Luminescent Materials for High Brightness LEDs

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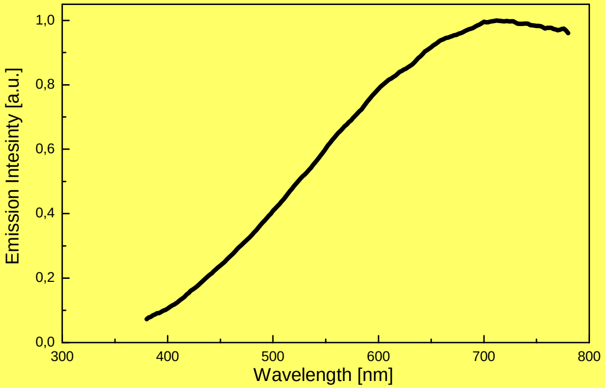
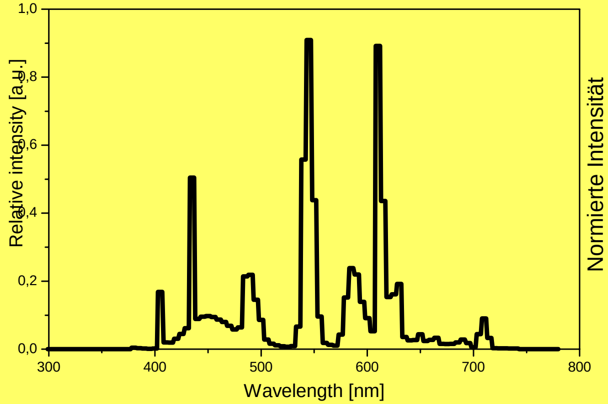
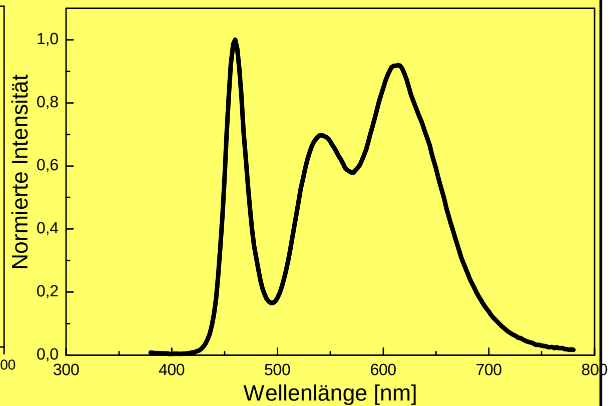
Evolution of Light Sources – General Lighting

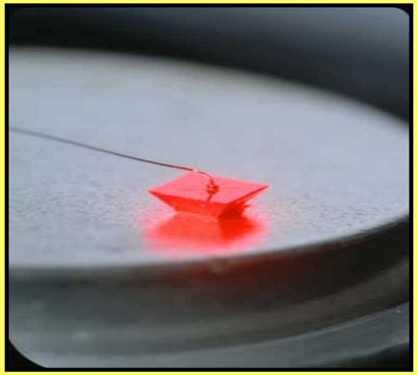
Light generation occurs from

19th century	→	20th century	→	21st century
solid state		gas discharge		solid state
C, Os, W		Hg, Na, Ne, Xe		AlInGaP,AlInGaN

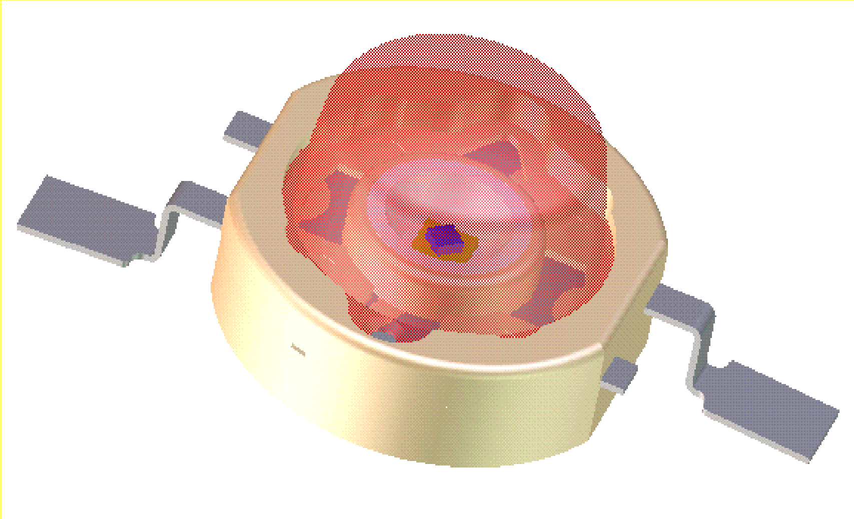






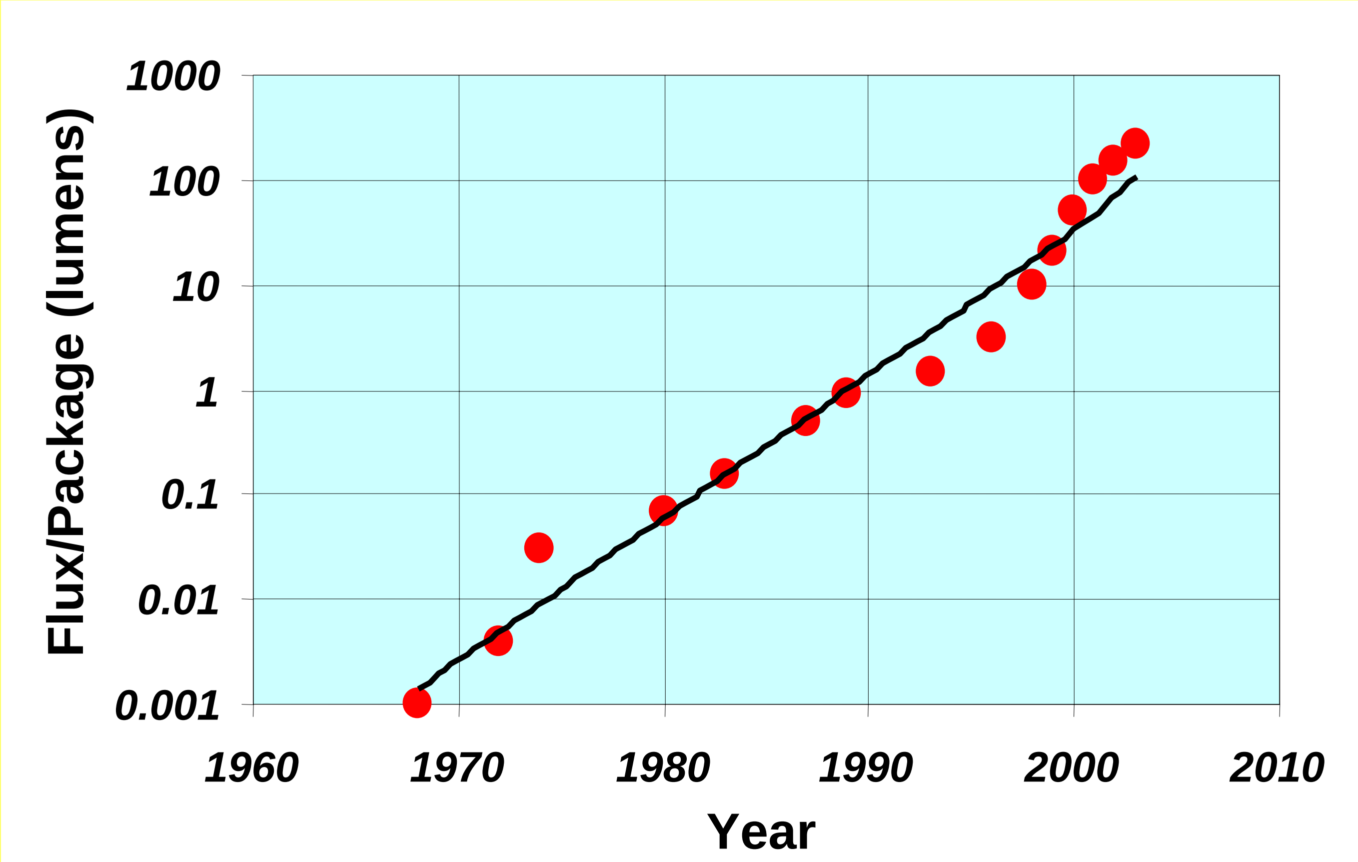


Evolution of Light Sources – LEDs



1970	2004
GaAsP	AlInGaP, AlInGaN
< 0.1 W	0.6 - 5 W
< 0.1 lm	10 - 150 lm
yellow, red	all colors + UV-A

