VUV Phosphors for Plasma Display Panels and Excimer Discharge Lamps

Thomas Jüstel

University of Applied Sciences Münster

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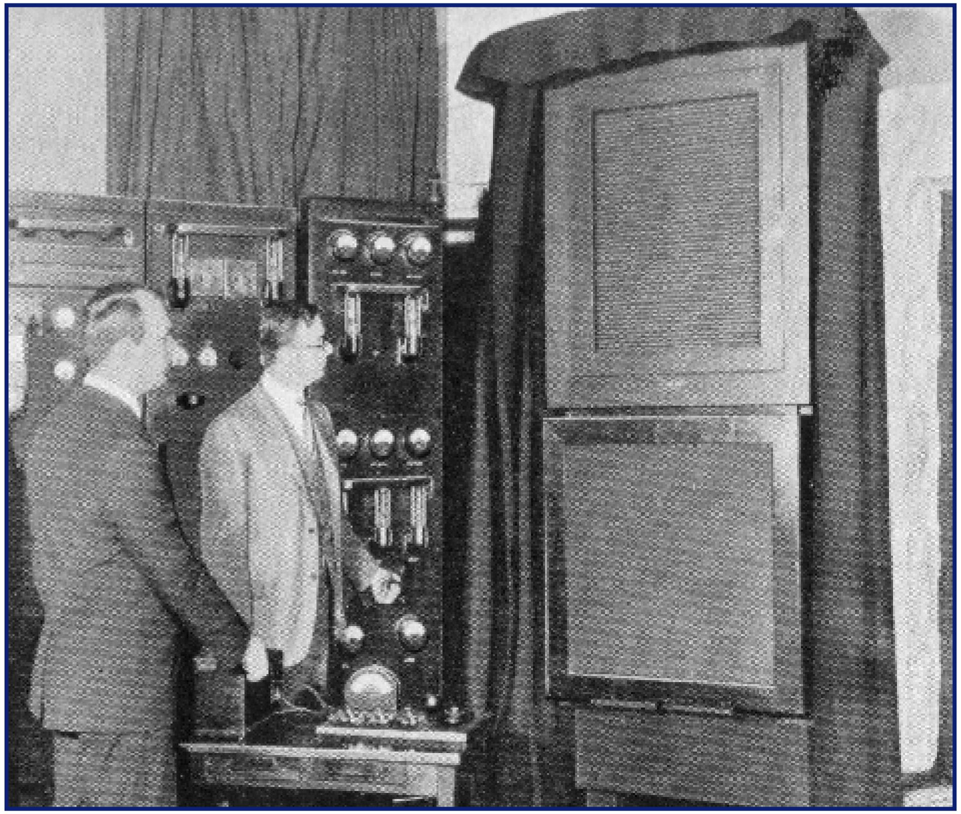
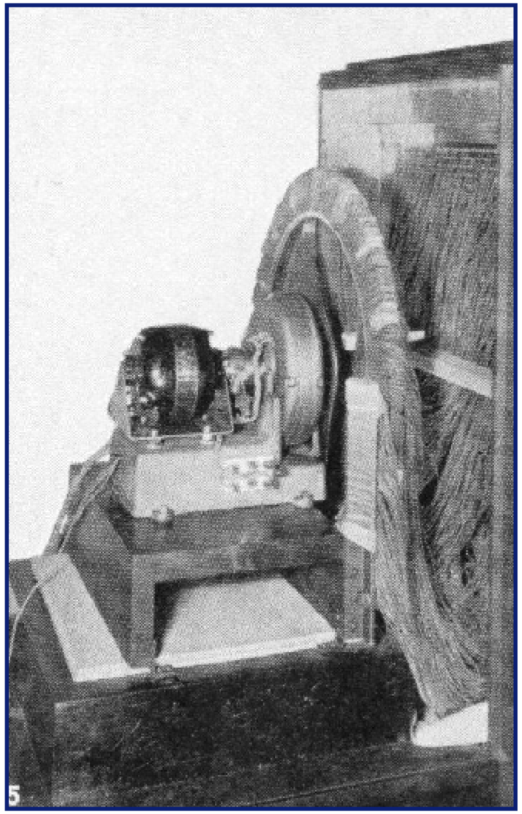
Plasma Display Panels 1929





