$ $\rightarrow$ [Xe]4f$^6$5d$^1$  250 nm (5.0 eV) and 310 nm (4.0 eV)
- Allowed transition $\Rightarrow$ Intense absorption bands and fast decay (~1 µs)
8.3 Excitation Mechanisms

Example: BaMgAl$_{10}$O$_{17}$ doped by 5% Mn$^{2+}$

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

Example: LaPO₄ doped by 20% Ce³⁺

- **Host material**  VB → CB  150 nm (8.2 eV)
- **Ce³⁺**  [Xe]⁴f¹ → [Xe]⁵d¹  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:** $\text{Y}_2\text{O}_3$ doped by 5% Eu$^{3+}$

**Reflection spectra**

**Emission and excitation spectra**

- **Host material** $\text{VB} \rightarrow \text{CB}$
  
  210 nm (5.9 eV)

- **Eu$^{3+}$** Charge-Transfer
  
  230 nm (5.4 eV)

  $[\text{Xe}]4f^6 \rightarrow [\text{Xe}]4f^6$

  395 nm (3.1 eV) and 465 nm (2.2 eV)

- **Forbidden transitions** $\Rightarrow$ Weak absorption bands and slow decay (~3 ms)
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 → $\text{Eu}^{3+}, \text{Yb}^{3+}$
  – Low-lying energy levels of the $[\text{Xe}]4f^n-15d^1$ configuration → $\text{Tb}^{3+}, \text{Eu}^{2+}, \text{Ce}^{3+}, \text{Pr}^{3+}$

• Sensitisation (via energy transfer)
  – $\text{Ce}^{3+}$ → $\text{Tb}^{3+}$
  – $\text{Pr}^{3+}$ → $\text{Tb}^{3+}$
  – $\text{Nd}^{3+}$ → $\text{Gd}^{3+}$
  – $\text{Pr}^{3+}$ → $\text{Gd}^{3+}$
  – $\text{Bi}^{3+}$ → $\text{Eu}^{3+}$
  – $\text{Sb}^{3+}$ → $\text{Mn}^{2+}$
  – $\text{Ce}^{3+}$ → $\text{Mn}^{2+}$
  – $\text{Eu}^{2+}$ → $\text{Mn}^{2+}$
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: \( P_{SA} = \left( \frac{1}{\tau_S} \right) \left( \frac{r_0}{r_{SA}} \right)^6 \)  
    \( \text{Ce}^{3+} - \text{Eu}^{2+} \)
    
    Dipole-Quadrupole: \( P_{SA} = \left( \frac{1}{\tau_S} \right) \left( \frac{r_0}{r_{SA}} \right)^8 \)  
    \( \text{Ce}^{3+} - \text{Tb}^{3+} \)
    
    Quadrupole-Quadrupole: \( P_{SA} = \left( \frac{1}{\tau_S} \right) \left( \frac{r_0}{r_{SA}} \right)^{10} \)  
    \( \text{unknown} \)

  - Exchange interaction
    
    \( P_{SA} \sim J \cdot \exp(-2r_{SA}) \)
    
    for \( r_{SA} < 5 \text{ Å} \) with \( J \) = coupling constant  
    \( \text{Mn}^{2+} - \text{Mn}^{2+} \)

- Spectral overlap \((\rightarrow \text{Energy conservation law!})\)
8.4 Energy Transfer

Probability $P_{ET}$

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

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

$\varphi_i$: Wave function of the initial state
$\varphi_f$: Wave function of the final state
$H$: Operator coupling the states
$\rho$: 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 (Eu$^{3+}$ - Eu$^{3+}$)
8.4 Energy Transfer

Example: ET in LaPO₄:Ce,Tb

LaPO₄:Ce
Ce³⁺ → (Ce³⁺)*
(Ce³⁺)* → Ce³⁺

Excitation 4f - 5d
Emission 5d - 4f

LaPO₄:Tb
Tb³⁺ → (Tb³⁺)***
(Tb³⁺)*** → (Tb³⁺)*
(Tb³⁺)* → Tb³⁺

Excitation 4f - 5d
Relaxation
Emission 4f - 4f

LaPO₄:Ce,Tb
Ce³⁺ → (Ce³⁺)*
(Ce³⁺)* + Tb³⁺ → Ce³⁺ + (Tb³⁺)*
(Tb³⁺)* → Tb³⁺

ET from Ce³⁺ to Tb³⁺
Emission 4f - 4f

Fluorescent lamps ⇒ Excitation at 254 nm

Incoherent Light Sources
Prof. Dr. T. Jüstel, FH Münster

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8.4 Energy Transfer

Example: ET in BaMgAl$_{10}$O$_{17}$:Eu co-doped by transition metal ions

<table>
<thead>
<tr>
<th>Divalent RE ions</th>
<th>Ba$^{2+}$ sites in the conduction layer</th>
<th>Eu$^{2+}$, Yb$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Divalent TM ions</td>
<td>tetrahedral gaps in the spinel blocks</td>
<td>Mn$^{2+}$, Co$^{2+}$</td>
</tr>
<tr>
<td>Trivalent TM ions</td>
<td>octahedral gaps in the spinel blocks</td>
<td>Cr$^{3+}$, Ti$^{3+}$</td>
</tr>
</tbody>
</table>
8.4 Energy Transfer

