8. Luminescence Mechanisms

Content

8.1 Luminescence – Definition, Materials and Processes
8.2 Absorption
8.3 Excitation Mechanisms
8.4 Energy Transfer
8.5 Cross-Relaxation
8.6 Loss Processes
8.7 Configuration Coordinate Diagram
8.8 Thermal Quenching
8.9 Lifetime of the Excited State
8.10 Luminescence of Transition Metal Ions
8.11 Luminescence of Ions with s²-Configuration
8.12 Luminescence of Rare Earth Ions
8.13 Down-Conversion
8.14 Up-Conversion
8.15 Afterglow
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!
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 – Requirements for high efficiency

Strong absorption, efficient energy transfer, and high internal quantum yield:

- Highly crystalline particles, low defect density
- High purity (99.99% or higher)
- Redox stable optical centres
- Homogeneous distribution of optical centres
- 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!
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8.1 Luminescence – Materials

Inorganic luminescent materials – The role of the host lattice

- Conduction band (CB)
- Band gap $E_g$
- Valence band (VB)

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

YBO$_3$ (Vaterite)
Band gap $E_g = 6.5$ eV
8.1 Luminescence – Materials

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
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8.1 Luminescence – Materials

Inorganic luminescent materials – The role of the dopants

YVO₄ (tetragonal), $E_g = 4.2 \text{ eV}$

YPO₄:V,Eu (tetragonal), $E_g = 8.2 \text{ eV}$

Absorption via

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

Inorganic luminescent materials – The role of the dopants

+ Host lattice
+ Defects (colour centers)
+ Dopants (impurities)
**8.1 Luminescence - Processes**

- **Energy** [eV]
  - **S0**, **S1**, **S2**, **T1**, **A0**, **A1** = Energy levels of activator and sensitizer ions

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

- **ET** = Energy transfer

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**The overall picture**

- **Conduction band (empty metal orbitals)**
  - **Excitation**
  - **Fluorescence** \( \sim 10^{-9}s \)
  - **Relaxation**

- **Valence band (anion orbitals filled by electrons)**
  - **Excitation**
  - **ET**

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Chapter Luminescence Mechanisms
Slide 8
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 > Eg

Eg

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### 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 $^{2S+1}L_J$</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\(^{3+}\) [Xe]4f\(^1\) (2F\(_{5/2}\)) \( \rightarrow \) [Xe]5d\(^1\) (2D\(_{3/2}\)) \( \Rightarrow \) allowed \( \sim \) ns
- Eu\(^{3+}\) [Xe]4f\(^6\) (7F\(_{0}\)) \( \rightarrow \) [Xe]4f\(^6\) (5D\(_{0}\)) \( \Rightarrow \) forbidden \( \sim \) ms
### Incoherent Light Sources

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<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>γ-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)**

Absorption by activators or sensitizers

Absorption by host lattice

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

\[
R = \frac{250A}{\rho Z^{n/2}} U^n \text{ with } n = \frac{1,2}{1 - 0,29\log_{10}Z}
\]

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

For 5.7 keV electrons

For a material with \( r = 5.0 \) g/cm³ (Y₂O₃)

10 kV electrons \( R \sim 400 \) nm
2 kV electrons \( R \sim 30 \) nm
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

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Chapter Luminescence Mechanisms
Slide 14
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: $\text{EQE} = \eta_{act} \times \eta_{transfer} \times \eta_{esc}$

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

**Activator excitation**

\[ \text{IQE} = \eta_{\text{act}} = \frac{k_r}{k_r + k_{nr}} = \frac{\tau}{\tau_0} \]

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

**Sensitizer excitation**

\[ \text{EQE} = \eta_{\text{act}} \times \eta_{\text{transfer}} \times \eta_{\text{esc}} \]
8.3 Excitation Mechanisms

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

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

---

**Reflection spectra**

- Host lattice
- Eu$^{2+}$
- 4f$^7$ - 4f$^6$5d$^1$

**Emission and excitation spectra**

- Host lattice
- 4f$^7$ - 4f$^6$5d$^1$
- 4f$^6$5d$^1$ - 4f$^7$
8.3 Excitation Mechanisms

