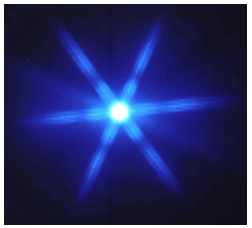
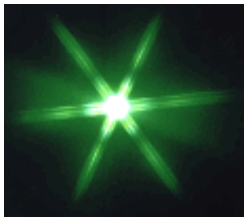
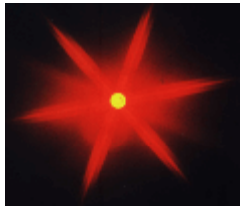
Session: LED Phosphors







Luminescent Materials for LEDs with Ultimate Efficiency and Color Quality

By

Prof. Dr. Thomas Jüstel

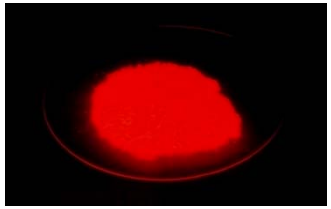
Department Head Chemical Engineering

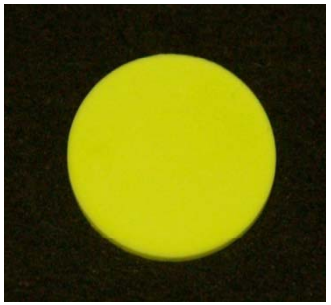
Münster University of Applied Sciences

Institut für Optische Technologien

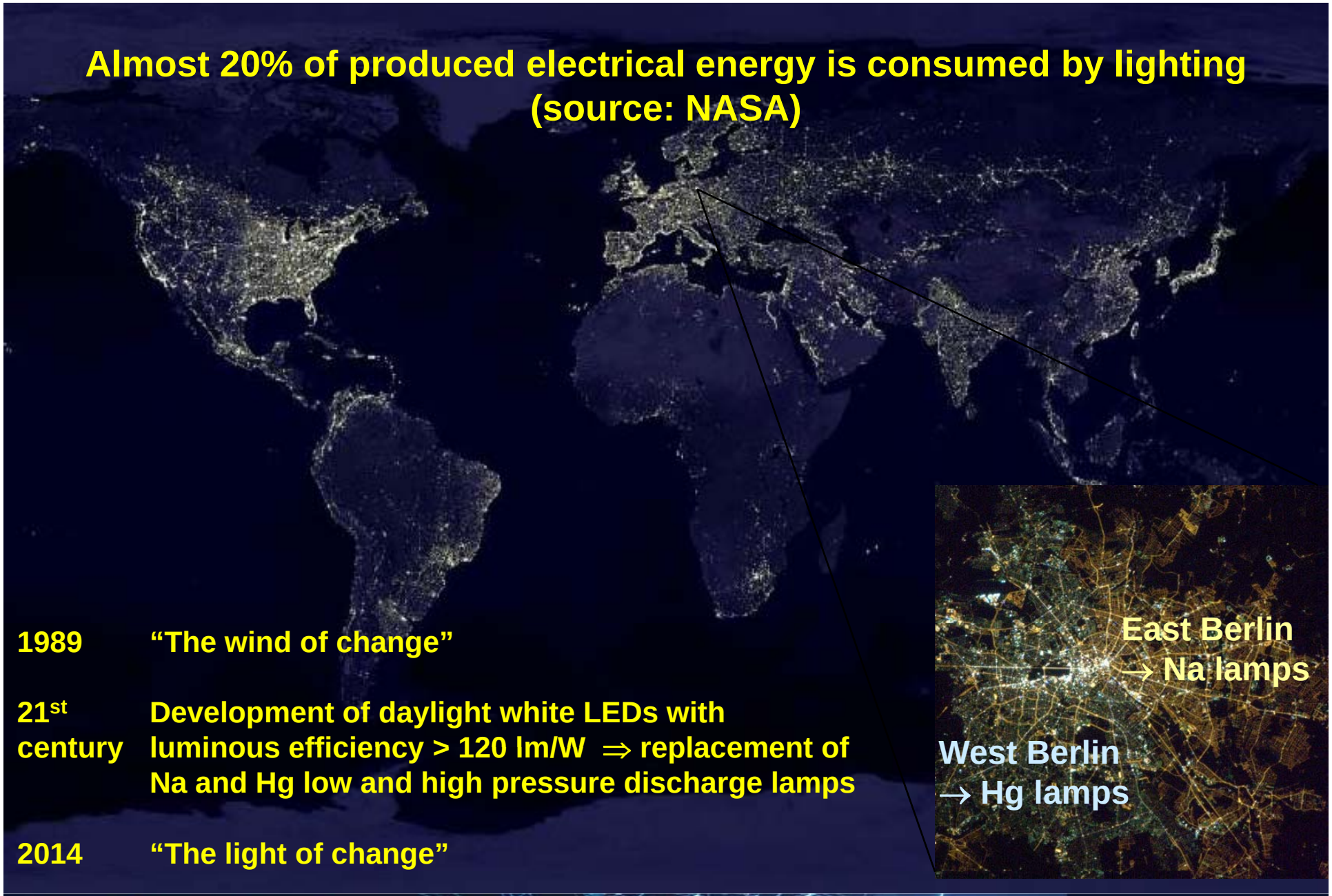
TOM Tailored Optical Materials

Fachhochschule Münster University of Applied Sciences





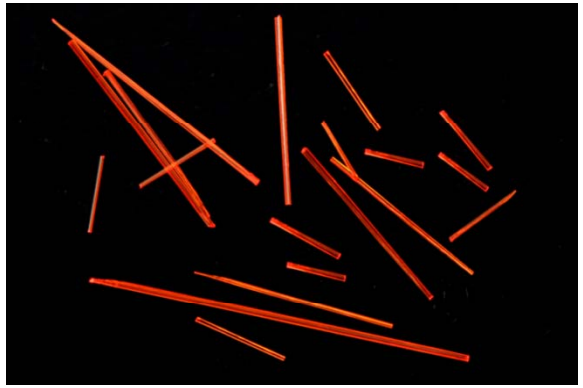
Almost 20% of produced electrical energy is consumed by lighting (source: NASA)

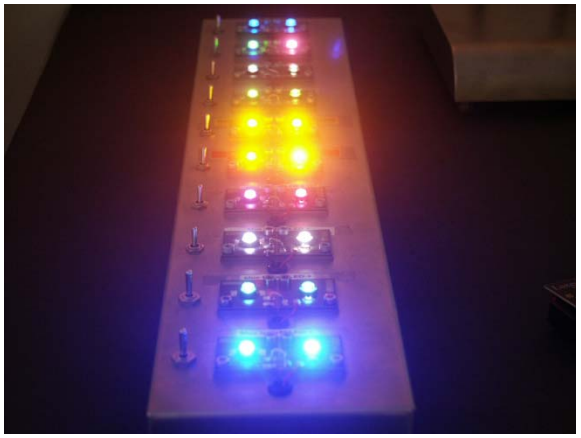


1989	"The wind of change"
21st century	Development of daylight white LEDs with luminous efficiency > 120 lm/W ⇒ replacement of Na and Hg low and high pressure discharge lamps
2014	"The light of change"

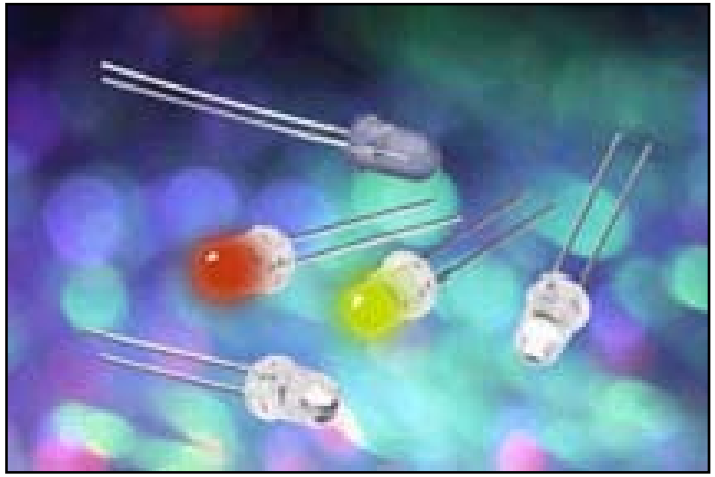
Outline

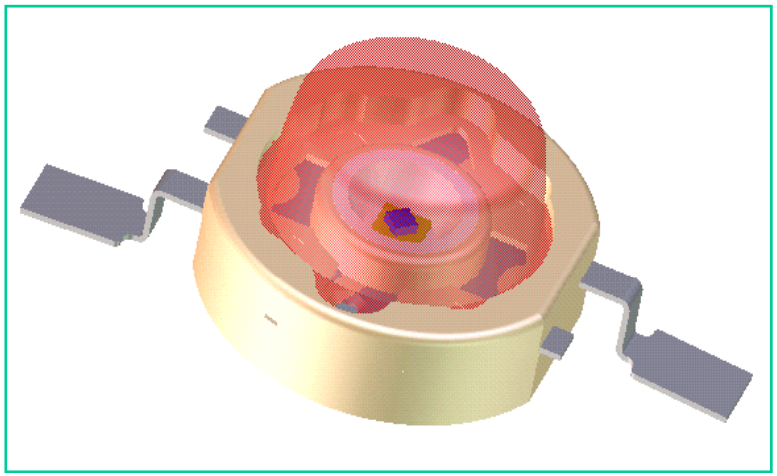
1. Advances in LED Technology
2. White Light Generation
3. Luminescent Materials (Phosphors)
4. Phosphor Converted LEDs (pcLEDs)
5. Towards Ultimate Efficiency and CRI
6. Conclusions and Outlook





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

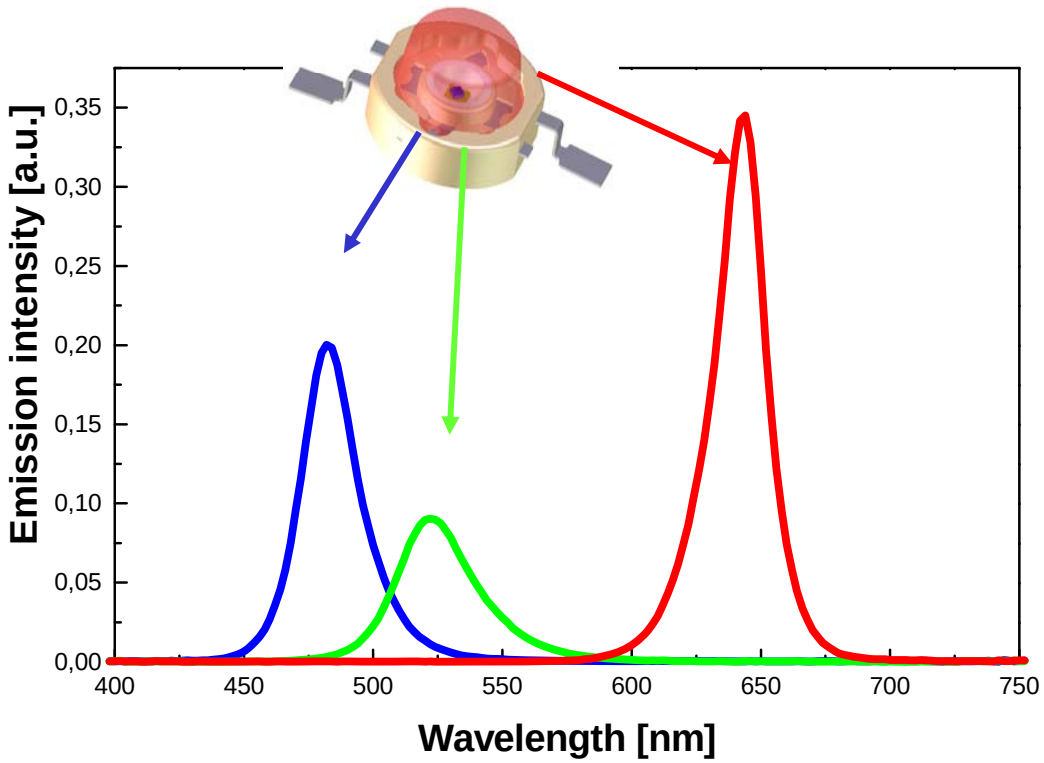
- **580 nm – 700 nm**
- **Yellow → Orange → Red**

(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**

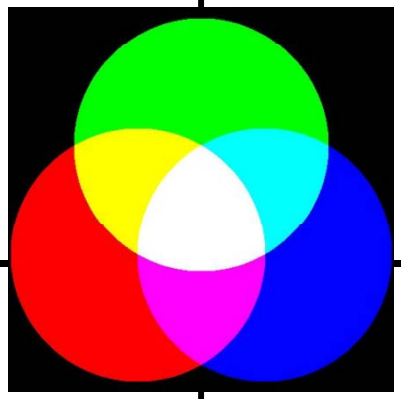
2. White Light Generation

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 → colour filter → Coloured light by absorption