Example: ET in BaMgAl$_{10}$O$_{17}$:Eu co-doped by transition metal ions

BaMgAl$_{10}$O$_{17}$:Eu

Eu$^{2+} \rightarrow (\text{Eu}^{2+})^*$

(Eu$^{2+}$)$^* \rightarrow \text{Eu}^3^+$

Absorption 4f - 5d

Emission 5d - 4f

BaMgAl$_{10}$O$_{17}$:Mn

Mn$^{2+} \rightarrow (\text{Mn}^{2+})^*$

(Mn$^{2+}$)$^* \rightarrow \text{Mn}^2^+$

Absorption 3d - 3d

Emission 3d – 3d

BaMgAl$_{10}$O$_{17}$:Eu,Mn

Eu$^{2+} \rightarrow (\text{Eu}^{2+})^*$

(Eu$^{2+}$)$^* + \text{Mn}^2^+ \rightarrow \text{Eu}^2^+ + (\text{Mn}^{2+})^*$

ET from Eu to Mn

(Eu$^{2+}$)$^* \rightarrow \text{Mn}^2^+$

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

$E_g = 7.0$ eV ($\sim 180$ nm)

172 nm

VUV Excitation

254 nm

[Ar]3d$^5$

Energy Transfer

453 nm

[Ar]3d$^5^*$

515 nm

[Ar]3d$^5$

Mn$^{2+}$

Energy

Conduction Band

Valence Band

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Prof. Dr. T. Jüstel, FH Münster

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8.6 Loss Processes

Overview of the most relevant processes leading to luminescence quenching

1. The absorbed energy does not reach the activator ion
   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
   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
   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
8.5 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.

Emission spectra of Tb$^{3+}$ activated Yttrium oxysulphides.
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8.6 Loss Processes

Related to the host lattice and host lattice activator interaction

\[ \eta_{\text{act}} = \frac{\eta_r}{\eta_r + \eta_{nr}} = \frac{\tau}{\tau_0} \]
(Anti proportional to decay time)

\[ \text{Internal Quantum Efficiency} \]
\[ \text{IQE} = \eta_{\text{act}} \]
\[ \text{External Quantum Efficiency} \]
\[ \text{EQE} = \frac{N_{hv(\text{emitted})}}{N_{hv(\text{absorbed})}} = \eta_{\text{transfer}} \times \eta_{\text{act}} \times \eta_{\text{esc}} \]
(No correlation to decay time!)

\[ \text{Light Yield} \]
\[ \text{LY} = \text{EQE} \times \eta_{\text{abs}} = \text{EQE} \times (1 - R) \]
(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

![Energy level diagram](Diagram)

\[ E_g \]

CB (Conduction Band)

$(A^{n+})^*$

$A^{n+}$ (Anion)

VB (Valence Band)
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 \( \sim \sqrt{S} \)

- **Quenching temperature 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
   - $4f \rightarrow 4f$ 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 photoionization
   - $4f \rightarrow 5d$ 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 $Pb^{2+}, Bi^{3+}, ...$
Width of the transitions can be explained by the model “harmonic oscillator”

\[ F = -k(r - r_0) \]

: Integration

\[ \Rightarrow E = -\frac{1}{2}k(r - r_0)^2 \]

Quantum mechanics provides: \( E_v = (v + 1/2)\hbar \nu \)

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 → 4f absorption lines)

\( r_{0g} < r_{0e} \Rightarrow \) broad bands (4fn → 4fn+1L⁻¹, 4fn → 4fn⁻15d, 6s² → 6s6p)
8.8 Thermal Quenching

Example: SrGa$_2$S$_4$:Eu$^{2+}$

- $T_{1/2}$ = 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**

![Graph showing light yield as a function of temperature.](image)

**Spectral width of the emission band of \(\text{BaMgAl}_{10}\text{O}_{17} \cdot \text{Eu} \)** as a function of the temperature

![Graph showing spectral width.](image)

**Stokes shift**

\(\text{BaMgAl}_{10}\text{O}_{17} \cdot \text{Eu} < (\text{Ba},\text{Sr})_{2}\text{SiO}_{4} \cdot \text{Eu} < (\text{Sr},\text{Ca})_{2}\text{SiO}_{4} \cdot \text{Eu}\)

**Thermal quenching**

\(\text{BaMgAl}_{10}\text{O}_{17} \cdot \text{Eu} < (\text{Ba},\text{Sr})_{2}\text{SiO}_{4} \cdot \text{Eu} < (\text{Sr},\text{Ca})_{2}\text{SiO}_{4} \cdot \text{Eu}\)

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

Incoherent Light Sources
Prof. Dr. T. Jüstel, FH Münster

Chapter Luminescence Mechanisms
Slide 39
8.8 Thermal Quenching

Some Rules

• Decreases 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!)

