Design and Degradation of UV Emitting Luminescent Materials for Xe Excimer Discharge Lamps

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Classification and impact of UV Radiation (100 - 380 nm)

Vacuum UV (100 - 200 nm)
- Photolysis of water
- Cleavage of N₂ and O₂
- Ozone formation

UV-C (200 - 280 nm) & UV-B (280 - 300 nm)
- Ozone cleavage

UV-B (300 - 320 nm) & UV-A (320 - 380 nm)
- Photochemical degradation of air pollutants
- Disinfection at photocatalytically active sites
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6. Phosphor Converted Xe Excimer Lamps - Degradation

7. Spin-off: Nanoscale UV Phosphors

8. Summary & Outlook
1. Motivation

Ongoing increase of water consumption and pollution

- UV-C Radiation (265 nm) inactivates microorganisms due to DNA modification
- VUV Radiation (180 - 200 nm) oxidizes due to H₂O cleavage into radical species

Industrial installations $\rightarrow$ discharge lamps
Mobile devices $\rightarrow$ discharge lamps or LEDs
1. Motivation

Ongoing increase of water consumption and pollution

Water impurities
- Microorganisms: Bacteria, viruses, spores, ...
- Chemical (micro)pollutants: Toxic, bioactive, or non-biodegradable organic compounds, NO$_3$-
- Micro & nanoplastics “Great Pacific Garbage Patch”

Trend to apply green chemistry for water treatment
- Avoid use of toxic/hazardous substances (Cl$_2$, ClO$_2$, NaOCl)
- Convert total organic compounds (TOC) to CO$_2$ and H$_2$O
- Introduce energy efficient and sustainable processes

- Biochemistry → Microorganism design, genetics
- Catalysis → Catalytic pigments and coatings
- Photochemistry → Frequency selective radiation sources
- Solar chemistry → Solar radiation + converter
- Fast analytics → Optical spectroscopy using radiation sources switchable in the ns-range

Ongoing increase of water consumption and pollution
2. Chemistry and Physics of LMs

A luminescent material (phosphor) converts absorbed energy into electromagnetic radiation beyond thermal equilibrium.

Host
- Coordination number and geometry
- Symmetry of activator sites
- Optical band gap
- Phonon spectrum

Dopants, impurities, and defects
- Concentration
- Phase diagram and miscibility gaps

Particle surface
- Zeta-potential
- Surface area
- Coatings → Light in- and outcoupling

Particle morphology
- Shape
- Particle size distribution
2. Chemistry and Physics of LMs

Relevant physical properties

- PL spectra
- CIE colour point
- Luminous efficacy
- Quantum yield (QY)
- Colour point consistency
- Decay curve
- Thermal quenching
- Linearity
- Stability under operation

**Excitation and emission spectrum of Mg$_2$TiO$_4$:Mn**

**Temp. dependent PL of selected LMs upon 254 nm excitation**

**Decay curves of SrSi$_2$N$_2$O$_2$:Eu**

**Linearity of YAG:Ce and LiEuMo$_2$O$_8$**
2. Chemistry and Physics of LMs

Quenching and degradation mechanisms

Reversible quenching

- Thermal quenching at high temperature
- Saturation at high power density

Irreversible degradation

- Dissolution/decomposition in applicat. medium
- Thermal oxidation or reduction of the activator
- Photo oxidation or reduction of the activator
- Reactions with the glass wall
- Reaction with discharge species, e.g. Hg or Xe
- Hydrolysis by moisture

Choose chemically stable and radiation hard host & activator e.g. Lu$_3$Al$_5$O$_{12}$:Gd$^{3+}$ (L80 => 10000 h!)

