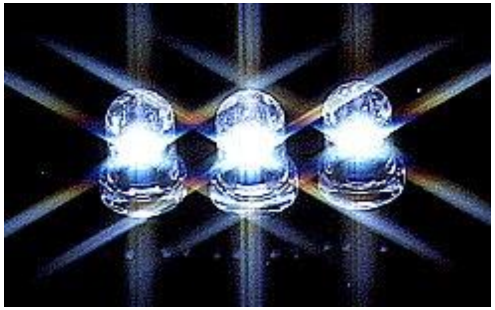
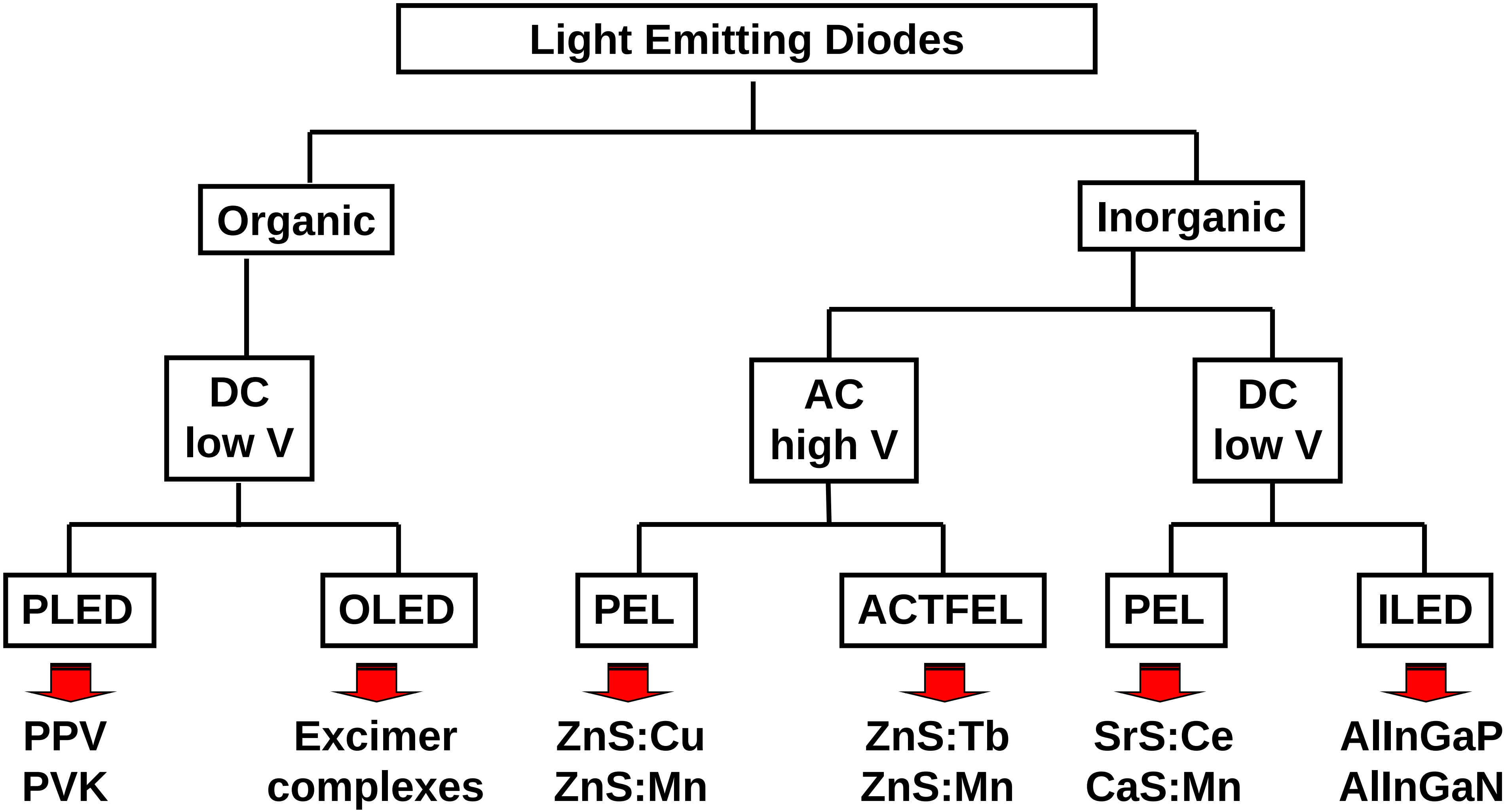
9. Inorganic LEDs

Content



9.1 Classification of LEDs



- Light Emitting Diodes
  - Organic
    - DC low V
      - PLED → PPV, PVK
      - OLED → Excimer complexes
  - Inorganic
    - AC high V
      - PEL → ZnS:Cu, ZnS:Mn
      - ACTFEL → ZnS:Tb, ZnS:Mn
    - DC low V
      - PEL → SrS:Ce, CaS:Mn
      - ILED → AlInGaP, AlInGaN

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

9.2 Evolution of LED Light Sources

A short history of LED

Shuji Nakamura

Destriau discovered indirect EL

Biard&Pittman discovered direct EL (first LED)

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

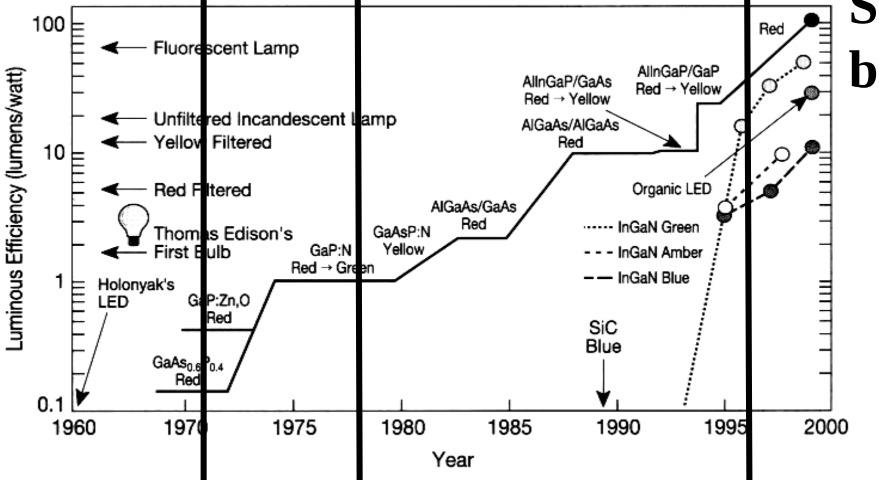
Friend&Burroughes invented PLED

S. Nakamura developed (In,Ga)N blue LED technology

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

5 W LED

White LED with 200 lm/W



1936 1961 1962 1990 1993 1999 2002 2010

Year

9.2 Evolution of LED Light Sources

Development of luminous efficiency and lumen output

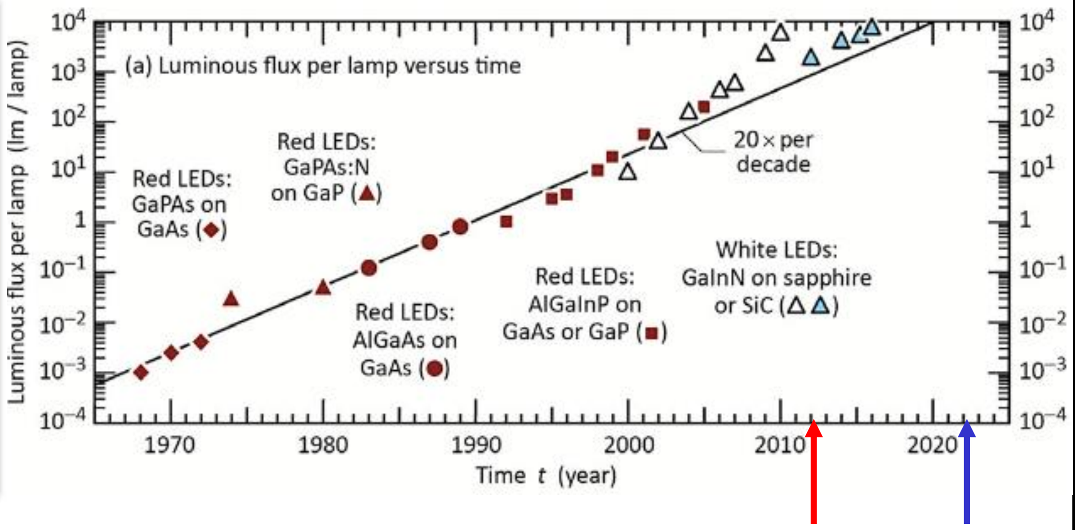
Luminous efficacy [lm/W]

Luminous flux per LED [lm]

BREAKING BARRIERS

Cree leads the industry in LED efficacy and innovation. We were the first company to hit these industry-leading performance milestones and we're not stopping!

Year



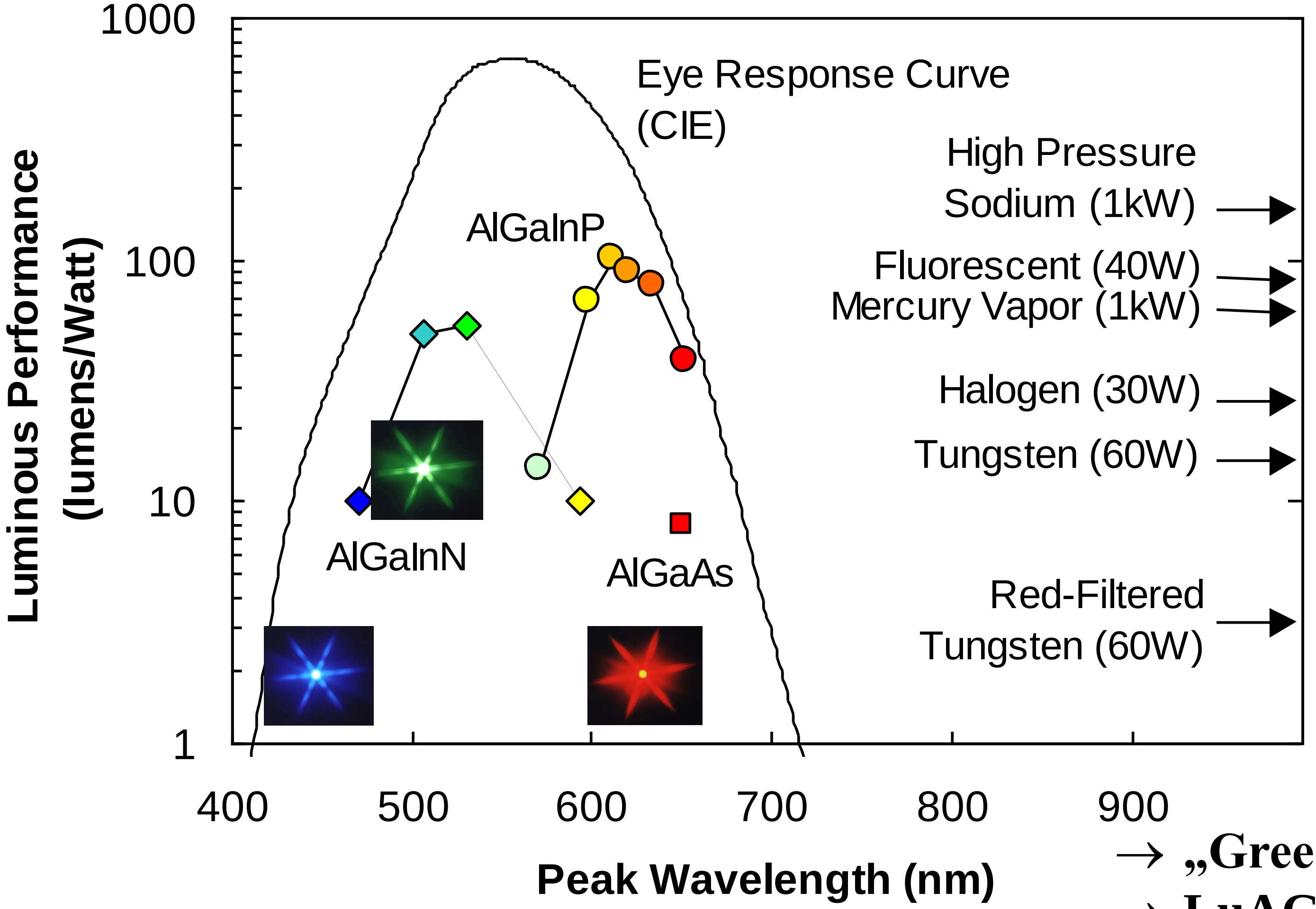
LEDs became more efficient than incandescent and fluorescent lamps

2012: LEDs > 1000 lm on the market

2022: LEDs with > 10000 lm commercially available

9.2 Evolution of LED Light Sources

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

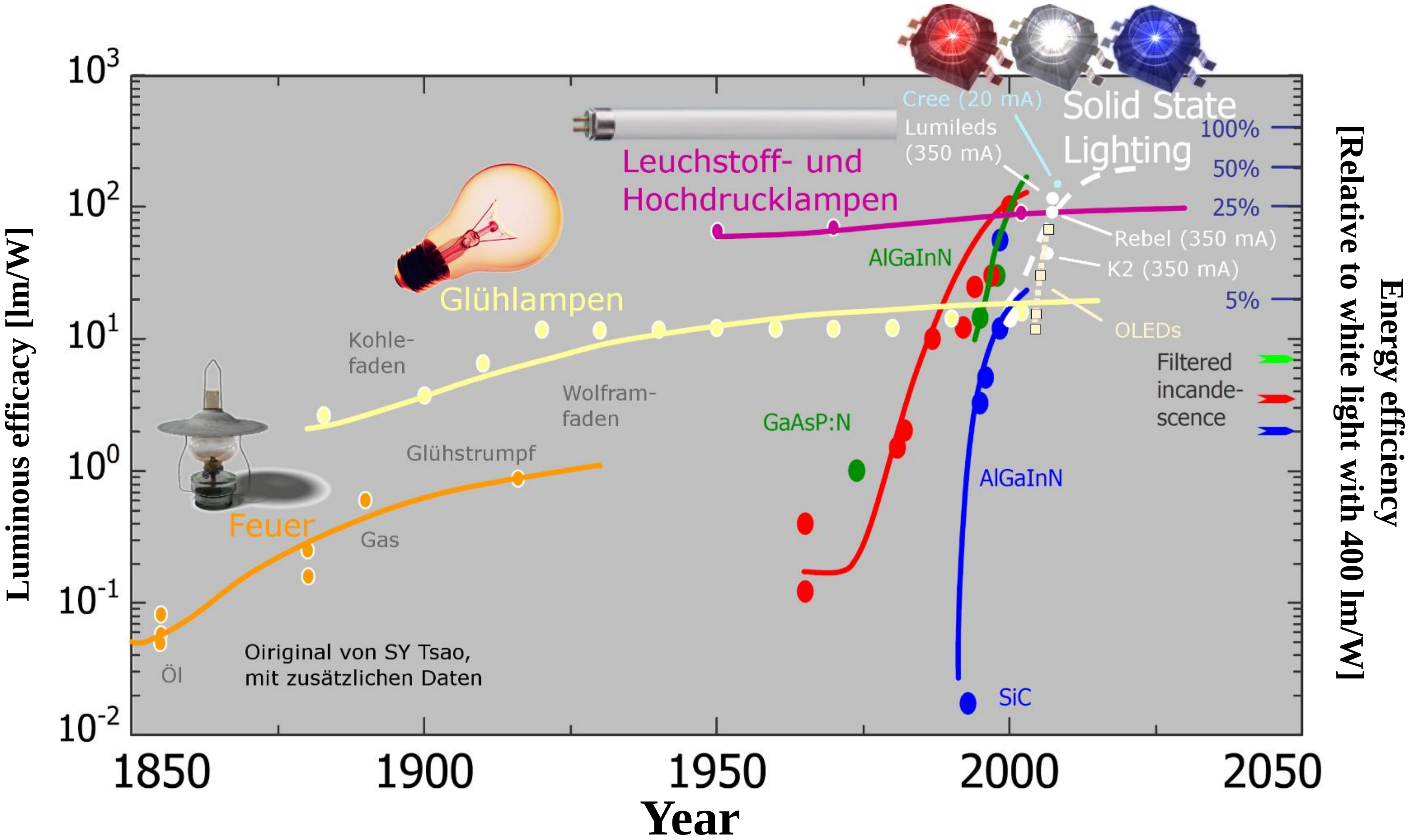


→ „Green/Yellow Gap“

→ LuAG:Ce/YAG:Ce

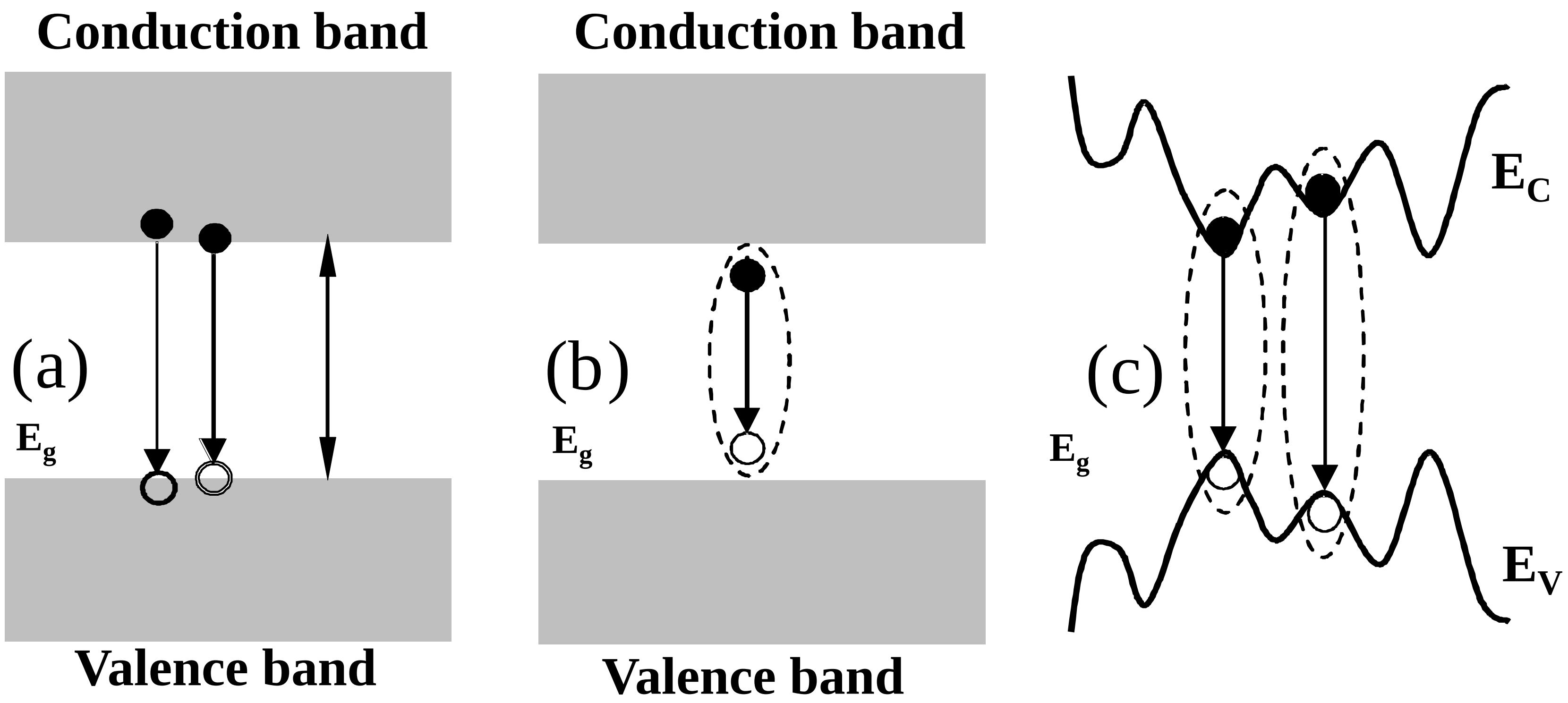
9.2 Evolution of LED Light Sources

Development of Luminous Efficacy and Energy Efficiency from Y1850 to Y2030



9.3 Generation of Light in Semiconductor LEDs

Electroluminescence: Recombination of electrons and holes



Intrinsic radiative transitions in semiconductors

(a) Band-to-band transitions

(b) Free-exciton annihilation

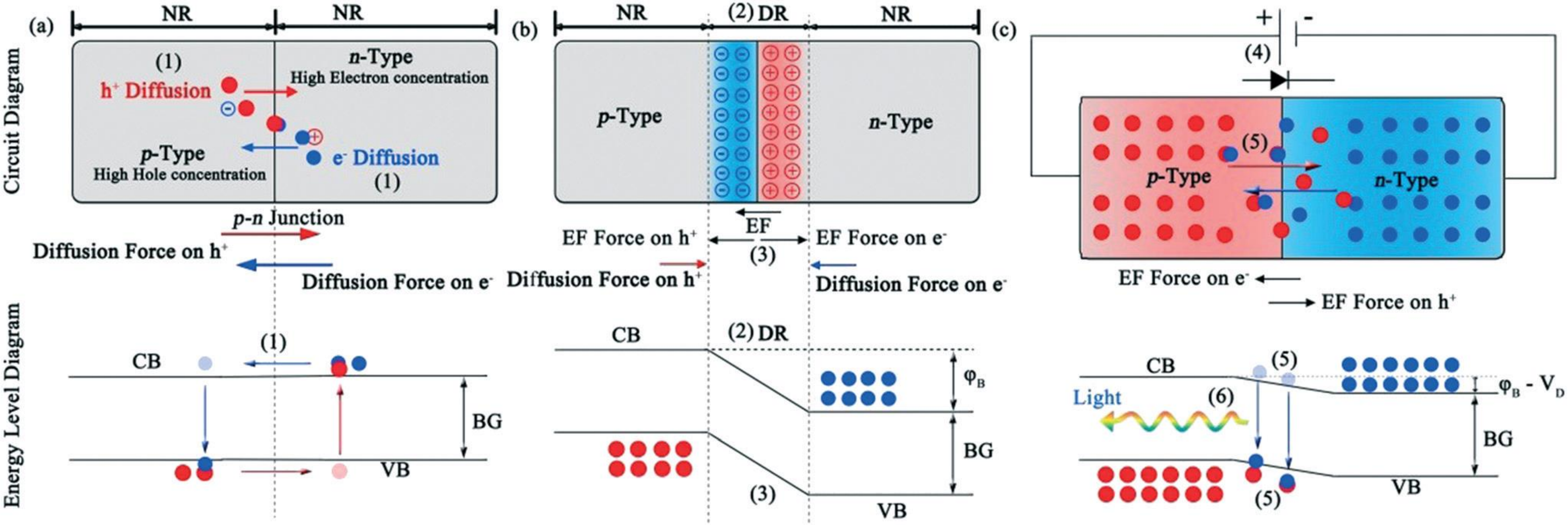
(c) Recombination of localized excitons caused by potential fluctuations (MQWs)

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 ⇒ Energy of emitted photons ~ optical band gap

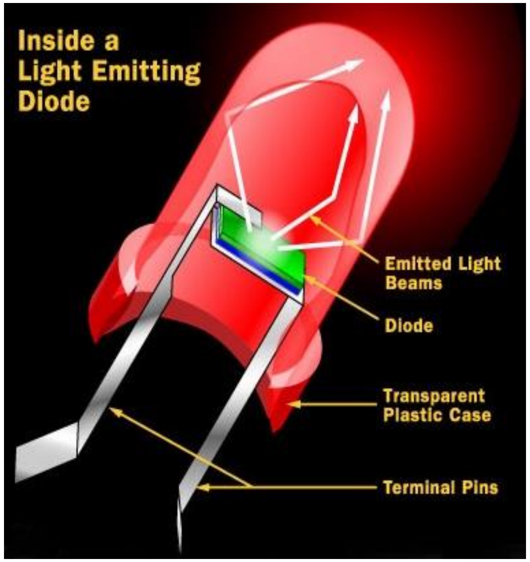
zero bias **forward bias**

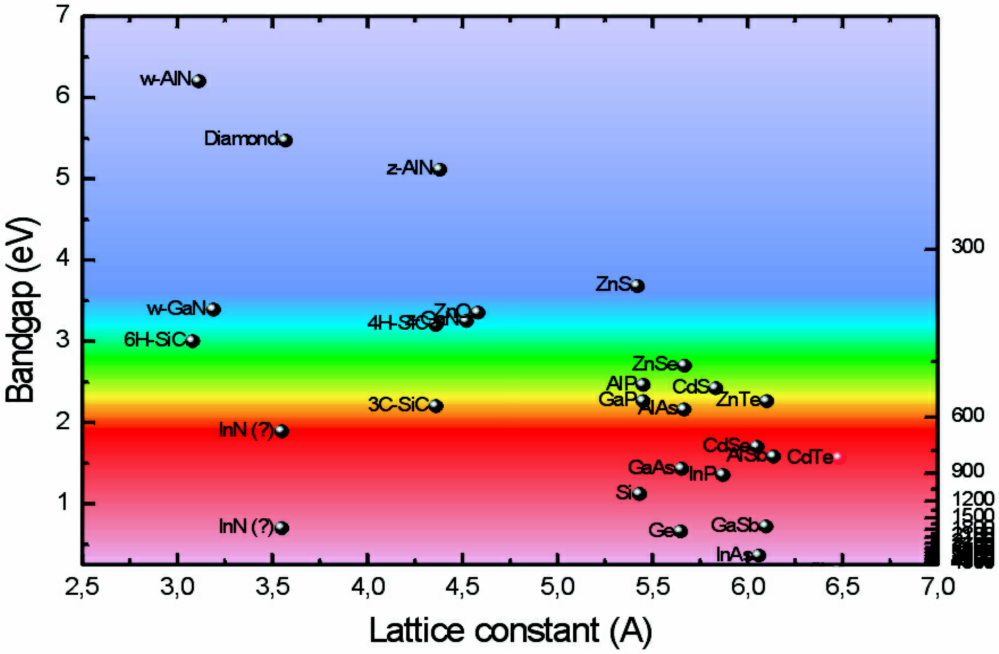


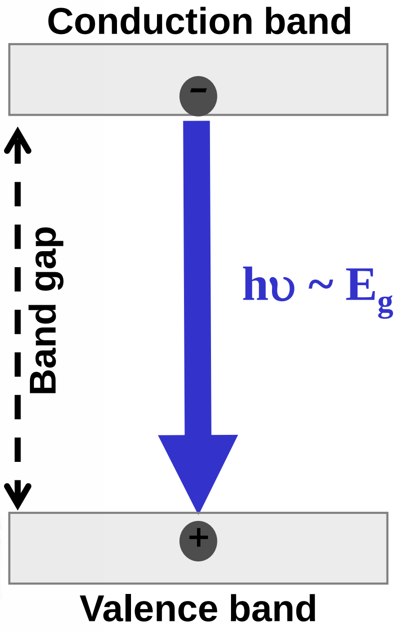
Lit.: LED revolution - Fundamentals and prospects for UV disinfection applications, Environ. Sci. Water Res. Technol. 3 (2017) 188

