9. Inorganic LEDs

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9.1 Classification of LEDs

Light Emitting Diodes

Organic

DC low V

PLED
PPV
PVK

OLED
Excimer complexes

PEL
ZnS:Cu
ZnS:Mn

Inorganic

AC high V

ACTFEL
ZnS:Tb
ZnS:Mn

PEL
SrS:Ce
CaS:Mn

DC low V

ILED
AllInGaP
AllInGaN

EL = Electroluminescence, I = Inorganic, P = Powder, TF = Thin Film

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9.2 Evolution of LED-Light Sources

Destriau discovered indirect EL

Biard&Pittman discovered direct EL (first LED)

Holonyak developed the first visible LED: Ga(As,P)

Friend&Burroughes invented PLED

Nakamura developed (In, Ga) N blue LED technology

Agilent Inc. presented red LED with 102 lm/W (55% ext. efficiency)

5 W LED

2002

White LED with 200 lm/W

2010
9.2 Evolution of LED-Light Sources

Development of luminous efficiency and lumen output

LEDs are now more efficient than incandescent and fluorescent lamps
2012: LEDs > 1000 lm on the market
9.2 Evolution of LED-Light Sources

Luminous efficiency of (Al,In,Ga)N, (Al,In,Ga)P and (Al,Ga)As LEDs (Stand 2002, source: Lumileds)

Eye Response Curve (CIE)

High Pressure Sodium (1kW)
Fluorescent (40W)
Mercury Vapor (1kW)
Halogen (30W)
Tungsten (60W)

Red-Filtered Tungsten (60W)

„Green/Yellow Gap“
9.3 Generation of Light in Semiconductor LEDs

Recombination of electrons and holes

Intrinsic radiative transitions in semiconductors:
(a) Band-to-band transitions
(b) Free-exciton annihilation
(c) Recombination of localized excitons by potential fluctuations in the bands
9.3 Generation of Light in Semiconductor LEDs

**Principle of semiconductor LED**

Recombination of electrons and holes at the p/n junction according to the energy and momentum conservation rule $\Rightarrow$ Energy of the emitted photon corresponds to the band gap.
9.3 Generation of Light in Semiconductor LEDs

Band gap of suitable semiconductor materials: Band gap engineering

![Diagram showing the band gap of various semiconductor materials against lattice constant.]

<table>
<thead>
<tr>
<th>Material</th>
<th>Band Gap (eV)</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>6.2</td>
<td>200</td>
</tr>
<tr>
<td>GaN</td>
<td>3.5</td>
<td>370</td>
</tr>
<tr>
<td>InN</td>
<td>0.9</td>
<td>1400</td>
</tr>
<tr>
<td>AlP</td>
<td>2.5</td>
<td>500</td>
</tr>
<tr>
<td>GaP</td>
<td>2.3</td>
<td>520</td>
</tr>
<tr>
<td>InP</td>
<td>1.4</td>
<td>900</td>
</tr>
</tbody>
</table>

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9.4 Chip Structure of (Al,In,Ga)N/Al₂O₃ LEDs

Structure of a semiconductor LED chip

- 0.5 µm
- 0.15 µm
- 4 µm
- ~100 µm

- Ni/Au p-electrode
- Transparent metal layer (Au/Ni)
- p-GaN contact layer
- InGaN/AlGaN DH, SQW or MQW structure
- Ti/Al n-electrode
- n-GaN contact layer
- Buffer layer
- Transparent sapphire substrate

9.4 Chip Structure of (Al,In,Ga)N/Al₂O₃ LEDs

Current paths in (Al,In,Ga)N LEDs on sapphire

(a) Asymmetrical design

(b) Symmetrical design

9.5 Spectra of LEDs

(In,Ga)N LEDs

(In,Ga)N yield a complete solid solution series without a miscibility gap

Effect of increasing In$^{3+}$ content

- Energy of the (In,Ga)N quantum well transition decreases
- Emission bands broaden
- Decrease in quantum yield due to increase of defect density
9.5 Spectra of LEDs

High Brightness LEDs (HB LEDs)

<table>
<thead>
<tr>
<th>LED</th>
<th>Voltage (U(V))</th>
<th>Current (I(A))</th>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue</td>
<td>3.7</td>
<td>0.29</td>
<td>0.096</td>
<td>0.208</td>
</tr>
<tr>
<td>Green</td>
<td>3.7</td>
<td>0.29</td>
<td>0.185</td>
<td>0.723</td>
</tr>
<tr>
<td>Red</td>
<td>3.1</td>
<td>0.30</td>
<td>0.703</td>
<td>0.328</td>
</tr>
<tr>
<td>White</td>
<td>3.4</td>
<td>0.30</td>
<td>0.328</td>
<td>0.329</td>
</tr>
</tbody>
</table>

(Al,In,Ga)P
500 – 900 nm
Depletion ~ 0.7%/K

(Al,In,Ga)N
250 – 550 nm
Depletion ~ 0.1%/K

Platform concept!

