Efficiency and Thermal Quenching of UV Phosphors


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Outline

• Application areas of UV-R radiation
• (Fluorescent) UV Light Sources
• Overview UV-R phosphors
• VUV Efficiency of UV-R Phosphors
• Thermal quenching
• From micro to nanoscale materials
• Conclusions
## Applications Areas of UV-R Radiation

<table>
<thead>
<tr>
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<th>VUV</th>
<th>UV-C</th>
<th>UV-B</th>
<th>UV-A</th>
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<tbody>
<tr>
<td>100 nm</td>
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<td>200 nm</td>
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<td>280 nm</td>
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</table>

### 12.5 - 6.9 eV
- Cleavage of $\text{H}_2\text{O}$ and $\text{O}_2$ into radicals
- Ozone formation
- Cleavage of $\text{C-C}$, $\text{C-H}$, $\text{C-O}$ bonds
- Waver cleaning
- Photochemistry

### 6.2 – 4.5 eV
- Excitation of $\text{C=C}$ bonds
- Excitation of nucleobases
- Cleavage of $\text{O}_3$, $\text{ClO}_2$ and $\text{H}_2\text{O}_2$
- Disinfection of air, $\text{H}_2\text{O}$ and surfaces
- Photochemistry

### 4.5 - 3.9 eV
- Vitamine D production
- Transcription of repair enzymes
- Melanosome formation (skin)
- Treatment of skin diseases, e.g. psoriasis
- Tanning

### 3.9 – 3.1 eV
- Photocatalytic reactions
- Melanine oxidation (skin)
- Decomposition of organic pigments
- Water and air purification by means of $\text{TiO}_2$ photocatalyst
- Tanning
Biological Effects of UV-R Radiation

UV-C

- Excitation of nucleobases (point mutations + cell death)
- Cleavage of $O_3$, $H_2O_2$, $ClO_2$

UV-B and UV-A

- Immediate pigmentation (melanin oxidation)
- Persistent pigmentation (melanosome formation)
- Vitamin D production
- Psoriasis treatment
- Erythema (sunburn)

Prof. Dr. T. Jüstel, March 1st, 2005
UV Light Sources

Sunlight

> 300 nm

Hg discharge lamps

• low pressure 185, 254 nm
• medium pressure (+ filter) 200 - 400 nm
• low pressure + phosphor 200 - 400 nm

Excimer discharge lamps

• $\text{Xe}_2^*$ 172 nm
• $\text{XeCl}^*$ 308 nm
• $\text{Xe}_2^*$ + phosphor 200 - 400 nm

Solar UV spectrum

TUV lamp

Xeradex lamp

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Fluorescent UV Light Sources

**Hg low pressure discharge lamp**

- Wavelength: 185 nm, 254 nm

**Xe₂⁺ excimer discharge lamp**

- Wavelength: 147 nm, 150 nm, 172 nm

### Graphs

- **Normalized emission intensity**
  - X-axis: Wavelength [nm]
  - Y-axis: Normalized emission intensity

- **Emission intensity**
  - X-axis: Wavelength [nm]
  - Y-axis: Emission intensity

**UV Phosphor layer**

- Desired lamp spectrum

**German Patent**

- DE 199 19 169.7

**Lamp glass**

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Overview UV-R Phosphors

Commercial phosphors for fluorescent Hg low pressure lamps

- $\text{SrAl}_{12}\text{O}_{19}:\text{Ce}^{3+}$ 305 nm
- $\text{LaB}_3\text{O}_6:\text{Bi}^{3+},\text{Gd}^{3+}$ 311 nm
- $\text{LaPO}_4:\text{Ce}^{3+}$ 320 nm
- $\text{LaMgAl}_{11}\text{O}_{19}:\text{Ce}^{3+}$ 340 nm
- $(\text{Y},\text{Gd})\text{PO}_4:\text{Ce}^{3+}$ 335, 355 nm
- $\text{BaSi}_2\text{O}_5:\text{Pb}^{2+}$ 350 nm
- $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Pb}^{2+}$ 365 nm
- $\text{SrB}_4\text{O}_7:\text{Eu}^{2+}$ 370 nm
- $\text{BaSO}_4:\text{Eu}^{2+}$ 375 nm
Overview UV-R Phosphors