9.3 Generation of Light in Semiconductor LEDs

“5 mm LEDs” and band gap engineering



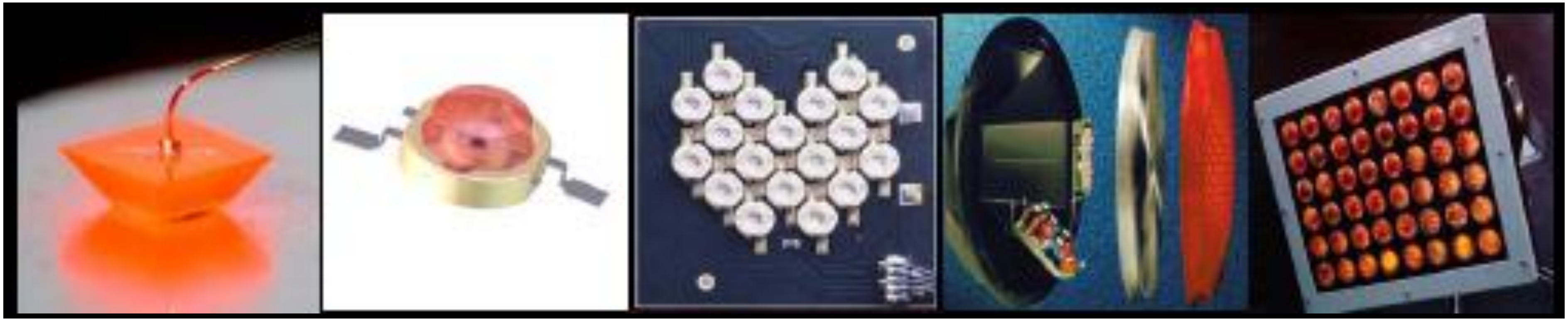




AlN	6.2 eV	(200 nm)	AlP	2.5 eV	(500 nm)
GaN	3.5 eV	(370 nm)	GaP	2.3 eV	(520 nm)
InN	1.9 eV	(650 nm)	InP	1.4 eV	(900 nm)

9.3 Generation of Light in Semiconductor LEDs

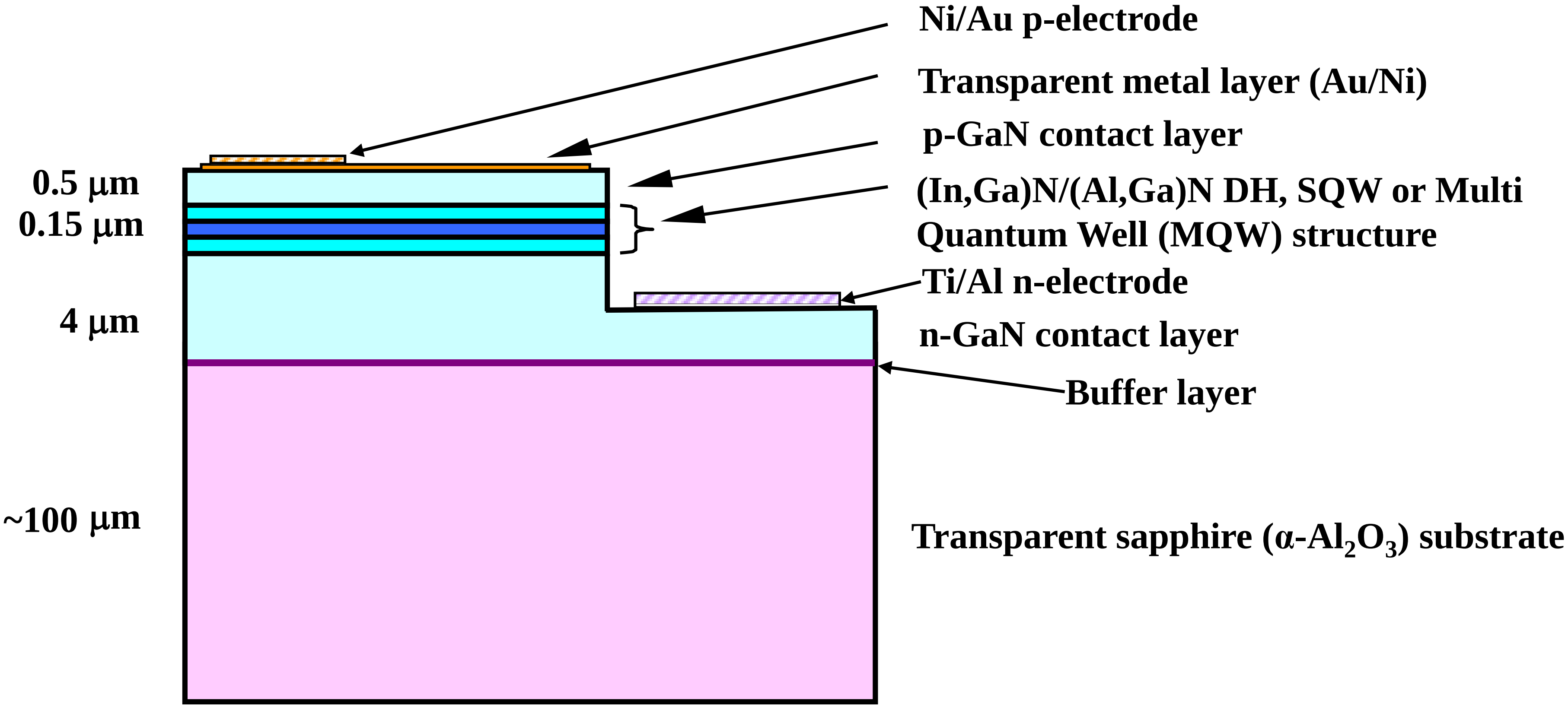
LED Light source build-up by the manufacturing levels



Level 0	Level 1	Level 2	Level 3	Level 4
Semiconductor	+ Primary optics + Contacts + Cooling body	+ circuit board	+ Secondary optics + Driver	+ Frame + Holder + „Design“
LED-Chip	LED-Lamp	LED-Modul	LED-System	LED-Luminaire
“wire”	“bulb”	“bulb array”	“array + driver”	“luminaire”

9.4 Chip Structure of (Al,In,Ga)N/Al_2O_3 LEDs

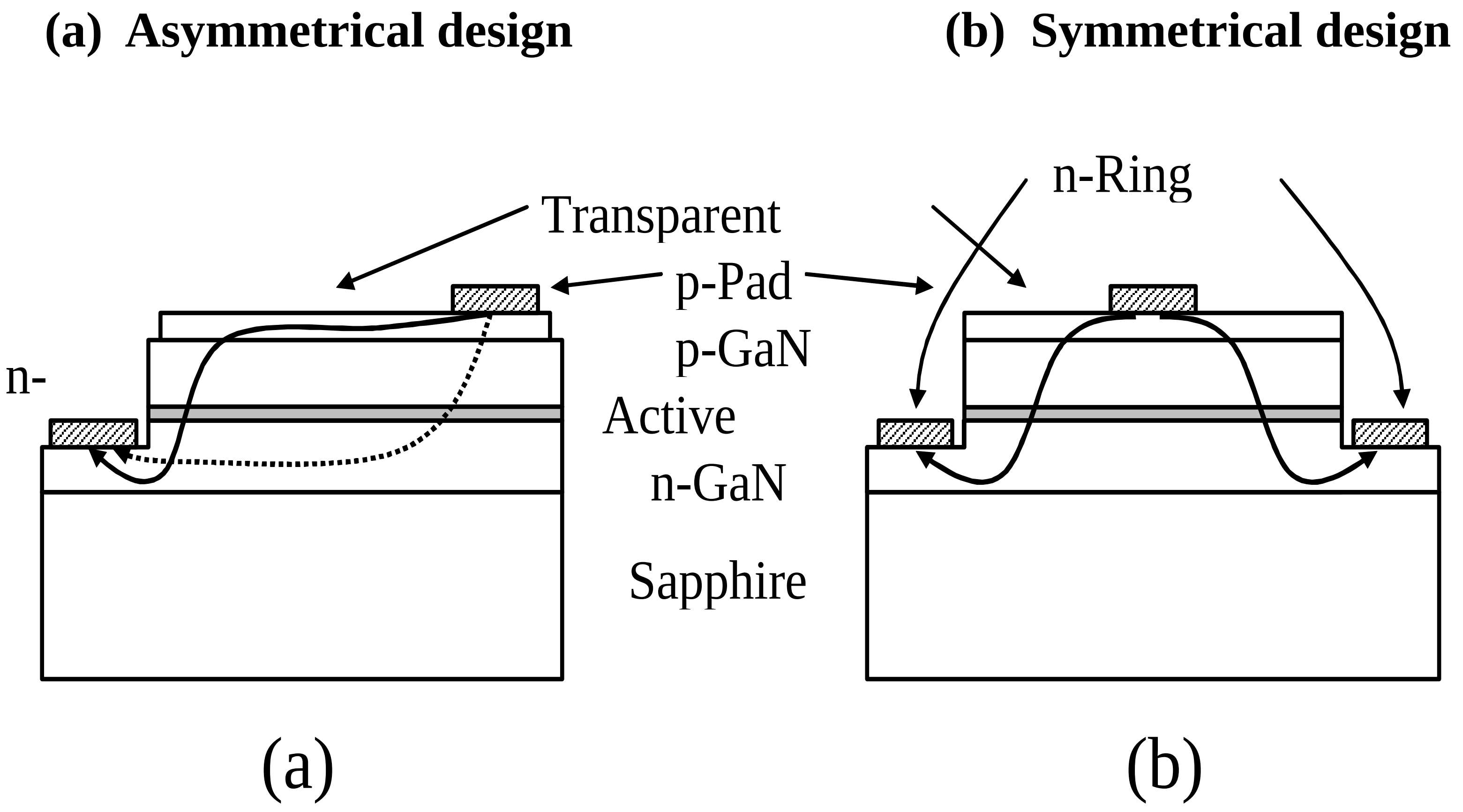
Structure of a semiconductor LED chip



Lit.: S. Nakamura and G. Fasol, The Blue Laser Diode: GaN Based Light Emitters and Lasers, Springer, Berlin, 1997

9.4 Chip Structure of (Al,In,Ga)N/Al_2O_3 LEDs

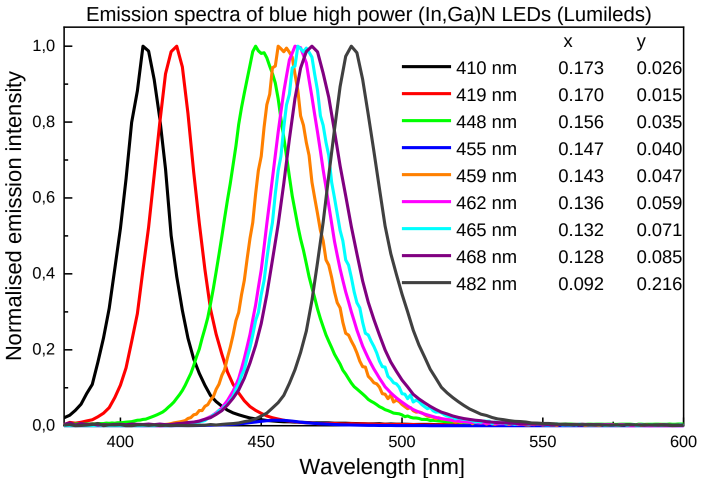
Current paths in (Al,In,Ga)N LEDs on sapphire

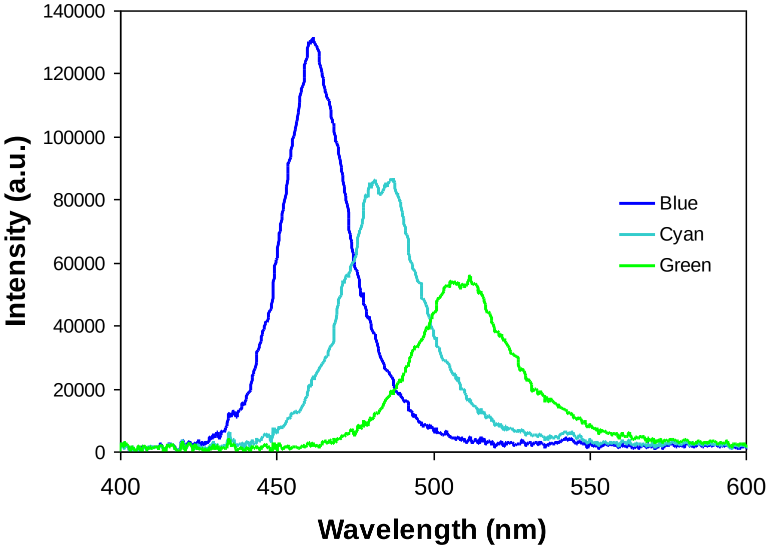


Lit.: M.R. Krames et al., Proc. SPIE 3938, 2, 2000

9.5 Spectra of LEDs

(In,Ga)N LEDs - Spectra





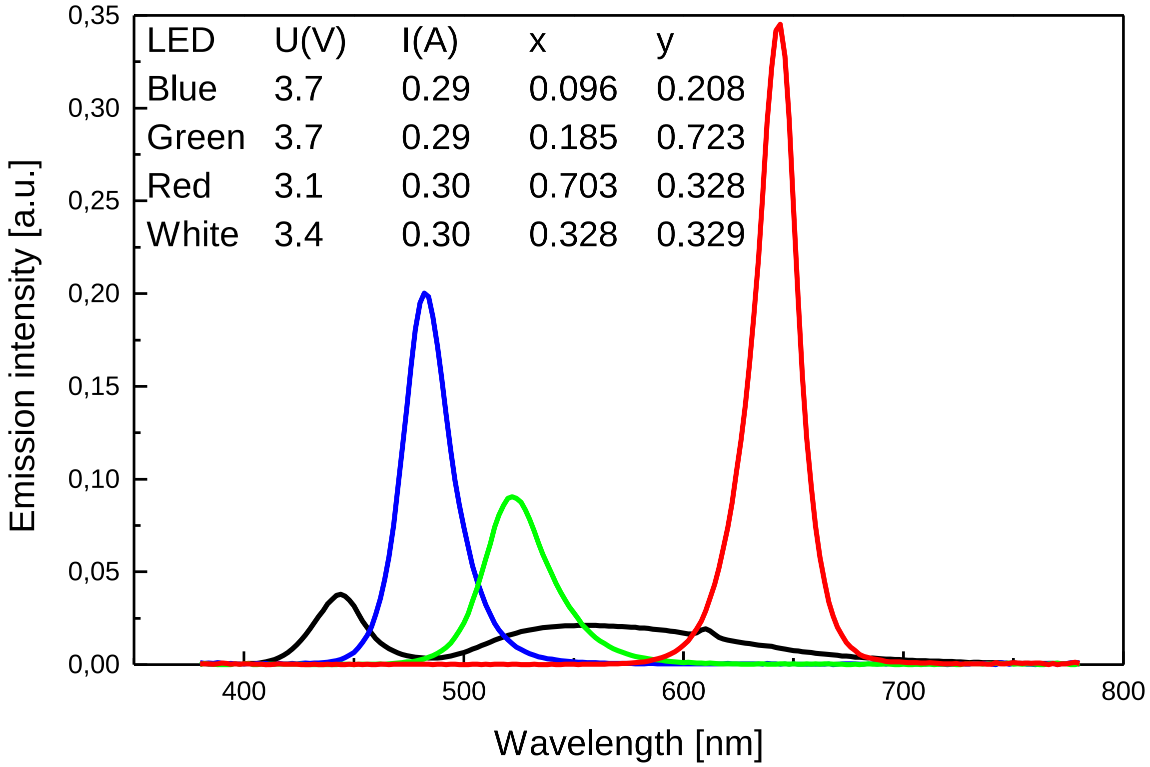
(In,Ga)N yield a complete solid solution series without a miscibility gap

Effect of the increasing In^{3+} concentration

- **Energy of the (In,Ga)N quantum well transition decreases**
- **Emission band broadens**
- **Decrease in quantum yield due to increase of defect density**
- **Increase in thermal quenching**
- **Loss of color consistency**

9.5 Spectra of LEDs

High Brightness LEDs (HB LEDs)



LED	U(V)	I(A)	x	y
Blue	3.7	0.29	0.096	0.208
Green	3.7	0.29	0.185	0.723
Red	3.1	0.30	0.703	0.328
White	3.4	0.30	0.328	0.329

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

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

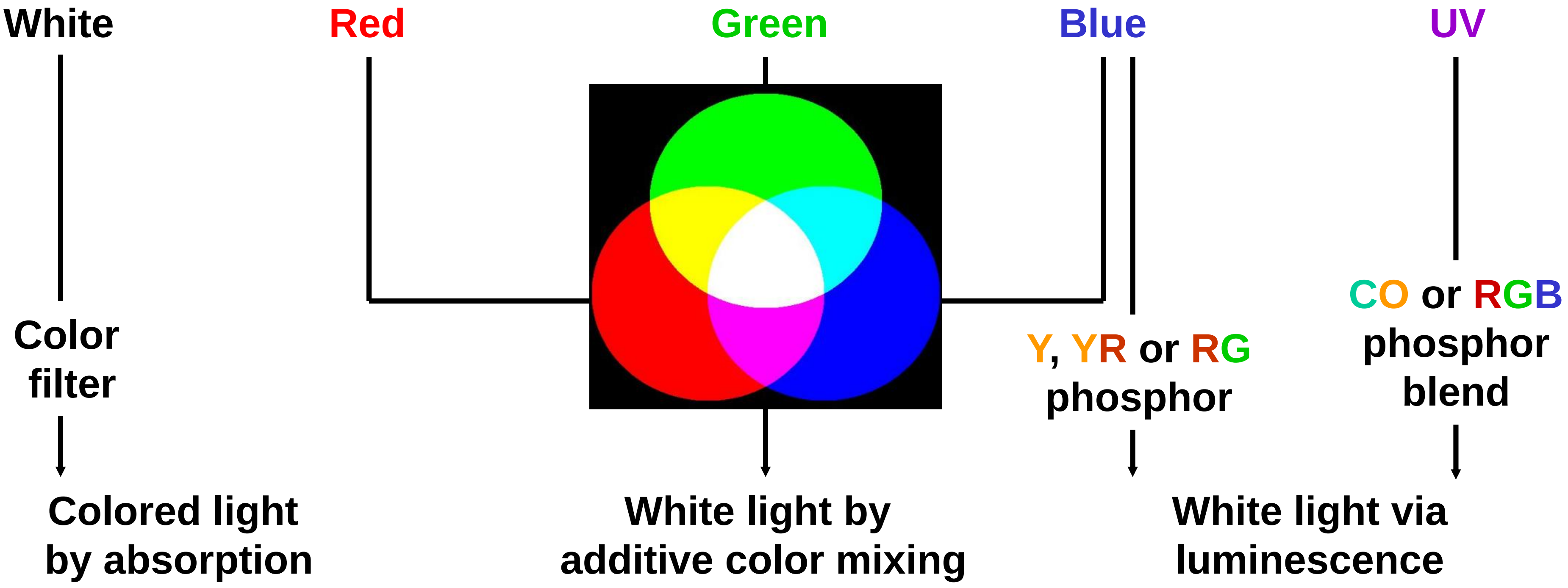
LEDs are a "platform" for many lighting products

Power input	Voltage	Amperage	Chip temperature
1 W (2000)	4.5 V	0.2 A	~120 °C
5 W (2002)	4.5 V	1.1 A	>150 °C

9.6 Concepts of White Light Production

By additive color mixing

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



White → **Color filter** → **Colored light by absorption**

Red, **Green**, **Blue** → **White light by additive color mixing**

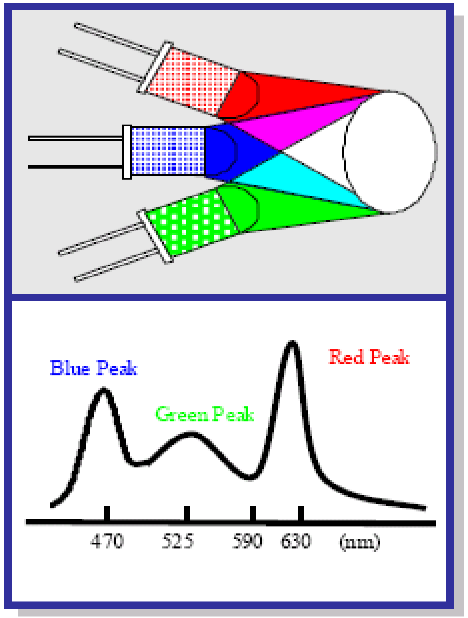
Blue → **Y, YR or RG phosphor** → **White light via luminescence**

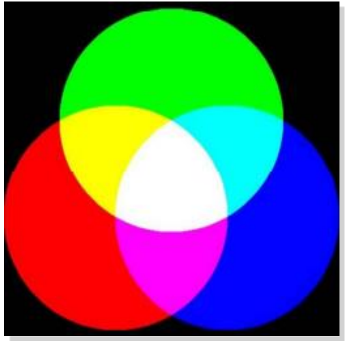
UV → **CO or RGB phosphor blend** → **White light via luminescence**