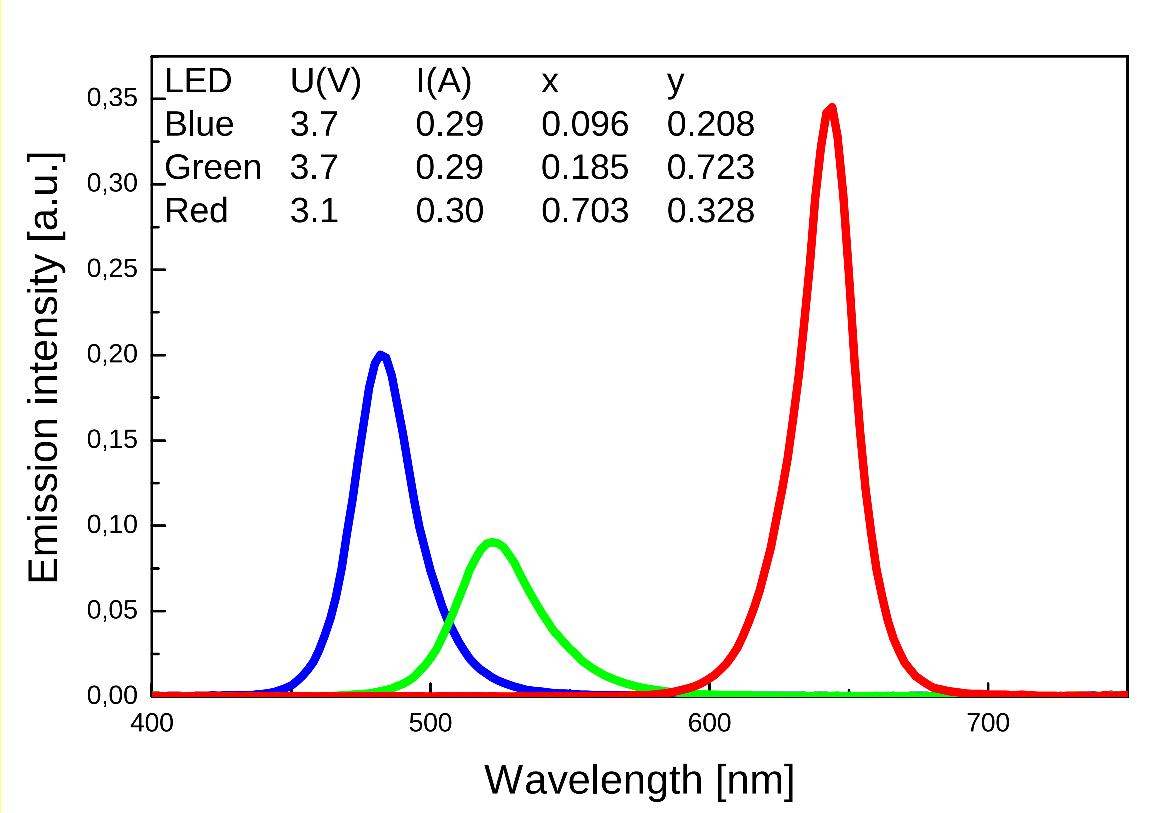
Evolution of Light Sources - LED Lumen Package



LED Flux per package has doubled every 18 - 24 months for last 30 years!

500 lm LED (30 W) demonstrated in lab!

Evolution of Light Sources – High Brightness LEDs



AlInGaP
580 – 900 nm
Quenching ~0.7%/K

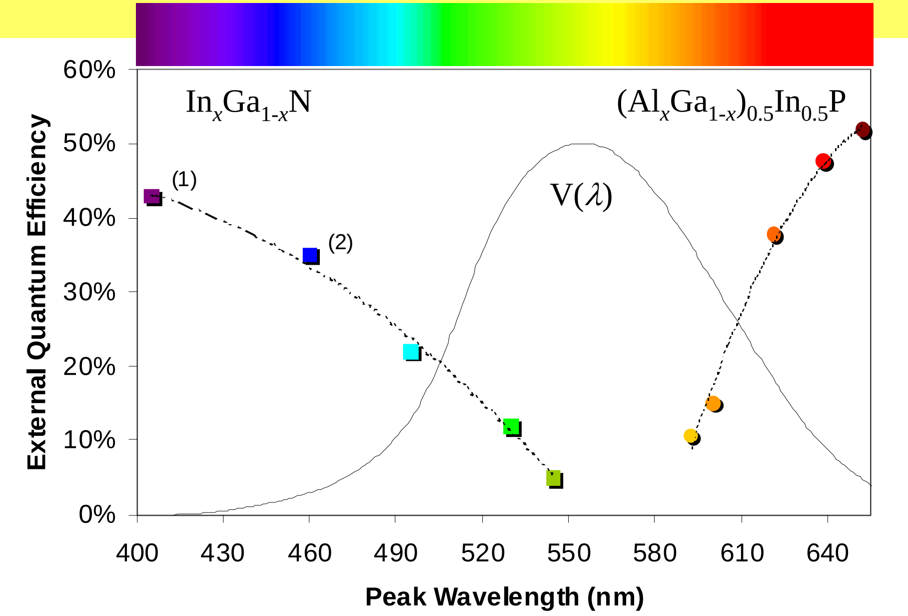
AlInGaN
250 – 550 nm
Quenching ~0.1%/K

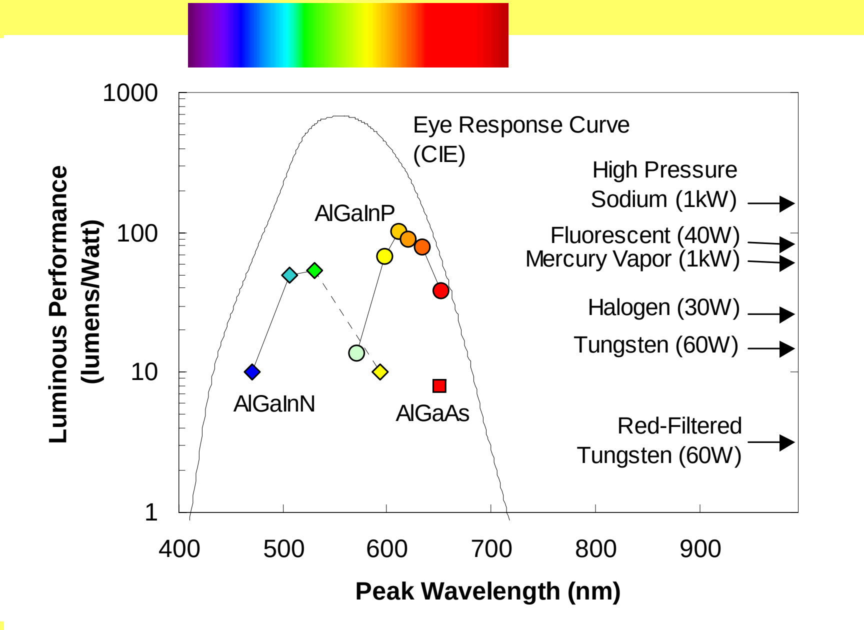
Spectral shift with drive and temperature

Input power	Voltage	Current	Chip temperature
1 W (2000)	4.5 V	0.2 A	120°C
5 W (2002)	4.5 V	1.1 A	150°C

Evolution of Light Sources – Efficiency of LEDs

Energy efficiency —Eye response→ **Luminous efficiency**

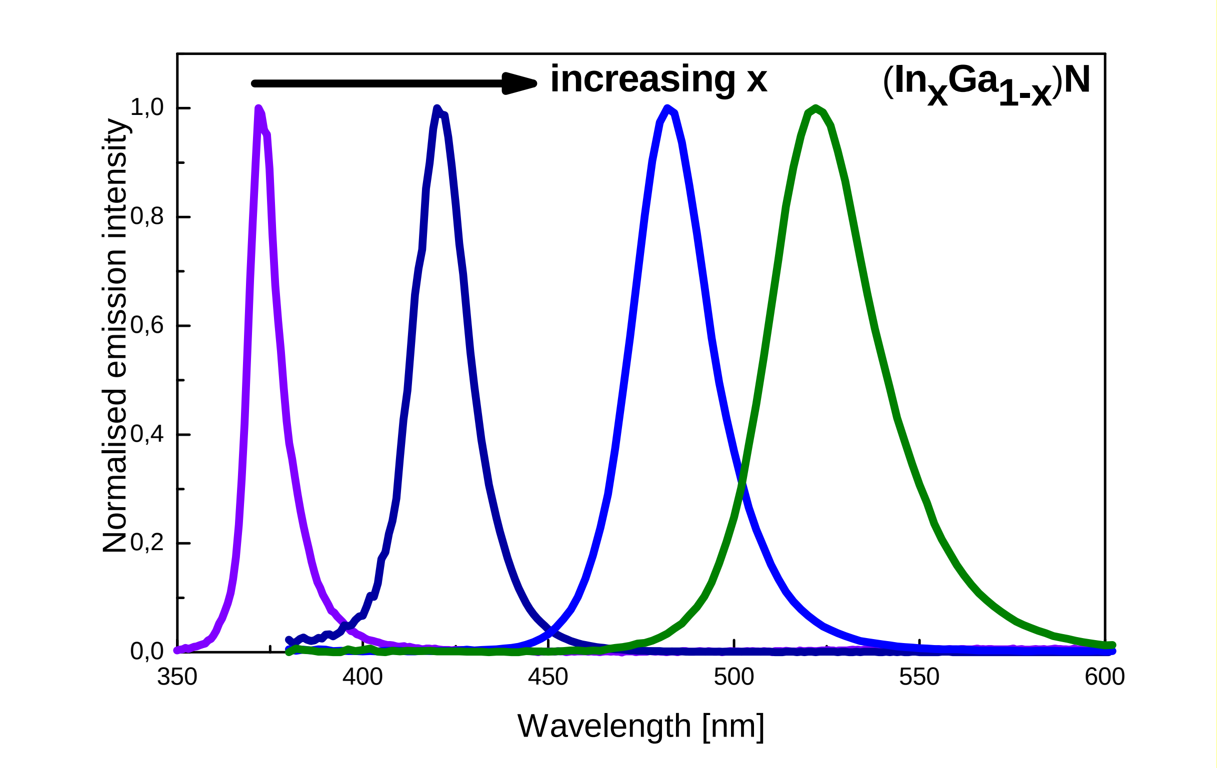




Yellow Efficiency Gap

LEDs are already more efficient than (filtered) incandescent and halogen lamps

Spectra of InGaN LEDs



<u>Increasing In concentration</u>

InGaN quantum well transition energy decreases: 370 nm → 550 nm

Broadening of emission band

Decrease in quantum efficiency

White Light Generation by LEDs

UV LED → Phosphor blend → White light by fluorescence

Blue LED → Single phosphor or phosphor blend → White light by fluorescence

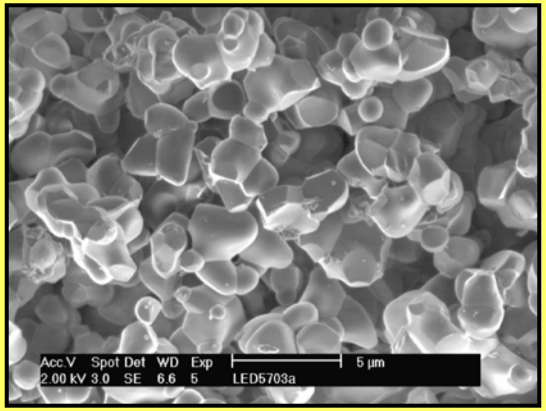
Blue LED + Green LED + Red LED → Additive color mixing by secondary optics → White light by colour mixing

