Luminescent Materials for Sophisticated Operation Conditions

Thomas Jüstel
RG Tailored Optical Materials
Institute for Optical Technologies
Münster Univ. of Applied Sciences

University Wuppertal
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About 20% of the produced electrical energy is used for lighting (source: NASA)

Even more than 25 years after Germany’s reunification
East and West Berlin can be diminished by lighting

1989  End of the Berlin Wall “The wind of change”
1990  Germany’s reunification
1993  Blue LED: (In,Ga)N
1996  White LED: YAG
2014  White LED > 300 lm/W & Nobel price
2016  LED dominates lighting business ”The light of change”

East Berlin  → Na lamps
West Berlin  → Hg lamps
Luminescent Materials - Almost Everywhere

Optical brightening
Paint, pulp and paper, washing powder

Product anticounterfeiting
Bills, stamps, credit cards, tickets, etc.

Advertisement illumination
Ne discharge lamps

Emergency illumination
Emergency exits and signs, runways

Medical imaging and treatment
x-ray converter films, scintillator crystals
Psoriasis and jaundice treatment
Dental ceramics

Astronomy
EUV/VUV-Amplifier

Biochemistry
Labels for DNA, RNA, proteins

Solar Cells
Down-Shifter
Down-Converter
Up-Converter

Solar Cells (INTERNATIONAL YEAR OF LIGHT 2015)

Telecommunication
NIR Amplifier

High energy physics
Scintillator crystals, neutron detectors, …
Outline

1. Motivation
2. Chemistry and Physics of LMs
3. LMs for High Power LEDs
4. VUV to UV Converter for Xe excimer lamps
5. Nanoscale UV Phosphors
6. Summary
7. Outlook
8. Literature
1. Motivation

Increasing requirements on the performance of lamps and displays results in higher wall load, luminescent screen temperature, linearity, …

Miniaturisation of fluorescent light sources

- Lamp temperature depends on lamp diameter
  - TL 36 mm: 40 °C
  - TL 13 mm: 60 °C
  - PL types: 70 – 80 °C
  - CFL: 90 – 110 °C
  - CFL “GLS look-a-like”: 100 – 160 °C
  - QL: 200 – 250 °C
- Quantum yield decreases with increasing temperature
- Excitation and emission spectra shift and broaden with increasing temperature

Higher resolution and image quality of emissive displays

- Reduction of particle size distribution (PSD)
- Reduction of decay time to enhance linearity (fps↑)
- Narrow band green and red to enlarge colour gamut
- Increase (photothermal)stability for laser projection displays
1. Motivation

Tremendous advances in LED technology (2nd semiconductor revolution)

<table>
<thead>
<tr>
<th>Year</th>
<th>Material</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970</td>
<td>(Ga,As)P</td>
<td>&lt; 0.1 W, &lt; 1.0 lm, &lt; 10 lm/W, &lt; 120 °C, &lt; 100 W/cm², &gt; 120 K/W, yellow, red, NIR</td>
</tr>
<tr>
<td>2018</td>
<td>(Al,In,Ga)P, (In,Ga)N, (Al,Ga)N</td>
<td>1 - 10 W, &gt; 100 lm, up to 303 lm/W, 120 – 200 °C, 100 – 200 W/cm², 2 – 12 K/W, UV-A/B/C, all colors, NIR</td>
</tr>
</tbody>
</table>

Optical power density of the LED light sources (source: fairchildsemi.com)
1. Motivation

Increase of energy density drives search for novel materials

Excitation energy [eV]

- High energy particles
- x-rays (< 1 nm)
- EUV (1 – 100 nm)
- VUV (100 – 200 nm)
- UV-C (200 – 280 nm)
- UV-B (280 – 320 nm)
- UV-A (320 – 400 nm)
- VIS (400 – 700 nm)
- NIR (700 – 1400 nm)

Power density [W/cm²]

Rare Earth Phosphors
Garnets
Crystals/Ceramics

Host lattice
Sensitiser
Activator
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
- Photochemical stability

Excitation and emission spectrum of Mg\textsubscript{2}TiO\textsubscript{4}:Mn

Decay curves of SrSi\textsubscript{2}N\textsubscript{2}O\textsubscript{2}:Eu

T-dependent PL of selected LMs upon 254 nm excitation

Linearity of YAG:Ce and LiEuMo\textsubscript{2}O\textsubscript{8}
2. Chemistry and Physics of LMs

Thermal quenching of the red emitting LED converter CaAlSiN$_3$:Eu$^{2+}$

Luminescent materials show a reduction of the photoluminescent quantum yield and a colour point shift with increasing temperature

$T_{1/2}$(CaAlSiN$_3$:Eu) $\sim$ 650 K ($\sim$ 380 °C)