9.6 Concepts of White Light Production

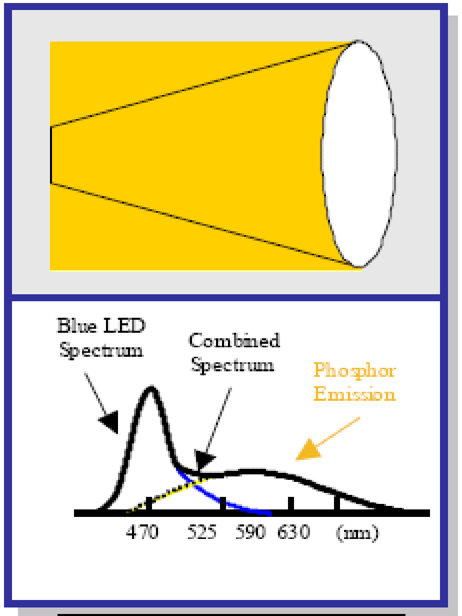
Overview: White light by LEDs

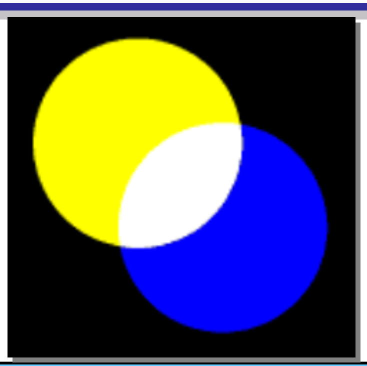
Red + Green + Blue LEDs



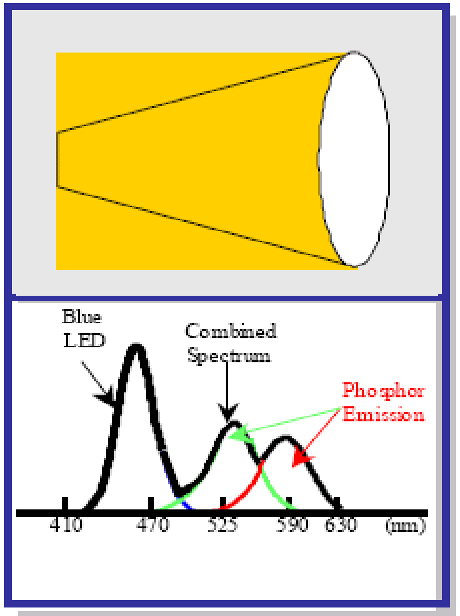


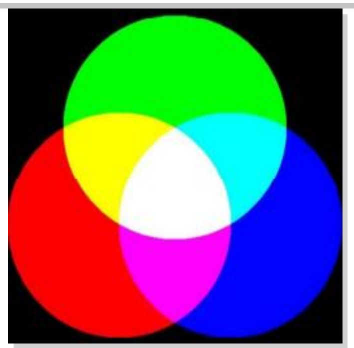
Blue LED + yellow phosphor



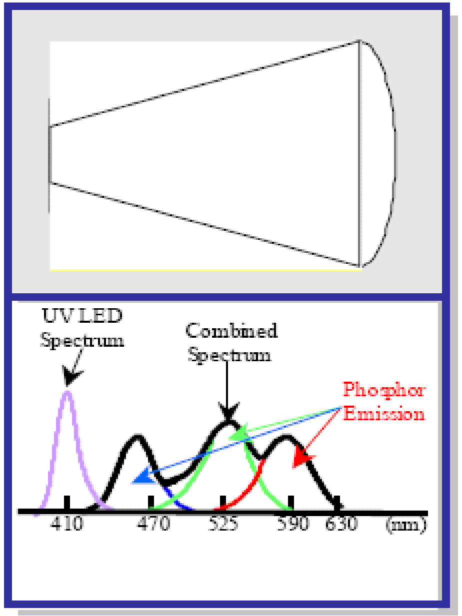


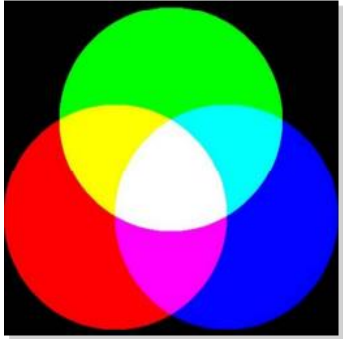
Blue LED + RG phosphor blend





UV LED + RGB phosphor blend

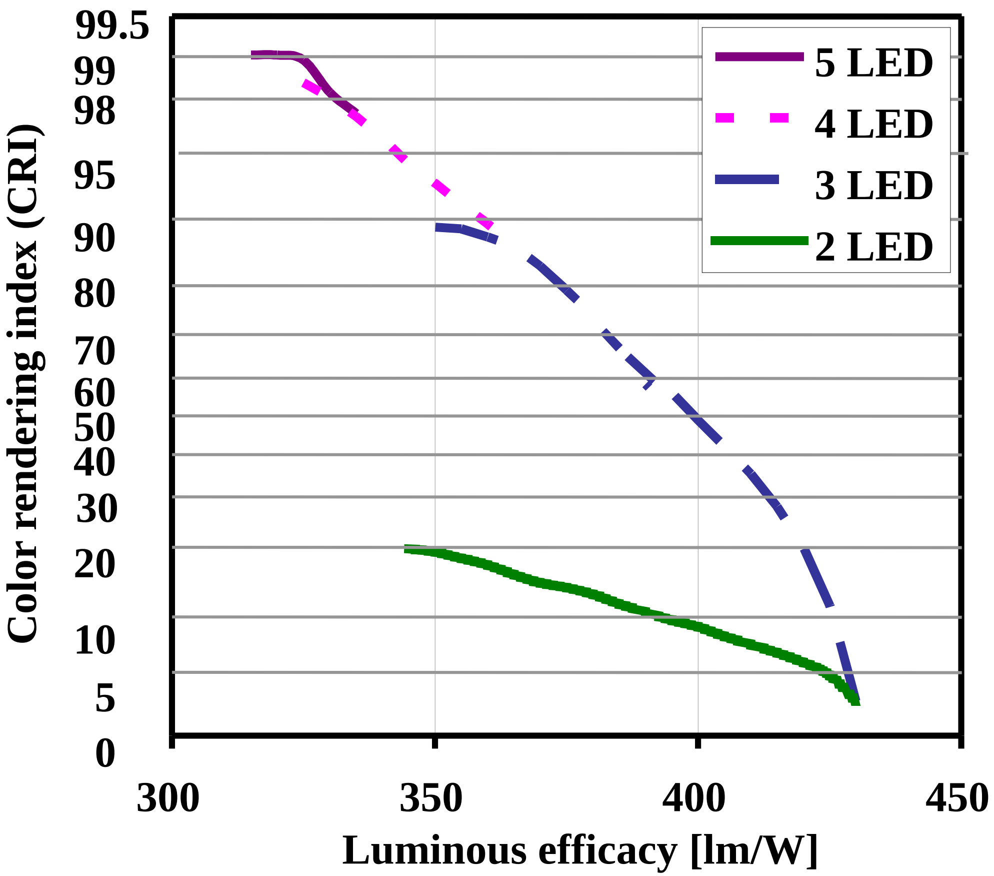




9.6 Concepts of White Light Production

White light by multichip LED Lamps

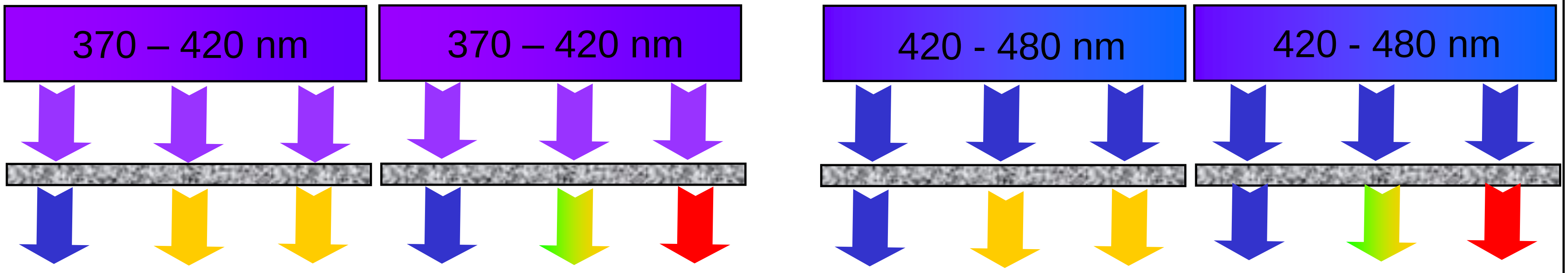
- Narrow band emitter e.g. LEDs
  - $\lambda_{½}$ = 30 nm
  - Several colored LEDs
- Theoretical maximum
  - 430 lm/W for
  - CCT = 4870 K
  - CRI = 3 (!)
- Feasible values
  - ~ 350 lm/W for CRI 90, n = 3 - 4
  - max. 320 lm/W for CRI 99, n = 5
- Problems
  - Thermal stability of the LEDs
  - LED efficiency
    - Red and blue high
    - Green moderate



Lit.: Zukauskas, A., et. al.., Optimization of white polychromatic semiconductor lamps", Applied Physics Letters 80 (2002) 234-236

9.6 Concepts of White Light Production

White light by near UV or blue LEDs



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

UV light causes polymer degradation and requires security measures

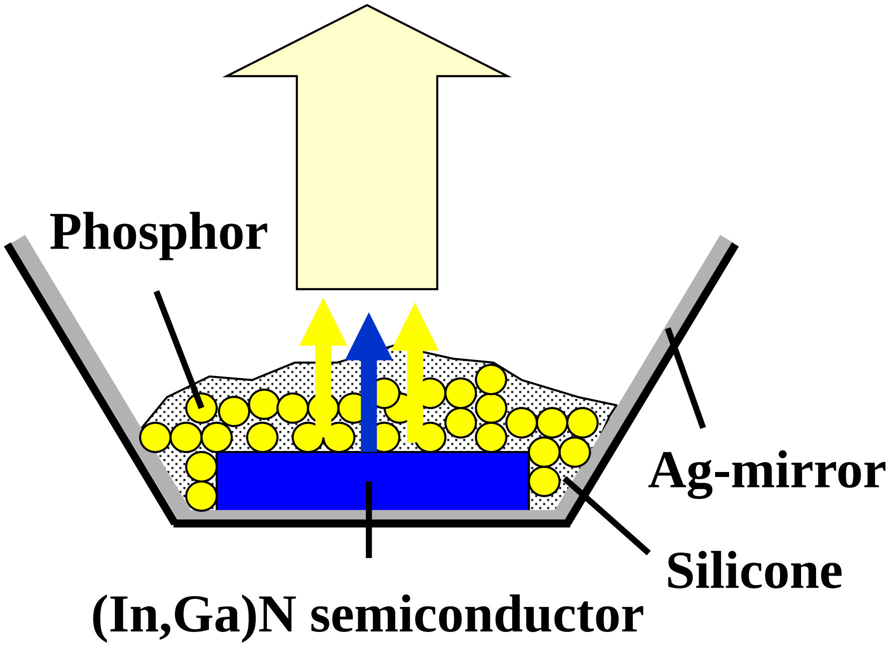
390 nm LED (3.2 eV) → 570 nm (2.2 eV)
Quantum deficit = 0.69

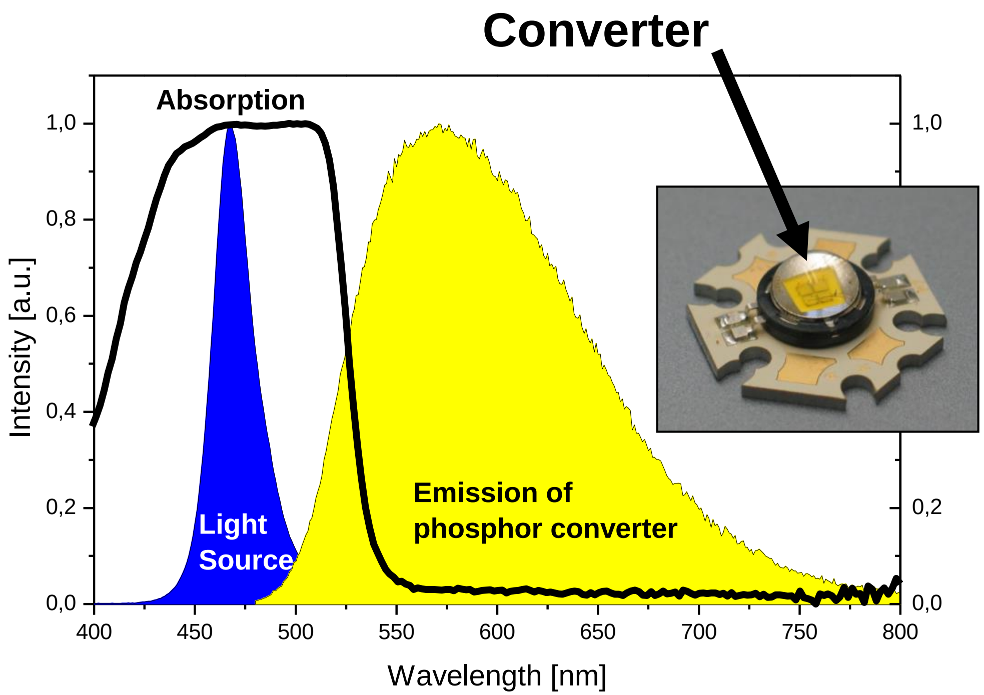
Transmission of blue depends on the optical path length through the phosphor layer
Color point = f(viewing angle)

460 nm LED (2.7 eV) → 570 nm (2.2 eV)
Quantum deficit = 0.78

9.7 Phosphor Converted LEDs (pcLEDs)

White light by blue LEDs





Blue LED chip: **420 – 480 nm emitting (In,Ga)N LED**

Phosphor layer:

Phosphor layer:	**(1) Yellow**	**$T_c > 4000$ K „cool white“**
	(2) Yellow + red	**$T_c < 4000$ K „warm white“**
	(3) Green + red	**$2000\text{ K} < T_c < 8000\text{ K}$**
	(4) Red	**magenta colors**

9.8 Requirements on LED Phosphors

General

- Strong absorption at the emission wavelength of the semiconductor-LED
  → spin-and parity-allowed transitions, e.g. $4f^n – 4f^{n-1}5d^1$
- Quantum yield > 90%
- Stability with respect to O_2, CO_2, NH_3, and H_2O
- Stability at high excitation density (100 - 200 W/cm^2)
- Compatibility with the LED production process
- Environmentally compliable

Blue + yellow (1st approach)

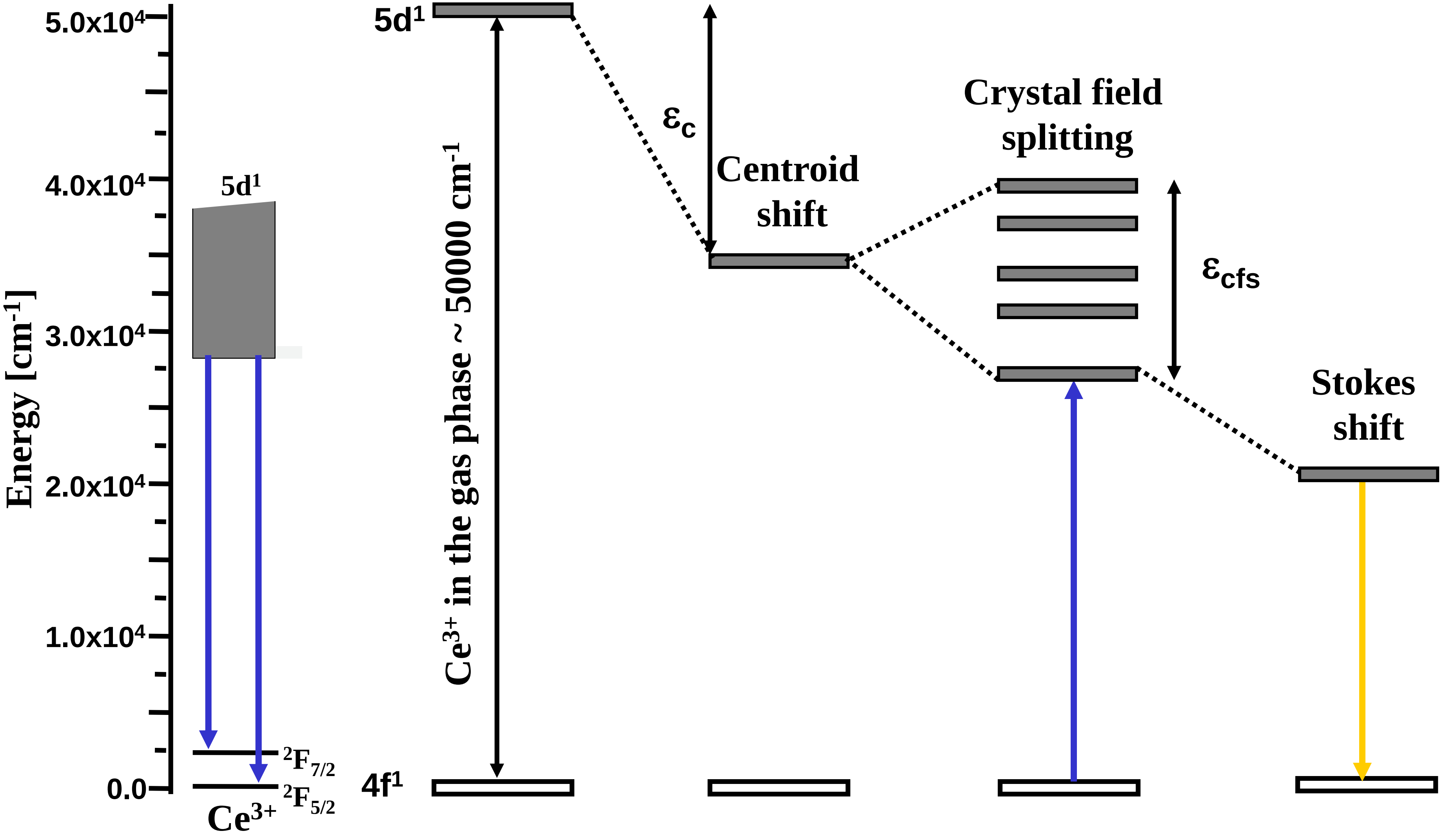
- Broad emission band between 560 - 580 nm
  → Ce^{3+}- phosphors (splitting of the ground state $^2F_{5/2}$ + $^2F_{7/2}$)

Blue + green/yellow + red (2nd and 3rd 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]$4f^1$)



9.9 Ce^{3+} Phosphors

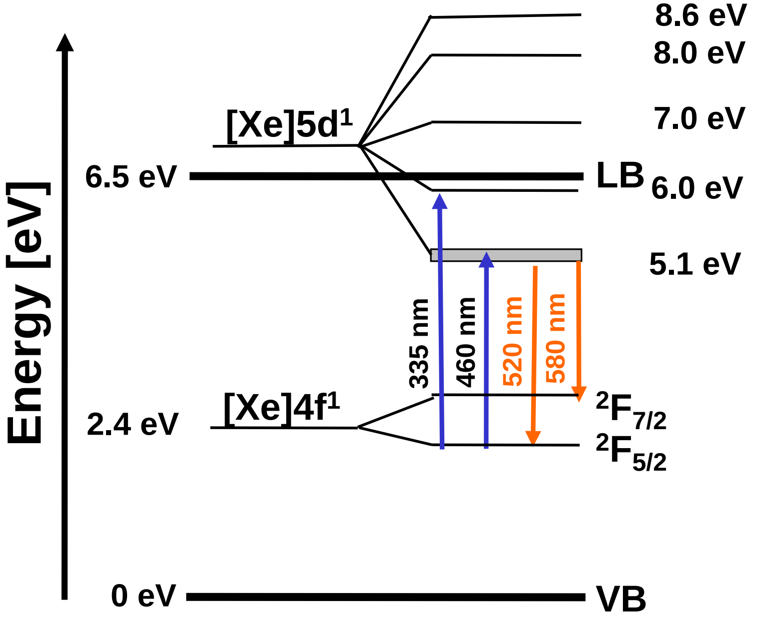
Established materials

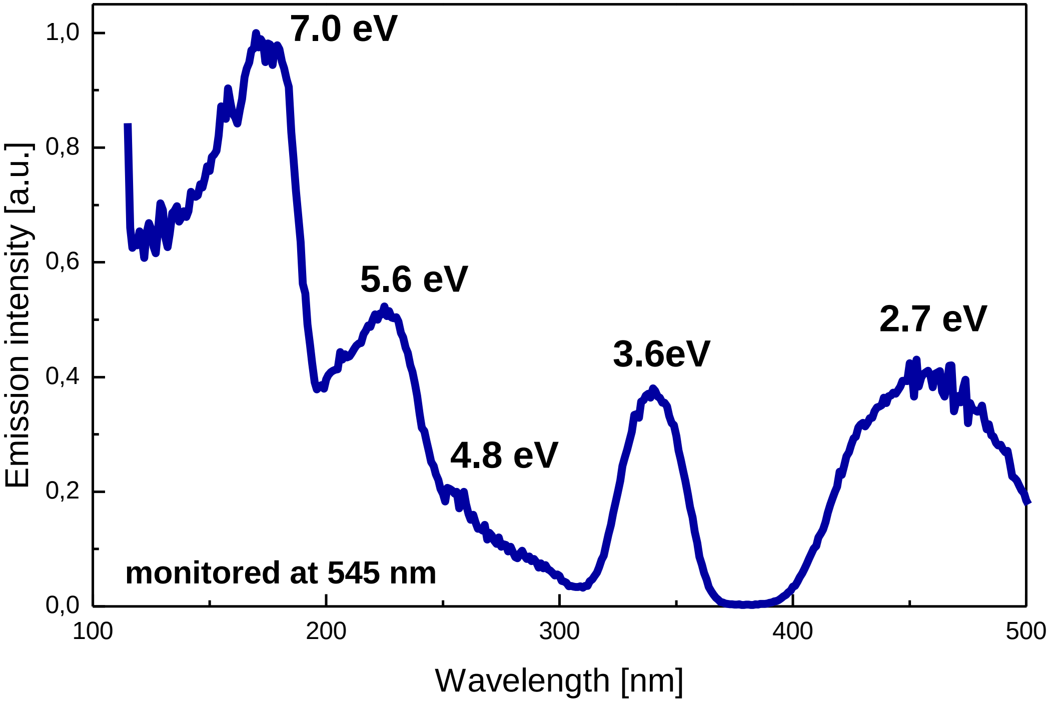
Host matrix	λ_{abs} [nm]	λ_{em} [nm]	ε_{cfs} [cm^{-1}]	ε_{c} [cm^{-1}]
$SrAl_{12}O_{19}$	224, 235, 244, 252, 261	290, 315	6300	10000
$LaPO_4$	203, 225, 238, 250, 323	320, 335	11900	8700
$LaMgAl_{11}O_{19}$	220, 232, 243, 255, 270	345	8400	10000
YPO_4	203, 225, 238, 250, 323	335, 355	18000	9600
$YAlO_3$	219, 237, 275, 291, 303	370	12700	12900
$LuAlO_3$	216, 230, 275, 292, 308	370	12650	13800
$LaMgB_5O_{10}$	202, 225, 239, 257, 272	385, 410	9000	12700
YBO_3	219, 245, 338, 357	390, 415	17600	13300
Lu_2SiO_5	205, 215, 267, 296, 356	405, 420	20700	12300
$Lu_3Al_5O_{12}$	205, 225, 265, 350, 445	525, 540		
$Y_3Al_5O_{12}$	205, 225, 261, 340, 458	545, 555	27000	14700

Lit.: P. Dorenbos, J. Luminescence 99 (2002) 283

9.9 Ce^{3+} Phosphors

Energy levels and excitation spectrum of Ce^{3+} in $Y_3Al_5O_{12}$

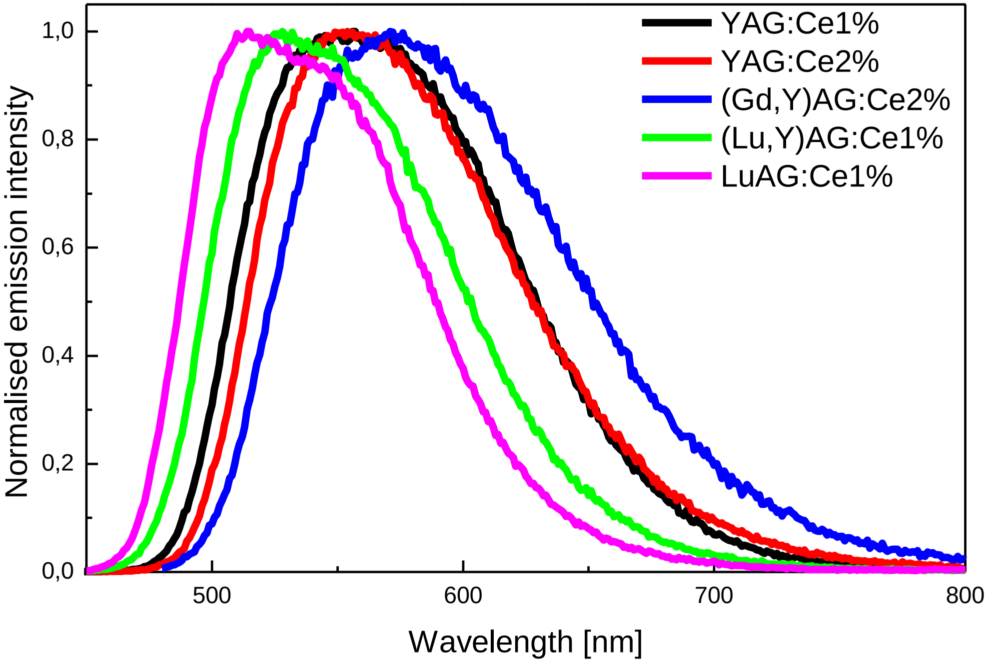


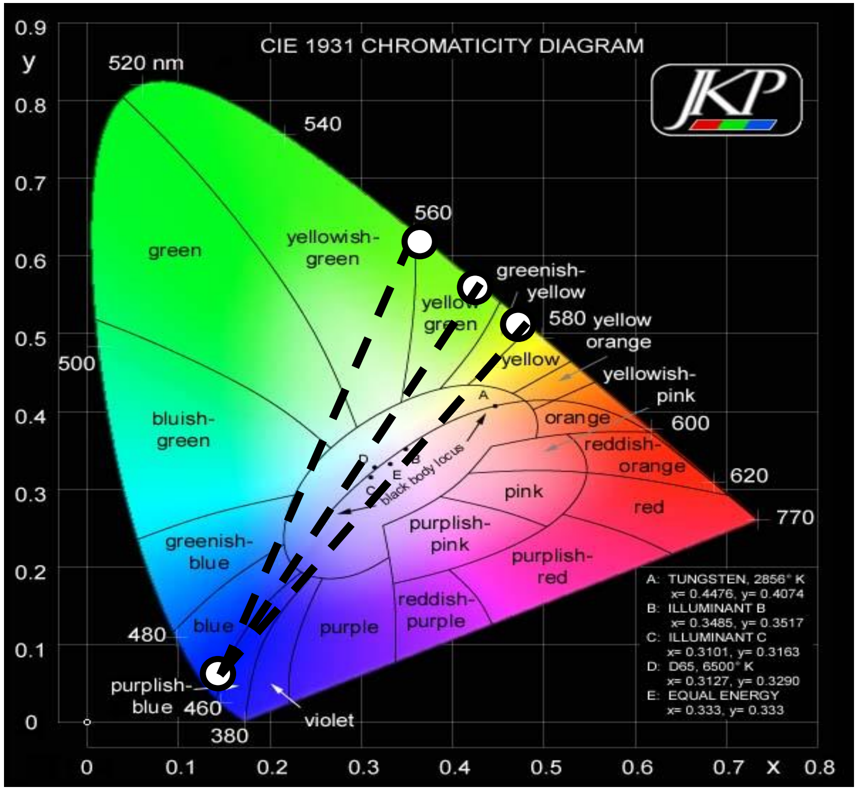


Lit.: M. Batenschuk et al., MRS Symp. Proc. 560 (1999) 215

9.9 Ce^{3+} Phosphors

$Ln_3Me_5O_{12}$:Ce - emission spectra and color points



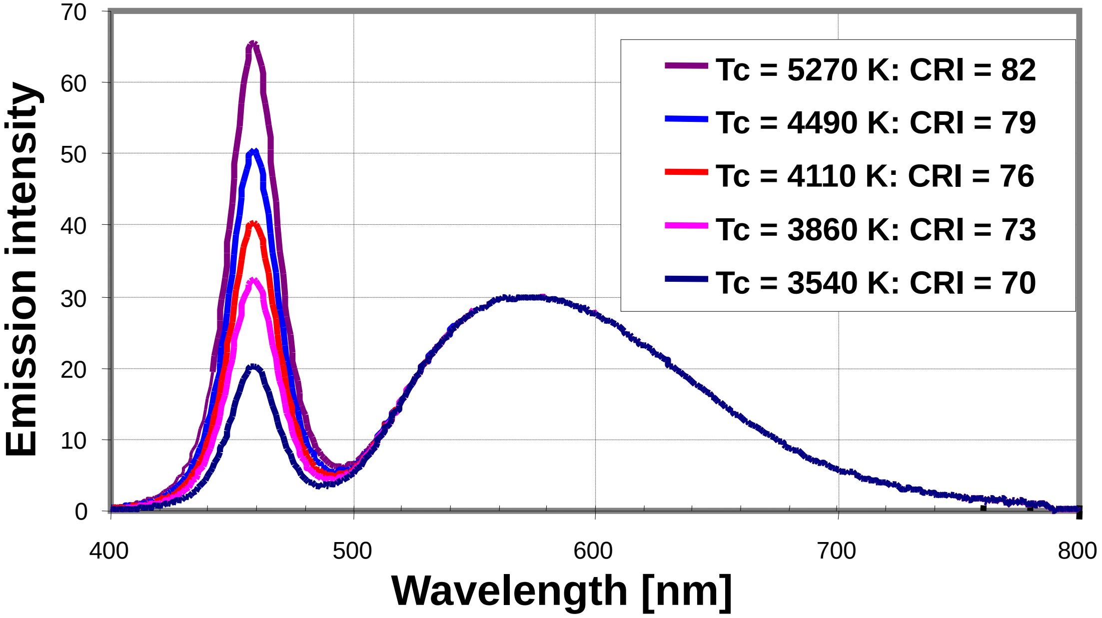


Garnet structure $Ln_3Me_5O_{12}$

- **Ln = Y, Ce, Gd, Tb, Lu dodecahedral**
- **Me = Al, Ga tetrahedral (3), Al, Ga, Sc octahedral (2)**
- **Substitution of Y by Gd, Tb or increasing the Ce^{3+}-content ⇒ Red shift**
- **Substitution of Y by Lu or Al by Sc or Ga ⇒ Blue shift**
- **Substitution of Y by Ca and Al by Zr or Hf ⇒ Blue shift**