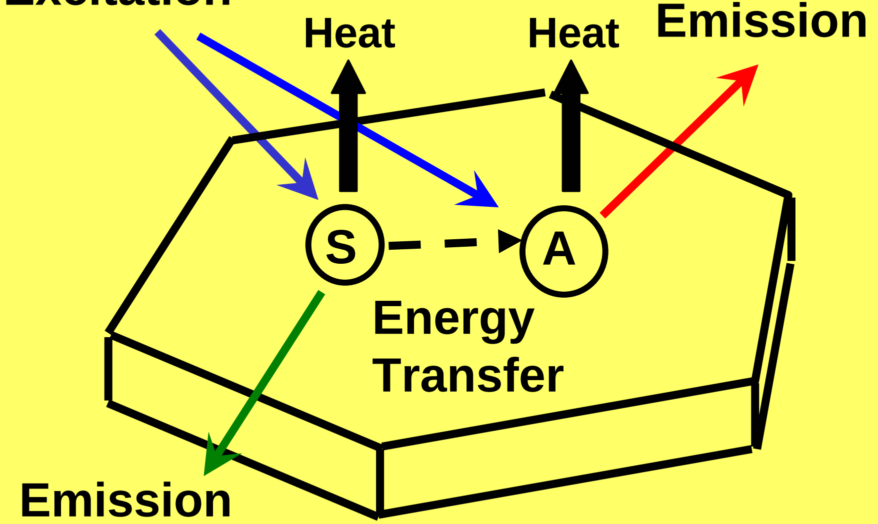
White Light Generation by Fluorescence

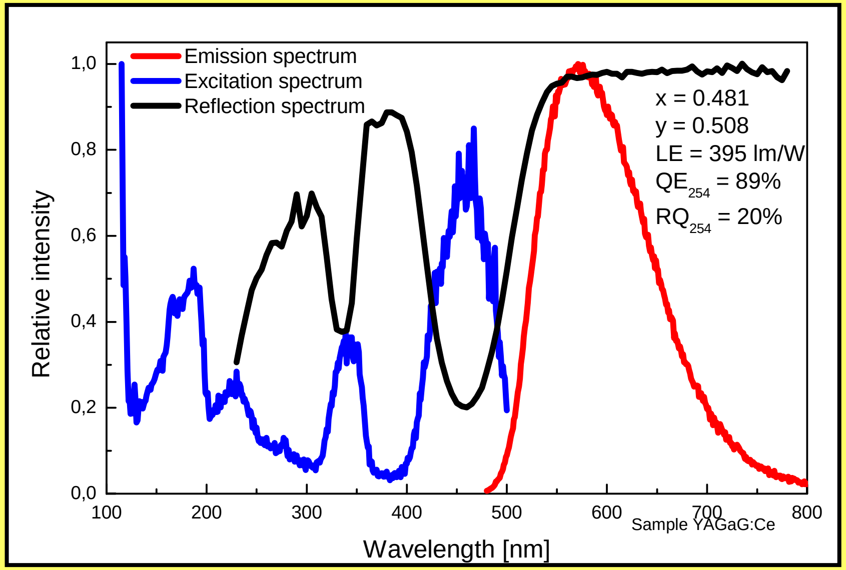
Fluorescent light sources comprise a luminescent screen, which convert absorbed energy into visible light by means of luminescent materials (phosphors)

How does a phosphor work?

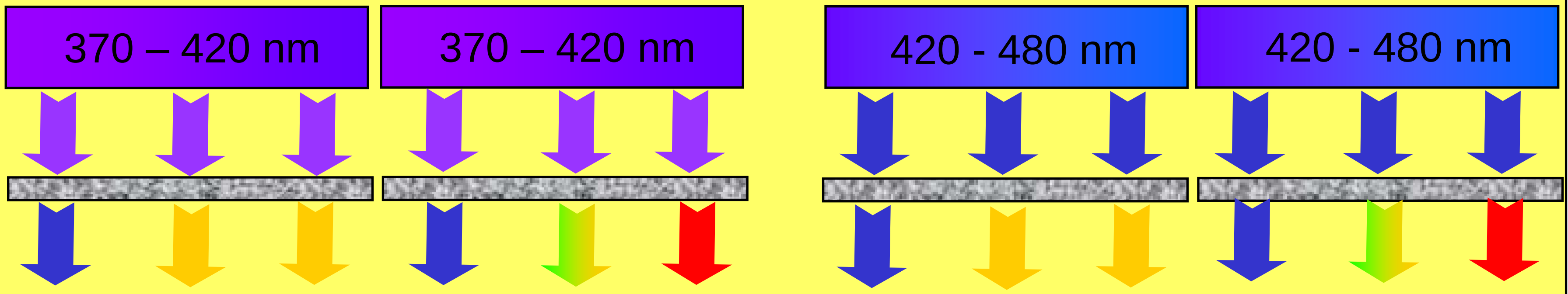
Layer of YAG:Ce µ-particles







White Light Generation by pcLEDs



290 – 330 lm/W	**320 – 360 lm/W**	**290 – 330 lm/W**	**320 – 360 lm/W**
CRI = 70 – 85	**CRI = 85 - 95**	**CRI = 70 – 85**	**CRI = 85 - 95**
low CRI at low T_c	**high CRI at all T_c**	**low CRI at low T_c**	**high CRI at all T_c**

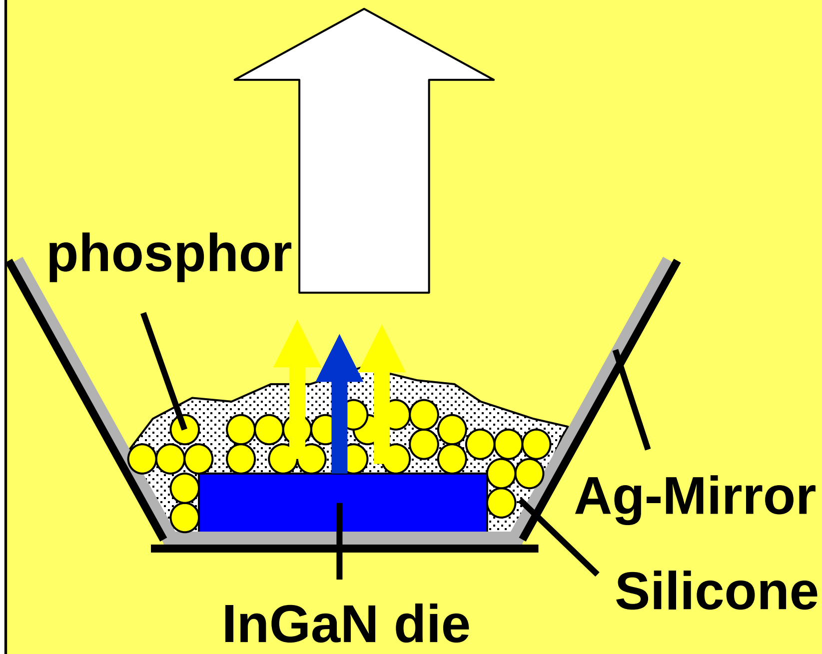
UV light causes polymer degradation and requires safety measures

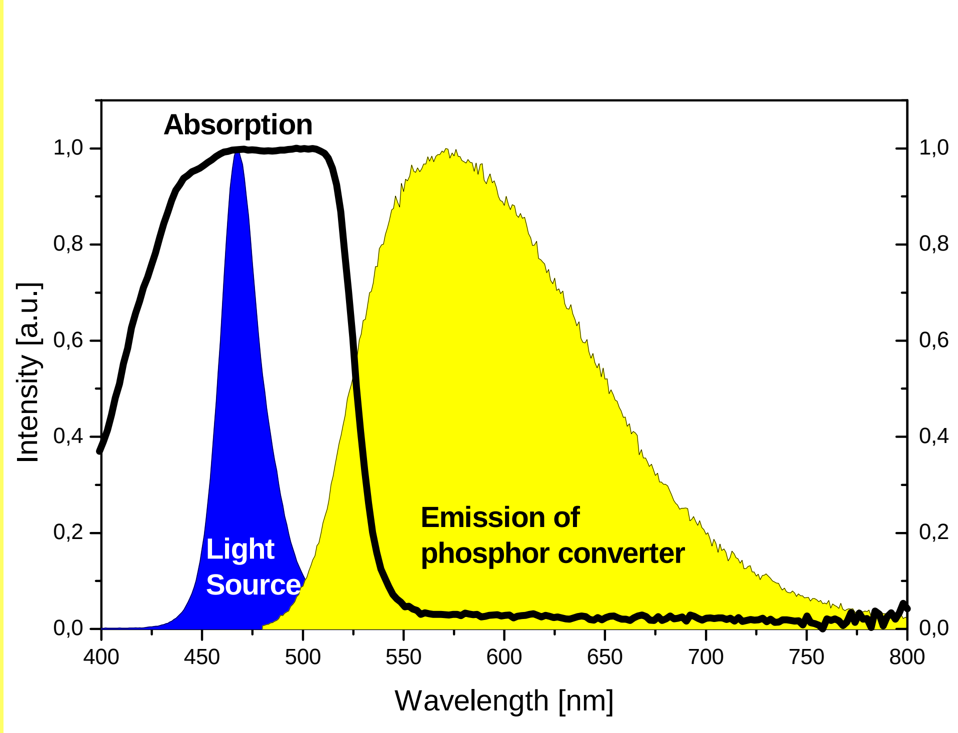
Leak through of blue light depends on optical pathway
Colour point = f(viewing angle)

390 nm LED (3.2 eV) $\rightarrow$ 570 nm (2.2 eV)
Quantum deficit = 0.69

460 nm LED (2.7 eV) $\rightarrow$ 570 nm (2.2 eV)
Quantum deficit = 0.78

Phosphor Converted LEDs (pcLEDs)





