Session: LED Phosphors

Luminescent Materials for LEDs with Ultimate Efficiency and Color Quality

By

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Almost 20% of produced electrical energy is consumed by lighting (source: NASA)

1989 “The wind of change”
21st century Development of daylight white LEDs with luminous efficiency > 120 lm/W ⇒ replacement of Na and Hg low and high pressure discharge lamps
2014 “The light of change”

East Berlin → Na lamps
West Berlin → Hg lamps
Outline

1. Advances in LED Technology
2. White Light Generation
3. Luminescent Materials (Phosphors)
4. Phosphor Converted LEDs (pcLEDs)
5. Towards Ultimate Efficiency and CRI
6. Conclusions and Outlook
1. Advances in LED Technology

1970
(Ga,As)P
< 0.1 W
< 1.0 lm
< 10 lm/W
< 120 °C
< 100 W/cm²
> 120 K/W
Yellow, red, NIR

2014
(Al,In,Ga)P, (In,Ga)N, (Al,Ga)N
0.6 - 5 W
> 100 lm
up to 303 lm/W (CREE)
120 – 200 °C
100 – 200 W/cm²
2 – 12 K/W
All colours and UV!
1. Advances in LED Technology

(Al,In,Ga)P
- 580 nm – 700 nm
- Yellow → Orange → Red

(In,Ga)N
- 370 – 530 nm
- UV-A → Blue → Green

(Al,Ga)N
- 210 – 370 nm
- UV-C → UV-A

- All spectral colours by LEDs without colour filter accessible!
- EL of semiconductors results in emission bands with small FWHM < 30 nm
- But white light cannot be efficiently produced by a single LED type so far....
1. Advances in LED Technology

Technical Status 2014

Lumen output: > 200 lm/W (cool white)
> 100 lm/W (warm white)
CRI: 70 – 95
Liftime: > 30000 h
Design: Very flexible

Presently: Retrofits für fluorescent tubes and light bulbs

Advantages of LED over Incandescent lamps | Fluorescent lamps (CFL + TL)
---|---
Higher lifetime | Simpler driving and dimming
Higher effiziency | Higher colour rendering
Better robustness | Better robustness
No IR radiation | No UV radiation
2. White Light Generation

General concepts

1. Glowing solids
   ⇒ visible light + IR
2. Gas discharges
   ⇒ VUV + UV-C/B/A + visible light
3. Semiconductors
   ⇒ UV-A or visible light or IR-A

White Light Generation

- **White**
  - colour filter
  - Coloured light by absorption
  - White light by luminescence

- **Red**
  - White light by additive colour mixing

- **Green**
  - Y or YR or RG phosphor

- **Blue**
  - White light by additive colour mixing

- **(V)UV**
  - CO or RGB phosphor blend

White Light by luminescence

Additive colour mixing

Absorption
2. White Light Generation

- **Red + Green + Blue LEDs**
- **Blue LED + yellow phosphor**
- **Blue LED + RG phosphor blend**
- **UV LED + RGB phosphor blend**
2. White Light Generation

Multichip LEDs
- Narrow band emitter
  - $\lambda_{1/2} = 30$ nm typical
  - 2 - 5 monochromatic LEDs
- Theoretical limit
  - 430 lm/W with
  - CCT = 4870 K
  - CRI = 3 (!)
- Possible values
  - 360 lm/W for CRI 90, $n = 3 - 4$
  - 320 lm/W for CRI 99, $n = 5$
- Problems
  - Thermal quenching of (Al,In,Ga)P
  - LED Efficiency
    - Red / Blue high
    - Green low “The green gap”

2. White Light Generation

300 – 350 lm/W\textsubscript{opt.}  
CRI = 70 – 85  
low CRI at low T\textsubscript{c}  
single phosphor screen

250 – 300 lm/W\textsubscript{opt.}  
CRI = 85 – 95  
high CRI at low T\textsubscript{c}  
phosphor blend

280 – 330 lm/W\textsubscript{opt.}  
CRI = 80 – 85  
CRI ~ independent of T\textsubscript{c}  
phosphor blend
2. White Light Generation

Blue band emitter + green + red converter

Conclusion: Blue LEDs emitting in the range 460 – 470 nm yield best compromise between CRI and luminous efficacy.
2. White Light Generation

**Lumen output of a light source**

- Strongly dependent on emission spectrum

- Optimal for pure 555 nm radiation
  - \( V(\lambda) = 683 \text{ lm/W} (\eta = 100\%) \)