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

- **Host material** $\text{VB} \rightarrow \text{CB}$
- **$\text{Mn}^{2+}$** $\text{[Ar]}3\text{d}^5 \rightarrow \text{[Ar]}3\text{d}^5$
- **Forbidden transition** $\Rightarrow$ Weak absorption bands and slow decay (~10 ms)

- Reflection spectra
- Emission and excitation spectra

- Wavelength [nm]:
  - VB $\rightarrow$ CB: 180 nm (7.0 eV)
  - 3d$^5$ $\rightarrow$ 3d$^5$: 200 nm (6.2 eV) and 450 nm (2.8 eV)

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Chapter Luminescence Mechanisms
Slide 18
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% $\text{Eu}^{3+}$

Reflection spectra

Emission and excitation spectra

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

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

- Forbidden transitions $\Rightarrow$ Weak absorption bands and slow decay ($\sim$3 ms)

$[\text{Xe}]4f^6 \rightarrow [\text{Xe}]4f^6$  
395 nm (3.1 eV) and 465 nm (2.2 eV)
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 $[\text{Xe}]4f^{n-1}5d^1$ configuration → $\text{Tb}^{3+}, \text{Eu}^{2+}, \text{Ce}^{3+}, \text{Pr}^{3+}$

- Sensitisation (via energy transfer)
  - $\text{Ce}^{3+}$ → $\text{Tb}^{3+}$
  - $\text{Pr}^{3+}$ → $\text{Tb}^{3+}$
  - $\text{Nd}^{3+}$ → $\text{Gd}^{3+}$
  - $\text{Pr}^{3+}$ → $\text{Gd}^{3+}$
  - $\text{Bi}^{3+}$ → $\text{Eu}^{3+}$
  - $\text{Sb}^{3+}$ → $\text{Mn}^{2+}$
  - $\text{Ce}^{3+}$ → $\text{Mn}^{2+}$
  - $\text{Eu}^{2+}$ → $\text{Mn}^{2+}$
Requirements for ET ($S^* + A \rightarrow S + A^*$)

- Sensitizer $S$ and activator $A$ interact with each other by
  - Coulomb interaction (multipolar interaction)
    
    Dipole-Dipole: \[ P_{SA} = \frac{1}{\tau_S} \frac{r_0}{r_{SA}}^6 \] \( \text{Ce}^{3+} - \text{Eu}^{2+} \)
    
    Dipole-Quadrupole: \[ P_{SA} = \frac{1}{\tau_S} \frac{r_0}{r_{SA}}^8 \] \( \text{Ce}^{3+} - \text{Tb}^{3+} \)
    
    Quadrupole-Quadrupole: \[ P_{SA} = \frac{1}{\tau_S} \frac{r_0}{r_{SA}}^{10} \] unknown

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

- Spectral overlap (\( \rightarrow \) Energy conservation law!)
Probability $P_{ET}$

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

$$P_{ET} = (2\pi/\hbar) \rho \langle \phi_i | H | \phi_f \rangle^2$$

- $\phi_i$: Wave function of the initial state
- $\phi_f$: Wave function of the final state
- $H$: Operator coupling the states
- $\rho$: Spectral overlap (energy conservation)

Spectral overlap

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

$g_S(E)$ 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 LaPO$_4$:Ce,Tb

LaPO$_4$:Ce

\[ \text{Ce}^{3+} \rightarrow (\text{Ce}^{3+})^* \]
\[ (\text{Ce}^{3+})^* \rightarrow \text{Ce}^{3+} \]

Excitation 4f - 5d

LaPO$_4$:Tb

\[ \text{Tb}^{3+} \rightarrow (\text{Tb}^{3+})^{**} \]
\[ (\text{Tb}^{3+})^{**} \rightarrow (\text{Tb}^{3+})^* \]
\[ (\text{Tb}^{3+})^* \rightarrow \text{Tb}^{3+} \]

Relaxation

Excitation 4f - 5d

LaPO$_4$:Ce,Tb

\[ \text{Ce}^{3+} \rightarrow (\text{Ce}^{3+})^* \]
\[ (\text{Ce}^{3+})^* + \text{Tb}^{3+} \rightarrow \text{Ce}^{3+} + (\text{Tb}^{3+})^* \]
\[ (\text{Tb}^{3+})^* \rightarrow \text{Tb}^{3+} \]