\[
\frac{dN_e}{dt} = -N_e * P_{eg}
\]

\[\Rightarrow \frac{dN_e}{N_e} = -P_{eg} * dt : \text{Integration} \]

\[\Rightarrow \ln\left(\frac{dN_e(t)}{N_e(0)}\right) = -P_{eg} * t \]

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

<table>
<thead>
<tr>
<th>Transition</th>
<th>Time scale</th>
<th>Oscillator strength</th>
<th>Activators</th>
</tr>
</thead>
<tbody>
<tr>
<td>“allowed”</td>
<td>~ 10^{-9} s</td>
<td>f ~ 0.1</td>
<td>Eu^{2+}, Ce^{3+}</td>
</tr>
<tr>
<td>“weak”</td>
<td>~ 10^{-6} s</td>
<td>f ~ 0.001</td>
<td>Pr^{3+}, Nd^{3+}</td>
</tr>
<tr>
<td>“forbidden”</td>
<td>~ 10^{-3} s</td>
<td>f ~ 10^{-5}</td>
<td>Eu^{3+}, Mn^{2+}</td>
</tr>
</tbody>
</table>
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 \(\Rightarrow\) No energy transfer e.g. to impurities such as Fe$^{3+}$ or Cr$^{3+}$

Deviation from mono-exponential decay \(\Rightarrow\) quenching, energy transfer, afterglow, ....
8.10 Luminescence of Transition Metal Ions

Absorption processes of $d^n$-ions $\rightarrow$ Tanabe-Sugano diagrams

Energy level diagram of a $d^1$-ion (Ti$^{3+}$, V$^{4+}$, Cr$^{5+}$, Mn$^{6+}$): RS-terms $\Rightarrow 2D_{3/2}$

<table>
<thead>
<tr>
<th>Ion</th>
<th>Configuration</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$^{3+}$</td>
<td>[Ar]$d^1$</td>
<td>Al$_2$O$_3$:Ti (Sapphire)</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>[Ar]$d^3$</td>
<td>Al$_2$O$_3$:Cr (Ruby)</td>
</tr>
<tr>
<td>Mn$^{4+}$</td>
<td>[Ar]$d^3$</td>
<td>Mg$<em>4$GeO$</em>{5.5}$F:Mn</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>[Ar]$d^5$</td>
<td>Zn$_2$SiO$_4$:Mn (Willemite)</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>[Ar]$d^5$</td>
<td>LiAlO$_2$:Fe</td>
</tr>
</tbody>
</table>

$d$-$d$ transitions are parity-forbidden
$\Rightarrow$ low absorption coefficient
$\Rightarrow$ high concentration needed
## 8.10 Luminescence of Transition Metal Ions

### Absorption in glasses, laser crystals and phosphors

<table>
<thead>
<tr>
<th>Ion</th>
<th>Configuration</th>
<th>Colour</th>
<th>Pigment</th>
<th>Structure type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$^{3+}$</td>
<td>d$^1$</td>
<td>violet, brown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V$^{3+}$</td>
<td>d$^2$</td>
<td>green</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V$^{4+}$</td>
<td>d$^1$</td>
<td>green, blue</td>
<td>(Zr,V)SiO$_4$</td>
<td>Zircon</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>d$^3$</td>
<td>green, yellow</td>
<td>Cr$_2$O$_3$</td>
<td>Corundum</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>d$^5$</td>
<td>light pink</td>
<td>MnO</td>
<td>NaCl</td>
</tr>
<tr>
<td>Mn$^{3+}$</td>
<td>d$^4$</td>
<td>violet</td>
<td>Mn$_2$O$_3$</td>
<td>Corundum</td>
</tr>
<tr>
<td>Mn$^{4+}$</td>
<td>d$^3$</td>
<td>red, brown</td>
<td>MnO$_2$</td>
<td>Rutile</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>d$^5$</td>
<td>yellow, brown</td>
<td>Fe$_2$O$_3$</td>
<td>Corundum</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>d$^6$</td>
<td>blue, green</td>
<td>Fe(C$_2$O$_4$)$\cdot$2H$_2$O</td>
<td></td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>d$^7$</td>
<td>blue, violet</td>
<td>CoAl$_2$O$_4$</td>
<td>Spinel</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>d$^8$</td>
<td>green</td>
<td>NiO</td>
<td>NaCl</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>d$^9$</td>
<td>blue, green</td>
<td>CuO</td>
<td></td>
</tr>
</tbody>
</table>
8.10 Luminescence of Transition Metal Ions

Absorption processes of transition metal ions with d⁰-configuration

Examples: VO₄³⁻, NbO₄³⁻, TaO₄³⁻, CrO₄²⁻, MoO₄²⁻, WO₄²⁻, MnO₄⁻

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

\[ \text{O}^{2-} \rightarrow \text{Me}^{n+} \text{ or } \text{p(non-bonding)} \rightarrow \text{d(e₉: anti-bonding)} \]
Bond is weakened \( \Rightarrow \Delta R \gg 0 \Rightarrow \) broad absorption band