Otherwise: Particle coatings or lower activator conc.
# 3. UV Radiation Sources

## Overview

<table>
<thead>
<tr>
<th>Source</th>
<th>Wavelengths</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar radiation</td>
<td>&gt; 300 nm</td>
</tr>
<tr>
<td>Hg discharge lamps</td>
<td></td>
</tr>
<tr>
<td>low-pressure</td>
<td>185, 254 nm</td>
</tr>
<tr>
<td>amalgam</td>
<td>185, 254 nm</td>
</tr>
<tr>
<td>medium-pressure</td>
<td>200 – 400 nm</td>
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<tr>
<td>Xe discharge lamps</td>
<td>230 – 800 nm</td>
</tr>
<tr>
<td>D₂ discharge lamps</td>
<td>110 – 400 nm</td>
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<tr>
<td>Excimer laser</td>
<td>193 nm</td>
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<tr>
<td>Solid state laser Nd³⁺ 4ᵗʰ harmon.</td>
<td>266 nm</td>
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<tr>
<td>Excimer discharge lamps</td>
<td></td>
</tr>
<tr>
<td>Xe₂⁺</td>
<td>172 nm</td>
</tr>
<tr>
<td>KrCl⁺</td>
<td>222 nm</td>
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<tr>
<td>XeBr⁺</td>
<td>282 nm</td>
</tr>
<tr>
<td>XeCl⁺</td>
<td>308 nm</td>
</tr>
<tr>
<td>(Al,Ga)N LEDs</td>
<td>210 – 365 nm</td>
</tr>
<tr>
<td>(In,Ga)N LEDs</td>
<td>365 – 400 nm</td>
</tr>
</tbody>
</table>
3. UV Radiation Sources

Solar Radiation

~ 5% UV
~ 60% VIS
~ 35% IR

The solar spectrum depends on daytime & season, air pressure, clouds, particles (dust) and so on.
3. UV Radiation Sources

Direct radiation:
Filtered solar radiation

Diffuse radiation:
Scattered solar radiation

CCT = 5500 - 6500 K

~ 1000 W/m²

CCT = 10600 K

~ 50 W/m²

50 W/m² UV total and 0.1 W/m² UV-B

almost no UV radiation
3. UV Radiation Sources

Present trend: Use solar light & combine with traditional light sources, e.g. for water, air, and surface disinfection or for indoor illumination.
3. UV Radiation Sources

Hg vapour discharge lamps - Overview

<table>
<thead>
<tr>
<th></th>
<th>Low Pressure Hg</th>
<th>Amalgam</th>
<th>Medium Pressure Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-C wavelength</td>
<td>254 nm</td>
<td>254 nm</td>
<td>200 - 280 nm</td>
</tr>
<tr>
<td>Typical lamp power</td>
<td>4 ... 100 W</td>
<td>100 ... 300 W</td>
<td>1 ... 17 kW</td>
</tr>
<tr>
<td>Lamp efficiency</td>
<td>&lt; 40%</td>
<td>30 ... 35%</td>
<td>10 ... 15%</td>
</tr>
<tr>
<td>GAC factor</td>
<td>85%</td>
<td>85%</td>
<td>80%</td>
</tr>
<tr>
<td>UV-C power per length</td>
<td>0.2 W / cm</td>
<td>0.7 W / cm</td>
<td>15 W / cm</td>
</tr>
<tr>
<td>Wall temperature</td>
<td>40 °C</td>
<td>100 °C</td>
<td>600 - 800 °C</td>
</tr>
</tbody>
</table>

⇒ Selection based on application area and life cycle cost
3. UV Radiation Sources

**LEDs and laser diodes**

<table>
<thead>
<tr>
<th>Wavelength [nm]</th>
<th>LEDs</th>
<th>Laser diodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>375</td>
<td></td>
<td>400 nm</td>
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<tr>
<td>400</td>
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<td>425 nm</td>
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<td>450 nm</td>
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<td>465 nm</td>
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<tr>
<td>500</td>
<td></td>
<td>500 nm</td>
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<tr>
<td>525</td>
<td></td>
<td>525 nm</td>
</tr>
<tr>
<td>550</td>
<td></td>
<td>550 nm</td>
</tr>
</tbody>
</table>

**“LED platform“**

- 465 nm LEDs: Illumination
- 410 nm LEDs: Full conversion
- 365 nm LEDs: Black light
- 265 nm LEDs: Disinfection

**“Laserdiode platform“**

- 940 nm: Remote control
- 785 nm: CD
- 655 nm: DVD
- 405 nm: Blue ray DVD

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4. Xe Excimer Discharge Lamps

Devices using a dielectric barrier excimer discharge (either $O_2$ or $Xe$)

- **Ozone generator** (Wedeco AG)
- **Exhaust treatment** (Siemens AG)
- **UV Radiation sources** (Xenon) (Siemens AG)
- **Triton** (Heraeus Noblelight)
- **Flat lamp** for LCD backlighting (Osram AG)
- **Osram Xeradex**

**Devices using a dielectric barrier excimer discharge:**

- Ozone generator (Wedeco AG)
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- UV Radiation sources (Xenon) (Siemens AG)
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- Osram Xeradex
4. Xe Excimer Discharge Lamps

Lamp sketch and principle of working

\[ h\nu (190 - 700 \text{ nm}) = f(\text{luminescent screen}) \]