Red, Green, Blue → White light by additive colour mixing

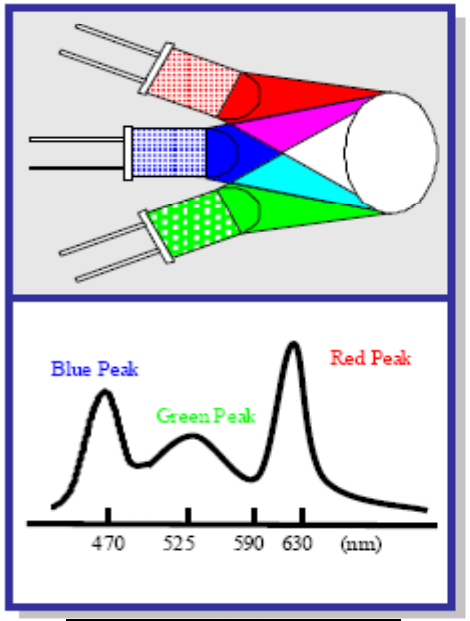


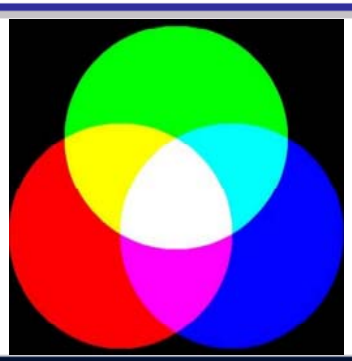
Y or YR or RG phosphor → White light by luminescence

(V)UV → CO or RGB phosphor blend → White light by luminescence

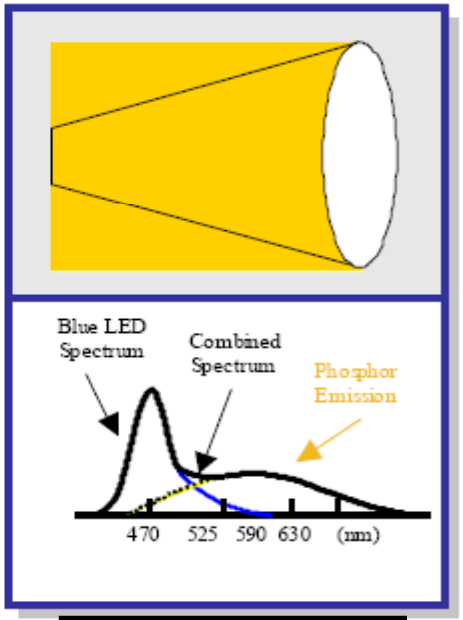
2. White Light Generation

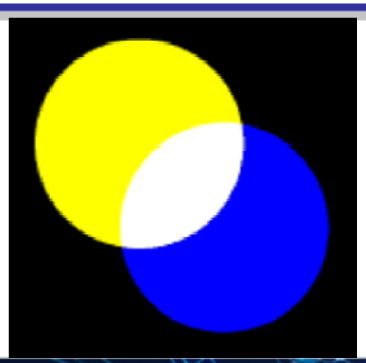
Red + Green + Blue LEDs



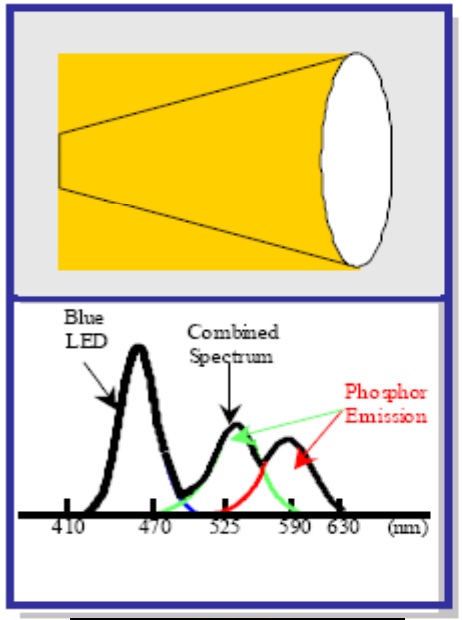


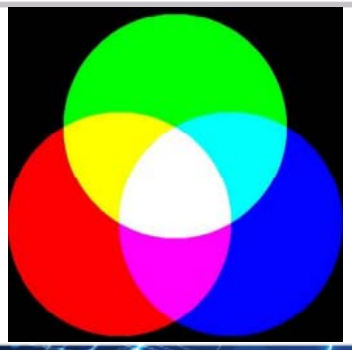
Blue LED + yellow phosphor



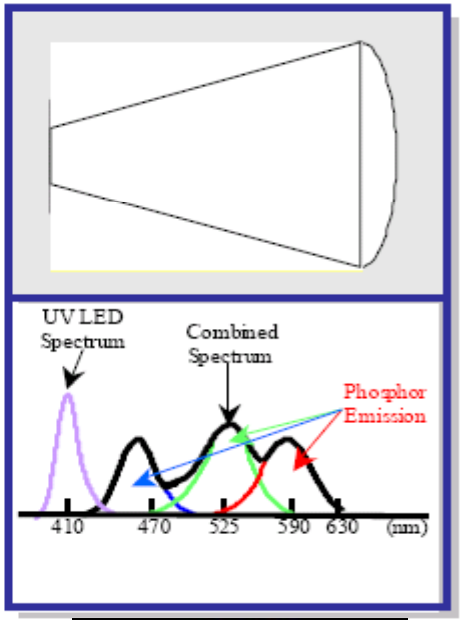


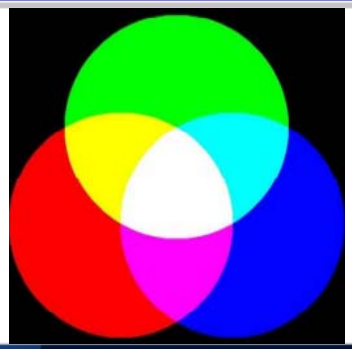
Blue LED + RG phosphor blend





UV LED + RGB phosphor blend

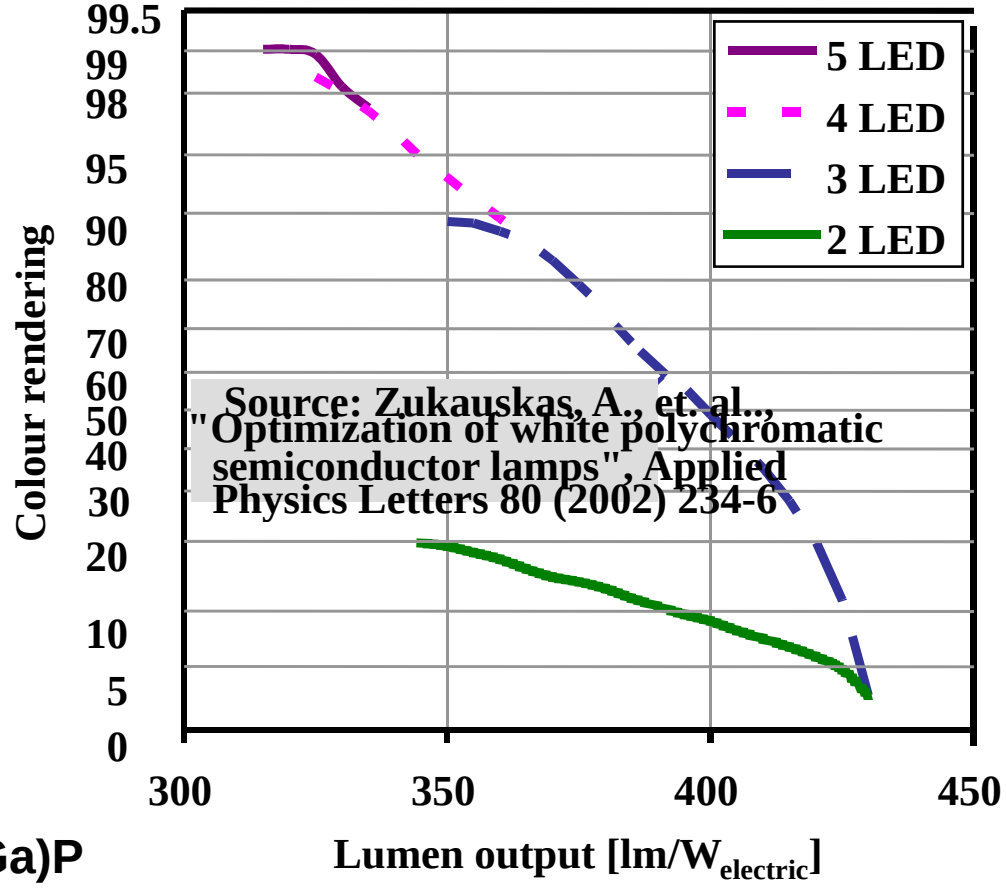




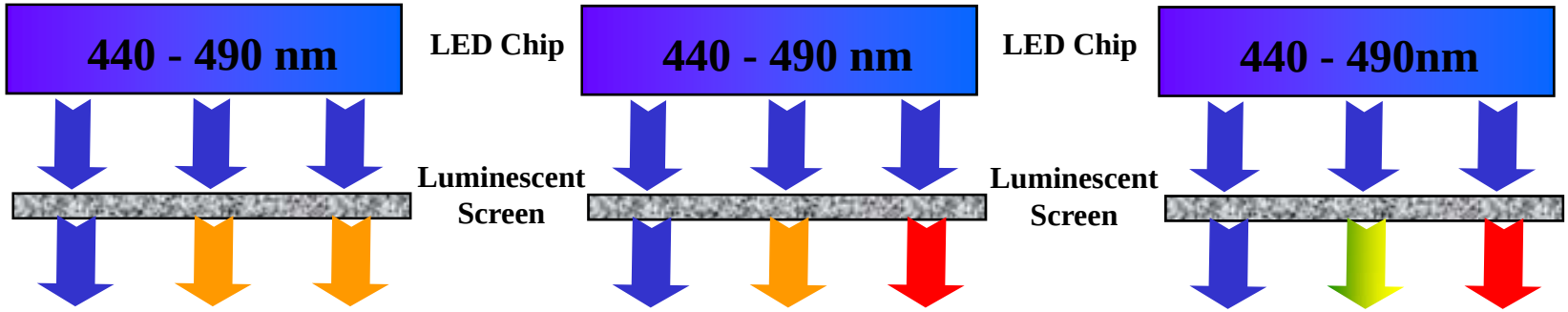
2. White Light Generation

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”



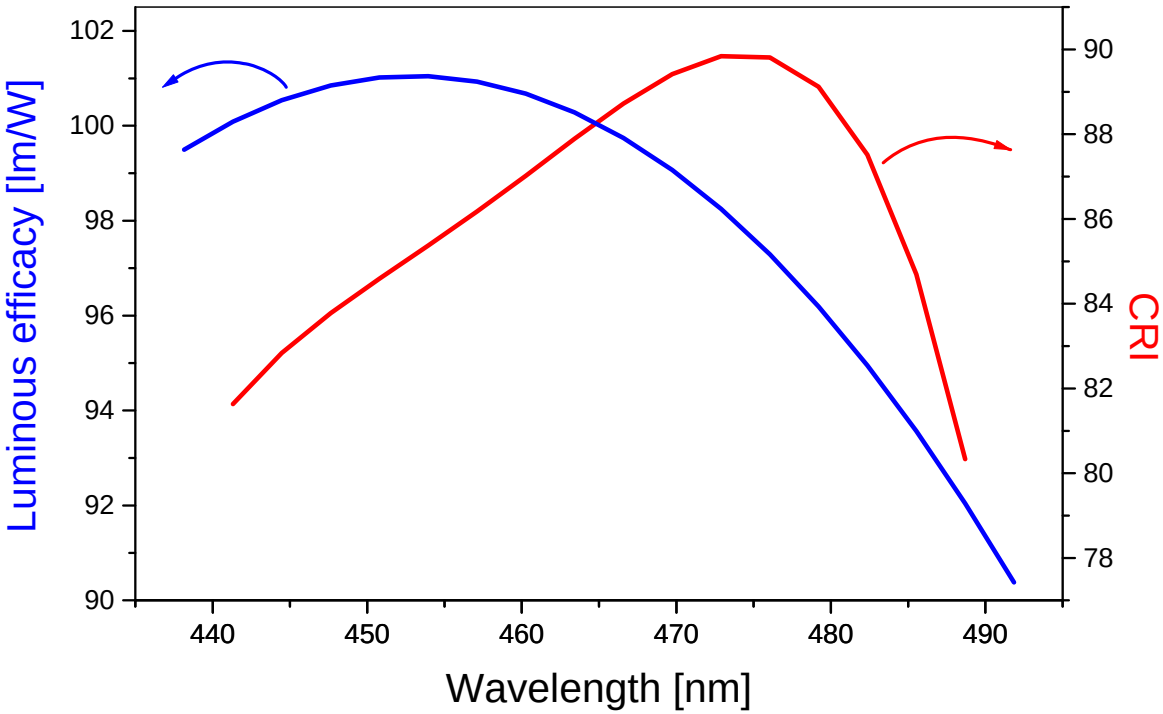
2. White Light Generation



300 – 350 lm/$W_{opt.}$	250 – 300 lm/$W_{opt.}$	280 – 330 lm/$W_{opt.}$
CRI = 70 – 85	CRI = 85 – 95	CRI = 80 – 85
low CRI at low T_c	high CRI at low T_c but decreases with T_c	CRI ~ independent of T_c
single phosphor screen	phosphor blend	phosphor blend