$T_{1/2}$ depends on chemical composition → Stokes Shift, band gap and distance of the excited state to the conduction band edge, phonon spectrum and so on
3. LMs for High Power LEDs

Multichip LED Lamps
- Narrow band emitter e.g. LEDs
  - $\lambda_{1/2} = 30$ nm
  - Several visible LED types $n = 2 - 5$
- Theoretical maximum, $n = 2$
  - Luminous efficacy (LE) = 430 lm/W
  - Corr. colour temp. (CCT) = 4870 K
  - Colour rendering index (CRI) = 3
- Practical values
  - LE $\sim$ 350 lm/W for CRI 90, $n = 3 - 4$
  - LE$_{max}$ $\sim$ 320 lm/W for CRI 99, $n = 5$
- Problems
  - Thermal quenching of EL and LE lifetime = f(semiconductor)
  - LED efficiency
    - Red and blue high
    - Green and yellow moderate → Luminescent materials

3. LMs for High Power LEDs

"Phosphor Converted" (pc) LED

**Diagram:**
- Plastic lens
- Contact
- Gold wire
- Heat sink (Cu)

**Formula:**
(In$_{1-x}$Ga$_x$)N semiconductor

**Graph:**
- Normalised emission intensity vs. Wavelength [nm]
- CIE1931 x y values for different wavelengths:
  - 410 nm: 0.173, 0.026
  - 419 nm: 0.170, 0.015
  - 448 nm: 0.156, 0.035
  - 455 nm: 0.147, 0.040
  - 459 nm: 0.143, 0.047
  - 462 nm: 0.136, 0.059
  - 465 nm: 0.132, 0.071
  - 468 nm: 0.128, 0.085
  - 482 nm: 0.092, 0.216

**Notes:**
- Photons are converted to visible light through the phosphor screen.
3. LMs for High Power LEDs

Micropowders or Ceramics

Aluminates $\rightarrow$ Ce$^{3+}$
(Y,Gd,Tb)$_3$Al$_5$O$_{12}$:Ce
Lu$_3$(Ga,Al)$_5$O$_{12}$:Ce

Sulphides $\rightarrow$ Eu$^{2+}$
(Ca,Sr)S:Eu

Oxides $\rightarrow$ Eu$^{2+}$ or Ce$^{3+}$
CaSc$_2$O$_4$:Ce,Mg
(Ca,Sr,Ba)$_2$SiO$_4$:Eu
(Ca,Sr,Ba)$_3$SiO$_5$:Eu

(Oxy)Nitrides $\rightarrow$ Eu$^{2+}$ or Ce$^{3+}$
(Sr,Ca,Ba)$_2$Si$_5$N$_8$:Eu “2-5-8”
(Sr,Ca,Ba)Si$_2$N$_2$O$_2$:Eu “1-2-2-2”
(Ca,Sr)AlSiN$_3$:Eu “1-1-1-3”
La$_3$Si$_6$N$_{11}$:Ce “3-6-11”
Ba$_3$Si$_6$O$_{12}$N$_2$:Eu
$\alpha,\beta$-Si$_{3-x}$Al$_x$N$_{4-x}$O$_x$:Eu

Silicon Nitride Alloys (SiAlON)

Typical spectra of Eu$^{2+}$ phosphors

Simplified energy level scheme of Eu$^{2+}$
3. LMs for High Power LEDs

1st Generation pcLEDs: Wall Plug efficiency (WPE) >> Discharge lamps

*(In,Ga)*N LED  *(Y,Gd)*₃Al₅O₁₂:Ce

Status quo cool white phosphor converted LEDs @ 2018

- Yellow phosphors
  - garnets: *(Y,Gd,Tb)*₃Al₅O₁₂:Ce³⁺
  - ortho-silicates: *(Ca,Sr,Ba)*₂SiO₄:Eu²⁺
- LE  300 lm/W (WPE > 80%)
- CRI  70 - 80
- CCT > 5000 K

<table>
<thead>
<tr>
<th>Element</th>
<th>Y</th>
<th>Gd</th>
<th>Ce</th>
<th>Al</th>
<th>O</th>
<th>*(Y₀.₇₇Gd₀.₂Ce₀.₀₃)*₅O₁₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar Mass (g/mol)</td>
<td>88,91</td>
<td>157,25</td>
<td>140,12</td>
<td>26,98</td>
<td>16,0</td>
<td>639,243</td>
</tr>
<tr>
<td>Coefficient</td>
<td>2,31</td>
<td>0,6</td>
<td>0,09</td>
<td>5</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Mass fraction</td>
<td>32%</td>
<td>15%</td>
<td>2%</td>
<td>21%</td>
<td>30%</td>
<td>100%</td>
</tr>
</tbody>
</table>
3. LMs for High Power LEDs