- **Electrode**
- **Dielectric**
- **Phosphor layer**

\[
\begin{align*}
  \text{Xe} & \rightarrow \text{Xe}^* \\
  \text{Xe}^* + 2 \text{Xe} & \rightarrow \text{Xe}_2^* \\
  \text{Xe}_2^* + \text{Xe} & \rightarrow 2 \text{Xe} + h\nu (172 \text{ nm}) \\
\end{align*}
\]

- **Surface discharge**
- **Micro discharge channel**
- **Surface discharge**

**Parameters:**

- \( p(\text{Xe}) = 300 \text{ mbar} \)
- \( P = 10 - 100 \text{ W} \)
- \( U = 3 - 5 \text{ kV} \)
- \( f = 10 - 50 \text{ kHz} \)
4. Xe Excimer Discharge Lamps

Xe and Xe₂* energy levels and discharge emission spectrum

**Excited monomeric Xe species:**
- Emits 147 nm (8.44 eV) Xe resonance line

**1st Emission continuum:**
- 148 nm (8.38 eV) 
  \[ \text{Xe}_2[0^+_{\text{U}}(3P_1)_{\text{high } n}] \rightarrow \text{Xe}_2[0^+_{\text{g}}(1S_0)] \]
- 152 nm (8.16 eV) 
  \[ \text{Xe}_2[1^+_{\text{U}}(3P_2)_{\text{high } n}] \rightarrow \text{Xe}_2[0^+_{\text{g}}(1S_0)] \]

**2nd Emission continuum:**
- 186 nm (7.38 eV) 
  \[ \text{Xe}_2[0^+_{\text{U}}(3P_1)_{\text{low } n}] \rightarrow \text{Xe}_2[0^+_{\text{g}}(1S_0)] \]
- 172 nm (7.21 eV) 
  \[ \text{Xe}_2[1^+_{\text{U}}(3P_2)_{\text{low } n}] \rightarrow \text{Xe}_2[0^+_{\text{g}}(1S_0)] \]
4. Xe Excimer Discharge Lamps

Xe excimer spectrum and typical lamp parameter

**Simplified reaction scheme**

\[ \text{Xe}(^1\text{S}_0) + e^- \rightarrow \text{Xe}(^3\text{P}_1) + e^- \]

\[ \text{Xe}(^3\text{P}_1) \rightarrow \text{Xe}(^1\text{S}_0) + h\nu_{147\text{nm}} \]

\[ \text{Xe}(^3\text{P}_1) + 2 \text{Xe} \rightarrow \text{Xe}_2(^3\Sigma_u^+) + \text{Xe} \]

\[ \text{Xe}_2(^3\Sigma_u^+) \rightarrow 2 \text{Xe}(^1\text{S}_0) + h\nu_{172\text{nm}} \]

**Example:** Osram XERADEX L40/120/SB-S46/85

- Power consumption = 20 W
- Diameter = 4 cm
- Length = 12 cm
- Wall load \( \sim 0.15 \) W/cm\(^2\)
- Output power = 6 W
- Power density = 0.04 W/cm\(^2\)
- Wall plug efficiency \( \sim 30\% \) (including driver)
5. VUV to UV Converter Design

UV Emitter - Suitable host lattices and activator ions

<table>
<thead>
<tr>
<th>VUV</th>
<th>UV-C</th>
<th>UV-B</th>
<th>UV-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 nm</td>
<td>200 nm</td>
<td>280 nm</td>
<td>320 nm</td>
</tr>
</tbody>
</table>

Host lattices

- Fluorides
- Phosphates
- Borates
- Silicates
- Aluminates

Activator ions

- Nd$^{3+}$
- Tl$^+$, Pb$^{2+}$, Pr$^{3+}$, Bi$^{3+}$
- Gd$^{3+}$, Bi$^{3+}$, Pr$^{3+}$, Ce$^{3+}$
- Tm$^{3+}$, Pb$^{2+}$, Ce$^{3+}$, Eu$^{2+}$
5. VUV to UV Converter Design

Pr$^{3+}$ energy level scheme - Host impact

Pr$^{3+}$ energy level scheme - Host impact
### 5. VUV to UV Converter Design

#### Pr³⁺ energy level scheme - Host impact

- **UV band emission**
  - YF₃:Pr
  - NaYF₄:Pr
  - SrAl₁₂O₁₉:Pr
  - LaMgB₅O₁₀:Pr
  - LaB₃O₆:Pr
  - Energy of the lowest crystal-field component of [Xe]⁴f¹⁵d¹