- Luminous flux
  - 1000 lm for 555 nm requires solely 1.5 W radiation
  - „green light“

- Blue and red radiation
  - \( V(\lambda) < 70 \text{ lm/W} (<10\%) \)
  - reduces lumen equivalent
  - is required for generating white light with high CRI

**Emission of lines or narrow bands in the blue and or red desired....**

InGaN LED / Eu\(^{2+}\) Eu\(^{2+}/\) Eu\(^{3+}/\)Mn\(^{4+}\)

\[\text{Lumen output [ lm/W ]}\]

\[\lambda [ \text{ nm } ]\]
3. Luminescent Materials (Phosphors)

Definition

An (inorganic) luminescent material (phosphor) is a material which converts absorbed energy into electromagnetic radiation beyond thermal equilibrium.
3. Luminescent Materials (Phosphors)

Type of converter materials

1. Inorganic phosphors
   Microscale powders
   - SrY\textsubscript{3}Si\textsubscript{4}N\textsubscript{7}:Ce
   - (Ba,Sr)\textsubscript{2}SiO\textsubscript{4}:Eu
   - (Ca,Sr,Ba)Si\textsubscript{2}N\textsubscript{2}O\textsubscript{2}:Eu
   - SrYSi\textsubscript{4}N\textsubscript{7}:Eu
   - (Y,Gd,Tb,Lu)AG:Ce
   - CaAlSiN\textsubscript{3}:Ce
   - (Ca,Sr)\textsubscript{2}SiO\textsubscript{4}:Eu
   - (Ca,Sr)S:Eu
   - (Ca,Sr,Ba)\textsubscript{2}Si\textsubscript{5}N\textsubscript{8}:Eu
   - (Ca,Sr)AlSiN\textsubscript{3}:Eu

   Nanoscale powders
   - (Y,Gd,Tb,Lu)AG:Ce

   Quantum dots
   - (Zn,Cd)(S,Se), (In,Ga)(P,As),

2. Organic dyes
   Polycyclic aromatic compounds
   - Perylenes
   - Coumarines
   Metal complexes
   - Ln\textsuperscript{3+}-complexes Ln = Tm, Tb, Eu
   - Ru- and Ir-complexes
3. Luminescent Materials (Phosphors)

Garnets
- \((Y,Tb)_{3}Al_{5}O_{12}:Ce\)
- \(Lu_{3}Al_{5}O_{12}:Ce\)
- \(Lu_{3}(Ga,Al)_{5}O_{12}:Ce\)
- \((Lu,Y)_{3}Sc_{2}Al_{3}O_{12}:Ce\)
- \((Y,Lu)_{3}(Al,Mg, Si)_{5}O_{12}:Ce\)
- \(Ca(Y,Lu)_{2}Al_{4}SiO_{12}:Ce\)

Ortho-silicates
- \((Ca,Sr,Ba)_{2}SiO_{4}:Eu\)
- \((Ca,Sr,Ba)_{3}SiO_{5}:Eu\)

(Oxy)Nitrides
- \((Sr,Ca,Ba)_{2}Si_{5}N_{8}:Eu\) „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“
- \((Ca,Sr,Ba)SiN_{2}:Eu\) „1-1-2“
- \(La_{3}Si_{6}N_{11}:Ce\) „3-6-11“
- \(Ba_{3}Si_{6}O_{12}N_{2}:Eu\)
- \(\alpha,\beta-SiAlONes:Eu\)

Selection criteria for LED phosphors
- Patent situation
- Price and access
- (Photo)Chemical stability
- Colour point stability
- Conversion efficiency (IQA and EQA)
- Thermische quenching
- Absorption strength
- Saturation/Linearity
- Environmental issues
4. Phosphor Converted LEDs

High Power LEDs → low thermal resistance ~ 2-3 K/W typical

\[(\text{In,Ga})N \text{ semiconductor} + \text{phosphor (converter)} \rightarrow \text{Colour temperature range}\]

- **Blue** 420 – 480 nm
  - Yellow
  - Yellow + Red
  - Green + Red
  - Cool white
  - Cool and warm white

- **Near UV** 370 – 420 nm
  - Blue + Green + Red
  - Warm white
  - Cool and warm white


![Diagram showing components and color temperature ranges](image-url)
4. Phosphor Converted LEDs