2. White Light Generation

Blue band emitter + green + red converter



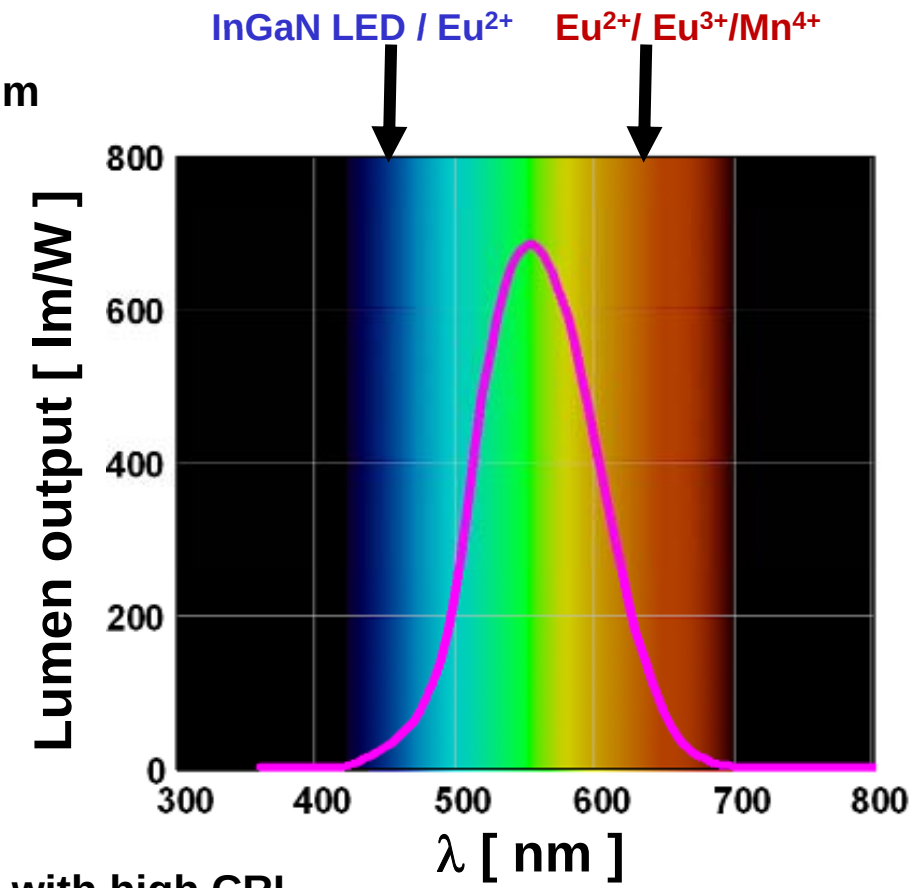
Conclusion: Blue LEDs emitting in the range 460 – 470 nm yield best compromise between CRI and luminous efficacy

2. White Light Generation

Lumen output of a light source

- Strongly dependent on emission spectrum
- Optimal for pure 555 nm radiation
  - V(λ) = 683 lm/W (η = 100%)
- Luminous flux
  - 1000 lm for 555 nm
    requires solely 1.5 W radiation
  - „green light“
- Blue and red radiation
  - V(λ) < 70 lm/W (<10%)
  - reduces lumen equivalent
  - is required for generating white light with high CRI

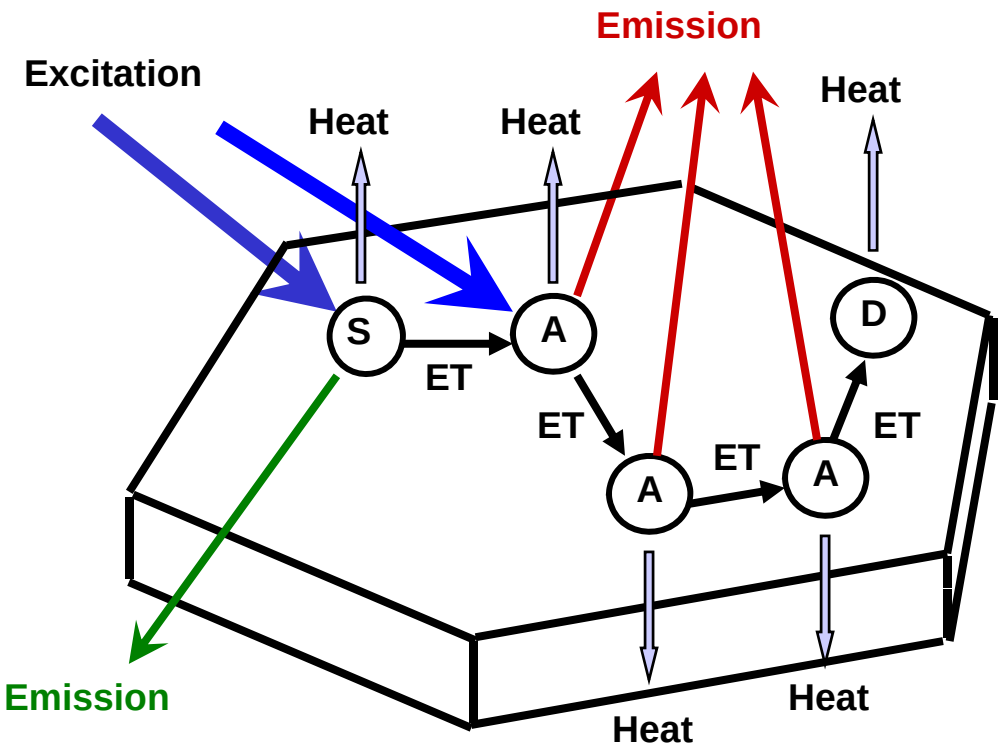
Emission of lines or narrow bands in the blue and or red desired….



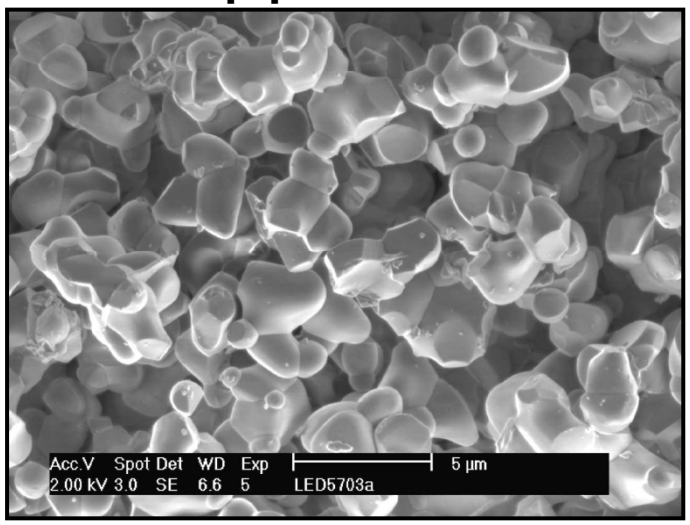
3. Luminescent Materials (Phosphors)

Definition

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



Layer of $Y_3Al_5O_{12}$:Ce µ-particles

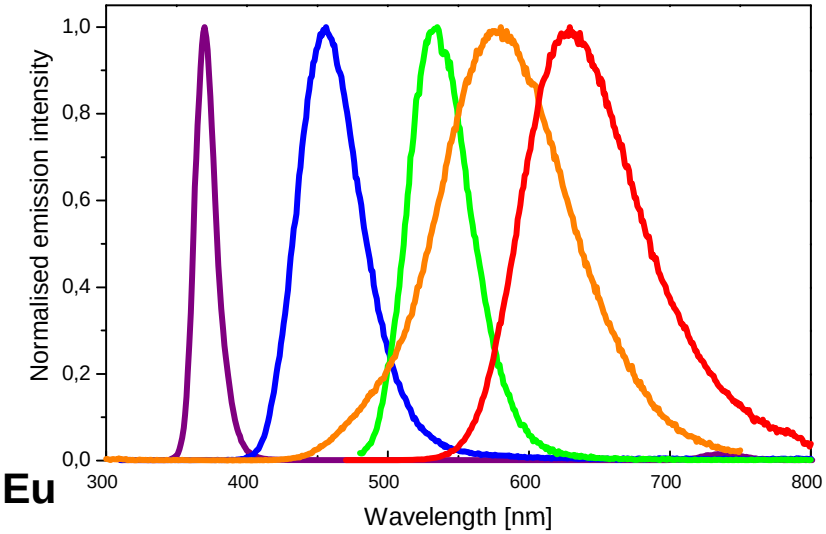


Average particle size ~ 1 – 10 µm

3. Luminescent Materials (Phosphors)

Type of converter materials

1. Inorganic phosphors
    - Microscale powders
        - $SrYSi_4N_7$:Ce
        - $(Ba,Sr)_2SiO_4$:Eu
        - $(Ca,Sr,Ba)Si_2N_2O_2$:Eu
        - $SrYSi_4N_7$:Eu
        - (Y,Gd,Tb,Lu)AG:Ce
        - $CaAlSiN_3$:Ce
        - $(Ca,Sr)_2SiO_4$:Eu
        - (Ca,Sr)S:Eu
        - $(Ca,Sr,Ba)_2Si_5N_8$:Eu
        - $(Ca,Sr)AlSiN_3$: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^{3+}-complexes Ln = Tm, Tb, Eu
        - Ru- and Ir-complexes



3. Luminescent Materials (Phosphors)

Garnets

- $(Y,Tb)_3Al_5O_{12}$:Ce
- $Lu_3Al_5O_{12}$:Ce
- $Lu_3(Ga,Al)_5O_{12}$:Ce
- $(Lu,Y)_3Sc_2Al_3O_{12}$:Ce
- $(Y,Lu)_3(Al,Mg,Si)_5O_{12}$:Ce
- $Ca(Y,Lu)_2Al_4SiO_{12}$:Ce

Ortho-silicates

- $(Ca,Sr,Ba)_2SiO_4$:Eu
- $(Ca,Sr,Ba)_3SiO_5$:Eu

(Oxy)Nitrides

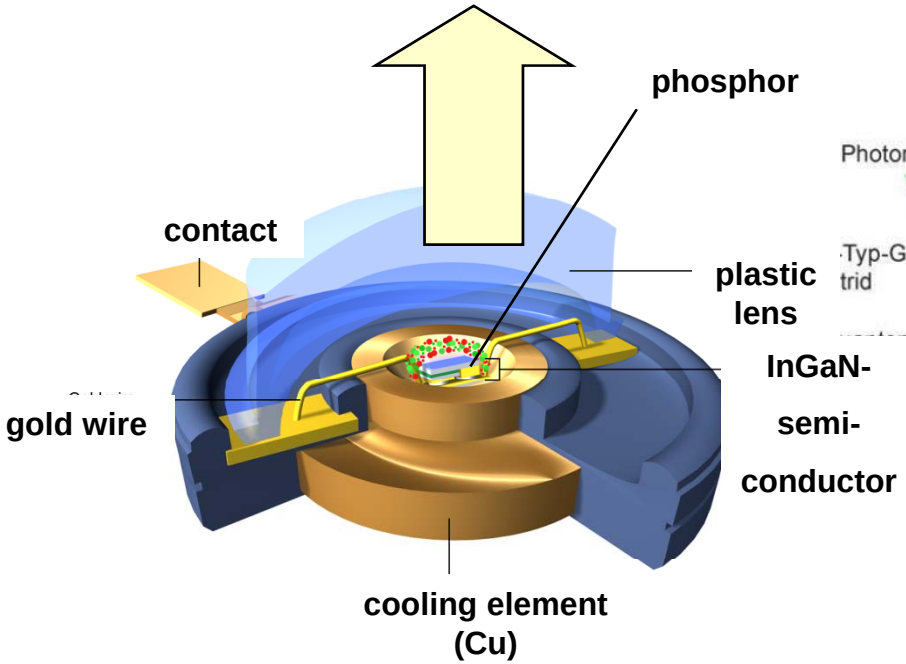
- $(Sr,Ca,Ba)_2Si_5N_8$:Eu „2-5-8“
- $(Sr,Ca,Ba)Si_2N_2O_2$:Eu „1-2-2-2“
- $(Ca,Sr)AlSiN_3$:Eu „1-1-1-3“
- $(Ca,Sr,Ba)SiN_2$:Eu „1-1-2“
- $La_3Si_6N_{11}$:Ce „3-6-11“
- $Ba_3Si_6O_{12}N_2$:Eu
- α,ß-SiAlONes:Eu

