Luminescent Materials for Cool and Warm White LEDs

Thomas Jüstel

University of Applied Sciences Münster

Materials Valley Workshop
January 20th, 2011

19% of the Electrical Energy is Consumed for Lighting (Source: NASA)

If a 150 lm/Watt Solid State White Light Source were developed, then in the US alone

- we save 273 TWh/year in energy
- we alleviate the need of 133 new power stations
- we Eliminate 258 Mill. tons of carbon dioxide

http://www.netl.doe.gov/ssl/PDFs/oida led-oled rpt.pdf

http://www.eere.energy.gov/buildings/info/documents/pdfs/ssl_final_report3.pdf

Outline

1. Evolution of Light Sources

2. Principles of White Light Generation

3. Inorganic Luminescent Materials

4. Phosphor Converted White LEDs

5. Summary and Outlook

1. Evolution of Light Sources - General

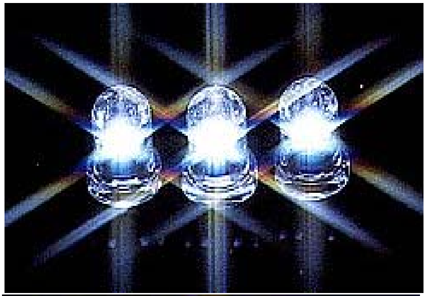
10000 B.C. | 19^{th} century | 20^{th} century | 21^{st} century

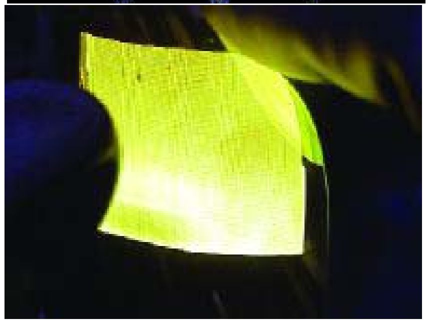
First there was open fire...

...then the fire was tamed...

...put into a glass bulb...

...and made more efficient...



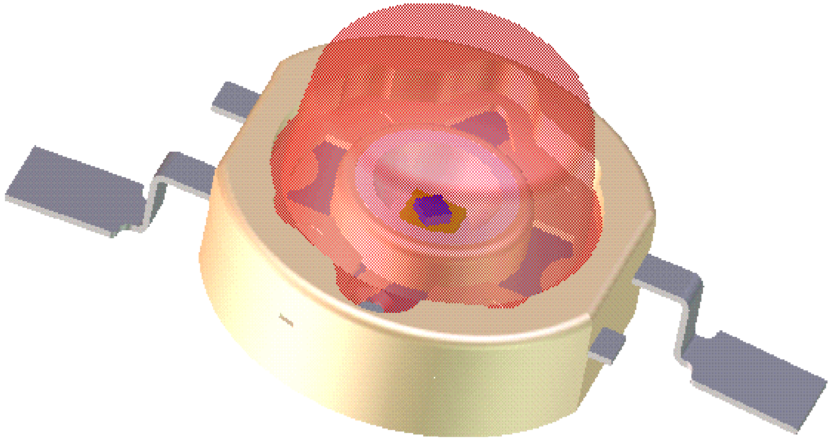


...then the fire vanished and light only prevailed !

Chemical light sources

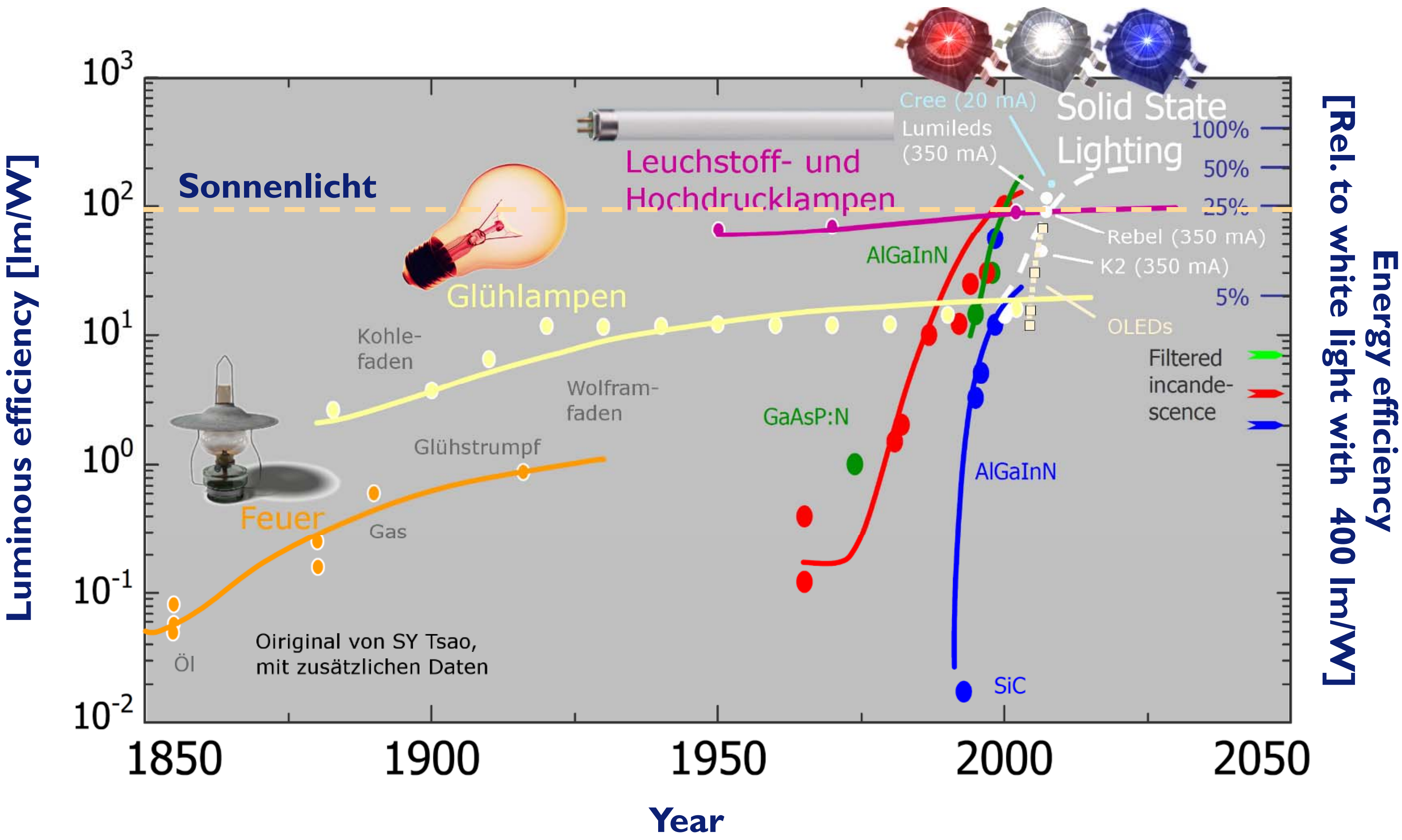
Electrical light sources

1. Evolution of Light Sources - LEDs



1970	2011
$(Ga_{1-x}As_x)P$	$(Al_{1-x-y}In_xGa_y)P$ $(Al_{1-x-y}In_xGa_y)N$
< 0.1 W	< 30 W
< 0.1 lm	> 200 lm
yellow, red	all colours + UV-A/B/C

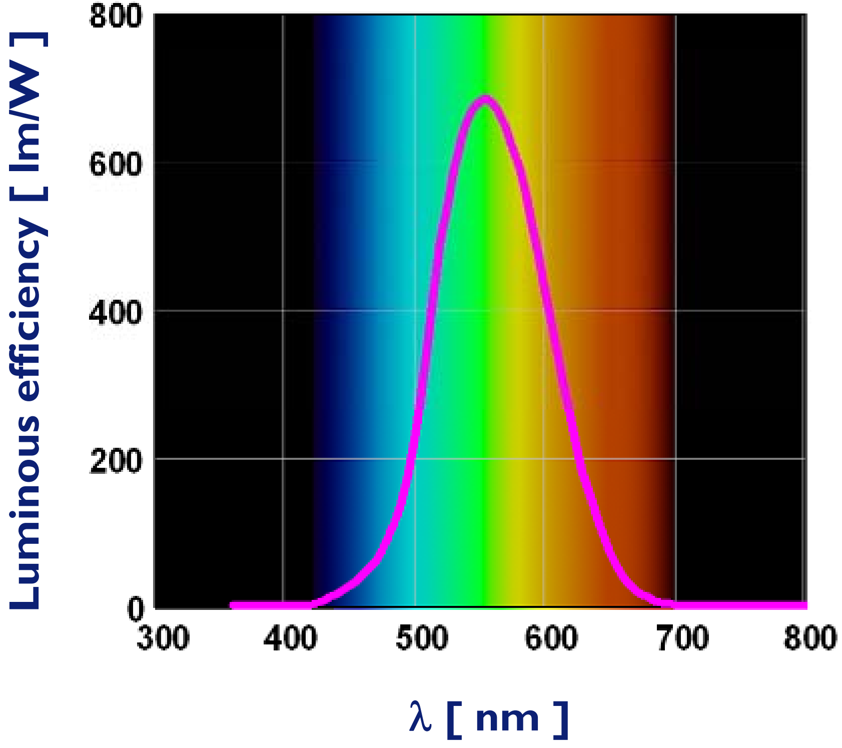
1. Evolution of Light Sources – Efficiency



2. Principles of White Light Generation

Luminous efficiency of light sources

- Strong dependence on the spectrum
- Optimum is at 555 nm
  - V(λ) = 683 lm/W (100%)
- Lumen output
  - 1000 lm at 555 nm requires 1.5 W
  - Incandescent bulb ~ 80 W, i.e. 12.5 lm/W
- Blue and red radiation
  - V(λ) < 70 lm/W (10%)