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>Absorption [cm⁻¹]</th>
<th>CN</th>
<th>Polyhedron</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaWO₄</td>
<td>40000</td>
<td>4</td>
<td>Tetrahedron</td>
</tr>
<tr>
<td>Ca₃WO₆</td>
<td>35000</td>
<td>6</td>
<td>Octahedron</td>
</tr>
</tbody>
</table>

\( \Rightarrow \) 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: $\text{Ga}^+, \text{In}^+, \text{Tl}^+, \text{Ge}^{2+}, \text{Sn}^{2+}, \text{Pb}^{2+}, \text{As}^{3+}, \text{Sb}^{3+}, \text{Bi}^{3+}$

Electron configuration of $s^2$-ions

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

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

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

Energy level diagram of $s^2$-ions

Excitation and emission spectra of $\text{BaYB}_9\text{O}_{16}:\text{Sb}^{3+}$

![Energy level diagram and spectra](image-url)
**8.11 Luminescence of Ions with $s^2$-Configuration**

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

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>Structure type</th>
<th>Stokes shift [cm$^{-1}$]</th>
<th>Half width [cm$^{-1}$]</th>
<th>QY [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaSi$_2$O$_5$:Pb</td>
<td>Sanbornite</td>
<td>10600</td>
<td>2700</td>
<td>90</td>
</tr>
<tr>
<td>Sr$_2$MgSi$_2$O$_7$:Pb</td>
<td>Akermanite</td>
<td>12000</td>
<td>4300</td>
<td>75</td>
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<tr>
<td>SrLaBO$_4$:Pb</td>
<td></td>
<td>17700</td>
<td>5300</td>
<td>65</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Parity</th>
<th>l</th>
<th>m_l</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>g</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>p</td>
<td>u</td>
<td>1</td>
<td>-1, 0, 1</td>
</tr>
<tr>
<td>d</td>
<td>g</td>
<td>2</td>
<td>-2, ..., 2</td>
</tr>
<tr>
<td>f</td>
<td>u</td>
<td>3</td>
<td>-3, ..., 3</td>
</tr>
</tbody>
</table>
# 8.12 Luminescence of Rare Earth Ions

## Electron configuration of rare earth metals and ions

### Metals

<table>
<thead>
<tr>
<th>[Xe]</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Pm</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
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<tbody>
<tr>
<td>6s</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
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<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>5d</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>4f</td>
<td>0</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>7</td>
<td>9</td>
<td>10</td>
<td>11</td>
<td>12</td>
<td>13</td>
<td>14</td>
<td>14</td>
</tr>
</tbody>
</table>

### Ions

<table>
<thead>
<tr>
<th>[Xe]</th>
<th>La$^{3+}$</th>
<th>Ce$^{3+}$</th>
<th>Pr$^{3+}$</th>
<th>Nd$^{3+}$</th>
<th>Pm$^{3+}$</th>
<th>Sm$^{3+}$</th>
<th>Eu$^{3+}$</th>
<th>Gd$^{3+}$</th>
<th>Tb$^{3+}$</th>
<th>Dy$^{3+}$</th>
<th>Ho$^{3+}$</th>
<th>Er$^{3+}$</th>
<th>Tm$^{3+}$</th>
<th>Yb$^{3+}$</th>
<th>Lu$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$^{4+}$</td>
<td>Pr$^{4+}$</td>
<td>Nd$^{4+}$</td>
<td>Sm$^{2+}$</td>
<td>Eu$^{2+}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4f</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
<td>11</td>
<td>12</td>
<td>13</td>
<td>14</td>
</tr>
</tbody>
</table>

### Example

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

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

- **4f**: ↑↑↑↑↑↑
- **5d**:         
- **6s**:         
- **6p**:         

**S** = $\Sigma s = 7/2$  
**L** = $|\Sigma l| = 0$

$S = 2S+1 = 8$  
L = „S“  
$\rightarrow$ strongly paramagnetic ions  
$\rightarrow$ LS-Term symbol $^8S$

### Spectroscopic terms

$2S+1L_J$
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]4fⁿ ions

Partly filled 4f-shell results in multiple electron configurations
Example: Tb³⁺ [Xe]4f⁸ → 8 electrons in 7 f-orbitals: 3003 different arrangements!

Free ion energy levels due to:
1. Electrostatic interactions (comparable to 3dⁿ ions)
2. Spin-orbit coupling (larger than for 3dⁿ ions)
3. Crystal field splitting (smaller than for 3dⁿ ions)

Ground state \( m_l = -3\ -2\ -1\ 0\ 1\ 2\ 3 \) \( 7F_6 \)

\[
\begin{array}{ccccccc}
\uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
4f
\end{array}
\]

1st excited state \( m_l = -3\ -2\ -1\ 0\ 1\ 2\ 3 \) \( 5D_4 \)

\[
\begin{array}{ccccccc}
\uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
4f
\end{array}
\]
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

<table>
<thead>
<tr>
<th>Incoherent Light Sources</th>
<th>Chapter Luminescence Mechanisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prof. Dr. T. Jüstel, FH Münster</td>
<td>Slide 54</td>
</tr>
</tbody>
</table>