Blue LED chip:	**420 – 480 nm emitting InGaN**	
Phosphor conversion 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**

Selection Criteria for pcLED Phosphors

In General

- strong absorption at LED chip emission wavelength
  → spin and parity allowed transition, e.g. $4f^n – 4f^{n-1}5d^1$
- quantum efficiency higher than 90%
- stability towards O_2, CO_2, and H_2O
- stability under high photoexcitation density

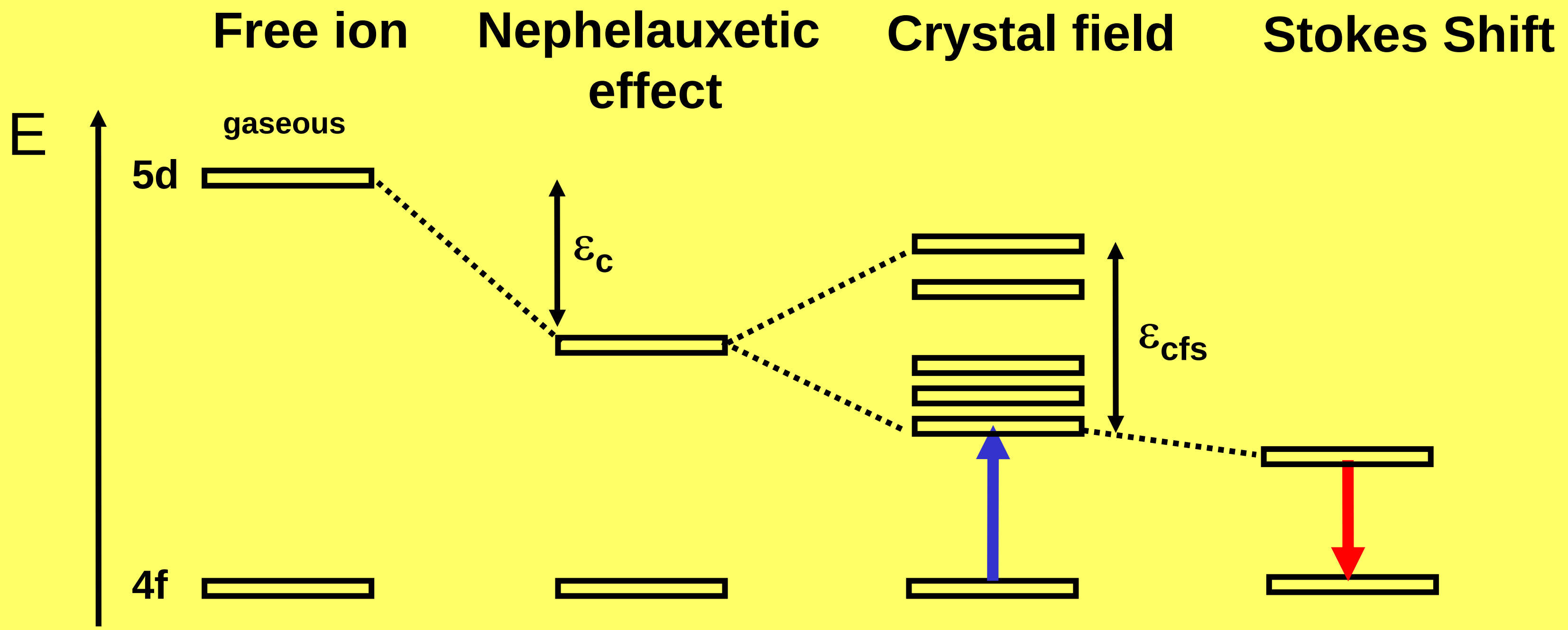
Blue + Yellow Concept

- broad emission band at around 560 - 580 nm
  → Ce^{3+} phosphors (ground state depletion $^2F_{5/2}$ + $^2F_{7/2}$)

Blue + Green/Yellow + Red Concept

- green/yellow phosphor → Eu^{2+} or Ce^{3+}
- red phosphor → Eu^{2+}

Spectra of Ce^{3+} and Eu^{2+} Phosphors



Free ion: **Eu^{2+}** **Ce^{3+}**

$4f^{n-1}5d^1$ level: **34000 cm^{-1}** **50000 cm^{-1}**

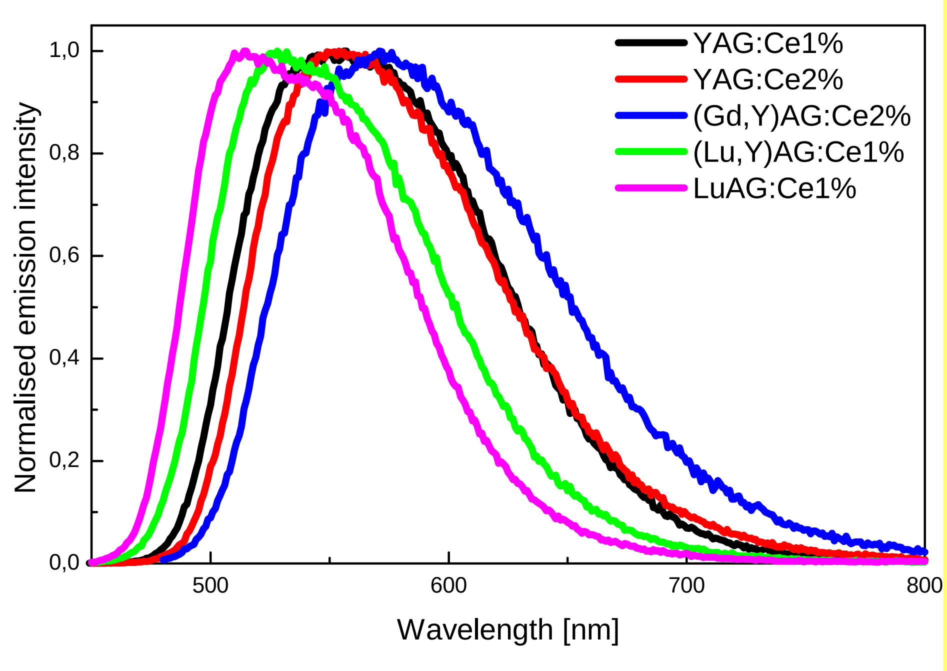
ε_c: centroid shift due to nephelauxetic effect

ε_{cfs}: crystal field splitting

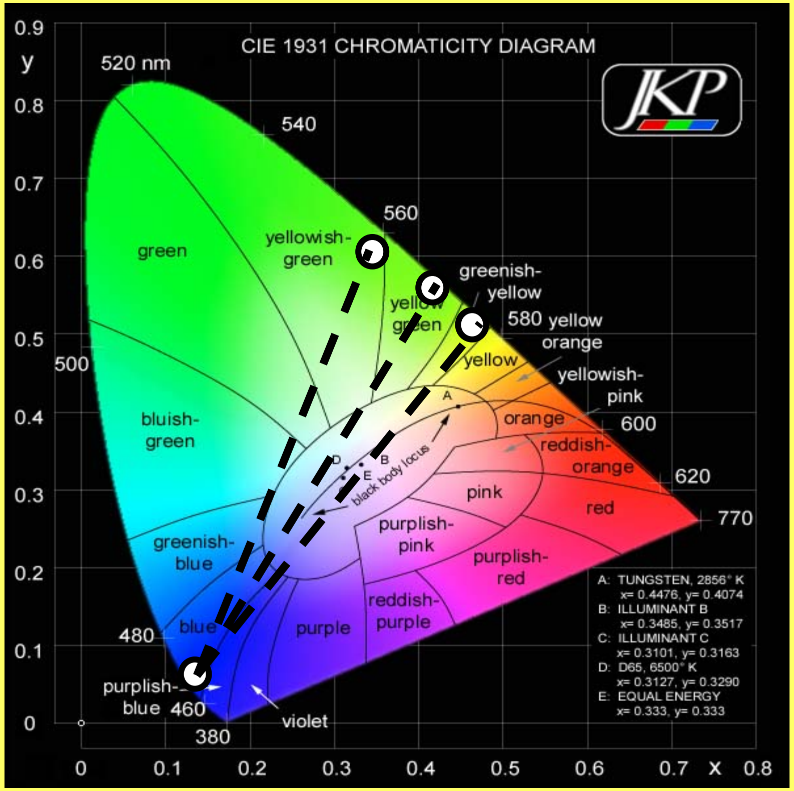
Both parameters depend on type of host lattice, i.e. composition