Fluorescent Hg low pressure lamps for cosmetic purposes

1st Generation

Ba$_2$Si$_2$O$_5$:Pb
or Sr$_2$MgSi$_2$O$_7$:Pb

2nd Generation

Ba$_2$Si$_2$O$_5$:Pb
+ LaPO$_4$:Ce

3rd Generation

YPO$_4$:Ce
+ LaPO$_4$:Ce

Stability of Pb$^{2+}$ phosphors limits lamp lifetime
Quantum efficiency upon 254 nm excitation of these phosphors is larger than 90%
Overview UV-R Phosphors

Fluorescent Hg low pressure lamps for medical purposes

Standard phosphor
LaB$_3$O$_6$:Bi$^{3+}$,Gd$^{3+}$

Novel material
Ce$^{3+}$ sensitised Gd$^{3+}$ phosphor

Shortcomings:
- Long-term stability
due to photochemistry of Bi$^{3+}$
- Hg consumption

Advantages:
- Efficient ET to Gd$^{3+}$
- Broad and intense Ce$^{3+}$ absorption
- Higher efficiency
VUV Efficiency of UV-R Phosphors

High VUV efficiency
⇒ potential application in fluorescent $Xe_2^*$ excimer discharge lamps

UV-A phosphors ($Ce^{3+}$ and $Pb^{2+}$ activated)

Efficiency: $LaMgAl_{11}O_{19}:Ce > YPO_4:Ce \sim BaSi_2O_5:Pb > Sr_2MgSi_2O_7:Pb$
VUV Efficiency of UV-R Phosphors

UV-B phosphors (Gd$^{3+}$ activated)

**Sensitisation of Gd$^{3+}$ for 172 nm excitation by**

- **Host lattice** suitable band edge required
- **Bi$^{3+}$** large lattice position (e.g. La$^{3+}$) required
- **Ce$^{3+}$** suitable 4f5d states required
- **Nd$^{3+}$** suitable 4f5d states required
- **Pr$^{3+}$** suitable 4f5d states required

**Nd$^{3+}$ sensitised Gd$^{3+}$ phosphor**

**Pr$^{3+}$ sensitised Gd$^{3+}$ phosphor**
VUV Efficiency of UV-R Phosphors

UV-B phosphors (Gd$^{3+}$ activated)

**Bi$^{3+}$ sensitised Gd$^{3+}$ phosphor**

$\text{Lu}_3\text{Al}_5\text{O}_{12}:1\% \text{Bi}, 0.1\% \text{Gd}$

- Band gap
- $6s \rightarrow 6p$
- $311 \text{ nm (Gd}^{3+}\text{)}$

**HL sensitised Gd$^{3+}$ phosphor**

$\text{YAl}_3(\text{BO}_3)_4:50\% \text{Gd}$

- $6P_{7/2} \rightarrow 6S_{7/2}$
- $6S_{7/2} \rightarrow 6I_{J}$

Co-doping by Gd$^{3+}$ results in 311 nm emission

Efficient ET from the host lattice to Gd$^{3+}$
VUV Efficiency of UV-R Phosphors

UV-C phosphors ⇒ Fluorescent $\text{Xe}_2^*$ excimer lamps for disinfection purposes

**Excitation Spectra**

- $\text{Pb}^{2+}$ sensitised
- $\text{Pr}^{3+}$ sensitised

**Emission Spectra**

- $\text{Pb}^{2+}$ sensitised
- $\text{Pr}^{3+}$ sensitised
**Xe$_2^*$ - Excimer Lamp with YBO$_3$:Pr**

