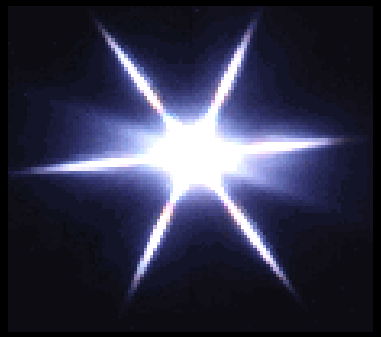
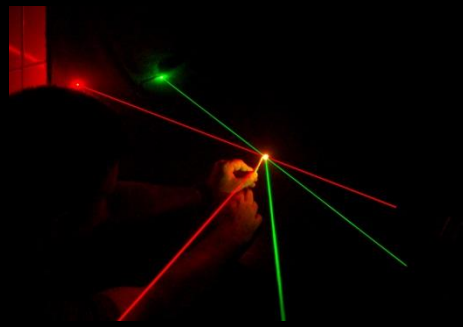
Luminescent Materials for Sophisticated Operation Conditions

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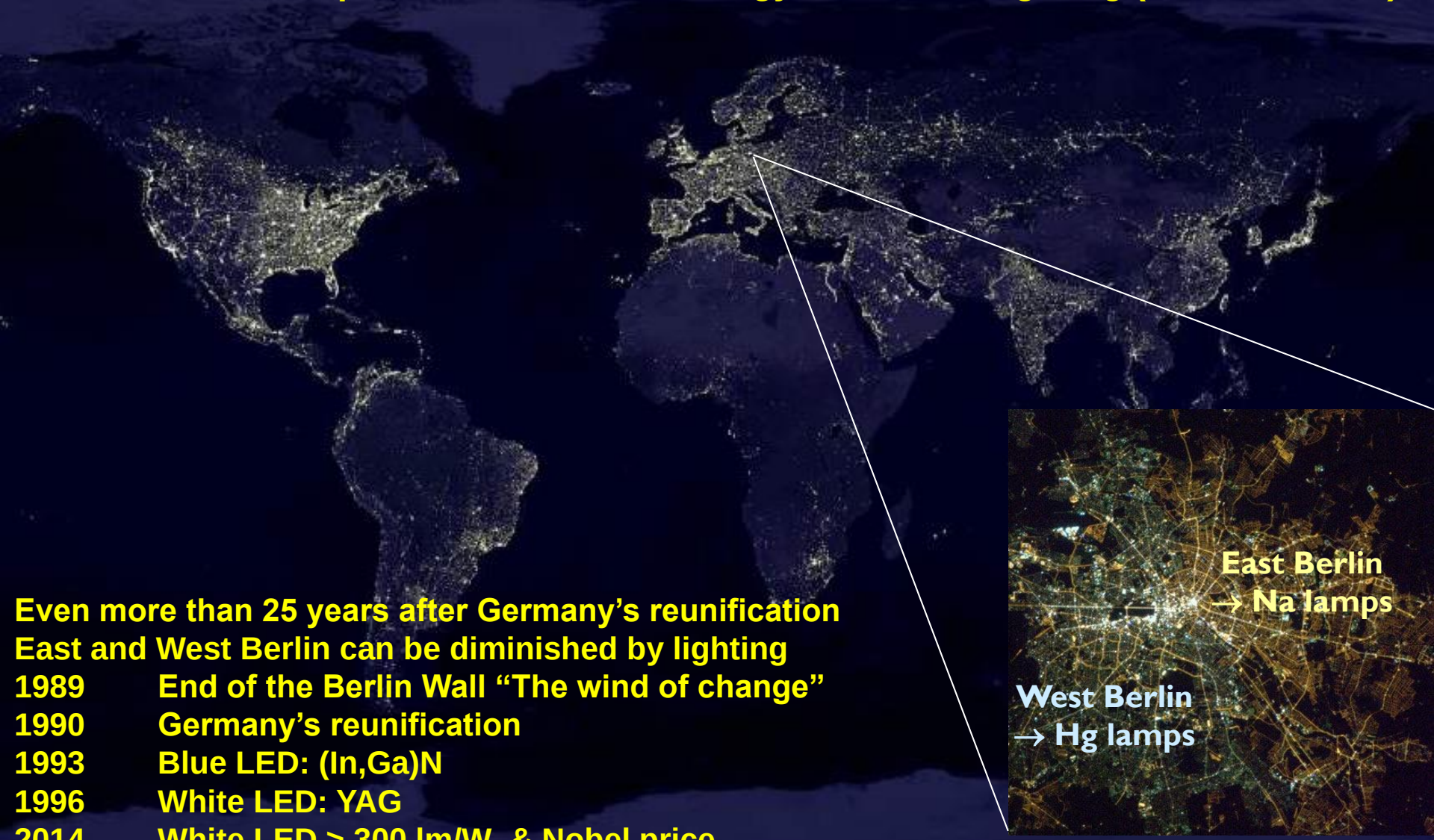
Münster Univ. of Applied Sciences

University Wuppertal
@ January 15th, 2018

About 20% of the produced electrical energy is used for lighting (source: NASA)



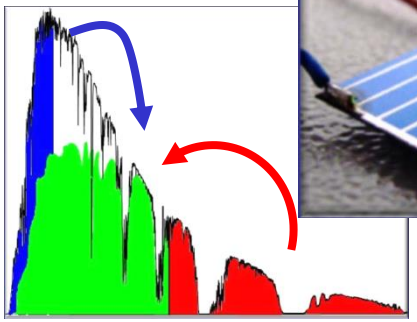
Even more than 25 years after Germany's reunification
East and West Berlin can be diminished by lighting

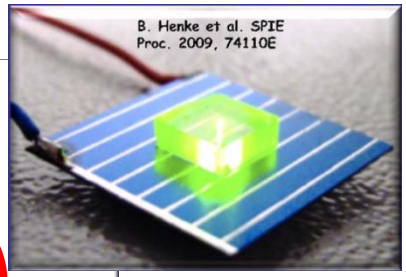
1989	End of the Berlin Wall "The wind of change"
1990	Germany's reunification
1993	Blue LED: (In,Ga)N
1996	White LED: YAG
2014	White LED > 300 lm/W & Nobel price
2016	LED dominates lighting business "The light of change"

Luminescent Materials - Almost Everywhere

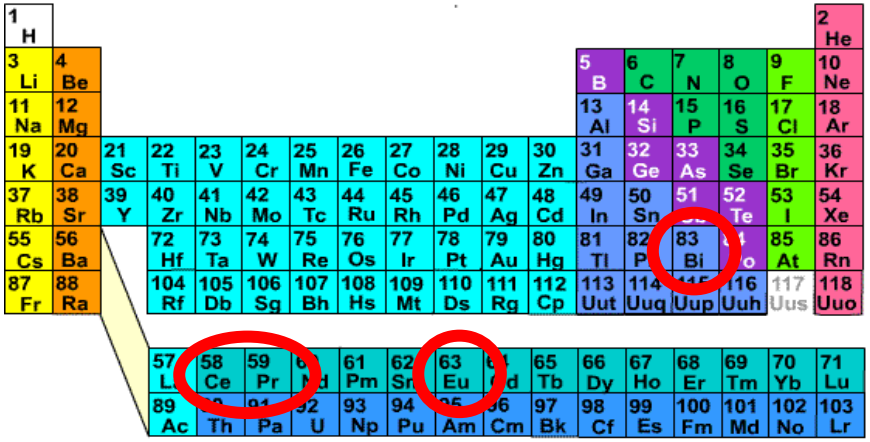
Optical brightening	Paint, pulp and paper, washing powder
Product anticounter feiting	Bills, stamps, credit cards, tickets, etc.
Advertisement illumination	Ne discharge lamps
Emergency illumination	Emergency exits and signs, runways
Medical imaging and treatment	x-ray converter films, scintillator crystals Psoriasis and jaundice treatment Dental ceramics
Astronomy	EUV/VUV-Amplifier
Biochemistry	Labels for DNA, RNA, proteins
Solar Cells	Down-Shifter Down-Converter Up-Converter
Telecommunication	NIR Amplifier
High energy physics	Scintillator crystals, neutron detectors, …

INTERNATIONAL YEAR OF LIGHT 2015





Outline



1. Motivation
2. Chemistry and Physics of LMs
3. LMs for High Power LEDs
4. VUV to UV Converter for Xe excimer lamps
5. Nanoscale UV Phosphors
6. Summary
7. Outlook
8. Literature

1. Motivation

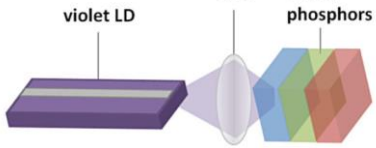
Increasing requirements on the performance of lamps and displays results in higher wall load, luminescent screen temperature, linearity, …

Miniaturisation of fluorescent light sources

- Lamp temperature depends on lamp diameter
  - TL 36 mm 40 °C
  - TL 13 mm 60 °C
  - PL types 70 – 80 °C
  - CFL 90 – 110 °C
  - CFL "GLS look-a-like" 100 – 160 °C
  - QL 200 – 250 °C
- Quantum yield decreases with increasing temperature
- Excitation and emission spectra shift and broaden with increasing temperature

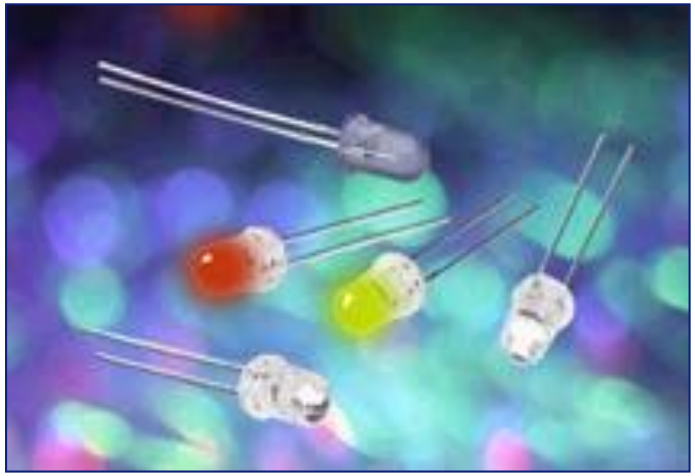
Higher resolution and image quality of emissive displays

- Reduction of particle size distribution (PSD)
- Reduction of decay time to enhance linearity (fps↑)
- Narrow band green and red to enlarge colour gamut
- Increase (photothermal)stability for laser projection displays

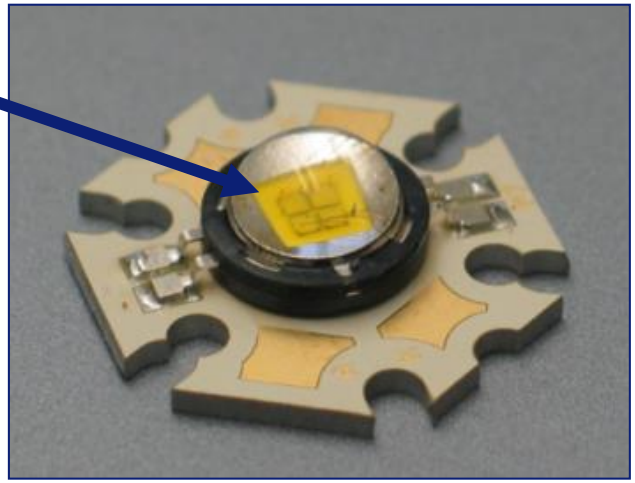


1. Motivation

Tremendous advances in LED technology (2nd semiconductor revolution)

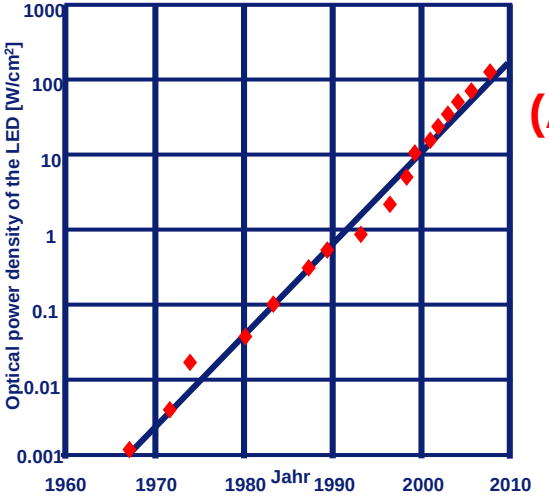


Luminescent screen



1970

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



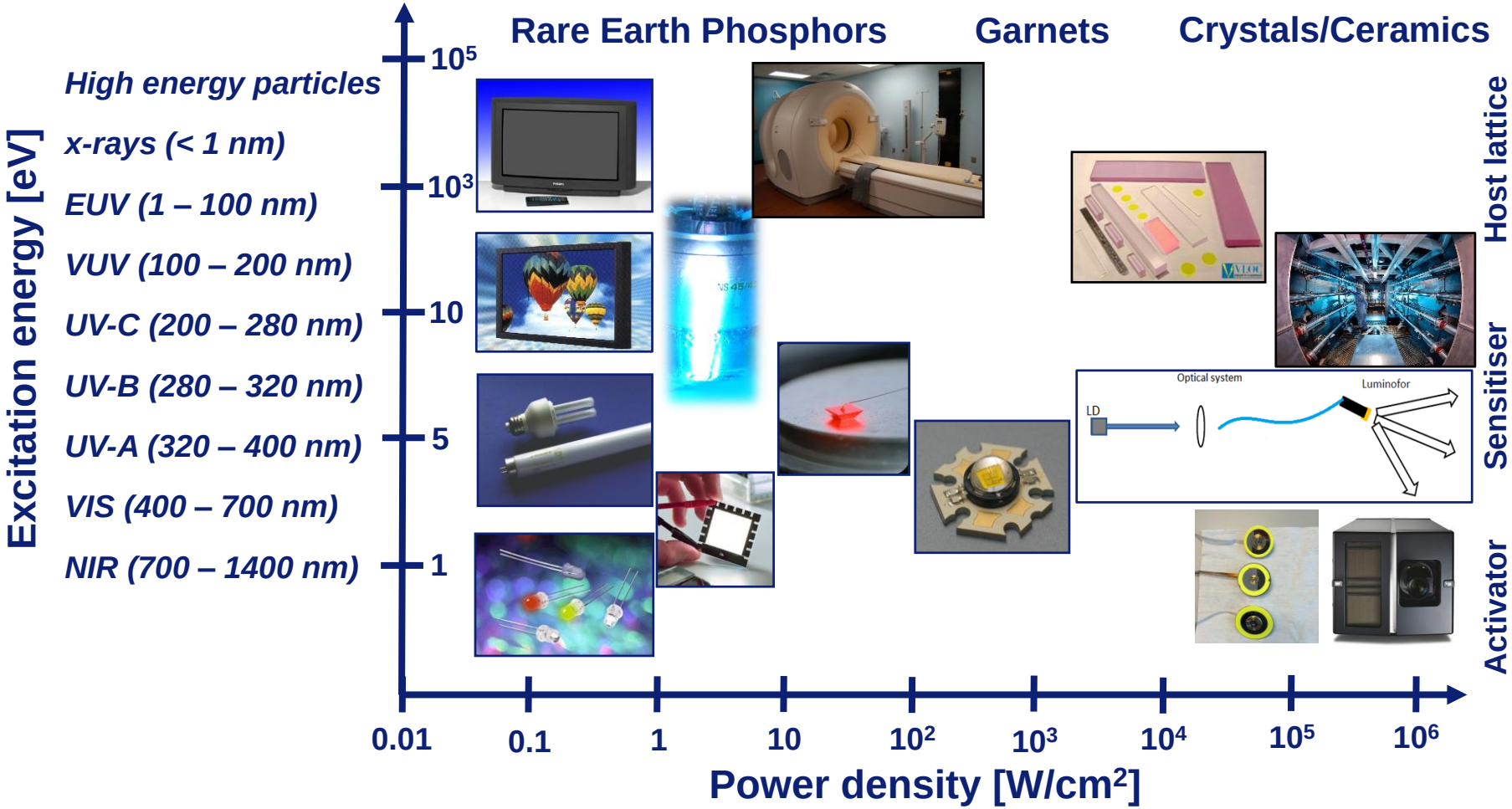
Development of the optical power density of LED light sources (source: fairchildsemi.com)

2018

(Al,In,Ga)P, (In,Ga)N, (Al,Ga)N
1 - 10 W
> 100 lm
up to 303 lm/W
120 – 200 °C
100 – 200 W/cm²
2 – 12 K/W
UV-A/B/C, all colors, NIR

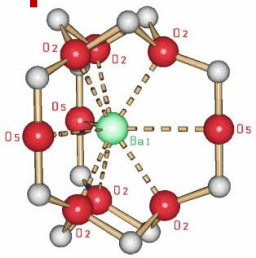
1. Motivation

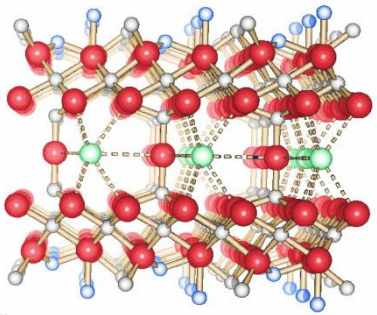
Increase of energy density drives search for novel materials



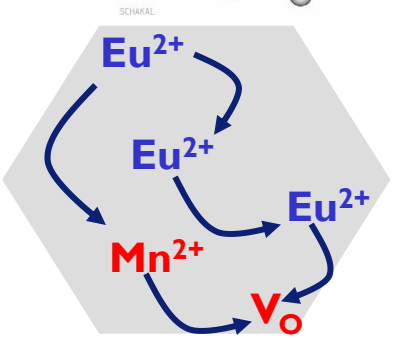
2. Chemistry and Physics of LMs

A luminescent material (phosphor) converts absorbed energy into electromagnetic radiation beyond thermal equilibrium

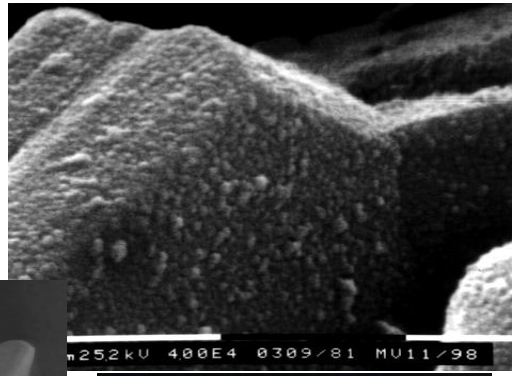




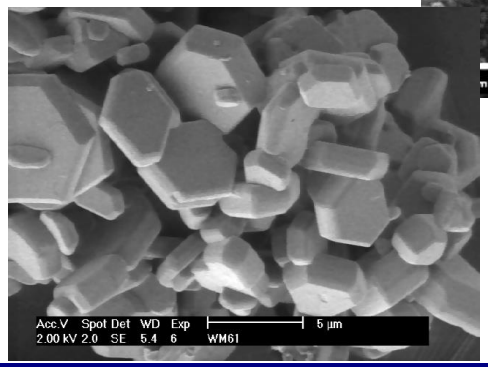
Host
- Coordination number and geometry
- Symmetry of activator sites
- Optical band gap
- Phonon spectrum



Dopants, impurities, and defects
- Concentration
- Phase diagram and miscibility gaps



Particle surface
- Zeta-potential
- Surface area
- Coatings → Light in- and outcoupling



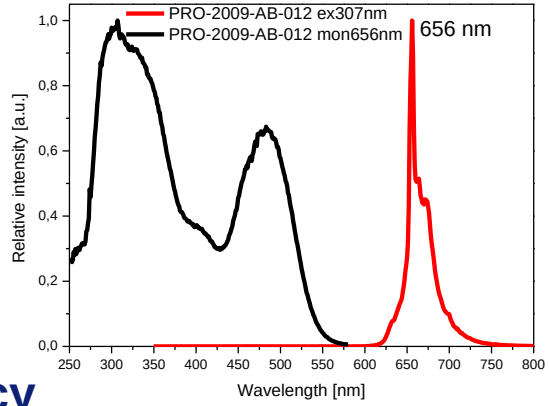
Particle morphology
- Shape
- Particle size distribution

2. Chemistry and Physics of LMs

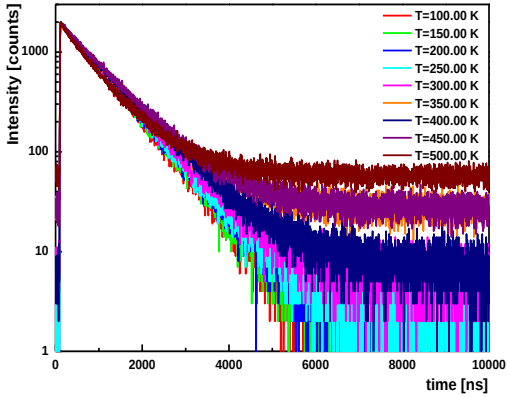
Relevant physical properties

- PL spectra
- CIE colour point
- Luminous efficacy
- Quantum yield (QY)
- Colour point consistency
- Decay curve
- Thermal quenching
- Linearity
- Photochemical stability

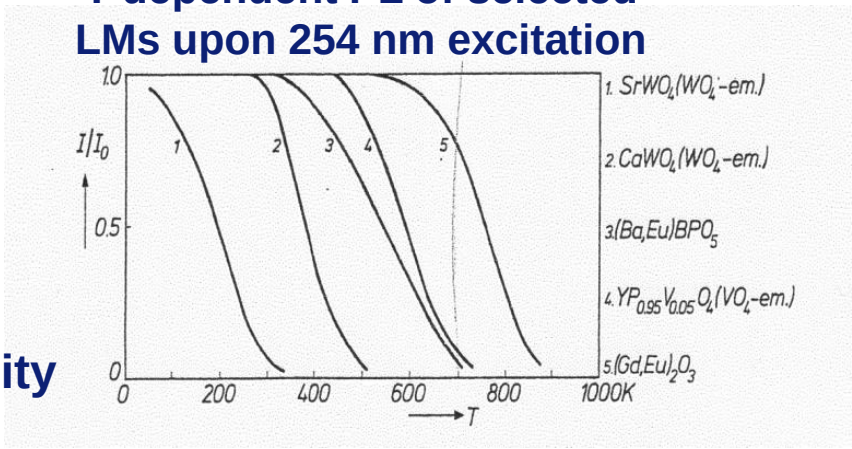
Excitation and emission spectrum of Mg_2TiO_4:Mn