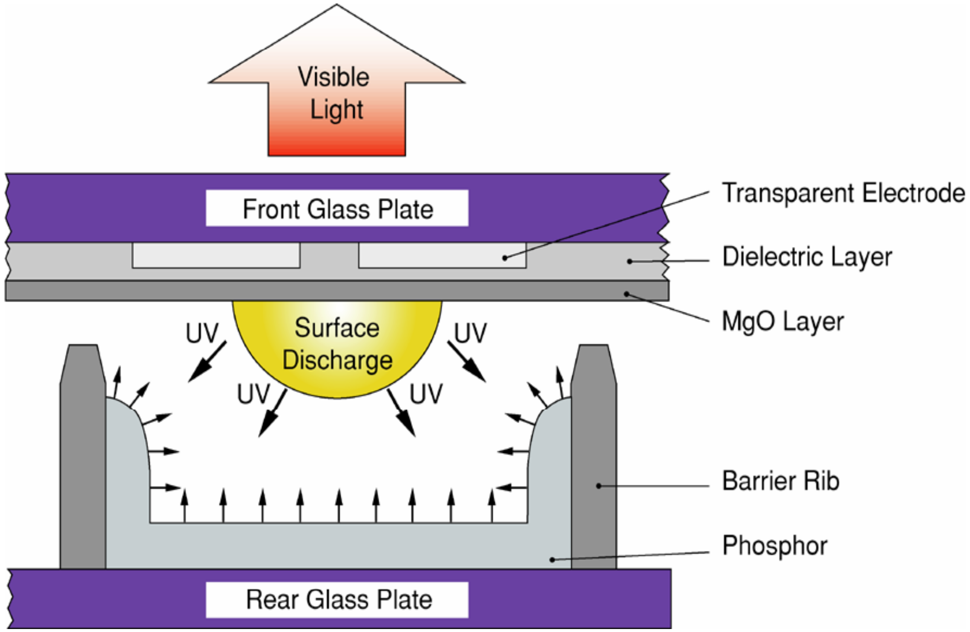
Outlines

1. Introduction
2. Xe and Xe/Ne Discharges
3. Inorganic luminescent materials
4. Phosphors for plasma display panels
5. Phosphors for Xe_2* discharge lamps
6. Application areas
7. Conclusions

1. Introduction

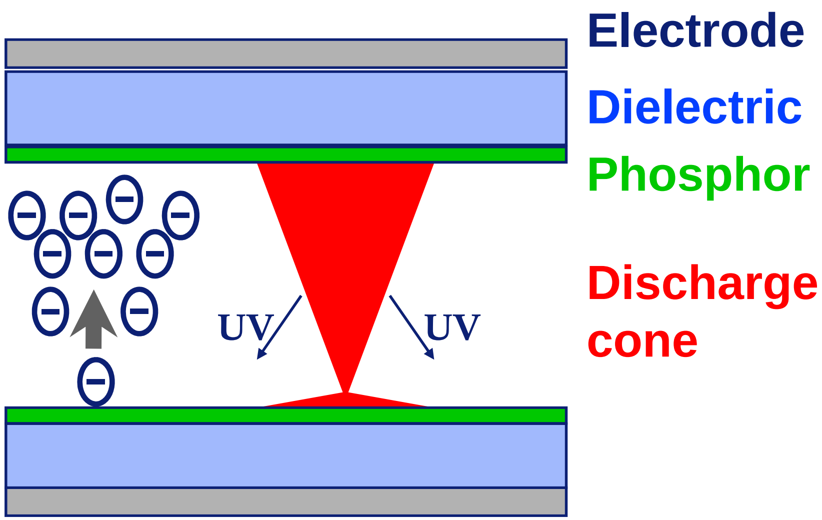
- Light Generation in PDPs and Discharge Lamps -