**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$^{2+}$
1. Electrostatic interactions

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

\[ F^{(k)} = \frac{e^2}{4\pi \varepsilon_0} \int_0^\infty \int_0^\infty \frac{r_i^k}{r_{i+1}^k} \left[ R_{4f}^{\prime}(r_i) R_{4f}^{\prime}(r_j) \right]^2 r_i^2 r_j^2 \, dr_i \, dr_j \]

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)
2. Spin-orbit coupling

Spin-orbit coupling constant $\zeta$ increases throughout the lanthanide series, i.e. from $\zeta$(Ce) = 650 cm$^{-1}$ to $\zeta$(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 $2J+1$ levels
Crystal field splitting $\sim 100 \text{ cm}^{-1}$ + sensitive function of site symmetry

**Lu$_3$Al$_5$O$_{12}$:Nd$^{3+}$**

$^4F_{3/2} - ^4I_{11/2}$

$\Delta E = 203 \text{ cm}^{-1}$

six levels without external magnetic field

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

\[
\mathcal{H}_{c}^{O_{n}} = B_0^4 \left[ C_0^{(4)} + \sqrt{\frac{5}{14}} (C_{-4}^{(4)} + C_4^{(4)}) \right] + B_0^6 \left[ C_0^{(6)} - \sqrt{\frac{7}{2}} (C_{-4}^{(6)} + C_4^{(6)}) \right]
\]
In summary: RE ions exhibit a great number of energy levels $^{2S+1}L_J$

<table>
<thead>
<tr>
<th></th>
<th>Ce (Yb)</th>
<th>Pr (Tm)</th>
<th>Nd (Er)</th>
<th>Pm (Ho)</th>
<th>Sm (Dy)</th>
<th>Eu (Tb)</th>
<th>Gd</th>
</tr>
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<tbody>
<tr>
<td>n</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
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<td>6</td>
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<td>364</td>
<td>1001</td>
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<td>3432</td>
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</tbody>
</table>

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”
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

8.12 Luminescence of Rare Earth Ions

Complete energy level diagram

<table>
<thead>
<tr>
<th>Ion</th>
<th>Energy Level Splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$^{3+}$</td>
<td>~</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>~ ~</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>~ ~ ~</td>
</tr>
<tr>
<td>Pm$^{3+}$</td>
<td>~ ~ ~ ~</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>~ ~ ~ ~ ~</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>~ ~ ~ ~ ~ ~</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td></td>
</tr>
</tbody>
</table>

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 $\sim 0 \, \text{cm}^{-1}$

2) Little influence of environment on energy level scheme

3) Parity forbidden transitions ($\sim \text{ms life time, } f \sim 10^{-5}$)

**Origin:** Shielding of $4f^n$ electrons by outer filled 5s and 5p shells

$\rightarrow$ 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\(_2\)SiO\(_5\):Eu)
8.12 Luminescence of Rare Earth Ions

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

- LuBO$_3$:Eu
  - Calcite

- (Y,Gd)BO$_3$:Eu
  - Vaterite

- Y$_2$O$_3$:Eu
  - Bixbyite

- Y(V,P)O$_4$:Eu
  - Xenotime
8.12 Luminescence of Rare Earth Ions

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

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>CIE1931 colour point</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Y,Gd)BO$_3$:Eu</td>
<td>x: 0.640 y: 0.360</td>
</tr>
<tr>
<td>Y$_2$O$_3$:Eu</td>
<td>x: 0.641 y: 0.344</td>
</tr>
<tr>
<td>YVO$_4$:Eu</td>
<td>x: 0.645 y: 0.343</td>
</tr>
<tr>
<td>Y$_2$O$_2$S:Eu</td>
<td>x: 0.650 y: 0.342</td>
</tr>
</tbody>
</table>

Colour saturation: Y$_2$O$_2$S:Eu > YVO$_4$:Eu > Y$_2$O$_3$:Eu > (Y,Gd)BO$_3$:Eu
8.12 Luminescence of Rare Earth Ions

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

- Observed emission spectrum due to \(^5\!D_0 \rightarrow \!^7\!F_J\) transitions (lines)
  - a) Inversion symmetry (\(S_6, D_{3d}\))
    - Magnetic dipole transitions, e.g. \(^5\!D_0 - \!^7\!F_1\)
    - \(\Delta J = 0, \pm 1\) (\(J = 0 \rightarrow J = 0\) forbidden)
    - MeBO\(_3\):Eu (Calcite, Vaterite)
      - \(\tau \sim 8 - 16\) ms
  - b) No inversion symmetry
    - Electric dipole transitions \(^5\!D_0 - \!^7\!F_{2,4}\)
    - \(\Delta J \leq 6\) (\(J_i = 0 \rightarrow J_f = 2, 4, 6\))
    - Y\(_2\)O\(_3\):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$^{3+}$**

- Spin- and parity forbidden transitions
- Strong CT absorption band (broad)
- Weak 4f-4f absorption lines (narrow)