Lamp spectrum shows strong overlap with the germicidal action spectrum.
<table>
<thead>
<tr>
<th>Phosphor</th>
<th>exc. band max.</th>
<th>em. band max.</th>
<th>light output 172 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaPO$_4$:Pr</td>
<td>165, 200 nm</td>
<td>225 nm</td>
<td>70%</td>
</tr>
<tr>
<td>YPO$_4$:Pr</td>
<td>160, 190 nm</td>
<td>233 nm</td>
<td>70%</td>
</tr>
<tr>
<td>Best practice</td>
<td>170 nm</td>
<td>241 nm</td>
<td>90%</td>
</tr>
<tr>
<td>(Ca,Mg)SO$_4$:Pb</td>
<td>170 nm</td>
<td>245 nm</td>
<td>80%</td>
</tr>
<tr>
<td>LuBO$_3$:Pr</td>
<td>240 nm</td>
<td>257 nm</td>
<td>50%</td>
</tr>
<tr>
<td>YBO$_3$:Pr</td>
<td>240 nm</td>
<td>261 nm</td>
<td>50%</td>
</tr>
<tr>
<td>Y$_2$SiO$_5$:Pr</td>
<td>170, 245 nm</td>
<td>270 nm</td>
<td>20%</td>
</tr>
<tr>
<td>SrSiO$_3$:Pb</td>
<td>170, 235 nm</td>
<td>275 nm</td>
<td>80%</td>
</tr>
<tr>
<td>LaPO$_4$:Ce</td>
<td>170, 270 nm</td>
<td>320 nm</td>
<td>90%</td>
</tr>
<tr>
<td>YPO$_4$:Ce</td>
<td>170, 270 nm</td>
<td>335, 355 nm</td>
<td>55%</td>
</tr>
<tr>
<td>LaMgAl$<em>{11}$O$</em>{19}$:Ce</td>
<td>170, 275 nm</td>
<td>340 nm</td>
<td>90%</td>
</tr>
</tbody>
</table>
Thermal Quenching - UV-A Phosphors

**Phosphor**  | **Stokes Shift [cm⁻¹]** | **FWHM [cm⁻¹]** | **QE_{254 RT} [%]** | **TQ_{1/2} [°C]**
---|---|---|---|---
BaSi₂O₅:Pb | 10600 | 2700 | 95 | 375
Sr₂MgSi₂O₇:Pb | 12000 | 4300 | 80 | 316
Thermal Quenching - UV-A Phosphors

**YPO$_4$:Ce**

*Emission spectra (254 nm excitation)*

- **TQ$_{1/2}$** is estimated to be above 700°C!
- **UV-B to UV-A ratio remains constant between RT and 330°C**
- **355 nm band increases at the cost of the 335 nm band with increasing temp.**
TQ_{1/2} of commercially available UV-B phosphors is above 400°C
VUV efficiency of LaPO_4:Ce increases from RT to 200°C
(more efficient ET from host lattice to Ce^{3+}?)
Thermal Quenching - UV-C Phosphors

**TQ\(_{1/2}\) of both phosphors is beyond 400°C**

Emission band of best practice phosphor shifts towards 250 nm upon heating
LnPO₄ is a stable host for many activators: Ce, Pr, Gd, Tb, ...
Synthesis in organic solvents with a high boiling point

LaPO₄:Ce,Tb from M. Haase et al.
Quantum efficiency ~ 60 % (40 % Tb³⁺ + 20 % Ce³⁺)
Microscale LaPO₄:Ce,Tb ~ 95%
From Micro to Nanoscale Materials

Alternative LnPO$_4$ synthesis approach
1. Complexation of Ln$^{3+}$
2. Destabilisation of Ln-complex
3. Precipitation of the phosphate

SEM: particle size < 50 nm
XRD: crystalline particles, particle size ~ 10 nm (Debye-Scherrer)
From Micro to Nanoscale Materials

Quantum efficiency of LaPO$_4$:Pr
- µm particles: ~ 70 %
- nm particles: ~ 55 %

Further materials synthesised: YPO$_4$:Pr, LuPO$_4$:Pr, YPO$_4$:Ce, LaPO$_4$:Ce
From Micro to Nanoscale Materials

YPO₄:Pr and LuPO₄:Pr as 235 nm Emitter

YPO₄:Pr (30 nm particles)

LuPO₄:Pr (5 nm particles)

\[ 4f^2 \rightarrow 5d^1 4f^1 \]
\[ 5d^1 4f^1 \rightarrow 3H_4 \]
Conclusions

UV Phosphors for Hg discharge lamps
- very efficient materials known, in particular LnPO$_4$:Ce (Ln = Y, La)
- wall load and lamp temperature increase results in stability problems ⇒ use coatings + avoid Pb$^{2+}$ phosphors
- thermal quenching is not a matter of concern

UV Phosphors for Xe$_2^*$ excimer discharge lamps
- UV-A phosphor with a high VUV efficiency is LaMgAl$_{11}$O$_{19}$:Ce
- Gd$^{3+}$ activated UV-B phosphors have to be sensitised
- efficient UV-C phosphors have been identified
- thermal quenching is not a matter of concern

Nanoscale Phosphors
- nanoscale ortho-phosphates (monazite and xenotime structure) can be synthesised via hydrolysis of RE-complexes
- efficiency is about 60 – 70% of microscale phosphors