9.10 White pcLEDs

Blue (In,Ga)N chip + $(Y,Gd)_3Al_5O_{12}$:Ce



The first commercially available LEDs are based on this approach (1st)

- **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**

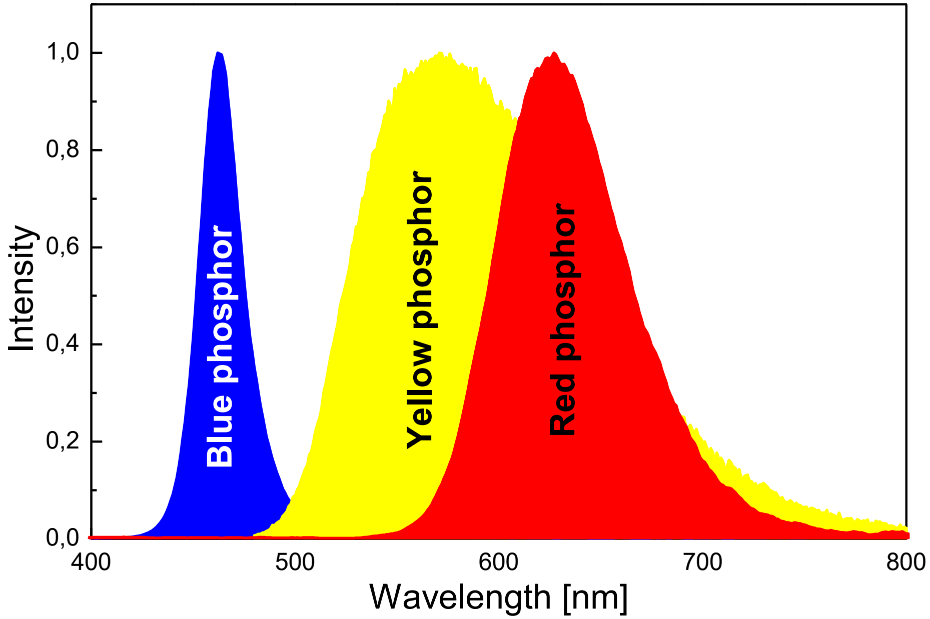
9.10 White pcLEDs

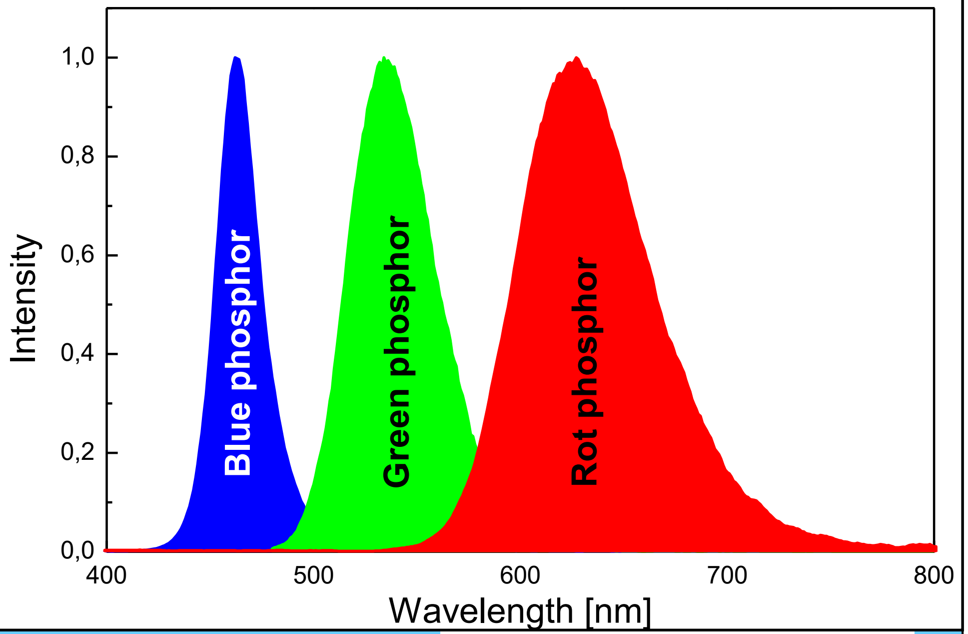
White pcLEDs with high color rendering

(1st) Blue LED + $(Y,Gd)_3Al_5O_{12}$ ⇒ CRI > 75 only for $T_c > 4000$ K

(2nd) Blue LED + $(Y,Gd)_3Al_5O_{12}$ + red ⇒ CRI > 85 for $T_c < 4000$ K

(3rd) Blue LED + green + red ⇒ CRI > 85 for $2700 < T_c < 8000$ K





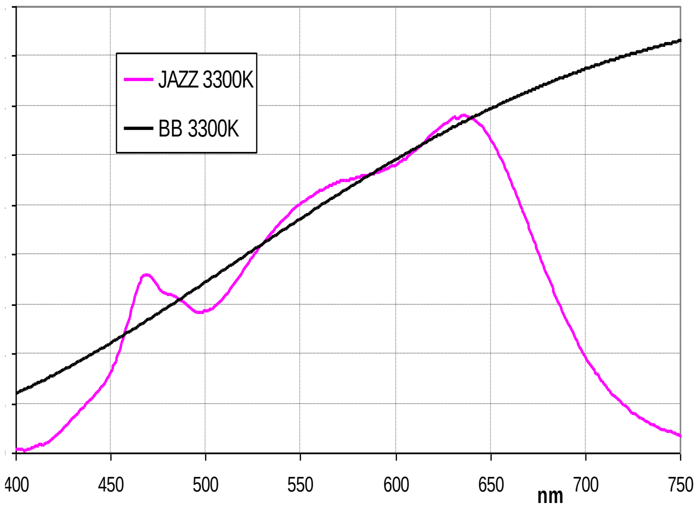
9.10 White pcLEDs

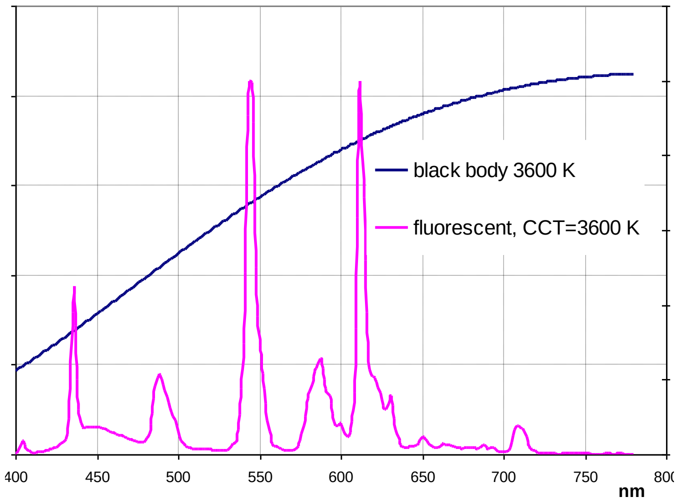
White pcLEDs with high color rendering

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

2^{nd} Approach

- **$(Y,Gd)_3Al_5O_{12}$ + red phosphor**
- **CRI = 85 - 95**
- **T_c = 2800 to 4000 K**
- **1 W LEDs**
- **20 - 25 lm at 350 mA**
- **Reduced luminous flux by 30 – 40%**





9.11 Problems of Ce^{3+}-Phosphors

General properties

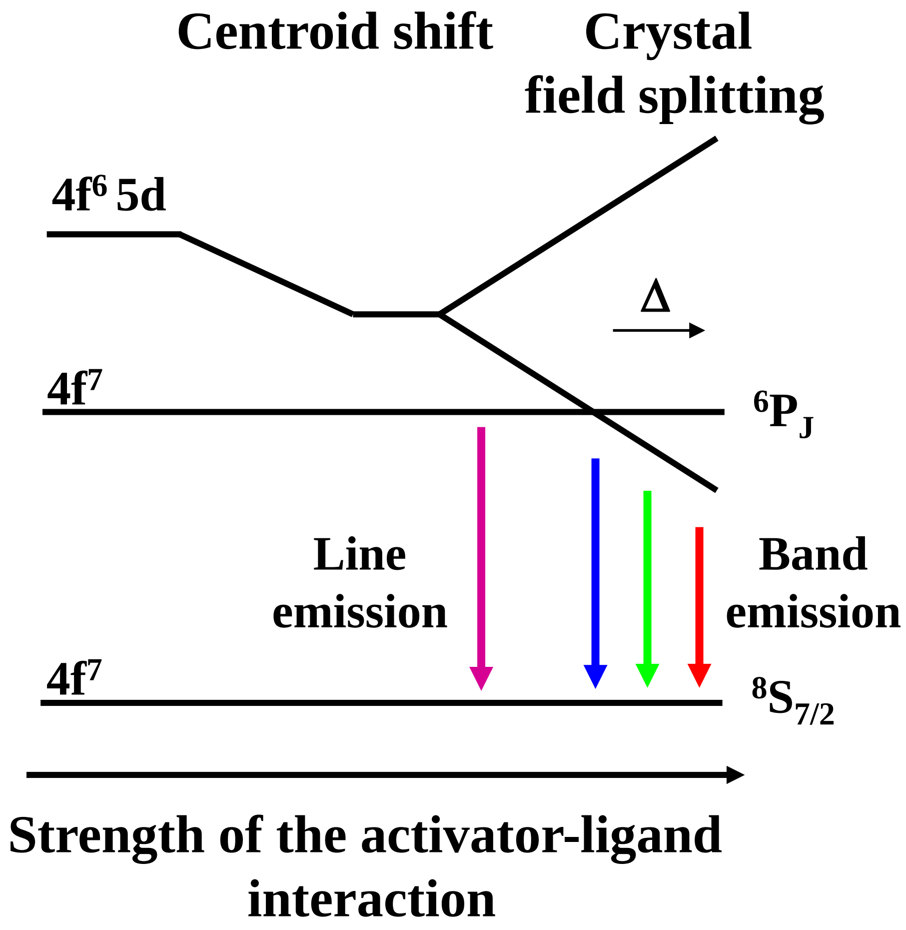
- Relatively narrow absorption bands
- Relatively broad emission band
- Ce^{3+} activated phosphors with red emission and high thermal quenching temperature are not known

Suitable activators for red-emitting phosphors

Activator	Spectral range [nm]	Lumen equivalent [lm/W_{opt}]	Decay time τ	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	moderate	weak
Pr^{3+}	590 - 680	100 – 220	0.1 ms	moderate - 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

9.12 Eu^{2+}-Phosphors

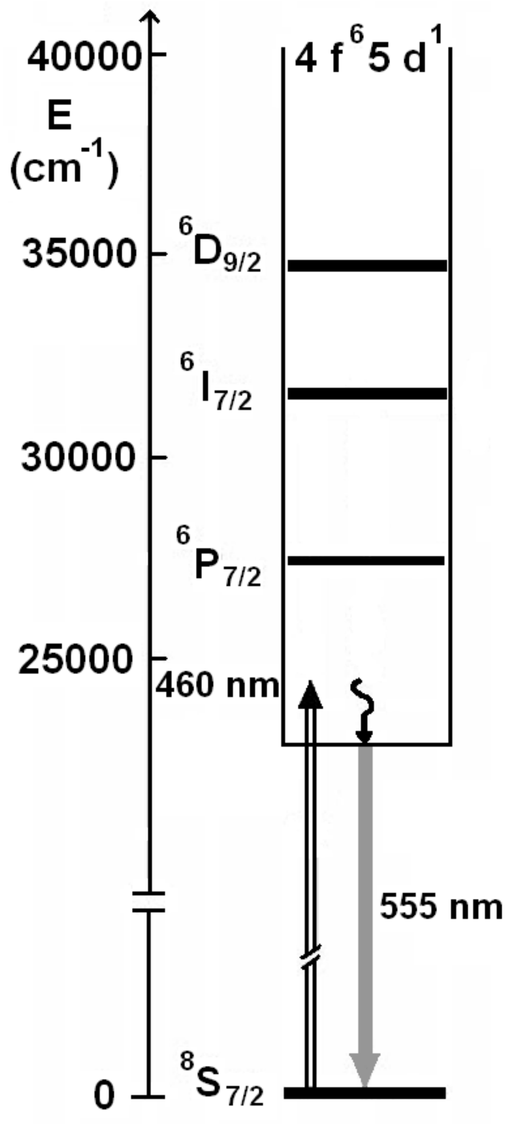
Simplified energy level diagram



Spectral position of the dipole-allowed $5d^14f^6 \rightarrow 4f^7$ emissions-bands is determined by

- *Crystal field splitting* of the 5d levels
- *Centroid shift* reduces the energy gap between the $4f^7$- and $4f^65d^1$-configuration (nephelauxetic effect, spectroscopic polarizibility, covalency)
- *Stokes shift*

9.12 Eu^{2+}-Phosphors



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

9.12 Eu^{2+}-Phosphors

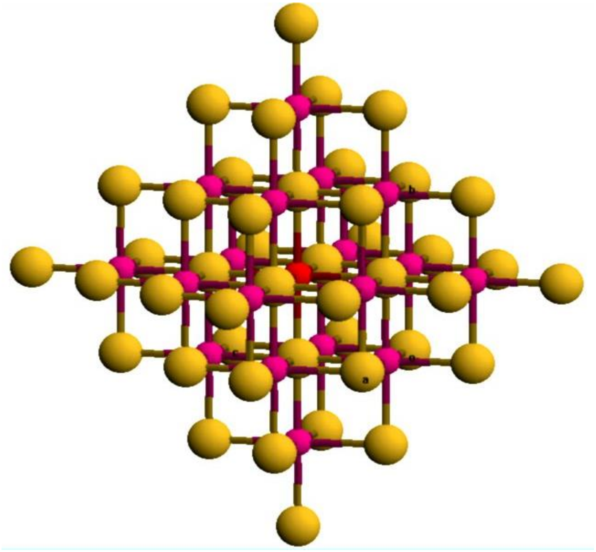
Bonding interaction in MeS:Eu

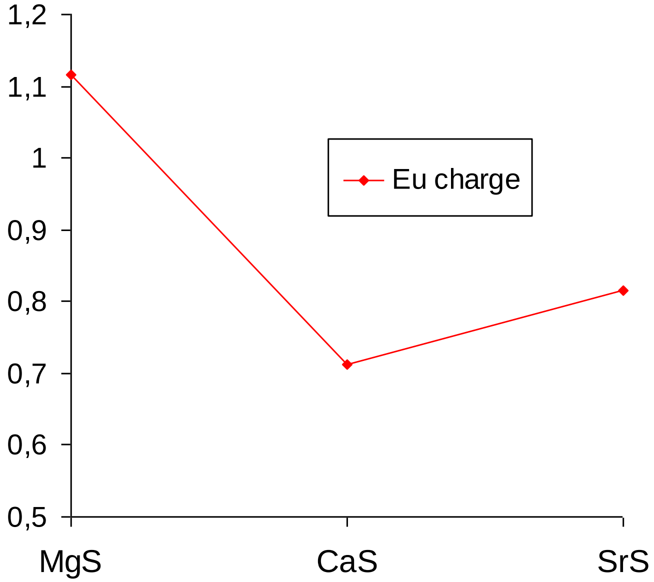
- MgS:Eu $\lambda_{em} = 588$ nm
- CaS:Eu $\lambda_{em} = 651$ nm
- SrS:Eu $\lambda_{em} = 620$ nm

↑ 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

9.13 Warm White pcLEDs

Phosphors for concept (2)

Yellow: 550 – 560 nm

Red: 600 – 620 nm

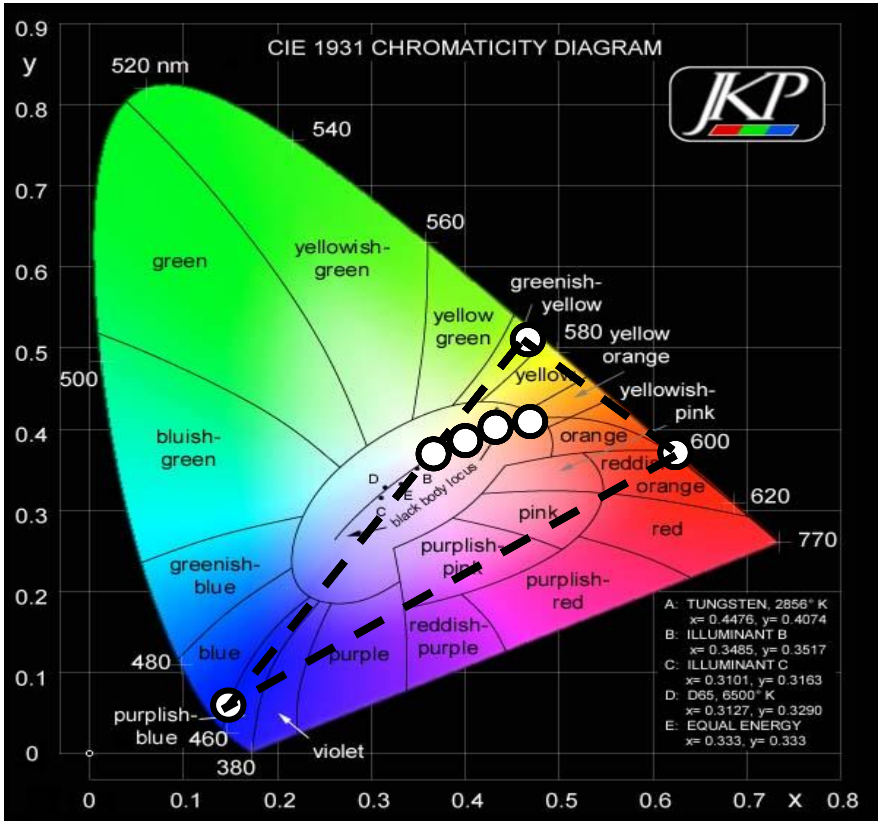
$(Y,Gd)_3Al_5O_{12}$:Ce and $(Ca,Sr)S$:Eu

⇒ CRI > 85 for $T_c < 4000$ K

$(Y,Gd)_3Al_5O_{12}$:Ce and $(Ca,Sr,Ba)_2Si_5N_8$:Eu or $(Ca,Sr)AlSiN_3$:Eu

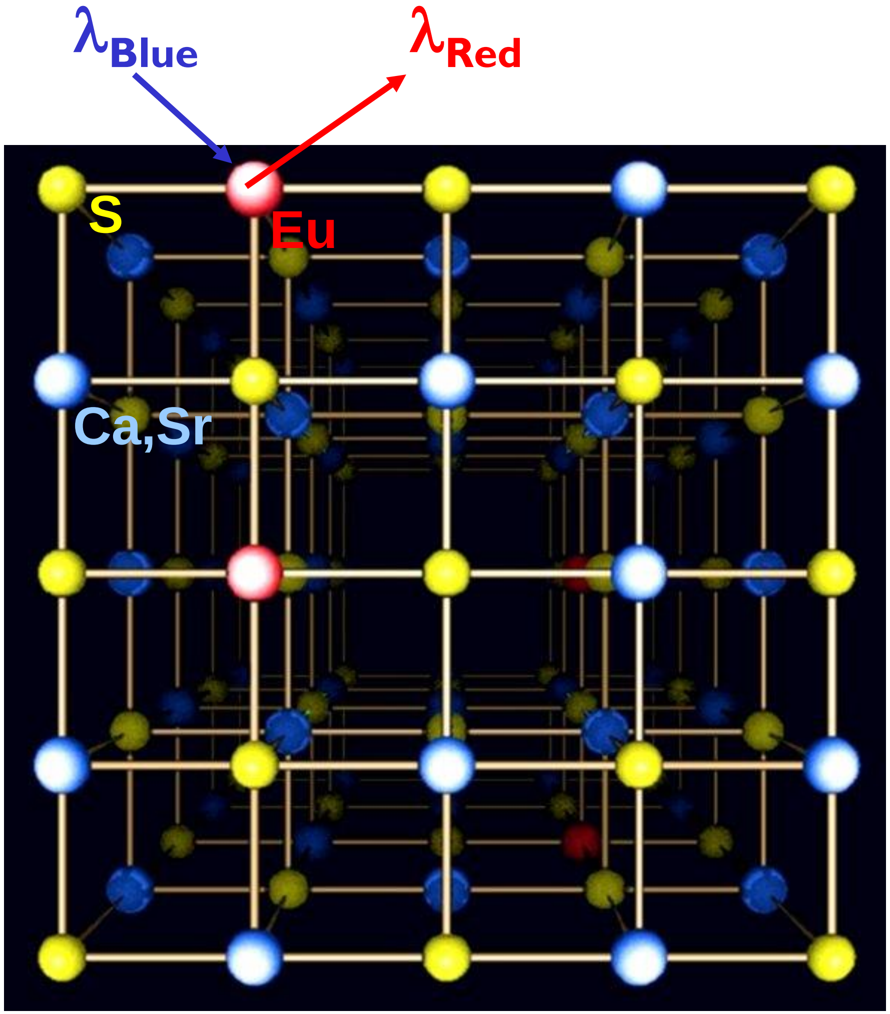
⇒ CRI > 75 for $T_c = 2700 – 4000$ K

Products available since 2004



9.13 Warm White pcLEDs

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

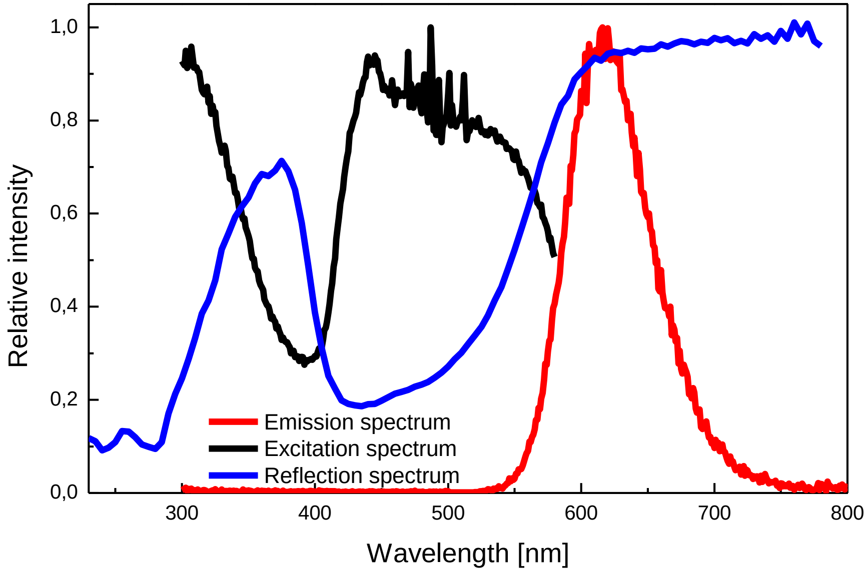


- **Rock salt (NaCl) structure**
- **High sensitivity towards O_2, H_2O and diluted acids → H_2S**
- **Activator: Eu^{2+}**
  - **onto octahedral Ca^{2+}/Sr^{2+} site**
  - **strong 4f-5d absorption bands below 550 nm**
  - **quantum efficiency > 90%**
  - **red emission tunable by adjustment of Sr/Ca content**