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

- Spin- and parity allowed transitions
- Strong 4f-5d absorption bands (broad)

$\text{Eu}^{3+} \rightarrow (\text{Eu}^{3+})^{**}$

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

$(\text{Eu}^{3+})^{**} \rightarrow (\text{Eu}^{3+})^*$

$(\text{Eu}^{2+})^{**} \rightarrow (\text{Eu}^{2+})^*$  
Relaxation

$(\text{Eu}^{3+})^* \rightarrow \text{Eu}^{3+}$

$(\text{Eu}^{2+})^* \rightarrow \text{Eu}^{2+}$  
Relaxation

4f-4f

5d-4f

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Energy gap between the \([\text{Xe}]4f^n\) and \([\text{Xe}]4f^{n-1}5d^1\) states

\[
\begin{align*}
\varepsilon_c & : \text{Centroid energy proportional to the spectroscopic polarizability } \alpha_{sp} \\
(3000 – 20000 \text{ cm}^{-1}) \\
\varepsilon_{cfs} & : \text{Crystal field splitting (< 23000 cm}^{-1})
\end{align*}
\]
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 akermanite benitoite montmorillonite
  - zircon thortveitite talc
  - olivine kaolinite

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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)
  \[ D = \frac{35Ze}{4R^5} \]
  \[ R = \text{Cation-anion distance} \]
  \[ Z = \text{Valence of the anion} \]
  \[ e = \text{Electron charge} \]
## 8.12 Luminescence of Rare Earth Ions

### Covalent character of ionic bonds

<table>
<thead>
<tr>
<th>Host lattice</th>
<th>Cation</th>
<th>Type of network former</th>
<th>Covalent character of ionic bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>YPO$_4$</td>
<td>Y$^{3+}$</td>
<td>$\text{PO}_4^{3-}$</td>
<td>Low charge density $3/4^-$ per oxygen</td>
</tr>
<tr>
<td>Y$_3$Al$<em>5$O$</em>{12}$</td>
<td>Y$^{3+}$</td>
<td>$\text{AlO}_4^{5-}$, $\text{AlO}_6^{9-}$</td>
<td>High charge density $5/4^-$ or $9/4^-$ per oxygen</td>
</tr>
</tbody>
</table>

$P^{5+}$ 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$_4$**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$4 \times O(1)$</td>
<td>7.248</td>
</tr>
<tr>
<td>$4 \times O(2)$</td>
<td>7.193</td>
</tr>
</tbody>
</table>

Low charge density on oxygen

**$Y_3Al_5O_{12}$**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$4 \times O(1)$</td>
<td>7.528</td>
</tr>
<tr>
<td>$4 \times O(2)$</td>
<td>7.504</td>
</tr>
</tbody>
</table>

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
- 4f $\varepsilon_{cfs}$

Crystal field splitting $\sim$ 18000 cm$^{-1}$
Centroid shift $\sim$ 9600 cm$^{-1}$

(P. Dorenbos, Phys. Rev. B, 64, 2001, 1251)

$\Rightarrow$ Large 4f-5d energy gap
$\Rightarrow$ Emission bands at 335 and 355 nm
8.12 Luminescence of Rare Earth Ions

Luminescence of $\text{Y}_3\text{Al}_5\text{O}_{12} \cdot \text{Ce}$

- Distorted dodecahedral

Y-O distances
- $4x$ 2.30 Å
- $4x$ 2.44 Å

Crystal field splitting $\sim 27000$ cm$^{-1}$
Centroid shift $\sim 14700$ cm$^{-1}$


$\Rightarrow$ Small 4f-5d energy gap
$\Rightarrow$ Emission bands at 560 nm
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

\[ [\text{Xe}]4f^2 \rightarrow 13 \text{ SLJ-States} \]

\[ \begin{array}{c}
\uparrow \uparrow \uparrow \\
4f \\
\downarrow \downarrow \\
5d
\end{array} \]

Pr\(^{3+}\) excited state configuration

\[ [\text{Xe}]4f^15d^1 \rightarrow 2 \text{ SLJ-States} \]

\[ \begin{array}{c}
\uparrow \\
4f \\
\uparrow
\end{array} \]

\[ \downarrow \]

\[ 5d \]

\[ \Rightarrow [\text{Xe}]4f^2 - [\text{Xe}]4f^2 \text{ transitions} \]

\[ \Rightarrow [\text{Xe}]4f^2 - [\text{Xe}]4f^15d^1 \text{ transitions} \]
8.12 Luminescence of Rare Earth Ions

Fundamentals of Pr$^{3+}$ luminescence

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8.12 Luminescence of Rare Earth Ions

Emission spectra of Pr\(^{3+}\) phosphors

\(^1\)S\(_0\) \(-\) \(^{2}\)S\(_1\) \(L_J\) line emission

- YF\(_3\):Pr
- NaYF\(_4\):Pr
- SrAl\(_{12}\)O\(_{19}\):Pr
- LaMgB\(_5\)O\(_{10}\):Pr
- LaB\(_3\)O\(_6\):Pr