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9.6 Concepts of White Light Production

By additive color mixing

1. Black body radiation \(\Rightarrow\) visible light + IR
2. Gas discharge \(\Rightarrow\) VUV + UV-C/B/A + visible light
3. Semiconductor \(\Rightarrow\) UV-A, visible or IR-A radiation

White light via luminescence

- **Y, YR or RG phosphor**
- **CO or RGB phosphor blend**

Colored light by absorption

- **Color filter**
- **Incoherent light sources**

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Chapter Inorganic LEDs
Folie 13
9.6 Concepts of White Light Production

By LEDs

Red + Green + Blue LEDs

Blue LED + yellow phosphor

Blue LED + RG phosphor blend

UV LED + RGB phosphor blend

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9.6 Concepts of White Light Production

By near UV or blue LEDs

![Diagram showing light transitions and yields.]

- **370 – 420 nm**
  - 290 – 330 lm/W
  - CRI = 70 – 85
- **370 – 420 nm**
  - 320 – 360 lm/W
  - CRI = 85 - 95

- **420 - 480 nm**
  - 290 – 330 lm/W
  - CRI = 70 – 85
  - Transmission of blue depends on the optical path length through the phosphor layer
  - Color point = f(viewing angle)
  - Quantum deficit = 0.78
- **420 - 480 nm**
  - 320 – 360 lm/W
  - CRI = 85 - 95

UV light causes polymer degradation and requires security measures

- 390 nm LED (3.2 eV) → 570 nm (2.2 eV)
  - Quantum deficit = 0.69
- 460 nm LED (2.7 eV) → 570 nm (2.2 eV)
  - Quantum deficit = 0.78
9.7 Phosphor-LEDs (pcLEDs)

By blue LEDs

Blue LED chip: 420 – 480 nm emitting (In,Ga)N LED
Phosphor layer:
(1) Yellow $T_c > 4000$ K „cool white“
(2) Yellow + red $T_c < 4000$ K „warm white“
(3) Green + red $2000$ K $< T_c < 8000$ K
(4) Red magenta colors
9.8 Requirements for LED Phosphors

General
- Strong absorption at the emission wavelength of the semiconductor-LED → spin-and parity-allowed transition, e.g. $4f^n - 4f^{n-1}5d^1$
- Quantum yield > 90%
- Stability with respect to $O_2$, $CO_2$ and $H_2O$
- Stability at high excitation density (100 - 200 W/cm$^2$)
- Compatibility with the LED production process

Blue + yellow (1$^{st}$ approach)
- Broad emission band between 560 - 580 nm → $Ce^{3+}$- phosphors (splitting of the ground state $^2F_{5/2} + ^2F_{7/2}$)

Blue + green/yellow + red (2$^{nd}$ and 3$^{rd}$ approach)
- Green / yellow phosphor → $Eu^{2+}$ or $Ce^{3+}$ 530 - 560 nm
- Red phosphor → $Eu^{2+}$ 590 - 620 nm
9.9 Ce$^{3+}$ Phosphors

Simplified energy level scheme of Ce$^{3+}$ ([Xe]4f$^1$)

Centroid shift

Crystal field splitting

Stokes shift

Energy [cm$^{-1}$]