2. Principles of White Light Generation

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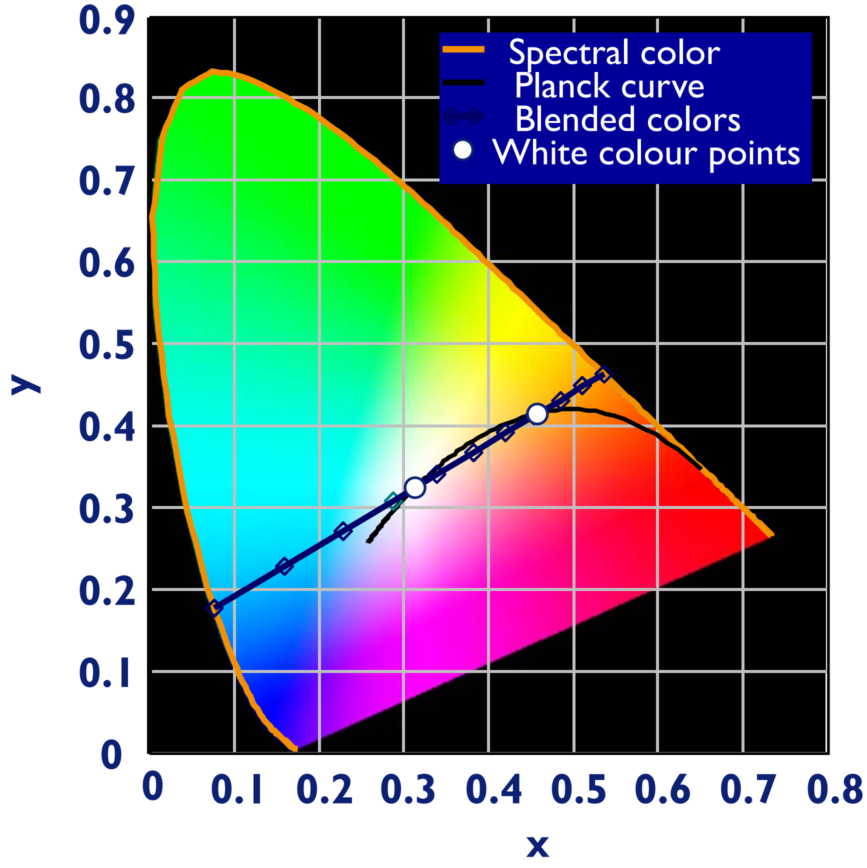
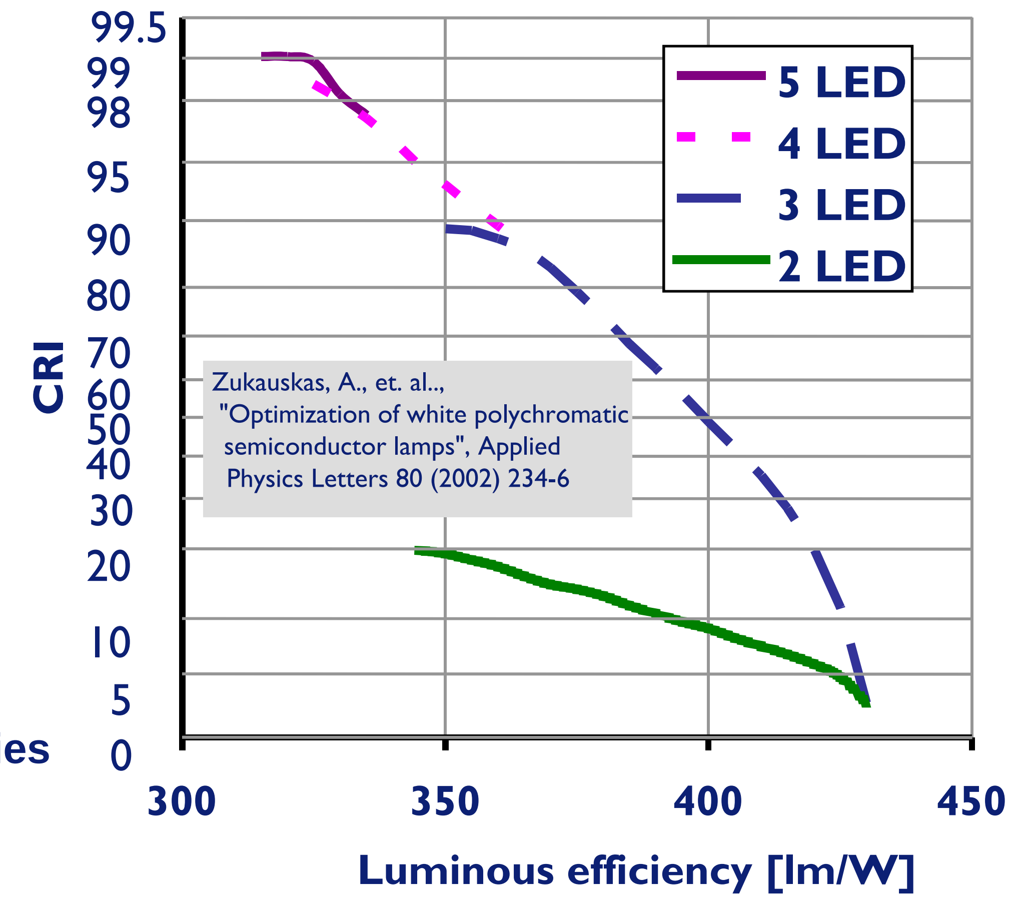
- White light is achieved by blending several spectral colors
  - At least two spectral lines („pure colors“
  - Or two broad bands (less color saturation)
- The maximum of luminous efficiency for white light is 430 lm/W!!!
- Perceived differences
  - Color point, e.g. cool vs. warm white
  - Effect on illuminated objects

  → Color Rendering Index CRI
- A high color rendering index requires a line multiplett or broad bands



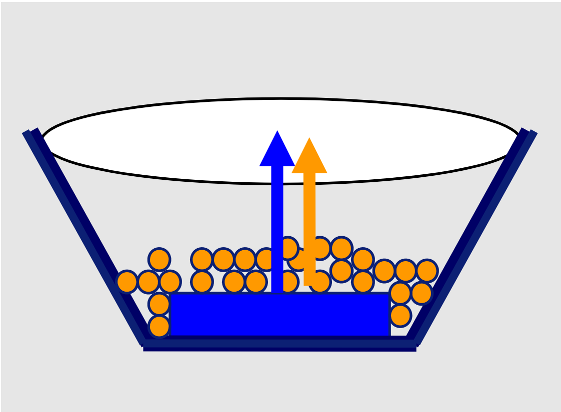
2. Principles of White Light Generation

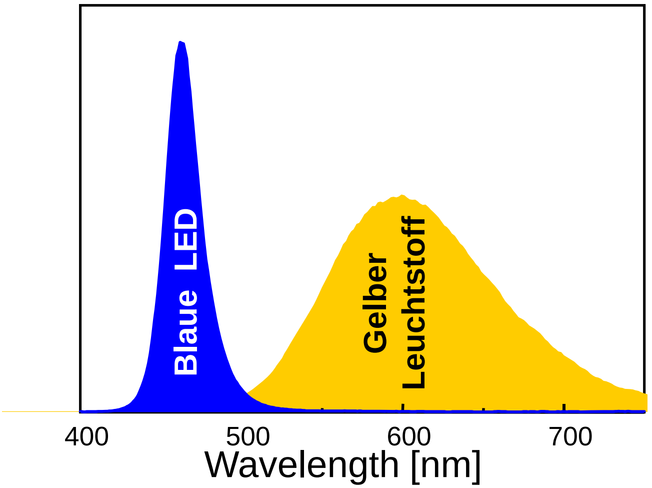
- Narrow band emitter (e.g. LEDs)
  - $\lambda_{1/2}$ = 30 nm
  - Array of colored light sources
- Theoretical maximum
  - 430 lm/W at
  - CCT : 4870 K
  - CRI = 3 (!)
- Useful values
  - ~ 350 lm/W at CRI 90, n = 3 - 4
  - max. 320 lm/ W a CRI 99, n = 5
- Problems
  - Thermal stability of the primaries
  - LED effiziency
    - Red and blue high
    - Green moderate



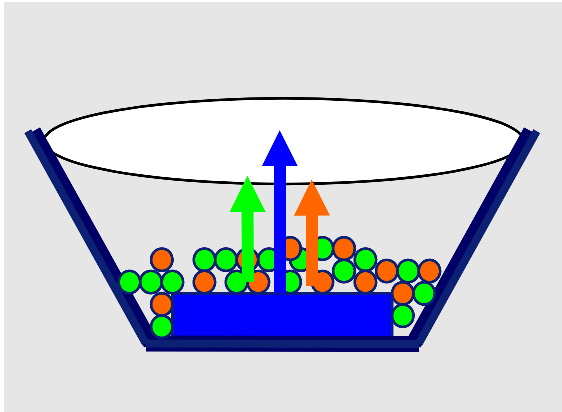
2. White Light Generation

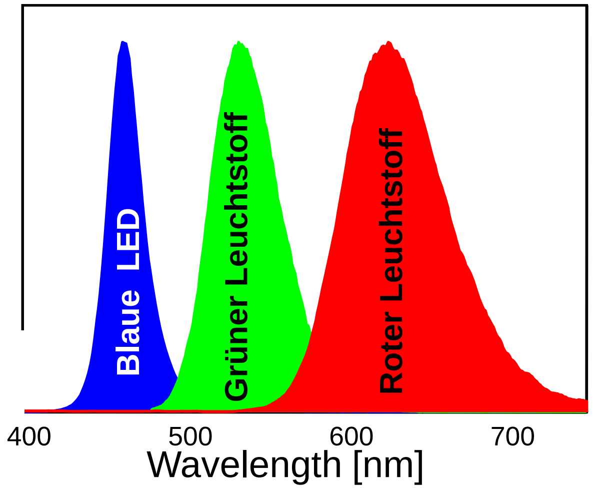
Blue LEDs + yellow phosphor



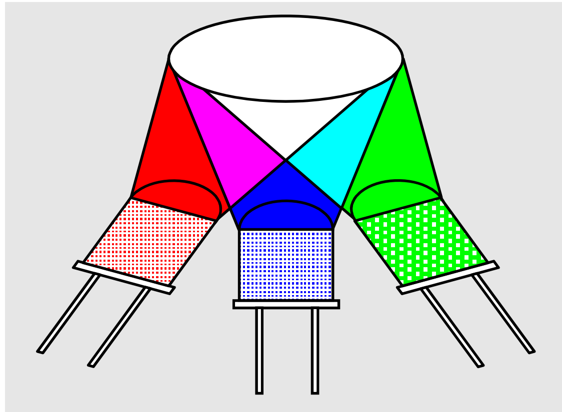


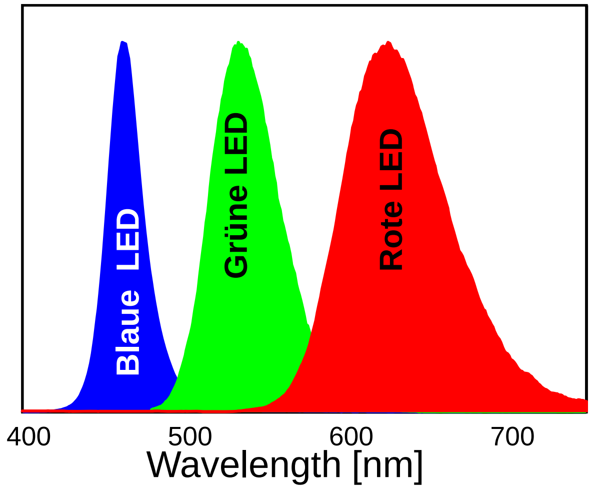
Blue LED + green phosphor + red phosphor





Red + green+ blue LEDs





3. Inorganic Luminescent Materials

Requirements on color converters

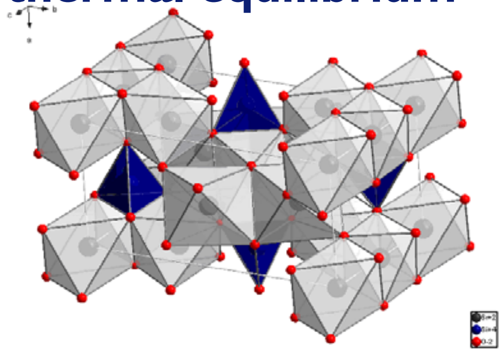
- Strong absorption ⇒ allowed optical transitions
- Suitable emission band position and width
- High conversion efficiency
- High stability in device manufacturing process
- High stability under device operation

→ Suitable optical centres (activator ions) are mainly Rare Earth ions!