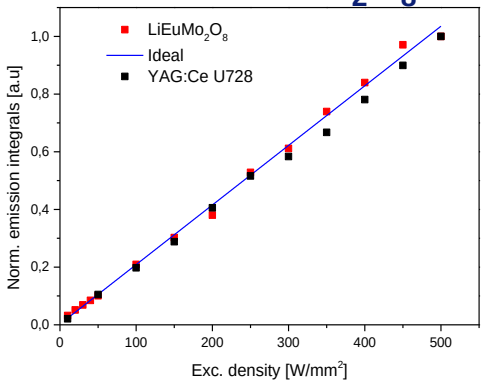
Decay curves of $SrSi_2N_2O_2$:Eu



T-dependent PL of selected LMs upon 254 nm excitation

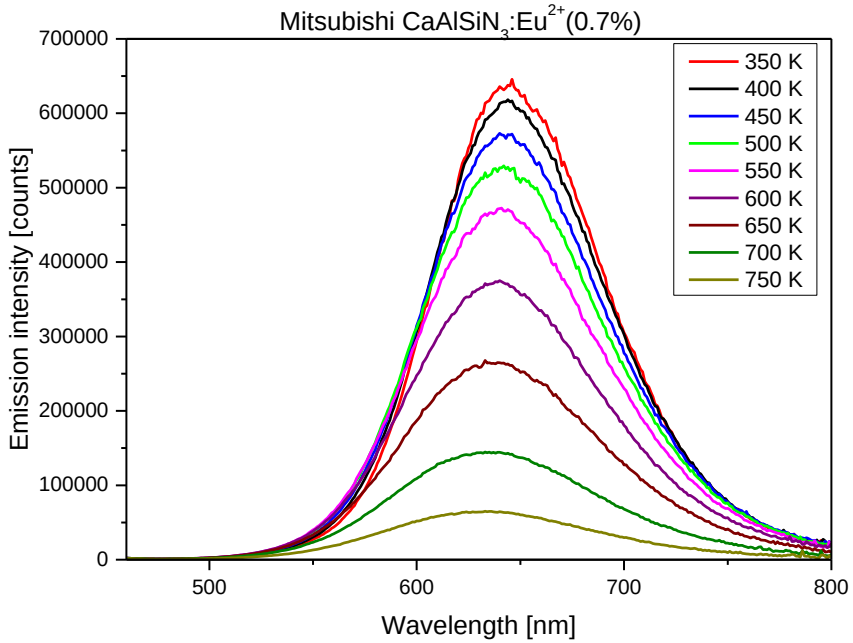


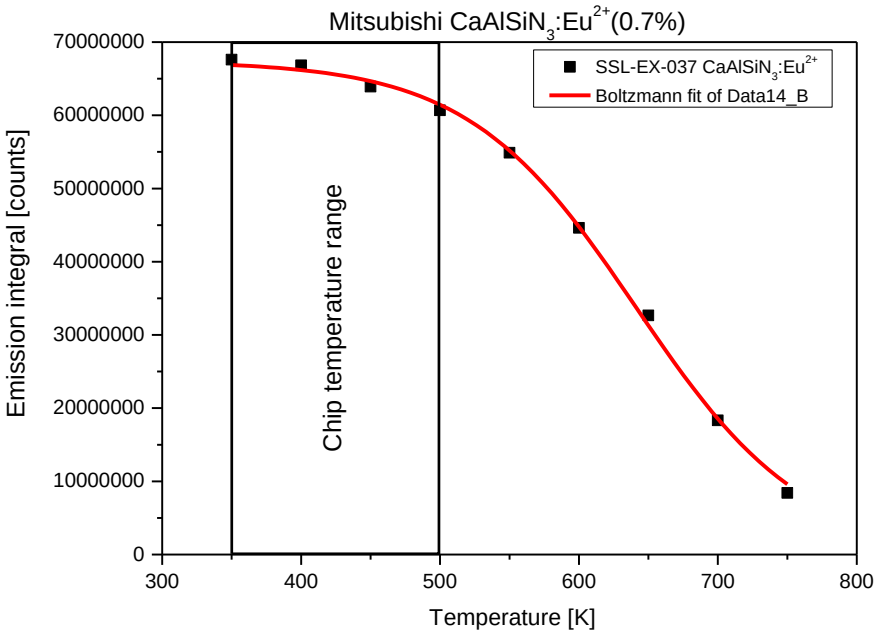
Linearity of YAG:Ce and $LiEuMo_2O_8$



2. Chemistry and Physics of LMs

Thermal quenching of the red emitting LED converter $CaAlSiN_3:Eu^{2+}$





Luminescent materials show a reduction of the photoluminescent quantum yield and a colour point shift with increasing temperature

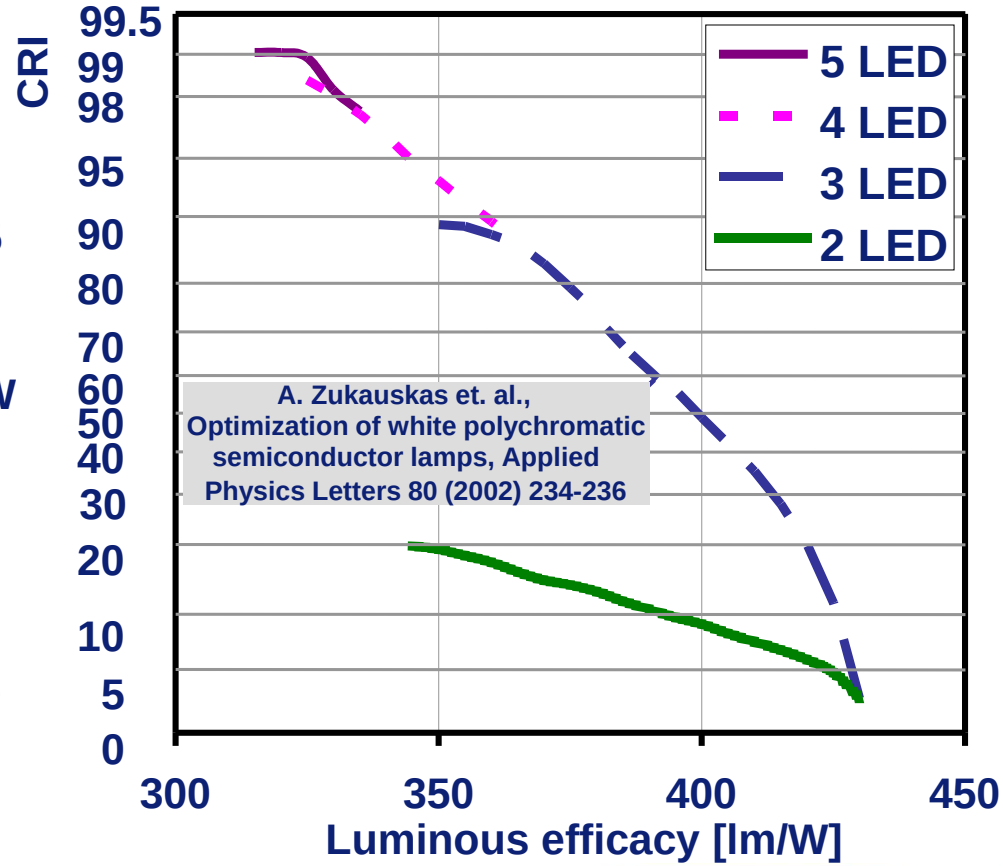
$T_{1/2}(CaAlSiN_3:Eu) \sim 650$ K (~ 380 °C)

$T_{1/2}$ depends on chemical composition → Stokes Shift, band gap and distance of the excited state to the conduction band edge, phonon spectrum and so on

3. LMs for High Power LEDs

Multichip LED Lamps

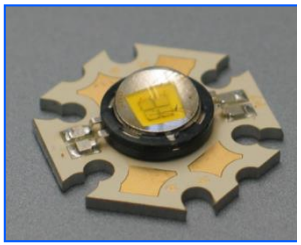
- Narrow band emitter e.g. LEDs
  - $\lambda_{1/2}$ = 30 nm
  - Several visible LED types n = 2 - 5
- Theoretical maximum, n = 2
  - Luminous efficacy (LE) = 430 lm/W
  - Corr. colour temp. (CCT) = 4870 K
  - Colour rendering index (CRI) = 3
- Practical values
  - LE ~ 350 lm/W for CRI 90, n = 3 - 4
  - LE_{max} ~ 320 lm/W for CRI 99, n = 5

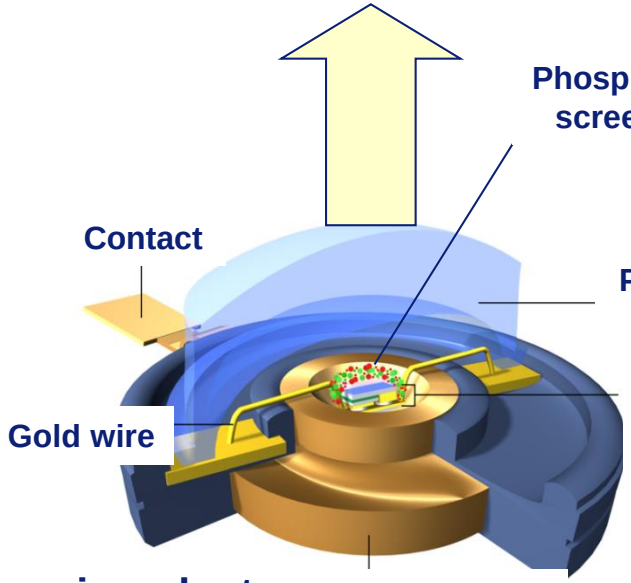


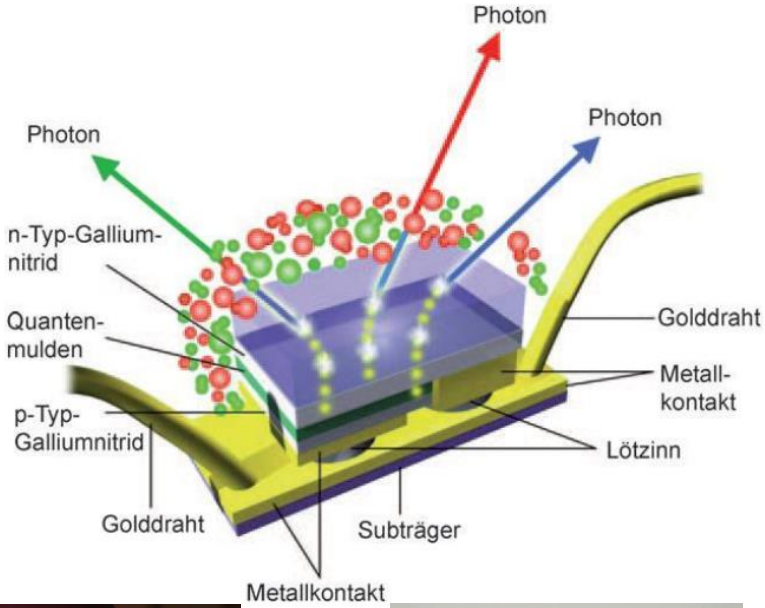
- Problems
  - Thermal quenching of EL and LE lifetime = f(semiconductor)
  - LED efficiency
    - Red and blue high
    - Green and yellow moderate → Luminescent materials

3. LMs for High Power LEDs

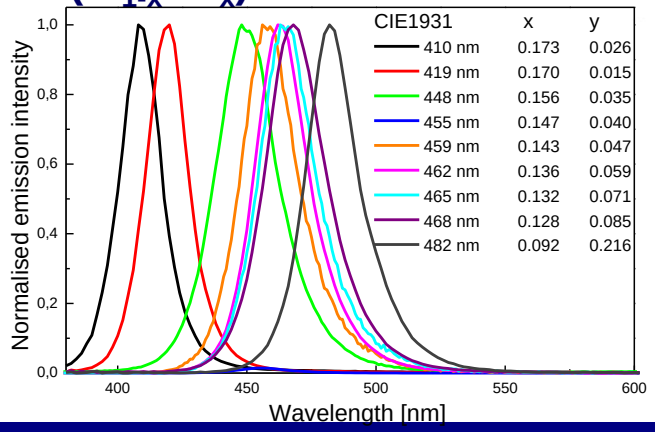
"Phosphor Converted" (pc) LED

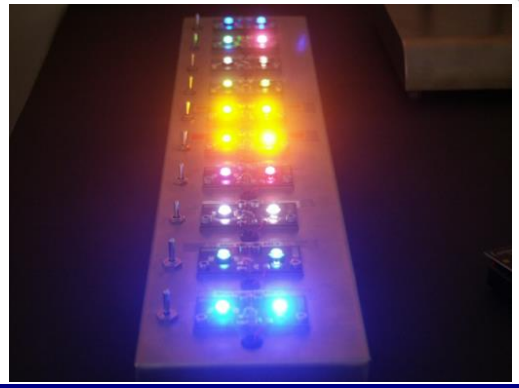


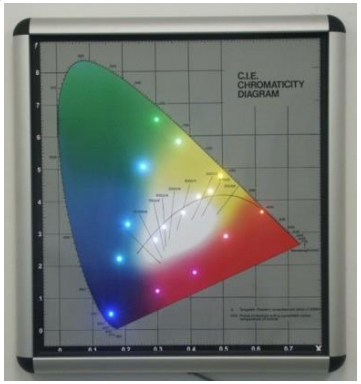




$(In_{1-x}Ga_x)N$ semiconductor







3. LMs for High Power LEDs

Micropowders or Ceramics

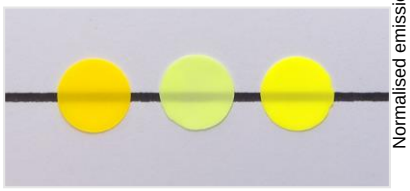
Aluminates → Ce^{3+}

$(Y,Gd,Tb)_3Al_5O_{12}$:Ce

$Lu_3(Ga,Al)_5O_{12}$:Ce

Sulphides → Eu^{2+}

(Ca,Sr)S:Eu

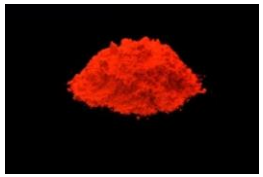


Oxides → Eu^{2+} or Ce^{3+}

$CaSc_2O_4$:Ce,Mg

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

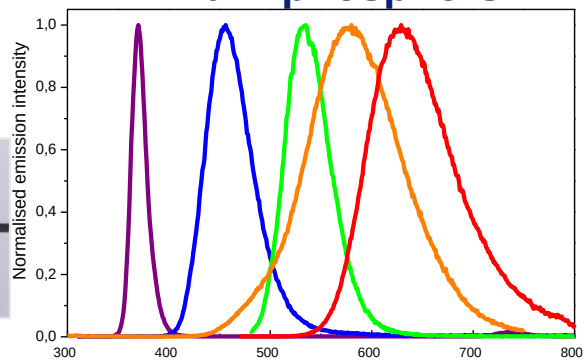
$(Ca,Sr,Ba)_3SiO_5$:Ce

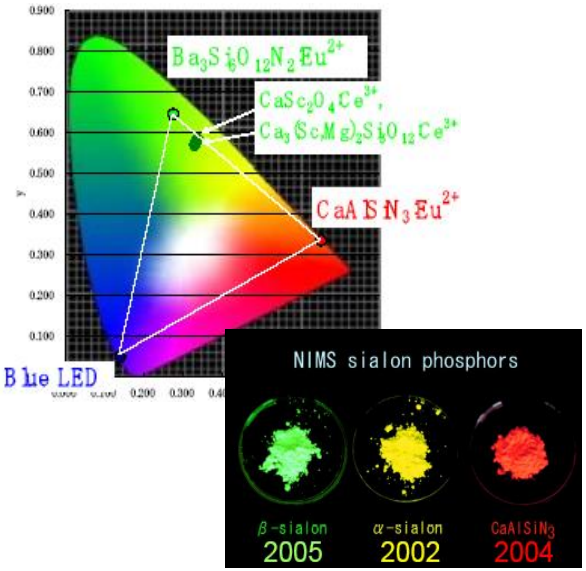


(Oxy)Nitrides → Eu^{2+} or Ce^{3+}

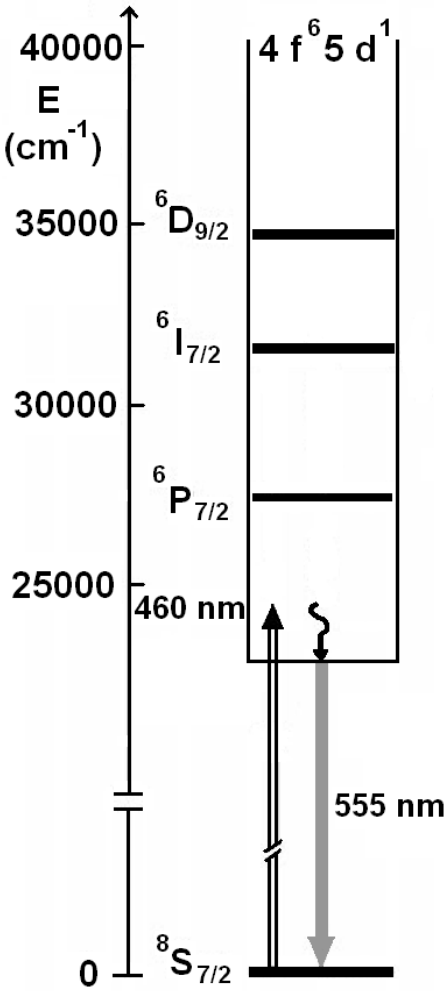
$(Sr,Ca,Ba)_2Si_5N_8$:Eu	„2-5-8“
$(Sr,Ca,Ba)Si_2N_2O_2$:Eu	„1-2-2-2“
(Ca,Sr)$AlSiN_3$:Eu	„1-1-1-3“
$La_3Si_6N_{11}$:Ce	„3-6-11“
$Ba_3Si_6O_{12}N_2$:Eu	
α,ß-$Si_{3-x}Al_xN_{4-x}O_x$:Eu	SiAlON

Typical spectra of Eu^{2+} phosphors





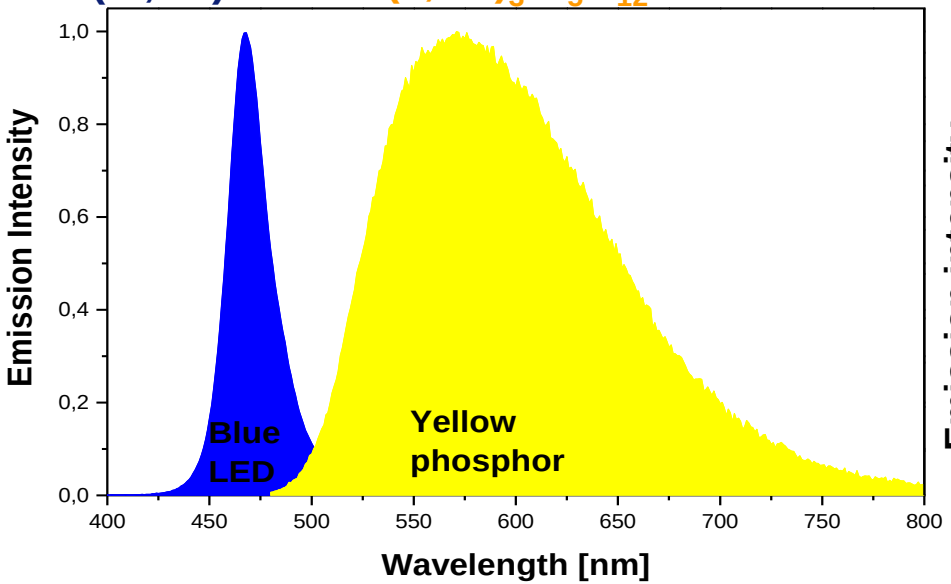
Simplified energy level scheme of Eu^{2+}

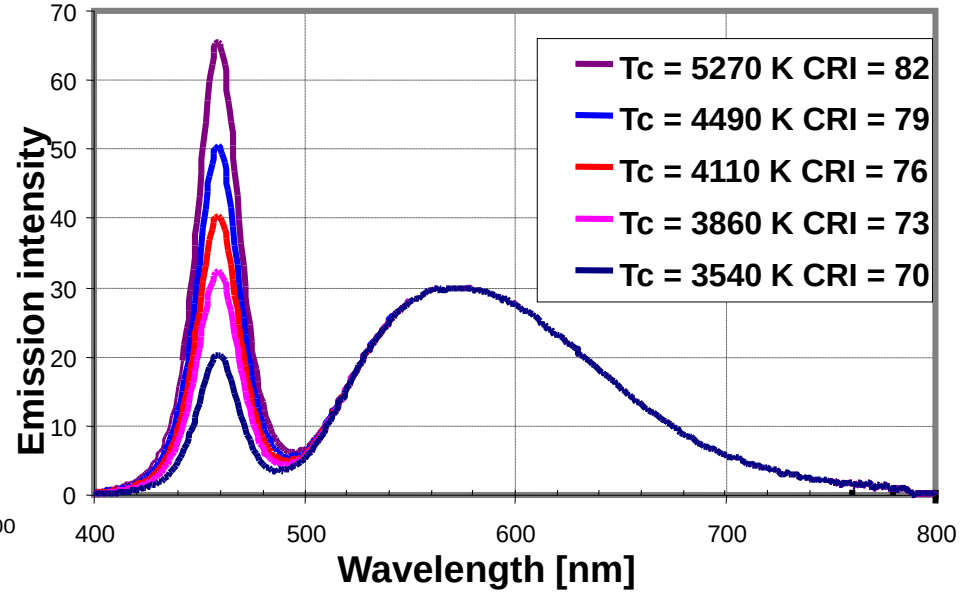


3. LMs for High Power LEDs

1st Generation pcLEDs: Wall Plug efficiency (WPE) >> Discharge lamps

(In,Ga)N LED $(Y,Gd)_3Al_5O_{12}$:Ce





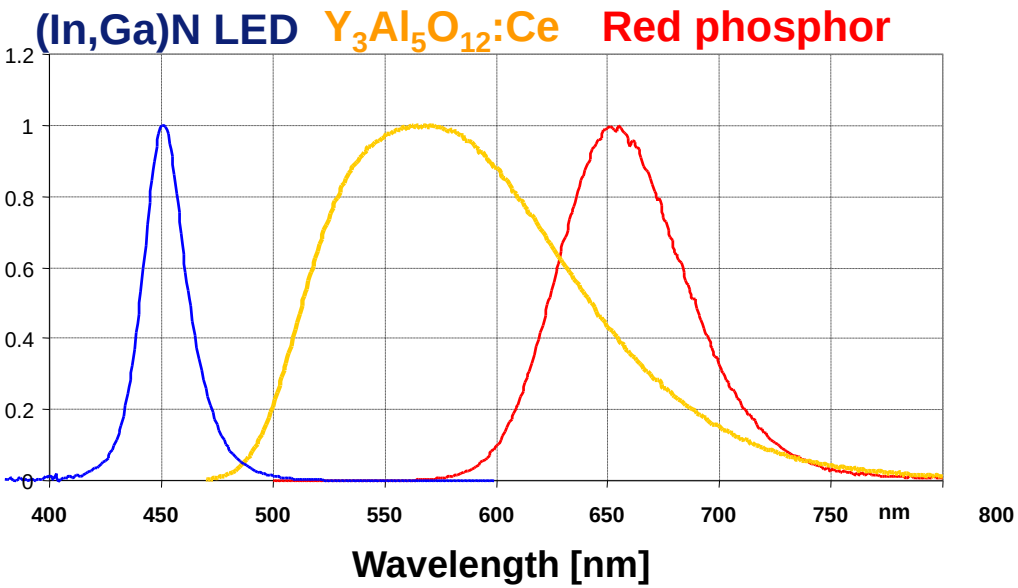
Status quo cool white phosphor converted LEDs @ 2018