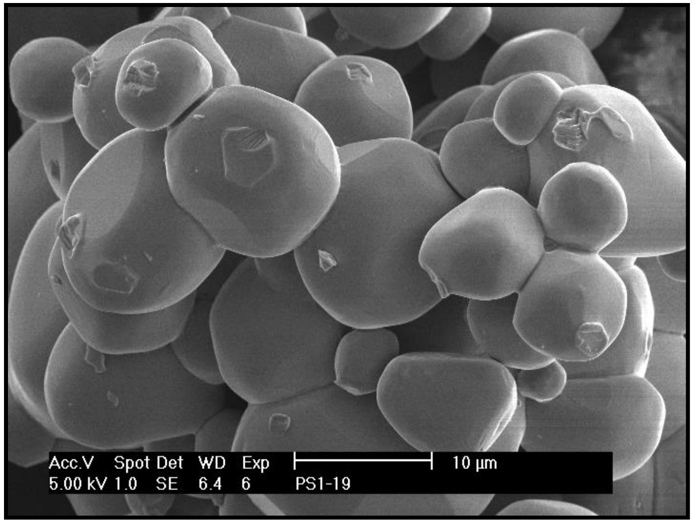
9.13 Warm White pcLEDs

Properties of (Sr,Ca)S:Eu

Luminescence and reflection spectra



Particle morphology



Quantum yield [%]	Lumen equivalent [lm/W]	CIE1931 color point x, y
> 90	260 - 265	0.629 0.370

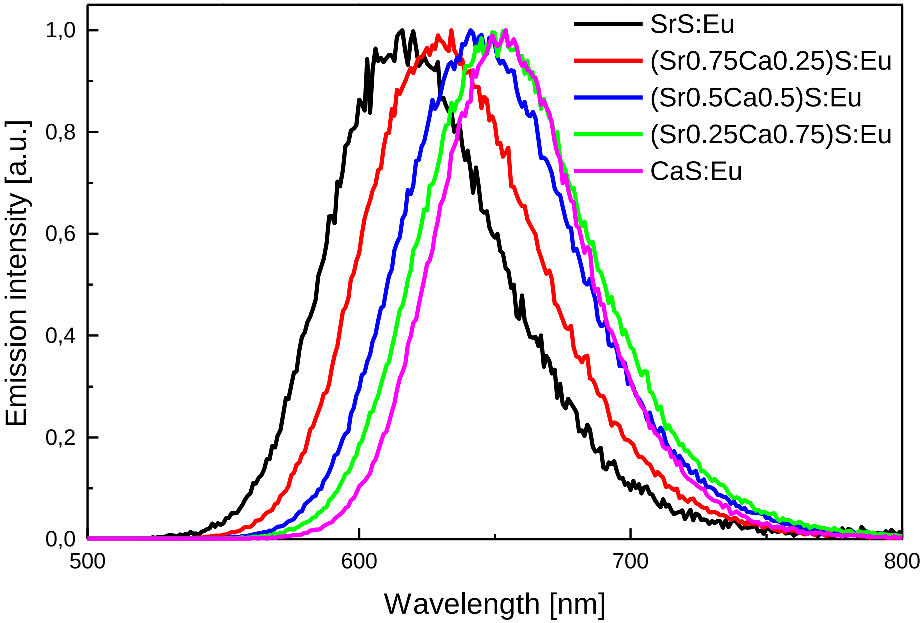
Hydrolysis of SrS: $SrS + 2\,H_2O \rightarrow H_2S\uparrow + Sr(OH)_2$

Oxidation of SrS: $SrS + 2\,O_2 \rightarrow SrSO_4$

Solution: Particle coatings or reduction of the basicity

9.13 Warm White pcLEDs

Improving the stability of SrS:Eu

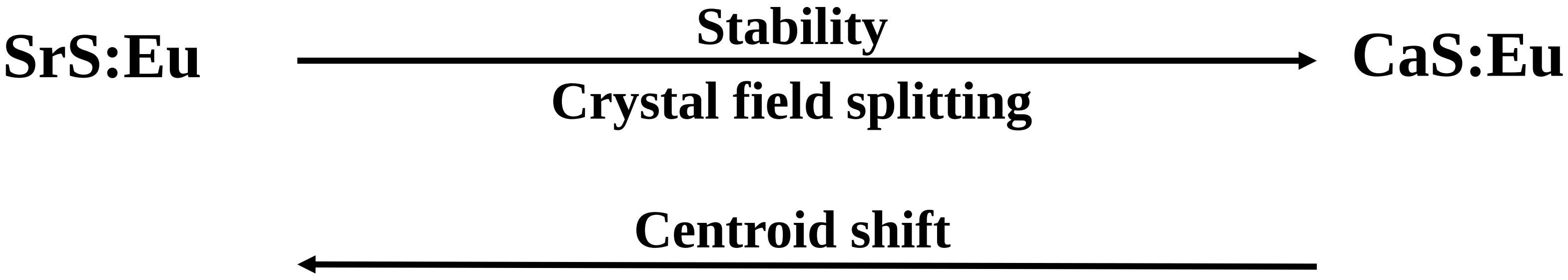


1. Reduction of the basicity of the (Ca,Sr)S host lattice
(electron density on the anions):
Replacement of Sr by Ca
Red shift of the emission band
⇒ Reduction in the lumen equivalent

2. Reduction of susceptibility to hydrolysis:
Application of a particle coating i.e., encapsulation of the particles with an impermeable wide band gap material: Al_2O_3, CaPP, $LaPO_4$, MgO, $MgAl_2O_4$, SiO_2, SrPP, YPO_4, or ZrO_2

9.13 Warm White pcLEDs

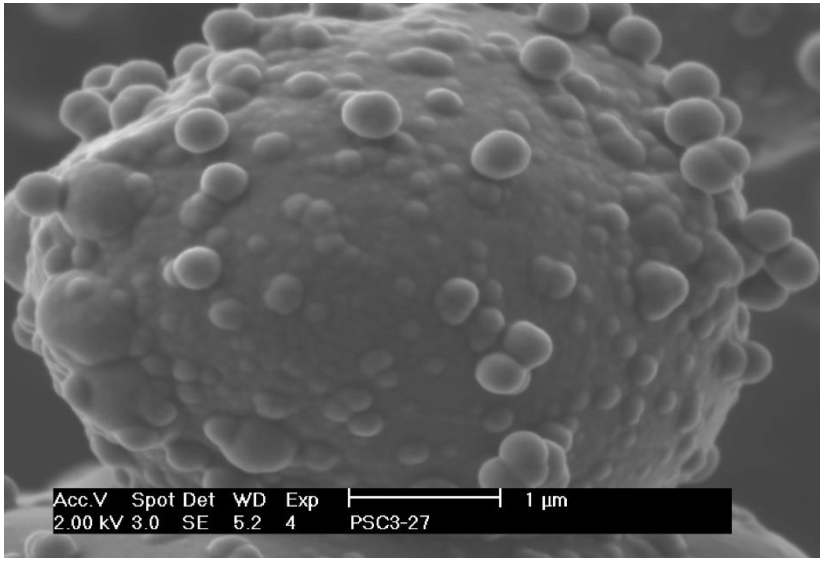
Improving the chemical stability of SrS:Eu → Compositional change



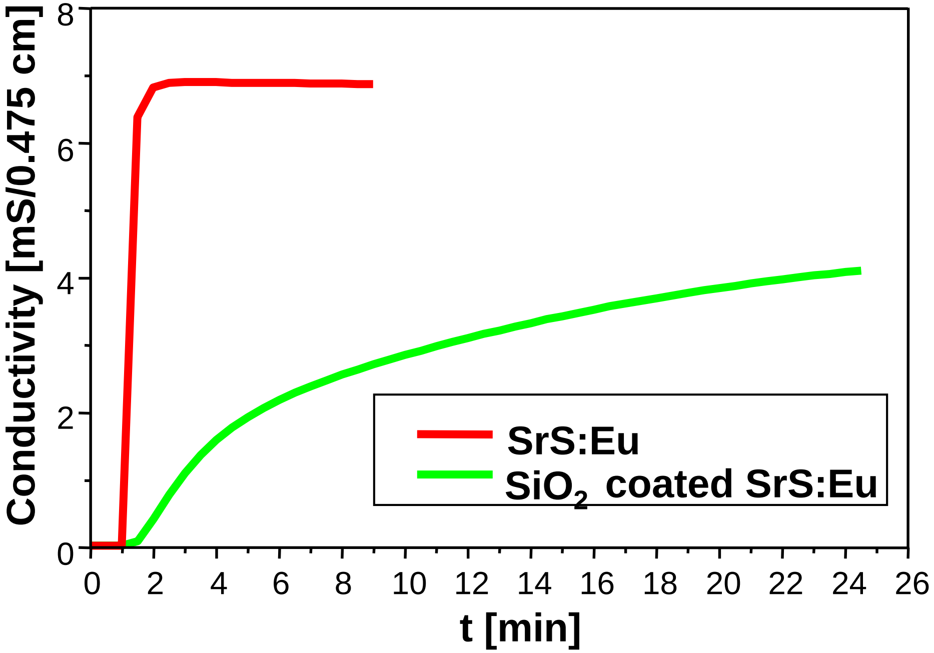
Composition	QE [%]	Abs. [%]	LE [lm/W]	CIE1931 x	CIE1931 y
CaS:Eu	> 95	> 80	90	0.697	0.303
SrS:Eu	> 95	> 80	260	0.629	0.370

9.13 Warm White pcLEDs

Improving the stability of SrS:Eu → Particle Coatings



Solubility in H_2O monitored by conductometry



SiO_2 Particle coating acts as a diffusion barrier for H_2O and CO_2 and thus improves phosphor stability

9.14 Nitride Phosphors

Advantages over oxides and sulfides

- Highly condensed anionic networks

  ⇒ high density, high chemical stability, high hardness, high thermal quenching temperature
- High charge density between the activator and the anions:

  oxide < oxynitrides < nitrides < nitridocarbide

  ⇒ strong red shift of the 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

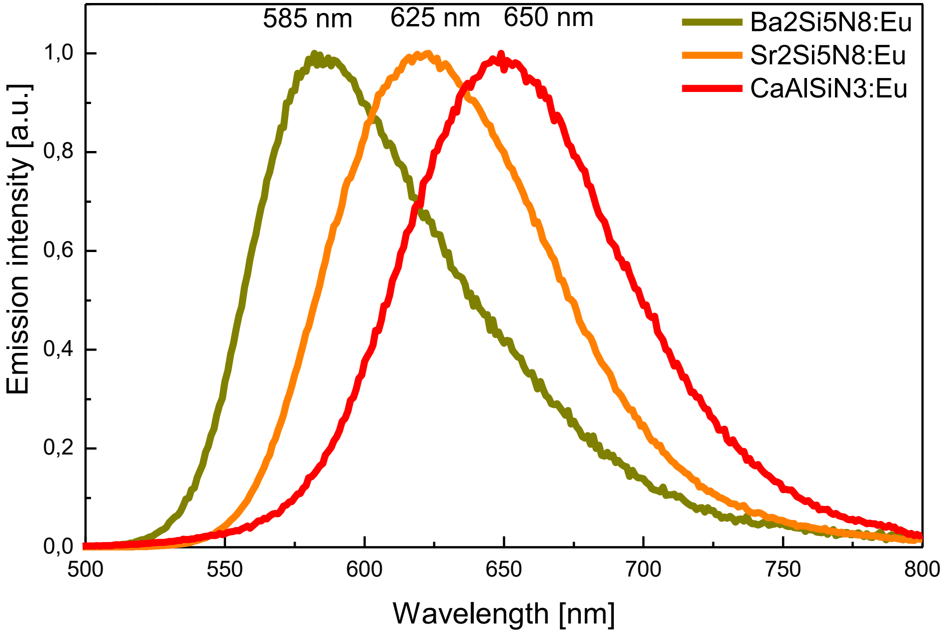
First example: $Eu_2Si_5N_8$ (640 nm)

Lit.: W. Schnick et al., Acta Cryst. C 53 (1997) 1751

9.14 Nitride Phosphors

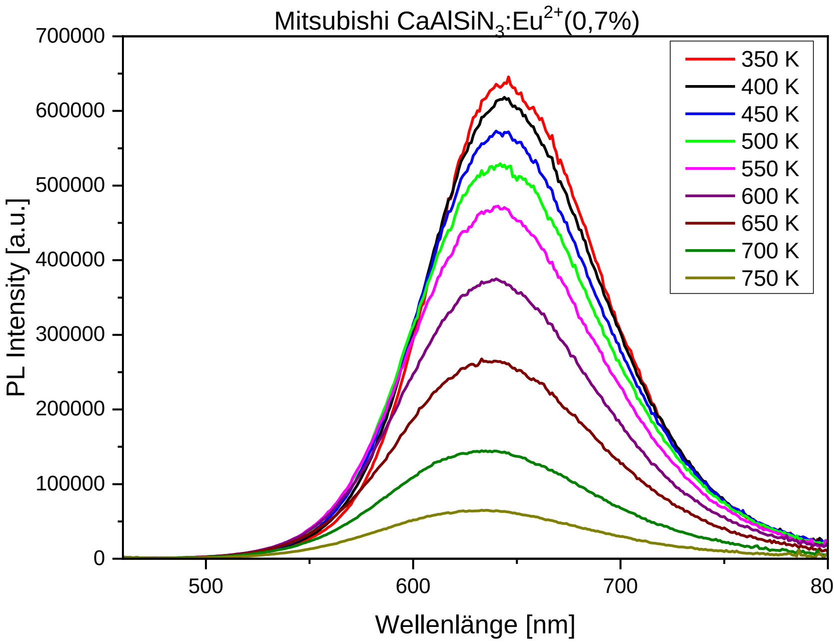
Composition and emission spectra of commercial orange/red emitting materials

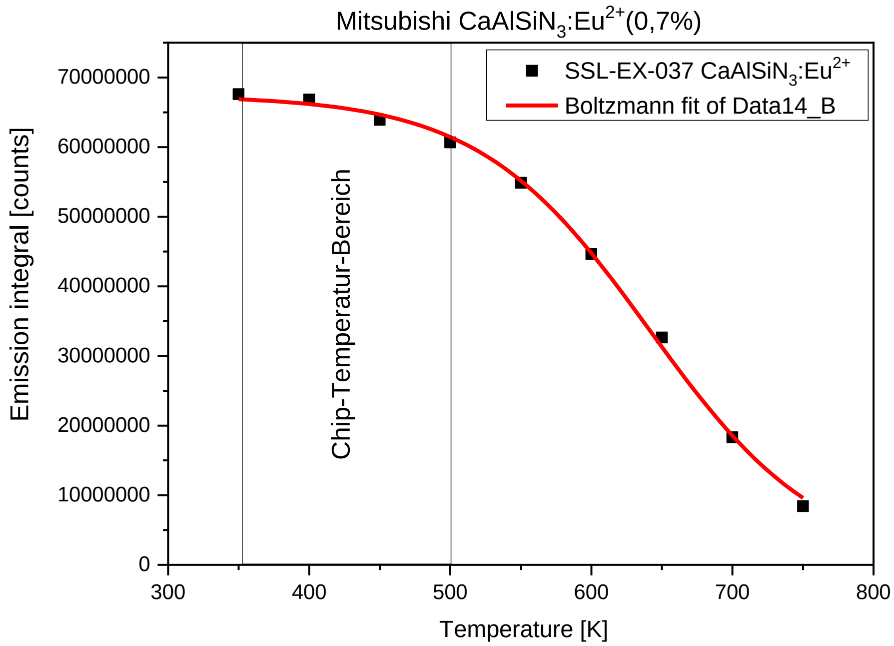
$(Ba,Sr,Ca)_2Si_5N_8$:Eu	**580 – 625 nm**
$(Ca,Sr)AlSiN_3$:Eu,O	**610 – 650 nm**



9.14 Nitride Phosphors

Thermal quenching of LED phosphors: Example $CaAlSiN_3:Eu,O$



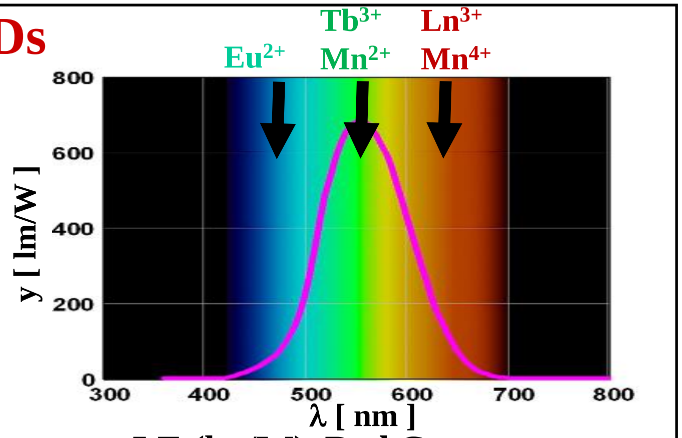


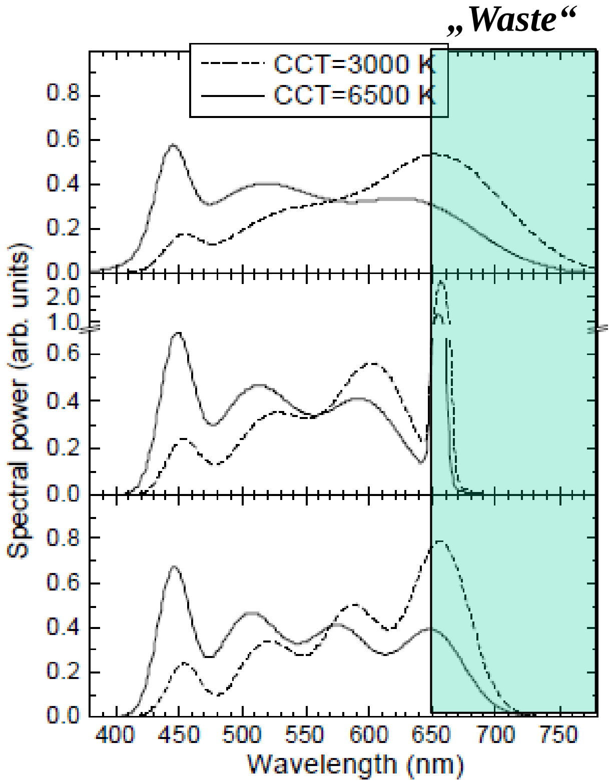
- **High absorption intensity between 200 and 500 nm**
- **Quantum yield > 90% at 450 nm excitation**
- **High thermal quenching temperature $T_{1/2}$ = Temperature at which the light output is reduced by 50%, here ~ 625 K**
- **Slight blue shift with increasing T due to thermal expansion of the host lattice**

9.15 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



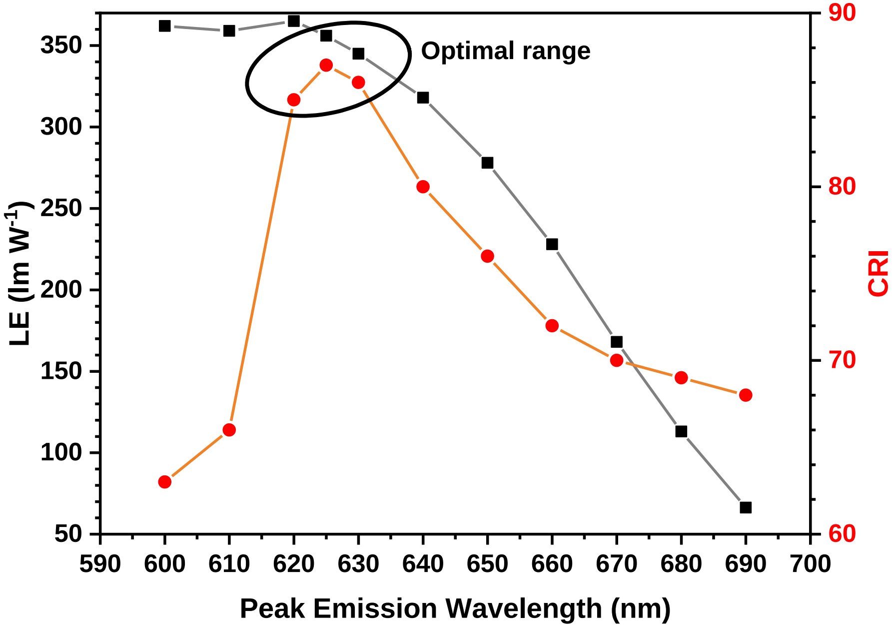


FWHM [nm]	Position (nm)	LE (lm/W)	Red Converter
90 - 120	635	257	(Ca,Sr)S:Eu $(Ca,Sr,Ba)_2Si_5N_8$:Eu $(Ca,Sr)AlSiN_3$:Eu
20 – 30	655	278	$Mg_2TiO_4:Mn^{4+}$
20 – 30	620	320	$K_2SiF_6:Mn^{4+}$ Ln^{3+} activated (Ln = Pr, Sm, Eu)
50 – 60	655	269	Eu^{2+} activated
50 – 60	620	300	Eu^{2+} activated

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

9.15 Narrow Band Red Emitter

Requirements to the „ideal“ red phosphor



- Emission wavelength ~ 615 – 635 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(λ) weighed brightness value > 60% relative to $(Ca,Sr)AlSiN_3$:Eu,O
- Decay time < 10 ms
- No saturation to 100 W/mm^2
- High (photo)chemical and thermal stability

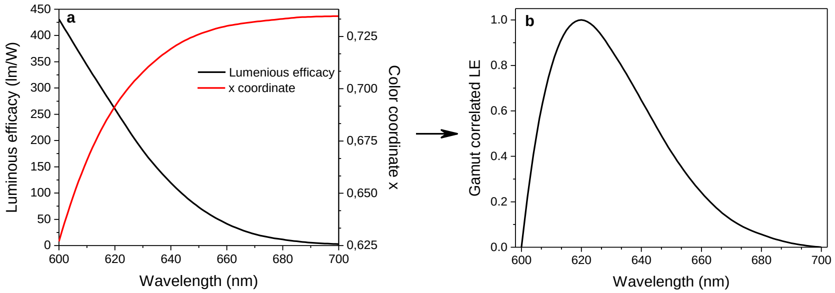
→ Eu^{2+} activated red emitting phosphors meet almost all requirements!