Emission Spectra of $Ln_3Me_5O_{12}$:Ce

Emission spectra



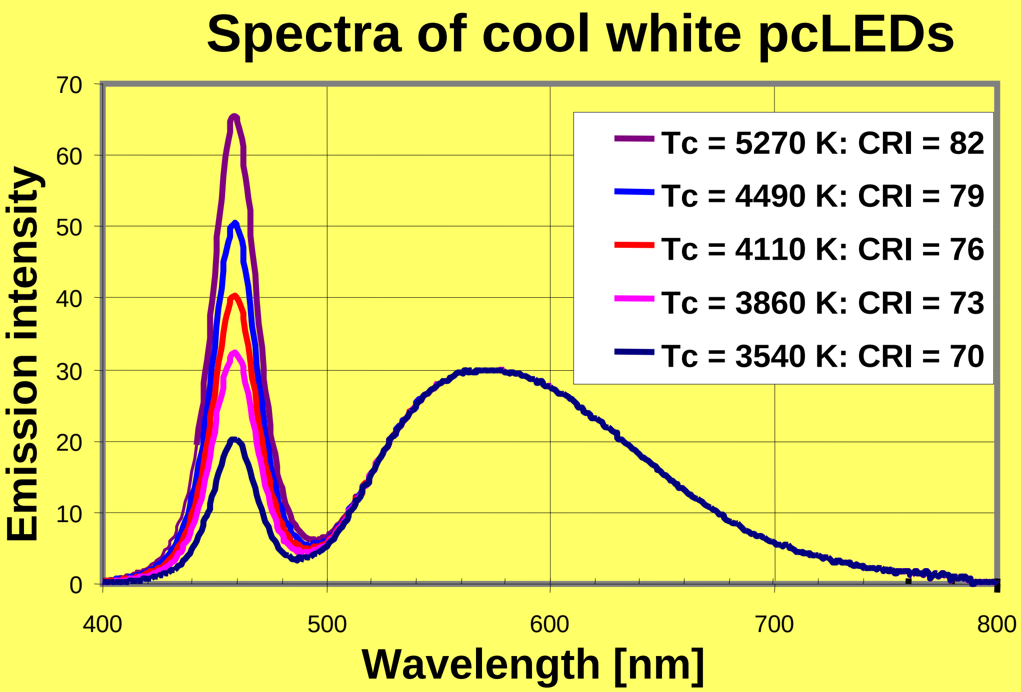
Color points



Garnet structure $Ln_3Me_5O_{12}$

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

White pcLEDs based on $(Y,Gd)_3Al_5O_{12}$:Ce



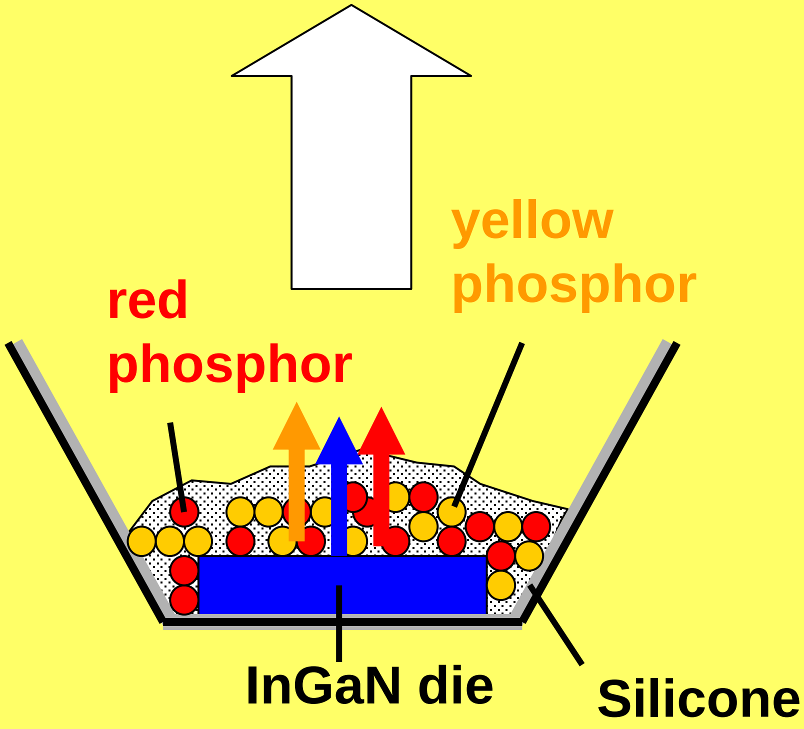
- **Color rendition CRI = 70 – 80**
- **Cool white light emission**
- **Wall plug efficiency:**
  high brightness 30 lm/W
  low brightness 50 lm/W
- **Lifetime 50000h, 90% at 12000h**
- **Lack of red radiation and colour rendering is f(T_c)!**

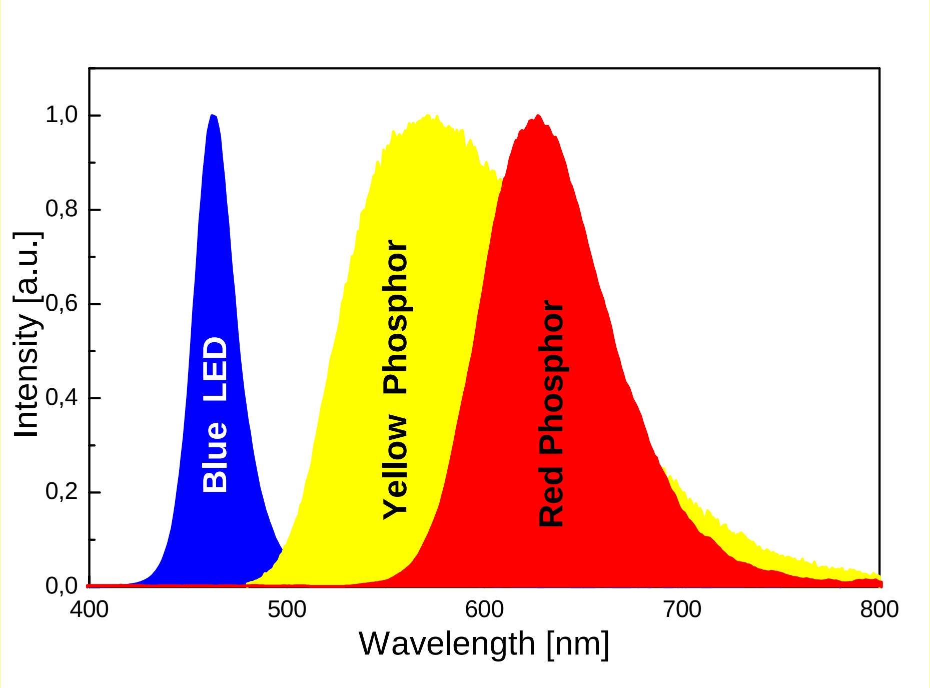
$(Y,Gd)_3Al_5O_{12}$:Ce is very efficient and (photo)chemically stable, but high color rendering at low color temperature requires additional red emitter!

White pcLEDs with a high Color Rendition

1. Blue LED + (Y,Gd)AG:Ce ⇒ CRI > 75 only for T_c > 4000 K

2. Blue LED + YAG:Ce + Red ⇒ CRI > 85 for T_c < 4000 K





Red Phosphors

Shortcomings of Ce^{3+} Phosphors

- **Rather narrow absorption band**
- **Rather broad emission band**
- **No known red-emitting Ce^{3+} phosphor with a high thermal quenching temperature at the same time**

Alternatives

- **Mn^{2+} activated: Sensitisation required, saturation**
- **Eu^{3+} activated: Y_2O_2S:Eu, CT band < 360 nm**
- **Eu^{2+} activated: Strong covalency and CFS required**

Best choice are Eu^{2+} activated luminescent materials

Color of Eu^{2+} Phosphors

Chemical composition	λ_{max}
– $CaS:Eu$	655 nm
– $Sr_2Si_5N_8:Eu$	615 nm
– $SrS:Eu$	610 nm
– $Ba_2Si_5N_8:Eu$	580 nm
– $Sr_2SiO_4:Eu$	575 nm
– $SrGa_2S_4:Eu$	535 nm
– $SrAl_2O_4:Eu$	520 nm
– $Ba_2SiO_4:Eu$	505 nm
– $Sr_4Al_{14}O_{25}:Eu$	490 nm
– $SrSiAl_2O_3N:Eu$	480 nm
– $BaMgAl_{10}O_{17}:Eu$	450 nm
– $Sr_2P_2O_7:Eu$	420 nm
– $SrB_4O_7:Eu$	368 nm

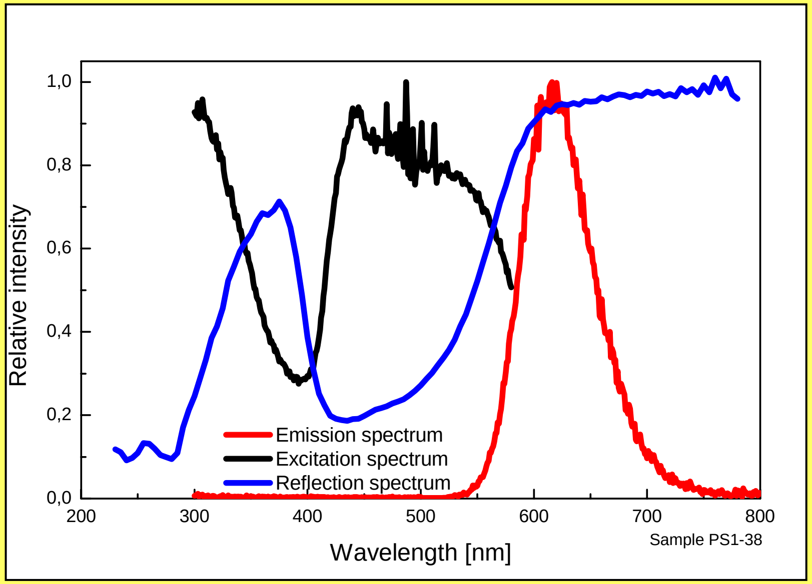
Increase fo covalency or crystal-field strength