2nd Generation pcLEDs: Enhancement of CRI and reduction of CCT

Status quo warm white phosphor converted LEDs @ 2018

- Red phosphor \( \text{Eu}^{2+} \) activated
- LE 80 - 150 lm/W
- CRI 85 – 95
- CCT 2500 - 4000 K

**Table:**

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>Molar Mass (g/mol)</th>
<th>Coefficient for ( \text{Eu}^{2+} )</th>
<th>Mass fraction ( \text{Eu}^{2+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ca}<em>{0.5}\text{Sr}</em>{0.45}\text{Eu}_{0.05}\text{S} )</td>
<td>99,14</td>
<td>0,05</td>
<td>8%</td>
</tr>
<tr>
<td>( \text{Ca}<em>{0.5}\text{Sr}</em>{0.45}\text{Eu}_{0.05}\text{Si}_5\text{N}_8 )</td>
<td>434,12</td>
<td>0,1</td>
<td>4%</td>
</tr>
<tr>
<td>( \text{Ca}<em>{0.5}\text{Sr}</em>{0.45}\text{Eu}_{0.05}\text{Al}_3\text{Si}_3\text{N}_8 )</td>
<td>168,14</td>
<td>0,05</td>
<td>5%</td>
</tr>
</tbody>
</table>

3. LMs for High Power LEDs

First all nitride LED demonstrated in 2005 (QY > 0.9, QY_{rel}(200 °C) > 0.95)

(\text{In,Ga})N LED + \text{SrSi}_2\text{N}_2\text{O}_2:Eu + \text{Sr}_2\text{Si}_5\text{N}_8:Eu

or (\text{Sr,Ca})\text{AlSiN}_3:Eu or (\text{Sr,Ca})_2\text{SiO}_4:Eu

Colour rendering index CRI > 88
Excellent colour point consistency with drive is achieved
3. LMs for High Power LEDs

\[(\text{Sr}, \text{Ca}), \text{SiO}_4: \text{Eu}^{2+}\]
\[(\text{Ca}, \text{Sr}) \text{AlSiN}_3: \text{Eu}^{2+}\]
\[(\text{Sr}, \text{Ba})_2 \text{Si}_5 \text{N}_8: \text{Eu}^{2+}\]

Saturation by photoioinsation

\[\text{E}_g\]

Aktivator

Leitungsband

Valenzband

\[x_0 + x_1 = N\]

\[\beta_{h,1} x_1\]

\[g\]

\[x_1 / \tau_r\]

\[x_1 / \tau_{nr}\]

\[\beta_{as,1} x_1^\beta\]

Prof. Dr. T. Jüstel, Münster University of Applied Sciences, Germany
3. LMs for High Power LEDs

Red band emitter cause reduction in lum. efficacy

1. Spectral interaction due to re-absorption
2. Reduction in lumen equivalent

<table>
<thead>
<tr>
<th>Band width [nm]</th>
<th>Position (nm)</th>
<th>LE (lm/W)</th>
<th>Red LED Phosphor</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 - 120</td>
<td>635</td>
<td>257</td>
<td>(Ca,Sr)S:Eu</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Ca,Sr,Ba)<em>{2}Si</em>{5}N_{8}:Eu</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Ca,Sr)AlSiN_{3}:Eu</td>
</tr>
<tr>
<td>20 – 30</td>
<td>655</td>
<td>278</td>
<td>Mg_{2}TiO_{4}:Mn^{4+}</td>
</tr>
<tr>
<td>20 – 30</td>
<td>620</td>
<td>320</td>
<td>Ln^{3+} activated</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Ln = Eu, Sm, Pr)</td>
</tr>
<tr>
<td>50 – 60</td>
<td>655</td>
<td>269</td>
<td>Eu^{2+}- activated</td>
</tr>
<tr>
<td>50 – 60</td>
<td>620</td>
<td>300</td>
<td>Eu^{2+}- activated</td>
</tr>
</tbody>
</table>

3. LMs for High Power LEDs

Requirements to an „ideal“ LED phosphor

- Narrow FWHM ~ 20 - 60 nm
- Emission peak at ~ 630 nm
- QY (excitation at 450 nm) > 90%
- Absorption at 450 nm > 50%
- $T_{1/2} > 200$ °C
- Decay time < 10 ms
- No saturation up to 100 W/mm$^2$ (good linearity)
- High (photo)chemical and thermal stability