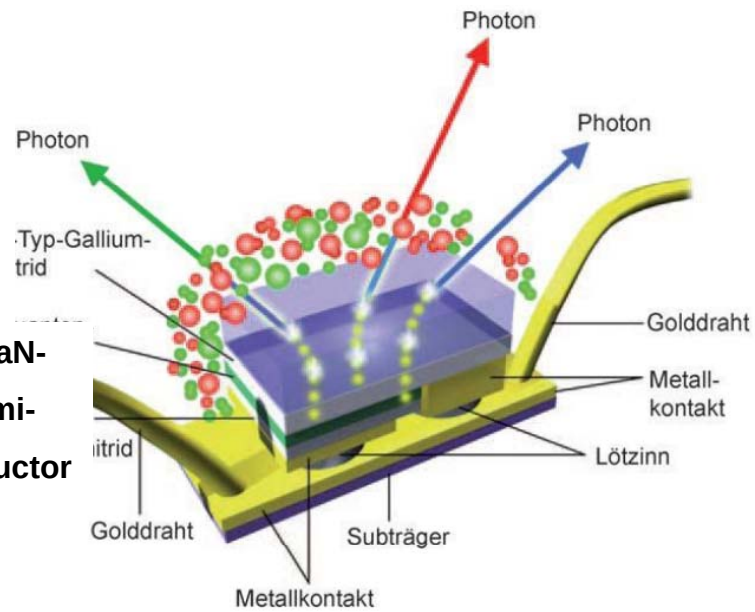
Selection criteria for LED phosphors

- 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

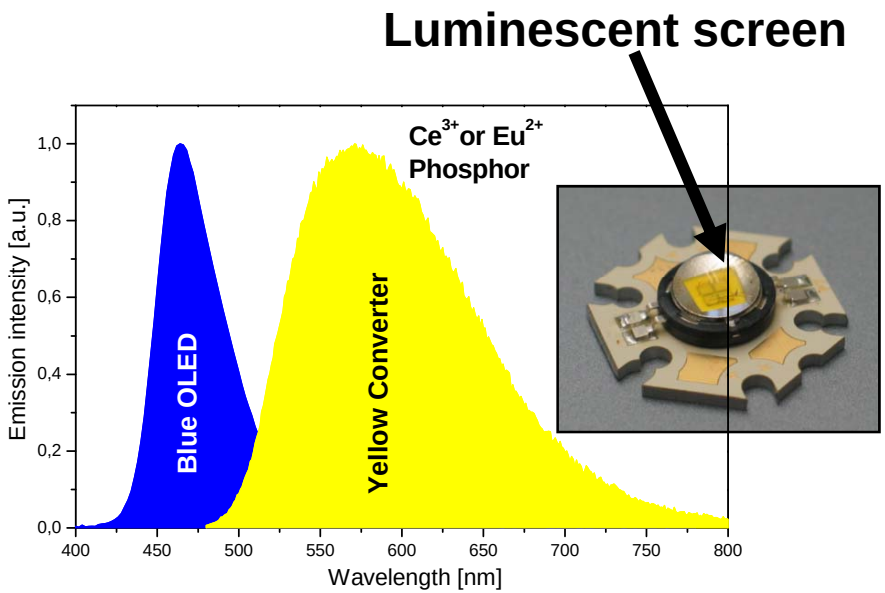
High Power LEDs → low thermal resistance ~ 2-3 K/W typical

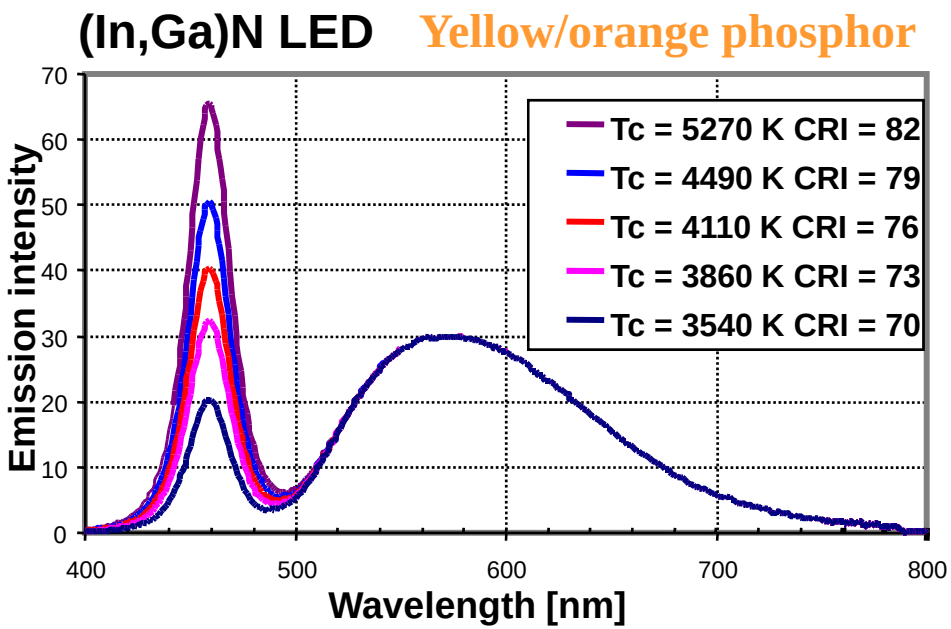




(In,Ga)N semiconductor	+ phosphor (converter)	→ Colour temperature range
Blue 420 – 480 nm	Yellow	cool white
	Yellow + Red	warm white
	Green + Red	cool and warm white
Near UV 370 – 420 nm	Blue + Green + Red	cool and warm white

4. Phosphor Converted LEDs





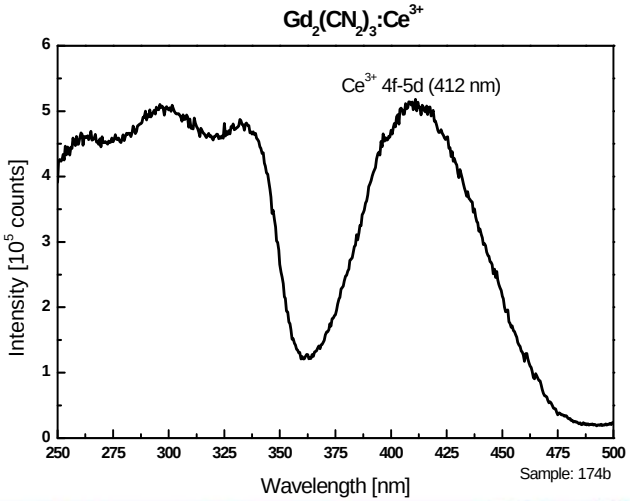
Status quo cool white pcLEDs @ 2014

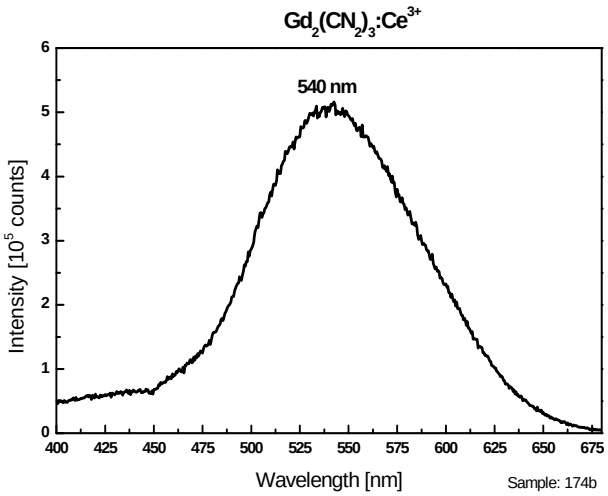
- **Phosphor** — $(Y,Gd,Tb,Lu)_3Al_5O_{12}:Ce^{3+}$, $(Ca,Sr,Ba)_2SiO_4:Eu^{2+}$
- **Luminous efficacy** — LE = 303 lm/W! (WPE ~ 80%)
- **Colour rendering index** — CRI ~ 70 - 80
- **Corr. colour temperature** — Tc > 5000 K

4. Phosphor Converted LEDs

Yellow Converters

Ortho-Silicates	A_2SiO_4:Eu, Sr_2LiSiO_4:Eu		
Oxynitrides	$(Ca,Sr)Si_2N_2O_2$:Eu		
α-SiAlONes	α-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	$Gd_2(CN_2)_3$:Ce	540 nm	UniTübingen/Münster



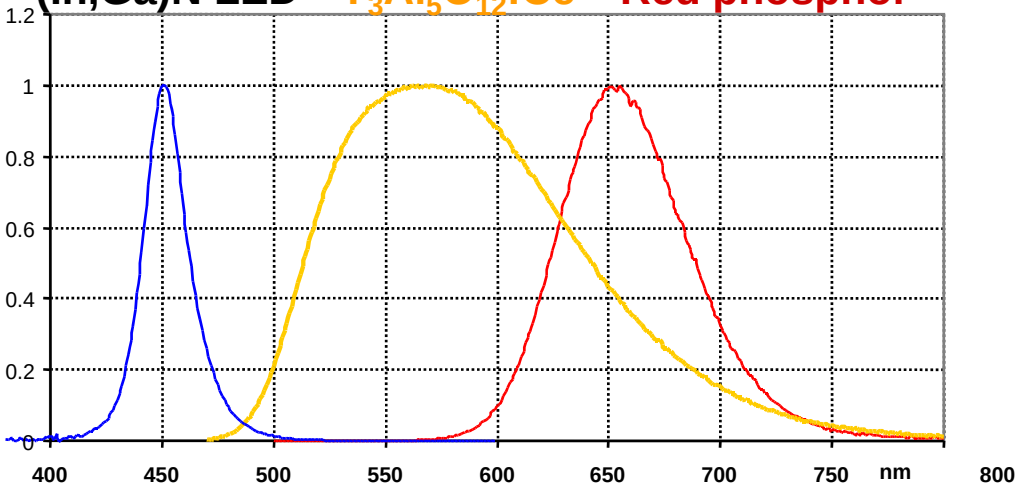


4. Phosphor Converted LEDs

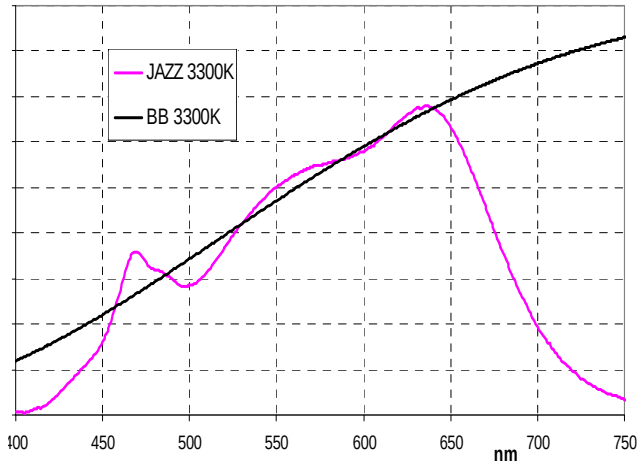
CRI Enhancement and colour temperature reduction of pcLEDs

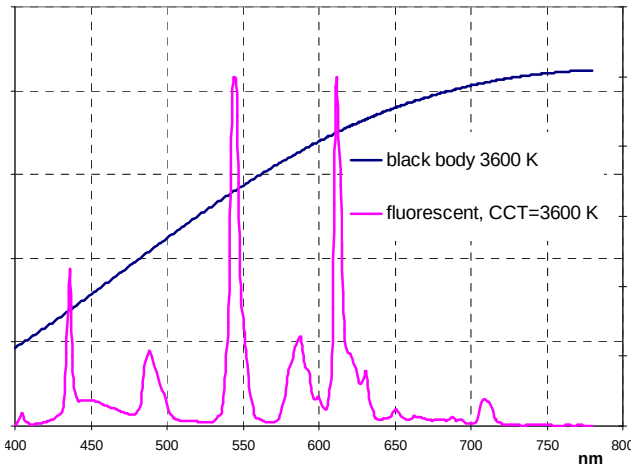
LUXEON LEDs (Philips Lumileds)

(In,Ga)N LED **$Y_3Al_5O_{12}$:Ce** **Red phosphor**



Wavelength [nm]





Status quo warm white pcLEDs @ 2014

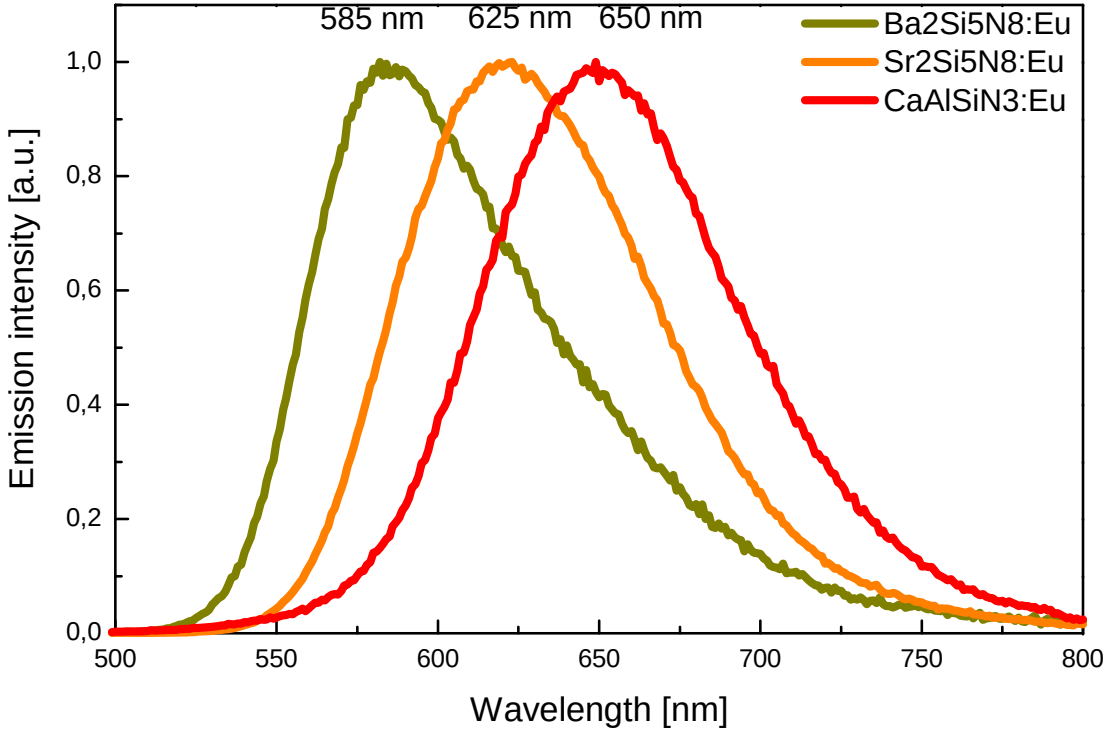
- **Red phosphor** — **Eu^{2+} activated**
- **Luminous efficacy LE** — **80 - 150 lm/W**
- **Colour rendering index CRI** — **85 – 95**
- **Corr. colour temperature Tc** — **2500 - 4000 K**