Nitrides + Sulfides

Oxynitrides + Oxides

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

Substitution of Sr by Ca yields a red-shift and improves stability



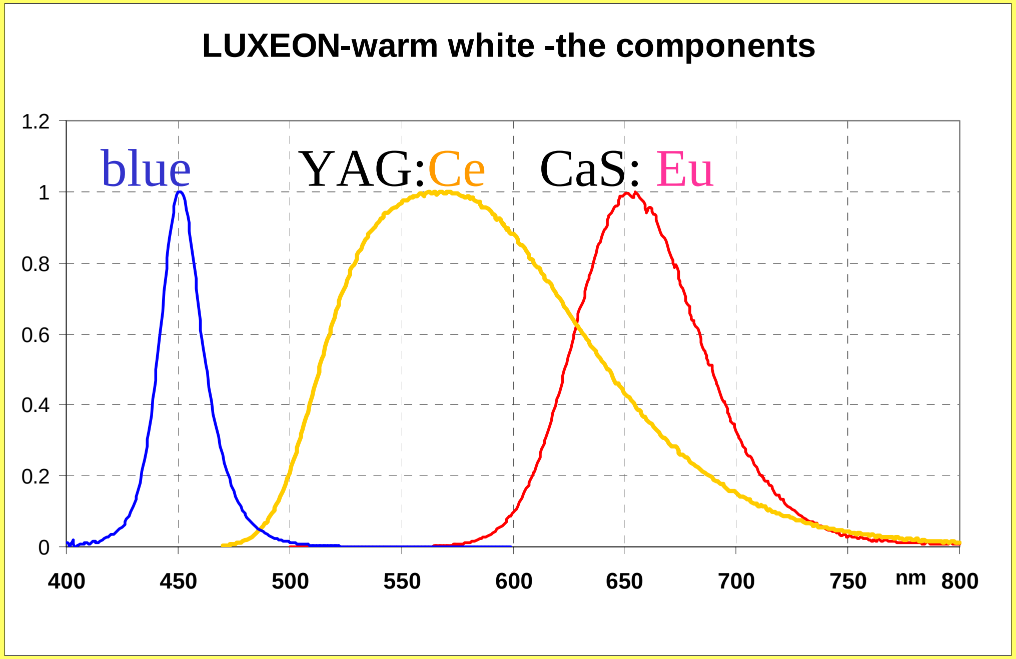
SrS:Eu → **stability** → **CaS:Eu**

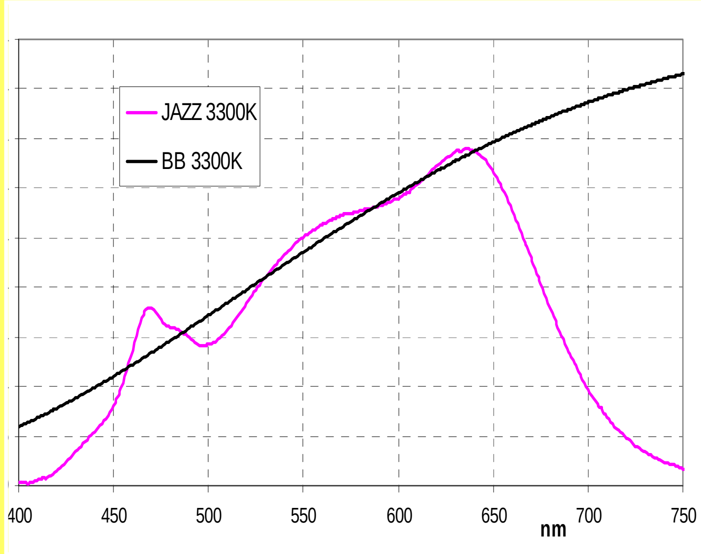
Crystal field strength →

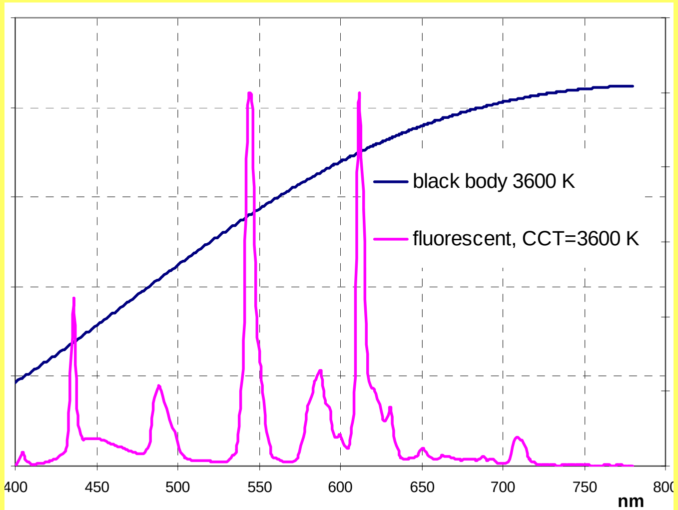
← **Centroid shift**

Composition	QE [%]	Abs. [%]	LE [lm/W]	x	y
SrS:Eu	> 95	> 80	260	0.629	0.370
CaS:Eu	> 95	> 80	90	0.697	0.303

Warm White pcLEDs



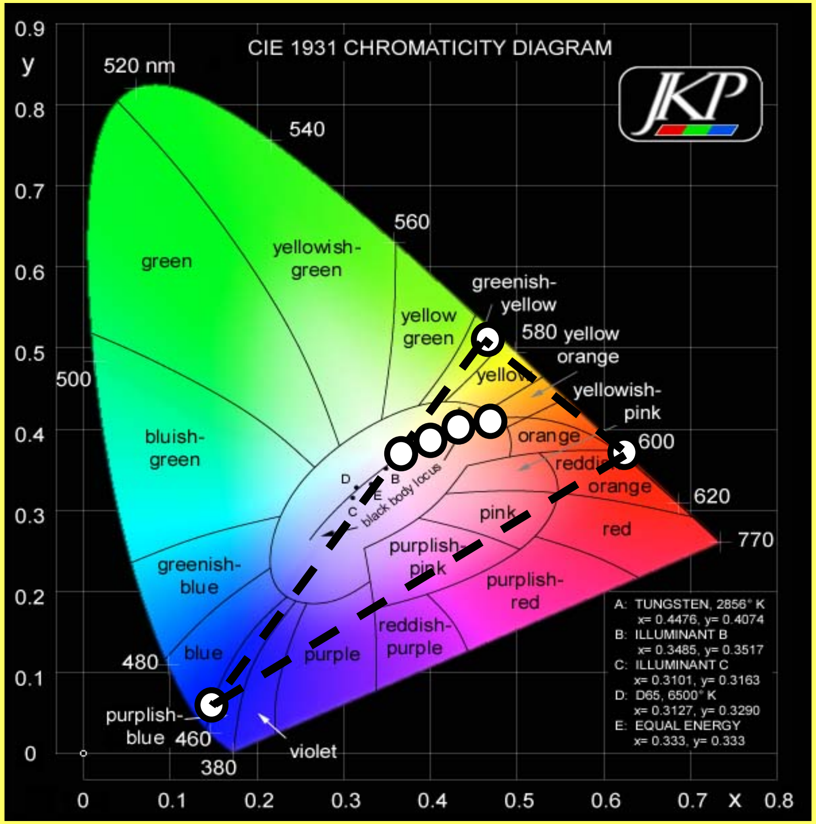




Red emitter is added to the plain (cold) white of blue +YAG:Ce.
We chose CaS:Eu^{2+} (Philips + Lumileds IP)
More red: lower CCT, more blue: higher CCT.

CCT range: 2700 to 5500 K
with excellent CRI > 90

Warm White pcLEDs



Warm white pcLEDs comprising YAG:Ce and CaS:Eu

⇒ CRI > 90 for T_c between 2700 and 5500 K

Colour cannot be better but efficiency....

Standard White ((Y,Gd)AG:Ce)
5500 K, CRI ~ 75
330 $lm/W_{opt.} \rightarrow$ ~ 30 $lm/W_{el.}$

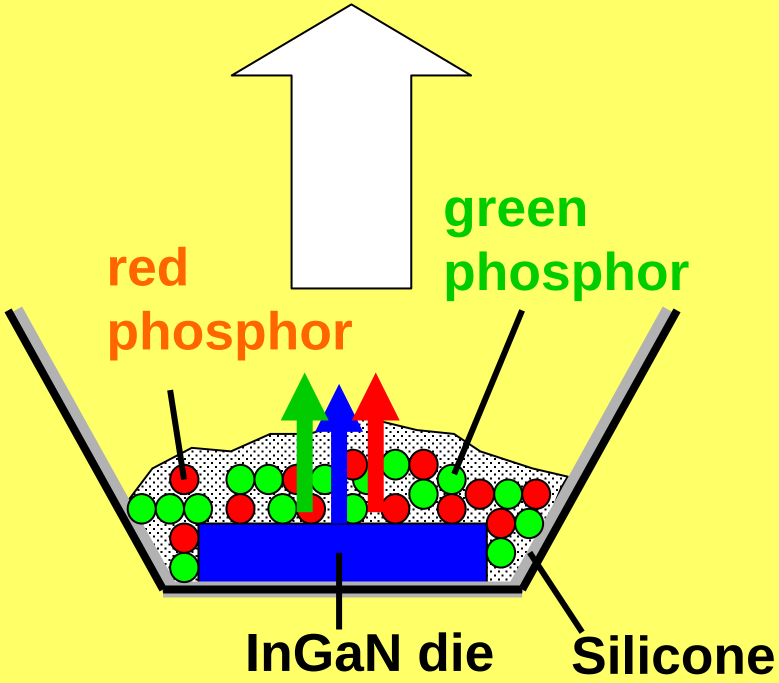
Warm White (YAG:Ce + CaS:Eu)
3200 K, CRI ~ 90
300 $lm/W_{opt.} \rightarrow$ ~ 20 – 25 $lm/W_{el.}$