Luminescent screen

\((\text{In,Ga})\text{N LED}\) Yellow/orange phosphor

\begin{align*}
\text{Intensity} & \quad \text{Emission intensity [a.u.]} \\
\text{Wavelength [nm]} & \quad 400, 450, 500, 550, 600, 650, 700, 750, 800
\end{align*}

\begin{align*}
\text{Energy} & \quad \text{Emission intensity [a.u.]} \\
\text{Wavelength [nm]} & \quad 400, 450, 500, 550, 600, 650, 700, 750, 800
\end{align*}

Status quo cool white pcLEDs @ 2014

- Phosphor \((\text{Y,Gd,Tb,Lu)}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}\) \((\text{Ca,Sr,Ba})_2\text{SiO}_4:\text{Eu}^{2+}\)
- Luminous efficacy \(\text{LE} = 303 \text{ lm/W! (WPE} \sim 80\%)\)
- Colour rendering index \(\text{CRI} \sim 70 - 80\)
- Corr. colour temperature \(T_c > 5000 \text{ K}\)
4. Phosphor Converted LEDs

Yellow Converters
Ortho-Silicates $A_2SiO_4:Eu$, $Sr_2LiSiO_4:Eu$
Oxynitrides $(Ca,Sr)Si_2N_2O_2:Eu$
$\alpha$-SiAlONes $\alpha$-SiAlON:Eu

Garnets $A_3B_2B'_3O_{12}:Ce$
Oxynitrides $(Sr_{1-x}Ba_x)_2SiO_4:Ce,N$ 470 – 525 nm UCSB
Nitrides $La_3Si_6N_{11}:Ce$ 560 nm Mitsubishi
$Sr_2Si_5N_8:Ce$ 535 nm Philips
Cyanamides $Gd_2(CN)_2:Ce \quad 540 \text{ nm}$ UniTübingen/Münster

![Graph 1](image1.png)
![Graph 2](image2.png)
4. Phosphor Converted LEDs

CRI Enhancement and colour temperature reduction of pcLEDs

LUXEON LEDs (Philips Lumileds)

(IN,Ga)N LED \( Y_3Al_5O_{12}:Ce \) Red phosphor

Status quo warm white pcLEDs @ 2014

- Red phosphor \( \text{Eu}^{2+} \) activated
- Luminous efficacy LE 80 - 150 lm/W
- Colour rendering index CRI 85 – 95
- Corr. colour temperature Tc 2500 - 4000 K

4. Phosphor Converted LEDs

Red emitting LED phosphors $\Rightarrow$ Eu$^{2+}$ doped nitrides

$\text{Ba}_2\text{Si}_5\text{N}_8$:Eu
$\text{Sr}_2\text{Si}_5\text{N}_8$:Eu
$\text{Ca}_2\text{Si}_5\text{N}_8$:Eu
$(\text{Ca},\text{Sr})\text{AlSiN}_3$:Eu
$\text{CaAlSiN}_3$:Eu

![Graph showing emission spectra of different phosphors](chart.png)
4. Phosphor Converted LEDs

Blue LED + Green + Red (band emitter) ⇒ CRI will only slightly depend on $T_c$

- **Green emitter** (AE = Ca, Sr, Ba)
- **Ortho-Silicates**
- **Oxynitrides**
- **β-SiAlONes**
- **Garnets**
- **$\text{CaSi}_2\text{N}_2\text{O}_2$ - $\text{SrSi}_2\text{N}_2\text{O}_2$ Solid solution without miscibility gap** ⇒ fine-tuning of green emission band position possible

**Emission spectrum**

- **Emission intensity [a.u.]**
- **Wavelength [nm]**

**Excitation spectrum**

- **Relative intensity [a.u.]**
- **Wavelength [nm]**

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**Graphs:**

- **Graph 1:** Emission and excitation spectra of a blue LED, green converter, and red converter.
- **Graph 2:** Emission and excitation spectra of various compounds, including $\text{CaSi}_2\text{N}_2\text{O}_2$, $\text{SrSi}_2\text{N}_2\text{O}_2$, and oxynitrides.
4. Phosphor Converted LEDs

First all nitride LED demonstrated in 2005 (QE > 0.9, \(Q_{E\text{rel}}(200 \, ^\circ\text{C}) > 0.95\))

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

Colour rendering index > 88
Excellent colour point stability
with drive is achieved