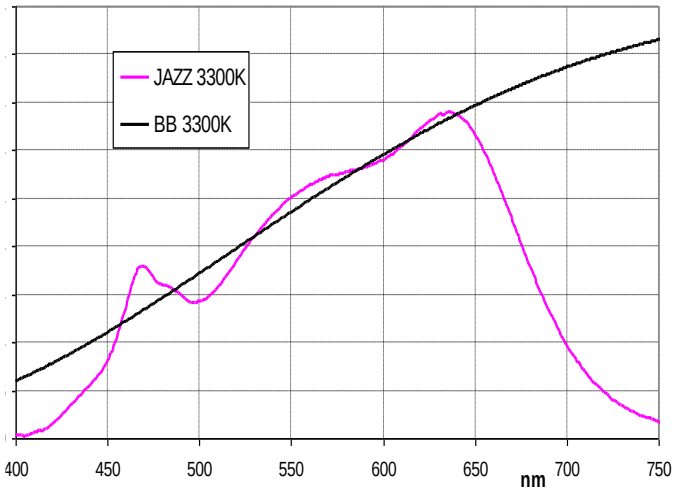
- Yellow phosphors garnets: $(Y,Gd,Tb)_3Al_5O_{12}:Ce^{3+}$
  ortho-silicates: $(Ca,Sr,Ba)_2SiO_4:Eu^{2+}$
- LE 300 lm/W (WPE > 80%)
- CRI 70 - 80
- CCT > 5000 K

Element	Y	Gd	Ce	Al	O	$(Y_{0,77}Gd_{0,2}Ce_{0,03})_3Al_5O_{12}$
Molar Mass (g/mol)	88,91	157,25	140,12	26,98	16,0	639,243
Coefficient	2,31	0,6	0,09	5	12	
Mass fraction	32%	15%	2%	21%	30%	100%

3. LMs for High Power LEDs

2nd Generation pcLEDs: Enhancement of CRI and reduction of CCT





Status quo warm white phosphor converted LEDs @ 2018

- **Red phosphor** **Eu^{2+} activated**
- **LE 80 - 150 lm/W**
- **CRI 85 – 95**
- **CCT 2500 - 4000 K**

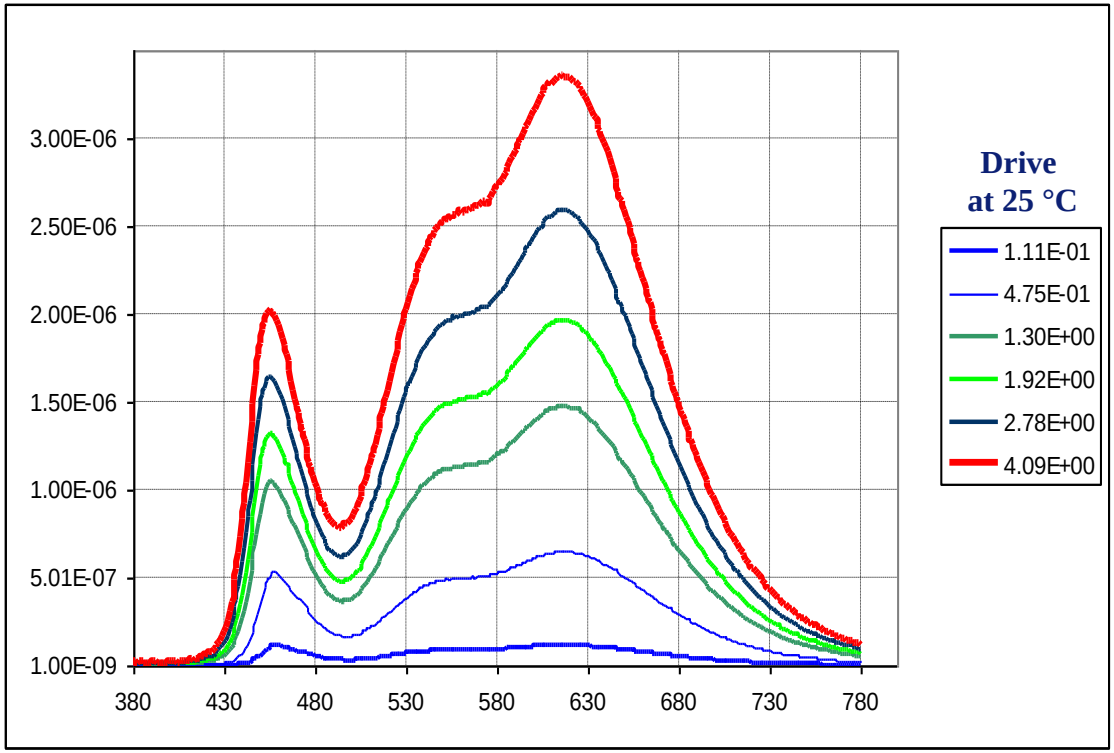
Phosphor	Molar Mass (g/mol)	Coeffi-cient for Eu^{2+}	Mass fraction Eu^{2+}
$Ca_{0,5}Sr_{0,45}Eu_{0,05}S$	99,14	0,05	8%
$(Sr_{0,95}Eu_{0,05})_2Si_5N_8$	434,12	0,1	4%
$Ca_{0,5}Sr_{0,45}Eu_{0,05}AlSiN_3$	168,14	0,05	5%

R. Mueller-Mach, G.O. Mueller, P.J. Schmidt, T. Jüstel, Red Deficiency Compensating Phosphor LED, Light Emitting Device, US Patent 2003/0006702

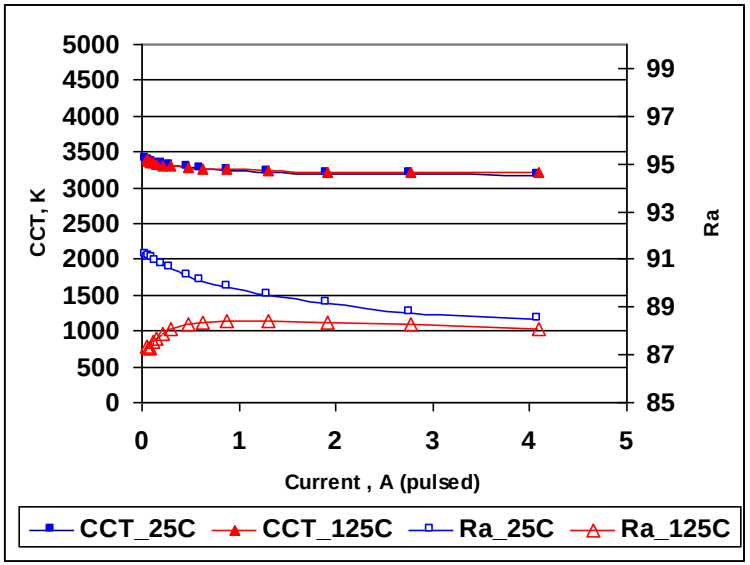
3. LMs for High Power LEDs

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

(In,Ga)N LED + $SrSi_2N_2O_2$:Eu + $Sr_2Si_5N_8$:Eu or (Sr,Ca)$AlSiN_3$:Eu or $(Sr,Ca)_2SiO_4$:Eu

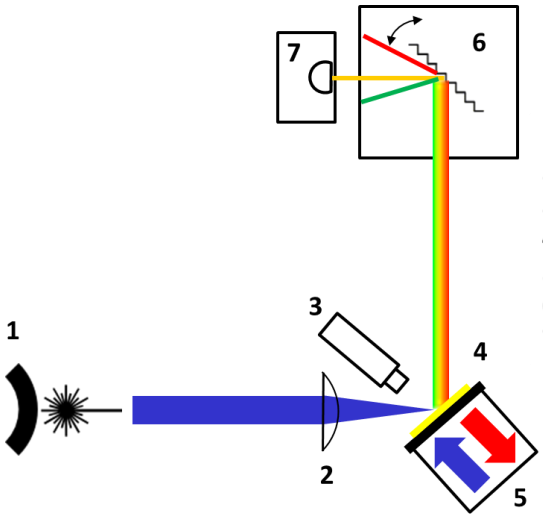


Colour rendering index CRI > 88
Excellent colour point consistency with drive is achieved



R. Mueller-Mach, G.O. Mueller, M.R. Krames, H.A. Höppe, F. Stadler, W.S. Schnick, T. Jüstel, P.J. Schmidt, Highly efficient all nitride phosphor converted white light emitting diode, Phys. Stat. Sol. A 202 (2005) 1727

3. LMs for High Power LEDs



1 - Laserdiode
2 - Fokussierlinse (Fleckdurchmeser: 11 µm)
3 - Infrarotkamera (7.5 … 14 µm)
4 - Probe
5 - Kühlung (Ag-Probenhalter)
6 - Emissionsmonochromator
7 - Detektor

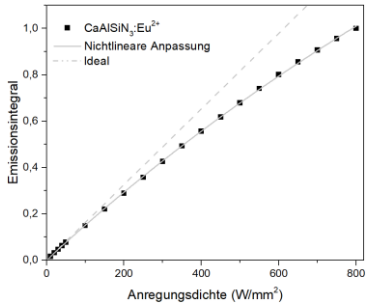
Saturation by photoioinsation

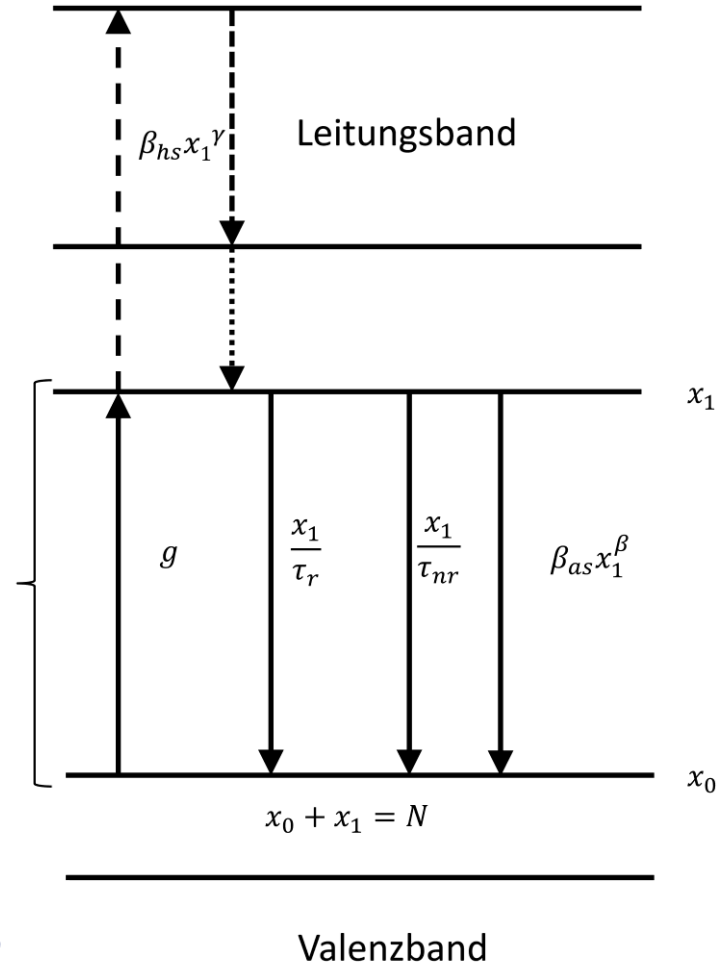
E_g

$(Sr_{1,6}Ca_{0,4})SiO_4:Eu^{2+}$

$(Ca,Sr)AlSiN_3:Eu^{2+}$

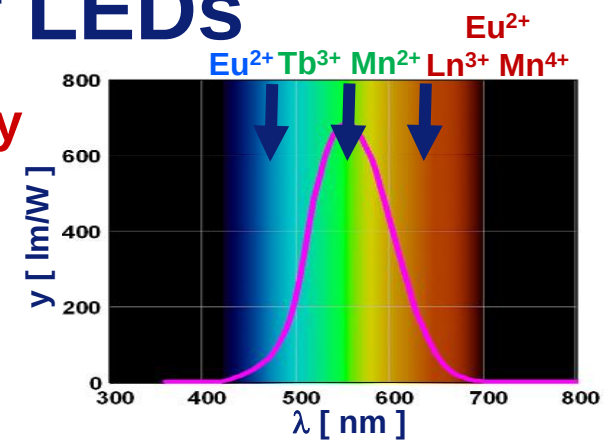
$(Sr,Ba)_2Si_5N_8:Eu^{2+}$





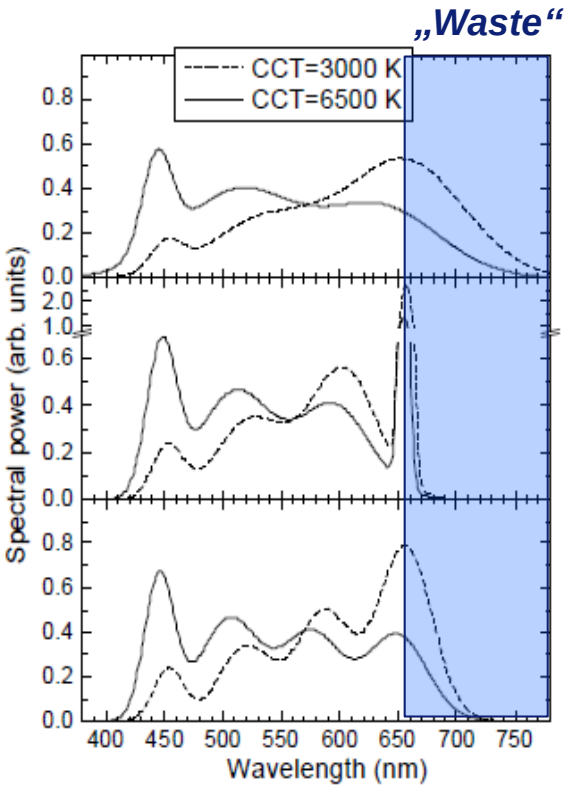
T. Jansen, D. Böhnisch, T. Jüstel, On the Photoluminescence Linearity of Eu^{2+} based LED Phosphors upon High Excitation Density, ECS J. Solid State Sci. Technol. 5 (2016) R91

3. LMs for High Power LEDs



Red band emitter cause reduction in lum. 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 = Eu, Sm, Pr) 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

3. LMs for High Power LEDs

Requirements to an „ideal“ LED phosphor

- Narrow FWHM ~ 20 - 60 nm
- Emission peak at ~ 630 nm
- QY (excitation at 450 nm) > 90%
- Absorption at 450 nm > 50%
- $T_{1/2}$ > 200 °C
- Decay time < 10 ms
- No saturation up to 100 W/mm^2 (good linearity)
- High (photo)chemical and thermal stability

Activator	Spectral range [nm]	Lumen equivalent [lm/W_{opt}]	Decay time τ	QY [%]	Absorption at 450 nm
RE-Ions					
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	weak
TM-Ions					
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

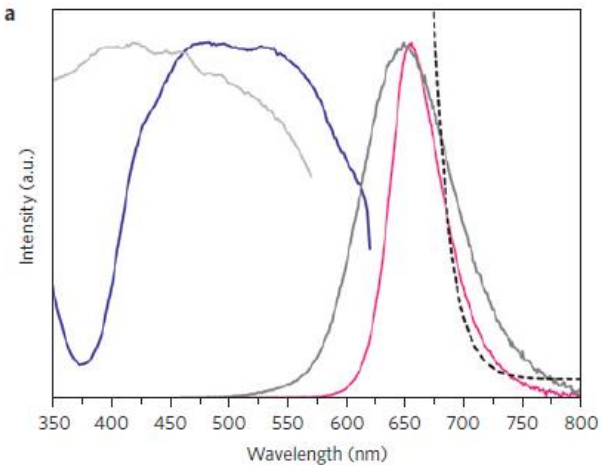
3. LMs for High Power LEDs

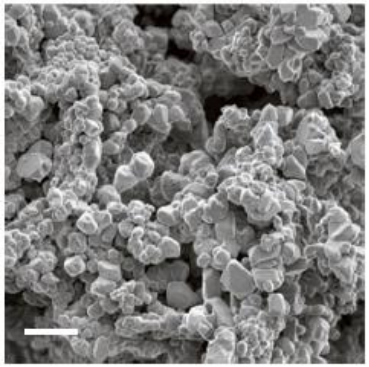
Narrow band red emitter $Sr[LiAl_3N_4]:Eu^{2+}$

Claimed as next generation LED-phosphor material"

Synthesis

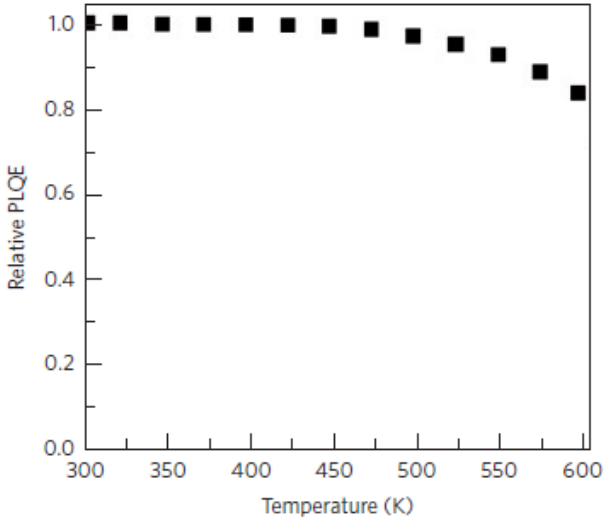
$LiAlH_4 + (1-x)\ SrH_2 + x\ EuF_3 + 2\ AlN + N_2$
$\rightarrow\ (Sr_{1-x}Eu_x)[LiAl_3N_4] + 3x\ HF + (3-x)\ H_2$
RF-Furnace, 1000 °C





Optical Properties

λ_{max} = 651 nm for 5% Eu^{2+}
FWHM = 1180 cm^{-1} (~ 60 nm)
QY(200 °C) > 95% rel. to QY(RT)
Decay time of Eu^{2+} ~ 1.1 µs



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

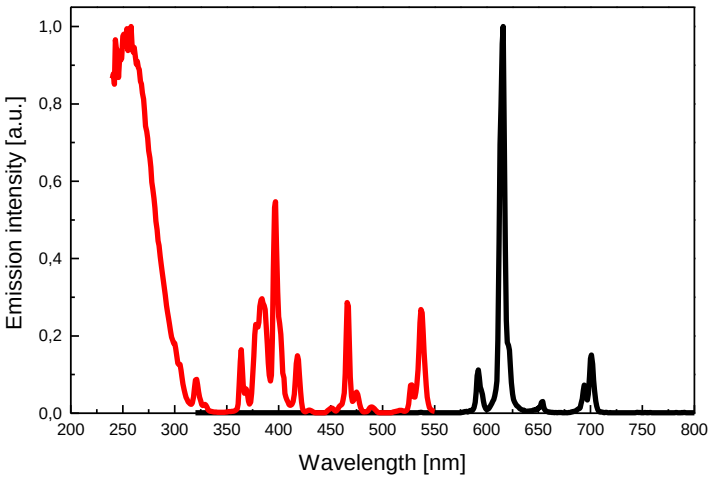
W.S. Schnick et al., Nature Materials (2014) 1-6

3. LMs for High Power LEDs

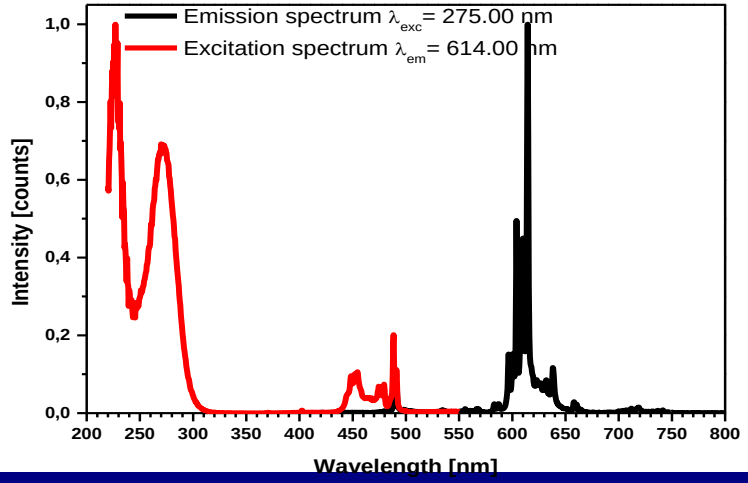
Remaining Options

Red emitter	LE [lm/$W_{opt.}$]	QY at RT
Eu^{3+}	220 – 360	high
Pr^{3+}	200 – 220	moderate
Mn^{4+}	20 – 200	high