ET from Ce$^{3+}$ to Tb$^{3+}$

Emission 4f - 4f

Fluorescent lamps \(\Rightarrow\) Excitation at 254 nm

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Slide 25
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
- **Divalent TM ions**: tetrahedral gaps in the spinel blocks
- **Trivalent TM ions**: octahedral gaps in the spinel blocks

Energy Transfer

- $\lambda_{UV}$
- $\lambda_1$
- $\lambda_2$
Example: ET in BaMgAl_{10}O_{17}:Eu co-doped by transition metal ions

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

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

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

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

\[ \text{Mn}^{2+} \rightarrow (\text{Mn}^{2+})^* \]  
Absorption 3d - 3d

\[ (\text{Mn}^{2+})^* \rightarrow \text{Mn}^{2+} \]  
Emission 3d – 3d

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

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

\[ (\text{Eu}^{2+})^* + \text{Mn}^{2+} \rightarrow \text{Eu}^{2+} + (\text{Mn}^{2+})^* \]  
ET from Eu to Mn

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

- **Energy pathways**:
  - VUV Excitation: 172 nm
  - UV Excitation: 254 nm, 370 nm, 453 nm
  - Energy Transfer: 515 nm

- **Energy levels**:
  - $E_g = 7.0$ eV ($\sim 180$ nm)
  - $\text{[Xe]}4f^7$
  - $\text{[Xe]}4f^65d^1$
  - $\text{[Ar]}3d^5$
  - $\text{[Ar]}3d^{5*}$

- **Excitation sites**:
  - EUV Excitation
  - UV Excitation

- **Emission**:
  - 515 nm

- **Defect**
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.

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Chapter Luminescence Mechanisms
Slide 30
### 8.6 Loss Processes

Related to the host lattice and host lattice activator interaction

#### Internal Quantum Efficiency

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

(Anti proportional to decay time)

#### External Quantum Efficiency

- **EQE** = $N_{hv(\text{emitted})} / N_{hv(\text{absorbed})}$
- **EQE** = $\eta_{\text{transfer}} \times \eta_{act} \times \eta_{esc}$

(No correlation to decay time!)

#### Light Yield

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

(No correlation to decay time!)
Photoionization

\[ E_g \]
\[ \text{CB} \]
\[ (A^{n+})^* \]
\[ A^{n+} \]
\[ \text{VB} \]

- 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
  \[ S = S_e \hbar \omega_e + S_g \hbar \omega_g \]

- **Full width at half maximum of the emission band**
  \[ \text{FWHM} \sim \sqrt{S} \]

- **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
   - $4f \to 4f$ transitions (shielded 4f-shell: small crystal field splitting [CFS])
   - Lines $Eu^{3+}, Tb^{3+}, \ldots$

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

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

Width of the transitions can be explained by the model “harmonic oscillator”

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

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

Franck-Condon principle: Electrons motion is much faster than nuclear motion \( \rightarrow \) “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\textsuperscript{n} \( \rightarrow \) 4f\textsuperscript{n+1}L\textsuperscript{-1}, 4f\textsuperscript{n} \( \rightarrow \) 4f\textsuperscript{n-1}5d, 6s\textsuperscript{2} \( \rightarrow \) 6s6p)
8.8 Thermal Quenching

Model based on a two-level systems: Example SrGa$_2$S$_4$:Eu$^{2+}$

- Mathematical fit: $I(T) = A_0 + I_0/(1 + B \exp(-\Delta E/k_B T))$ „Struck-Fonger-Model“
- $T_{1/2} = \text{Temperature at which the phosphor loses 50\% of its initial emission intensity (here \sim 170 \, ^\circ C)} \sim \text{activator-host lattice interaction}$
- In many industrially applied phosphors the quantum yield starts to decline between 100 and 150 \, ^\circ C
8.8 Thermal Quenching

Eu$^{2+}$ activated phosphors

Stokes shift

Thermal quenching

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

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Chapter Luminescence Mechanisms
Slide 37
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 $\Delta r = r_e - r_g$ and thus with Stokes Shift

• 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!)