R. Mueller-Mach, G.O. Mueller, P.J. Schmidt, T. Jüstel,
Red Deficiency Compensating Phosphor LED , Light Emitting Device, US Patent 20030006702

4. Phosphor Converted LEDs

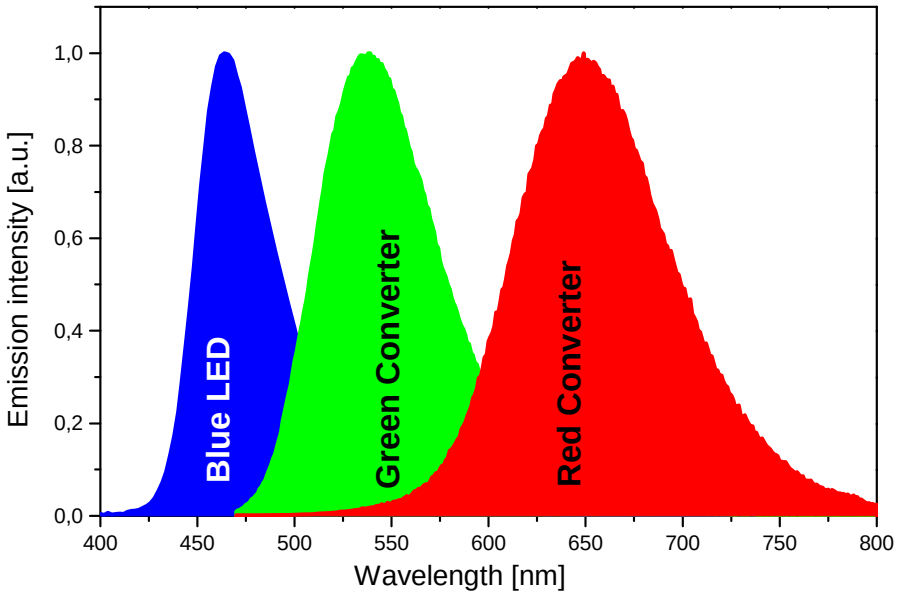
Red emitting LED phosphors ⇒ Eu^{2+} doped nitrides

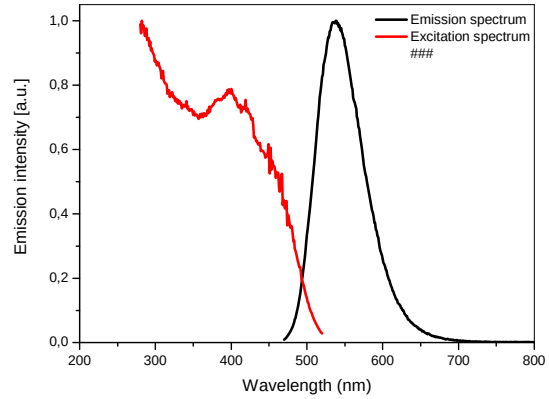
$Ba_2Si_5N_8$:Eu
$Sr_2Si_5N_8$:Eu
$Ca_2Si_5N_8$:Eu
(Ca,Sr)$AlSiN_3$:Eu
$CaAlSiN_3$:Eu

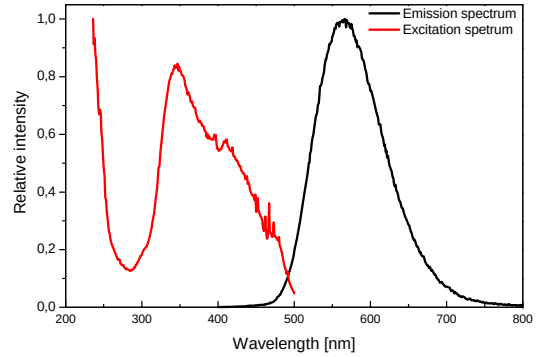


4. Phosphor Converted LEDs

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







Green emitter (AE = Ca, Sr, Ba)

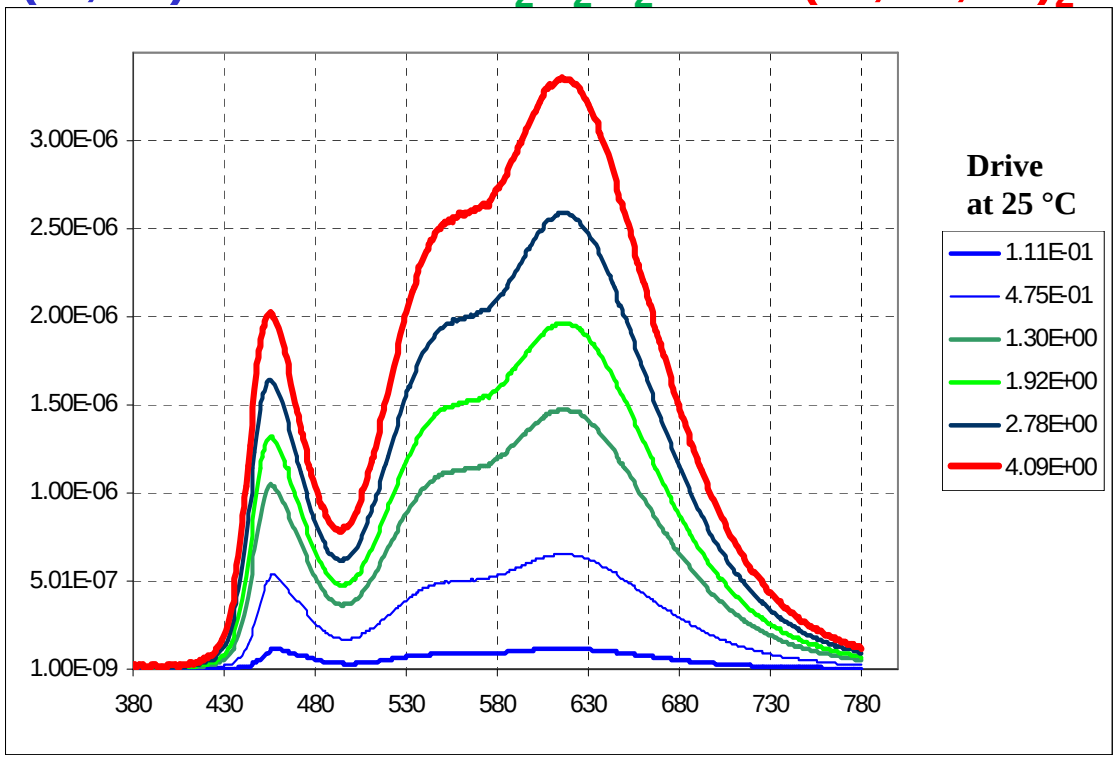
ortho-Silicates — AE_2SiO_4:Eu
Oxynitrides — $AESi_2N_2O_2$:Eu
ß-SiAlONes — ß-SiAlON:Eu
Garnets — $Lu_3Al_5O_{12}$:Ce

$CaSi_2N_2O_2$ - $SrSi_2N_2O_2$ Solid solution without miscibility gap
⇒ fine-tuning of green emission band position possible

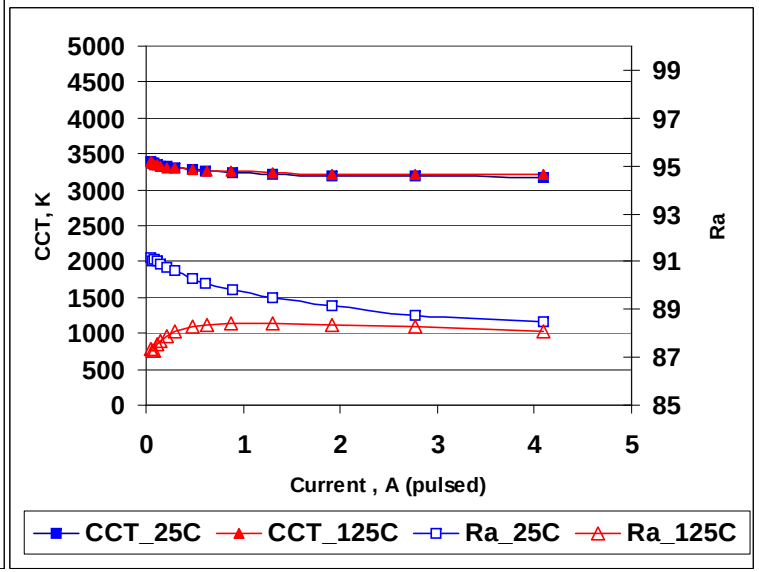
4. Phosphor Converted LEDs

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

(In,Ga)N LED + $SrSi_2N_2O_2$:Eu + $(Sr,Ca,Ba)_2Si_5N_8$:Eu



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



R. Mueller-Mach, G.O. Mueller, M.R. Krames, H.A. Höppe, F. Stadler, W. Schnick, T. Jüstel, P.J. Schmidt, All Nitride White Light Emitting Diodes, Phys. Stat. Sol. A 202 (2005) 1727

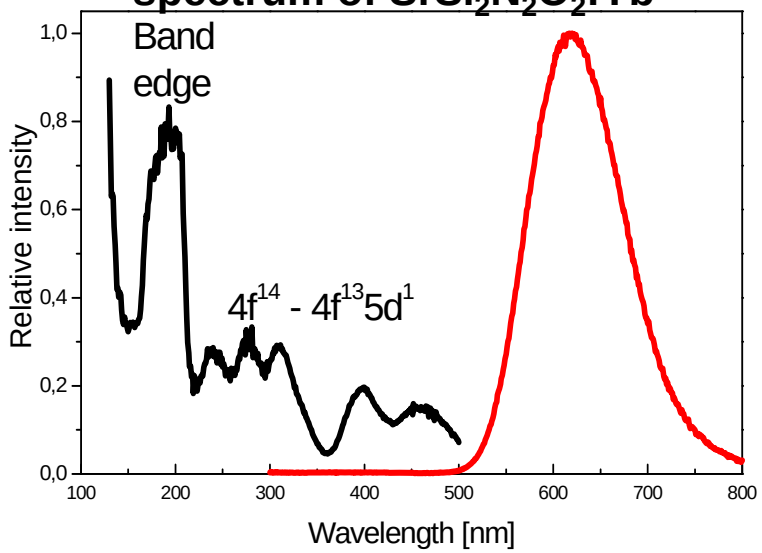
4. Phosphor Converted LEDs

Eu^{2+} and Yb^{2+} Phosphors

Phosphor	Emission at
Eu^{2+} $[Xe]4f^7$	
$BaSi_2N_2O_2$:Eu	490 nm
$SrSi_2N_2O_2$:Eu	540 nm
$CaSi_2N_2O_2$:Eu	565 nm
$Ba_2Si_5N_8$:Eu	580 nm
$Sr_2Si_5N_8$:Eu	610 nm
(Ca,Sr)$AlSiN_3$:Eu	630 nm
$Ca_2Si_5N_8$:Eu	650 nm
$CaAlSiN_3$:Eu	650 nm
Yb^{2+} $[Xe]4f^{14}$	
$Ca_{m/2}Si_{12-m-n}Al_{m+n}O_nN_{16-n}$:Yb	550 nm