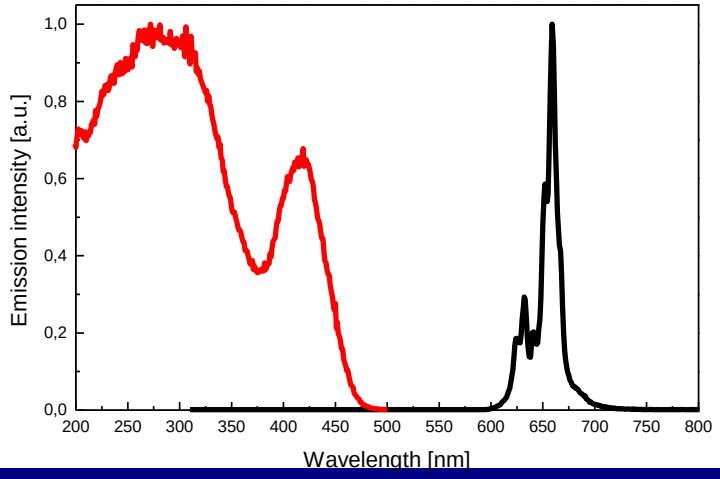
$La_2W_3O_{12}$:Eu



$LuTaO_4$:Pr



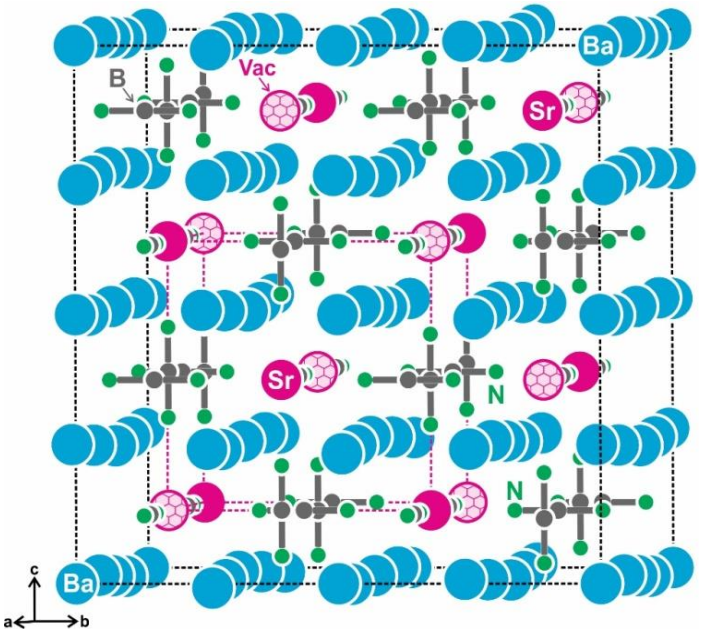
$Mg_4GeO_{5.5}F$:Mn

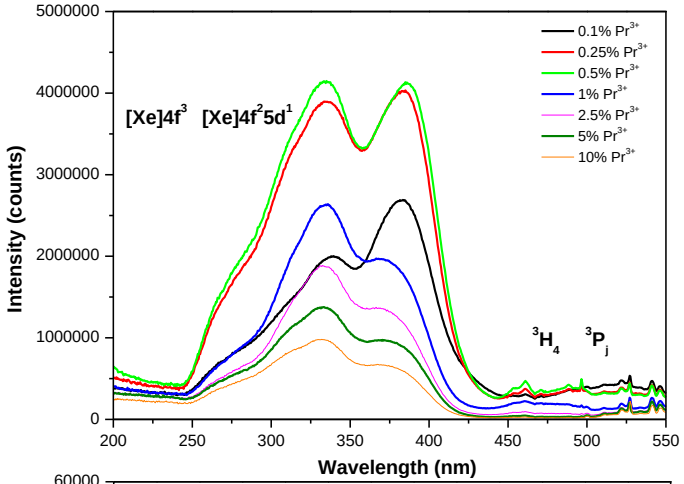


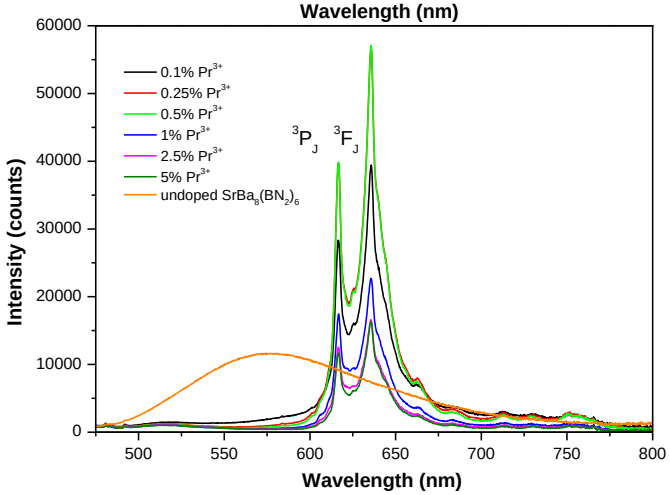
3. LMs for High Power LEDs

Red line emitter → Pr^{3+}

Example: $SrBa_8(BN_2)_6$
Space group Fd3m, Z = 8





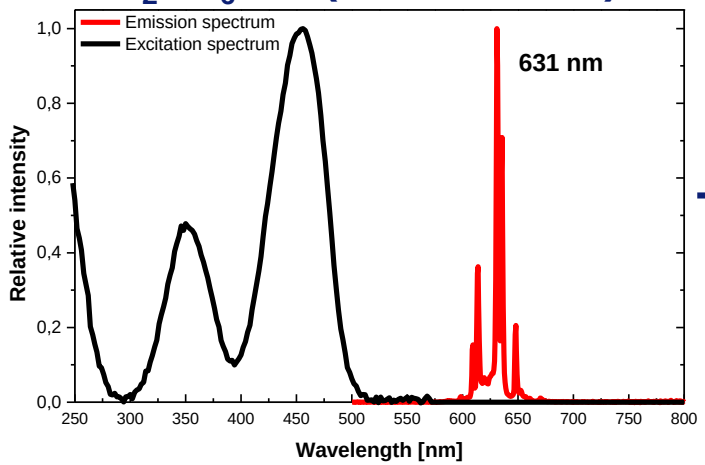


T. Dierkes, T. Jüstel, J. Luminescence 187 (2017) 513
T. Dierkes, S. Seidel, C. Benndorf, L. Heletta, M. de Oliveira Jr., M. Holtkamp, U. Karst, T. Block, T. Jüstel, H. Eckert, R. Poettgen,T. Jüstel, Solid State Science 70 (2017) 86

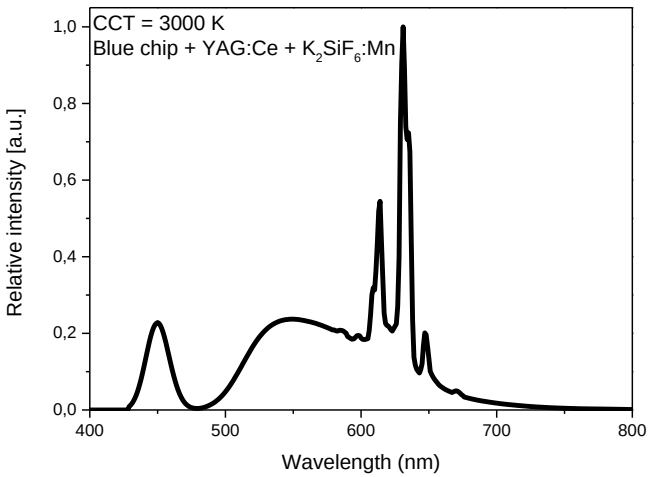
3. LMs for High Power LEDs

Red 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+}- phosphor**
Typical yellow/red blend	**$Tb_3Al_5O_{12}$:3%Ce + $K_2[MF_6]:Mn^{4+}$ (M = Si, Ge, Sn, Ti, Zr)**	
Problems	**Absorption strength, linearity, and stability of Mn^{4+}**	
	$MnF_4 \rightarrow MnF_3 + ½ F_2$	

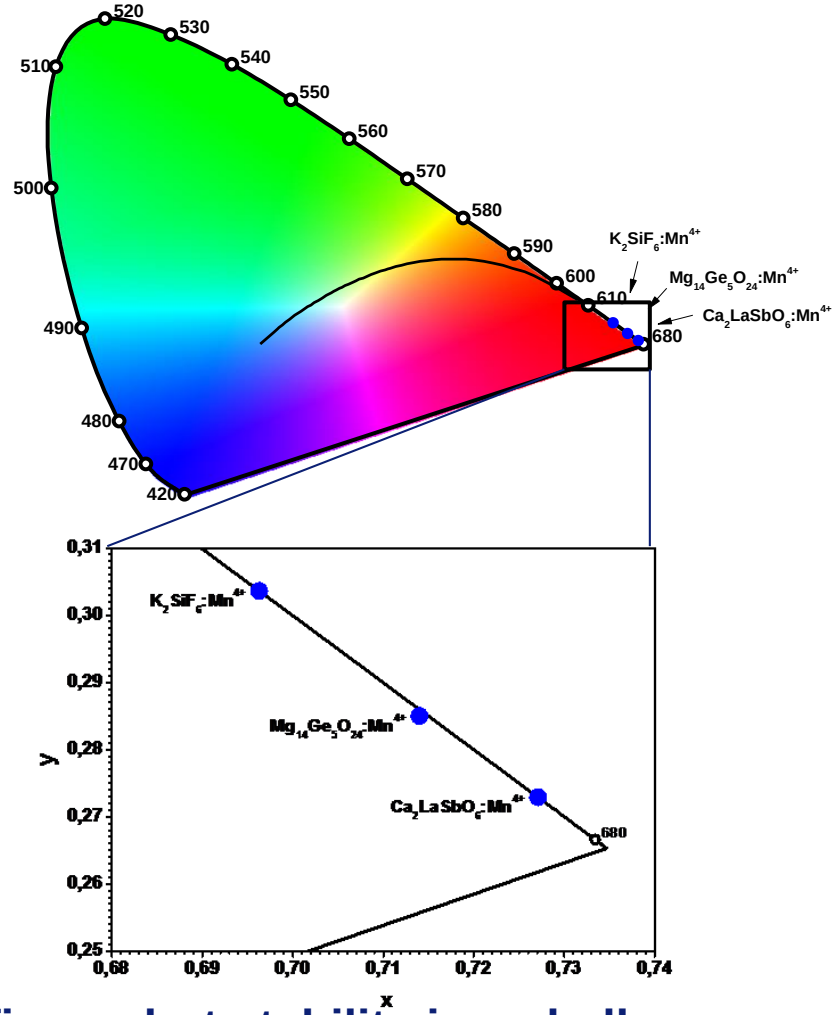
A. Srivastava et al., GE, US Patent US2006/0169998

3. LMs for High Power LEDs

Red line emitter → Mn^{4+}

Phosphor	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

**F. Baur, T. Jüstel, J. Luminescence 177 (2016) 354*

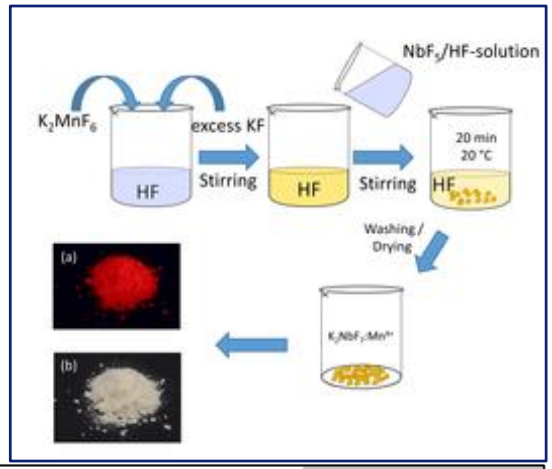


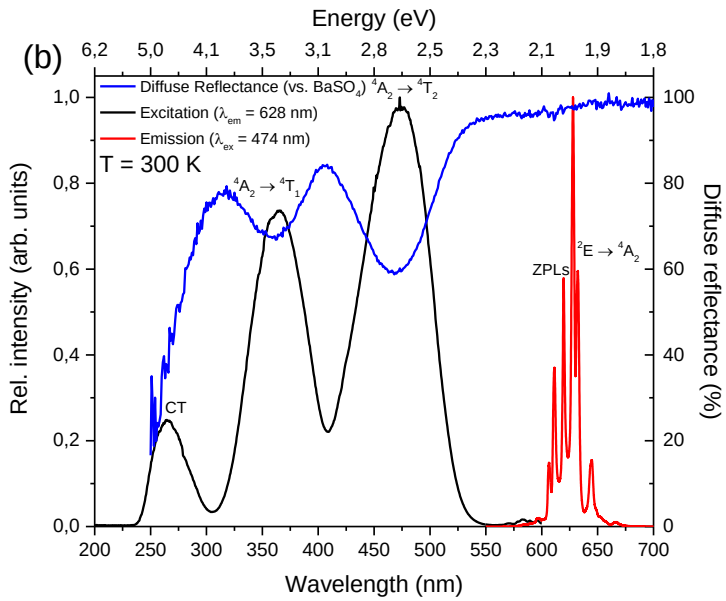
Fluorides → Rather high luminous efficacy, but stability is a challenge
Oxides → Very stable, but low luminous efficacy

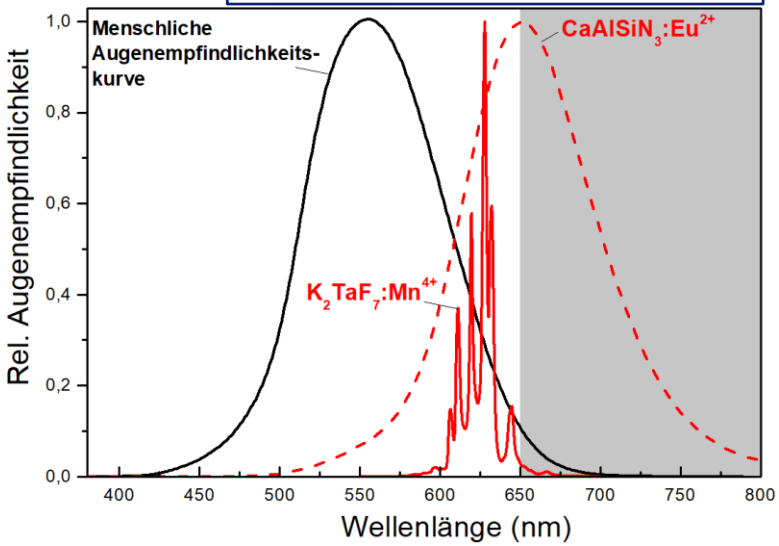
3. LMs for High Power LEDs

Red line emitter → $K_2(Nb,Ta)F_7:Mn^{4+}$

λ_{max} = 628 nm
LE = 228 lm/W
CIE1931: x = 0.690; y = 0.310





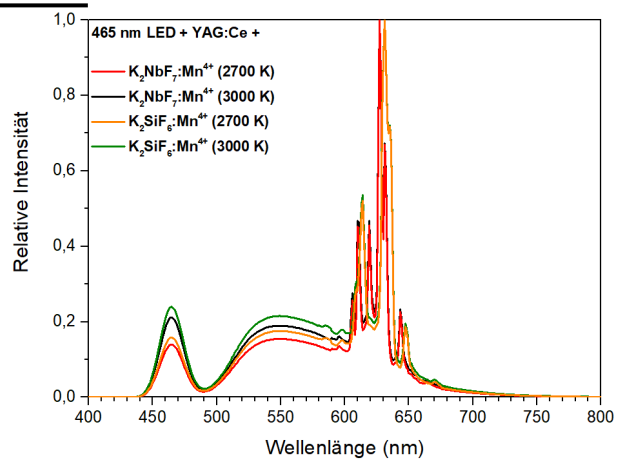


T. Jansen, F. Baur, T. Jüstel, Red Emitting $K_2NbF_7:Mn^{4+}$ and $K_2TaF_7:Mn^{4+}$ for Warm-White LED Applications, J. Luminescence 192 (2017) 644

3. LMs for High Power LEDs

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

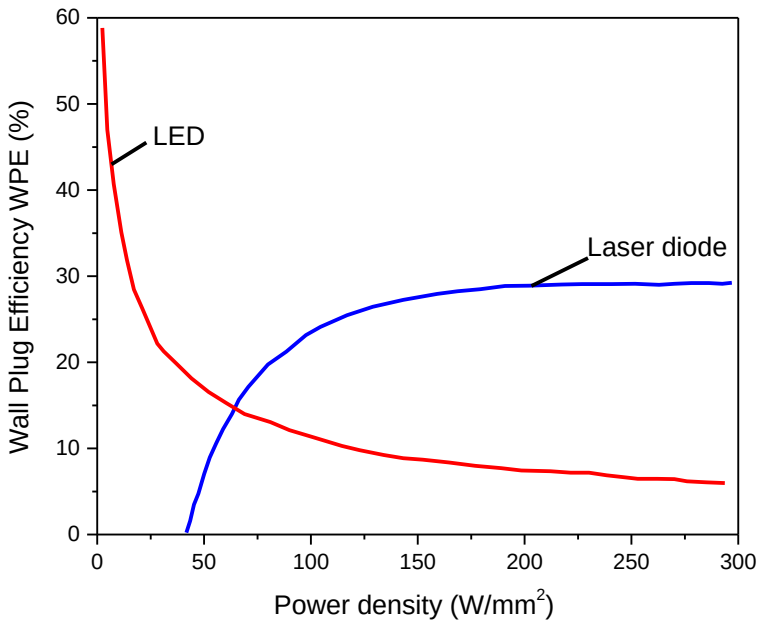
Blue LED + YAG:Ce +	CCT [K]	LE [lm/W_{opt}]	CRI
$K_2NbF_7:Mn^{4+}$	3000	346	95
	2700	345	95
$K_2TaF_7:Mn^{4+}$	3000	345	95
	2700	345	94
$Na_3AlF_6:Mn^{4+}$	3000	345	95
	2700	344	95
$K_2SiF_6:Mn^{4+}$	3000	339	95
	2700	297	95
$Mg_{14}Ge_5O_{24}:Mn^{4+}$	3000	254	83
	2700	241	78
$Y_2Mg_3Ge_3O_{12}:Mn^{4+}$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



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

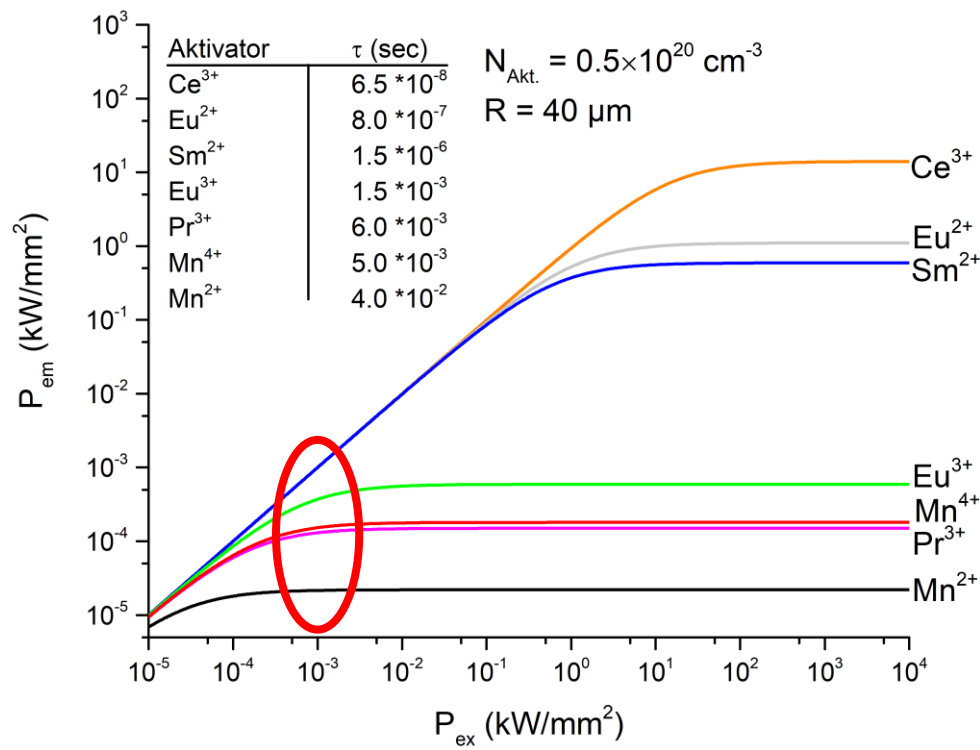
3. LMs for High Power LEDs

Red line emitter → Remaining problem: Saturation at ~ 1 W/mm²



Brils Modell*: $P_{em,max} = Nact\ E_{h\nu} C_{extraction}\ R/\tau_r$

$$\eta = \frac{P_{em}}{P_{abs}} = \frac{\eta_0}{1 + \left(P_{abs}\,\eta_0 / P_{em,max}\right)}$$

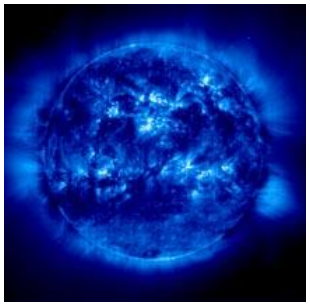
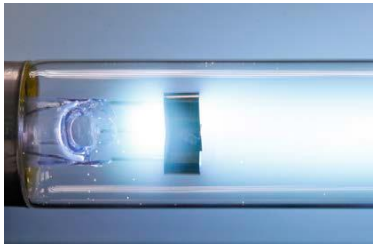
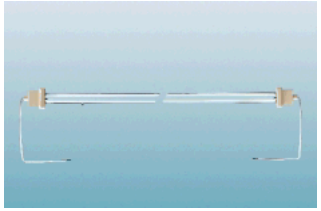


A. Bril, Physica 15 (1949) 361-379

4. VUV to UV Converter for Xe Excimer Lamps

Sources of UV Radiation

Solar radiation	**> 300 nm**
Hg discharge lamps	
low-pressure	**185, 254 nm**
amalgam	**185, 254 nm**
medium-pressure	**200 – 400 nm**
Xe discharge lamps	**230 – 800 nm**
D_2 discharge lamps	**110 – 400 nm**
Excimer laser	**193 nm**
Solid state laser Nd^{3+} 4th harmon.	**266 nm**
Excimer discharge lamps	
Xe_2*	**172 nm**
KrCl*	**222 nm**
XeBr*	**282 nm**
XeCl*	**308 nm**
(Al,Ga)N LEDs	**210 – 365 nm**
(In,Ga)N LEDs	**365 – 400 nm**

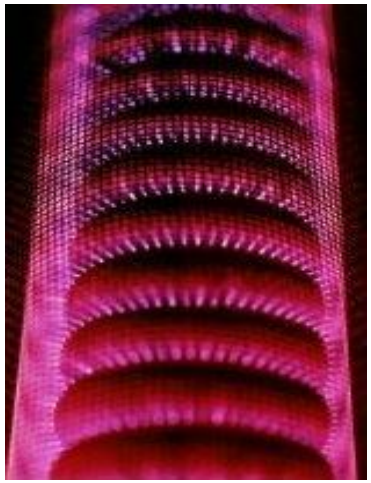





4. VUV to UV Converter for Xe Excimer Lamps

Devices using a dielectric barrier excimer discharge (either O_2 or Xe)

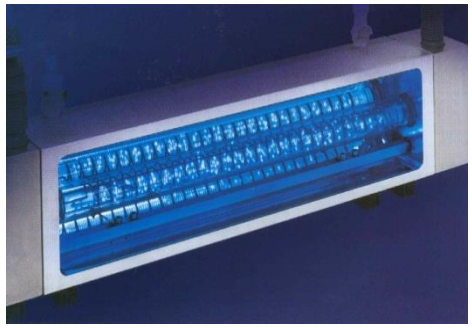
Ozone generator (Wedeco AG)

Exhaust treatment (Siemens AG)



UV Radiation sources (Xenon)