$5d^1$

$2F_{7/2}$

$2F_{5/2}$

$4f^1$

$Ce^{3+}$ in the gas phase $\approx 50000$ cm$^{-1}$

$Ce^{3+}$ in the gas phase ~ 50000 cm$^{-1}$

$\varepsilon_c$

$\varepsilon_{cfs}$

$0.0$

$1.0 \times 10^4$

$2.0 \times 10^4$

$3.0 \times 10^4$

$4.0 \times 10^4$

$5.0 \times 10^4$
# Established materials

<table>
<thead>
<tr>
<th>Host lattice</th>
<th>$\lambda_{\text{abs}}$ [nm]</th>
<th>$\lambda_{\text{em}}$ [nm]</th>
<th>$\varepsilon_{\text{cfs}}$ [cm$^{-1}$]</th>
<th>$\varepsilon_{\text{c}}$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrAl$<em>{12}$O$</em>{19}$</td>
<td>224, 235, 244, 252, 261</td>
<td>290, 315</td>
<td>6300</td>
<td>10000</td>
</tr>
<tr>
<td>LaPO$_4$</td>
<td>203, 225, 238, 250, 323</td>
<td>320, 335</td>
<td>11900</td>
<td>8700</td>
</tr>
<tr>
<td>LaMgAl$<em>{11}$O$</em>{19}$</td>
<td>220, 232, 243, 255, 270</td>
<td>345</td>
<td>8400</td>
<td>10000</td>
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<tr>
<td>YPO$_4$</td>
<td>203, 225, 238, 250, 323</td>
<td>335, 355</td>
<td>18000</td>
<td>9600</td>
</tr>
<tr>
<td>YAlO$_3$</td>
<td>219, 237, 275, 291, 303</td>
<td>370</td>
<td>12700</td>
<td>12900</td>
</tr>
<tr>
<td>LuAlO$_3$</td>
<td>216, 230, 275, 292, 308</td>
<td>370</td>
<td>12650</td>
<td>13800</td>
</tr>
<tr>
<td>LaMgB$<em>5$O$</em>{10}$</td>
<td>202, 225, 239, 257, 272</td>
<td>385, 410</td>
<td>9000</td>
<td>12700</td>
</tr>
<tr>
<td>YBO$_3$</td>
<td>219, 245, 338, 357</td>
<td>390, 415</td>
<td>17600</td>
<td>13300</td>
</tr>
<tr>
<td>Lu$_2$SiO$_5$</td>
<td>205, 215, 267, 296, 356</td>
<td>405, 420</td>
<td>20700</td>
<td>12300</td>
</tr>
<tr>
<td>Lu$_3$Al$<em>5$O$</em>{12}$</td>
<td>205, 225, 265, 350, 445</td>
<td>525, 540</td>
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<td></td>
</tr>
<tr>
<td>Y$_3$Al$<em>5$O$</em>{12}$</td>
<td>205, 225, 261, 340, 458</td>
<td>545, 555</td>
<td>27000</td>
<td>14700</td>
</tr>
</tbody>
</table>

Lit.: P. Dorenbos, J. Luminescence 99 (2002) 283
Energy levels and excitation spectrum of Ce$^{3+}$ in Y$_3$Al$_5$O$_{12}$

9.9 Ce$^{3+}$ Phosphors

**Ln$_3$Me$_5$O$_{12}$:Ce - emission spectra and color points**

Garnet structure Ln$_3$Me$_5$O$_{12}$
- Ln = Y, Ce, Gd, Lu dodecahedral
- Me = Al, Ga tetrahedral (3), Al, Ga, Sc octahedral (2)
- Substitution of Y by Gd, Tb or increasing the Ce$^{3+}$-concentration
  \[ \Rightarrow \] Red shift
- Substitution of Y by Lu or Al by Sc or Ga \[ \Rightarrow \] Blue shift

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9.10 White pcLEDs

Blue (In,Ga)N chip + (Y,Gd)$_3$Al$_5$O$_{12}$:Ce

The first commercially available LEDs followed this approach (1)

- Color rendering CRI = 70 – 85
- Cool white light
- Luminous efficiency up to 303 lm/W
- Problem: Low color rendering for red color and low color temperature
9.10 White pcLEDs

White pcLEDs with high color rendering

(1) Blue LED + (Y,Gd)$_3$Al$_5$O$_{12}$ \[\Rightarrow \text{CRI} > 75 \text{ only for } T_c > 4000 \text{ K}\]

(2) Blue LED + (Y,Gd)$_3$Al$_5$O$_{12}$ + red \[\Rightarrow \text{CRI} > 85 \text{ for } T_c < 4000 \text{ K}\]

(3) Blue LED + green + red \[\Rightarrow \text{CRI} > 85 \text{ for } 2700 < T_c < 8000 \text{ K}\]
9.10 White pcLEDs

White pcLEDs with high color rendering

Light sources for general lighting require high color rendering even at low color temperatures

2\textsuperscript{nd} Approach
- \((\text{Y},\text{Gd})_3\text{Al}_5\text{O}_{12} + \text{red phosphor}\)
- \(\text{CRI} = 85 - 95\)
- \(T_c = 2800\) to \(4000\) K
- 1 W LEDs
- 20 - 25 lm at 350 mA
- Reduced luminous flux (30 – 40%)
9.11 Problems of Ce$^{3+}$-Phosphors