<table>
<thead>
<tr>
<th>Activator</th>
<th>Spectral range [nm]</th>
<th>Lumen equivalent [lm/W$_{opt}$]</th>
<th>Decay time $\tau$</th>
<th>QY [%]</th>
<th>Absorption at 450 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>RE-ions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu$^{2+}$</td>
<td>360 - 700</td>
<td>50 – 550</td>
<td>~ 1 µs</td>
<td>high</td>
<td>strong</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>590 - 710</td>
<td>200 – 360</td>
<td>~ 1 ms</td>
<td>high</td>
<td>weak</td>
</tr>
<tr>
<td>Sm$^{2+}$</td>
<td>670 - 770</td>
<td>&lt; 100</td>
<td>~ 1 µs</td>
<td>high</td>
<td>moderate</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>560 - 710</td>
<td>240 – 260</td>
<td>0.5 ms</td>
<td>moderate</td>
<td>weak</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>590 - 680</td>
<td>100 – 220</td>
<td>0.1 ms</td>
<td>moderate</td>
<td>weak</td>
</tr>
<tr>
<td><strong>TM-ions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>500 - 650</td>
<td>100 - 550</td>
<td>5-15 ms</td>
<td>high</td>
<td>weak</td>
</tr>
<tr>
<td>Mn$^{4+}$</td>
<td>620 - 680</td>
<td>80 – 230</td>
<td>1-10 ms</td>
<td>high</td>
<td>moderate</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>680 - 750</td>
<td>&lt; 100</td>
<td>1-10 ms</td>
<td>high</td>
<td>moderate</td>
</tr>
</tbody>
</table>
3. LMs for High Power LEDs

Narrow band red emitter $\text{Sr}[\text{LiAl}_3\text{N}_4]$:Eu$^{2+}$

Claimed as next generation LED-phosphor material’’

Synthesis

$\text{LiAlH}_4 + (1-x)\text{SrH}_2 + x\text{EuF}_3 + 2\text{AlN} + \text{N}_2$

$\rightarrow (\text{Sr}_{1-x}\text{Eu}_x)[\text{LiAl}_3\text{N}_4] + 3x\text{HF} + (3-x)\text{H}_2$

RF-Furnace, 1000 °C

Optical Properties

$\lambda_{\text{max}} = 651$ nm for 5% Eu$^{2+}$

FWHM = 1180 cm$^{-1}$ (~ 60 nm)

QY(200 °C) > 95% rel. to QY(RT)

Decay time of Eu$^{2+}$ ~ 1.1 µs

Problems: Excitation @ 410 nm → photoionisation and strong re-absorption of YAG:Ce/LuAG:Ce PL

W.S. Schnick et al., Nature Materials (2014) 1-6
### 3. LMs for High Power LEDs

#### Remaining Options

<table>
<thead>
<tr>
<th>Red emitter</th>
<th>LE [lm/W_{opt.}]</th>
<th>QY at RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu^{3+}</td>
<td>220 – 360</td>
<td>high</td>
</tr>
<tr>
<td>Pr^{3+}</td>
<td>200 – 220</td>
<td>moderate</td>
</tr>
<tr>
<td>Mn^{4+}</td>
<td>20 – 200</td>
<td>high</td>
</tr>
</tbody>
</table>

**La_{2}W_{3}O_{12}**:Eu

- Emission spectrum \(\lambda_{\text{exc}} = 275.00\) nm
- Excitation spectrum \(\lambda_{\text{em}} = 614.00\) nm

**LuTaO_{4}**:Pr

**Mg_{4}GeO_{5.5}F**:Mn
3. LMs for High Power LEDs

Red line emitter $\rightarrow$ Pr$^{3+}$

Example: SrBa$_8$(BN$_2$)$_6$

Space group Fd3m, Z = 8

3. LMs for High Power LEDs

**Red line emitter → Mn⁴⁺**

K₂MF₆:Mn (M = Si, Ge, Ti)

**LED Chip**

- Blue: 420 – 480 nm
- Yellow: (Y,Gd,Tb,Lu)Al₅O₁₂:Ce
- Red: Mn⁴⁺-phosphor

**Typical yellow/red blend**

Tb₃Al₅O₁₂:3%Ce + K₂[MF₆]:Mn⁴⁺ (M = Si, Ge, Sn, Ti, Zr)