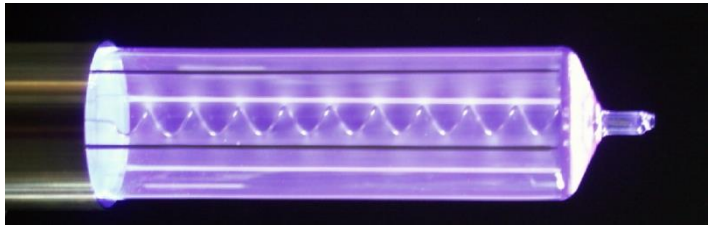
Heraeus Noblelight



Triton

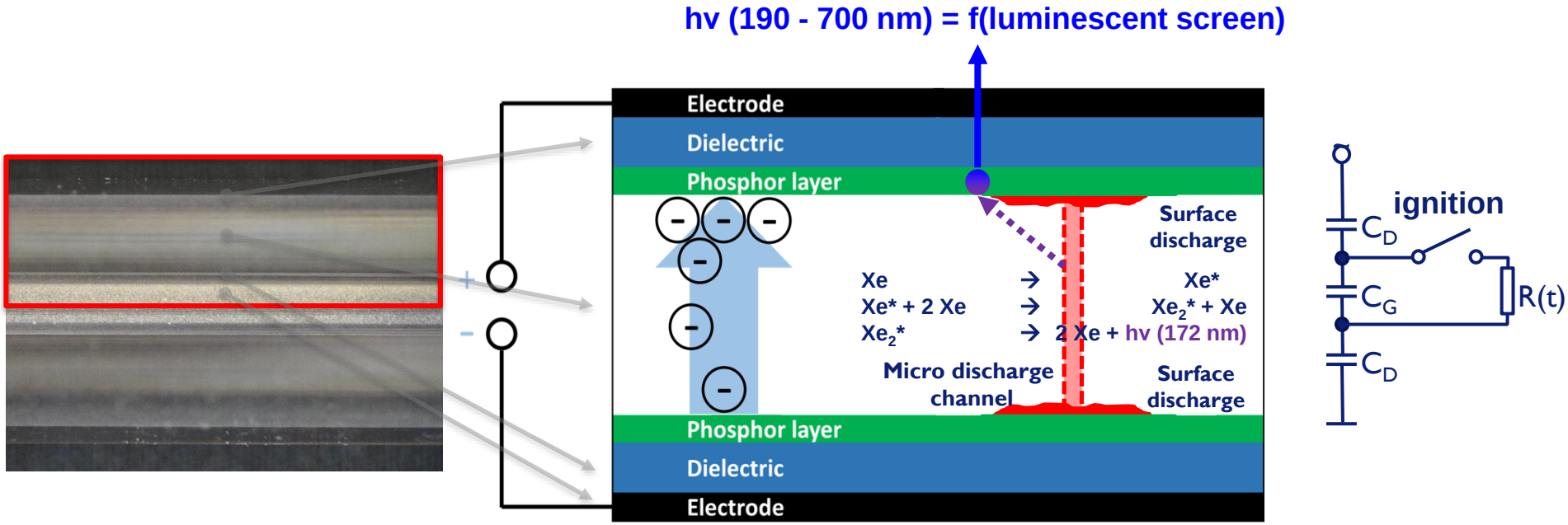
Flat lamp for LCD Backlighting (Osram AG)

Osram Xeradex



4. VUV to UV Converter for Xe Excimer Lamps

Lamp sketch and principle of working



p(Xe) = 300 mbar

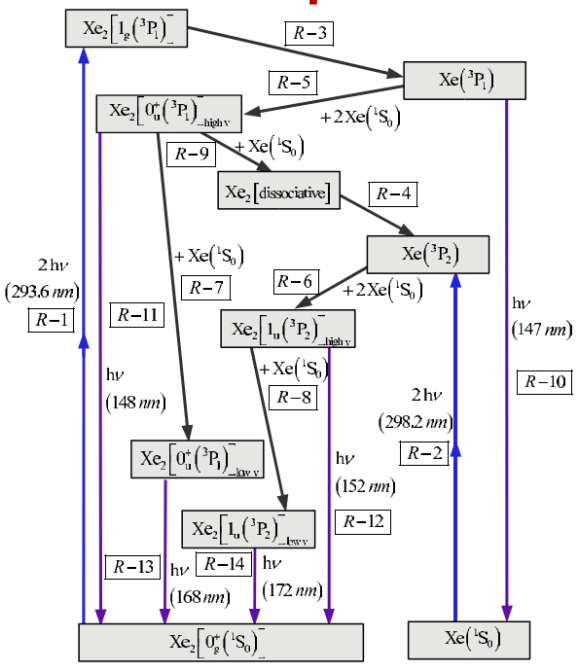
P = 10 - 100 W

U = 3 - 5 kV

f = 10 - 50 kHz

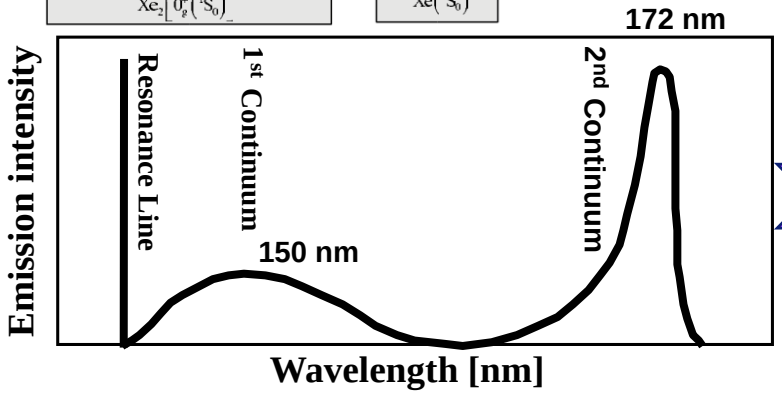
4. VUV to UV Converter for Xe Excimer Lamps

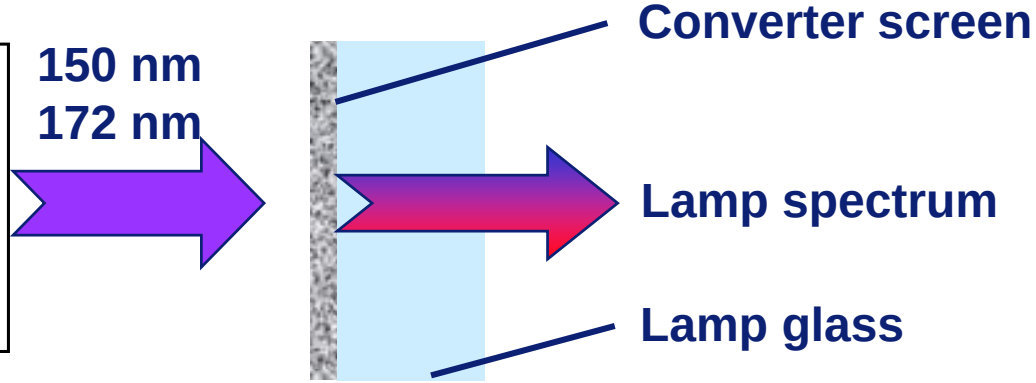
Xe excimer spectrum and typical lamp parameter



Example: Osram XERADEX L40/120/SB-S46/85

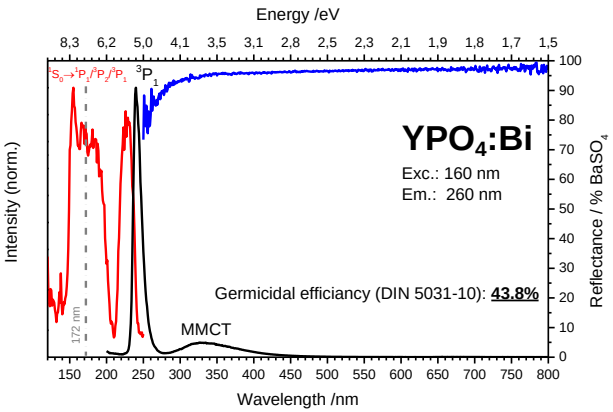
Power consumption = 20 W
Diameter = 4 cm
Length = 12 cm
Wall load ~ 0.15 W/cm²
Output power = 6 W
Power density = 0.04 W/cm²
Wall plug efficiency ~ 30% (including driver)





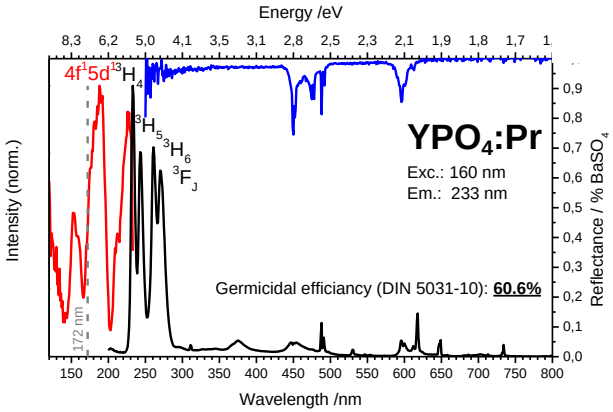
4. VUV to UV Converter for Xe Excimer Lamps

Chosen converter material must be radiation hard

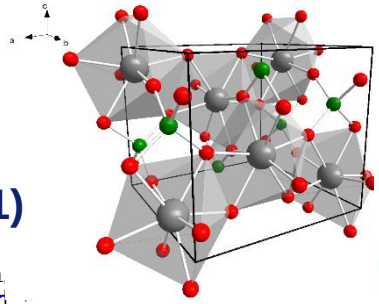


$\lambda_{max}(YPO_4:Bi) = 241$ nm

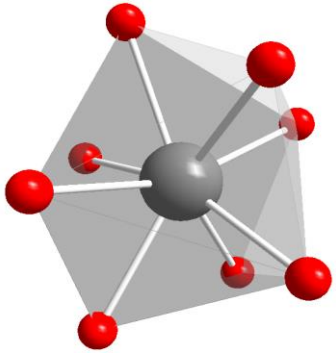
YPO_4 as the host material
mineral: Xenotime
structure: Zircon type
crystal system: tetragonal
space group: *I4₁amd* (#141)



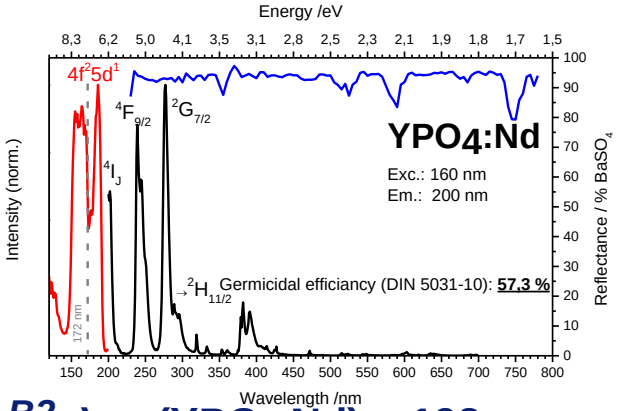
$\lambda_{max}(YPO_4:Pr) = 235$ nm



unit cell



Y^{3+} site: CN = 8

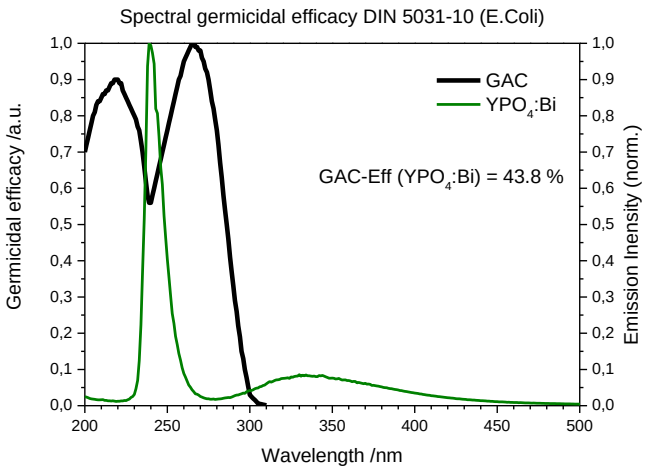


$\lambda_{max}(YPO_4:Nd) = 193$ nm

T. Jüstel, H. Nikol, J. Dirscherl, W. Busselt, US 6398970 B1
T. Jüstel, H. von Busch, G. Heussler, W. Mayr, US 7298077 B2
G.F. Gärtner, G. Greuel, T. Jüstel, W. Schiene, US 7687997 B2
T. Jüstel, J. Meyer, W. Mayr, US 7808170 B2
T. Jüstel, P. Huppertz, D.U. Wiechert, W. Mayr, H. von Busch, US 7855497 B2
G. Greuel, T. Jüstel. J.M. Kuc, US 9334442 B2

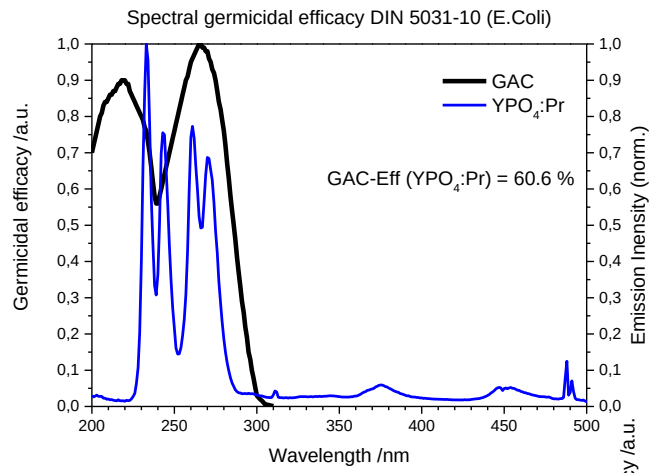
4. VUV to UV Converter for Xe Excimer Lamps

Germicidal efficacy of doped ortho-phosphate YPO_4

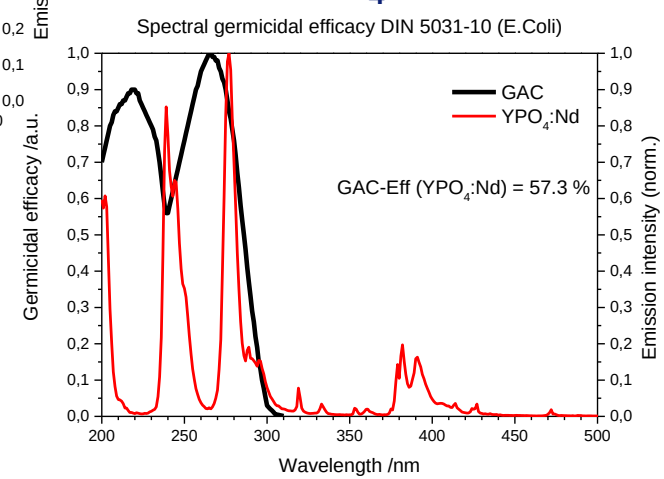


YPO_4:Bi

YPO_4:Pr



YPO_4:Nd



Germicidal Action Curve (GAC):
Efficacy of deactivation of E. Coli (DIN 5031-10)

$$Eff_{GAC}(Phosphor) = \frac{\int (Em_{Phosphor} \times GAC)}{\int Em_{Phosphor}}$$

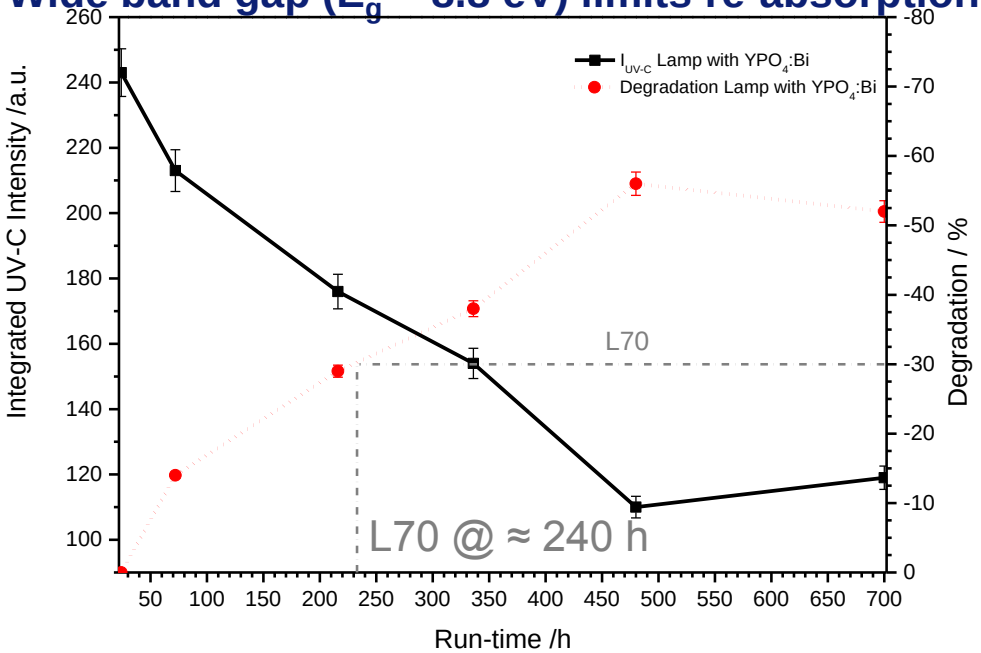
4. VUV to UV Converter for Xe Excimer Lamps

Lifetime of Xe excimer lamp comprising YPO_4:Bi or YPO_4:Ln

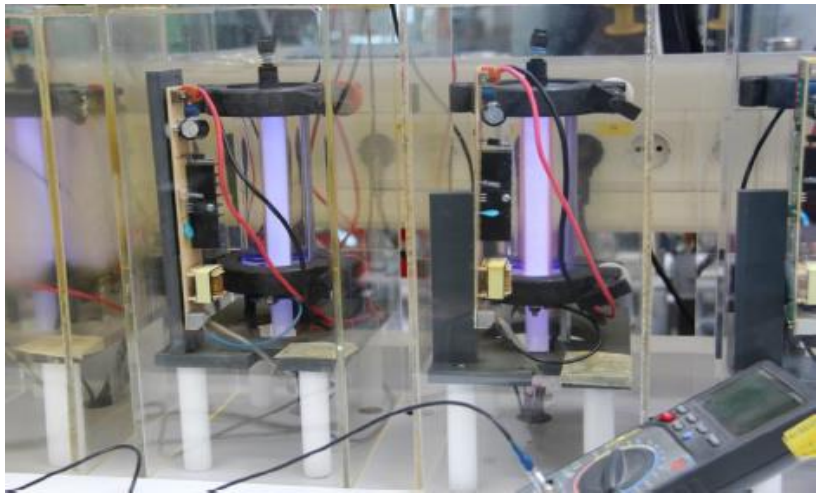
Choice was based on

$LnPO_4$ phosphors are stable in discharge lamps

Wide band gap (E_g ~ 8.8 eV) limits re-absorption



But: An YPO_4:Bi lamp has reached its rated end of life after just about 240 hours of operation if L70 is applied



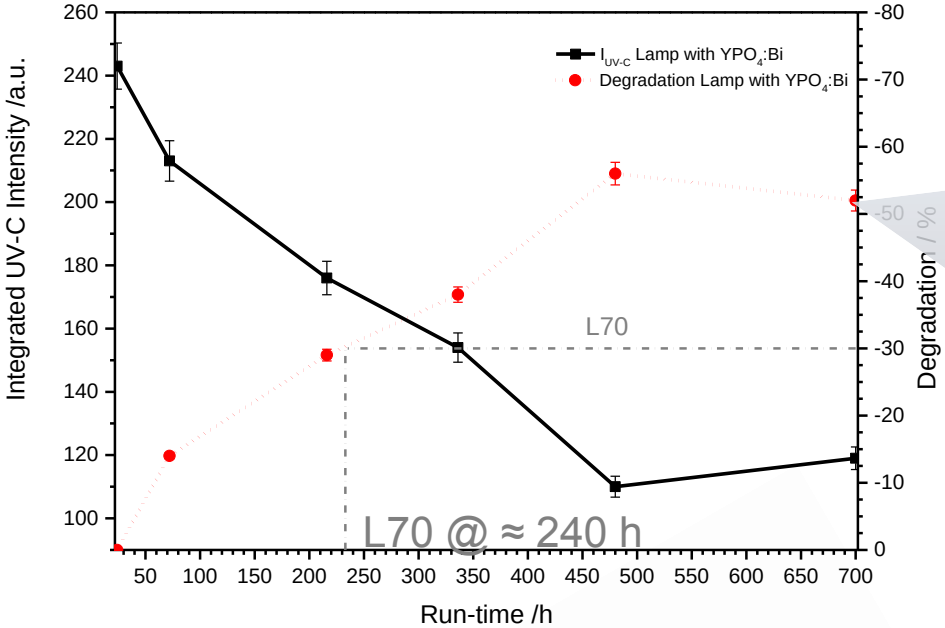
H_2O filled dive-in test stand for Xe excimer co-axial lamps

Converter screen	Operation period	Relative radiation intensity loss
YPO_4:Bi	792 hours	- 50 %
YPO_4:Pr	792 hours	- 60 %
YPO_4:Nd	763 hours	~ -50 %

4. VUV to UV Converter for Xe Excimer Lamps

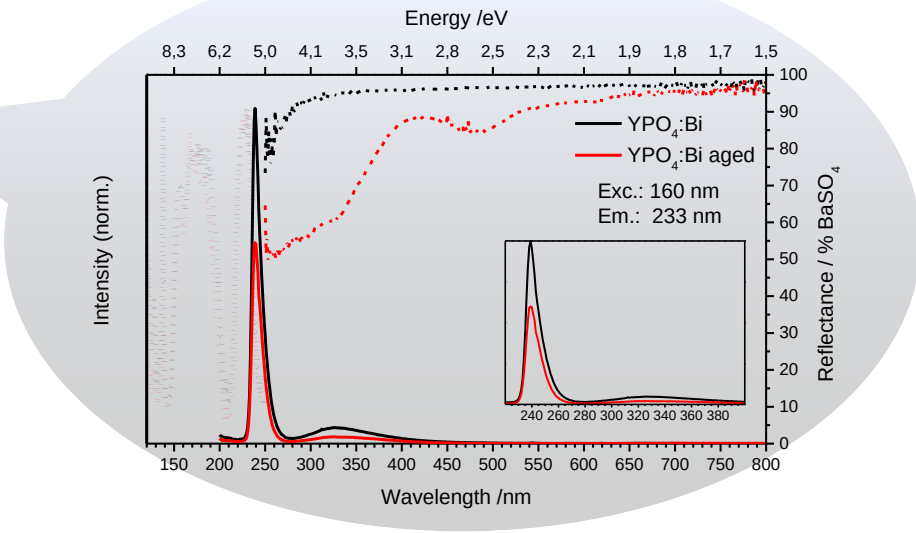
Lifetime of Xe excimer lamp comprising YPO_4:Bi or YPO_4:Ln

Lamp degradation due to several processes



YPO_4:Bi as-made and aged

(PL and reflection spectra)



Discharge related

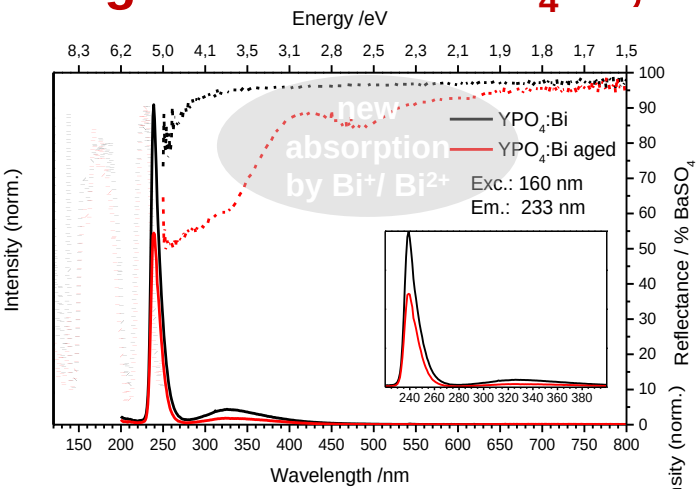
XeO* formation
Sputtering of central wire

Phosphor related

Reduction of $Bi^{3+} \rightarrow Bi^{2+}$, Bi^{+}
Degradation of ortho-phosphate host (defects or phosphate reduction?)