M. Mitomo, K. Uheda et al., J. Phys. Chem. B 109 (2005) 9490

Excitation and emission spectrum of $SrSi_2N_2O_2:Yb^{2+}$

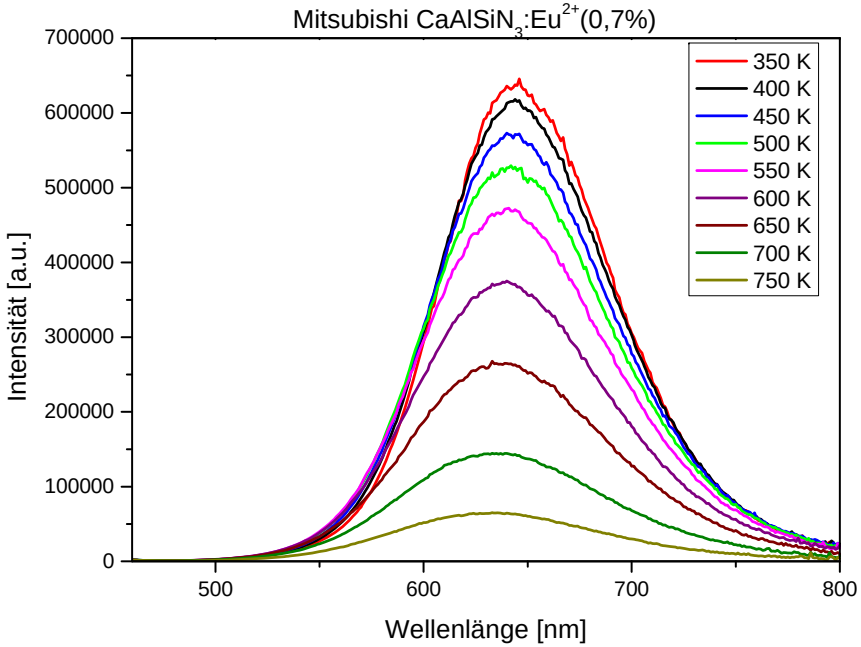


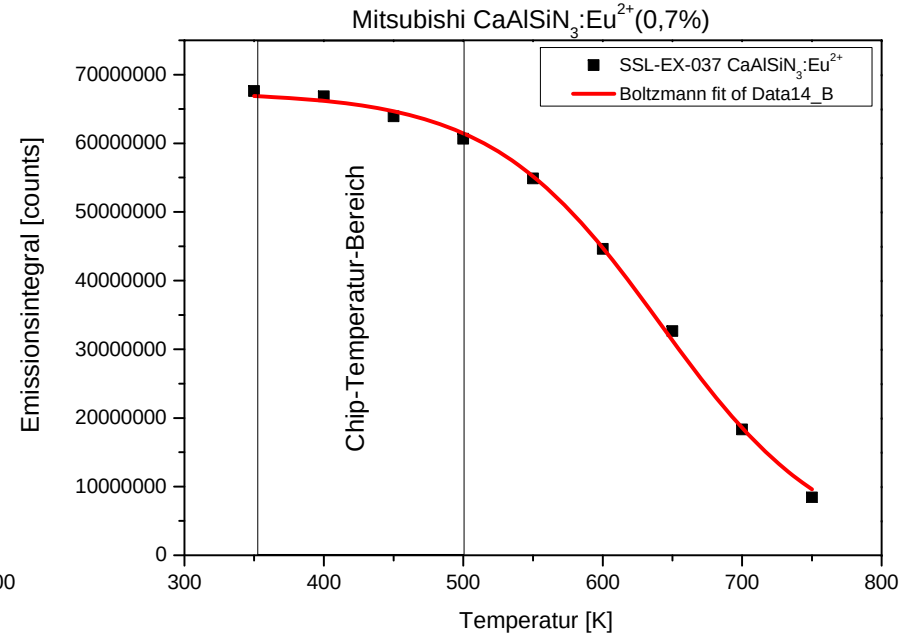
$SrSi_2N_2O_2$:Yb 615 nm **Problem: Thermal quenching**

V. Bachmann, T. Jüstel, A. Meijerink, C.R. Ronda, P.J. Schmidt, J. Luminescence (2006)

4. Phosphor Converted LEDs

Thermal quenching of a typical LED converter material



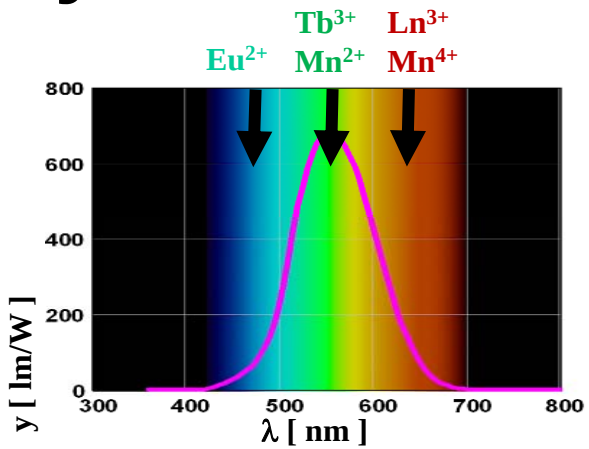


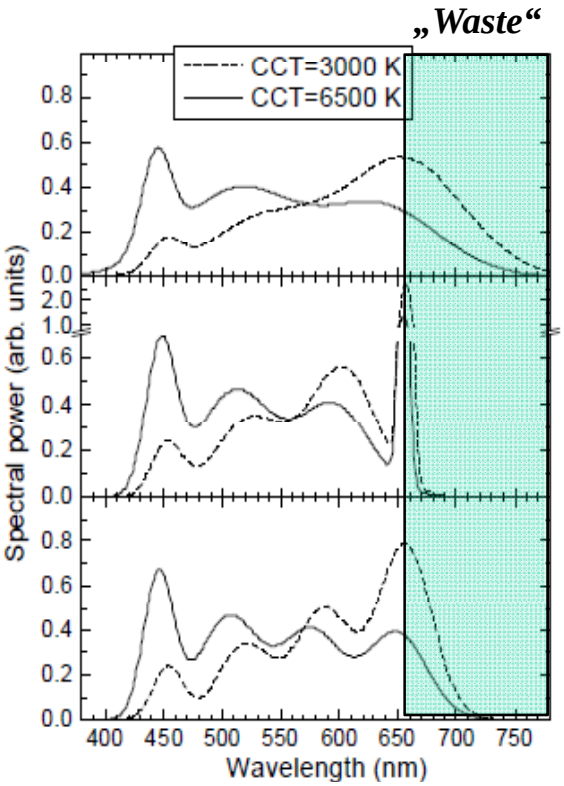
- **Thermal quenching is a reversible process and occurs for all kind of phosphors**
- **The quenching temperature is a strong function of the activator, host, and its interaction**

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





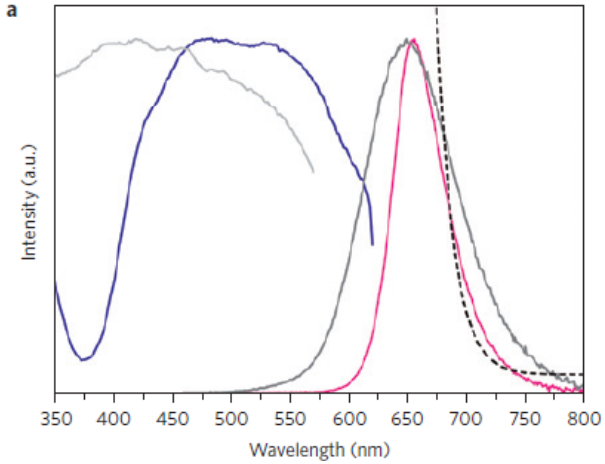
Band width [nm]	Position (nm)	LE (lm/W)	Red LED Phosphor
90 - 120	635	257	(Ca,Sr)S:Eu $(Ca,Sr,Ba)_2Si_5N_8$:Eu $(Ca,Sr)AlSiN_3$:Eu
20 – 30	655	278	$Mg_2TiO_4:Mn^{4+}$
20 – 30	620	320	Ln^{3+} activated (Ln = Pr, Sm, Eu) Mn^{4+} activated
50 – 60	655	269	Eu^{2+}- activated
50 – 60	620	300	Eu^{2+}- activated

A. Zukauskas et al., Appl. Phys.Lett. 93 (2008) 051115

5. Towards Ultimate Efficiency and CRI

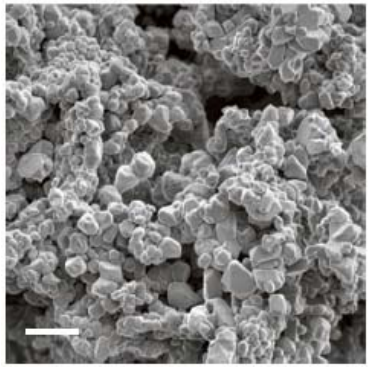
Narrow-band red-emitting $Sr[LiAl_3N_4]:Eu^{2+}$

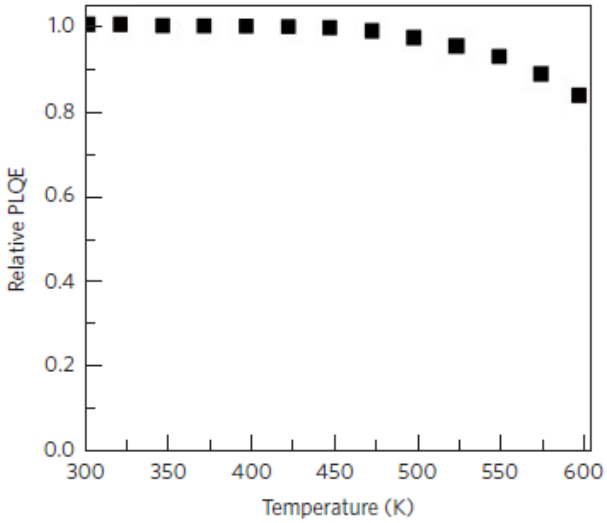
as a next-generation LED-phosphor material"
W. Schnick et al., *Nature Materials (2014) 1-6*
Appeared on-line June 22nd



Synthesis

$LiAlH_4 + (1\text{-}x)\ SrH_2 + x\ EuF_3 + 2\ AlN + N_2$
$\rightarrow\ (Sr_{1-x}Eu_x)[LiAl_3N_4] + 3x\ HF + (3\text{-}x)\ H_2$
RF-furnace, 1000 °C

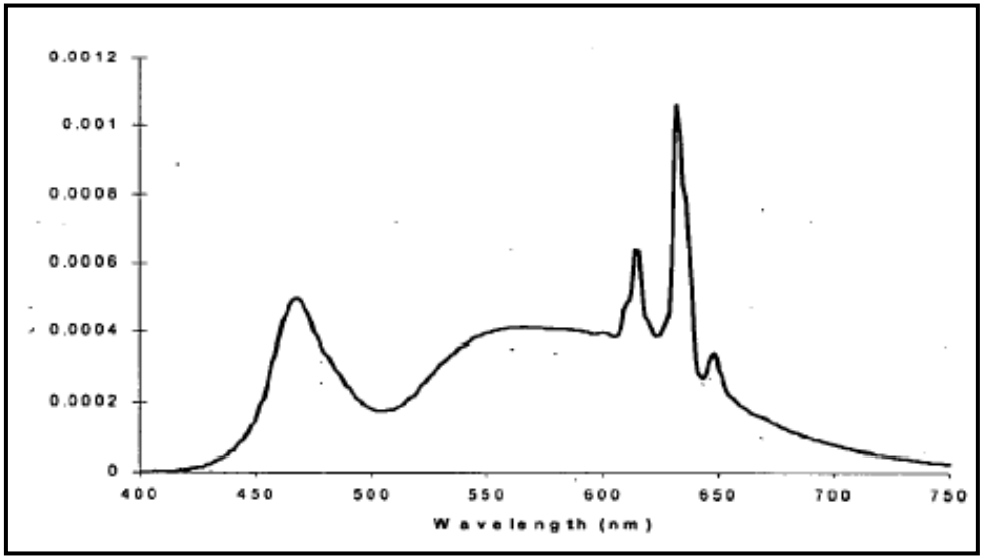




Optical Properties

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

Problems: **Absorption strength, decay time and stability of red line emitter**

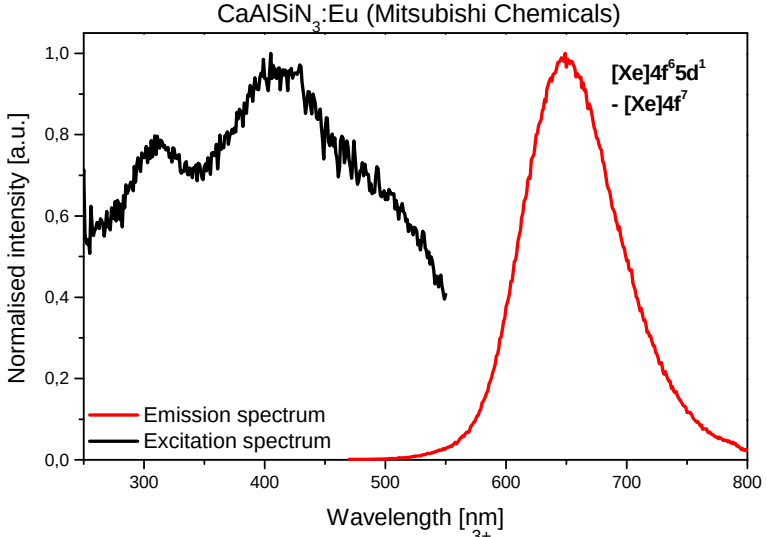
5. Towards Ultimate Efficiency and CRI

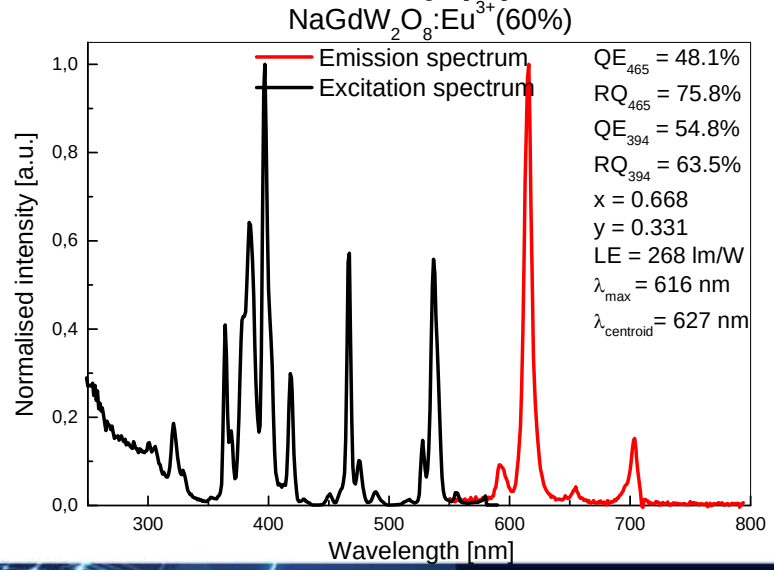
Challenges

- **Red narrow band or line emitter**
  → to increase lumen equivalent

- **Reduced re-absorption**
  → to increase package gain

Red emitting ion	LE [lm/$W_{opt.}$]
Eu^{2+}	80 - 200
Eu^{3+}	220 – 360
Sm^{3+}	240 – 260
Pr^{3+}	200 – 220
Mn^{4+}	80 – 150
Cr^{3+}	< 100
Fe^{3+}	< 100