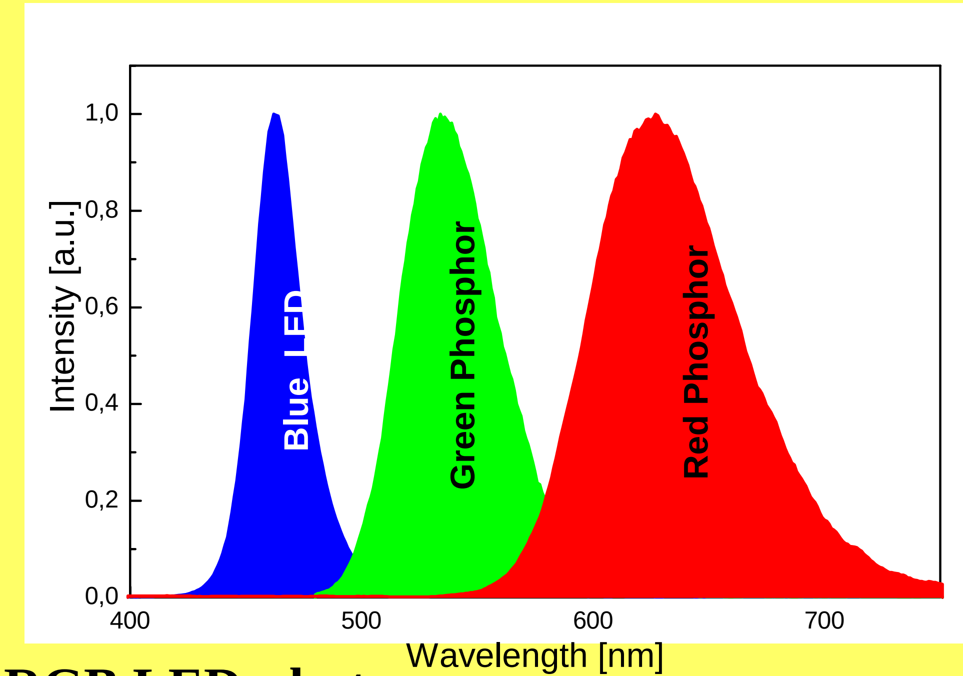
Trichromatic RGB White pcLEDs

1. Blue LED + (Y,Gd)AG:Ce ⇒ CRI > 75 only for T_c > 4000 K

2. Blue LED + YAG:Ce + Red ⇒ CRI > 90 for T_c < 4000 K

3. Blue LED + Green + Red ⇒ CRI > 85 for T_c = 2700 – 8000 K

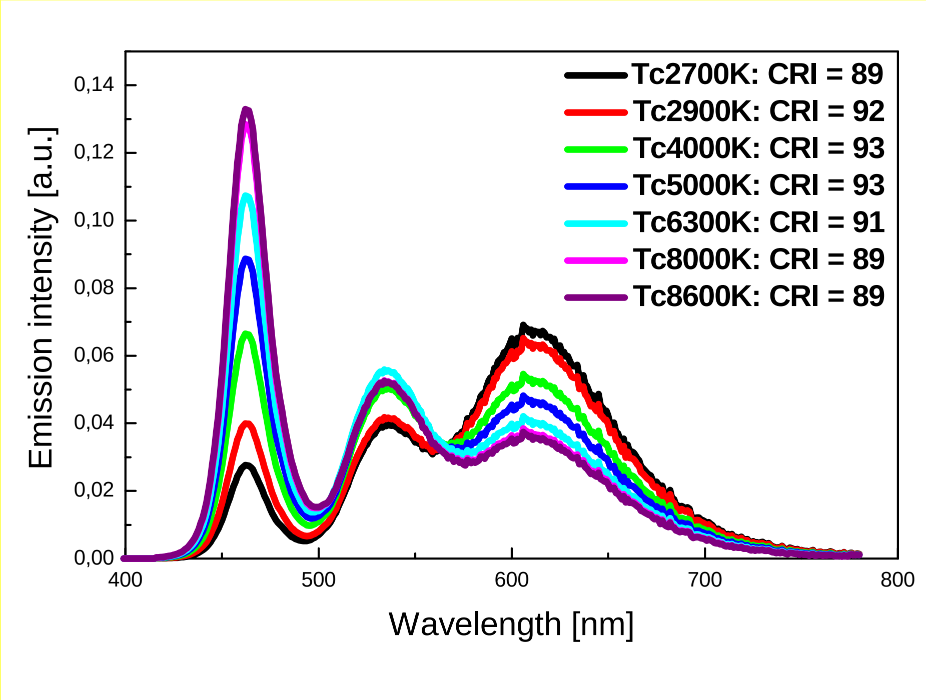


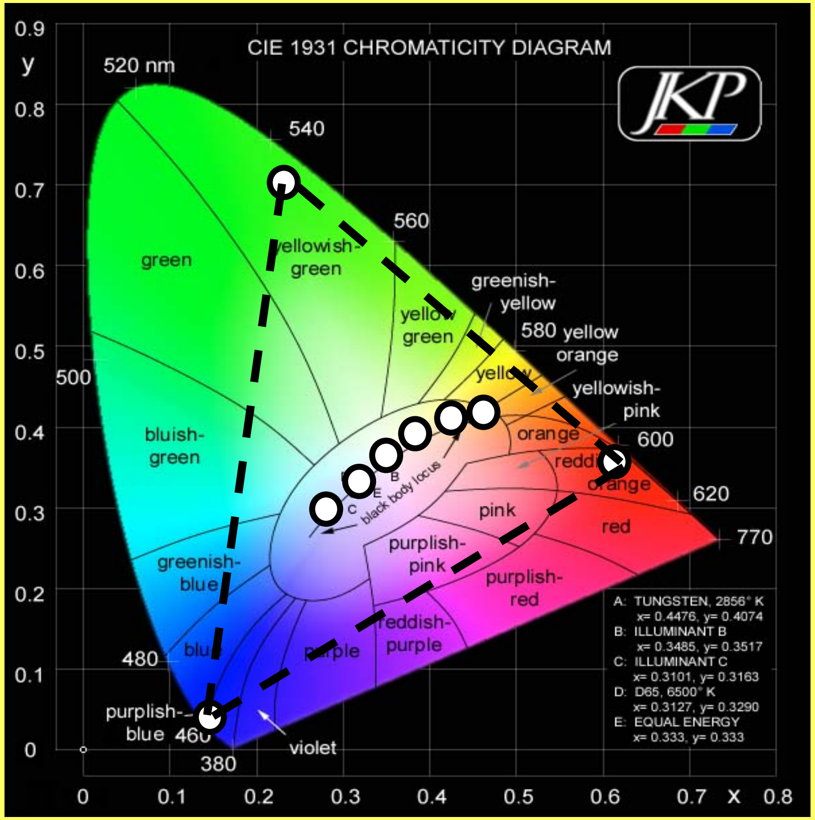


Alternative concept: Application of RGB LEDs, but.....

Trichromatic RGB White pcLEDs

Blue LED + $SrGa_2S_4$:Eu + SrS:Eu





Color rendition is > 89 for 2700 K < CCT < 8000 K

(R. Mueller-Mach, G.O. Mueller, Proc. SPIE 3938, 2000, 29)

Problem: Stability of phosphor blend (sulfides)

Nitride Phosphors

Advantages over oxides and sulfides

- **highly condensed anionic networks**
  - ⇒ **high density**
  - ⇒ **high chemical stability**
  - ⇒ **high hardness**
  - ⇒ **high quenching temperature**

- **higher charge density between activator and nitride ligands:**
  oxides < oxynitrides < nitrides < nitridocarbides
  - ⇒ **large red-shift of emission band**

	Si	$X = O^{2-}$	$X = N^{3-}$	$X = C^{4-}$
r [pm]	26	138	146	160
Electronegativity χ	1.92	3.61	3.07	2.54
Ionic bonding Si-X [%]	-	51	28	9

Nitride Phosphors

Several efficient phosphors have been recently developed for LED purposes

$(Ca,Sr,Ba)_2Si_5N_8:Eu^{2+}$ — **λ_{em}= 580 - 625 nm**
W.S. Schnick et al.

$YSiO_2N:Tb^{3+}$ — **λ_{em}= 545 nm**
$Y_2Si_3O_3N_4:Tb^{3+}$
$Gd_2Si_3O_3N_4:Tb^{3+}$
B. Hintzen et al. — **"but low absorption at 450 nm"**

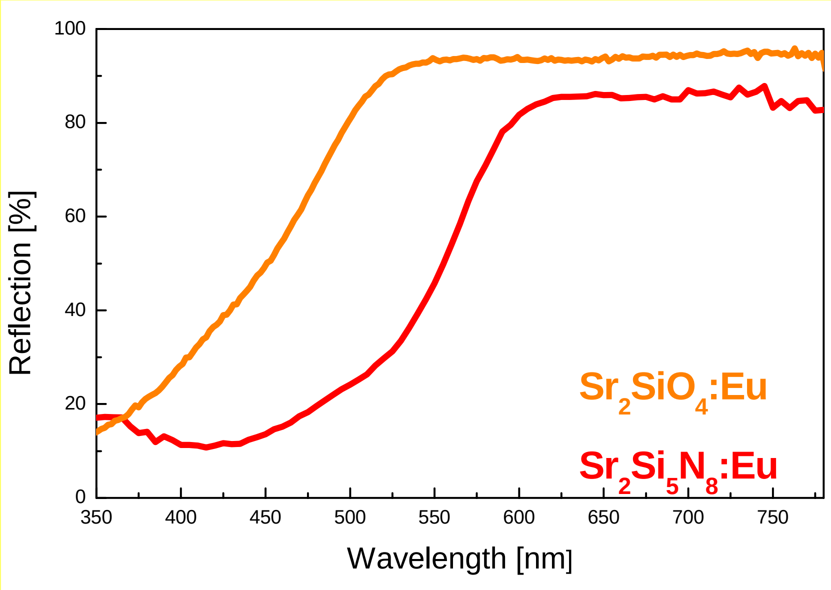
Green Nitride:Eu^{2+} — **λ_{em}= 505 - 565 nm**
P.J. Schmidt et al.