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

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

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

\[ \Rightarrow N_e(t) = N_e(0) \exp\left(-\frac{P_{eg}}{\tau}\right) \quad \text{with} \quad \tau = \frac{1}{P_{eg}} \]

<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>$\sim 10^{-9}$ s</td>
<td>$f \sim 0.1$</td>
<td>Eu$^{2+}$, Ce$^{3+}$</td>
</tr>
<tr>
<td>“weak”</td>
<td>$\sim 10^{-6}$ s</td>
<td>$f \sim 0.001$</td>
<td>Pr$^{3+}$, Nd$^{3+}$</td>
</tr>
<tr>
<td>“forbidden”</td>
<td>$\sim 10^{-3}$ s</td>
<td>$f \sim 10^{-5}$</td>
<td>Eu$^{3+}$, Mn$^{2+}$</td>
</tr>
</tbody>
</table>
8.9 Lifetime of the Excited State

Typical decay curves

\( \text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+} \) (\( \tau = 1 \ \mu\text{s} \))

\( \text{(Y,Gd)BO}_3:\text{Eu}^{3+} \) (\( \tau = 3.5 \ \text{ms} \))

Mono-exponential decay \( \Rightarrow \) No energy transfer e.g. to impurities such as \( \text{Fe}^{3+} \) or \( \text{Cr}^{3+} \)

Deviation from mono-exponential decay \( \Rightarrow \) quenching, energy transfer to defects or impurity ions, afterglow and so on
8.10 Luminescence of Transition Metal Ions

Absorption processes of \(d^n\)-ions → Tanabe-Sugano diagrams

Energy level diagram of a \(d^1\)-ion (Ti\(^{3+}\), V\(^{4+}\), Cr\(^{5+}\), Mn\(^{6+}\)):

- **RS-terms**: \(\Delta \Rightarrow ^2D_{3/2}\)
- **CF-terms**: \(\Rightarrow ^2T_2 + ^2E\)

<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>(\text{Al}_2\text{O}_3:\text{Ti}) (Sapphire)</td>
</tr>
<tr>
<td>Cr(^{3+})</td>
<td>[Ar](d^3)</td>
<td>(\text{Al}_2\text{O}_3:\text{Cr}) (Ruby)</td>
</tr>
<tr>
<td>Mn(^{4+})</td>
<td>[Ar](d^3)</td>
<td>(\text{Mg}<em>4\text{GeO}</em>{5.5}\text{F}:\text{Mn})</td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>[Ar](d^5)</td>
<td>(\text{Zn}_2\text{SiO}_4:\text{Mn}) (Willemite)</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>[Ar](d^5)</td>
<td>(\text{LiAlO}_2:\text{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>Al$_2$O$_3$ : Ti</td>
<td>Corundum</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$_4$) · 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 $d^0$-configuration

Examples: $\text{VO}_4^{3-}$, $\text{NbO}_4^{3-}$, $\text{TaO}_4^{3-}$, $\text{CrO}_4^{2-}$, $\text{MoO}_4^{2-}$, $\text{WO}_4^{2-}$, $\text{MnO}_4^{-}$

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

$\text{O}^{2-} \rightarrow \text{Me}^{n+}$ or $\text{p(non-bonding)} \rightarrow \text{d(e}_{g} \text{: anti-bonding)}$

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>CaWO$_4$</td>
<td>40000</td>
<td>4</td>
<td>Tetrahedron</td>
</tr>
<tr>
<td>Ca$_3$WO$_6$</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: 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$_9$O$_{16}$:Sb$^{3+}$

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Chapter Luminescence Mechanisms
Slide 44
8.11 Luminescence of Ions with $s^2$-Configuration

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

<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>
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<tbody>
<tr>
<td>BaSi$_2$O$_5$·Pb</td>
<td>Sanbornite</td>
<td>10600</td>
<td>2700</td>
<td>90</td>
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<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>
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</table>

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Chapter Luminescence Mechanisms  
Slide 45
Lanthanides originate 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>
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<tr>
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<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>
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</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