General properties

- Relatively narrow absorption bands
- Relatively broad emission band
- Ce$^{3+}$-phosphors with red emission and high thermal quenching temperature are not known

Alternative activators for red-emitting phosphors

<table>
<thead>
<tr>
<th>Activator</th>
<th>Spectral range [nm]</th>
<th>Lumen equivalent [lm/W$_{opt}$]</th>
<th>Decay time $\tau$</th>
<th>Efficiency</th>
<th>Absorption at 450 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu$^{2+}$</td>
<td>360 - 700</td>
<td>50 – 550</td>
<td>~ 1 $\mu$s</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 $\mu$s</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 - high</td>
<td>weak</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>
<tr>
<td>Fe$^{3+}$</td>
<td>&gt; 700</td>
<td>&lt; 50</td>
<td>5-15 ms</td>
<td>medium</td>
<td>weak</td>
</tr>
</tbody>
</table>
9.12 Eu\(^{2+}\)-Phosphors

**Simplified energy level diagram**

- **Centroid shift**
- **Crystal field splitting**
- **Line emission**
- **Band emission**

Spectral position of the dipole-allowed 5d\(^1\)-4f\(^6\) \(\rightarrow\) 4f\(^7\) emissions-bands is determined by:

- **Crystal field splitting** of the 5d levels
- **Centroid shift** reduces the energy gap between the 4f\(^7\)- and 4f\(^6\)5d\(^1\)-configuration (nephelauxetic effect, spectroscopic polarizibility, covalency)
- **Stokes shift**

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9.12 Eu$^{2+}$-Phosphors

<table>
<thead>
<tr>
<th>Eu$^{2+}$ activated phosphor</th>
<th>Emission max. [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrB$_4$O$_7$:Eu</td>
<td>368</td>
</tr>
<tr>
<td>BaSO$_4$:Eu</td>
<td>374</td>
</tr>
<tr>
<td>Sr$_2$P$_2$O$_7$:Eu</td>
<td>420</td>
</tr>
<tr>
<td>CaAl$_2$O$_4$:Eu</td>
<td>440</td>
</tr>
<tr>
<td>BaMgAl$<em>{10}$O$</em>{17}$:Eu</td>
<td>450</td>
</tr>
<tr>
<td>Sr$_2$MgSi$_2$O$_7$:Eu</td>
<td>467</td>
</tr>
<tr>
<td>SrAl$_4$O$_7$:Eu</td>
<td>473</td>
</tr>
<tr>
<td>SrSiAl$_2$O$_3$N:Eu</td>
<td>480</td>
</tr>
<tr>
<td>Sr$<em>4$Al$</em>{14}$O$_{25}$:Eu</td>
<td>490</td>
</tr>
<tr>
<td>BaSi$_2$N$_2$O$_2$:Eu</td>
<td>490</td>
</tr>
<tr>
<td>Ba$_2$SiO$_4$:Eu</td>
<td>505</td>
</tr>
<tr>
<td>SrAl$_2$O$_4$:Eu</td>
<td>520</td>
</tr>
<tr>
<td>SrGa$_2$S$_4$:Eu</td>
<td>535</td>
</tr>
<tr>
<td>SrSi$_2$N$_2$O$_2$:Eu</td>
<td>540</td>
</tr>
<tr>
<td>CaSi$_2$N$_2$O$_2$:Eu</td>
<td>565</td>
</tr>
<tr>
<td>Sr$_2$SiO$_4$:Eu</td>
<td>575</td>
</tr>
<tr>
<td>Ba$_2$Si$_5$N$_8$:Eu</td>
<td>585</td>
</tr>
<tr>
<td>SrS:Eu</td>
<td>610</td>
</tr>
<tr>
<td>Sr$_2$Si$_5$N$_8$:Eu</td>
<td>615</td>
</tr>
<tr>
<td>CaAlSiN$_3$:Eu</td>
<td>650</td>
</tr>
<tr>
<td>CaS:Eu</td>
<td>655</td>
</tr>
<tr>
<td>SrSiN$_2$:Eu</td>
<td>700</td>
</tr>
</tbody>
</table>

Centroid shift + crystal field splitting
9.12 Eu$^{2+}$-Phosphors

Bonding interaction in MeS:Eu

- **MgS:Eu** \(\lambda_{em} = 588\) nm
- **CaS:Eu** \(\lambda_{em} = 651\) nm
- **SrS:Eu** \(\lambda_{em} = 620\) nm