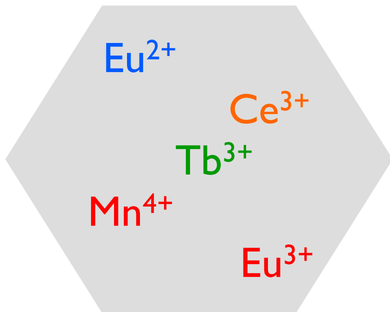
Emission color	UV LEDs	Blue LEDs
Blue	Eu^{2+}, Ce^{3+}, Bi^{3+}	-
Cyan	Eu^{2+}, Ce^{3+}	Eu^{2+}
Green	Eu^{2+}, Ce^{3+}, Tb^{3+}, Mn^{2+}	Eu^{2+}, Ce^{3+}
Yellow	Ce^{3+}, Eu^{2+}, Mn^{2+}	Ce^{3+}, Eu^{2+}, Mn^{2+}
Red	Eu^{2+}, Mn^{2+}, Eu^{3+}	Eu^{2+}, Mn^{2+}

3. Inorganic Luminescent Materials

An (inorganic) luminescent material (phosphor) is a material which converts absorbed energy into electromagnetic radiation beyond thermal equilibrium

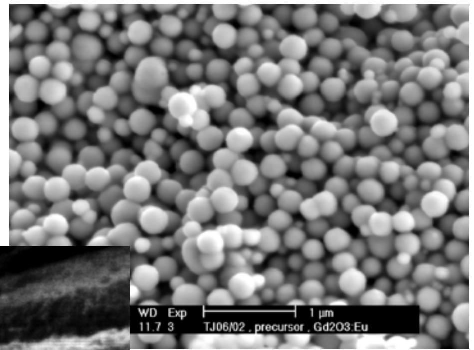


Inorganic Host
- Chemical stability
- Photostability
- Absorption and color point

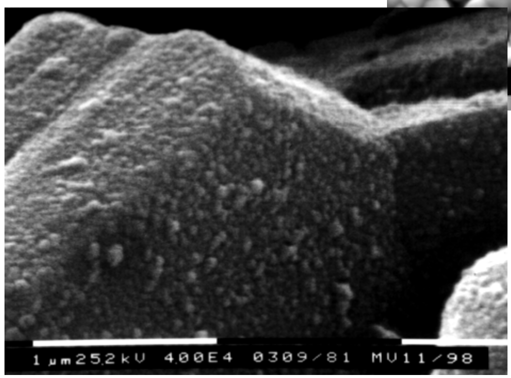


Dopants
- Quantum efficiency
- Absorption and color point
- Thermal quenching

Morphology
- Efficiency
- Stability

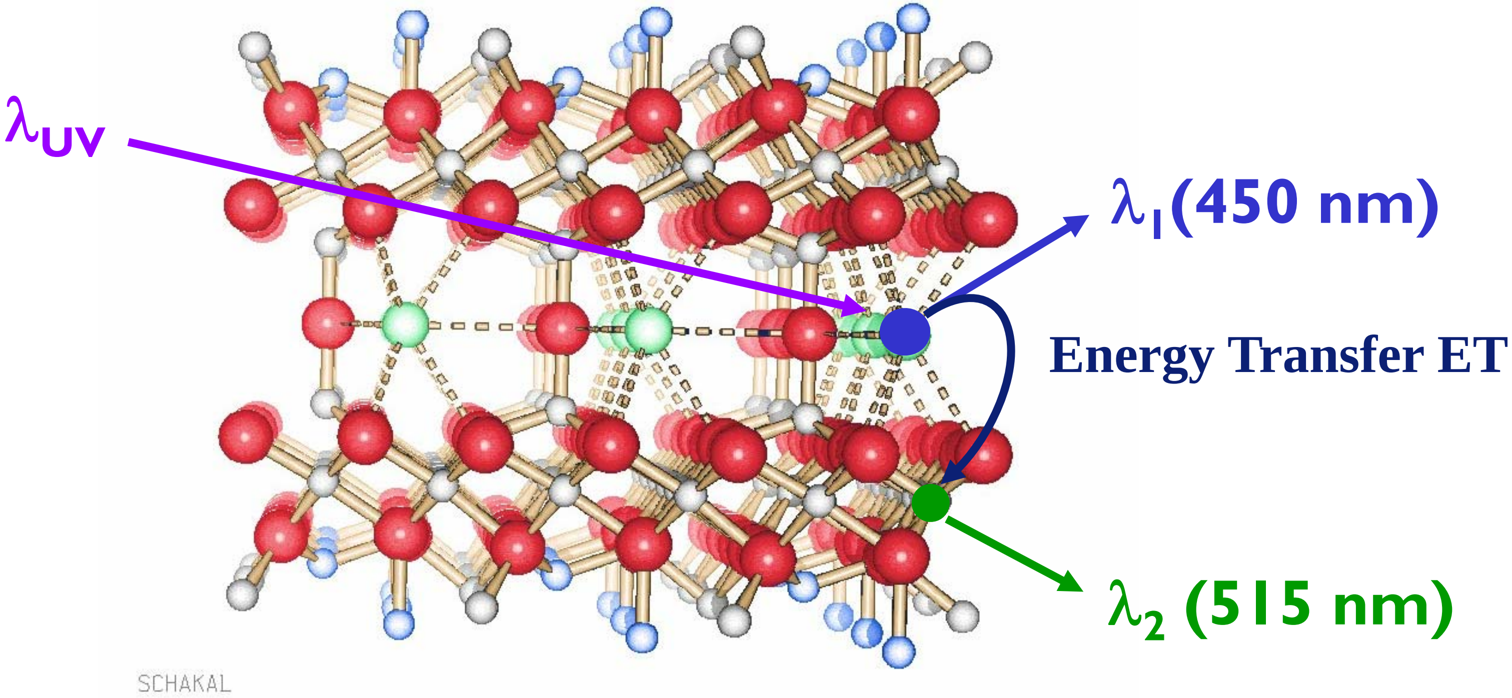


Coatings
- Chemical stability
- Light in- and out-coupling (efficiency)



3. Inorganic Luminescent Materials

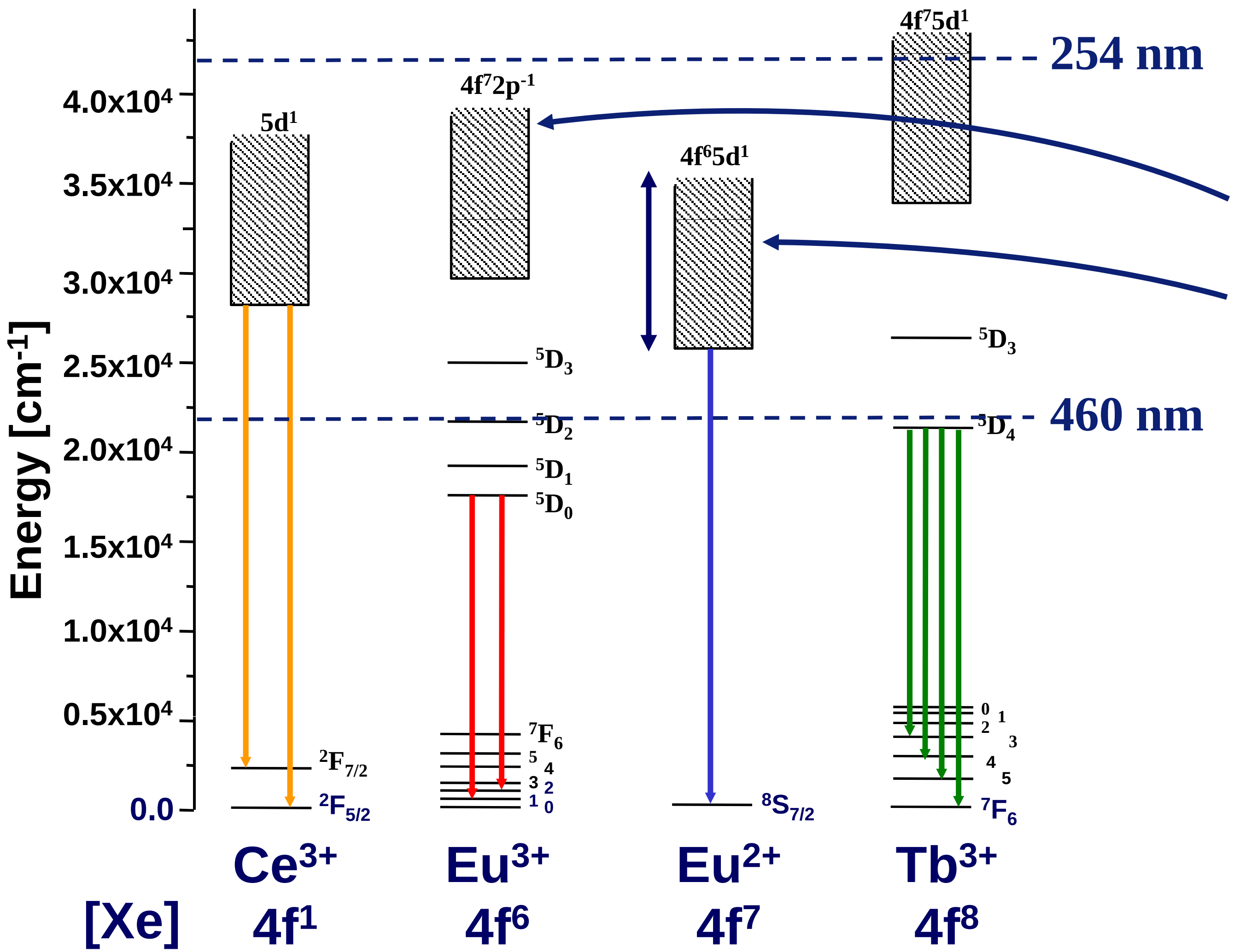
Example $BaMgAl_{10}O_{17}$:S,A



Divalent RE ions	**Ba^{2+} sites in the conduction layer**	**Eu^{2+}**
Divalent TM ions	**tetrahedral gaps in the spinel blocks (weak absorption)**	**Mn^{2+}**