→ Main problem: FWHM >> 60 nm

9.15 Narrow Band Red Emitter

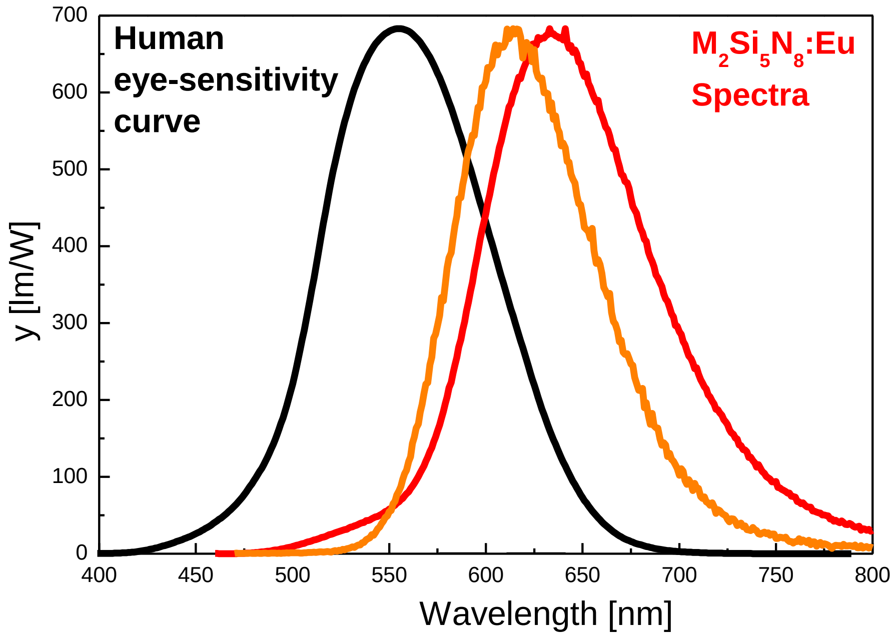
Requirements to the „ideal“ red phosphor

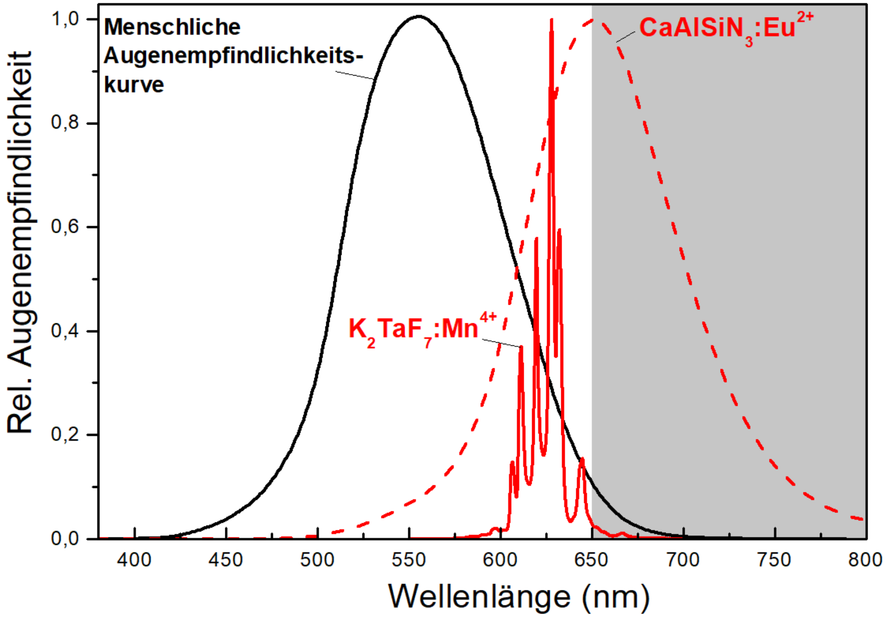
Development goals:



Find Eu^{2+} phosphor with FWHM ≤ 60 nm

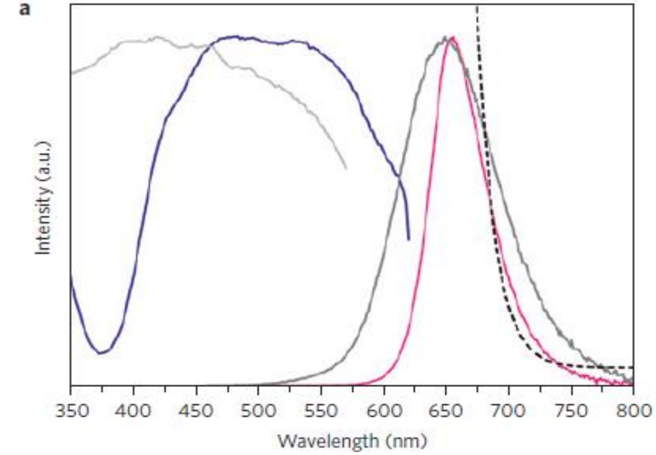
Replace Eu^{2+} by Mn^{4+} (or Eu^{3+})





9.15 Narrow Band Red Emitter

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



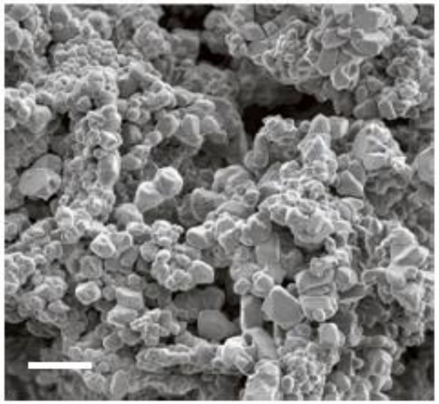
Claimed as next generation LED-phosphor material”

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



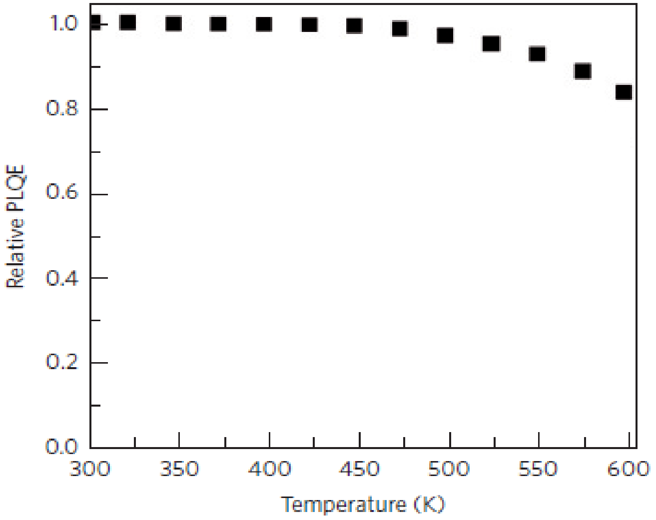
Optical Properties

λ_{max} = 651 nm for 5% Eu^{2+}

FWHM = 1180 cm^{-1} (~ 60 nm)

QE(200 °C) > 95%rel. to QE(RT)

Decay time of Eu^{2+} ~ 1.1 µs

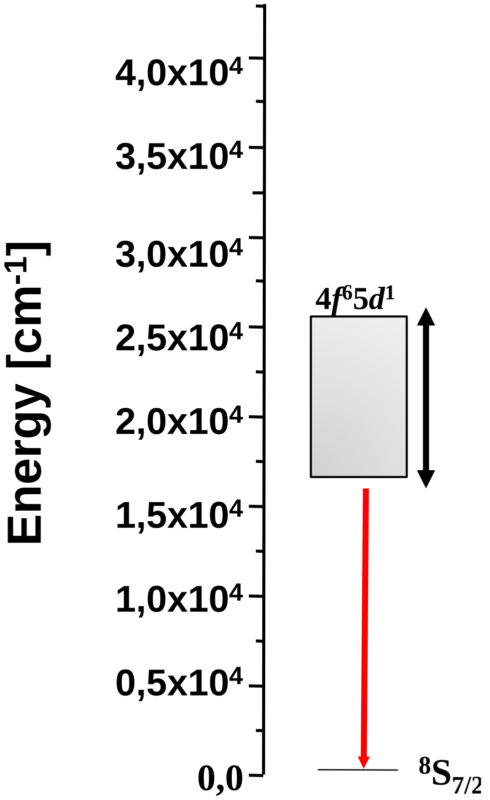


Problems: Excitation @ 410 nm → photoionisation and strong re-absorption of YAG:Ce/LuAG:Ce PL

Lit.: W.S. Schnick et al., Nature Materials (2014) 1-6

9.15 Narrow Band Red Emitter

Narrow band red emitter: Eu^{2+} vs. Mn^{4+} or Eu^{3+} emitter

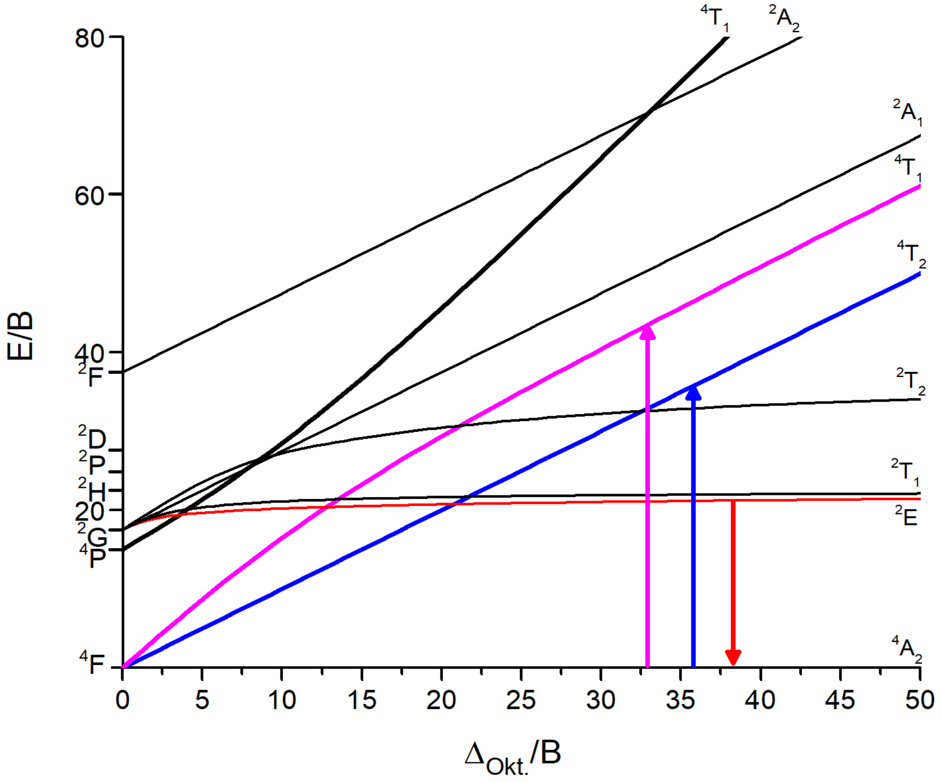


Eu^{2+}

[Xe]4f^7

Dq ≈ 2000 cm^{-1}

Δ_{SO} ≈ 2000 cm^{-1}

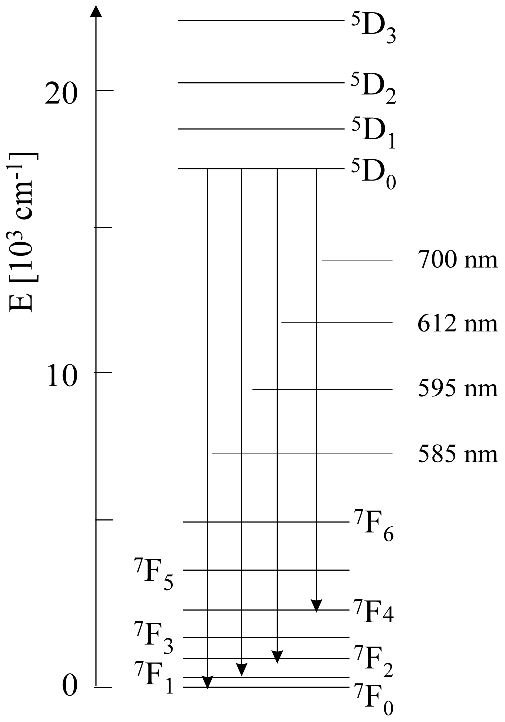


Mn^{4+}

[Ar]3d^3

Dq ≈ 10000 cm^{-1}

Δ_{SO} ≈ 400 cm^{-1}



Eu^{3+}

[Xe]4f^6

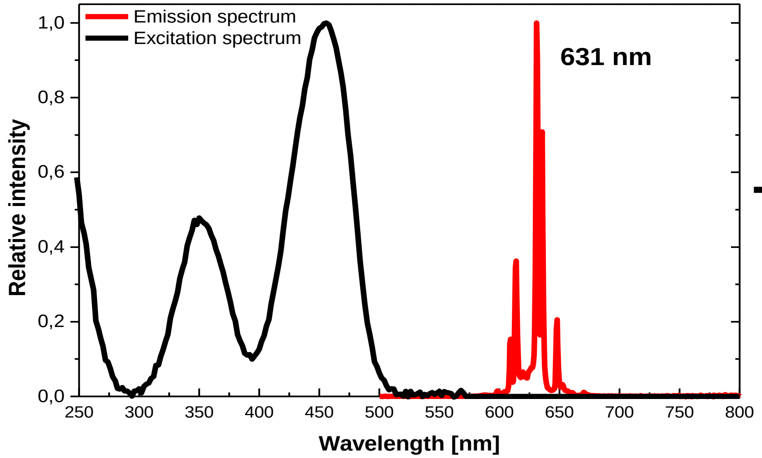
Dq ≈ 200 cm^{-1}

Δ_{SO} ≈ 3000 cm^{-1}

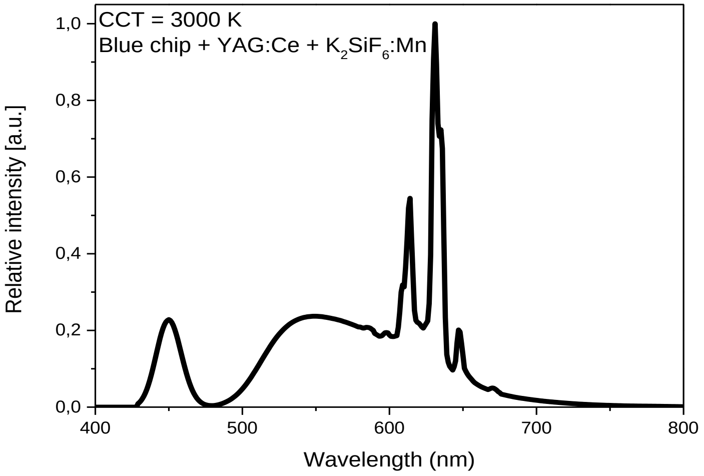
9.15 Narrow Band Red Emitter

Red emitting line emitter → Mn^{4+}

K_2MF_6:Mn (M = Si, Ge, Ti)



Warm white pcLED



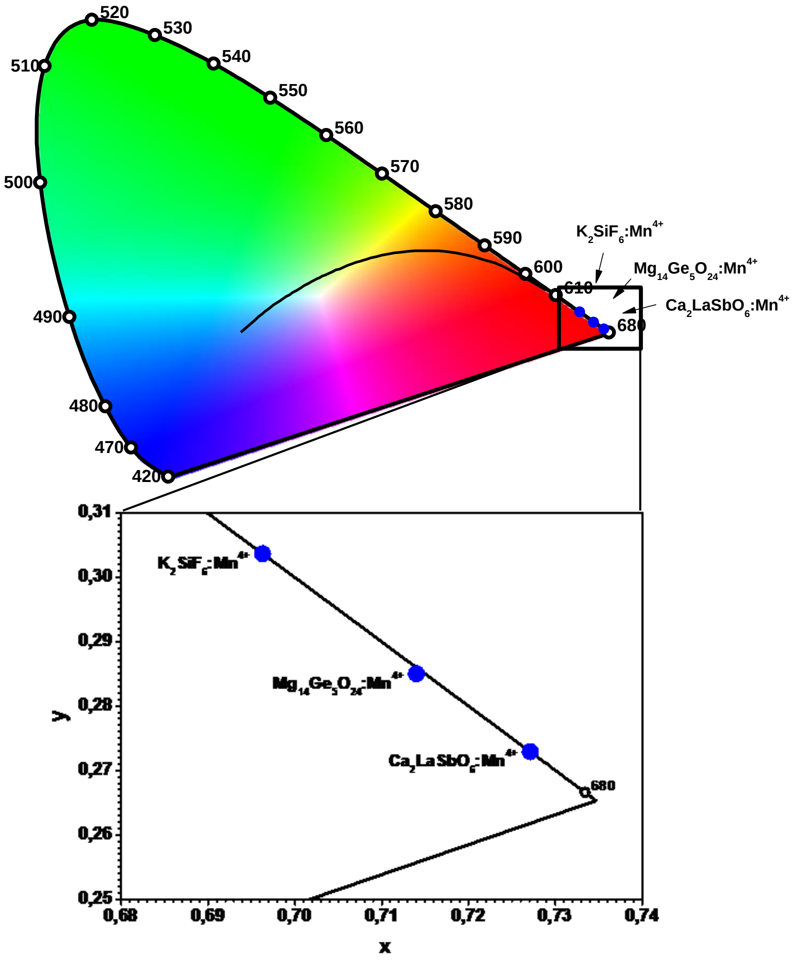
LED Chip	**Blue**	**420 – 480 nm**
Converter	**Yellow**	**(Y,Gd,Tb,Lu)Al_5O_{12}:Ce**
	Red	**Mn^{4+}- phosphors**
Typical yellow/red blend	**$Tb_3Al_5O_{12}$:3%Ce + $K_2[MF_6]$:Mn^{4+} (M = Si, Ge)**	
Problems	**Absorption strength, linearity, and stability of Mn^{4+}**	
	$MnF_4 \rightarrow MnF_3 + \frac{1}{2} F_2$	

Lit.: A. Srivastava et al., GE, US Patent US2006/0169998

9.15 Narrow Band Red Emitter

Red emitting line emitter → Mn^{4+}

Compound	LE (lm/W)	Peak λ_{em} (nm)
$K_2SiF_6:Mn^{4+}$	196	631.0
$K_2TiF_6:Mn^{4+}$	192	631.8
$K_2GeF_6:Mn^{4+}$	191	632.0
$Mg_{14}Ge_5O_{24}:Mn^{4+}$	80	658
$K_2Ge_4O_9:Mn^{4+}$	46	663
$Rb_2Ge_4O_9:Mn^{4+}$	38	667
$Ca_2YNbO_6:Mn^{4+}$	15	680
$Ca_2LaSbO_6:Mn^{4+}$	7	699
$LaScO_3:Mn^{4+}$	7	703

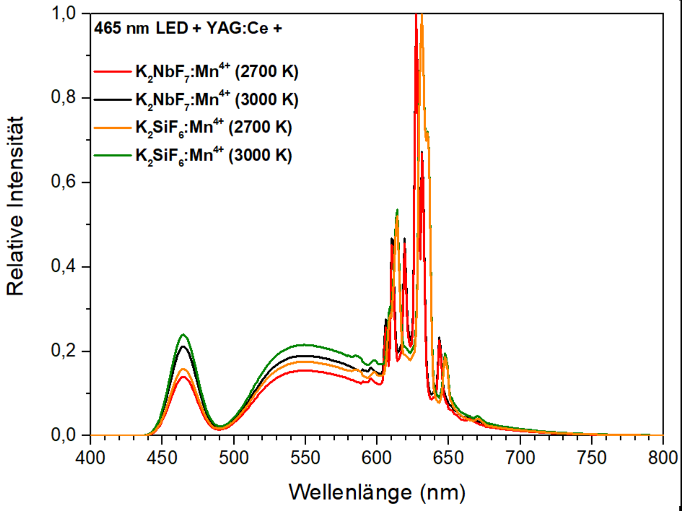


Fluorides → Rather high luminous efficacy, but stability is a challenge
Oxides → Very stable, but low luminous efficacy
Perowskites/Garnets → Very stable, NIR Emitter for Horticulture Lighting

9.15 Narrow Band Red Emitter

Red emitting line emitter → $K_2(Nb,Ta)F_7:Mn^{4+}$ with superior luminous efficacy (LE)

Blue LED + YAG:Ce +	CCT [K]	LE [lm/W_{opt}]	CRI
$K_2NbF_7:Mn^{4+}$	3000	346	95
	2700	345	95
$K_2TaF_7:Mn^{4+}$	3000	345	95
	2700	345	94
$Na_3AlF_6:Mn^{4+}$	3000	345	95
	2700	344	95
$K_2SiF_6:Mn^{4+}$	3000	339	95
	2700	297	95
$Mg_{14}Ge_5O_{24}:Mn^{4+}$	3000	254	83
	2700	241	78
$Y_2Mg_3Ge_3O_{12}:Mn^{4+}$	3000	255	84
	2700	242	79
$CaAlSiN_3:Eu^{2+}$	3000	272	93
	2700	260	95



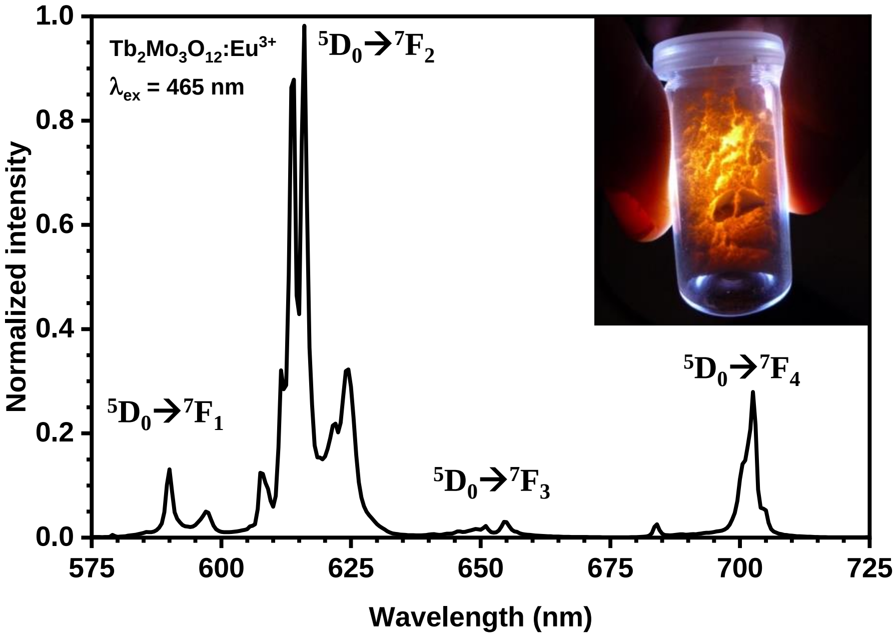
A 2700 K LED comprising YAG:Ce and $K_2TaF_7:Mn^{4+}$ yields 15% higher LE than an LED comprising YAG:Ce and $K_2SiF_6:Mn^{4+}$

9.15 Narrow Band Red Emitter

Red emitting line emitter → Eu^{3+}

Eu^{3+} is an ideal red emitter for CRTs, PDPs, TLs, CFLs, and so on due to

- line emission at around 620 nm
- high thermal quenching temperature
- high quantum yield
- not prone to concentration quenching
- stable oxidation state



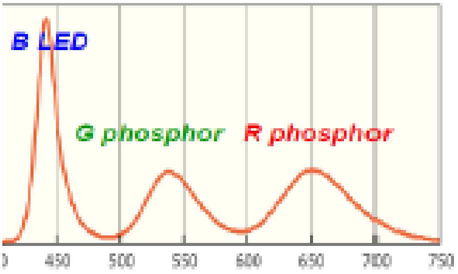
Main problem: Very low absorption cross section in the spectral range 350 – 480 nm due to strongly forbidden $[Xe]4f^6$ - $[Xe]4f^6$ transitions …..

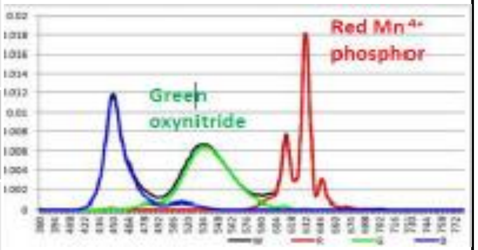
9.15 Narrow Band Red Emitter

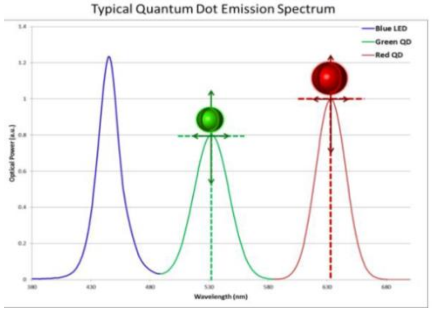
The quest for a narrow band red emitter goes on ….

Eu^{2+} → Mn^{4+} → CdSe or InP QDots → Tb^{3+} or $[UO_2]^{2+}$ sensitised Eu^{3+}

Material	Peak at [nm]	FWHM [nm]	Pros	Cons
(Sr,Ca)S:Eu	615 - 650	60 - 70	Rather narrow band	Low chemical stability
$(Sr,Ba)_2Si_5N_8$:Eu	585 - 625	80 - 100	Reliability	IR spillover
$(Ca,Sr)AlSiN_3$:Eu	610 – 655	80 – 90	Reliability	IR spillover
$SrLiAl_3N_4$:Eu	650	50 nm	Narrow band	Self-absorption, some IR spillover
K_2SiF_6:Mn	631	Lines < 2 nm	Very narrow band	Moderate absorption
CdSe QDots	Tunable green to red	30 – 50	Narrow band	Reliability, Reabsorption
InP QDots	Tunable green to red	45 – 65	Narrow band	Reliability, Reabsorption
Direct red LEDs	Tunable red	25 – 35	No Stokes loss Narrow band	Strong TQ, more complex
$Tb_2Mo_3O_{12}:Eu^{3+}$ [1]	615	Lines < 1 nm	Very high LE and stability	Weak absorption





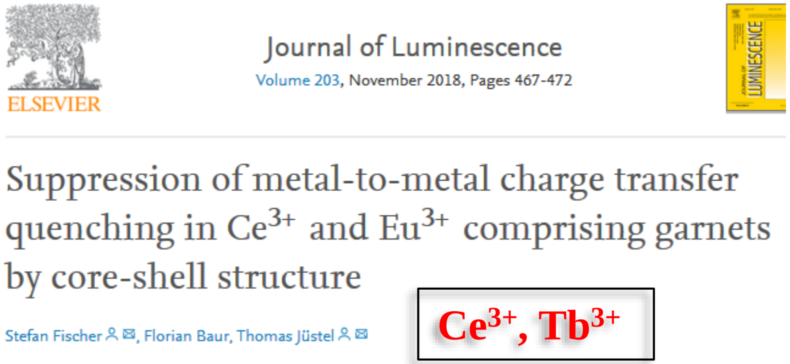


Modified from GE, PGS2016, Newport Beach, CA, USA

[1] Lit.: F. Baur, F. Glocker, T. Jüstel, J. Mater. Chem. C 3 (2015) 2054

9.15 Narrow Band Red Emitter

Ways to circumvent the problem of weak absorption of Eu^{3+}: Sensitisation!