- **UV line emission**
  - ⁴f¹⁵d¹ – ⁴f² band emission
    - LiYF₄:Pr
    - YPO₄:Pr
    - KYF₄:Pr
    - YAIO₃:Pr
    - YBO₃:Pr
    - Lu₂Si₂O₇:Pr
    - Lu₃Al₅O₁₂:Pr
    - Y₃Al₅O₁₂:Pr
    - ⁴f¹⁵d¹ – ³H_J line emission
      - Y₂O₃:Pr
      - CaTiO₃:Pr,Na

- **Red emission**
  - Y₂O₃:Pr
  - CaTiO₃:Pr,Na
Pr³⁺ energy level scheme - Host impact

[Xe]⁴f¹⁵d¹ – [Xe]⁴f² vs. [Xe]⁴f² – [Xe]⁴f² emission

NaYF₄:Pr³⁺  213, 236 nm  hexagonal  CN 9  E([Xe]⁴f¹⁵d¹) > E(¹S₀)

KYF₄:Pr³⁺  235 nm  hexagonal  CN 7  E([Xe]⁴f¹⁵d¹) < E(¹S₀)
5. VUV to UV Converter Design

Pr\(^{3+}\) energy level scheme - Impact of the host

Situation in YPO\(_4\)  
\(E_g = 9.0\) eV

Distorted dodecahedra  
CN = 8

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

CF splitting  
\(~ 12000\) cm\(^{-1}\)

Centroid shift  
\(~ 9600\) cm\(^{-1}\)

CFS and centroid shift reduces energy of lowest crystal-field component of the [Xe]4f\(^1\)5d\(^1\) configuration by \(~ 22000\) cm\(^{-1}\)

\(\Rightarrow\) E(4f\(^1\)5d\(^1\)) below E(\(^1\)S\(_0\))  
\(\Rightarrow\) [Xe]4f\(^1\)5d\(^1\) - [Xe]4f\(^2\) band emission
5. VUV to UV Converter Design

Converter for different Xe excimer radiator applications

1. Water splitting and NO\textsubscript{x} removal
   - YPO\textsubscript{4}:Nd $190\ \text{nm}$

2. Mineralisation of $\mu$-pollutants: Pharmaceuticals, hormones, …
   - YPO\textsubscript{4}:Bi $241\ \text{nm}$
   - YPO\textsubscript{4}:Pr $235\ \text{nm}$
   - LaPO\textsubscript{4}:Pr $225\ \text{nm}$
   - CaSO\textsubscript{4}:Pr,Na $218\ \text{nm}$

3. Disinfection: Water, surfaces, air, …
   - YPO\textsubscript{4}:Bi $241\ \text{nm}$
   - CaLi\textsubscript{2}SiO\textsubscript{4}:Pr,Na $252\ \text{nm}$
   - YBO\textsubscript{3}:Pr $265\ \text{nm}$
   - Y\textsubscript{2}Si\textsubscript{2}O\textsubscript{7}:Pr $275\ \text{nm}$

4. Photopolymerisation: UV curing
   - Lu\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}:Gd $311\ \text{nm}$
   - LaMgAl\textsubscript{11}O\textsubscript{19}:Gd $311\ \text{nm}$
   - Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}:Pr $320\ \text{nm}$
5. VUV to UV Converter Design

Chosen converter material must be radiation hard

**YPO$_4$** as the host material
- mineral: Xenotime
- structure: Zircon type
- crystal system: tetragonal
- space group: $I4_1/amd$ (#141)

$\lambda_{\text{max}}$(YPO$_4$:Bi) = 241 nm

$\lambda_{\text{max}}$(YPO$_4$:Pr) = 235 nm

$\lambda_{\text{max}}$(YPO$_4$:Nd) = 193 nm

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T. Jüstel, H. Nikol, J. Dirscherl, W. Busselt, US 6398970 B1
5. VUV to UV Converter Design

Germicidal efficacy of doped ortho-phosphate YPO$_4$

Germicidal Action Curve (GAC): Efficacy of deactivation of E. Coli (DIN 5031-10)

$$\text{Eff}_{GAC}(\text{Phosphor}) = \frac{\int (Em_{\text{Phosphor}} \times GAC)}{\int Em_{\text{Phosphor}}}$$

Goal: Log-4 reduction

GAC-Eff (YPO$_4$:Bi) = 43.8 %

GAC-Eff (YPO$_4$:Pr) = 60.6 %

GAC-Eff (YPO$_4$:Nd) = 57.3 %
6. Phosphor Converted Xe Excimer Lamps

YP\textsubscript{4}O\textsubscript{4}:Bi or YP\textsubscript{4}O\textsubscript{4}:Pr comprising lamps