3. Inorganic Luminescent Materials

Energy level schemes of selected rare earth ions



Excitation via

a) CT transitions

b) $4f^n$ - $4f^{n-1}5d^1$ transitions

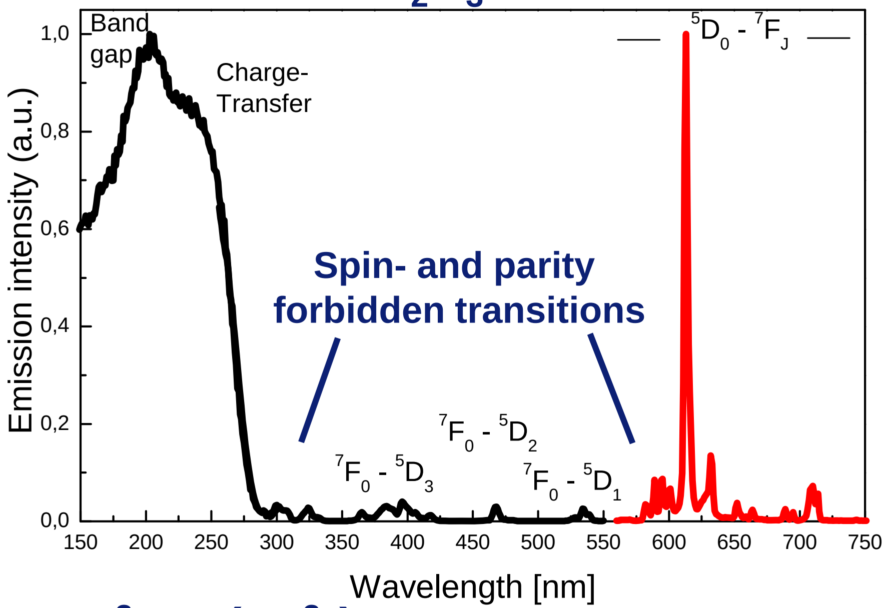
c) Sensitisers

Rare earth ions enable materials with a quantum yield of ~ 100%

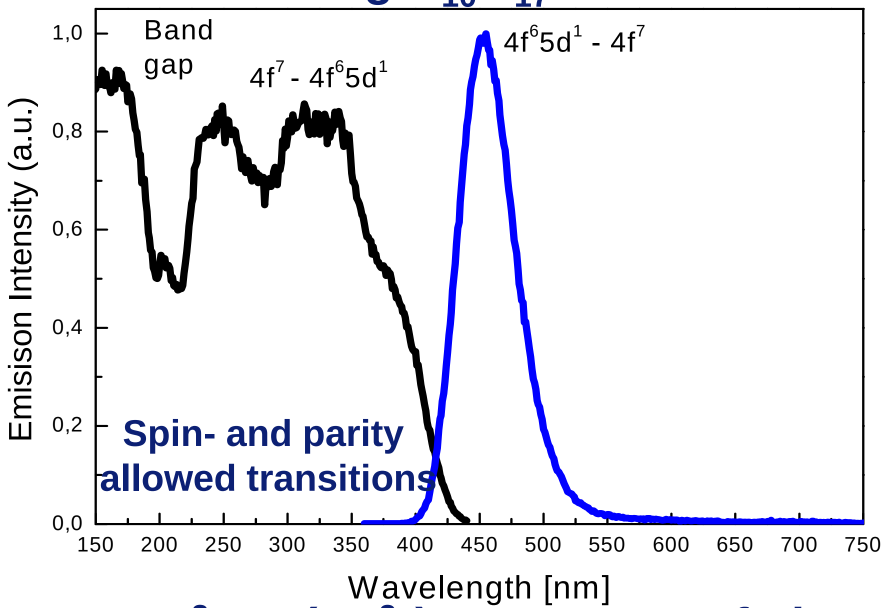
3. Inorganic Luminescent Materials

Excitation and emission spectra of Eu^{n+} phosphors

$Y_2O_3:Eu^{3+}$



$BaMgAl_{10}O_{17}:Eu^{2+}$



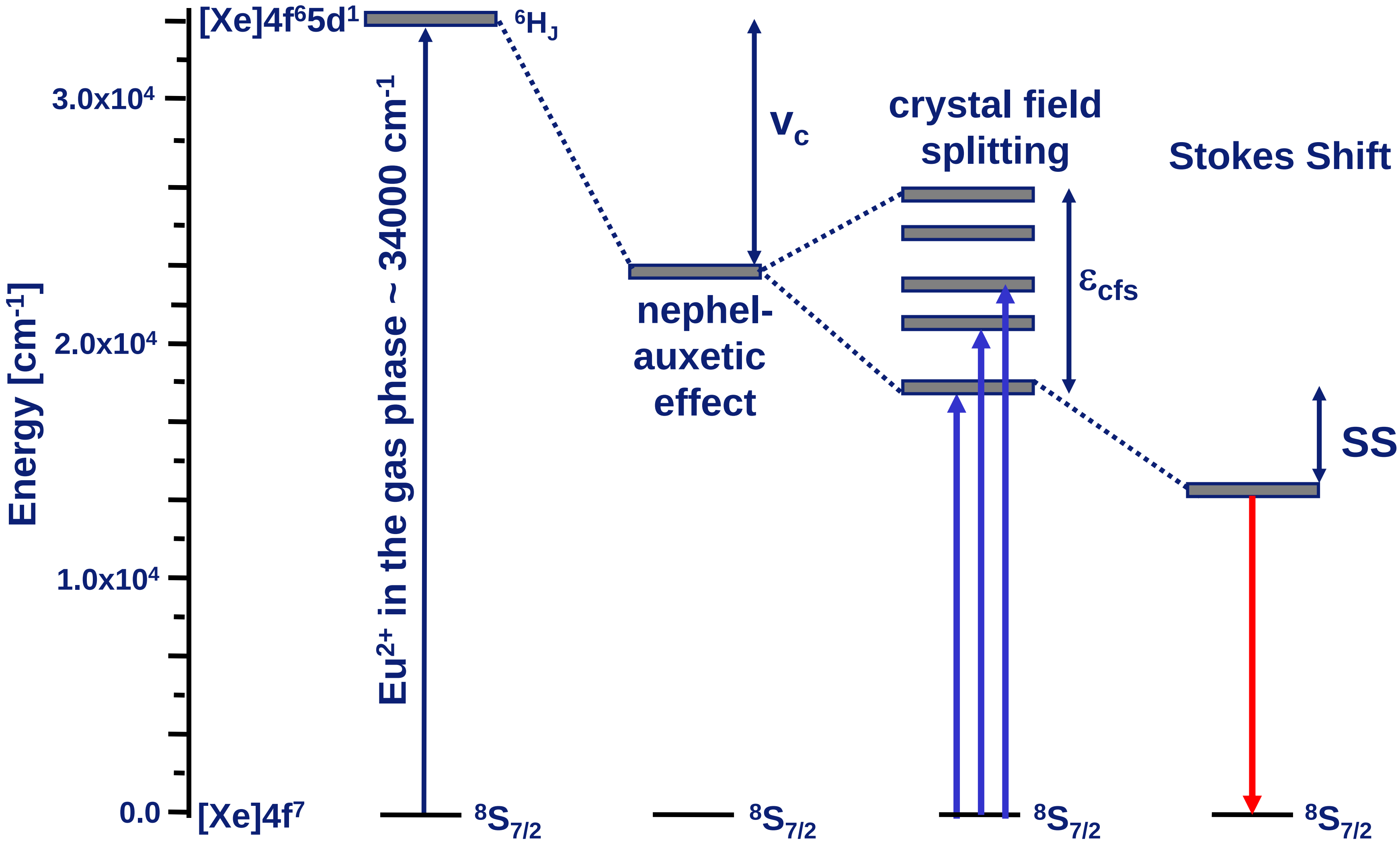
$Eu^{3+} \rightarrow (Eu^{3+})^{**}$	CT
$(Eu^{3+})^{**} \rightarrow (Eu^{3+})^{*}$	Relaxation
$(Eu^{3+})^{*} \rightarrow Eu^{3+}$	4f4f

$Eu^{2+} \rightarrow (Eu^{2+})^{**}$	4f5d
$(Eu^{2+})^{**} \rightarrow (Eu^{2+})^{*}$	Relaxation
$(Eu^{2+})^{*} \rightarrow Eu^{2+}$	5d4f

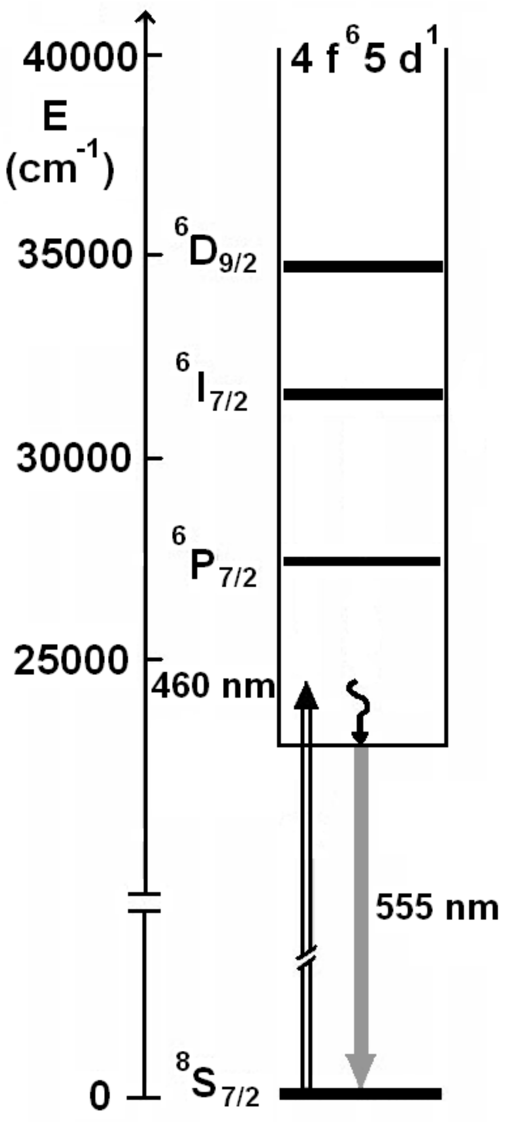
Strong CT absorption band
Weak 4f4f absorption lines at 394 and 465 nm

Strong 4f5d absorption bands
Weak and invisible 4f4f absorption lines

3. Inorganic Luminescent Materials



3. Inorganic Luminescent Materials

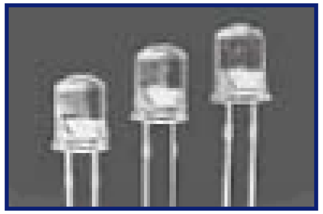


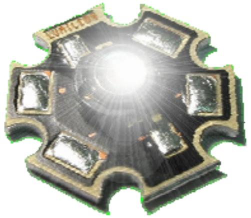
Eu^{2+} activated phosphor	Emission max. [nm]
SrB_4O_7:Eu	368
$BaSO_4$:Eu	374
$Sr_2P_2O_7$:Eu	420
$CaAl_2O_4$:Eu	440
$BaMgAl_{10}O_{17}$:Eu	450
$Sr_2MgSi_2O_7$:Eu	467
$SrAl_4O_7$:Eu	473
$SrSiAl_2O_3N$:Eu	480
$Sr_4Al_{14}O_{25}$:Eu	490
$BaSi_2N_2O_2$:Eu	490
Ba_2SiO_4:Eu	505
$SrAl_2O_4$:Eu	520
$SrGa_2S_4$:Eu	535
$SrSi_2N_2O_2$:Eu	540
$CaSi_2N_2O_2$:Eu	565
Sr_2SiO_4:Eu	575
$Ba_2Si_5N_8$:Eu	585
SrS:Eu	610
$Sr_2Si_5N_8$:Eu	615
$CaAlSiN_3$:Eu	650
CaS:Eu	655
$SrSiN_2$:Eu	700