<table>
<thead>
<tr>
<th>Metals</th>
<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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<td>1</td>
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<td>10</td>
<td>11</td>
<td>12</td>
<td>13</td>
<td>14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ions</th>
<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>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Ce$^{4+}$</td>
<td>Pr$^{4+}$</td>
<td>Nd$^{4+}$</td>
<td>Sm$^{2+}$</td>
<td>Eu$^{2+}$</td>
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<td>9</td>
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<td>12</td>
<td>13</td>
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</table>

#### Example

<table>
<thead>
<tr>
<th>Gd$^{3+}$/Eu$^{2+}$</th>
<th>m_l</th>
<th>-3</th>
<th>-2</th>
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</tr>
</tbody>
</table>

### Spectroscopic terms

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

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

$2S+1L_J$
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
Energy level structure of $[\text{Xe}]4f^n$ ions

Partly filled 4f-shell results in multiple electron configurations
Example: Tb$^{3+}$ $[\text{Xe}]4f^8 \rightarrow$ 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 \( m_l = -3 \ -2 \ -1 \ 0 \ 1 \ 2 \ 3 \ \ 7F_6 \)

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

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

\[
\begin{array}{cccccc}
\uparrow & \uparrow & \uparrow & \uparrow & \downarrow & \uparrow & \downarrow \\
4f
\end{array}
\]
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>Energy [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
</tr>
<tr>
<td>0.5x10$^4$</td>
</tr>
<tr>
<td>1.0x10$^4$</td>
</tr>
<tr>
<td>1.5x10$^4$</td>
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<tr>
<td>2.0x10$^4$</td>
</tr>
<tr>
<td>2.5x10$^4$</td>
</tr>
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<td>3.0x10$^4$</td>
</tr>
<tr>
<td>3.5x10$^4$</td>
</tr>
<tr>
<td>4.0x10$^4$</td>
</tr>
</tbody>
</table>

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Chapter Luminescence Mechanisms
Slide 52
1. Electrostatic interactions

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

\[
F^{(k)}(k) = \frac{e^2}{4\pi\varepsilon_0} \int_0^\infty \int_0^\infty \frac{r_i^k}{r_{i+1}^k} \left[ R'_4(r_i)R'_4(r_j) \right] r_i^2 r_j^2 \, dr_i \, dr_j
\]

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:

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

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

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

$^4F_{3/2} \rightarrow ^4I_{11/2}$

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

six levels without external magnetic field

Extra fitting parameters $B_{kq}$ to graphically fit experimentally observed levels:

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

Dodecahedral coordination
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>
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<td>91</td>
<td>364</td>
<td>1001</td>
<td>2002</td>
<td>3003</td>
<td>3432</td>
</tr>
</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

Complete energy level diagram

\[
\begin{align*}
\text{Ce}^{3+} & \sim \text{Yb}^{3+} \\
\text{Pr}^{3+} & \sim \text{Tm}^{3+} \\
\text{Nd}^{3+} & \sim \text{Er}^{3+} \\
\text{Pm}^{3+} & \sim \text{Ho}^{3+} \\
\text{Sm}^{3+} & \sim \text{Dy}^{3+} \\
\text{Eu}^{3+} & \sim \text{Tb}^{3+} \\
\text{Gd}^{3+} &
\end{align*}
\]

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)
Example: Eu$^{3+}$ - Typical excitation and emission spectra (Example: 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 col. point applications</th>
<th>x</th>
<th>y</th>
<th>applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Y,Gd)BO$_3$:Eu</td>
<td></td>
<td>0.640</td>
<td>0.360</td>
<td>PDP</td>
</tr>
<tr>
<td>Y$_2$O$_3$:Eu</td>
<td></td>
<td>0.641</td>
<td>0.344</td>
<td>CFL, PL, TL</td>
</tr>
<tr>
<td>YVO$_4$:Eu</td>
<td></td>
<td>0.645</td>
<td>0.343</td>
<td>Hg-HP-Lamps</td>
</tr>
<tr>
<td>Y$_2$O$_2$S:Eu</td>
<td></td>
<td>0.650</td>
<td>0.342</td>
<td>CRT</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

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Chapter Luminescence Mechanisms
Slide 63
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Chapter Luminescence Mechanisms
Slide 64