Goal: Degradation of sulfamethoxazol (antibiotic)

Source: N. Braun, GVB

Photolytical degradation by the use of a phosphor converted Xe excimer lamp allows a reduction of the required dose by 95% compared to an amalgam lamp

Source: A. Nietzsch, DLR
6. Phosphor Converted Xe Excimer Lamps

Lifetime of Xe excimer lamp comprising YPO$_4$:Bi or YPO$_4$:Ln

Choice was based on

LnPO$_4$ phosphors are stable in discharge lamps

Wide band gap ($E_g \sim 8.8$ eV) limits re-absorption

But: An YPO$_4$:Bi lamp has reached its rated end of life after just about 240 hours of operation if L70 is applied.
6. Phosphor Converted Xe Excimer Lamps

Lifetime of Xe excimer lamp comprising YPO₄:Bi or YPO₄:Ln

Lamp degradation due to several processes

YPO₄:Bi as-made and aged (PL and reflection spectra)

Discharge related
XeO* formation
Sputtering of central wire

Phosphor related
Reduction of Bi³⁺ → Bi²⁺, Bi⁺
Degradation of ortho-phosphate host (defects or phosphate reduction?)
6. Phosphor Converted Xe Excimer Lamps

Degradation of YPO₄:Bi, YPO₄:Pr, and undoped YPO₄

- **YPO₄:Bi³⁺**
- **YPO₄:Pr³⁺**
- **undoped YPO₄**

New absorption due to host degradation.
Temperature dependent spectroscopy on aged YPO$_4$ samples

Aged undoped YPO$_4$ shows intense red photoluminescence

Nature of luminescence process?

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6. Phosphor Converted Xe Excimer Lamps

Bi³⁺ doping

Pr³⁺ doping

YPO₄ host

Gd³⁺ doping

Luminescence process:
- Independent of type of dopant ion
- Similar PL found for aged LuPO₄ and LaPO₄

→ PL related to phosphate
6. Phosphor Converted Xe Excimer Lamps

Further analytics on degraded LnPO₄ (Ln = Y, La, Gd, Lu)

- XRD and ³¹P-NMR → No phase transitions or impurity phase formation
- Photoluminescence spectroscopy → Spectral features characteristic for \( ns^2 \leftrightarrow ns^1np^1 \) luminescence, as already known for As³⁺, Sb³⁺, and Bi³⁺
- Decay curve → main component \( \tau_{1/e} = 5 \text{ ms} \) → PL of \( s^2 \)-ion with a small spin-orbit (S.-O.) coupling, which increases with atomic number!

Reduction of P⁵⁺ by hot e⁻ and Xe⁺ impingement due to intimate contact to barrier discharge

\[
P^{+V} + \text{O}_4^{3-} + \text{Xe}^+ + e^- \rightarrow P^{+\text{III}} \text{O}_3^{3-} + \text{XeO}^\uparrow
\]
6. Phosphor Converted Xe Excimer Lamps

Photoluminescence of degraded LnPO$_4$ (Ln = Y, La, Gd, Lu)

Simplified energy level diagram of an ns$^2$ ion

Conclusions:
• Formation of LnPO$_4$·P$^{3+}$
• First known example of P$^{3+}$ [Ne]3s$^2$ to [Ne]3s$^1$3p$^1$ photoluminescence


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6. Phosphor Converted Xe Excimer Lamps

Improvement of stability of LnPO$_4$:M (Ln = Y, La, Gd, Lu; M = Pr, Nd, Bi)

Approach: Particle coating with Al$_2$O$_3$ ($E_g \sim 7.5$ eV) to reduce interaction with Xe discharge and to absorb radiation from discharge below 160 nm

6. Phosphor Converted Xe Excimer Lamps

Improvement of stability of $\text{LnPO}_4$ ($\text{Ln} = \text{Y}, \text{La}, \text{Gd}, \text{Lu}$)

$\text{Al}_2\text{O}_3$ reduces efficacy upon 160 nm, but hardly upon 172 nm excitation.
6. Phosphor Converted Xe Excimer Lamps