\(^1\)S\(_0\) \(-\) \(^{2}\)S\(_1\) \(L_J\) lines and \(4f^15d^1 - 4f^2\) band emission

- KY\(_3\)F\(_{10}\):Pr 213, 236
- 252, 271
- 407 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\(_2\)Si\(_2\)O\(_7\):Pr 273 nm
- Lu\(_3\)Al\(_5\)O\(_{12}\):Pr 310 nm
- Y\(_3\)Al\(_5\)O\(_{12}\):Pr 320 nm + line emission

\(^1\)D\(_2\) \(-\) \(^3\)H\(_J\) line emission

- Y\(_2\)O\(_3\):Pr 615 nm
- CaTIO\(_3\):Pr,Na 615 nm

UV band emission

Blue emission

Red emission

Energy of the lowest crystal field component of \([\text{Xe}]4f^15d^1\) 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
- $\sim$ 8000 cm$^{-1}$

Centroid shift
- $\sim$ 5600 cm$^{-1}$

CFS + centroid shift reduces energy of lowest crystal field component of the [Xe]4f$^1$5d$^1$ configuration by $\sim$ 10000 cm$^{-1}$

$\Rightarrow$ E(4f$^1$5d$^1$) > E($^1$S$_0$)

$\Rightarrow$ $^1$S$_0$ $\rightarrow$ 2S+1$L_J$ line emission
**8.12 Luminescence of Rare Earth Ions**

**Luminescence of YPO$_4$:Pr**

![Diagram of YPO$_4$:Pr]

- **Y-O distances**
  - 4x 2.24 Å
  - 4x 2.24 Å

- **CF splitting**
  - ~ 12000 cm$^{-1}$

- **Centroid shift**
  - ~ 9600 cm$^{-1}$

**Energy Diagram**

- $\epsilon_{\text{cfs}}$

**Wavelength [nm]**

- Host lattice
- 4f$^1$5d$^1$
- $^3H_4$
- $^3H_5$
- $^3H_6$
- $^3F_J$

**Distorted dodecahedral**

- Centroid shift reduces energy of lowest crystal field component of the [Xe]4f$^1$5d$^1$ configuration by ~ 16000 cm$^{-1}$

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

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

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8.12 Luminescence of Rare Earth Ions

Luminescence of $Y_3Al_5O_{12}$:Pr

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]$4f^{1}5d^{1}$ configuration by ~ 26000 cm$^{-1}$

$\Rightarrow E(4f^{1}5d^{1}) \ll E(^{1}S_{0})$

$\Rightarrow$ UV band emission (320 nm) and visible line emission (> 450 nm)
First examples (1974)

Sources: Sommerdijk et al., J. Lumin. 8 (1974) 288 (Philips),
Sommerdijk et al., J. Lumin. 8 (1974) 341 (Philips), and
Piper et al., J. Lumin. 8 (1974) 344 (GE)

YF$_3$:Pr(0.1%) and NaYF$_4$:Pr(0.1%)

$^1$S$_0$ - $^3$P$_1$, $^1$I$_6$ transition @ 407 nm

$^3$P$_0$ - $^3$H$_J$, $^3$F$_2$ transitions in the red

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

Derived from line ratio UV to blue to green/red

Oxidic luminescent materials to show photon cascade emission (PCE)

Source: 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$_5$O$_{10}$:Pr

LaB$_3$O$_6$:Pr
8.13 Down-Conversion

Example: LiGdF$_4$:Eu

Energy level diagram

- Gd $\rightarrow$ 202 nm $\rightarrow$ Gd**
- Gd** + Eu $\rightarrow$ Eu* + Gd*
- Eu* $\rightarrow$ Eu + hv
- Gd* + Eu $\rightarrow$ Gd + Eu*
- Eu* $\rightarrow$ Eu + hv

QY$_A$ = 195%
8.13 Down-Conversion

Example: LiGdF₄:Er,Tb

Energy level diagram

\[
\begin{align*}
\text{Er} & \quad > 210 \text{ nm} & \quad \text{Er}^{**} \\
\text{Er}^{**} + \text{Gd} & \xrightarrow{\text{CR}} \text{Er}^{*} + \text{Gd}^{*} \\
\text{Er}^{*} & \quad \rightarrow \quad \text{Er} + \text{hv} \\
\text{Gd}^{*} + \text{Tb} & \xrightarrow{\text{ET}} \text{Gd} + \text{Tb}^{*} \\
\text{Tb}^{*} & \quad \rightarrow \quad \text{Tb} + \text{hv} \\
\text{QY}_A & = 130\% 
\end{align*}
\]

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8.14 Up-Conversion

**Principle**

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

**Examples**

- $\text{YF}_3:\text{Yb},\text{Tm}$
- $\text{YF}_3:\text{Yb},\text{Er}$
- $\text{NaYF}_4:\text{Yb},\text{Er}$
- $\text{BaY}_2\text{F}_8:\text{Yb},\text{Er}$
- $\text{YOCl}:\text{Yb},\text{Er}$