Journal of Luminescence
Volume 203, November 2018, Pages 467-472

Suppression of metal-to-metal charge transfer quenching in Ce^{3+} and Eu^{3+} comprising garnets by core-shell structure

Stefan Fischer, Florian Baur, Thomas Jüstel

Ce^{3+}, Tb^{3+}


Journal of Luminescence
Volume 196, April 2018, Pages 431-436

Uranyl sensitized Eu^{3+} luminescence in $Ln(UO_2)_3(PO_4)_2O(OH)\cdot 6H_2O$ phosphors (Ln = Y, Eu, La) for warm-white light emitting diodes

Florian Baur, Thomas Jüstel

$(UO_2)^{2+}$


From the journal:
Journal of Materials Chemistry C

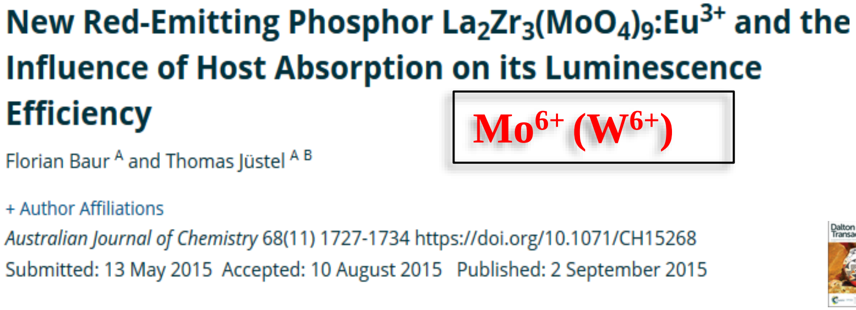

Photoluminescence and energy transfer rates and efficiencies in Eu^{3+} activated $Tb_2Mo_3O_{12}$†

Issue 26, 2018

Baur,[a] F. Glocker[b] and T. Jüstel*[a]

Tb^{3+}


From the journal:
Journal of Materials Chemistry C


New Red-Emitting Phosphor $La_2Zr_3(MoO_4)_9:Eu^{3+}$ and the Influence of Host Absorption on its Luminescence Efficiency

Florian Baur [A] and Thomas Jüstel [A B]

+ Author Affiliations

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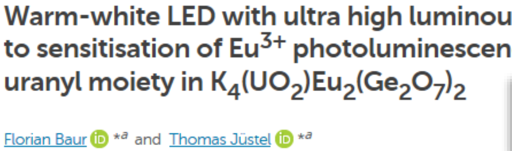
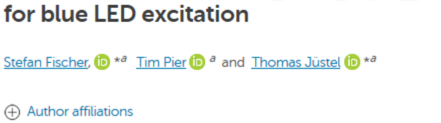
Mo^{6+} (W^{6+})


From the journal:
Dalton Transactions


Warm-white LED with ultra high luminous efficacy due to sensitisation of Eu^{3+} photoluminescence by the uranyl moiety in $K_4(UO_2)Eu_2(Ge_2O_7)_2$

Florian Baur *[a] and Thomas Jüstel *[a]

$(UO_2)^{2+}$


On the sensitization of Eu^{3+} with Ce and Tb by composite structured $Ca_2LuHf_2Al_3O_{12}$ garnet phosphors for blue LED excitation

Stefan Fischer, *[a] Tim Pier [a] and Thomas Jüstel *[a]

⊕ Author affiliations

Ce^{3+}, Tb^{3+}

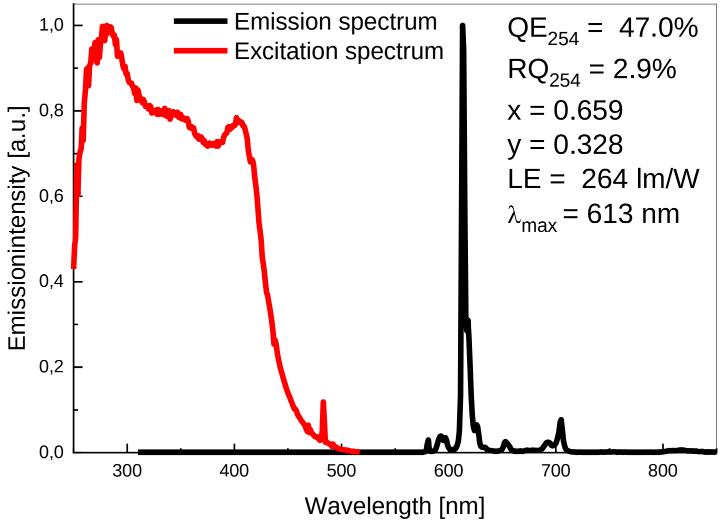
Moreover: Shift of the LMCT band to low energy (→ blue range):
Metallates or e^- rich anions $[Si(NCN)_4]^{4-}$ or ligands, e.g. ttfa

9.15 Narrow Band Red Emitter

Position of the LMCT band ($O^{2-} \rightarrow Eu^{3+}$)

Reduction in energy by alkaline anionic moieties, i.e. high electron density and/or polarizability

[Eu(thenoyltrifluoracetylacetone)$_3$ (diphenylphenanthroline)]



Organic π-donor ligands
→ e.g. diketonate, phenanthroline
→ [Eu(ttfa)$_3$(dpphen)]   CN = 8

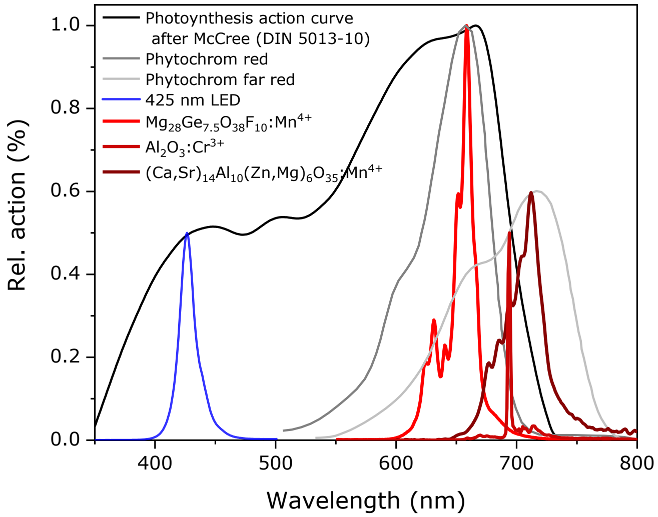
Metallates
→ VO_4^{3-}, MoO_4^{2-}, WO_4^{2-}, MoO_6^{6-}, WO_6^{6-}

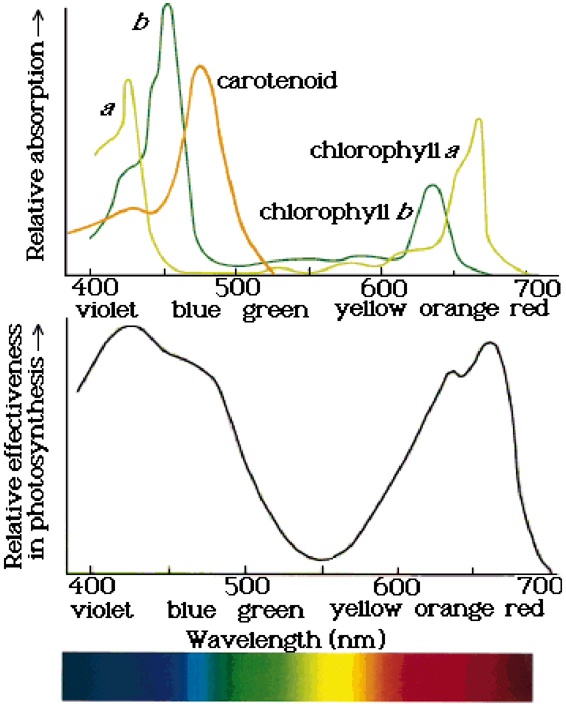
Other alkaline network formers
→ e.g.carbodiimides
→ $M^{I}Ln^{III}(M^{IV}(CN_2)_4]$:$Eu^{3+}$ M^{I} = K, Rb, Cs; Ln^{III} = Y, La, Gd and M^{IV} = Si, Ge

9.15 Narrow Band Red Emitter

Light sources in horticulture lighting

- Na low-pressure discharge lamps
- Fluorescent lamps with RB phosphor blend
- Blue and red LEDs (+ far red LED)
- Blue LEDs + red (~ 660 nm) + far red (~ 700 nm) phosphors





Grass cultivated upon daylight or upon LED illumination

Daylight (left vessel) and LED illumination (right vessel)

Plants

Roots

9.15 Narrow Band Red Emitter

Light sources in horticulture lighting - Spectra optimization

1. Blue (In,Ga)N and red & NIR (Al,In,Ga)P LED

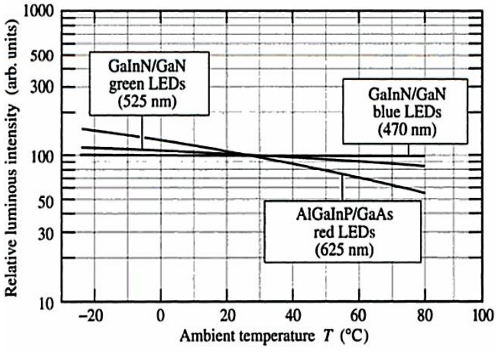
2. Blue (In,Ga)N LED and red & NIR phosphor

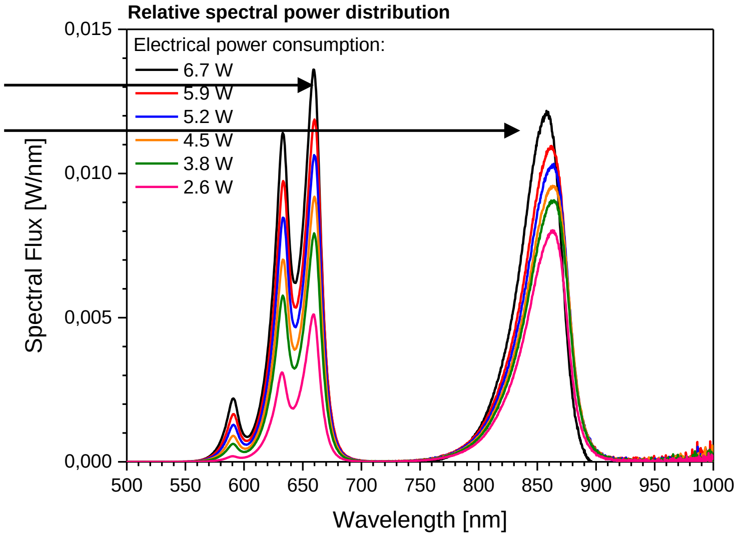
- 400 - 490 nm LED
- red phosphor: Mn^{4+}
- NIR phosphor: Cr^{3+}

(Al,In,Ga)P
500 - 900 nm
quenching ~ 0.7%/K
strong red-shift

(Al,In,Ga)N
210 - 550 nm
quenching ~ 0.1%/K
spectral consistent

→ (In,Ga)N platform is
more temperature stable

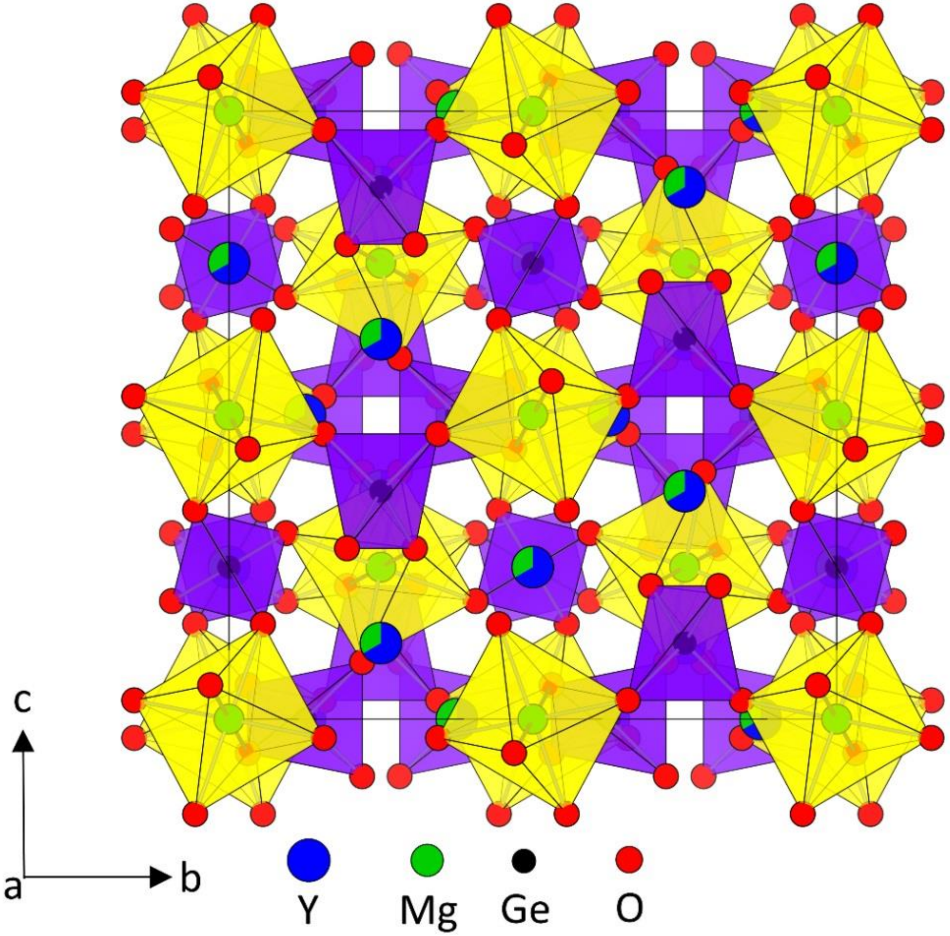


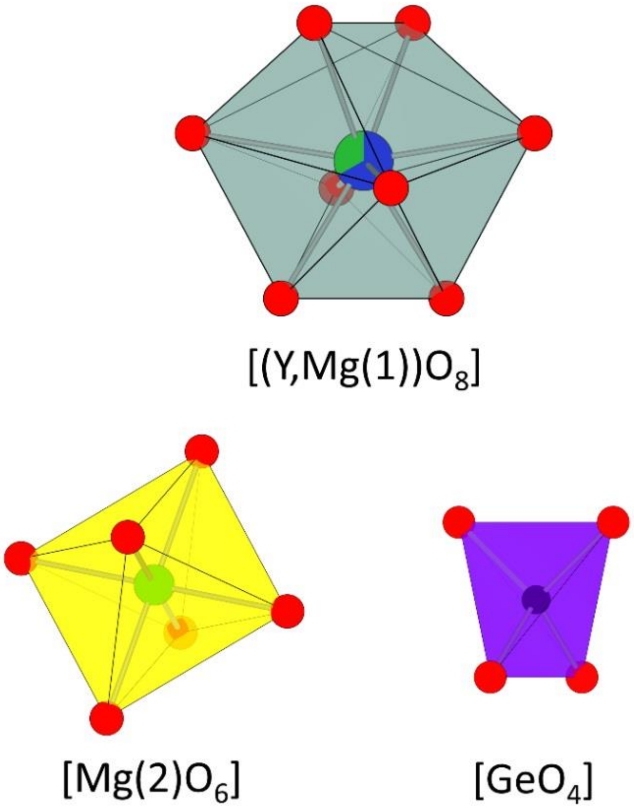


Power consumption	Voltage	Current	Chip temperature
1 W	4.5 V	0.2 A	~ 120 °C
5 W	4.5 V	1.1 A	> 150 °C

9.15 Narrow Band Red Emitter

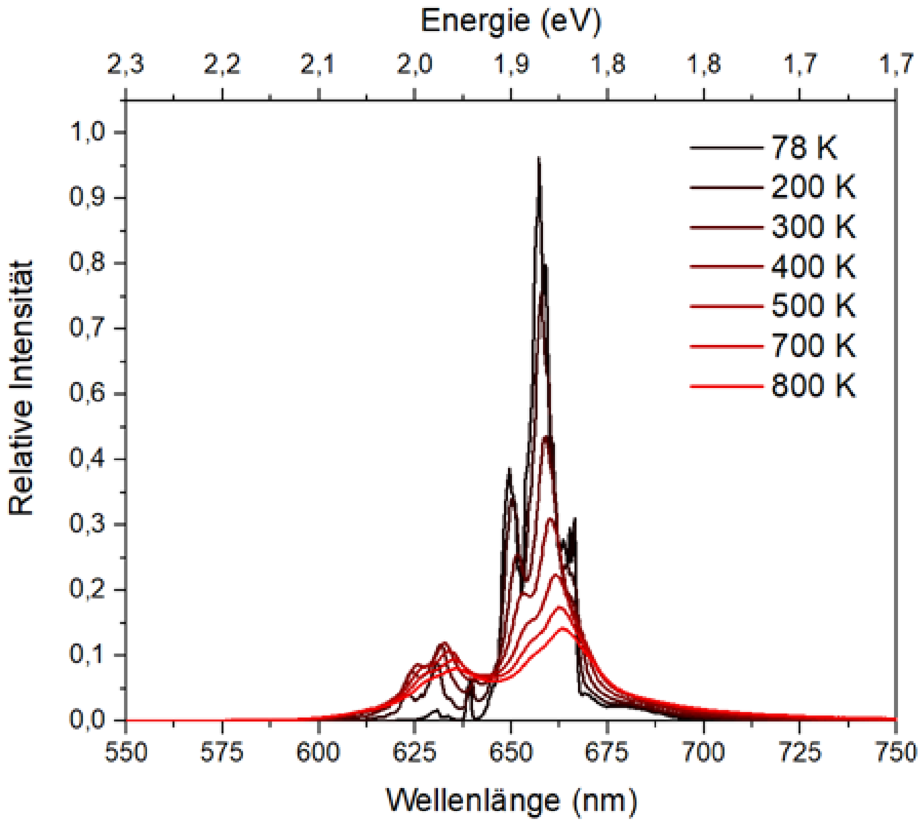
Garnet type phosphor $Y_2Mg_3Ge_3O_{12}$:Mn^{4+} (very rigid and stable host)

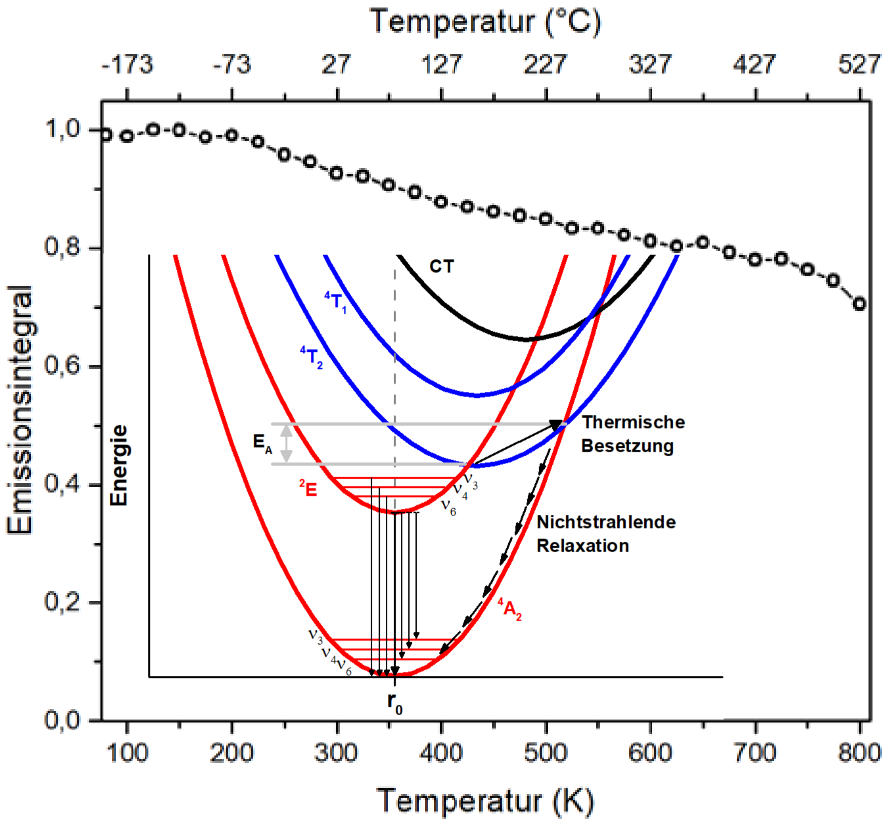




9.15 Narrow Band Red Emitter

Garnet type phosphor $Y_2Mg_3Ge_3O_{12}:Mn^{4+}$ (stable host)



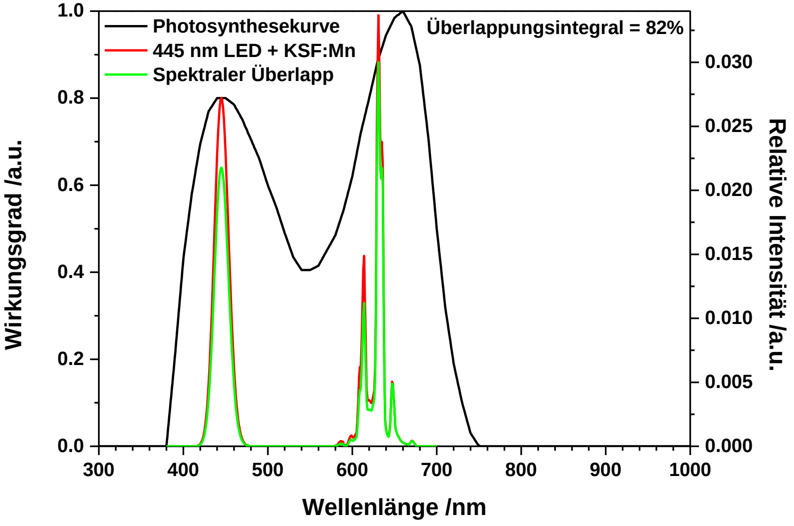


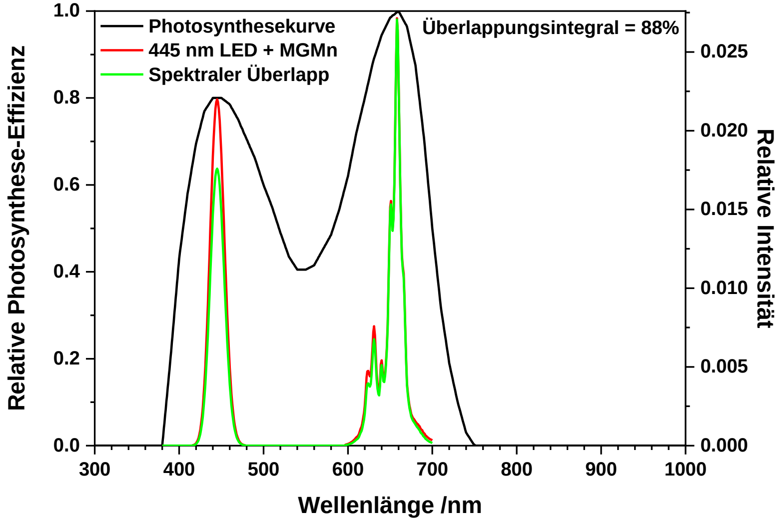
$Y_2Mg_3Ge_3O_{12}:Mn^{4+}$ has the highest known quenching temperature of Mn^{4+} phosphors known so far, which is most likely related to the high energy of the $^4T_2$ band and thus large E_A

Lit.: T. Jansen, M. Kirm, M.G. Brik, S. Vielhauer, M. Oja, N.M. Khaidukov, V.N. Makhov, T. Jüstel., ECS JSSST 7 (2018) R3086

9.15 Narrow Band Red Emitter

Blue and red emitting pcLEDs and its photosynthesis efficacy





445 nm LED (19 nm FWHM) and

K_2SiF_6:Mn^{4+} (PSF) phosphor (lines) **Mn^{4+} doped garnet phosphor**

intensity ratio 0.8:1 (LED:phosphor)

Spectral integral overlap ~ 82% **Spectral integral overlap ~ 88%**

9.16 Application Areas of Inorganic LEDs

Illumination

Strengths of inorganic LEDs

- Lifetime > 20000 h
- Ease of dimming
- Reduced depth
- High T-stability
- Fast switching cycles
- Low voltage < 4 V
- Any color temperature
- Robustness

Main challenges

- Luminous flux per LED ↑
- Color point consistency ↑
- Price per lumen ↓
- Thermal management ↑

Chronological deployment

Flashlights

Signal lights

Lighting panels

Spot lighting

Contour lighting

Backlighting (LCDs)