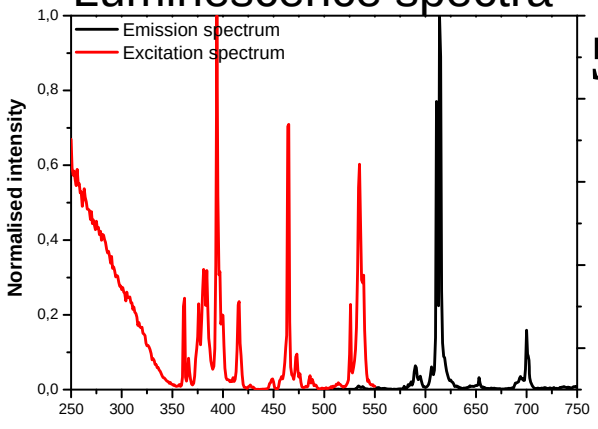




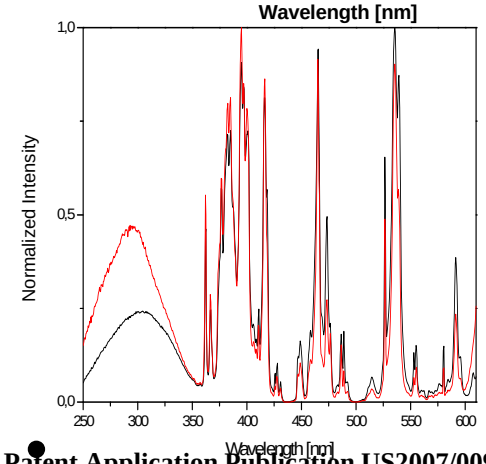
5. Towards Ultimate Efficiency and CRI

Eu^{3+} doped Molybdates, e.g. $LiLaMo_2O_8$:Eu and $Tb_2Mo_3O_{12}$:Eu

Luminescence spectra

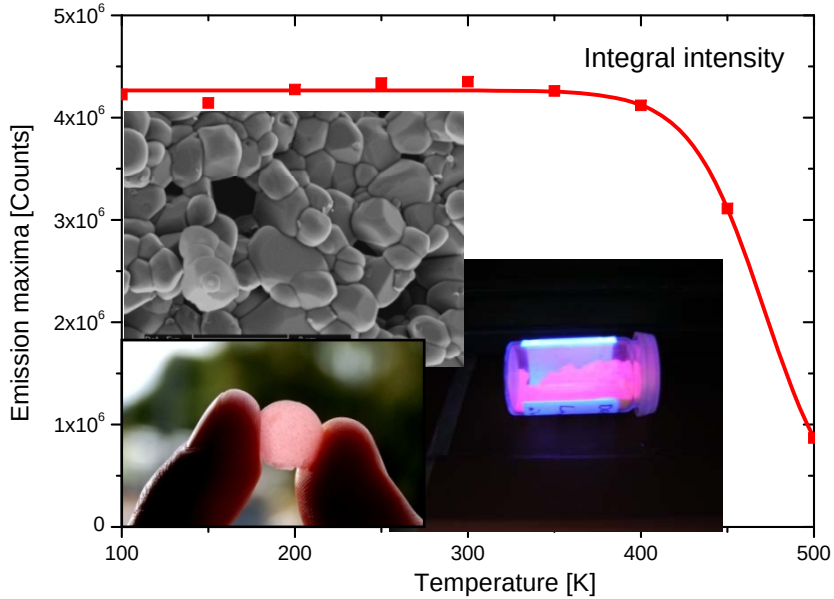


5% Eu^{3+}



100% Eu^{3+}

T-dependent integral emission intensity

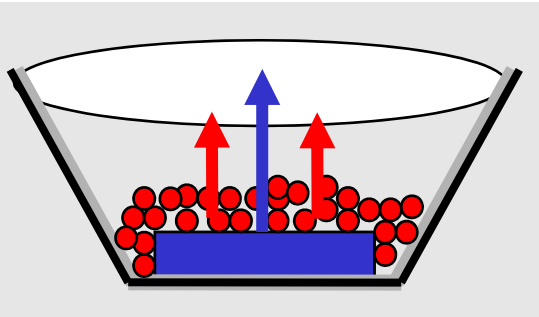


QE_{465} ~ 100%	LE = 269 lm/W_{opt}
R_{465} = 75%	λ_{max} = 614 nm
R_{395} = 60%	$\lambda_{centroid}$ = 623 nm
CIE x = 0.665	$\tau_{1/e}$ = 0.39 ms (0.2 x Y_2O_3:Eu)
CIE y = 0.333	d_{50} = 4.2 µm

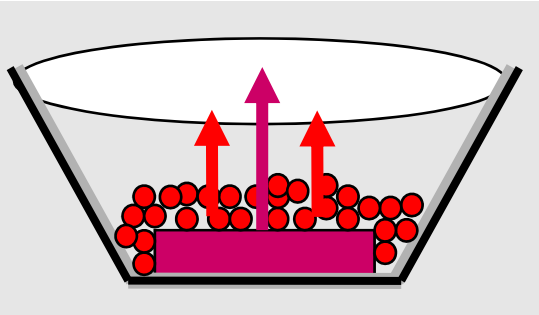
- Patent Application Publication US2007/0090327, "Novel red fluorescent powder", Industrial Technology Research Institute, Taiwan
- M. Rico, U. Giebner, et.al, "Growth, spectroscopy, and tunable laser operation of the disordered crystal $LiGd(MoO_4)_2$ doped with ytterbium", J. Opt. Soc. Am. B 22 (2005) 1083

5. Towards Ultimate Efficiency and CRI

Phosphor converted LED comprising $Tb_2Mo_3O_{12}$:Eu

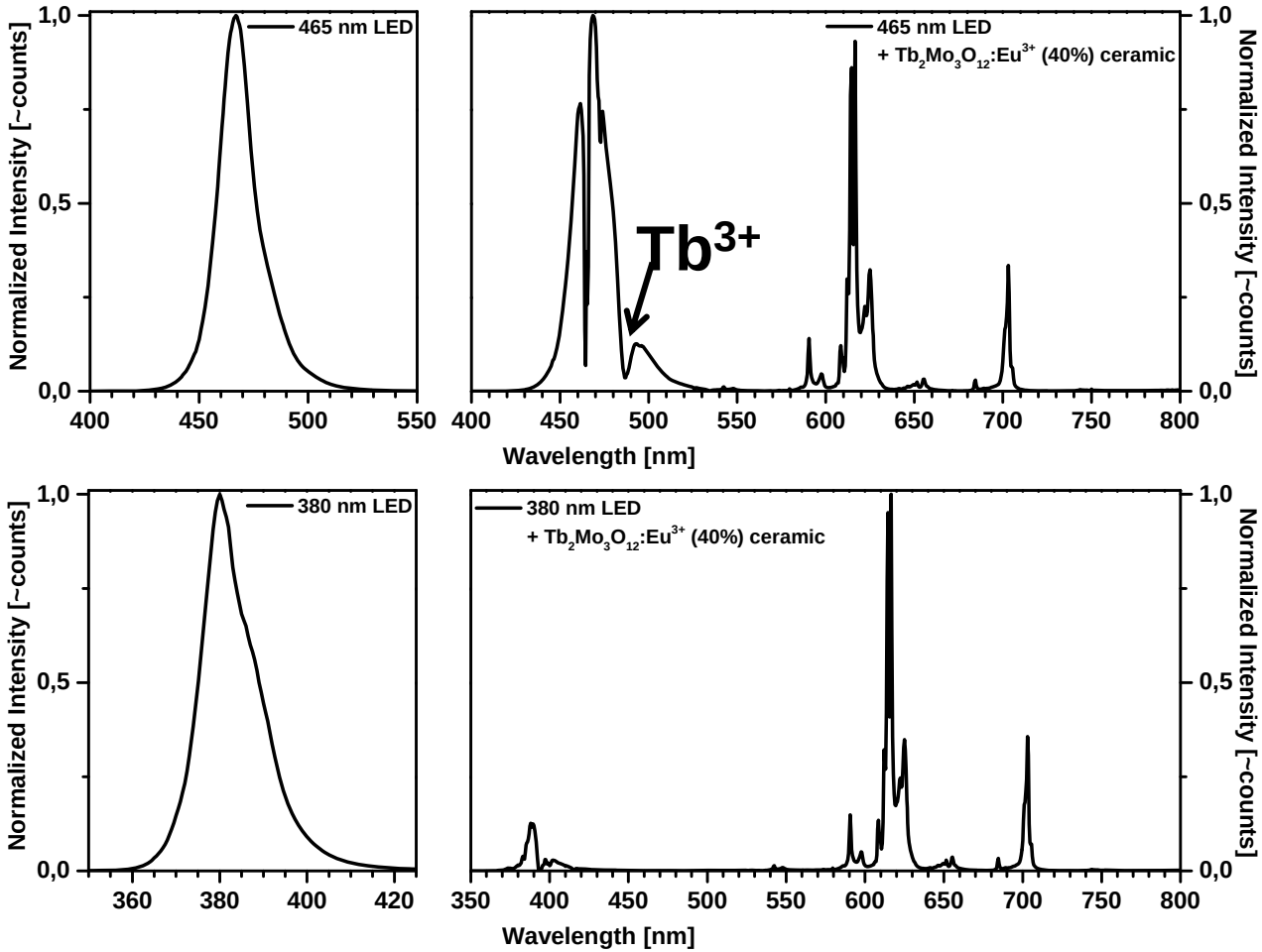


465 nm InGaN LED



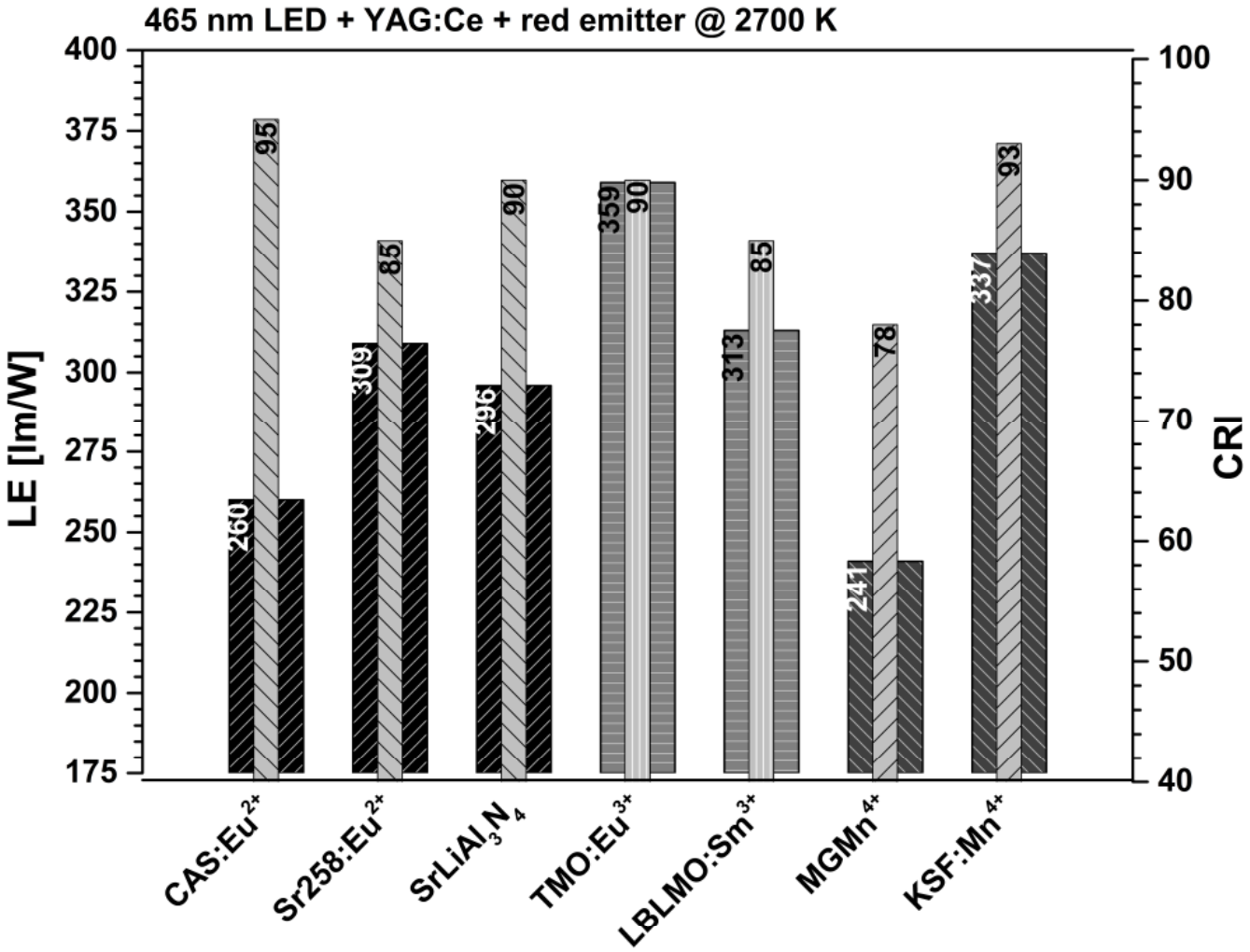
380 nm InGaN LED

⇒ Full conversion LED possible



5. Towards Ultimate Efficiency and CRI

LE and CRI calculations of warm-white phosphor converted LEDs



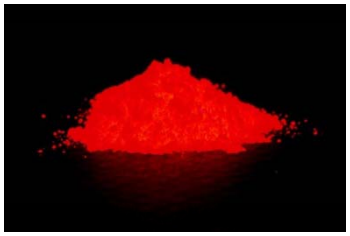
$Tb_2Mo_3O_{12}$:Eu gives 20% higher LE compared to $SrLiAl_3N_4$:Eu

The reduced re-absorption in Eu^{3+} phosphor comprising LEDs gives potentially higher package gain as well …..