- 20-35% $\text{Yb}^{3+}$
- 1-5% $\text{Er}^{3+}$ or $\text{Tm}^{3+}$
8.15 Afterglow

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

Shallow traps: Release of electrons from traps is done by ambient thermal energy
Deep traps: Release of electrons from traps is done by stimulation (PSL or TSL)

Example: Ba(F,Br):Eu Storage phosphor for imaging plates (detection of x-rays)
8.15 Afterglow

Deep traps: Storage phosphors - Example: $\text{Cs}_2\text{NaYF}_6:\text{Ce}$ and $\text{Cs}_2\text{NaYF}_6:\text{Pr}$ (elpasolite)

\[ A = \text{Ce, Pr} \]

Deep traps: Storage phosphors - Application

Process

1. Charging of the material, e.g. by high energy particles, x-rays, or UV radiation
2. Stimulation of energy release to induce luminescence
   - Thermally stimulated luminescence
     (TSL: $T \gg 300 \text{ K}$)
   - Photostimulated luminescence
     (PSL: Laser activation)

In a storage phosphor radiation energy is stored inside the material by traps and the light of interest is not produced until the material is activated, either by thermal or optical stimulation. Thus information on the radiation can be obtained at a time later than the actual interaction.
## 8.15 Afterglow

### Deep traps: Storage phosphors – Overview

#### Established materials

- **Ba(F,Br):Eu$^{2+}$**: PSL
- **RbBr:Tl$^+$**: PSL
- **SrS:Eu$^{2+}$,Sm$^{3+}$**: PSL
- **Ba$_3$(PO$_4$)$_2$:Eu$^{2+}$**: PSL
- **Ba$_2$B$_5$O$_9$Br:Eu$^{2+}$**: PSL
- **Ba$_7$Cl$_2$F$_{12}$:Eu$^{2+}$**: PSL
- **Ba$_{12}$Cl$_5$F$_{19}$:Eu$^{2+}$**: PSL
- **Y$_2$SiO$_5$:Ce$^{3+}$**: PSL
- **Ba$_5$SiO$_4$Br$_6$:Eu$^{2+}$,Nb$^{3+}$**: PSL and TSL (150 °C)
- **Sr$_5$(PO$_4$)$_3$Cl:Eu$^{2+}$**: PSL and TSL (157 °C)
- **Li$_6$Gd$_{0.5}$Y$_{0.5}$(BO$_3$)$_3$:Eu$^{3+}$**: PSL and TSL (177 °C)
- **LiSr$_4$(BO$_3$)$_3$:Ce$^{3+}$**: PSL and TSL (200 °C)
- **LiCaAlF$_6$:Eu$^{2+}$**: PSL and TSL (240 °C)
- **LiYSiO$_4$:Ce$^{3+}$**: PSL and TSL (260 °C)
8.15 Afterglow

Shallow traps: Thermal release of charge carriers at ambient temperature

Example
SrAl$_2$O$_4$:Eu,Dy

(Source: Nemoto Ltd., JECS 143 (1996) 2670)
### 8.15 Afterglow

#### Afterglow phosphors

<table>
<thead>
<tr>
<th>Composition</th>
<th>Colour</th>
<th>$\lambda_{\text{max}}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaAl$_2$O$_4$:Eu,Nd</td>
<td>blue</td>
<td>440 nm</td>
</tr>
<tr>
<td>Sr$_2$MgSi$_2$O$_7$:Eu,Dy</td>
<td>blue</td>
<td>469 nm</td>
</tr>
<tr>
<td>Sr$<em>4$Al$</em>{14}$O$_{25}$:Eu,Dy</td>
<td>cyan</td>
<td>490 nm</td>
</tr>
<tr>
<td>Mg$_2$SnO$_4$:Mn$^{2+}$</td>
<td>cyan</td>
<td>499 nm</td>
</tr>
<tr>
<td>SrAl$_2$O$_4$:Eu,Dy</td>
<td>green</td>
<td>520 nm</td>
</tr>
<tr>
<td>ZnS:Cu,Co</td>
<td>green</td>
<td>530 nm</td>
</tr>
<tr>
<td>Sr$_2$SiO$_4$:Eu,Dy</td>
<td>yellow</td>
<td>570 nm</td>
</tr>
<tr>
<td>Y$_2$O$_2$S:Eu,Ti,Mg</td>
<td>red</td>
<td>620 nm</td>
</tr>
<tr>
<td>CaZnGe$_2$O$_6$:Mn</td>
<td>red</td>
<td>648 nm</td>
</tr>
<tr>
<td>CaS:Eu,Tm</td>
<td>red</td>
<td>655 nm</td>
</tr>
<tr>
<td>MgSiO$_3$:Eu,Dy,Mn</td>
<td>red</td>
<td>660 nm</td>
</tr>
<tr>
<td>SrSc$_2$O$_4$:Eu</td>
<td>red</td>
<td>685 nm</td>
</tr>
</tbody>
</table>

**Example:** Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Ln$^{3+}$

![Graph showing emission spectra](image-url)