8.12 Luminescence of Rare Earth Ions

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. $^{5}D_{0} \rightarrow ^{7}F_{1}$
$\Delta J = 0, \pm 1 (J = 0 \rightarrow J = 0$ forbidden)
MeBO$_3$:Eu (Calcite, Vaterite)
$\tau \sim 8 - 16$ ms

b) No inversion symmetry
Electric dipole transitions $^{5}D_{0} \rightarrow ^{7}F_{2,4}$
$\Delta J \leq 6 (J_{i} = 0 \rightarrow J_{f} = 2, 4, 6)$
Y$_2$O$_3$:Eu (Bixbyite), Y(V,P)O$_4$:Eu (Xenotime)
$\tau \sim 2 - 5$ ms
Excitation and emission spectra of Eu$^{3+}$ and Eu$^{2+}$ activated phosphors

**Y$_2$O$_3$:Eu$^{3+}$**

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

**BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$**

- Strong 4f-5d absorption bands (broad)

Spin- and parity allowed transitions

Spin- and parity forbidden transitions

**Eu$^{3+}$ → (Eu$^{3+}$)**

CT

- Relaxation

- 4f-4f

Strong CT absorption band (broad)

Weak 4f-4f absorption lines (narrow)

**Eu$^{2+}$ → (Eu$^{2+}$)**

4f-5d

- Relaxation

- 5d-4f

Strong 4f-5d absorption bands (broad)
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Chapter Luminescence Mechanisms
Slide 66

8.12 Luminescence of Rare Earth Ions

Ce$^{3+}$

$[\text{Xe}]4f^1$ $[\text{Xe}]5d^1$

$^2F_{\text{7/2}}$ $^2D_J$

Eu$^{2+}$

$[\text{Xe}]4f^7$

$6P_{\text{7/2}} - 8S_{\text{7/2}}$

YPO$_4$:Ce(10%)

Intensity [a.u.]

Wavelength [nm]

$4f - 5d$ Excit.

$5d - 4f$ Emission

NaMgF$_3$:Eu$^{2+}$(1.0%)

$6D_{9/2}$ $6I_{7/2}$ $6P_{7/2}$ $8H_J$

Intensity [a.u.]

Wavelength [nm]

$Emission$ $Ex= 268 \text{ nm}$ $Em= 361 \text{ nm}$ $5d - 4f$
8.12 Luminescence of Rare Earth Ions

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

- **Electrostatic interaction**
- **Centroid shift**
- **Crystal field splitting**
- **Stokes shift**

\[ [\text{Xe}]^{4f^n-15d^1} \]

\[ \varepsilon_c : \text{Centroid energy proportional to the spectroscopic polarizability } \alpha_{sp} \]
\[ (3000 \text{ -- } 20000 \text{ cm}^{-1}) \]

\[ \varepsilon_{cfs} : \text{Crystal field splitting} \ (< 23000 \text{ cm}^{-1}) \]

**Energy [10^3 cm^{-1}]**

- Ce\(^{3+}\): 49340 cm\(^{-1}\)
- Pr\(^{3+}\): 61580 cm\(^{-1}\)
- Nd\(^{3+}\): 72100 cm\(^{-1}\)
- Gd\(^{3+}\): 95200 cm\(^{-1}\)
- Eu\(^{2+}\): 34000 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
  - $O^{2-}$    $\text{AlO}_4^{5-}$  $\text{SiO}_4^{4-}$  $\text{BO}_3^{3-}$  $\text{PO}_4^{3-}$  $\text{SO}_4^{2-}$
- **Degree of networking**
  - neso-silicate  soro-silicate  cyclo-silicate  phyllo-silicate
  - $[\text{SiO}_4]^{4-}$  $[\text{Si}_2\text{O}_7]^{6-}$  $[\text{Si}_3\text{O}_9]^{6-}$  $[\text{Si}_4\text{O}_{10}]^{4-}$
  - garnet  akermanite  benitoite  montmorillonite
  - zircon  thortveitite  talc
  - olivine  kaolinite
Crystal field splitting

Crystal field theory $\Rightarrow$ ionic interaction between metal center and point charges

Energy splitting of the d-orbitals depends on:

- Anionic charge / anionic radius (spectrochemical series of solid state compounds)
  \[ I^- < Br^- < Cl^- < S^{2-} < F^- < O^{2-} < N^{3-} < C^{4-} \]