Stability, crystal field splitting → Covalency between Eu and S

EHTB-MO calculations on EuAE$_{18}$S$_{44}$$^{50-}$ clusters (according to P.J. Schmidt)

Strongest binding Eu-S interaction and high covalency in CaS

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9.13 Warm White pcLEDs

Phosphors for concept (2)

Yellow: 550 – 560 nm
Red: 600 – 620 nm

(Y,Gd)$_3$Al$_5$O$_{12}$:Ce and (Ca,Sr)S:Eu
⇒ CRI > 85 for $T_c < 4000$ K

(Y,Gd)$_3$Al$_5$O$_{12}$:Ce and (Ca,Sr,Ba)$_2$Si$_5$N$_8$:Eu or (Ca,Sr)AlSiN$_3$:Eu
⇒ CRI > 75 for $T_c = 2700 – 4000$ K

Products available since 2004
9.13 Warm White pcLEDs

Structure and Properties of (Sr,Ca)S:Eu

- Rock salt (NaCl) structure
- High sensitivity towards O$_2$, H$_2$O and diluted acids
- Activator: Eu$^{2+}$
  - onto octahedral Ca$^{2+}$/Sr$^{2+}$ site
  - strong 4f-5d absorption bands below 550 nm
  - quantum efficiency > 90%
  - red emission tunable by adjustment of Sr/Ca content
9.13 Warm White pcLEDs

Properties of (Sr,Ca)S:Eu

Luminescence and reflection spectra

<table>
<thead>
<tr>
<th>Quantum yield [%]</th>
<th>Lumen equivalent [lm/W]</th>
<th>CIE1931 color point x, y</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 90</td>
<td>260 - 265</td>
<td>0.629 0.370</td>
</tr>
</tbody>
</table>

Hydrolysis of SrS:
 SrS + 2 H₂O → H₂S↑ + Sr(OH)₂

Oxidation of SrS:
 SrS + 2 O₂ → SrSO₄

Solution: Particle coatings or reduction of the basicity

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9.13 Warm White pcLEDs

Improving the stability of SrS:Eu

1. Reduction of the basicity of the (Ca,Sr)S host lattice (electron density on the anions):
   Replacement of Sr by Ca
   Red shift of the emission band
   ⇒ Reduction in the lumen equivalent

2. Reduction of susceptibility to hydrolysis:
   Application of a particle coating i.e., encapsulation of the particles with impermeable wide band gap material (Al₂O₃, LaPO₄, MgO, MgAl₂O₄, SiO₂, YPO₄, ZrO₂)
9.13 Warm White pcLEDs

Improving the stability of SrS:Eu → Compositional change

SrS:Eu ─── Stability ───> CaS:Eu

Crystal field splitting

Centroid shift

<table>
<thead>
<tr>
<th>Composition</th>
<th>QE [%]</th>
<th>Abs. [%]</th>
<th>LE [lm/W]</th>
<th>x</th>
<th>y</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaS:Eu</td>
<td>&gt; 95</td>
<td>&gt; 80</td>
<td>90</td>
<td>0.697</td>
<td>0.303</td>
</tr>
<tr>
<td>SrS:Eu</td>
<td>&gt; 95</td>
<td>&gt; 80</td>
<td>260</td>
<td>0.629</td>
<td>0.370</td>
</tr>
</tbody>
</table>
9.13 Warm White pcLEDs

Improving the stability of SrS:Eu → Particle Coatings

SiO$_2$ Particle coating acts as a diffusion barrier for H$_2$O and CO$_2$ and thus improves phosphor stability
9.14 Nitride Phosphors

Advantages over oxides and sulfides

- Highly condensed anionic networks
  \[\Rightarrow\text{high density, high chemical stability, high hardness, high thermal quenching temperature}\]
- High charge density between the activator and the anions:
  oxide < oxynitrides < nitrides < nitridocarbide
  \[\Rightarrow\text{strong red shift of the emission band}\]

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>X = O²⁻</th>
<th>X = N³⁻</th>
<th>X = C⁴⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>r [pm]</td>
<td>26</td>
<td>138</td>
<td>146</td>
<td>160</td>
</tr>
<tr>
<td>Electronegativity (\chi)</td>
<td>1.92</td>
<td>3.61</td>
<td>3.07</td>
<td>2.54</td>
</tr>
<tr>
<td>Ionic bonding Si-X [%]</td>
<td>-</td>
<td>51</td>
<td>28</td>
<td>9</td>
</tr>
</tbody>
</table>