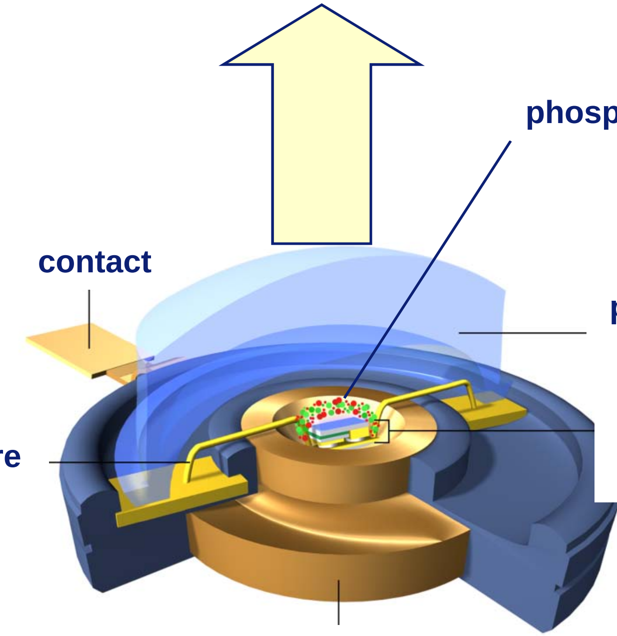
Centroid shift + crystal-field splitting

4. Phosphor Converted White LEDs

Principle of operation





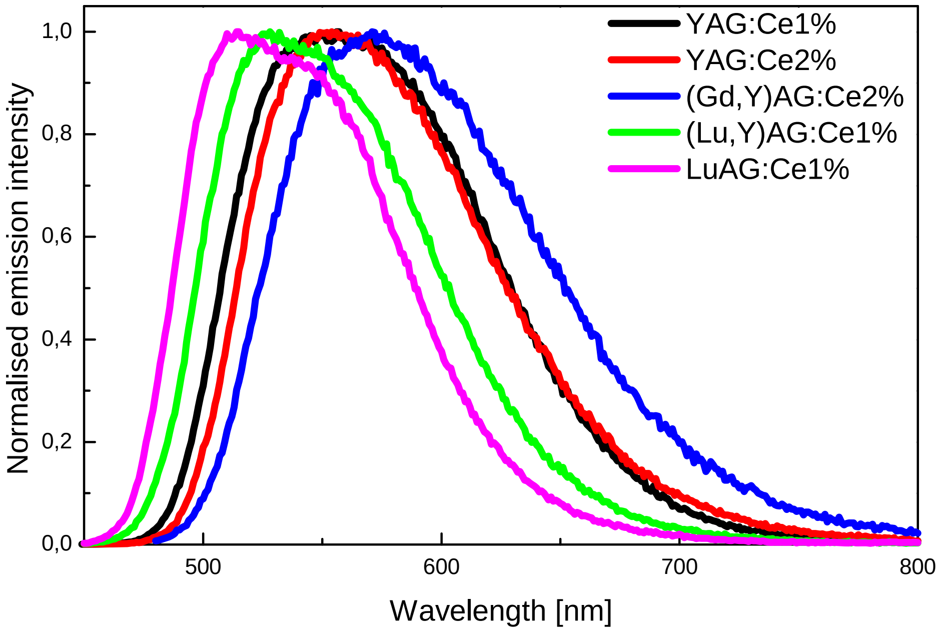


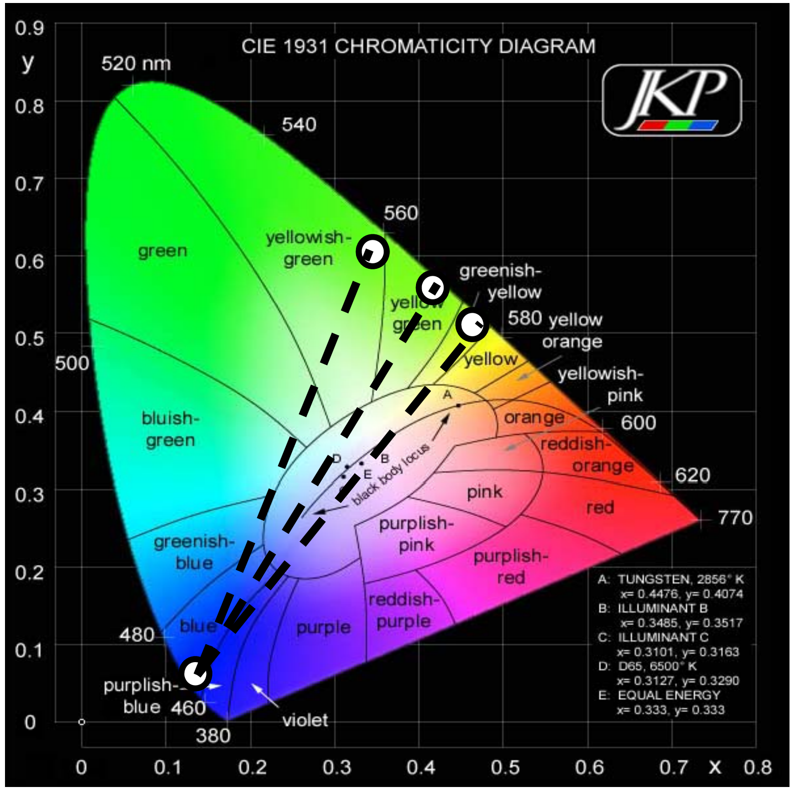
< 1.0 lm	10 – 150 lm
< 0.1 W	0.6 – 5 W
< 120 °C	120 – 200 °C
< 100 W/cm²	100 – 200 W/cm²
> 120 K/Wm	2 – 12 K/W

(In,Ga)N semiconductor	+ phosphor (converter)	→ Light colour
Blue 420 – 480 nm	Yellow	cool white
	Yellow + Red	warm white
	Green + Red	cool and warm white

4. Phosphor Converted White LEDs

Emission spectra of $Ln_3Al_5O_{12}:Ce$

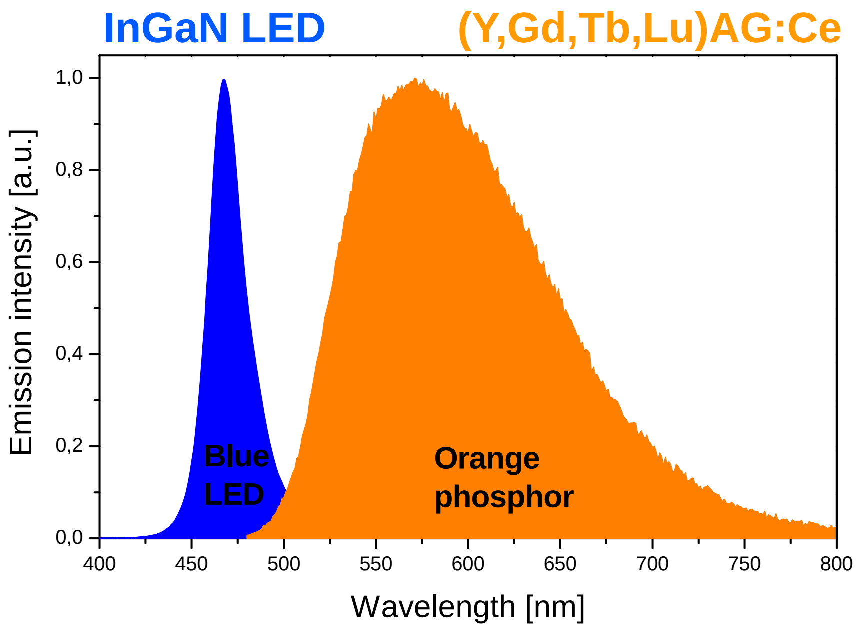


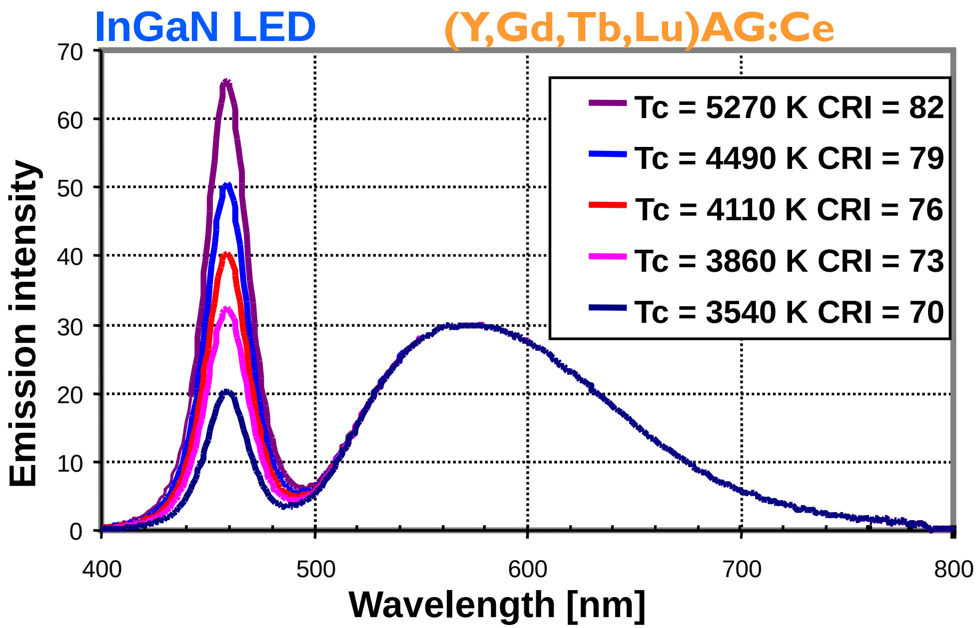


Garnet structure $Ln_3Me_5O_{12}$

- **Ln = Y, Ce, Gd, Lu dodecahedral**
- **Me = Al, Ga tetrahedral(3), octahedral(2)**
- **Substitute Y^{3+} by Ce^{3+} 560 nm → 565 nm (Red-Shift)**
- **Substitute Y^{3+} by Gd^{3+}, Dy^{3+}, or Tb^{3+} 560 nm → 580 nm (Red-Shift)**
- **Substitute Al^{3+} by Ga^{3+} or Y^{3+} by Lu^{3+} 560 nm → 520 nm (Blue-Shift)**

4. Phosphor Converted White LEDs





Status quo cool white LEDs @ 2011

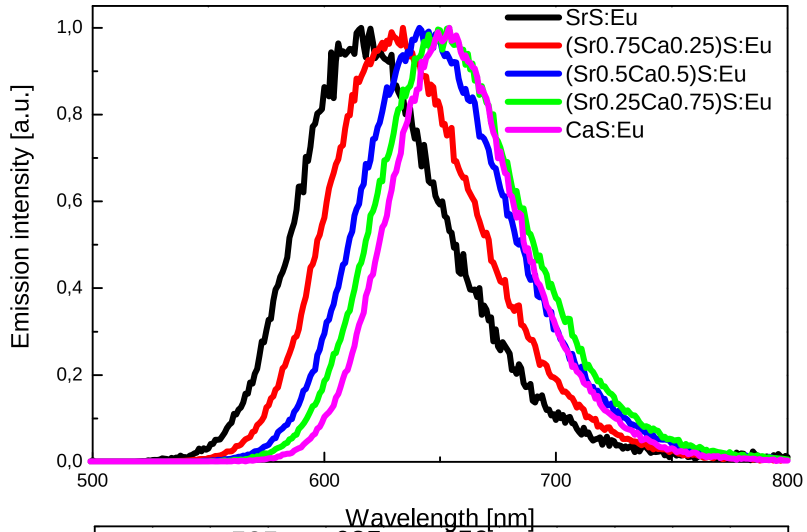
- **Luminous efficacy** 50 - 210 lm/W_{el}
- **Color rendering index** 70 – 80
- **Color temperature** > 4000 K due to lack of red light