- 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>
</tr>
</thead>
<tbody>
<tr>
<td>YPO₄</td>
<td>Y³⁺</td>
<td>Low charge density 3/4⁻ per oxygen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>tetrahedral PO₄⁻⁵⁻</td>
</tr>
<tr>
<td>Y₃Al₅O₁₂</td>
<td>Y³⁺</td>
<td>High charge density 5/4⁻ or 9/4⁻ per oxygen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>tetrahedral AlO₄⁻⁵⁻ + octahedral AlO₆⁻⁹⁻</td>
</tr>
</tbody>
</table>

- P⁵⁺ attracts more charge density of the O²⁻ anions than Al³⁺
8.12 Luminescence of Rare Earth Ions

Electron density on the anions

**YPO₄**

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

Low charge density on oxygen

**Y₃Al₅O₁₂**

- 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 YPO₄:Ce

Distorted dodecahedral

Y-O distances

4x 2.24 Å
4x 2.24 Å

Crystal field splitting \(\sim 18000 \text{ cm}^{-1}\)
Centroid shift \(\sim 9600 \text{ cm}^{-1}\)

\(\text{(P. Dorenbos, Phys. Rev. B, 64, 2001, 1251)}\)

\(\Rightarrow\) Large 4f-5d energy gap
\(\Rightarrow\) Emission bands at 335 and 355 nm

\(\varepsilon_{\text{cfs}}\)
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 $\sim 27000 \text{ cm}^{-1}$
Centroid shift $\sim 14700 \text{ cm}^{-1}$


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

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Chapter Luminescence Mechanisms
Slide 73
8.12 Luminescence of Rare Earth Ions

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

- **YF\(_3\):Pr**
- **YPO\(_4\):Pr**
- **Y\(_2\)O\(_3\):Pr**

**4f\(^1\)5d\(^1\)-4f\(^2\) band emission**

**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

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

\[ \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \]

\( 4f \quad 5d \)

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

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

\[ \uparrow \uparrow \uparrow \]

\( 4f \quad 5d \)

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

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

Fundamentals of Pr$^{3+}$ luminescence

- [Xe]4f$^2$ [Xe]4f$^1$5d$^1$ K$_h$ site
- O$_h$ site
- distorted O$_h$ site

Energy [10$^3$ cm$^{-1}$]

- $^1S_0$
- $^1D_2$
- $^1G_4$
- $^3P_0$, $^3P_1$, $^1I_6$
- $^3P_2$
- $^3F_3$, $^3F_4$
- $^3H_6$, $^3F_2$
- $^3H_4$, $^3H_5$

8.12 Luminescence of Rare Earth Ions

Emission spectra of Pr$^{3+}$ phosphors

- $^1S_0 - ^2S_{L_J}$ line emission
  - YF$_3$:Pr
  - NaYF$_4$:Pr
  - SrAl$_{12}$O$_{19}$:Pr
  - LaMgB$_5$O$_{10}$:Pr
  - LaB$_3$O$_6$:Pr
- $^1S_0 - ^2S_{L_J}$ lines and $4f^{15d_1} - 4f^2$ band emission
  - KY$_3$F$_{10}$:Pr  213, 236, 252, 271, 407 nm
  - KYF$_4$: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$_2$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
- $^1D_2 - ^3H_J$ line emission
  - Y$_2$O$_3$:Pr  615 nm
  - CaTiO$_3$:Pr,Na  615 nm
8.12 Luminescence of Rare Earth Ions

Luminescence of YF₃:Pr

Distorted square-antiprismatic

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

ε_{cfs}

CF splitting
- ~ 8000 cm⁻¹

Centroid shift
- ~ 5600 cm⁻¹

CFS + centroid shift reduces energy of lowest crystal field component of the [Xe]4f¹5d¹ configuration by ~ 10000 cm⁻¹

⇒ E(4f¹5d¹) > E(¹S₀)
⇒ ¹S₀ → ²S+¹L₂ line emission
Luminescence of YPO$_4$:Pr

- Distorted dodecahedral
- Y-O distances
  - $4 \times 2.24 \, \text{Å}$
  - $4 \times 2.24 \, \text{Å}$
- CF splitting
  - $\sim 12000 \, \text{cm}^{-1}$
- Centroid shift
  - $\sim 9600 \, \text{cm}^{-1}$