**Problems**

Absorption strength, linearity, and stability of Mn⁴⁺

MnF₄ → MnF₃ + ½ F₂

A. Srivastava et al., GE, US Patent US2006/0169998

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3. LMs for High Power LEDs

Red line emitter $\rightarrow$ Mn$^{4+}$

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>LE [lm/W]</th>
<th>Peak $\lambda_{em}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2SiF_6:Mn^{4+}$</td>
<td>196</td>
<td>631.0</td>
</tr>
<tr>
<td>$K_2TiF_6:Mn^{4+}$</td>
<td>192</td>
<td>631.8</td>
</tr>
<tr>
<td>$K_2GeF_6:Mn^{4+}$</td>
<td>191</td>
<td>632.0</td>
</tr>
<tr>
<td>$Mg_{14}Ge_5O_{24}:Mn^{4+}$</td>
<td>80</td>
<td>658</td>
</tr>
<tr>
<td>$K_2Ge_4O_9:Mn^{4+}$</td>
<td>46</td>
<td>663*</td>
</tr>
<tr>
<td>$Rb_2Ge_4O_9:Mn^{4+}$</td>
<td>38</td>
<td>667*</td>
</tr>
<tr>
<td>$Ca_2YNbO_6:Mn^{4+}$</td>
<td>15</td>
<td>680</td>
</tr>
<tr>
<td>$Ca_2LaSbO_6:Mn^{4+}$</td>
<td>7</td>
<td>699</td>
</tr>
<tr>
<td>$LaScO_3:Mn^{4+}$</td>
<td>7</td>
<td>703</td>
</tr>
</tbody>
</table>

*$F. Baur, T. Jüstel, J. Luminescence 177 (2016) 354$

Fluorides $\rightarrow$ Rather high luminous efficacy, but stability is a challenge
Oxides $\rightarrow$ Very stable, but low luminous efficacy
3. LMs for High Power LEDs

Red line emitter → $K_2(Nb,Ta)F_7:Mn^{4+}$

$\lambda_{\text{max}} = 628$ nm
LE = 228 lm/W
CIE1931: $x = 0.690; y = 0.310$

3. LMs for High Power LEDs

Red line emitter $\rightarrow$ $K_2(Nb,Ta)F_7:Mn^{4+}$ with superior luminous efficacy

<table>
<thead>
<tr>
<th>Blue LED + YAG:Ce +</th>
<th>CCT [K]</th>
<th>LE [Im/W_{opt}]</th>
<th>CRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2NbF_7:Mn^{4+}$</td>
<td>3000</td>
<td>346</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>2700</td>
<td>345</td>
<td>95</td>
</tr>
<tr>
<td>$K_2TaF_7:Mn^{4+}$</td>
<td>3000</td>
<td>345</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>2700</td>
<td>345</td>
<td>94</td>
</tr>
<tr>
<td>$Na_3AlF_6:Mn^{4+}$</td>
<td>3000</td>
<td>345</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>2700</td>
<td>344</td>
<td>95</td>
</tr>
<tr>
<td>$K_2SiF_6:Mn^{4+}$</td>
<td>3000</td>
<td>339</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>2700</td>
<td>297</td>
<td>95</td>
</tr>
<tr>
<td>$Mg_{14}Ge_5O_{24}:Mn^{4+}$</td>
<td>3000</td>
<td>254</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>2700</td>
<td>241</td>
<td>78</td>
</tr>
<tr>
<td>$Y_2Mg_3Ge_3O_{12}:Mn^{4+}$</td>
<td>3000</td>
<td>255</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>2700</td>
<td>242</td>
<td>79</td>
</tr>
<tr>
<td>$CaAlSiN_3:Eu^{2+}$</td>
<td>3000</td>
<td>272</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>2700</td>
<td>260</td>
<td>95</td>
</tr>
</tbody>
</table>

A 2700 K LED comprising YAG:Ce and $K_2TaF_7:Mn^{4+}$ shows a 15% higher LE than an LED comprising YAG:Ce and $K_2SiF_6:Mn^{4+}$
3. LMs for High Power LEDs

Red line emitter → Remaining problem: Saturation at ~ 1 W/mm²

Brils Modell*: \[ P_{em,max} = N_{act} E_{hv} C_{extraction} \frac{R}{\tau_r} \]

\[ \eta = \frac{P_{em}}{P_{abs}} = \frac{\eta_0}{1 + (P_{abs} \eta_0 / P_{em,max})} \]

*A. Bril, Physica 15 (1949) 361-379
### Sources of UV Radiation

<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>
</tr>
<tr>
<td>Xe discharge lamps</td>
<td>230 – 800 nm</td>
</tr>
<tr>
<td>D₂ discharge lamps</td>
<td>110 – 400 nm</td>
</tr>
<tr>
<td>Excimer laser</td>
<td>193 nm</td>
</tr>
<tr>
<td>Solid state laser Nd³⁺ 4th harmon.</td>
<td>266 nm</td>
</tr>
<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>
</tr>
<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>
4. VUV to UV Converter for Xe Excimer 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)**
  - Triton
  - Heraeus Noblelight

- **Flat lamp for LCD Backlighting** (Osram AG)
- **Osram Xeradex**
4. VUV to UV Converter for Xe Excimer Lamps