4. Phosphor Converted LEDs

Eu\textsuperscript{2+} and Yb\textsuperscript{2+} Phosphors

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>Emission at</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu\textsuperscript{2+} [Xe]4f\textsuperscript{7}</td>
<td></td>
</tr>
<tr>
<td>BaSi\textsubscript{2}N\textsubscript{2}O\textsubscript{2}:Eu</td>
<td>490 nm</td>
</tr>
<tr>
<td>SrSi\textsubscript{2}N\textsubscript{2}O\textsubscript{2}:Eu</td>
<td>540 nm</td>
</tr>
<tr>
<td>CaSi\textsubscript{2}N\textsubscript{2}O\textsubscript{2}:Eu</td>
<td>565 nm</td>
</tr>
<tr>
<td>Ba\textsubscript{2}Si\textsubscript{5}N\textsubscript{8}:Eu</td>
<td>580 nm</td>
</tr>
<tr>
<td>Sr\textsubscript{2}Si\textsubscript{5}N\textsubscript{8}:Eu</td>
<td>610 nm</td>
</tr>
<tr>
<td>(Ca,Sr)AlSiN\textsubscript{3}:Eu</td>
<td>630 nm</td>
</tr>
<tr>
<td>Ca\textsubscript{2}Si\textsubscript{5}N\textsubscript{8}:Eu</td>
<td>650 nm</td>
</tr>
<tr>
<td>CaAlSiN\textsubscript{3}:Eu</td>
<td>650 nm</td>
</tr>
</tbody>
</table>

Yb\textsuperscript{2+} [Xe]4f\textsuperscript{14}

Ca\textsubscript{m/2}Si\textsubscript{12-m-n}Al\textsubscript{m+n}O\textsubscript{n}N\textsubscript{16-n}:Yb | 550 nm |


SrSi\textsubscript{2}N\textsubscript{2}O\textsubscript{2}:Yb | 615 nm |

Problem: Thermal quenching

4. Phosphor Converted LEDs

Thermal quenching of a typical LED converter material

- Thermal quenching is a reversible process and occurs for all kind of phosphors
- The quenching temperature is a strong function of the activator, host, and its interaction

![Diagram showing thermal quenching](image)
5. Towards Ultimate Efficiency and CRI

Causes for the reduction in luminous 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)$_2$Si$_5$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 = Pr, Sm, Eu)</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>

5. Towards Ultimate Efficiency and CRI

Narrow-band red-emitting Sr[LiAl$_3$N$_4$]:Eu$^{2+}$
as a next-generation LED-phosphor material”
Appeared on-line June 22$^{nd}$

**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**
$\lambda_{\text{max}}$ = 651 nm for 5% Eu$^{2+}$
FWHM = 1180 cm$^{-1}$
QE(200 °C) > 95% of QE(RT)
Decay time Eu$^{2+}$ ~ 1.1 µs
Exc. @ 410 nm → Photoionisation!
Strong re-absorption of YAG/LuAG PL
5. Towards Ultimate Efficiency and CRI

**LED Converter**

- **Blue**: 420 – 480 nm Chip
- **Yellow**: (Y,Gd,Tb,Lu)Al$_5$O$_{12}$:Ce
- **Red**: Mn$^{4+}$- phosphor

*(GE Patent US2006/0169998)*

**Tb$_3$Al$_5$O$_{12}$:3%Ce + K$_2$[TiF$_6$]:Mn$^{4+}$

**Problems:** Absorption strength, decay time and stability of red line emitter
5. Towards Ultimate Efficiency and CRI

Challenges

• Red narrow band or line emitter
  → to increase lumen equivalent

• Reduced re-absorption
  → to increase package gain

<table>
<thead>
<tr>
<th>Red emitting ion</th>
<th>LE [lm/W_{opt.}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu$^{2+}$</td>
<td>80 - 200</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>220 – 360</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>240 – 260</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>200 – 220</td>
</tr>
<tr>
<td>Mn$^{4+}$</td>
<td>80 – 150</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>&lt; 100</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>&lt; 100</td>
</tr>
</tbody>
</table>
5. Towards Ultimate Efficiency and CRI

Eu$^{3+}$ doped Molybdates, e.g. LiLaMo$_2$O$_8$:Eu and Tb$_2$Mo$_3$O$_{12}$:Eu

T-dependent integral emission intensity

- QE$_{465}$ $\sim$ 100%
- $R_{465}$ = 75%
- $R_{395}$ = 60%
- CIE x = 0.665
- CIE y = 0.333
- $\lambda_{\text{max}}$ = 614 nm
- $\lambda_{\text{centroid}}$ = 623 nm
- $\tau_{1/e}$ = 0.39 ms (0.2 x Y$_2$O$_3$:Eu)
- $d_{50}$ = 4.2 µm