Automotive lighting

Aviation lighting

Interior lighting

General lighting

Street lighting

9.16 Application Areas of Inorganic LEDs

- Signal systems
  - Traffic lights
  - Railway signals
  - Airfield lighting

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

```
01 13162-000          100.9 ABCD12345678
02 17119               71.3 ABCD12345678
04 13821-00           160.0 WAIT MTL 34.7
05 78546-1D            75.3 SETUP     1.4
06 FAMILY             240.0 NO OPER   6.8
   54650/GF-F               NO OPER   6.8
07 14176-W             60.0 NO OPER   0.7
08 54558A-W            72.0 NO OPER   6.7
09 15078               72.0 TOOLPROB  5.7
10 E52205              32.7 ABCD12345678
11 400948             152.6 ABCD12345678
12 4501T-W             42.1 ABCD12345678
14 19700              108.0 ABCD12345678
15 4501N               39.7 ABCD12345678
16 51819-59            60.0 IDLE     11.9
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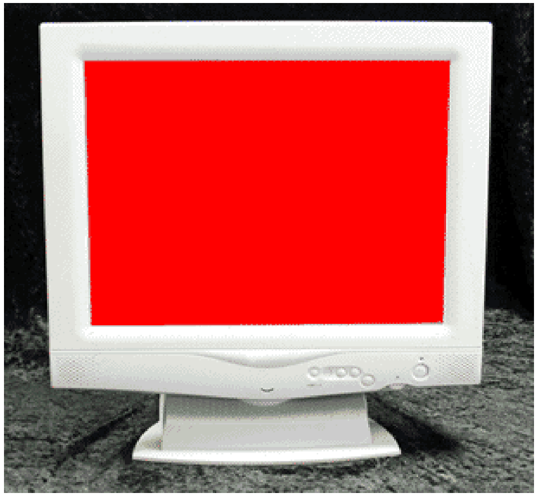


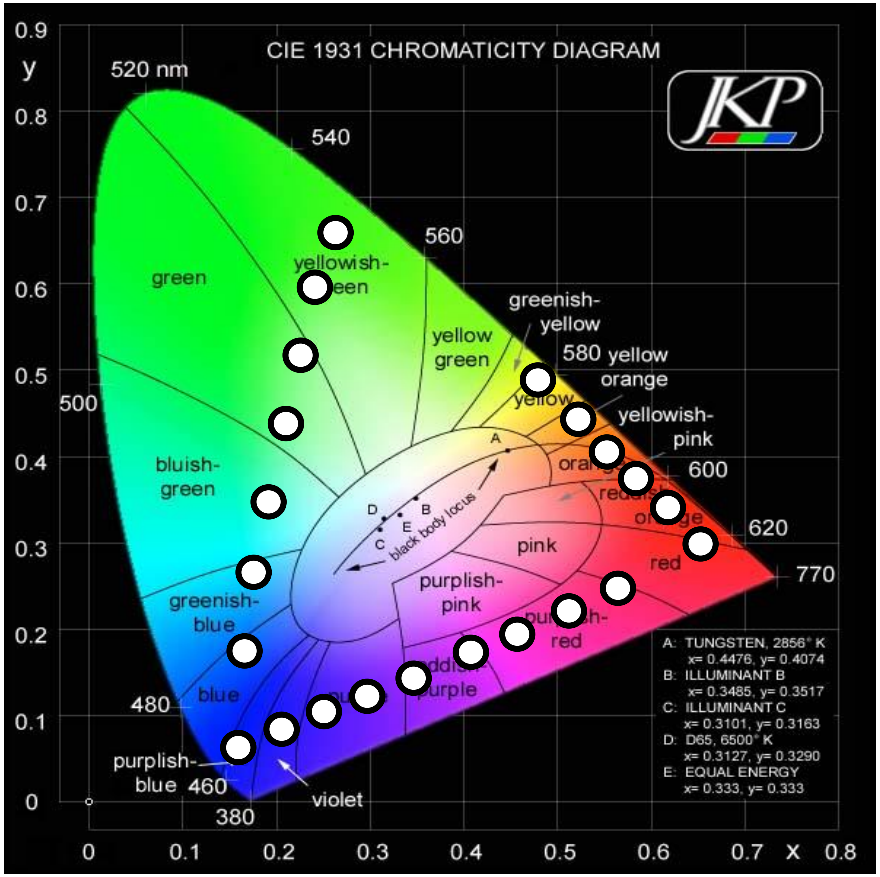
- Backlighting
  - LCD screens in TVs, laptops, smartphones, tablets, monitors

- LED screens
  - Scoreboards
  - Billboards
  - TV sets

9.16 Application Areas of Inorganic LEDs

“Color on Demand”

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



Examples

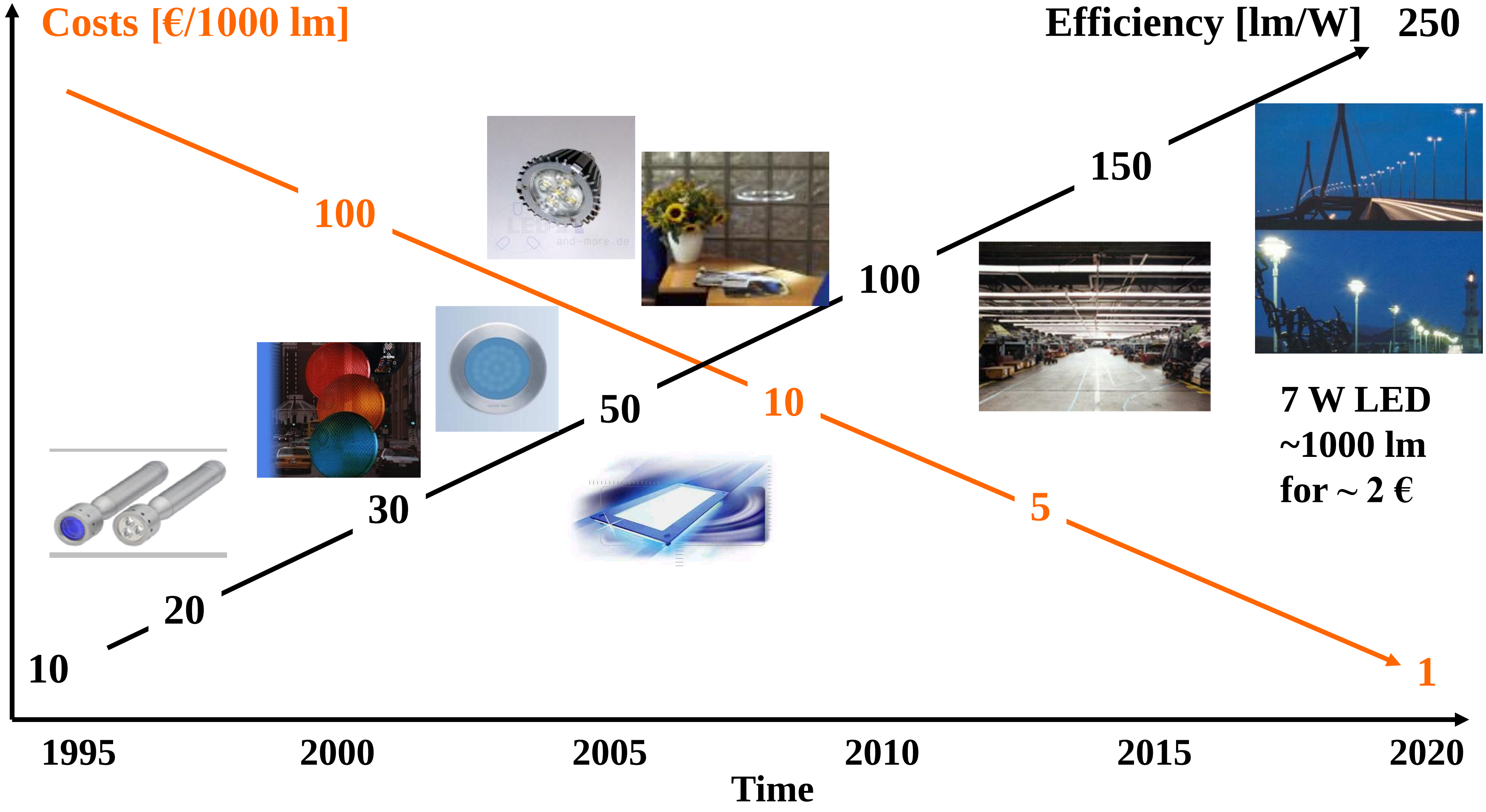
- **Magenta: Blue LED + red phosphor**
- **Cyan: Blue LED + green phosphor**

Application in

- **Company logos**
- **Signaling systems**
- **Decoration lighting**
- **Advertisement lighting**

9.17 The Future of LED

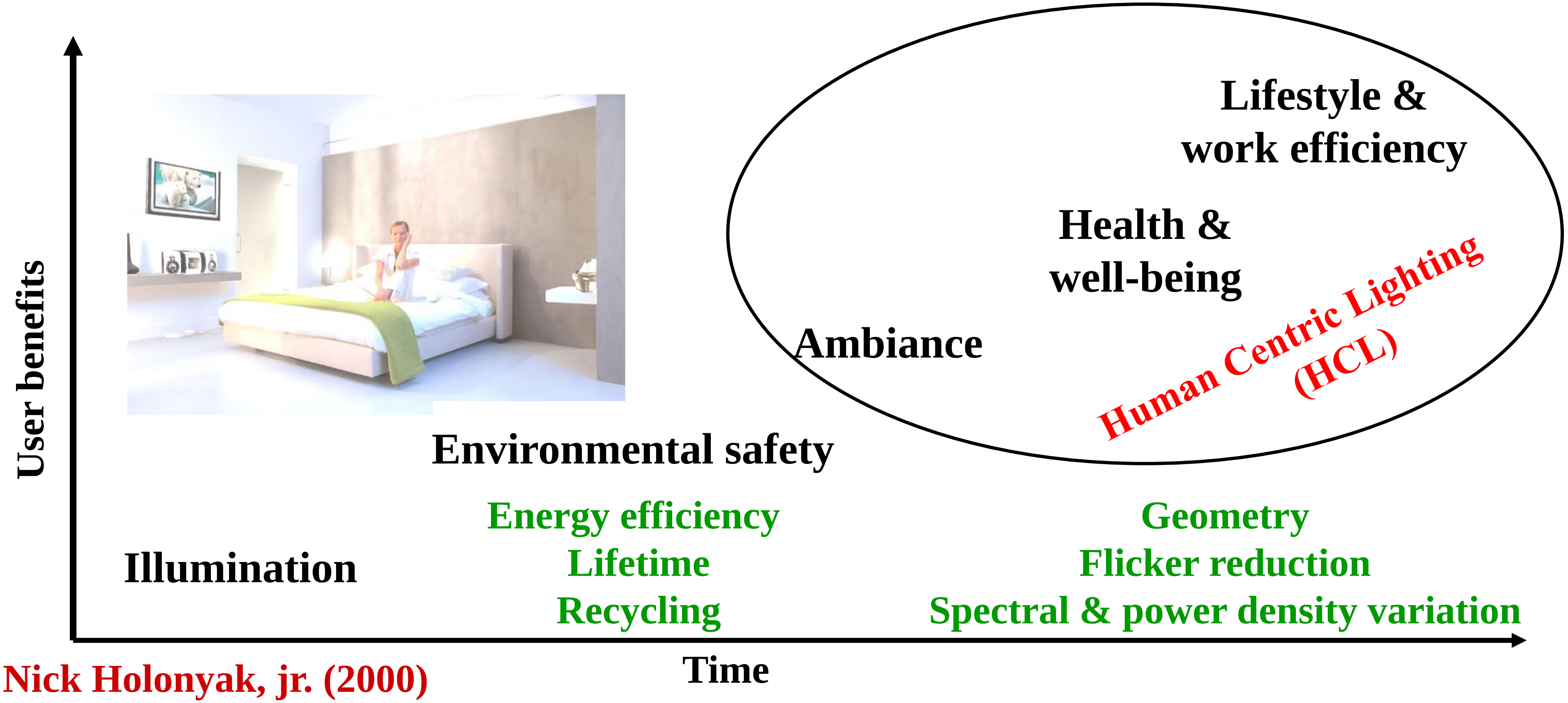
Cost and efficiency



7 W LED
~1000 lm
for ~ 2 €

9.17 The Future of LED

Market trends for LED light sources



Lifestyle &
work efficiency

Health &
well-being

Ambiance

Human Centric Lighting
(HCL)

Environmental safety

Illumination

Energy efficiency
Lifetime
Recycling

Geometry
Flicker reduction
Spectral & power density variation

User benefits

Time

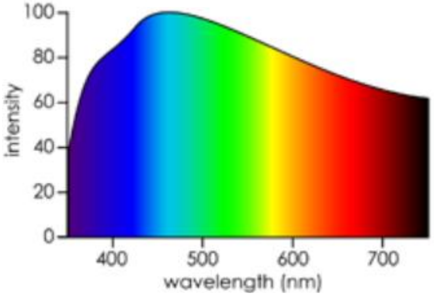
Nick Holonyak, jr. (2000)

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.

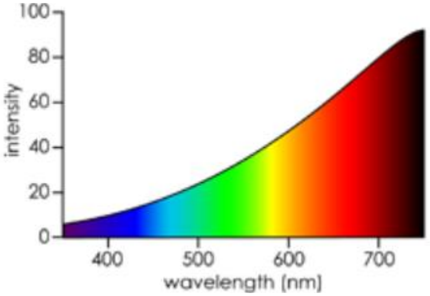
9.17 The Future of LED

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

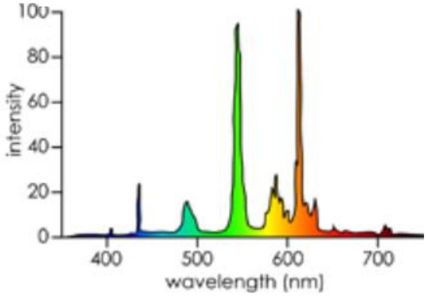
Day light



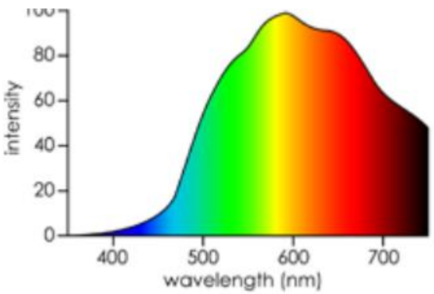
Incandescent lamp



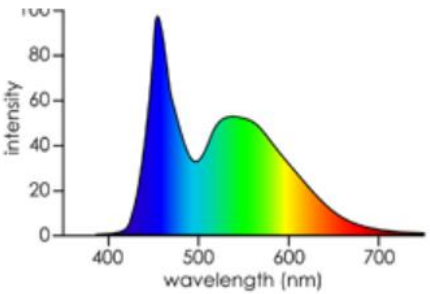
Fluorescent lamp



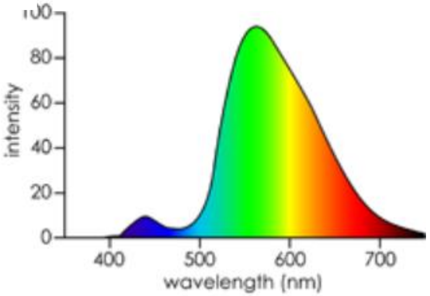
Halogen lamp with IR filter



Cool white LED



Warm white LED



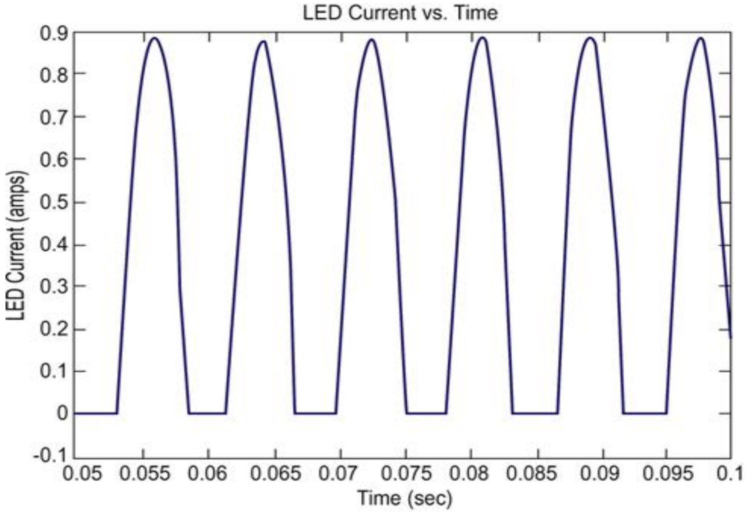
	Day light	Halogen lamp	Fluorescent lamp	LED lamp cool white	LED lamp warm white
Lux	100,000	500	500	500	500
UV	5%	< 1%	< 1%	0%	0%
VIS	60%	5%	90%	100%	90%
NIR	35%	95%	10%	0%	10%

9.17 The Future of LED

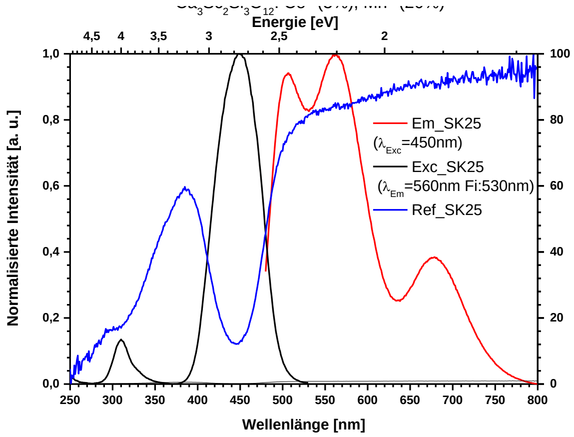
Human Centric Lighting (HCL): LED with reduced flickering (flicker index)

Potential solutions

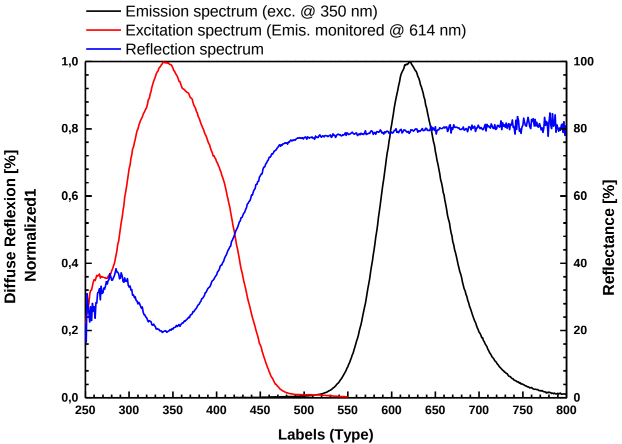
- **Electronics: Driver optimisation**
- **Afterglow pigments (s-min-h)**
- **Phosphors with delayed emission → risetime**
- **Phosphors with a long decay time (ms)**

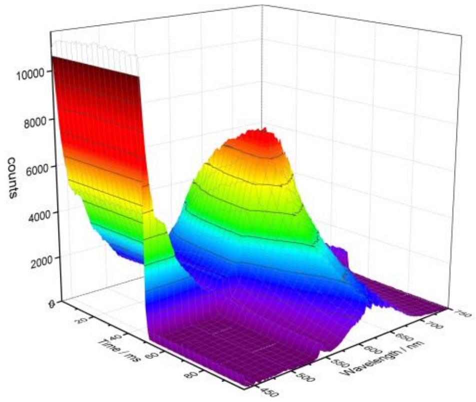


$Ca_3Sc_2Si_3O_{12}$:$Ce^{3+}Mn^{2+}$



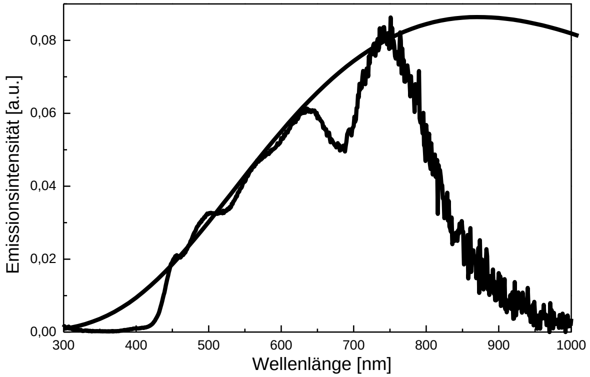
$CaSiO_3$:$Eu^{2+}Mn^{2+}$





9.17 The Future of LED

(In,Ga)N LEDs and laser diodes (LDs) with enhanced functionality

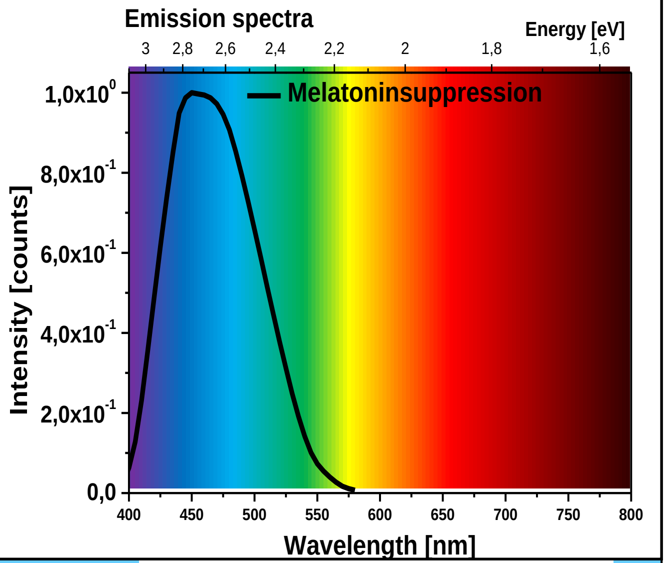


1. Physiological effects (HCL)

Full spectrum light sources: 300 - 1000 nm (see above)
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



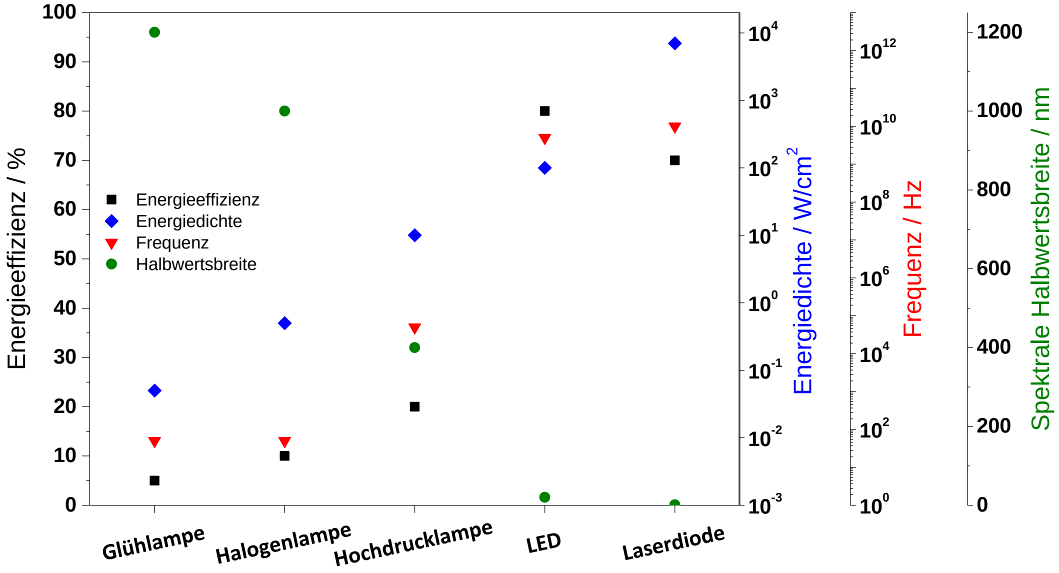
3. Data transmission

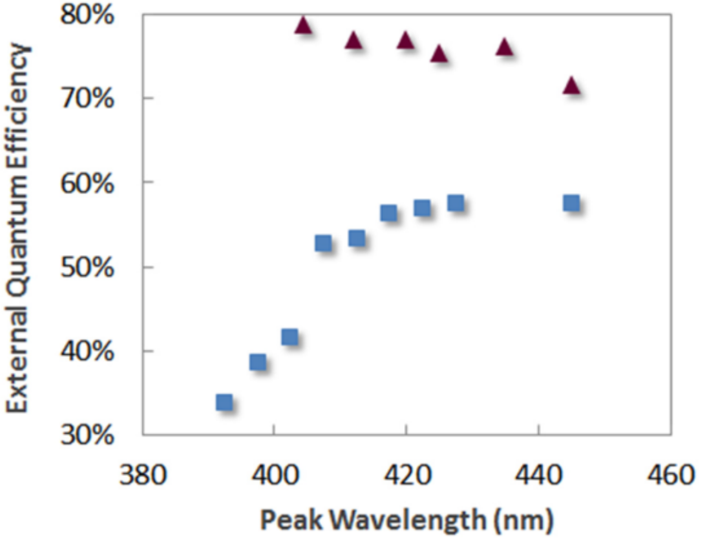
Local NIR LAN
ns-phosphors
700 – 3000 nm

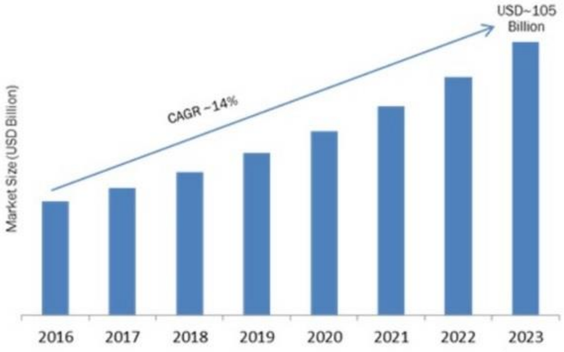
Wi-Fi	Li-Fi
10^9 Hz	10^{14} Hz
7 Gb/s	3 Tb/s

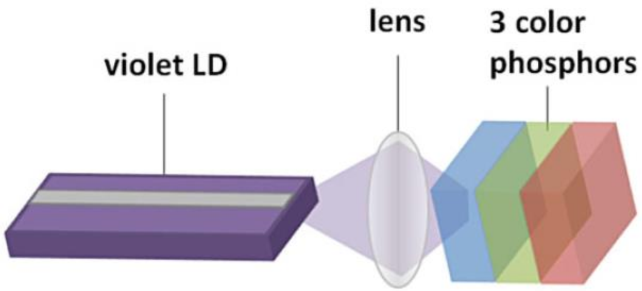
9.17 The Future of LED

(In,Ga)N LEDs and LDs are going to replace even high pressure discharge lamps









Lit.: C. Hurni et al., Applied Physics Letters 106, 031101 (2015)

9.17 The Future of LED

(In,Ga)N LEDs and LDs are going to replace NIR and UV radiation sources

VIS LED + NIR Phosphors

Transition metal activated phosphors

- e.g. Mn^{4+}, Cr^{3+}, Cr^{4+}, or Cu^{2+}
- usually broad band emission
- relatively strong absorption due to spin-allowed 3d-3d transitions
- sometimes strong thermal quenching

Lanthanides

- e.g. Nd^{3+}, Ho^{3+}, Er^{3+}, or Yb^{3+}
- show solely line emission
- very weak absorption due to spin- and parity-forbidden 4f-4f transitions
- usually higher thermal stability

Activator	$\lambda_{em,max}$	Typical host materials
Mn^{4+}	730 nm	$SrLaAlO_4$, $CaLaMgSbO_6$, perovskites
Mn^{6+}	1100 nm	$BaSO_4$
Cr^{3+}	850 nm	$Sr_8MgLa(PO_4)_7$, garnets, borates
Cr^{4+}	1250 nm	Mg_2SiO_4
Cu^{2+}	910 nm	$(Ca,Sr,Ba)CuSi_4O_{10}$
Ni^{2+}	1600 nm	$KMgF_3$
Co^{2+}	3200 nm	ZnSe
Eu^{2+}	840 nm	$Ca_3Sc_2Si_3O_{12}$
Nd^{3+}	1060 nm	$(Y,Gd,Lu)_3(Al,Sc,Ga)_2Al_3O_{12}$, $LiLnW_2O_8$
Ho^{3+}	2280 nm	$(Y,Gd,Lu)_3(Al,Sc,Ga)_2Al_3O_{12}$, $LiLnW_2O_8$
Er^{3+}	1550 nm	$(Y,Gd,Lu)_3(Al,Sc,Ga)_2Al_3O_{12}$, $LiLnW_2O_8$
Yb^{3+}	980 nm	$(Y,Gd,Lu)_3(Al,Sc,Ga)_2Al_3O_{12}$, $LiLnW_2O_8$

Deep UV LED + UV-A/B/C Phosphors → Chapter 12