Lamp sketch and principle of working

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

- **Lamp sketch and principle of working**

\[ 
\begin{align*}
\text{p(Xe)} & = 300 \text{ mbar} \\
\text{P} & = 10 - 100 \text{ W} \\
\text{U} & = 3 - 5 \text{ kV} \\
\text{f} & = 10 - 50 \text{ kHz}
\end{align*} \]
4. VUV to UV Converter for Xe Excimer Lamps

Xe excimer spectrum and typical lamp parameter

Example: Osram XERADEX L40/120/SB-S46/85
Power consumption = 20 W
Diameter = 4 cm
Length = 12 cm
Wall load ~ 0.15 W/cm²
Output power = 6 W
Power density = 0.04 W/cm²
Wall plug efficiency ~ 30% (including driver)
4. VUV to UV Converter for Xe Excimer Lamps

Chosen converter material must be radiation hard

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

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

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

YPO_4 as the host material

mineral: Xenotime

structure: Zircon type

crystal system: tetragonal

space group: \( I4_1/amd \) (#141)

Y^3+ site: CN = 8

Prof. Dr. T. Jüstel, Münster University of Applied Sciences, Germany
4. VUV to UV Converter for Xe Excimer Lamps

Germicidal efficacy of doped ortho-phosphate YPO₄

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

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

YPO₄:Bi

YPO₄:Pr

YPO₄:Nd

GAC-Eff (YPO₄:Bi) = 43.8 %
GAC-Eff (YPO₄:Pr) = 60.6 %
GAC-Eff (YPO₄:Nd) = 57.3 %
4. VUV to UV Converter for 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

<table>
<thead>
<tr>
<th>Converter screen</th>
<th>Operation period</th>
<th>Relative radiation intensity loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>YPO$_4$:Bi</td>
<td>792 hours</td>
<td>- 50 %</td>
</tr>
<tr>
<td>YPO$_4$:Pr</td>
<td>792 hours</td>
<td>- 60 %</td>
</tr>
<tr>
<td>YPO$_4$:Nd</td>
<td>763 hours</td>
<td>~ -50 %</td>
</tr>
</tbody>
</table>
4. VUV to UV Converter for Xe Excimer Lamps

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

Lamp degradation due to several processes

Discharge related
XeO* formation
Sputtering of central wire

Phosphor related
Reduction of Bi$^{3+} \rightarrow$ Bi$^{2+}$, Bi$^+$
Degradation of ortho-phosphate host (defects or phosphate reduction?)

YPO$_4$:Bi as-made and aged
(PL and reflection spectra)
4. VUV to UV Converter for Xe Excimer Lamps

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

YPO₄:Bi³⁺

YPO₄:Bi³⁺ aged

YPO₄:Pr

YPO₄:Pr aged

new absorption by Bi³⁺/Bi²⁺

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

VUV to UV Converter for Xe Excimer Lamps
4. VUV to UV Converter for Xe Excimer Lamps

Temperature dependent spectroscopy on aged YPO₄ samples

Aged undoped YPO₄ shows intense red PL!

Luminescence process?

YPO₄    YPO₄ aged    YPO₄ aged + 365 nm

YPO₄ aged @ Ex.: 350 Em.: 750

Prof. Dr. T. Jüstel, Münster University of Applied Sciences, Germany
4. VUV to UV Converter for Xe Excimer Lamps

**Bi³⁺ doping**

- YPO₄ host
- YPO₄:Bi aged

**Pr³⁺ doping**

- YPO₄:Bi aged
- YPO₄:Pr aged

**Gd³⁺ doping**

- YPO₄:Gd aged
- YPO₄:Gd aged + 365 nm

**Luminescence process?**

- Independent of type of dopant
- Similar PL found for aged LuPO₄ and LaPO₄
4. VUV to UV Converter for Xe Excimer Lamps

Further analytics on degraded LnPO$_4$ (Ln = Y, La, Gd, Lu)

- XRD and $^{31}$P-NMR $\rightarrow$ No phase transitions or impurity phase formation
- Photoluminescence spectroscopy $\rightarrow$ Spectral features characteristic for ns$^2$ $\leftrightarrow$ ns$^1$np$^1$ luminescence, as already known for As$^{3+}$, Sb$^{3+}$, and Bi$^{3+}$
- Decay curve $\rightarrow$ main component $\tau_{1/e} = 5$ ms $\rightarrow$ PL of s$^2$-ion with a small spin-orbit (S.-O.) coupling, which increases with atomic number!