5. Towards Ultimate Efficiency and CRI

Phosphor converted LED comprising \( \text{Tb}_2\text{Mo}_3\text{O}_{12}:\text{Eu} \)

465 nm InGaN LED

\( \Rightarrow \) Full conversion

LED possible
5. Towards Ultimate Efficiency and CRI

LE and CRI calculations of warm-white phosphor converted LEDs

465 nm LED + YAG:Ce + red emitter @ 2700 K

Tb$_2$Mo$_3$O$_{12}$:Eu gives 20% higher LE compared to SrLiAl$_3$N$_4$:Eu

The reduced re-absorption in Eu$^{3+}$ phosphor comprising LEDs gives potentially higher package gain as well ....
5. Towards Ultimate Efficiency and CRI

**Powder/polymer composites**
- Variable layer thickness
- Strong scattering
- High thermal resistance
- Drop-Stop

**Ceramics**
- Homogeneous layer thickness
- Little scattering
- Low thermal resistance
- Pick & Place

- Blue LED + inorganic luminescent powder in epoxy- or silicon resin

**Blue LED + ceramic converter**
(Lumiramic or c²)
5. Towards Ultimate Efficiency and CRI

Eu$^{3+}$ doped molybdates as red colour converter in white-emitting pcLEDs

→ Useful in near UV emitting LEDs (380 - 420 nm)

→ Conversion of red emitting powders into ceramics
6. Summary and Outlook

LiEuMo$_2$O$_8$, Li$_3$Ba$_2$Eu$_3$Mo$_8$O$_{32}$, Tb$_2$Mo$_3$O$_{12}$:Eu (Sm) - Are these luminescent converters applicable in white light emitting pcLEDs?

+ Cost effective and scalable synthesis routes
+ ~ 20% higher lumen equivalent than Eu$^{2+}$ doped sulphides and nitrides
+ Quantum yield at ambient temperature close to unity
+ Less than 20% thermal quenching upon heating to 150 °C
+ Reasonable absorption strength between 370 and 410 nm

- Narrow width of absorption 4f-4f line multiplets
- Diffuse reflectance at 465 and 535 nm still 70 - 80%

→ Useful in pcLEDs comprising a near UV emitting (In,Ga)N die (370 – 410 nm) as a pump source
→ Further optimisation by ceramic preparation or multiple activator ion sites, as inTb$_2$MoO$_6$:Eu
6. Summary and Outlook

<table>
<thead>
<tr>
<th>Cool white LEDs</th>
<th>Warm white LEDs</th>
<th>Warm White LEDs (near UV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Blue chip</td>
<td>Blue chip</td>
<td>Blue/cyan luminescent material</td>
</tr>
<tr>
<td>2. Ln\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}:Ce</td>
<td>Ln\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}:Ce</td>
<td>Ln\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}:Ce</td>
</tr>
<tr>
<td>3. None</td>
<td>CaS:Eu/Sr\textsubscript{2}Si\textsubscript{5}N\textsubscript{8}:Eu</td>
<td>CaS:Eu/Sr\textsubscript{2}Si\textsubscript{5}N\textsubscript{8}:Eu/CaAlSiN\textsubscript{3}:Eu</td>
</tr>
<tr>
<td></td>
<td>CaAlSiN\textsubscript{3}:Eu</td>
<td>Eu\textsuperscript{3+}-doped molybdates</td>
</tr>
</tbody>
</table>

Red line emitters Eu\textsuperscript{3+} doped molybdates/tungstates
- Strong absorption at 395, 465, 535 nm
- Quantum efficiency ~ 100%
- Problem: Absorption strength in the blue weak compared to CaS:Eu and Sr\textsubscript{2}Si\textsubscript{5}N\textsubscript{8}:Eu

Next steps
- Increase average particle size to enhance absorption strength
- Final goal: Transparent ceramics?
- Development of further stable green, yellow and red line phosphors with high luminous efficiency
6. Summary and Outlook

Increase of the power density

→ 8000 lm module (CREE)

Further power density increase will require phosphors with improved linearity

Development of the power density of LED
(source: fairchildsemi.com)
Acknowledgement

• Research Group “Tailored Optical Materials“ for synthesis, photographs, spectroscopy, and so on….

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