Lifetime of Xe excimer lamp comprising Al$_2$O$_3$ coated YPO$_4$:Bi particles

<table>
<thead>
<tr>
<th>Coating type</th>
<th>Lamp code</th>
<th>Operation time / h</th>
<th>72</th>
<th>216</th>
<th>336</th>
<th>480</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>837</td>
<td>loss / %</td>
<td>14.17</td>
<td>29</td>
<td>37.99</td>
<td>55.76</td>
<td>52.21</td>
</tr>
<tr>
<td>Al$_2$O$_3$ 2 wt-%, urea</td>
<td>838</td>
<td>loss / %</td>
<td>20.29</td>
<td>41.92</td>
<td>48.58</td>
<td>50.06</td>
<td>43.43</td>
</tr>
<tr>
<td>Al$_2$O$_3$ 4 wt-%, urea</td>
<td>827</td>
<td>loss / %</td>
<td>n. a.</td>
<td>22.47</td>
<td>24.04</td>
<td>30.37</td>
<td>32.58</td>
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<tr>
<td>Al$_2$O$_3$ 2 wt-%, UV-R</td>
<td>828</td>
<td>loss / %</td>
<td>12.40</td>
<td>24.91</td>
<td>33.81</td>
<td>32.35</td>
<td>40.23</td>
</tr>
<tr>
<td>Al$_2$O$_3$ 4 wt-%, UV-R</td>
<td>829</td>
<td>loss / %</td>
<td>12.61</td>
<td>26.95</td>
<td>24.94</td>
<td>32.72</td>
<td>42.01</td>
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<tr>
<td>Al$_2$O$_3$ 4 wt-%, UV-R, 1400 °C</td>
<td>830</td>
<td>loss / %</td>
<td>5.25</td>
<td>16.28</td>
<td>19.86</td>
<td>24.64</td>
<td>28.44</td>
</tr>
</tbody>
</table>

Optimal particle coating process
- Al$_2$(SO$_4$)$_3$ in water + NaN$_3$
- UV reactor (Hg high-pressure lamp)
- 4 wt-% Al$_2$O$_3$
- 1400 °C post annealing

Results so far
- Factor 2 - 3 less degradation
- Almost no loss of initial efficiency
7. Spin-off: Nanoscale UV Scintillators

YPO₄:Pr and LuPO₄:Pr as 235 nm UV-C emitting nanoparticle scintillators

YPO₄:Pr (30 nm)

LuPO₄:Pr (5 nm)

Probe EDTA 2

Emissionsspektrum
Anregungsspektrum

YPO₄:Pr³⁺(1%)

EDTA 16

Counts

LuPO₄:Pr(1%)
Idea: Conversion of x-rays to UV-C radiation by nanoscale particles to improve radiation therapy of cancer

Radiation therapy is a well established cancer treatment and applied all over the world, even though it has tremendous side effects, such as hair loss, diarrhea, ...

“UV Nanophors” would result in
- lower radiation dose
- fewer or none side effects
- lower treatment price
- shorter treatment periods


Image by S. Espinoza
Challenge: Provide UV-C scintillator which meet the following requirements

- High density
- Large GAC overlap
- Diameter: 50 - 150 nm
- Narrow PSD
- Homogeneous morphology
- Redispersibility
- Mainly UV-C emission
- Efficient CL and RL
- Suitable PZC
- Biocompatible host
- Low toxicity
- Stability in water to enable core-shell structure with linker

<table>
<thead>
<tr>
<th>Core material</th>
<th>Density [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lu₂O₃</td>
<td>9.4</td>
</tr>
<tr>
<td>LuLaO₃</td>
<td>8.2</td>
</tr>
<tr>
<td>Lu₂O₂S</td>
<td>8.9</td>
</tr>
<tr>
<td>Lu₂SiO₅</td>
<td>7.4</td>
</tr>
<tr>
<td>LuPO₄</td>
<td>6.53</td>
</tr>
<tr>
<td>Lu₂Si₂O₇</td>
<td>6.2</td>
</tr>
<tr>
<td>Lu₃Al₅O₁₂</td>
<td>6.7</td>
</tr>
<tr>
<td>LuAlO₃</td>
<td>8.4</td>
</tr>
<tr>
<td>LuBO₃</td>
<td>6.9</td>
</tr>
</tbody>
</table>