Reduction of P$^{5+}$ by hot e$^{-}$ and Xe$^{+}$ impingement due to intimate contact to barrier discharge

$$P^{+V}O_4^{3-} + Xe^+ + e^{-} \rightarrow P^{+III}O_3^{3-} + XeO^+$$
4. VUV to UV Converter for Xe Excimer Lamps

Photoluminescence of degraded LnPO₄ (Ln = Y, La, Gd, Lu)

Simplified energy level diagram of an ns² ion

Conclusions:
• Formation of LnPO₄·P³⁺
• First known example of P³⁺ [Ne]3s² to [Ne]3s¹3p¹ photoluminescence

M. Broxtermann, A. Meijerink, T. Jüstel, J. Luminescence, publication in progress
4. VUV to UV Converter for Xe Excimer Lamps

Improvement of stability of LnPO₄ (Ln = Y, La, Gd, Lu)

Approach: Particle coating with Al₂O₃ (E₉ ~ 7.5 eV) to reduce interaction with Xe discharge and to absorb radiation from discharge below 160 nm

5. Nanoscale UV Scintillators

YPO$_4$:Pr and LuPO$_4$:Pr as 235 nm UV-C emitting NP scintillators

![YPO$_4$:Pr (30 nm)](image)

![LuPO$_4$:Pr (5 nm)](image)

Emission spectrum and excitation spectrum for YPO$_4$:Pr$^{3+}$(1%) and LuPO$_4$:Pr(1%) samples.
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

5. Nanoscale UV Scintillators

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>
5. Nanoscale UV Scintillators

Emission peaks and GAC overlap of selected UV-C scintillators

<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda_{\text{max}}$(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$<em>5$O$</em>{12}$:Pr</td>
<td>310</td>
<td>2.3</td>
</tr>
<tr>
<td>Lu$_3$Al$<em>5$O$</em>{12}$:Gd</td>
<td>311</td>
<td>~ 0</td>
</tr>
<tr>
<td>Y$_3$Al$<em>5$O$</em>{12}$:Gd</td>
<td>311</td>
<td>~ 0</td>
</tr>
<tr>
<td>LaMgAl$<em>{11}$O$</em>{19}$:Gd</td>
<td>311</td>
<td>~ 0</td>
</tr>
<tr>
<td>Y$_3$Al$<em>5$O$</em>{12}$:Pr</td>
<td>320</td>
<td>~ 0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda_{\text{max}}$(Em.) /nm</th>
<th>GAC-Efficacy /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaPO$_4$:Ce</td>
<td>320</td>
<td>~ 0</td>
</tr>
<tr>
<td>Lu$_3$Al$<em>5$O$</em>{12}$:Tm</td>
<td>345</td>
<td>~ 0</td>
</tr>
<tr>
<td>Y$_3$Al$<em>5$O$</em>{12}$: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 showing relative proliferation](image)
5. Nanoscale UV Scintillators

GAC overlap and density of selected UV-C scintillators

Chosen materials

- LaPO$_4$
- LuPO$_4$
5. 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  
Average $d_{50} = 5.7$ µm
5. Nanoscale UV Scintillators

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

Reproducible synthesis of pure and highly crystalline LuPO$_4$:Pr$^3+$ 100 nm particle activated by 0.1 to 3% Pr$^3+$
5. Nanoscale UV Scintillators

Radioluminescence of LuPO₄:Pr and LaPO₄:Pr 100 nm particles

**LuPO₄:Pr**
- Energy (eV)
- \( \lambda_{\text{ex}} = \text{X-ray} \)
- 50 kV; 2 mA
- Tungsten Target
- 5 Repeats

- Pr³⁺: [Xe]4f⁵5d¹ - [Xe]4f⁶

**LaPO₄:Pr**
- Energy (eV)
- \( \lambda_{\text{ex}} = \text{X-ray} \)
- 50 kV; 2 mA
- Tungsten Target
- 5 Repeats

- YPO₄:Bi³⁺ UV-C 13/03 (4.2 µm)
- HMS-2017-AU-SS-103: LaPO₄:Pr³⁺ (0.1%)
- HMS-2017-AU-SS-104: LaPO₄:Pr³⁺ (0.25%)
- HMS-2017-AU-SS-105: LuPO₄:Pr³⁺ (0.5%)
- HMS-2017-AU-SS-106: LaPO₄:Pr³⁺ (1%)

**Density [g/cm³]**
- LuPO₄:Pr = 6.5
- LaPO₄:Pr = 4.2

**Main peak [nm]**
- LuPO₄:Pr = 235
- LaPO₄:Pr = 225

**Luminescence**
- LuPO₄:Pr = 4f-5d and 4f-4f
- LaPO₄:Pr = mainly 4f-5d

**GAC overlap [%]**
- LuPO₄:Pr = 61
- LaPO₄:Pr = 69
5. Nanoscale UV Scintillators

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

Colony formation assay
14 days after irradiation

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.
LED Materials in 2018 – State of the Art