4. Phosphor Converted White LEDs

Red emtting luminescent materials

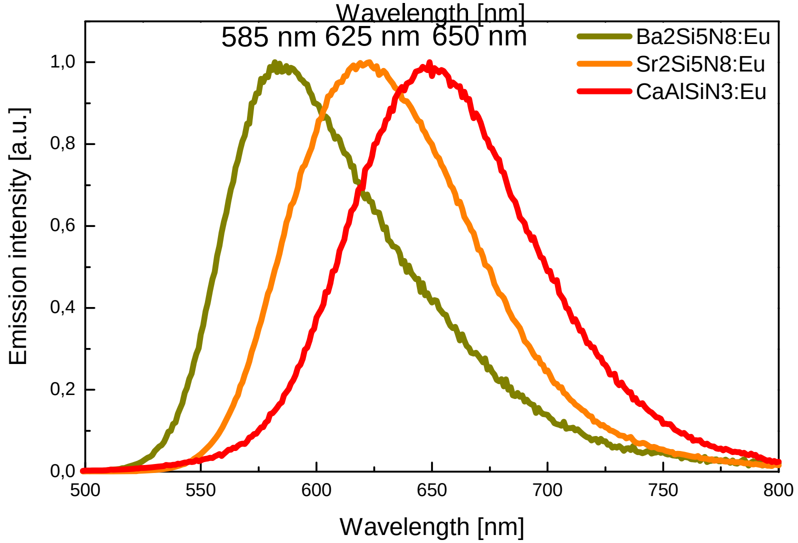
Sulphide lattices, e.g.

$(Ca_{1-x}Sr_x)S:Eu$

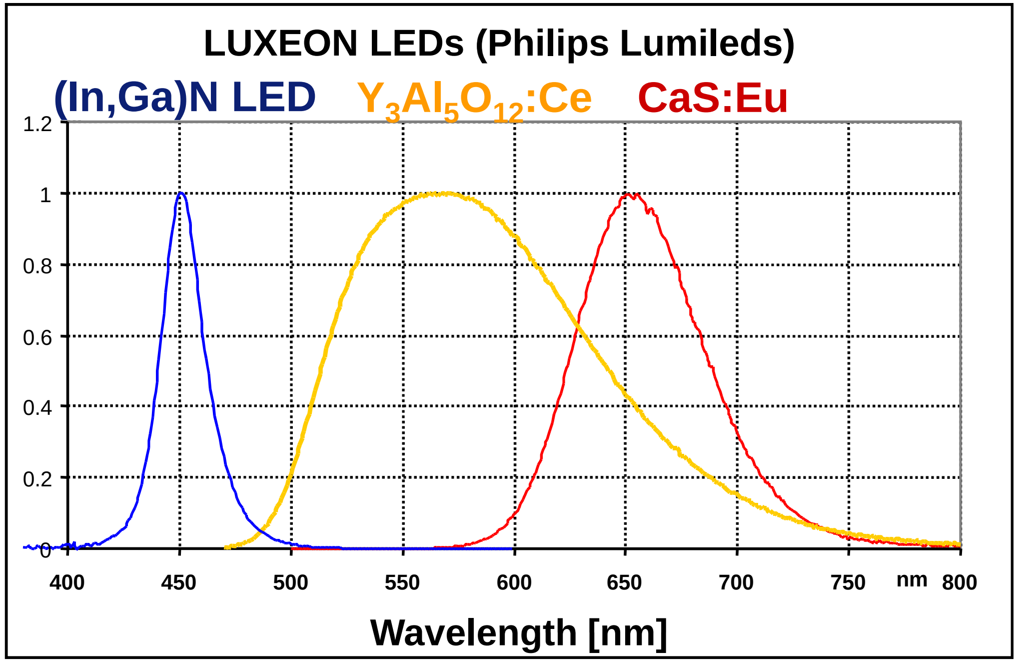


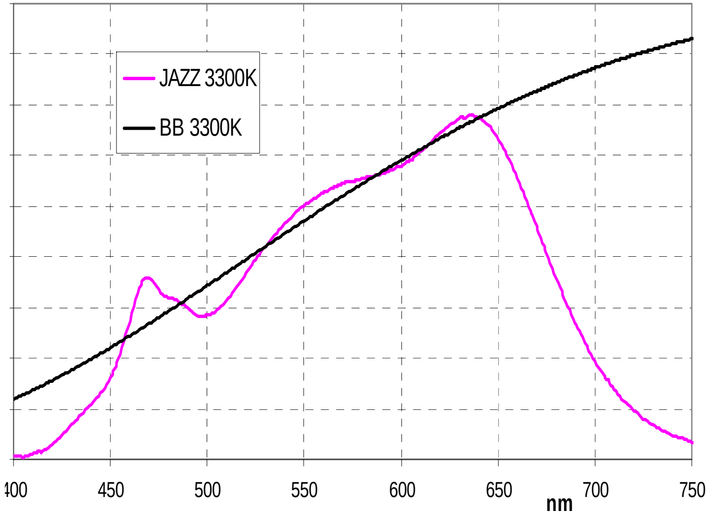
Nitride lattices, e.g.

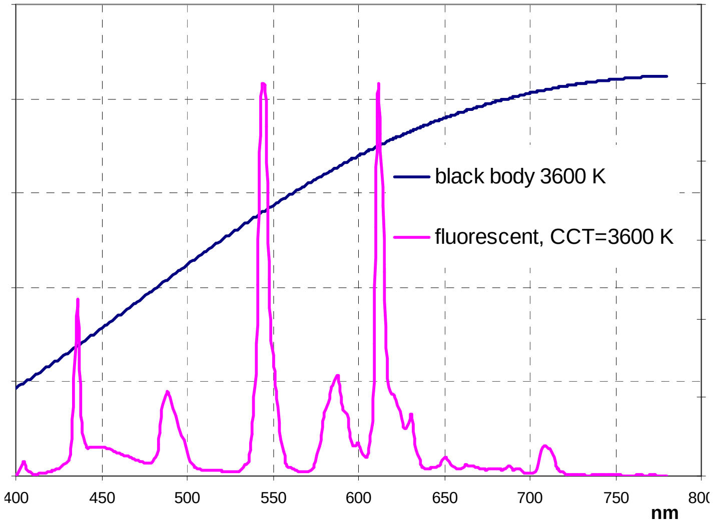
$(Ca_{1-x}Sr_x)AlSiN_3:Eu$



4. Phosphor Converted White LEDs







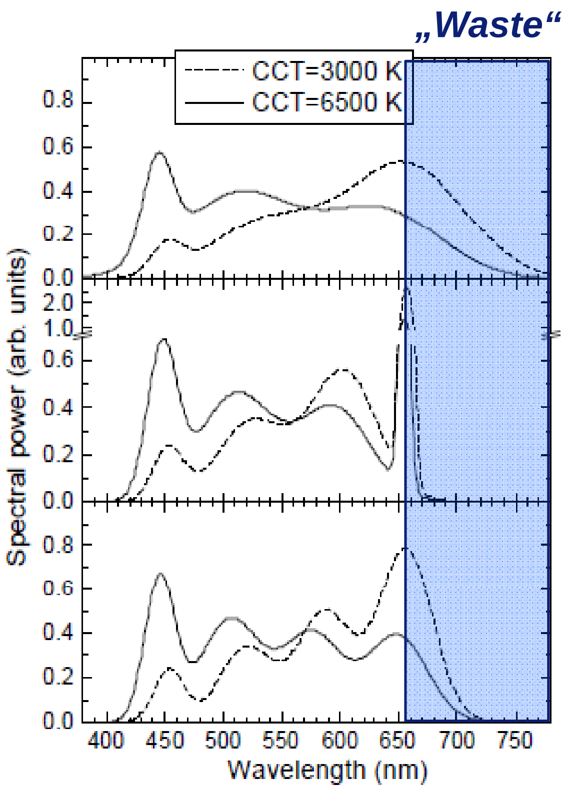
Status quo warm white LEDs @ 2011

- Luminous efficacy 60 - 80 lm/W_{el}
- Color rendering index 85 – 95
- Color temperature 2500 - 4000 K

4. Phosphor Converted White LEDs

Causes for the reduction in luminous efficacy

1. Spectral interaction between phosphors, i.e. re-absorption
2. Reduction in lumen equivalent



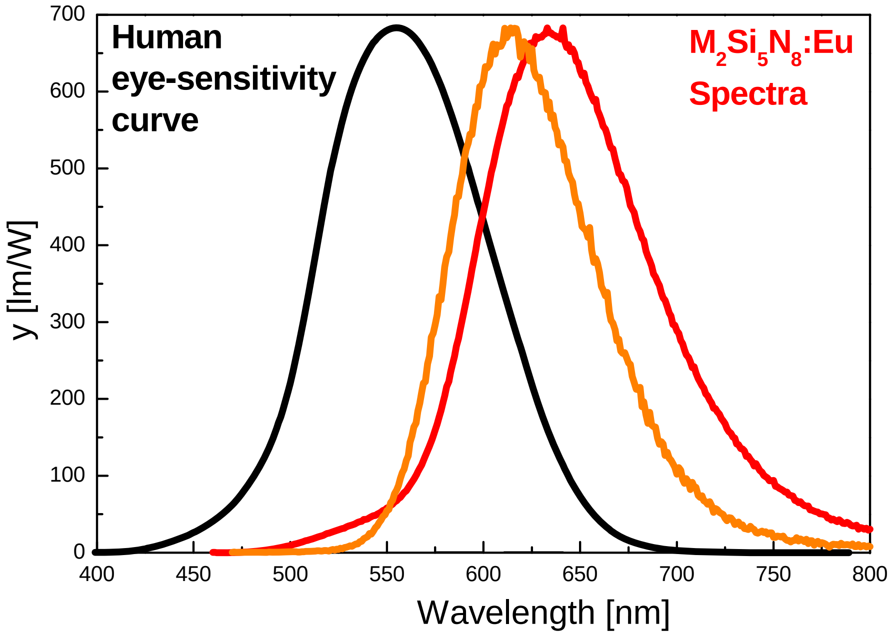
Band width [nm]	Peak @ (nm)	LE (lm/W)	Phosphor
115	635	257	$(Ca,Sr)AlSiN_3$:Eu
20 – 30	655	278	Mg_2TiO_4:Mn^{4+}
20 – 30	620	320	Mn^{4+} activated Eu^{3+} activated
50 – 60	655	269	Eu^{2+}- activated
50 – 60	590	300	Eu^{2+}- activated