First example: \(\text{Eu}_2\text{Si}_5\text{N}_8\) (640 nm)
9.14 Nitride Phosphors

Composition and emission spectra of commercial materials

\((\text{Ba}, \text{Sr}, \text{Ca})_2\text{Si}_5\text{N}_8: \text{Eu}\)  580 – 625 nm
\((\text{Ca}, \text{Sr})\text{AlSiN}_3: \text{Eu, O}\)  610 – 650 nm
9.14 Nitride Phosphors

Optical properties of $\text{Sr}_2\text{Si}_5\text{N}_8$:Eu

<table>
<thead>
<tr>
<th>Composition</th>
<th>Body color</th>
<th>Emission band</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Sr}_2\text{SiO}_4$:Eu</td>
<td>yellow</td>
<td>575 nm</td>
<td>Decomposition in $\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{Ba}_2\text{Si}_5\text{N}_8$:Eu</td>
<td>orange</td>
<td>580 nm</td>
<td>Decomposition in conc. acids</td>
</tr>
<tr>
<td>$\text{Sr}_2\text{Si}_5\text{N}_8$:Eu</td>
<td>orange-red</td>
<td>615 nm</td>
<td>Decomposition in conc. acids</td>
</tr>
</tbody>
</table>
9.14 Nitride Phosphors

Thermal quenching using the example of Sr$_2$Si$_5$N$_8$:Eu

- High absorption intensity between 200 and 500 nm
- Quantum yield $> 90\%$ at 450 nm excitation
- High thermal quenching temperature $T_{1/2} = \text{Temperature at which the light output is reduced by half}$
- Blue shift with increasing $T$ (thermal expansion of the lattice)

**Model:** Boltzmann-Sigmoidal

$$y = A_2 + \frac{(A_1-A_2)}{1 + \exp((x-x_0)/dx)}$$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (± Error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1.00087 ± 0.00272</td>
</tr>
<tr>
<td>A2</td>
<td>0 ± 0</td>
</tr>
<tr>
<td>x0</td>
<td>340.09306 ± 2.14197</td>
</tr>
<tr>
<td>dx</td>
<td>43.33371 ± 1.88373</td>
</tr>
</tbody>
</table>

Chi$^2$/DoF $= 0.00002$, $R^2 = 0.99868$
9.14 Nitride Phosphors / Narrow Band Red Emitter

Origin of the reduced luminous flux of warm-white LEDs

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

<table>
<thead>
<tr>
<th>FWHM [nm]</th>
<th>Position (nm)</th>
<th>LE (lm/W)</th>
<th>Red Converter</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)₂Si₅N₈:Eu</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Ca,Sr)AlSi₅N₃:Eu</td>
</tr>
<tr>
<td>20 – 30</td>
<td>655</td>
<td>278</td>
<td>Mg₂TiO₄:Mn⁴⁺</td>
</tr>
<tr>
<td>20 – 30</td>
<td>620</td>
<td>320</td>
<td>K₂SiF₆:Mn⁴⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ln³⁺ activated</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Ln = Pr, Sm, Eu)</td>
</tr>
<tr>
<td>50 – 60</td>
<td>655</td>
<td>269</td>
<td>Eu²⁺ activated</td>
</tr>
<tr>
<td>50 – 60</td>
<td>620</td>
<td>300</td>
<td>Eu²⁺ activated</td>
</tr>
</tbody>
</table>

9.14 Nitride Phosphors / Narrow Band Red Emitter

Requirements to the „ideal“ red phosphor

- Emission wavelength ~ 610 – 630 nm
- Narrow band, i.e. FWHM < 60 nm
- QE(RT) > 90% and QE(150 °C) > 80%
- Strong absorption at 410 nm and 450 nm
- \( T_{1/2} \) > 200 °C
- \( V(\lambda) \) weighed brightness value > 60% relative to (Ca,Sr)AlSiN₃:Eu,O
- Decay time < 10 ms
- No saturation to 100 W/mm²
- High (photo)chemical and thermal stability

Eu²⁺ activated red emitting phosphors meet almost all requirements!