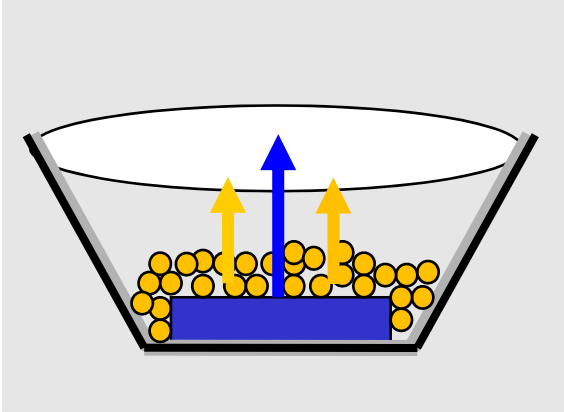
5. Towards Ultimate Efficiency and CRI

Powder/polymer composites

Variable layer thickness
Strong scattering
High thermal resistance
Drop-Stop

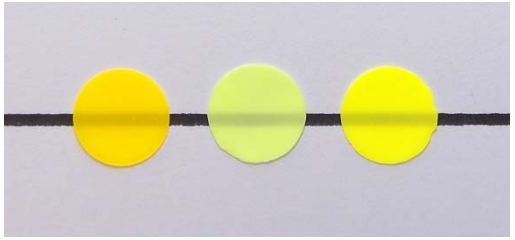



Blue LED + inorganic luminescent powder in epoxy- or silicon resin

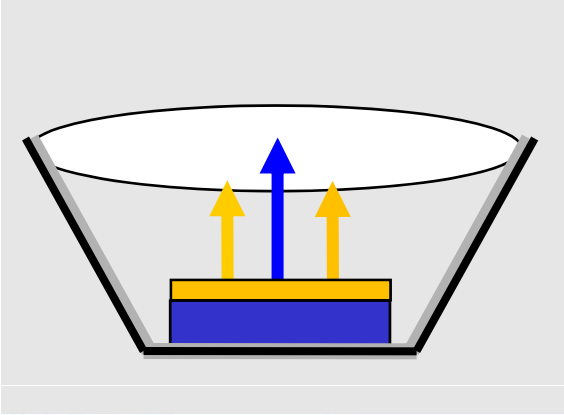


Ceramics

Homogeneous layer thickness
Little scattering
Low thermal resistance
Pick & Place



Blue LED + ceramic converter (Lumiramic or c^2)

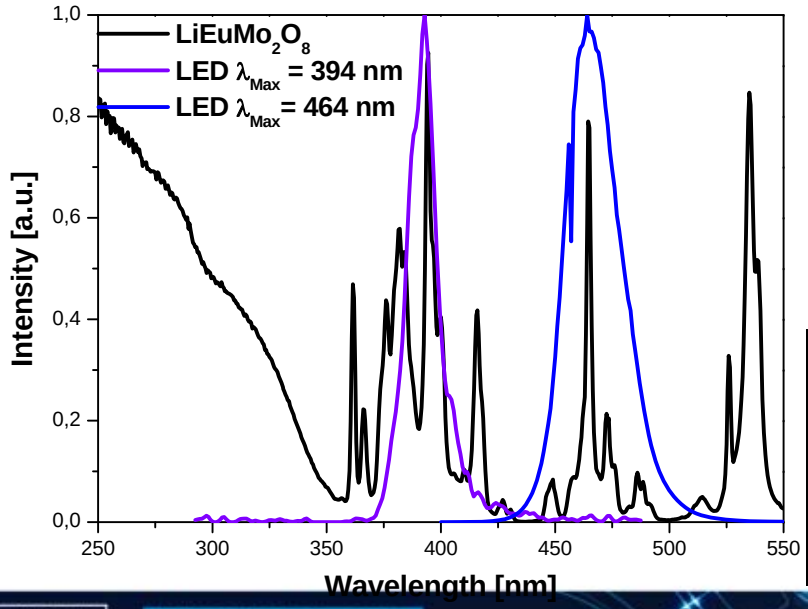


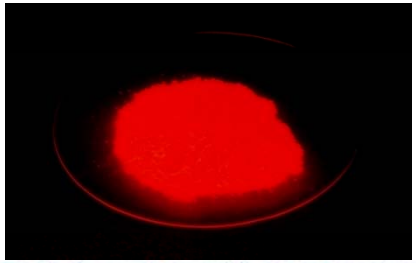
5. Towards Ultimate Efficiency and CRI

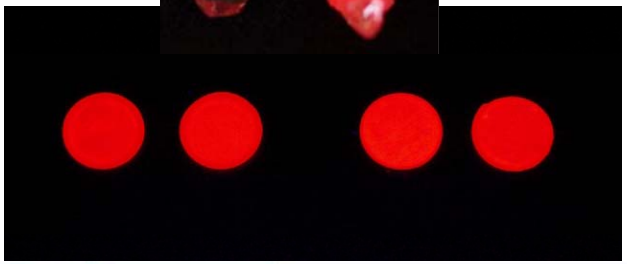
Eu^{3+} doped molybdates as red colour converter in white-emitting pcLEDs

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

→ **Conversion of red emitting powders into ceramics**







6. Summary and Outlook

$LiEuMo_2O_8$, $Li_3Ba_2Eu_3Mo_8O_{32}$, $Tb_2Mo_3O_{12}$: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

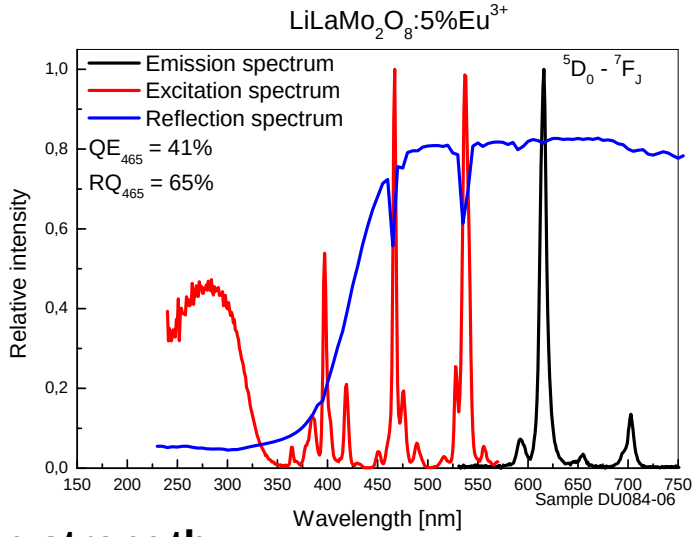
→ Further optimisation by ceramic preparation or multiple activator ion sites, as inTb_2MoO_6:Eu

6. Summary and Outlook

Cool white LEDs	Warm white LEDs	Warm White LEDs (near UV)
1. Blue chip	Blue chip	Blue/cyan luminescent material
2. $Ln_3Al_5O_{12}$:Ce	$Ln_3Al_5O_{12}$:Ce	$Ln_3Al_5O_{12}$:Ce
3. None	CaS:Eu/$Sr_2Si_5N_8$:Eu	CaS:Eu/$Sr_2Si_5N_8$:Eu/$CaAlSiN_3$:Eu
	$CaAlSiN_3$:Eu	Eu^{3+}-doped molybdates

Red line emitters Eu^{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 $Sr_2Si_5N_8$:Eu



Next steps

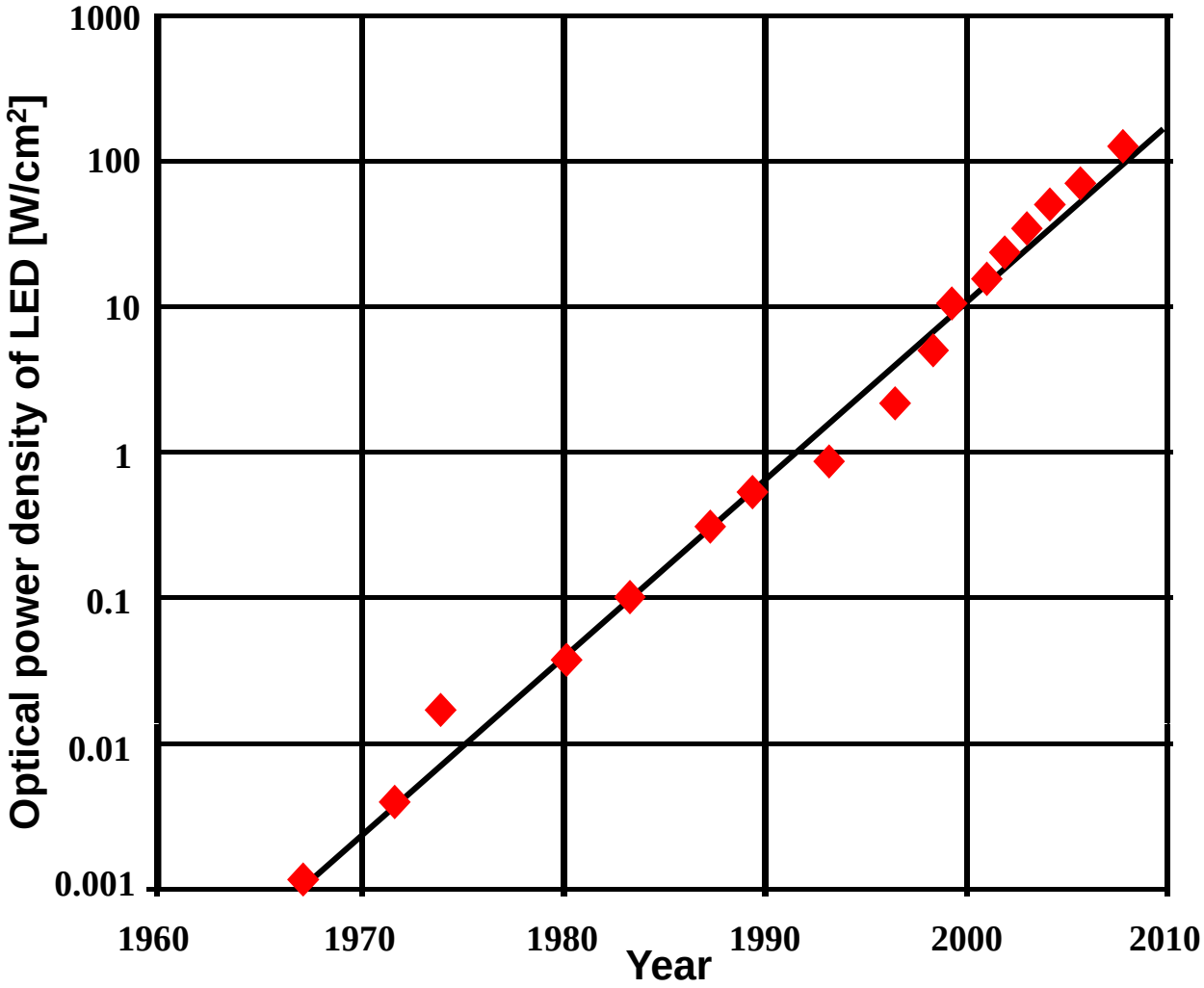
- Increase average particle size to enhance absorption strength
- Final goal: Transparent ceramics?
- Development of further stable green, yellow and red line phosphors with high luminous efficiency

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….
- University Tübingen, Germany
  Prof. Jürgen Meyer for inspiring discussions on solid state chemistry
- Universiteit Utrecht, The Netherlands
  Prof. Andries Meijerink for fruitful discussions on luminescence physics
- FEE Idar-Oberstein for crystal growth and fruitful collaboration on laser gain media
- Merck KGaA Darmstadt for generous financial support

Bundesministerium für Bildung und Forschung

MERCK