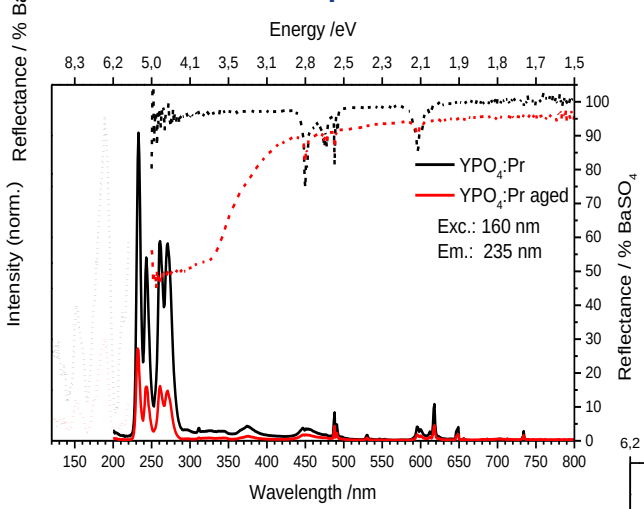
4. VUV to UV Converter for Xe Excimer Lamps

Degradation of YPO_4:Bi, YPO_4:Pr, and undoped YPO_4

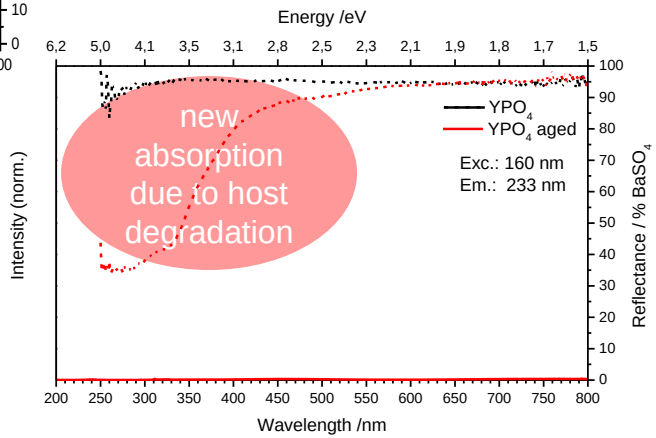


$YPO_4:Bi^{3+}$

$YPO_4:Pr^{3+}$

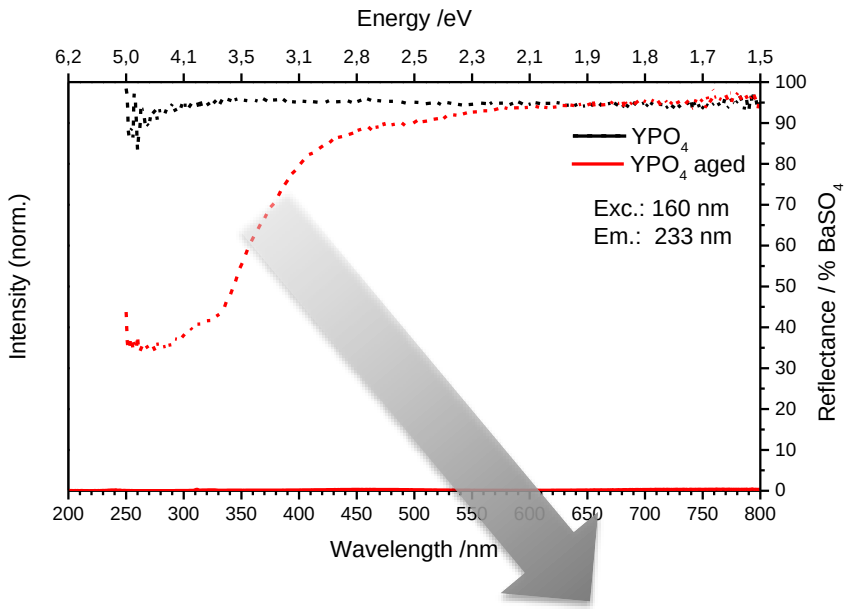


YPO_4



4. VUV to UV Converter for Xe Excimer Lamps

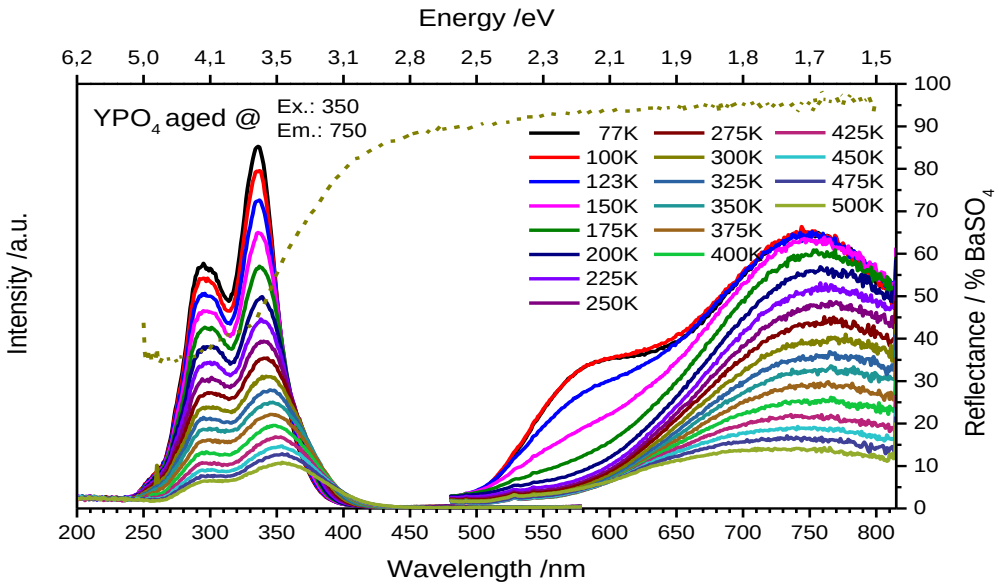
Temperature dependent spectroscopy on aged YPO_4 samples



Aged undoped YPO_4 shows intense red PL!

Luminescence process?

YPO_4 | **YPO_4 aged** | **YPO_4 aged + 365 nm**

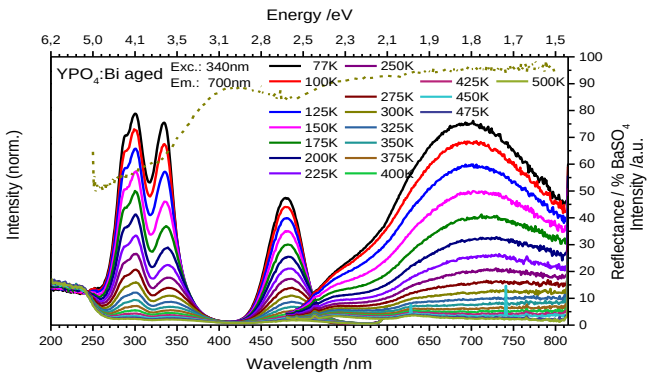


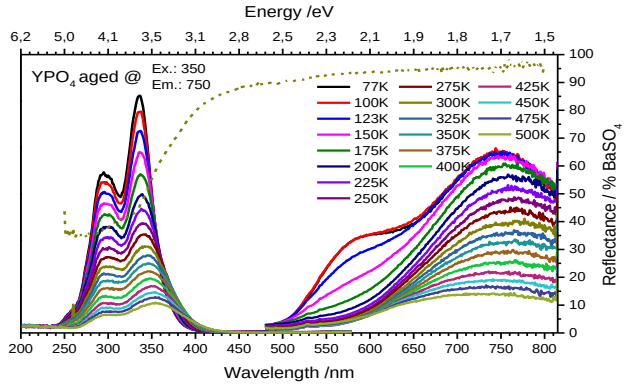
4. VUV to UV Converter for Xe Excimer Lamps

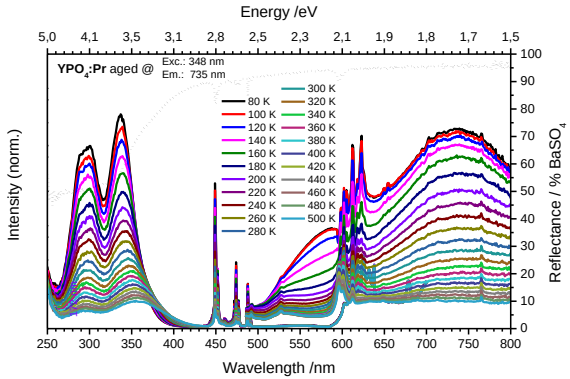
Bi^{3+} doping

Pr^{3+} doping

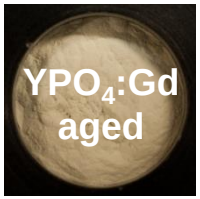
YPO_4 host

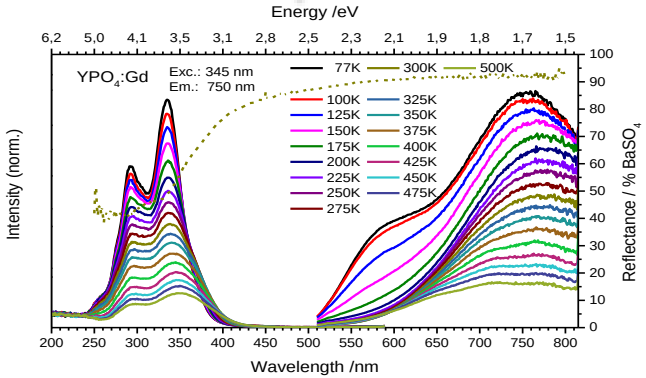






Gd^{3+} doping





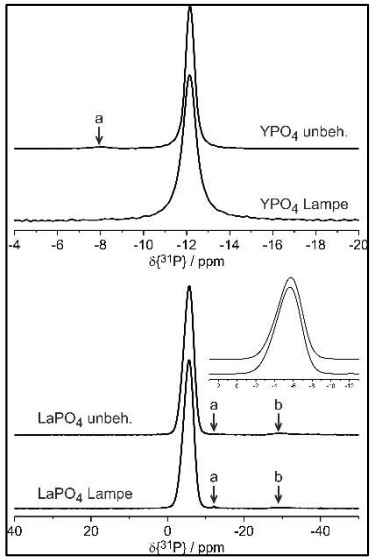
Luminescence process?

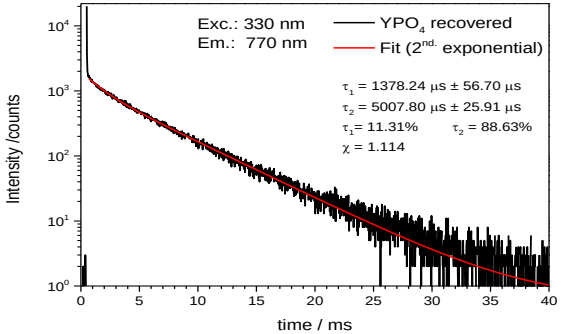
- Independent of type of dopant
- Similar PL found for aged $LuPO_4$ and $LaPO_4$

4. VUV to UV Converter for Xe Excimer Lamps

Further analytics on degraded $LnPO_4$ (Ln = Y, La, Gd, Lu)

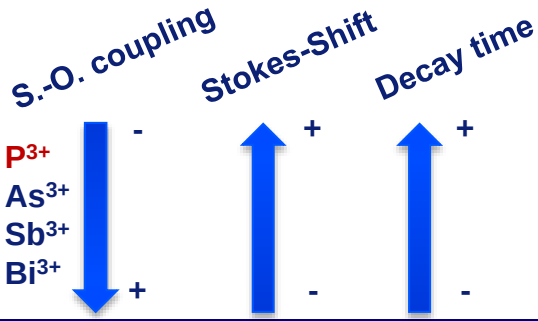
- XRD and ^{31}P-NMR → No phase transitions or impurity phase formation
- Photoluminescence spectroscopy → Spectral features characteristic for $ns^2 \leftrightarrow ns^1np^1$ luminescence, as already known for As^{3+}, Sb^{3+}, and Bi^{3+}
- Decay curve → main component $\tau_{1/e}$ = 5 ms → PL of s^2-ion with a small spin-orbit (S.-O.) coupling, which increases with atomic number!





P^{+V} → P^{+III}

$[Ne]3s^0$ $[Ne]3s^2$



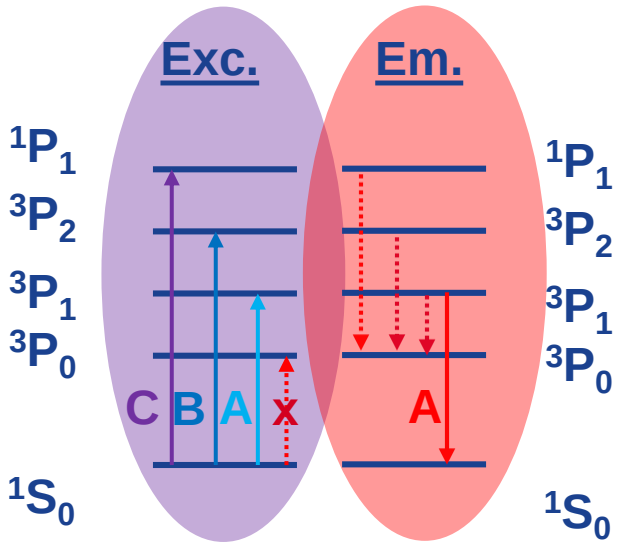
Reduction of P^{5+} by hot e^- and $Xe^{+\cdot}$ impingement due to intimate contact to barrier discharge

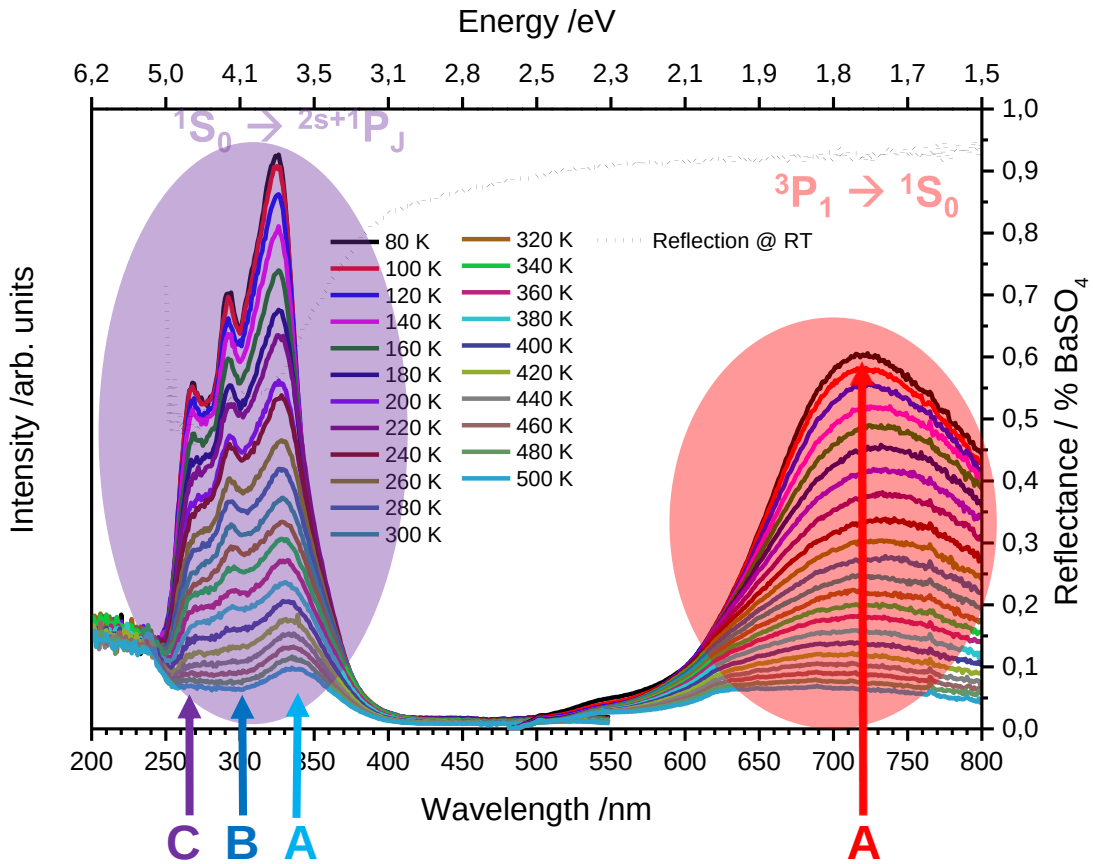
$$P^{+V}O_4^{3-} + Xe^+ + e^- \rightarrow P^{+III}O_3^{3-} + XeO\uparrow$$

4. VUV to UV Converter for Xe Excimer Lamps

Photoluminescence of degraded $LnPO_4$ (Ln = Y, La, Gd, Lu)

Simplified energy level diagram of an ns^2 ion





Conclusions:

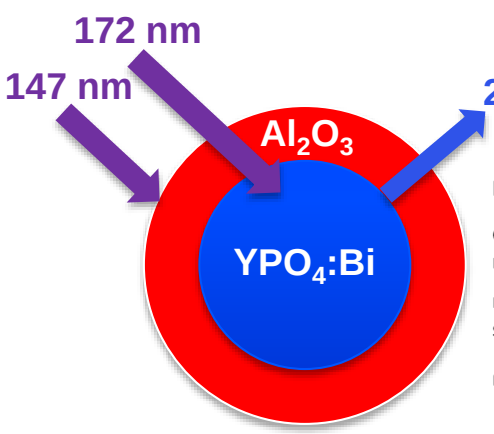
- Formation of $LnPO_4:P^{3+}$
- First known example of P^{3+} $[Ne]3s^2$ to $[Ne]3s^13p^1$ photoluminescence

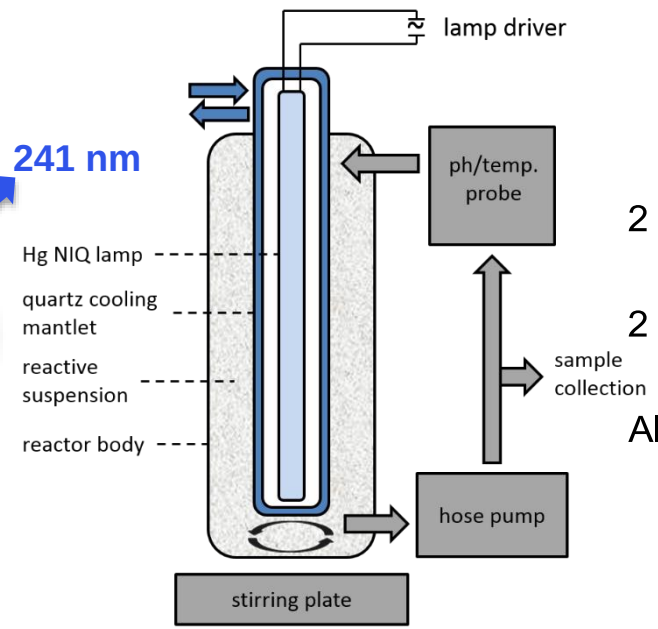
M. Broxtermann, A. Meijerink, T. Jüstel, J. Luminescence, publication in progress

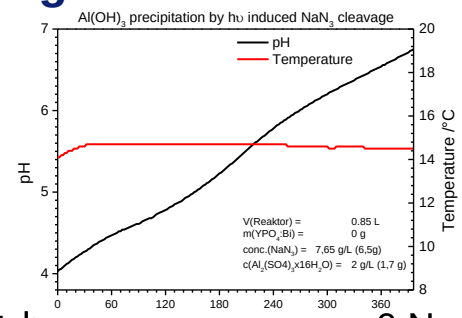
4. VUV to UV Converter for Xe Excimer Lamps

Improvement of stability of $LnPO_4$ (Ln = Y, La, Gd, Lu)

Approach: Particle coating with Al_2O_3 (E_g ~ 7.5 eV) to reduce interaction with Xe discharge and to absorb radiation from discharge below 160 nm





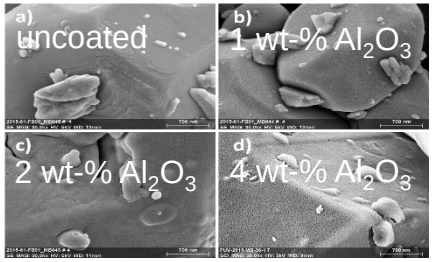


$$2\,N_3^-{}_{(aq)} + h\nu_{UV} \longrightarrow 3\,N_{2(g)} + 2\,e^-$$

$$2\,H_2O + 2\,e^- \longrightarrow 2\,H_{2(g)} + 2\,OH^-$$

$$Al^{3+}{}_{(aq)} + 3\,OH^- \xrightarrow{+\,YPO_4:Bi_{(s)}} Al_2O_3@YPO_4:Bi$$

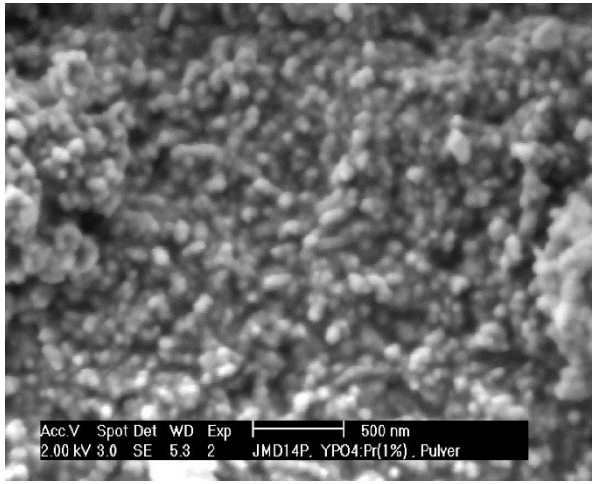
Calcination 1100°C/2h



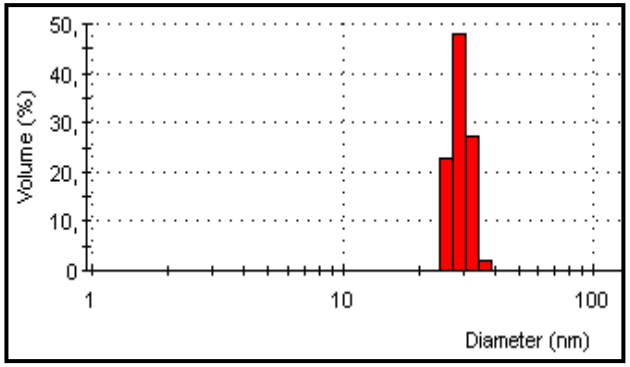
M. Broxtermann, T. Jüstel, Mat. Res. Bull. 80 (2016) 249