Main problem: FWHM >> 60 nm
Narrow band red emitter Sr[LiAl$_3$N$_4$]:Eu$^{2+}$

Claimed as next generation LED-phosphor material’’

Synthesis
LiAlH$_4$ + (1-x) SrH$_2$ + x EuF$_3$ + 2 AlN + N$_2$
→ (Sr$_{1-x}$Eu$_x$)[LiAl$_3$N$_4$] + 3x HF + (3-x) H$_2$
RF-Furnace, 1000 °C

Optical Properties
$\lambda_{max}$ = 651 nm for 5% Eu$^{2+}$
FWHM = 1180 cm$^{-1}$ (~ 60 nm)
QE(200 °C) > 95% rel. to QE(RT)
Decay time of Eu$^{2+}$ ~ 1.1 µs

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

Lit.: W.S. Schnick et al., Nature Materials (2014) 1-6
9.14 Nitride Phosphors / Narrow Band Red Emitter

**Red emitting line emitter → Mn**

K\(_2\)MF\(_6\):Mn (M = Si, Ge, Ti)

- **LED Chip**
  - Blue: 420 – 480 nm

- **Converter**
  - Yellow: \((Y,Gd,Tb,Lu)Al_5O_{12}:Ce\)
  - Red: Mn\(^{4+}\)- phosphors

- **Typical yellow/red blend**
  - Tb\(_3\)Al\(_5\)O\(_{12}\):3\%Ce + K\(_2\)[MF\(_6\)]:Mn\(^{4+}\) (M = Si, Ge)

- **Problems**
  - Absorption strength, linearity, and stability of Mn\(^{4+}\)
  - MnF\(_4\) → MnF\(_3\) + \(\frac{1}{2}\) F\(_2\)

**Lit.: A. Srivastava et al., GE, US Patent US2006/0169998**
9.14 Nitride Phosphors / Narrow Band Red Emitter

Red emitting line emitter → Mn$^{4+}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>LE (lm/W)</th>
<th>Peak $\lambda_{em}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$SiF$_6$:Mn$^{4+}$</td>
<td>196</td>
<td>631.0</td>
</tr>
<tr>
<td>K$_2$TiF$_6$:Mn$^{4+}$</td>
<td>192</td>
<td>631.8</td>
</tr>
<tr>
<td>K$_2$GeF$_6$:Mn$^{4+}$</td>
<td>191</td>
<td>632.0</td>
</tr>
<tr>
<td>Mg$_{14}$Ge$<em>5$O$</em>{24}$:Mn$^{4+}$</td>
<td>80</td>
<td>658</td>
</tr>
<tr>
<td>K$_2$Ge$_4$O$_9$:Mn$^{4+}$</td>
<td>46</td>
<td>663</td>
</tr>
<tr>
<td>Rb$_2$Ge$_4$O$_9$:Mn$^{4+}$</td>
<td>38</td>
<td>667</td>
</tr>
<tr>
<td>Ca$_2$YNbO$_6$:Mn$^{4+}$</td>
<td>15</td>
<td>680</td>
</tr>
<tr>
<td>Ca$_2$LaSbO$_6$: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>

Fluorides → Rather high luminous efficacy, but stability is a challenge

Oxides → Very stable, but low luminous efficacy

Perowskites → Very stable, NIR Emitter for Horticulture Lighting

Incoherent light sources
Prof. Dr. T. Jüstel

Chapter Inorganic LEDs
Folie 43
The quest for a narrow band red emitter goes on ….

\[ \text{Eu}^{2+} \rightarrow \text{Mn}^{4+} \rightarrow \text{CdSe or InP QDots} \rightarrow \text{Ln}^{3+} \text{ or } \text{[UO}_2\text{]}^{2+} \text{ sensitised } \text{Eu}^{3+} \]

<table>
<thead>
<tr>
<th>Material</th>
<th>Peak at [nm]</th>
<th>FWHM [nm]</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Sr,Ca)S:Eu</td>
<td>615 - 650</td>
<td>60 - 70</td>
<td>Rather narrow band</td>
<td>Low chemical stability</td>
</tr>
<tr>
<td>(Sr,Ba)\textsubscript{2}Si\textsubscript{5}N\textsubscript{8}:Eu</td>
<td>585 - 625</td>
<td>80 - 100</td>
<td>Reliability</td>
<td>IR spillover</td>
</tr>
<tr>
<td>(Ca,Sr)AlSiN\textsubscript{3}:Eu</td>
<td>610 – 655</td>
<td>80 – 90</td>
<td>Reliability</td>
<td>IR spillover</td>
</tr>
<tr>
<td>SrLiAl\textsubscript{3}N\textsubscript{4}:Eu</td>
<td>650</td>
<td>50 nm</td>
<td>Narrow band</td>
<td>Self-absorption, some IR spillover</td>
</tr>
<tr>
<td>K\textsubscript{2}SiF\textsubscript{6}:Mn</td>
<td>631</td>
<td>Lines &lt; 2 nm</td>
<td>Very narrow band</td>
<td>Moderate absorption</td>
</tr>
<tr>
<td>CdSe QDots</td>
<td>Tunable green to red</td>
<td>30 – 50</td>
<td>Narrow band</td>
<td>Reliability, Reabsorption</td>
</tr>
<tr>
<td>InP QDots</td>
<td>Tunable green to red</td>
<td>45 – 65</td>
<td>Narrow band</td>
<td>Reliability, Reabsorption</td>
</tr>
<tr>
<td>Direct red LEDs</td>
<td>Tunable red</td>
<td>25 – 35</td>
<td>No Stokes loss</td>
<td>Strong TQ, more complex</td>
</tr>
<tr>
<td>\text{Ti}<em>{2}\text{Mo}</em>{3}\text{O}_{12}:\text{Eu}^*</td>
<td>615</td>
<td>Lines &lt; 1 nm</td>
<td>Very high LE and stability</td>
<td>Weak absorption</td>
</tr>
</tbody>
</table>