CFS + centroid shift reduces energy of lowest crystal field component of the [Xe]4f$^1$5d$^1$ configuration by $\sim 16000 \, \text{cm}^{-1}$

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

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

Luminescence of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Pr}$

Distorted dodecahedral

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

- CF splitting:
  - $\sim 22500$ cm$^{-1}$

- Centroid shift:
  - $\sim 14700$ cm$^{-1}$

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

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

$\Rightarrow$ UV band emission (320 nm) and visible line emission (> 450 nm)
8.13 Down-Conversion

First examples (1974)


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 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: LiGdF₄:Eu

Energy level diagram

- Gd → Gd**
- Gd** + Eu$^{\text{CR}}$ → Eu* + Gd*
- Eu* → Eu + hν
- Gd* + Eu$^{\text{ET}}$ → Gd + Eu*
- Eu* → Eu + hν

QYA = 195%

202 nm

612 nm

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Chapter Luminescence Mechanisms
Slide 82
8.13 Down-Conversion

Example: LiGdF₄:Er,Tb

Energy level diagram

\[ \text{Er} \rightarrow > 210 \text{ nm} \rightarrow \text{Er}^{**} \]

\[ \text{Er}^{**} + \text{Gd} \rightarrow \text{Er}^* + \text{Gd}^* \]

\[ \text{Er}^* \rightarrow \text{Er} + \text{hv} \]

\[ \text{Gd}^* + \text{Tb} \rightarrow \text{Gd} + \text{Tb}^* \]

\[ \text{Tb}^* \rightarrow \text{Tb} + \text{hv} \]

\[ \text{QY}_A = 130\% \]
8.14 Up-Conversion

<table>
<thead>
<tr>
<th>Principle</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>YF₃:Yb,Tm</td>
</tr>
<tr>
<td></td>
<td>YF₃:Yb,Er</td>
</tr>
<tr>
<td></td>
<td>NaYF₄:Yb,Er</td>
</tr>
<tr>
<td></td>
<td>BaY₂F₈:Yb,Er</td>
</tr>
<tr>
<td></td>
<td>YOCl:Yb,Er</td>
</tr>
</tbody>
</table>

20-35% Yb³⁺
1-5% Er³⁺ or Tm³⁺

Implementation of IR radiation into visible
(in frequency multipliers, laser diodes, night vision goggles)
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: Cs$_2$NaYF$_6$:Ce and Cs$_2$NaYF$_6$:Pr (elpasolite)

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: $T \gg 300$ 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

- $\text{Ba}(\text{F,Br}):\text{Eu}^{2+}$
- $\text{RbBr}:\text{Tl}^+$
- $\text{SrS}:\text{Eu}^{2+},\text{Sm}^{3+}$
- $\text{Ba}_3(\text{PO}_4)_2:\text{Eu}^{2+}$
- $\text{Ba}_2\text{B}_5\text{O}_9\text{Br}:\text{Eu}^{2+}$
- $\text{Ba}_7\text{Cl}_2\text{F}_{12}:\text{Eu}^{2+}$
- $\text{Ba}_{12}\text{Cl}_5\text{F}_{19}:\text{Eu}^{2+}$
- $\text{Y}_2\text{SiO}_5:\text{Ce}^{3+}$
- $\text{Ba}_5\text{SiO}_4\text{Br}_6:\text{Eu}^{2+},\text{Nb}^{3+}$
- $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$
- $\text{Li}_6\text{Gd}_{0.5}\text{Y}_{0.5}(\text{BO}_3)_3:\text{Eu}^{3+}$
- $\text{LiSr}_4(\text{BO}_3)_3:\text{Ce}^{3+}$
- $\text{LiCaAlF}_6:\text{Eu}^{2+}$
- $\text{LiYSiO}_4:\text{Ce}^{3+}$

- PSL
- PSL (150 °C)
- PSL (157 °C)
- PSL (177 °C)
- PSL (200 °C)
- PSL (240 °C)
- PSL (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

Shallow traps: 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 and intensity over time for different phosphors.](attachment:image.png)