Image by S. Espinoza
### 7. Spin-off: Nanoscale UV Scintillators

#### Emission peaks and GAC overlap of selected UV-C scintillators

<table>
<thead>
<tr>
<th>Material</th>
<th>( \lambda_{\text{max}} \text{(Em.)} ) /nm</th>
<th>GAC-Efficacy /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Y,Lu)PO(_4)::Nd</td>
<td>193</td>
<td>57.3*</td>
</tr>
<tr>
<td>CaSO(_4)::Pr,Li</td>
<td>218</td>
<td>68.2</td>
</tr>
<tr>
<td>LaPO(_4)::Pr</td>
<td>225</td>
<td>68.9</td>
</tr>
<tr>
<td>(Y,Lu)PO(_4)::Pr</td>
<td>235</td>
<td>60.6</td>
</tr>
<tr>
<td>(Y,Lu)PO(_4)::Bi</td>
<td>241</td>
<td>43.8 – 50.7</td>
</tr>
<tr>
<td>YAlO(_3)::Pr</td>
<td>245</td>
<td>40.6</td>
</tr>
<tr>
<td>La(_2)Si(_2)O(_7)::Pr</td>
<td>247</td>
<td>33.4</td>
</tr>
<tr>
<td>CaLi(_2)SiO(_4)::Pr</td>
<td>253</td>
<td>44.0</td>
</tr>
<tr>
<td>CaMgSi(_2)O(_6)::Pr,Li</td>
<td>260</td>
<td>n. a.</td>
</tr>
<tr>
<td>YBO(_3)::Pr</td>
<td>265</td>
<td>45.9</td>
</tr>
<tr>
<td>Lu(_2)Si(_2)O(_7)::Pr</td>
<td>266</td>
<td>48.1</td>
</tr>
<tr>
<td>Y(_2)SiO(_5)::Pr</td>
<td>270</td>
<td>22.3</td>
</tr>
<tr>
<td>BaZrSi(_3)O(_9)</td>
<td>275</td>
<td>47.9</td>
</tr>
<tr>
<td>Lu(_2)SiO(_5)</td>
<td>277</td>
<td>15.9</td>
</tr>
<tr>
<td>Lu(_3)Al(_5)O(_12)::Pr</td>
<td>310</td>
<td>2.3</td>
</tr>
<tr>
<td>Lu(_3)Al(_5)O(_12)::Gd</td>
<td>311</td>
<td>~ 0</td>
</tr>
<tr>
<td>Y(_3)Al(_5)O(_12)::Gd</td>
<td>311</td>
<td>~ 0</td>
</tr>
<tr>
<td>LaMgAl(_11)O(_19)::Gd</td>
<td>311</td>
<td>~ 0</td>
</tr>
<tr>
<td>Y(_3)Al(_5)O(_12)::Pr</td>
<td>320</td>
<td>~ 0</td>
</tr>
<tr>
<td>LaPO(_4)::Ce</td>
<td>320</td>
<td>~ 0</td>
</tr>
<tr>
<td>Lu(_3)Al(_5)O(_12)::Tm</td>
<td>345</td>
<td>~ 0</td>
</tr>
<tr>
<td>Y(_3)Al(_5)O(_12)::Tm</td>
<td>345</td>
<td>~ 0</td>
</tr>
<tr>
<td>YPO(_4)::Ce</td>
<td>335, 355</td>
<td>~ 0</td>
</tr>
<tr>
<td>BaSi(_2)O(_5)::Pb</td>
<td>350</td>
<td>~ 0</td>
</tr>
</tbody>
</table>

![Graph](image.png)
7. Spin-off: Nanoscale UV Scintillators

GAC overlap and density of selected UV-C scintillators

Chosen materials:
- LaPO₄
- LuPO₄
7. Spin-off: Nanoscale UV Scintillators

From micro to nanoscale particles (bottom-up approach)

- A solution of NaH$_2$PO$_4$ (pH 12) is added dropwise to the second solution of LuCl$_3$ and Pr(NO$_3$)$_3$ dissolved in H$_2$O.
- The precipitate is separated by a centrifuge and washed with distilled H$_2$O several times to neutral pH value.
- Afterwards, the precipitate is annealed for 2 h at 1000 °C in a reducing atmosphere (CO).

- Lu$_2$O$_3$ and Pr$_6$O$_{11}$ are suspended in H$_2$O.
- H$_3$PO$_4$ is added to the suspension and mixed for 24 h.
- The precipitate is filtered and washed with distilled H$_2$O several times to neutral pH value.
- Afterwards, the precipitate is annealed for 4 h at 1000 °C under CO atmosphere and using 2 wt-% LiF.