Modified from GE, PGS2016, Newport Beach, CA, USA
9.15 Application Areas of Inorganic LEDs

**Strengths of inorganic LEDs**
- Lifetime > 20000 h
- Dimming
- Reduced depth
- High T-stability
- Fast switching cycles
- Low voltage < 4 V
- Any color temperature
- Robustness

**Problems to be solved**
- Luminous flux per LED ↑
- Color point consistency ↑
- Price per lumen ↓
- Thermal management ↑

**Chronological deployment**
- Flashlights
- Signal lights
- Lighting panels
- Spot lighting
- Contour lighting
- Backlighting (dislays)
- Automotive lighting
- Aviation lighting
- Interior lighting
- General lighting
- Street lighting
9.15 Application Areas of Inorganic LEDs

- Signal systems
  - Traffic lights
  - Airfield lighting

- Automotive lighting
  - Taillights
  - Brake lights
  - Dashboard lights
  - Dimmed headlight /driving light
  - Interior lights

- Backlight
  - LCD screens
  - Mobile phones

- LED screens
  - Scoreboards
  - Billboards
9.15 Application Areas of Inorganic LEDs

“Color on Demand”

Blue (In,Ga)N LED (420 – 480 nm) + phosphor layer

Examples
- Magenta: Blue LED + red phosphor
- Cyan: Blue LED + green phosphor

Application in
- Company logos
- Signaling systems
- Decoration lighting
- Advertisement lighting
9.16. The Future of LED

Cost and efficiency

Costs [€/1000 lm]

Efficiency [lm/W]


Time

100 100 150 250

7 W LED
~1000 lm
for ~ 2 €

10

20

30

50

10

5

1

10

Incoherent light sources
Prof. Dr. T. Jüstel

Chapter Inorganic LEDs
Folie 48
It is important to realize that the phosphor LED is the ultimate light source with respect to the principle of light production and the possibilities of the application and their development will continue as long as their efficiency and light output will exceed that of all other light sources.
9.16. The Future of LED

Human Centric Lighting (HCL): LED spectra can be optimised to human needs

Day light

Incandescent lamp

Fluorescent lamp

Halogen lamp with IR filter

Cool white LED

Warm white LED

- Lux: 100000, 500
- UV: 5%, <1%
- VIS: 60%, 5%
- NIR: 35%, 95%

- Lux: 500
- UV: <1%
- VIS: 90%
- NIR: 10%

- Lux: 500
- UV: 0%
- VIS: 100%
- NIR: 90%

- Lux: 500
- UV: 0%
- VIS: 90%
- NIR: 10%
(In,Ga)N LEDs and laser diodes (LDs) with enhanced functionality

1. Physiological effects
   - Full spectrum light sources: 300 – 1000 nm
   - Melatonin suppression: 420 nm
   - Stimulation of collagen synthesis: 800 - 850 nm
   - Stimulation of blood flow: 700 - 1000 nm

2. Spectroscopic and sensoric functions
   - IR Spectroscopy
   - NIR emission + up-conversion of reflected radiation

3. Data transmission
   - Local NIR LAN
   - ns-phosphors
     - 700 – 3000 nm
   - Wi-Fi, Li-Fi
     - $10^9$ Hz, $10^{14}$ Hz
     - 7 Gb/s, 3 Tb/s

Incoherent light sources
Prof. Dr. T. Jüstel
9.16. The Future of LED

(In,Ga)N LEDs and LDs will also replace high pressure discharge lamps