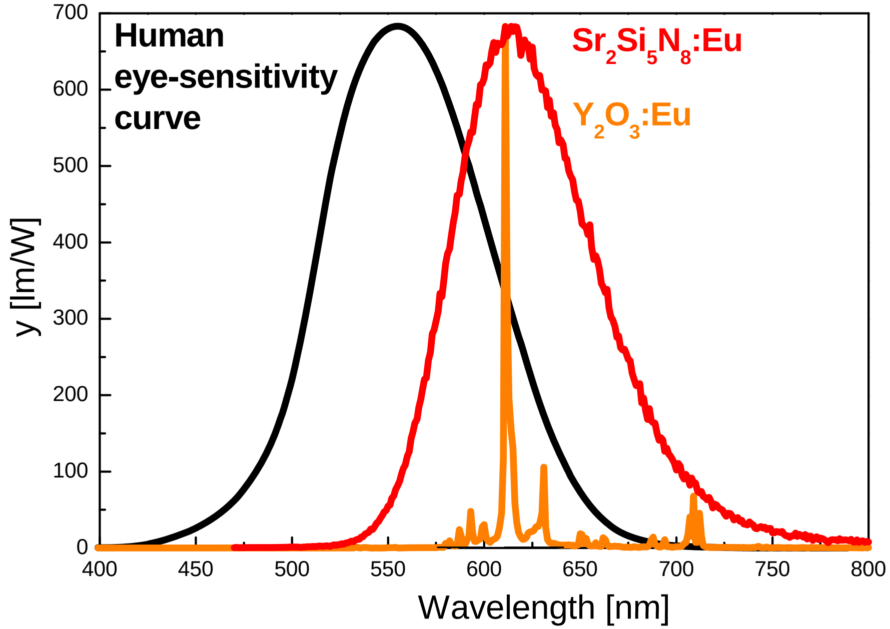
A. Zukauskas et al., APPLIED PHYSICS LETTERS 93 (2008) 051115

4. Phosphor Converted White LEDs

Next goal: Increase of the luminous efficacy of warm white LEDs!

Optimisation of the emission band position and width of Eu^{2+} phosphors	**Replacement of red Eu^{2+} phosphor by a narrow band emitter, e.g. Eu^{3+}**





4. Phosphor Converted White LEDs

Potential activators for red emitting phosphors are RE or TM ions

Ion	spectral range[nm]	LE [lm/W_{opt}]	Decay time	Efficiency	Absorption at 450 nm
Eu^{2+}	360 - 700	50 – 550	~ 1 µs	high	strong
Eu^{3+}	590 - 710	200 – 360	~ 1 ms	high	weak
Sm^{2+}	670 - 770	< 100	~ 1 µs	high	moderate
Sm^{3+}	560 - 710	240 – 260	0.5 ms	medium	weak
Pr^{3+}	590 - 680	100 – 220	0.1 ms	medium to high	weak
Mn^{2+}	500 - 650	100 - 550	5-15 ms	High	weak
Mn^{4+}	620 - 680	80 – 230	1-10 ms	High	moderate
Cr^{3+}	680 - 750	< 100	1-10 ms	High	moderate
Fe^{3+}	> 700	< 50	5-15 ms	Medium	weak

Rare earth ions are the best choice due to their high efficiency, short decay time, good linearity, strong absorption, and spectral flexibility

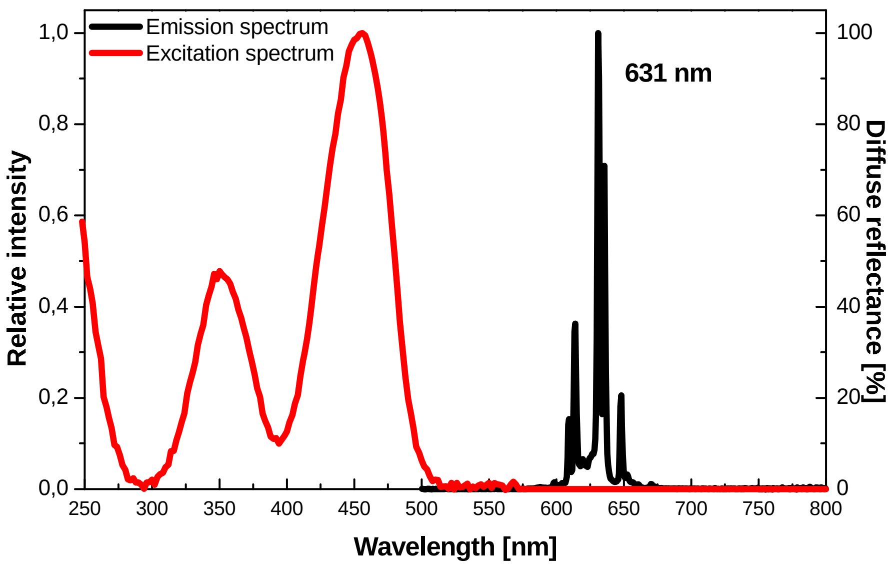
Problem areas:

- Redox stability (Eu^{2+}, Ce^{3+})
- Lumen equivalent
- Price development

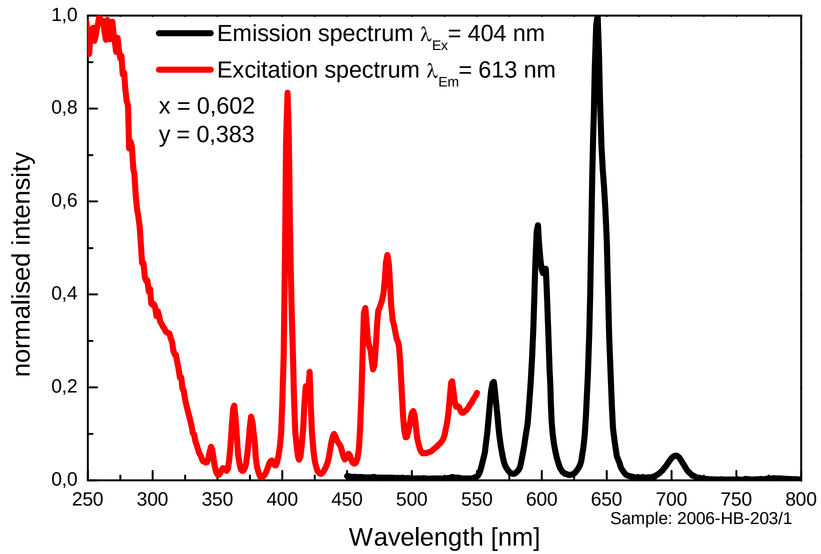
4. Phosphor Converted White LEDs

Potential activators for red line emitting phosphors are RE or TM ions

$K_2SiF_6:Mn^{4+}$



$La_2W_3O_{12}:Sm^{3+}$



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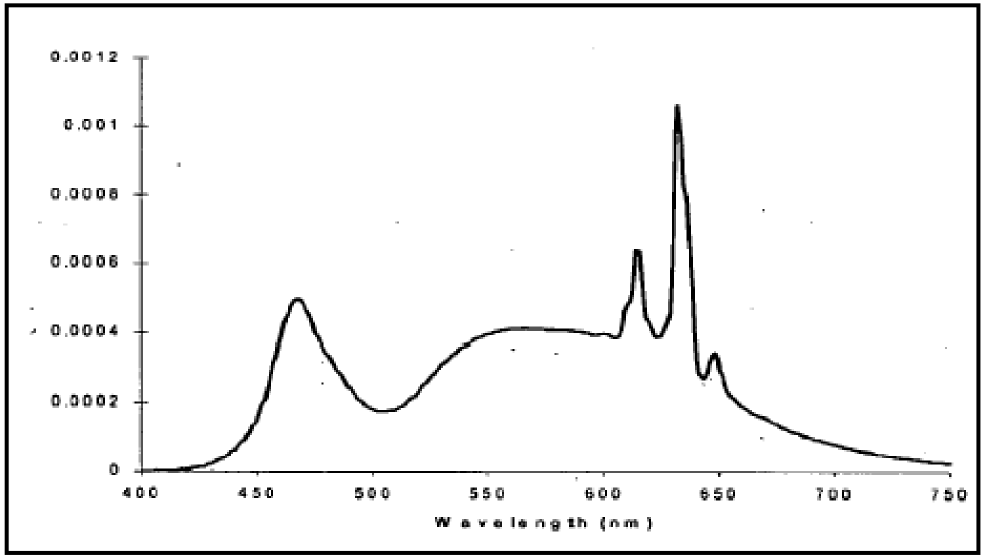
4. Phosphor Converted White LEDs

Application of a red line emitting luminescent material activated by Mn^{4+}

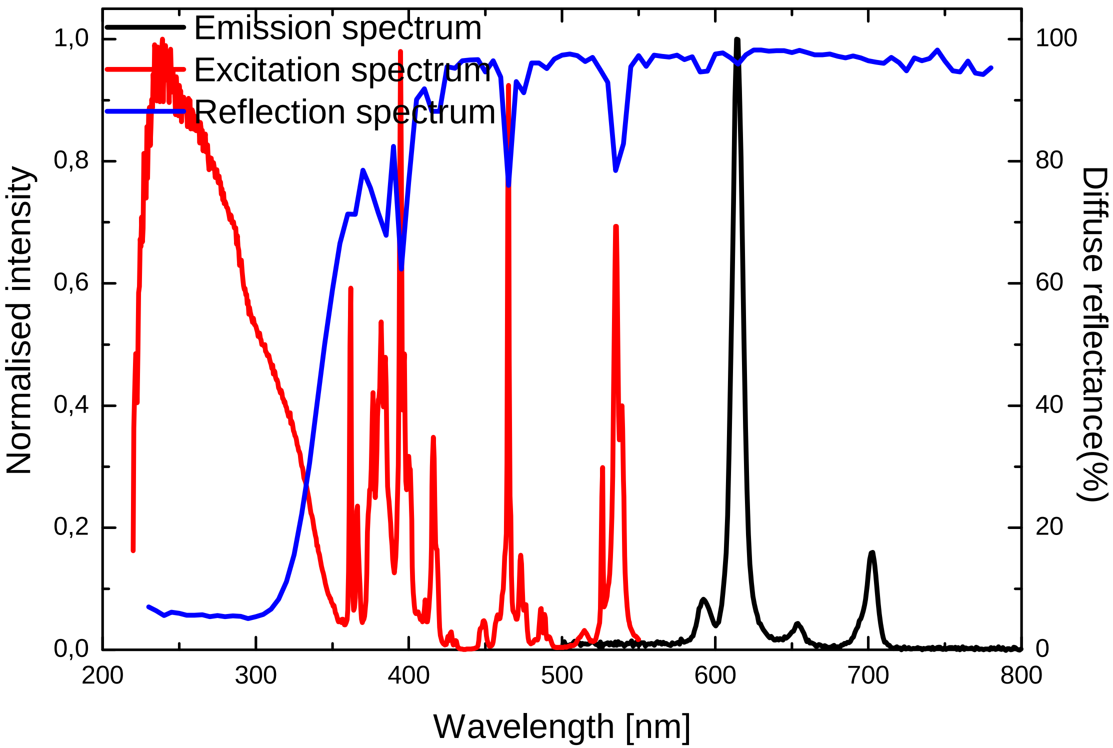


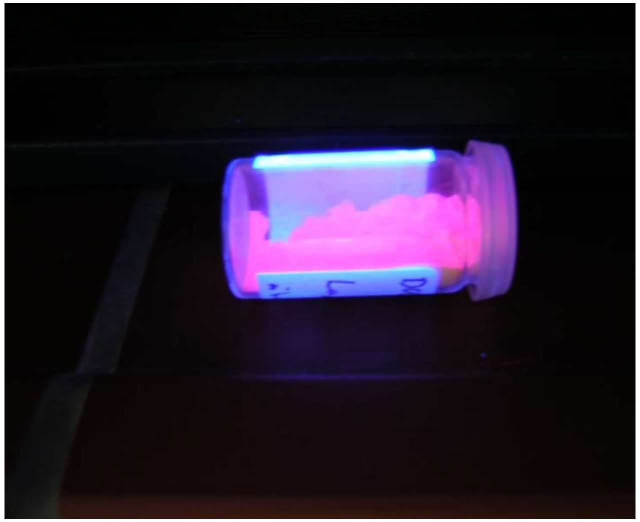
LED	**Blue**	**420 – 480 nm Chip**
Converters	**Yellow**	**$(Y,Gd,Tb,Lu)Al_5O_{12}:Ce$**
	Red	**Mn^{4+}- phosphor**
(GE Patent US2006/0169998)	**$Tb_3Al_5O_{12}:Ce^{3+} + K_2[TiF_6]:Mn^{4+}$**	