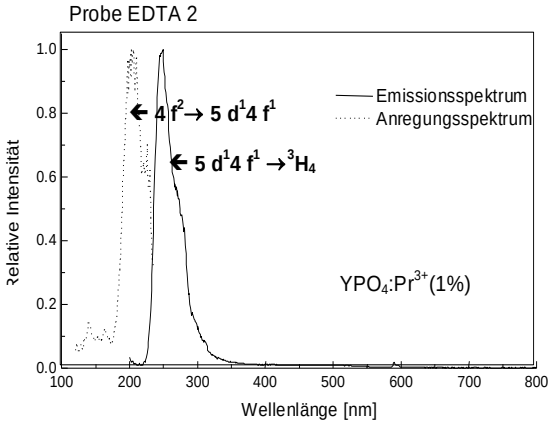
5. Nanoscale UV Scintillators

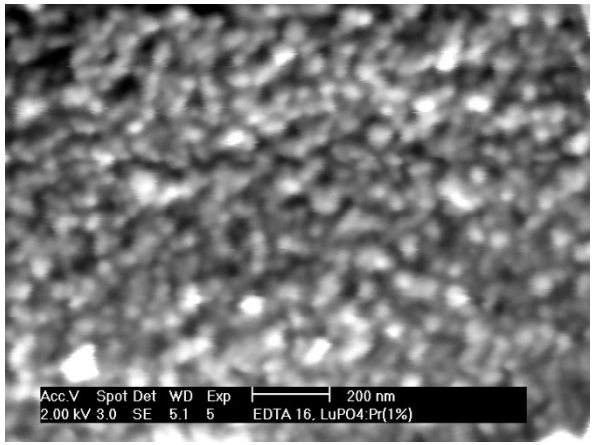
YPO_4:Pr and $LuPO_4$:Pr as 235 nm UV-C emitting NP scintillators



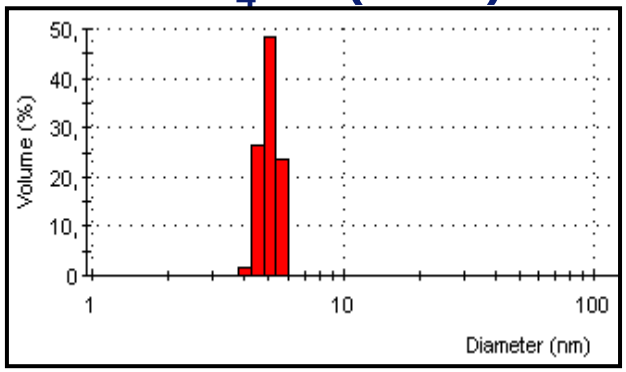
YPO_4:Pr (30 nm)

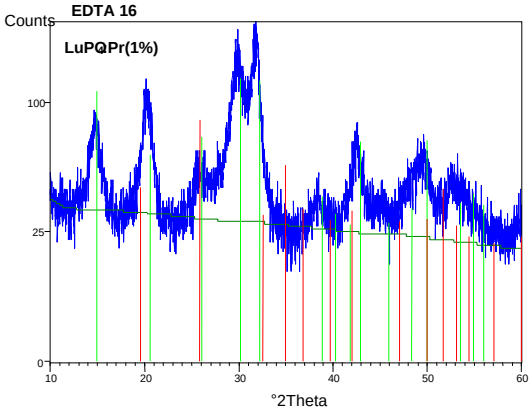






$LuPO_4$:Pr (5 nm)

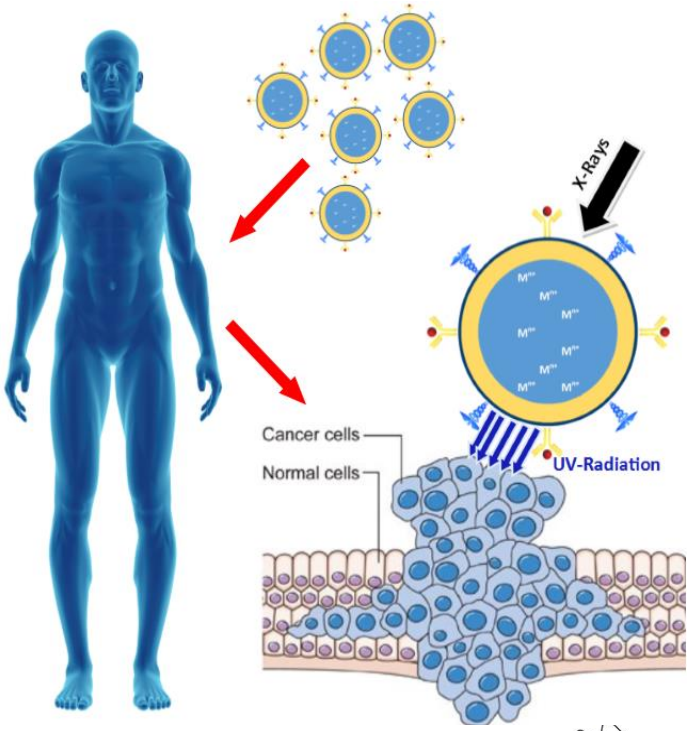




5. Nanoscale UV Scintillators

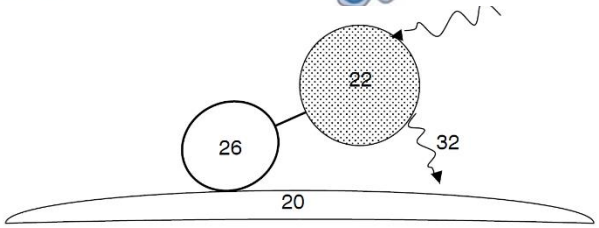
Idea: Conversion of x-rays to UV-C radiation by nanoscale particles to improve radiation therapy of cancer

Radiation therapy is a well established cancer treatment and applied all over the world, even though it has tremendous side effects, such as hair loss, diarrhea, …



"UV Nanophors" would result in

- **lower radiation dose**
- **fewer or none side effects**
- **lower treatment price**
- **shorter treatment periods**



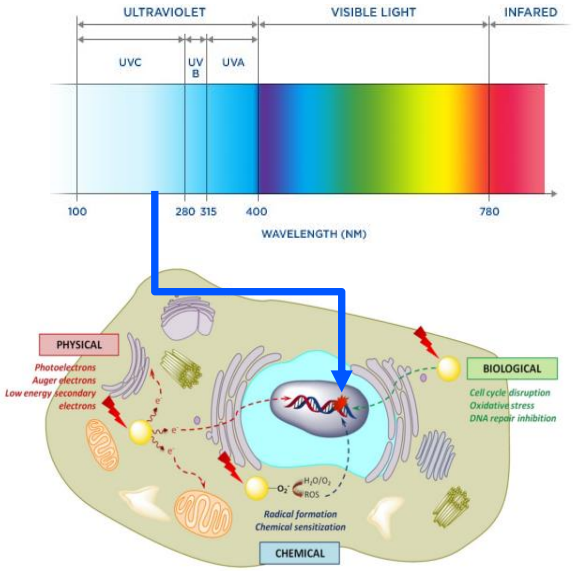
T. Jüstel, C. Feldmann, Philips Patent EP03104756, WO2005058360

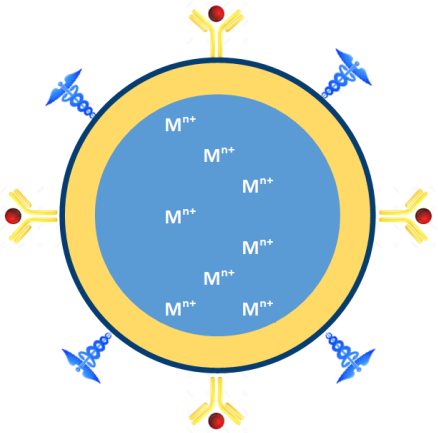
5. Nanoscale UV Scintillators

Challenge: Provide UV-C scintillator which meet the following requirements

- High density
- Large GAC overlap
- Diameter: 50 - 150 nm
- Narrow PSD
- Homogeneous morphology
- Redispersibility
- Mainly UV-C emission
- Efficient CL and RL
- Suitable PZC
- Biocompatible host
- Low toxicity
- Stability in water to enable core-shell structure with linker

Core material	Density [g/cm³]
Lu_2O_3	9.4
$LuLaO_3$	8.2
Lu_2O_2S	8.9
Lu_2SiO_5	7.4
$LuPO_4$	6.53
$Lu_2Si_2O_7$	6.2
$Lu_3Al_5O_{12}$	6.7
$LuAlO_3$	8.4
$LuBO_3$	6.9



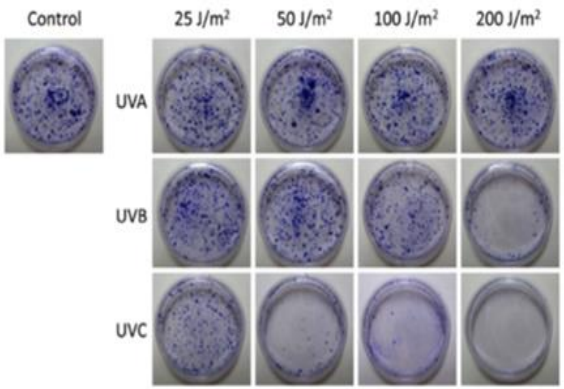


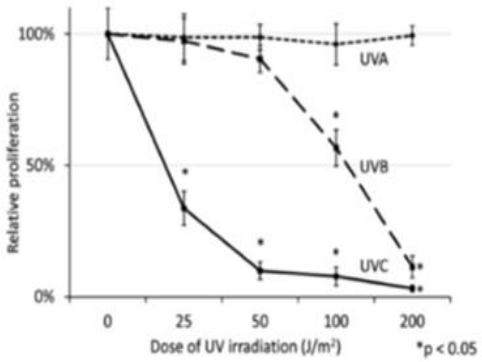
5. Nanoscale UV Scintillators

Emission peaks and GAC overlap of selected UV-C scintillators

Material	$\lambda_{max.}$(Em.) /nm	GAC-Efficacy /%
$(Y,Lu)PO_4$:Nd	193	57.3*
$CaSO_4$:Pr,Li	218	68,2
$LaPO_4$:Pr	225	68.9
$(Y,Lu)PO_4$:Pr	235	60.6
$(Y,Lu)PO_4$:Bi	241	43.8 – 50.7
$YAlO_3$:Pr	245	40.6
$La_2Si_2O_7$:Pr	247	33.4
$CaLi_2SiO_4$:Pr	253	44.0
$CaMgSi_2O_6$:Pr,Li	260	n. a.
YBO_3:Pr	265	45.9
$Lu_2Si_2O_7$:Pr	266	48.1
Y_2SiO_5:Pr	270	22.3
$BaZrSi_3O_9$	275	47.9
Lu_2SiO_5	277	15.9
$Lu_3Al_5O_{12}$:Pr	310	2.3
$Lu_3Al_5O_{12}$:Gd	311	~ 0
$Y_3Al_5O_{12}$:Gd	311	~ 0
$LaMgAl_{11}O_{19}$:Gd	311	~ 0
$Y_3Al_5O_{12}$:Pr	320	~ 0

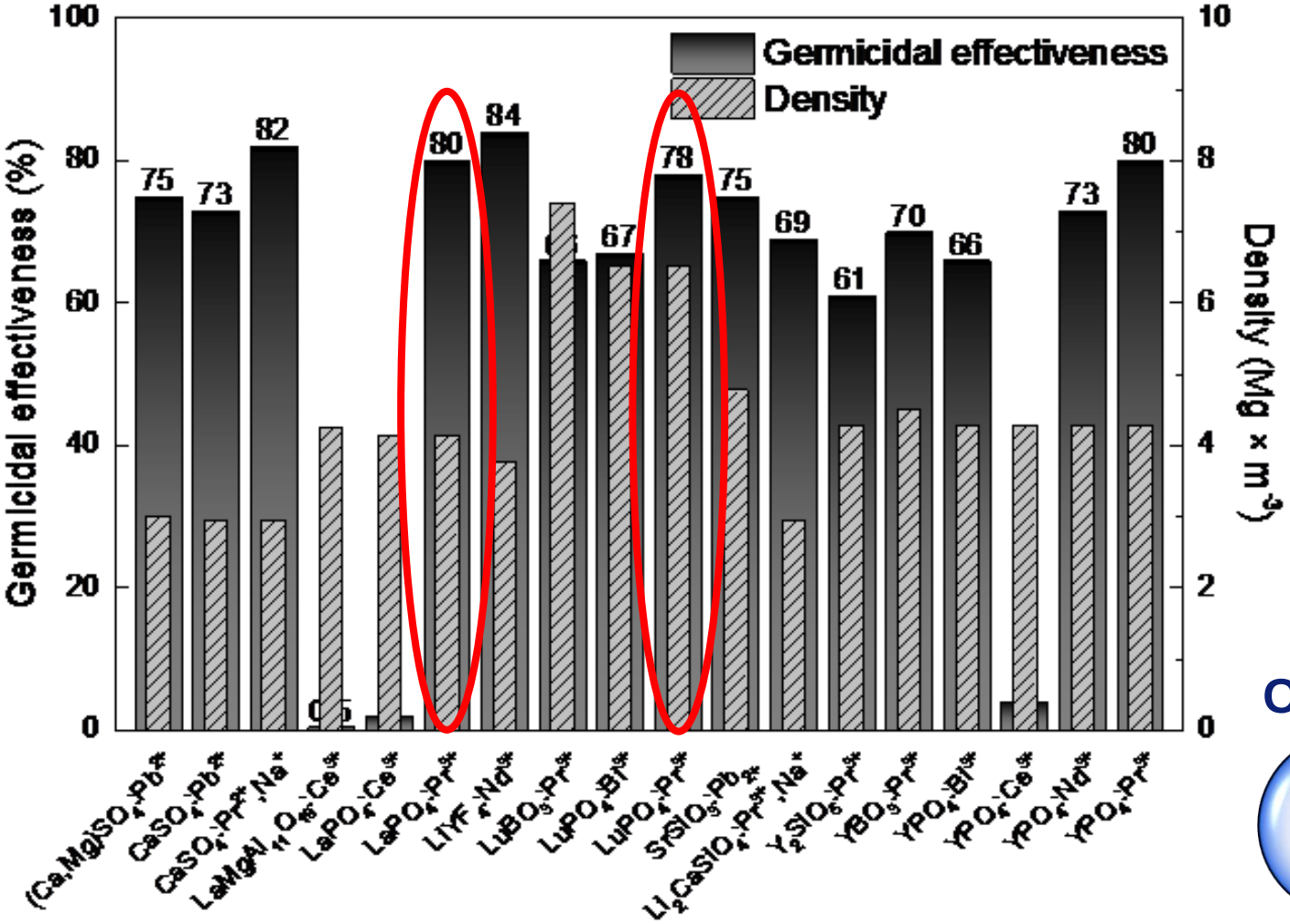
Material	$\lambda_{max.}$(Em.) /nm	GAC-Efficacy /%
$LaPO_4$:Ce	320	~ 0
$Lu_3Al_5O_{12}$:Tm	345	~ 0
$Y_3Al_5O_{12}$:Tm	345	~ 0
YPO_4:Ce	335, 355	~ 0
$BaSi_2O_5$:Pb	350	~ 0



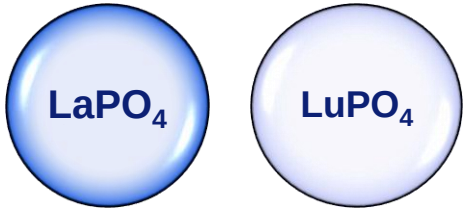


5. Nanoscale UV Scintillators

GAC overlap and density of selected UV-C scintillators

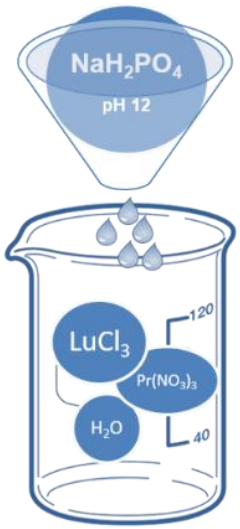


Chosen materials



5. Nanoscale UV Scintillators

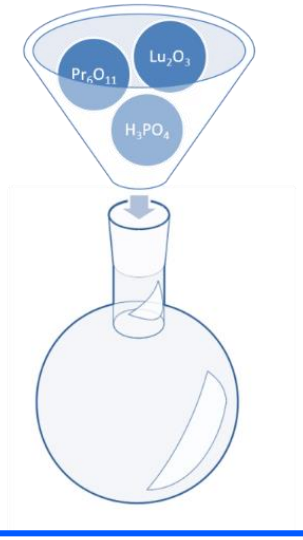
From micro to nanoscale particles (bottom-up approach)



$LuPO_4$

Sedimentation Nucleation (Modified)

Suspension



- A solution of NaH_2PO_4 (pH 12) is added dropwise to the second solution of $LuCl_3$ and $Pr(NO_3)_3$ dissolved in H_2O.
- The precipitate is separated by a centrifuge and washed with distilled H_2O several times to neutral pH value.
- Afterwards, the precipitate is annealed for 2 h at 1000 °C in a reducing atmosphere (CO).

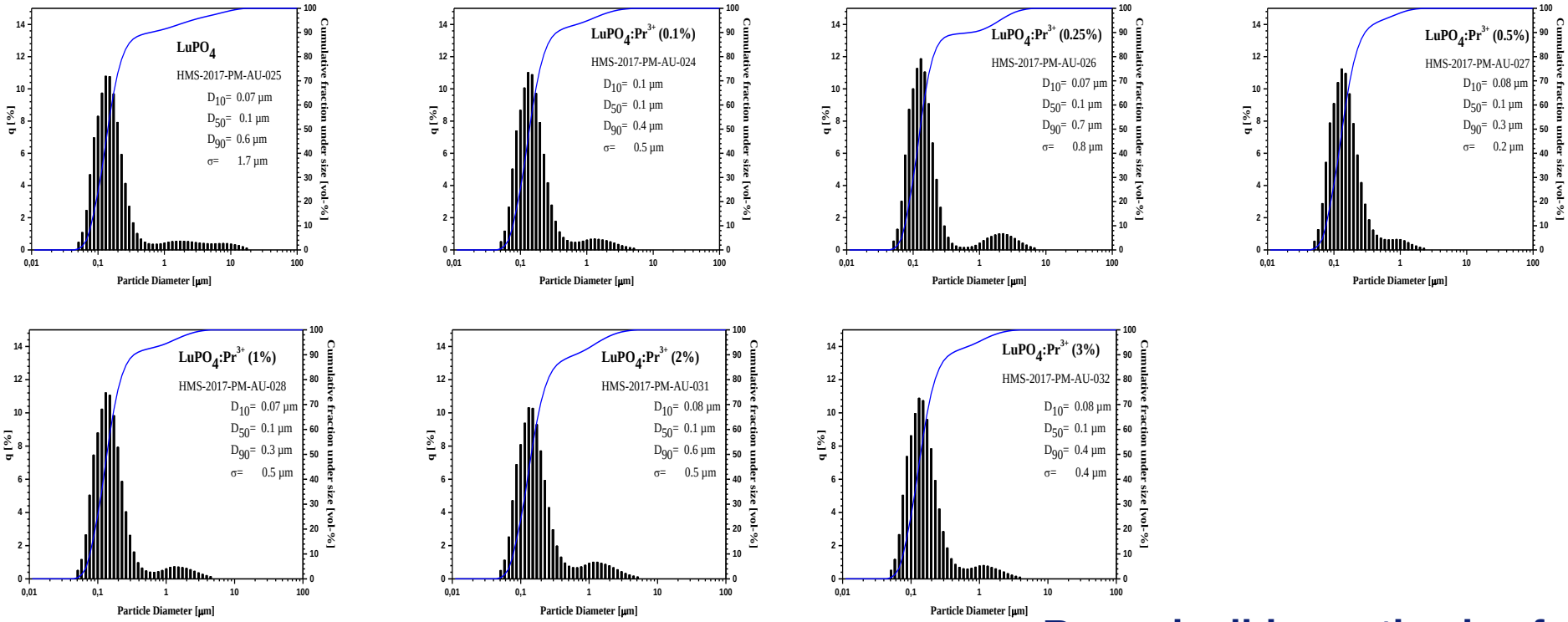
- Lu_2O_3 and Pr_6O_{11} are suspended in H_2O.
- H_3PO_4 is added to the suspension and mixed for 24 h.
- The precipitate is filtered and washed with distilled H_2O several times to neutral pH value.
- Afterwards, the precipitate is annealed for 4 h at 1000 °C under CO atmosphere and using 2 wt-% LiF.