Average $d_{50} = 0.1$ µm

Image by Sara Espinoza

Average $d_{50} = 5.7$ µm
7. Spin-off: Nanoscale UV Scintillators

PSD of nanoscale LuPO$_4$:$\text{Pr}(0.0 - 3.0 \text{ atom-\%})$ particles

Results from S. Espinoza, H. Jenneboer, H. Kaetker, and A. Uckelmann

Reproducible synthesis of pure and highly crystalline LuPO$_4$:Pr$^{3+}$ 100 nm particle activated by 0.1 to 3% Pr$^{3+}$
7. Spin-off: Nanoscale UV Scintillators

Radioluminescence of LuPO$_4$:Pr and LaPO$_4$:Pr 100 nm particles

LuPO$_4$:Pr

- Energy (eV)
- Intensity (a.u.)
- Wavelength (nm)

Pr$^{3+}$: [Xe]4f$^2$ - [Xe]4f$^2$

$\lambda_{ex}$= X-ray
50 kV; 2 mA
Tungsten Target
5 Repeats

- LuPO$_4$
- LuPO$_4$:Pr$^{3+}$ 0.1%
- LuPO$_4$:Pr$^{3+}$ 0.25%
- LuPO$_4$:Pr$^{3+}$ 0.5%
- LuPO$_4$:Pr$^{3+}$ 1%
- LuPO$_4$:Pr$^{3+}$ 2%
- LuPO$_4$:Pr$^{3+}$ 3%

LaPO$_4$:Pr

- Energy (eV)
- Intensity (a.u.)
- Wavelength (nm)

Pr$^{3+}$: [Xe]4f$^2$ - [Xe]4f$^2$

$\lambda_{ex}$= X-ray
50 kV; 2 mA
Tungsten Target
5 Repeats

- YPO$_4$:Bi$^{3+}$ UV-C 13/03 (4.2 $\mu$m)
- HMS-2017-AU-SS-103: LaPO$_4$:Pr$^{3+}$ (0.1%)
- HMS-2017-AU-SS-104: LaPO$_4$:Pr$^{3+}$ (0.25%)
- HMS-2017-AU-SS-105: LuPO$_4$:Pr$^{3+}$ (0.5%)
- HMS-2017-AU-SS-106: LaPO$_4$:Pr$^{3+}$ (1%)

Density [g/cm$^3$] 6.5
Main peak [nm] 235
Luminescence 4f-5d and 4f-4f
GAC overlap [%] 61

4.2
225
mainly 4f-5d
69
7. Spin-off: Nanoscale UV Scintillators

First results on cancer cell lines (source: HMS Boston, Dr. M. Purschke)

Colony formation assay
14 days after irradiation

Cyclobutane pyrimidine dimer assay as a proof of concept

Combined treatment causes an increased cell inactivation of 65 to 95%.
Combined treatment of cells with LuPO$_4$:Pr$^{3+}$ and 2 Gy is equivalent to 4 Gy alone
8. Summary

UV emitting (nanoscale) materials

⇒ Fluorescent Xe Excimer discharge lamps

• Tailored emission spectra possible by VUV → UV converter: 
  (Y,Lu)PO$_4$:Nd, LaPO$_4$:Pr, (Y,Lu)PO$_4$:Pr, YBO$_3$:Pr, BaZrSi$_3$O$_9$, …
• Lamp lifetime limited to ~1000 h yet
• Degradation mechanism clarified
• Improvement of stability of converter by photochemically deposited Al$_2$O$_3$ particle coatings
• Many application areas, such as disinfection, purification, photochemistry, NO$_3^-$ removal, food processing, …

⇒ Nanoscale UV emitting phosphors

• Excitation by x- or cathode-rays
• Local emission of harmful UV-C or VUV radiation
• Use for surface disinfection or therapeutic purposes
• Development of quantitative VUV/x-ray to UV-C spectroscopy
8. Outlook

UV emitting (Al,Ga)N LEDs and laser diodes

- Spectral range: 220 – 360 nm
- DUV-LED → DUV laser diodes: Challenging!
- Problems: Spectral consistency, efficiency, radiation out-coupling, mass production, encapsulation, …..

Fluorescent Xe excimer discharge lamps

- Spectral range: 190 – 700 nm
- Discharge – converter interaction determines yield & lifetime
- Advantages: Hg-free, fast switchable, high form factor, temperature independent
- Problems: Driver eff., lifetime, market access, but UNEP proposed Hg ban rom 2020 onwards …..
8. Outlook

UV emitting nanoscale core-shell particles for biomedical applications

Diagnostics
Imaging
Therapy
Delivery

Combination of these applications, e.g. for magneto-optical therapy
GdPO₄ (core) + LuPO₄:Pr (shell)

Her, S., Jaffray, D.A. and Allen, C., Gold nanoparticles for applications in cancer radiotherapy, Mechanisms and recent advancements, Advanced drug delivery reviews, 109 (2017) 84
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THANK YOU!