Mature LMs developed to encounter

- high luminous efficacy
  - cool-white > 200 lm/W
  - warm-white > 100 lm/W
- high CRI
  - 70 - 95
- superior lifetime L70
  - > 10000 h
- retrofit designs for TL, CFL, GLS, …

Efficient luminescent materials are

- Oxides
  - (Ca,Sr,Ba)$_2$SiO$_4$:Eu
- Oxynitrides
  - (Ca,Sr,Ba)$_2$Si$_2$N$_2$O$_2$:Eu
  - a,β-SiAlON
- Nitrides
  - (Ca,Sr,Ba)$_2$Si$_5$N$_8$:Eu
  - (Ca,Sr)AlSiN$_3$:Eu
  - (Sr,Ca)LiAl$_3$N$_4$:Eu
  - (Sr,Ba)Mg$_2$Ga$_2$N$_4$:Eu
- Fluorides
  - K$_2$SiF$_6$:Mn
  - Na$_3$AlF$_6$:Mn
  - K$_2$TaF$_7$:Mn
- Silicates
  - (Ca,Sr,Ba)$_2$SiO$_4$:Eu
- Aluminosilicates
  - (Y,Gd,Lu)$_3$Al$_5$O$_{12}$
- Aluminates
  - ZnGa$_2$O$_4$:Mn
- Gallates
  - Mg$_8$Ge$_2$O$_{11}$F$_2$:Mn
- Germanates
  - Tb$_2$Mo$_3$O$_{12}$:Eu
- Molybdates
- Tantalates

6. Summary

**LED Materials in 2018 – Remaining issues**

⇒ Red narrow band or line emitting phosphor
- Little thermal quenching
- Reduced photochemical aging
- Superior linearity
- Reduced sensitivity for photoionisation

⇒ Narrow band green and NIR Emitter
- Eu$^{2+}$ with small Stokes Shift, e.g. BaSi$_2$N$_2$O$_2$:Eu$^{2+}$
- Tb$^{3+}$ on cation sites with high symmetry: Oh, D$_{3d}$
- Mn$^{2+}$ on tetrahedral sites: Zn$_2$GeO$_4$

⇒ Ceramics and crystals
- Ceramics: Garnets, Ln$_2$O$_3$, (Oxy)Nitrides
- Composites: Garnet + Al$_2$O$_3$ or CaF$_2$
- Crystals: Garnets as PL references

6. Summary

UV emitting (nanoscale) materials

⇒ Fluorescent Xe Excimer discharge lamps

- Tailored emission spectra possible by VUV → UV converter: (Y,Lu)PO₄:Nd, LaPO₄:Pr, (Y,Lu)PO₄:Pr, YBO₃:Pr, BaZrSi₃O₉, ...
- Lamp lifetime limited yet
- Degradation mechanism clarified
- Improvement of stability of converter by photochemically deposited Al₂O₃ particle coatings
- Many application areas, such as disinfection, purification, photochemistry, NO₃⁻ removal, food processing, ...

⇒ Nanoscale UV emitting phosphors

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

**LEDs and laser diodes - Challenges**

- **Reduction of flicker**
  - Persistent luminescent materials
  - ET approaches to delay PL

- **Ongoing increase of LED power density**
  - Ceramics & crystals
  - Vis (460 nm) to UV-C (230 nm) up converter

- **Broad band NIR emitter for blue/near UV LEDs**
  - Cr³⁺ phosphors
  - Eu²⁺ or Ce³⁺ sensitised Nd³⁺/Yb³⁺ emitters

- **Photochemistry with high power density sources**
  - Novel reactor designs
  - Ceramic or crystalline photocatalyst
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 lamps

- Spectral range: 172 – 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 ….
7. Outlook

Nanoscale core-shell particles for biomedical applications

Diagnostics
Imaging
Therapy
Delivery

Combination of these applications, e.g. for magneto-optical diagnostics
$\text{GdPO}_4 \@ \text{MIR} \to \text{NIR}$ up-converter

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
8. Literature

Further Reading

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• M. Kubus, D. Enseling, T. Jüstel, H.-Jürgen Meyer, Synthesis and Luminescent Properties of Red-Emitting Phosphors: ZnSiF$_6$·6H$_2$O and ZnGeF$_6$·6H$_2$O Doped with Mn$^{4+}$, J. Luminescence 137 (2013) 88
• T. Jüstel, Anorganische Leuchtstoffe und LEDs, CHEManager 5 (2017)

Internet-Links

• Homepage T. Jüstel (PISA & LISA) www.fh-muenster.de/juestel
• Robert-Koch-Institut www.rki.de
• Dt. Krebsforschungszentrum www.dkfz.de
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