Average d_{50} = 0.1 µm

Average d_{50} = 5.7 µm

5. Nanoscale UV Scintillators

PSD of nanoscale $LuPO_4$:Pr(0.0 - 3.0 atom-%) particles

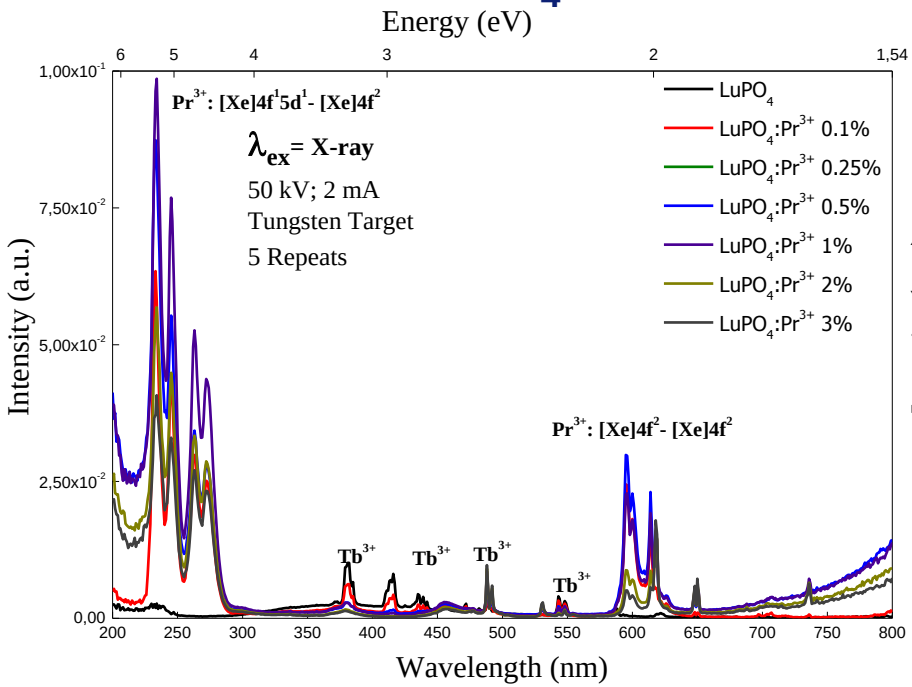


Reproducible synthesis of pure and highly crystalline $LuPO_4$:Pr^{3+} 100 nm particle activated by 0.1 to 3% Pr^{3+}

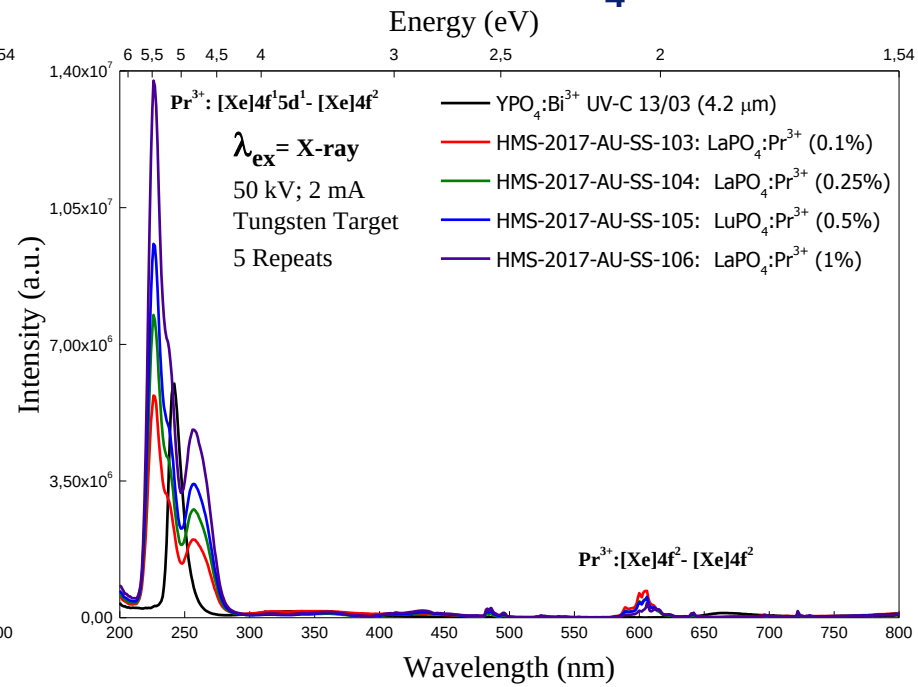
5. Nanoscale UV Scintillators

Radioluminescence of $LuPO_4$:Pr and $LaPO_4$:Pr 100 nm particles

$LuPO_4$:Pr



$LaPO_4$:Pr

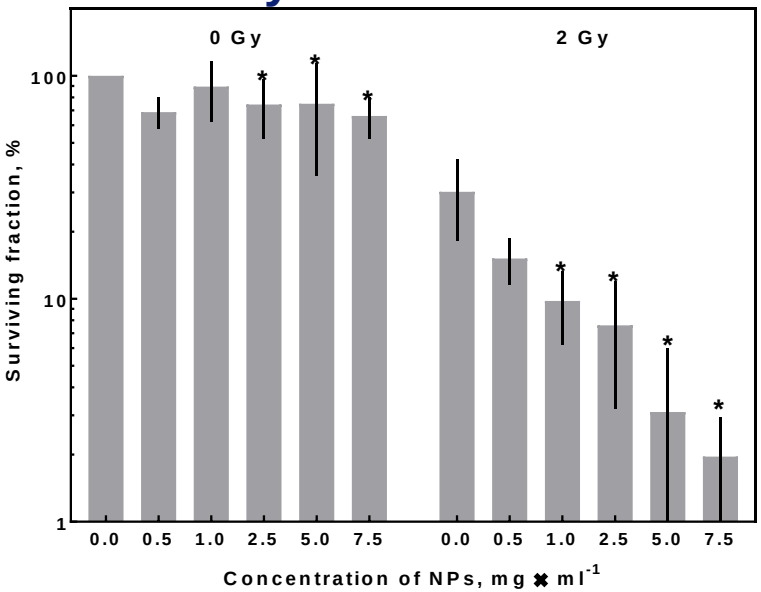


Density [g/cm³]	6.5	4.2
Main peak [nm]	235	225
Luminescence	4f-5d and 4f-4f	mainly 4f-5d
GAC overlap [%]	61	69

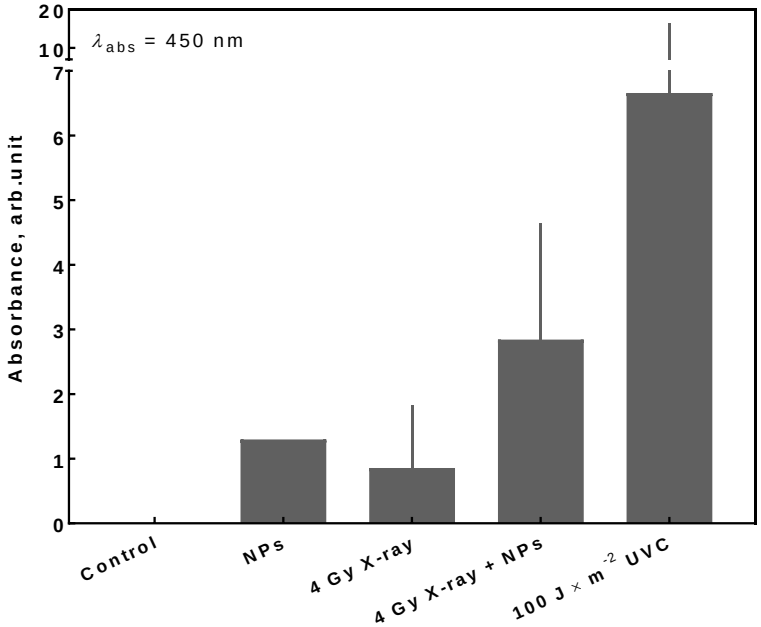
5. Nanoscale UV Scintillators

First results on cancer cell lines (HMS Boston, Dr. M. Purschke)

Colony formation assay 14 days after irradiation



Cyclobutane pyrimidine dimer assay as a proof of concept



Combined treatment causes an increased cell inactivation of 65 to 95%.

Combined treatment of cells with $LuPO_4:Pr^{3+}$ and 2 Gy is equivalent to 4 Gy alone

6. Summary

LED Materials in 2018 – State of the Art

Mature LMs developed to encounter

- high luminous efficacy — cool-white > 200 lm/W; warm-white > 100 lm/W
- high CRI — 70 - 95
- superior lifetime L70 — > 10000 h
- retrofit designs — for TL, CFL, GLS, …

Efficient luminescent materials are

	Oxides	Oxynitrides	Nitrides	Fluorides
Silicates	$(Ca,Sr,Ba)_2SiO_4$:Eu	$(Ca,Sr,Ba)Si_2N_2O_2$:Eu	$(Ca,Sr,Ba)_2Si_5N_8$:Eu	K_2SiF_6:Mn
Aluminosilicates		a,ß-SiAlON	$(Ca,Sr)AlSiN_3$:Eu	
Aluminates	$(Y,Gd,Lu)_3Al_5O_{12}$		$(Sr,Ca)LiAl_3N_4$:Eu	Na_3AlF_6:Mn
Gallates	$ZnGa_2O_4$:Mn		$(Sr,Ba)Mg_2Ga_2N_4$:Eu	
Germanates	$Mg_8Ge_2O_{11}F_2$:Mn			
Molybdates	$Tb_2Mo_3O_{12}$:Eu			
Tantalates				K_2TaF_7:Mn

6. Summary

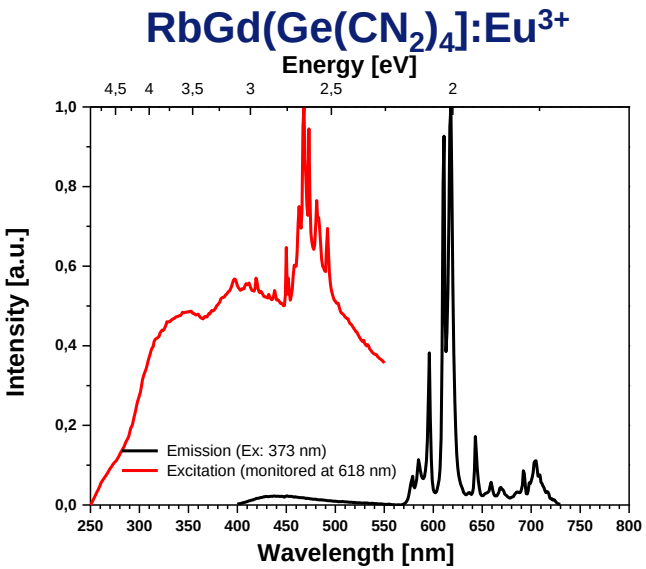
LED Materials in 2018 – Remaining issues

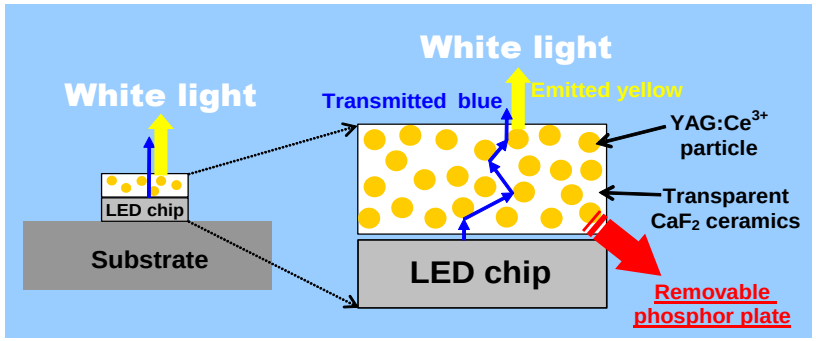
⇒ Red narrow band or line emitting phosphor
- Little thermal quenching
- Reduced photochemical aging
- Superior linearity
- Reduced sensitivity for photoionisation

⇒ Narrow band green and NIR Emitter
- Eu^{2+} with small Stokes Shift, e.g. $BaSi_2N_2O_2:Eu^{2+}$
- Tb^{3+} on cation sites with high symmetry: Oh, D_{3d}
- Mn^{2+} on tetrahedral sites: Zn_2GeO_4

⇒ Ceramics and crystals
- Ceramics: Garnets, Ln_2O_3, (Oxy)Nitrides
- Composites: Garnet + Al_2O_3 or CaF_2
- Crystals: Garnets as PL references

J. Glaser, H. Bettentrup, H.-J. Meyer, T. Jüstel, Inorg. Chem. 48 (2010) 2954



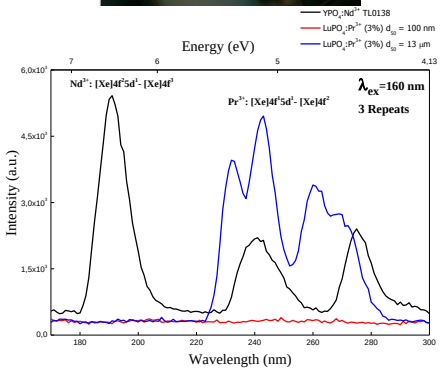


6. Summary

UV emitting (nanoscale) materials

⇒ **Fluorescent Xe Excimer discharge lamps**

- **Tailored emission spectra possible by VUV → UV converter: (Y,Lu)PO_4:Nd, $LaPO_4$:Pr, (Y,Lu)PO_4:Pr, YBO_3:Pr, $BaZrSi_3O_9$, …**
- **Lamp lifetime limited yet**
- **Degradation mechanism clarified**
- **Improvement of stability of converter by photochemically deposited Al_2O_3 particle coatings**
- **Many application areas, such as disinfection, purification, photochemistry, NO_3^- removal, food processing, …**



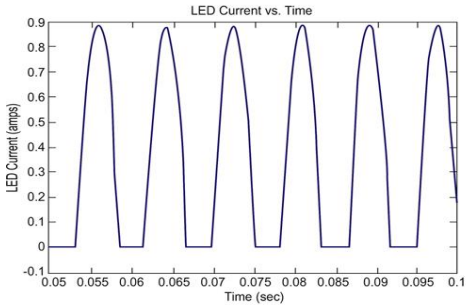
⇒ **Nanoscale UV emitting phosphors**

- **Excitation by x- or cathode-rays**
- **Local emission of harmful UV-C or VUV radiation**
- **Use for disinfection or therapeutic purposes**
- **Development of quantitative VUV/x-ray to UV-C spectroscopy**

7. Outlook

LEDs and laser diodes - Challenges

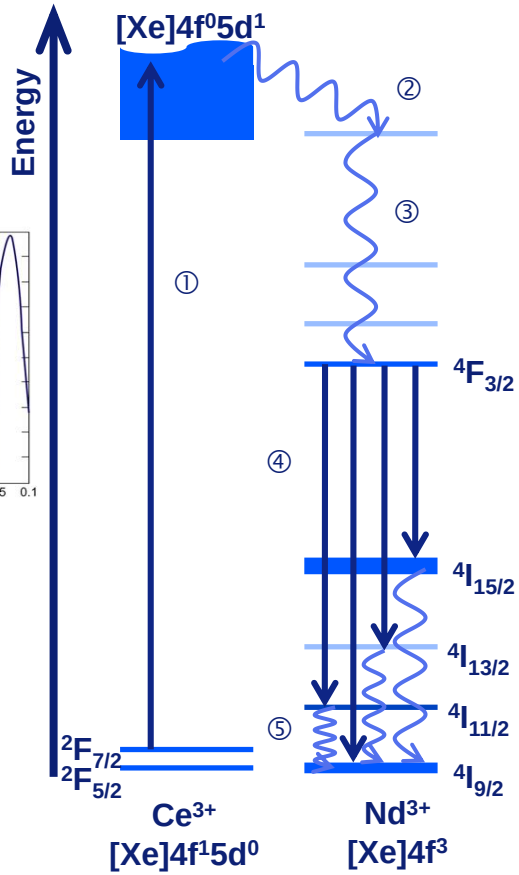
- **Reduction of flicker**
  - → Persistent luminescent materials
  - → ET approaches to delay PL



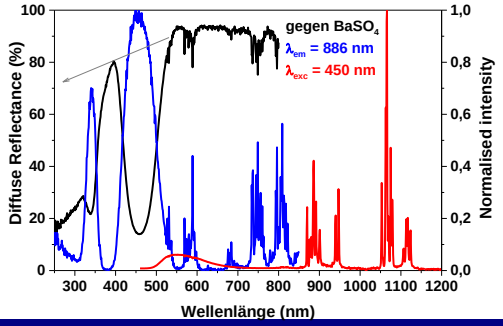
- **Ongoing increase of LED power density**
  - → Ceramics & crystals
  - → Vis (460 nm) to UV-C (230 nm) up converter

- **Broad band NIR emitter for blue/near UV LEDs**
  - → Cr^{3+} phosphors
  - → Eu^{2+} or Ce^{3+} sensitised Nd^{3+}/Yb^{3+} emitters

- **Photochemistry with high power density sources**
  - → Novel reactor designs
  - → Ceramic or crystalline photocatalyst



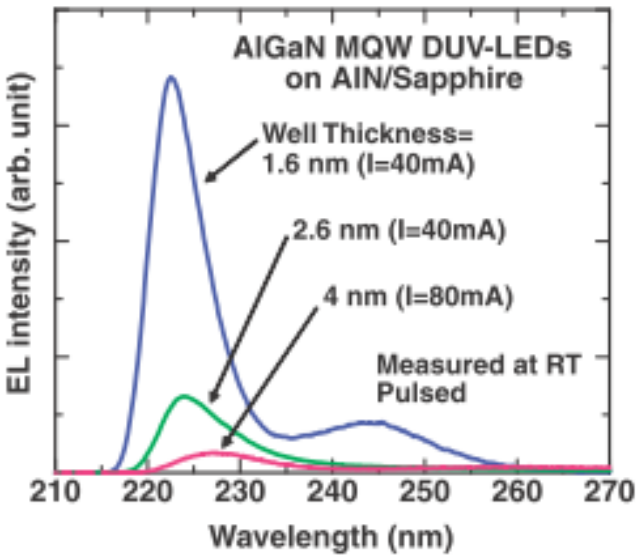
$(Y_{0,97}Ce_{0,02}Nd_{0,01})_3Al_5O_{12}$: Reflection, Excitation, Emission



7. Outlook

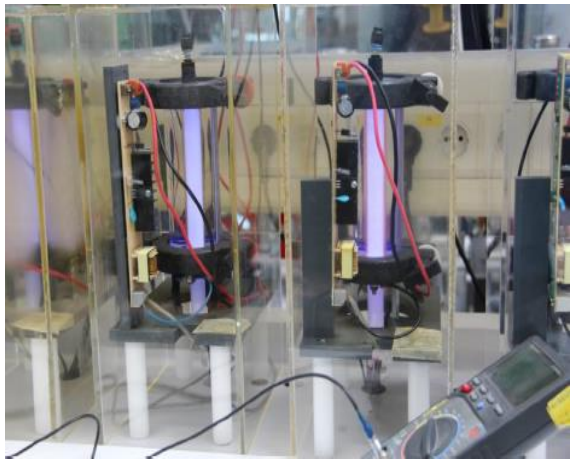
UV emitting (Al,Ga)N LEDs and laser diodes

- Spectral range: 220 – 360 nm
- DUV-LED → DUV laser diodes: Challenging!
- Problems: Spectral consistency, efficiency, radiation out-coupling, mass production, encapsulation, …..



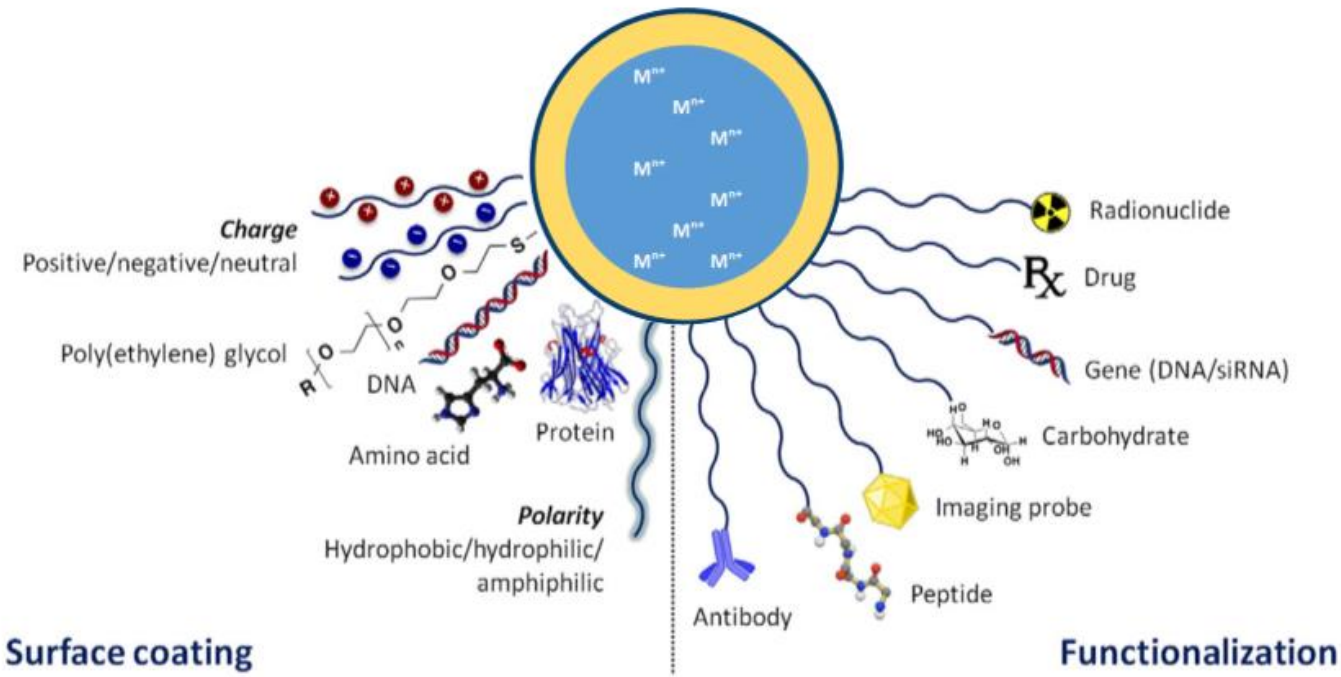
Fluorescent Xe excimer lamps

- Spectral range: 172 – 700 nm
- Discharge – converter interaction determines yield & lifetime
- Advantages: Hg-free, fast switchable, high form factor, temperature independent
- Problems: Driver eff., lifetime, market access, but UNEP proposed Hg ban rom 2020 onwards …..



7. Outlook

Nanoscale core-shell particles for biomedical applications



- Diagnostics
- Imaging
- Therapy
- Delivery

Combination of these applications, e.g. for magneto-optical diagnostics $GdPO_4$ @ MIR → NIR up-converter

Her, S., Jaffray, D.A. and Allen, C., Gold nanoparticles for applications in cancer radiotherapy, Mechanisms and recent advancements, Advanced drug delivery reviews, 109 (2017) 84

8. Literature

Further Reading

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- J. Chen, S. Loeb, J-H. Kim, LED Revolution: Fundamentals and Prospects for UV Disinfection Applications, Envir. Sci.: Water Res. Technol. 3 (2017) 188

Internet-Links

- Homepage T. Jüstel (PISA & LISA) — www.fh-muenster.de/juestel
- Robert-Koch-Institut — www.rki.de
- Dt. Krebsforschungszentrum — www.dkfz.de

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