$SrSiAl_2O_3N:Eu^{2+}$ — **λ_{max} = 480 nm**
Osram

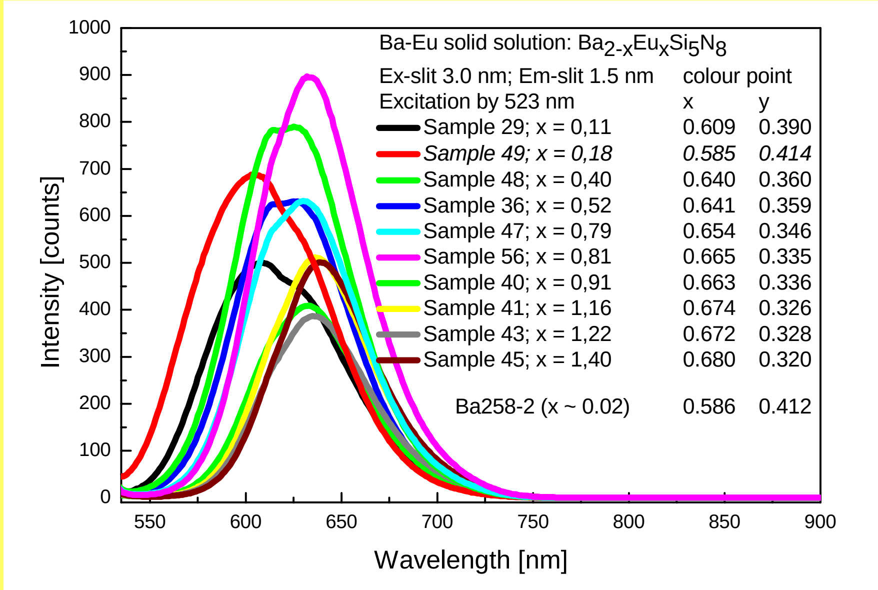
Nichia introduced first white LED comprising a nitride phosphor into the market, but due to low T-stability only low-power versions are sold (< 1 W)

Optical Properties of $(Ca,Sr,Ba)_2Si_5N_8$:Eu

Reflection Spectra



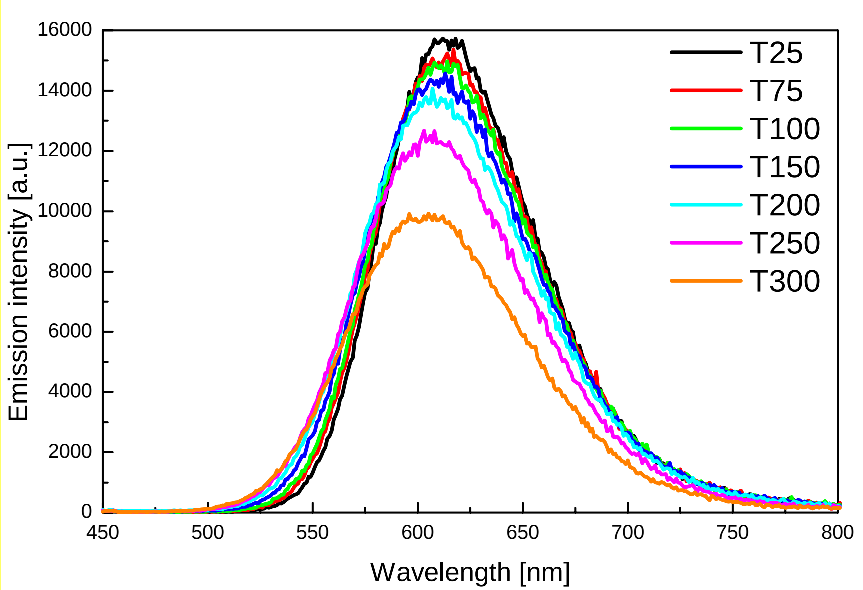
Emission Spectra



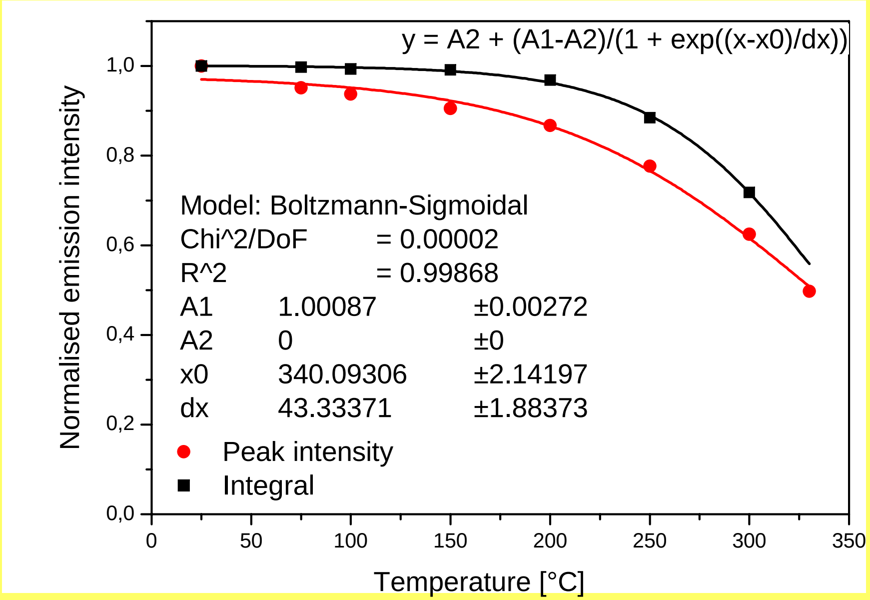
Composition	Body color	Emission band	Stability
Sr_2SiO_4:Eu	yellow	575 nm	decomposes in H_2O
$Ba_2Si_5N_8$:Eu	orange	580 nm	decomposes in conc. acids
$Sr_2Si_5N_8$:Eu	orange-red	615 nm	decomposes in conc. acids

Thermal Quenching of $Sr_2Si_5N_8$:Eu

Emission spectra



Thermal quenching



- **High absorption strength between 200 and 500 nm**
- **Quantum efficiency > 90% under 450 nm excitation**
- **Thermal quenching $TQ_{50\%}$ (450 nm excitation)**
  - **$Sr_2Si_5N_8$:Eu 340°C**
  - **SrS:Eu 300°C**

Application of pcLEDs - Illumination

Presently achieved performance of white LEDs

1. Standard white LEDs: (Y,Gd)AG:Ce

T_c = 5500 K CRI ~ 75 330 $lm/W_{opt.}$ → 30 $lm/W_{el.}$

2. Warm white LEDs: YAG:Ce + CaS:Eu

T_c = 3200 K CRI > 90 300 $lm/W_{opt.}$ → 20 – 25 $lm/W_{el.}$

3. Trichromatic white LEDs: Green nitride + $(Ca,Sr,Ba)_2Si_5N_8$:Eu

T_c = 2700 - 8000 K CRI ~ 90 350 $lm/W_{opt.}$ → 30 – 35 $lm/W_{el.}$

to address main concerns of LEDs

- **lumen package**
- **lifetime**
- **price per lumen**
- **colour homogeneity (has been solved)**

Application of pcLEDs - Illumination

Flash lights

Light tiles

Head lamps

Spot lighting

Architectural lighting

Contour lighting

Desktop lamps

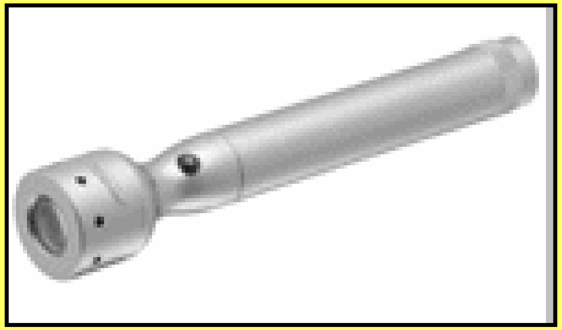
Automotive lighting

Backlighting

(General lighting)

(Street lighting)

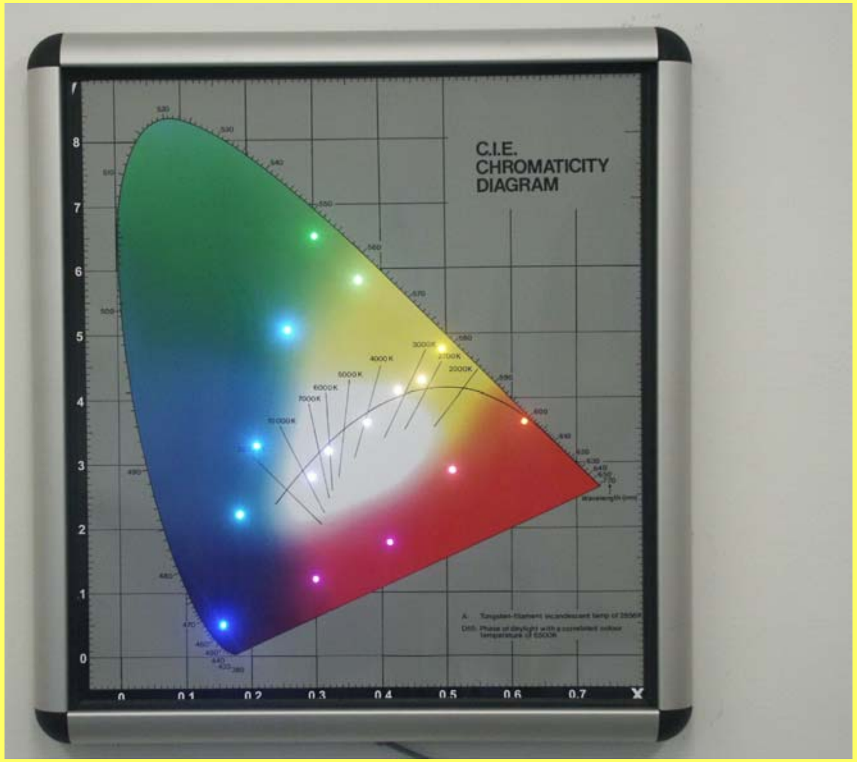
Advantages
- long lifetime
- easily dimmable
- slim profile
- little T-dependence
- fast switching speed
- low voltage
- arbitrary color (temperature)
- robustness
- …..



pcLEDs provide new opportunities for many illumination applications

Application of pcLEDs - Color on Demand

Blue LED (420 – 480 nm)
+ single phosphor conversion layer



Examples

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

Application in

- **corporate logos**
- **signals**
- **mood lighting**
- **advertisement lighting**

LEDs can provide almost all colors on demand without colour filters

Conclusions

- **Further increase in LED energy efficiency (→ 100 lm/W) and CRI (→ 90 - 95) expected this decade**
- **Next generation high color quality white LEDs will use Eu^{2+} activated luminescent materials**
- **Stable red-emitting phosphor has been found, e.g. CaS:Eu or $Sr_2Si_5N_8$:Eu**
- **Further increase in power and lumen package per LED**
  0.1 W (1970) → 1 W (2000) → 5 W (2002) → 20 W (2007)
- **Novel phosphors with a high stability and strong absorption are urgently required → green and yellow nitrides/oxynitrides**
- **Besides warm white, red and amber highly wanted for new applications (automotive, colour on demand, displays)**
- **Wide range of new nitride/oxynitride based color converters will be developed in the near future**

Phosphor converted LEDs will widely penetrate the lighting market!

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