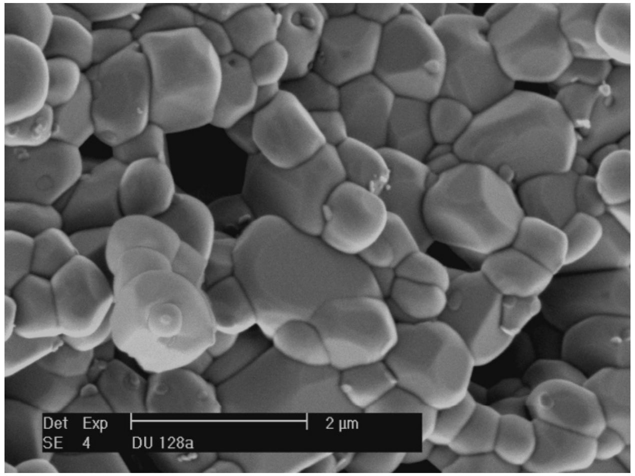
Problem: Absorption strength and decay time of red line emitter Mn^{4+}

4. Phosphor Converted White LEDs

Red line emitter $LiEuMo_2O_8$ (Result from BMBF project HELIOS)







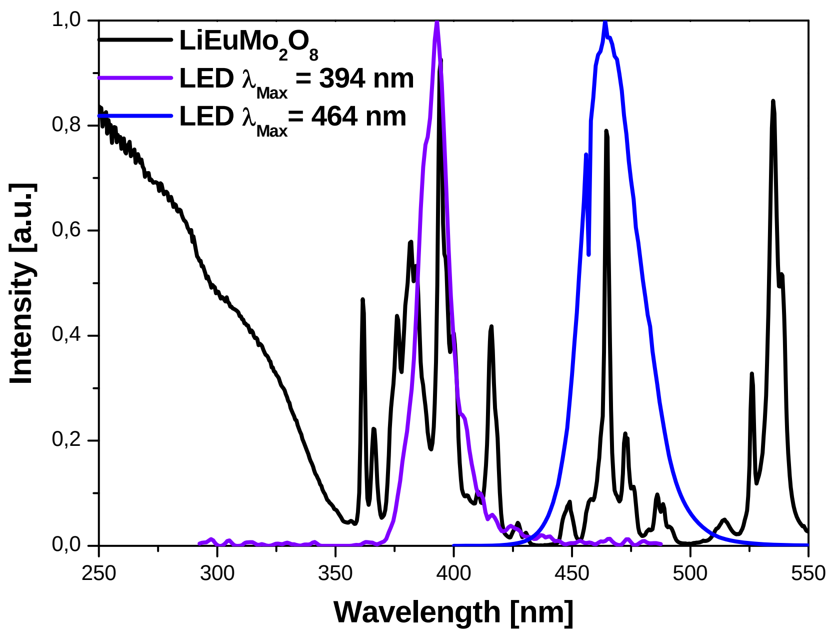
QE_{465} = 100%
RQ_{465} = 75%
x = 0.665
y = 0.333
d_{50} = 4.2 µm

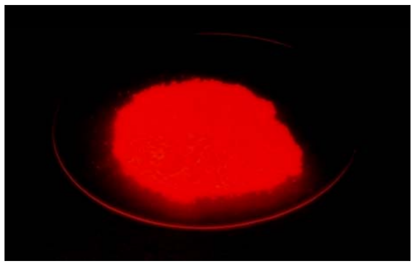
LE = 269 lm/W_{opt}
λ_{max} = 614 nm
$\lambda_{centroid}$ = 623 nm
$\tau_{1/e}$ = 0.39 ms

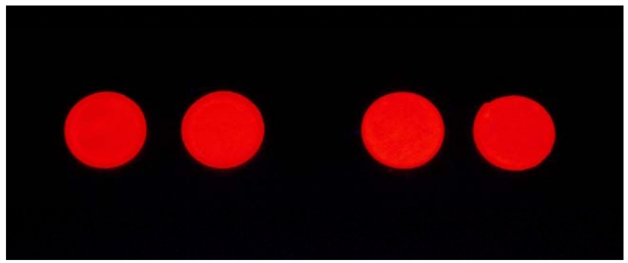
4. Phosphor Converted White LEDs

Are Eu^{3+} phosphors, such as $LiEuMo_2O_8$, applicable in white pcLEDs?

→ Suitable for near UV emitting LEDs, e.g, 394 nm chips
→ Enhance particle size to reduce scattering







5. Summary and Outlook

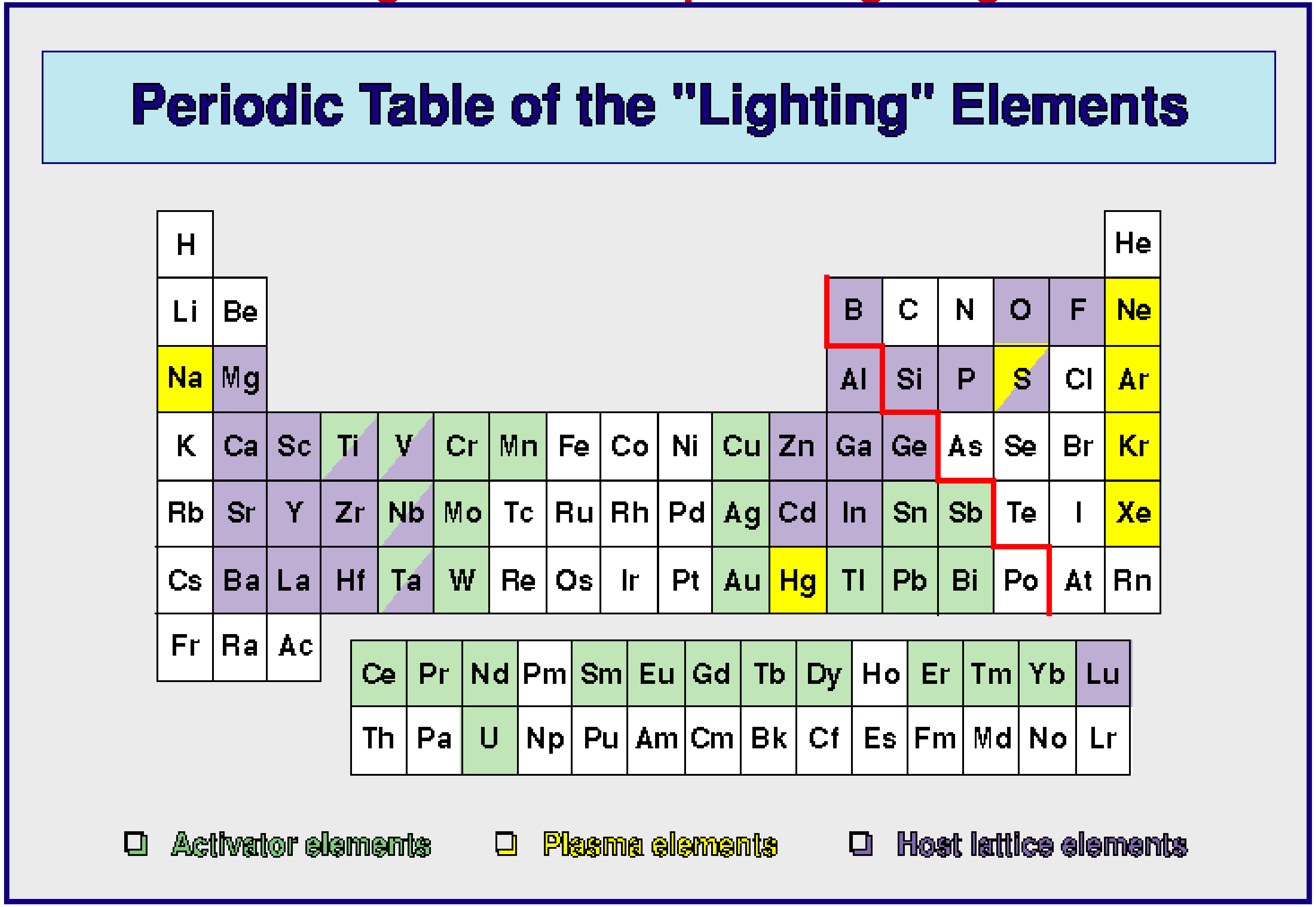
Rare Earths in Solid State Lighting
- Eu^{2+} and Ce^{3+} dominate luminescent materials for LEDs
- Required amount of converter materials will be much lower compared to gas discharge lighting

Cool white LEDs
- CRI ~ 70 – 80 and thus sufficiently high for outdoor lighting
- Examples with more than 200 lm/W already exist in industrial labs!
- Ce^{3+} activated garnets and Eu^{2+} ortho-silicates

Warm white LEDs
- Low CCT and high CRI are desired for indoor lighting
- To achieve a luminous efficiency > 100 lm/W improved luminescent materials, in particular for red emission, are required
- Rare earth ions are very difficult to substitute, maybe by Mn^{2+} or Mn^{4+}

5. Summary and Outlook

Rare earth elements in general and special lighting



Acknowledgement

- Dr. Helga Bettentrup
- Andre Bleise
- Ewelina Broda
- Danuta Dutczak
- Linda Eickhoff
- Rolf Gerdes
- Joanna Gondek
- Arturas Katelnikovas
- Beata Koziara
- Jagoda Kuc
- Daniel Michalik
- Stephanie Möller
- Dr. Julian Plewa
- Simas Sakirzanovas
- Dr. Dominik Uhlich

Bundesministerium für Bildung und Forschung

MERCK

PHILIPS

Thanks for your kind attention!