PDP pixel



Xe/Ne excimer discharge

Lamp burner



Xe_2* excimer discharge

2. Xe and Xe/Ne Discharges

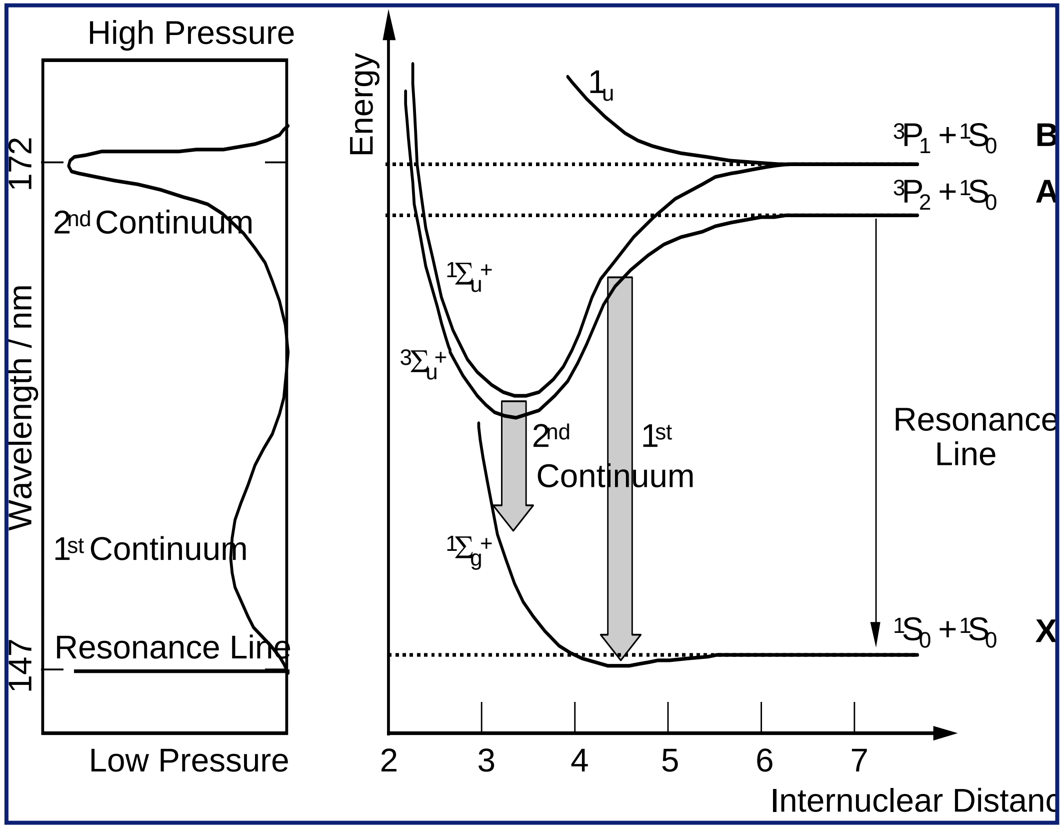
Radiation generation (Xe)

$Xe + e^- \rightarrow Xe(^3P_1) + e^-$
$\rightarrow Xe(^3P_2) + e^-$
$\rightarrow Xe^{**}$

$Xe^{**} \rightarrow Xe(^3P_1) + h\nu$ (828 nm)
$\rightarrow Xe(^3P_2) + h\nu$ (823 nm)

$Xe(^3P_1) \rightarrow Xe + h\nu$ (147 nm)

$Xe(^3P_1) + Xe + M \rightarrow Xe_2^* + M$



$Xe_2^* \rightarrow 2\ Xe + h\nu$ (150 nm and 172 nm)

Application of 50–90% Ne reduces discharge ignition voltage → plasma displays

2. Xe and Xe/Ne Discharges

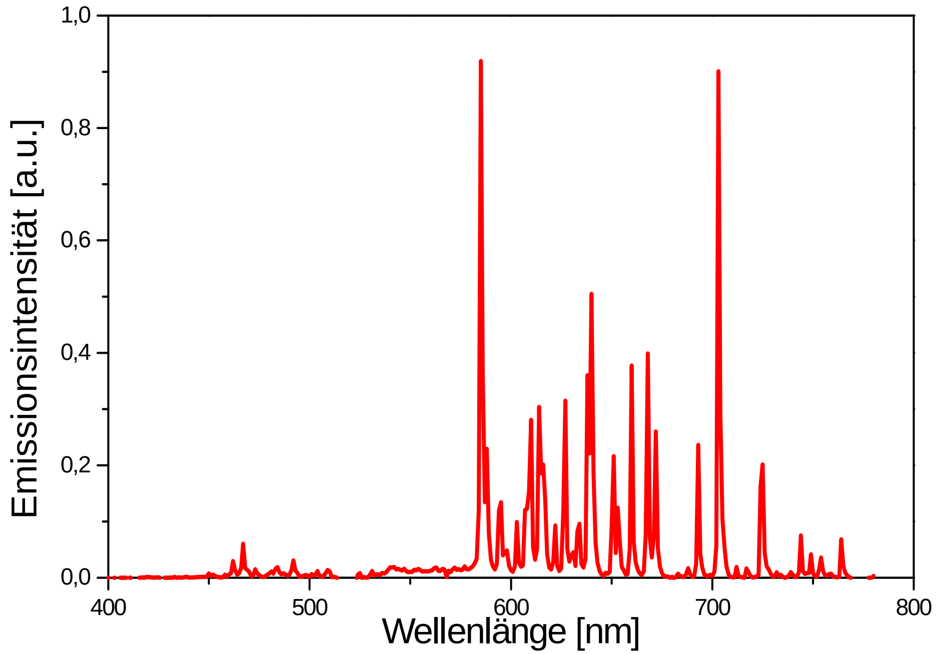
Radiation generation (Ne)

$Ne + e^- \rightarrow Ne^* + e^-$

$Ne^* \rightarrow Ne + h\nu$(74 nm + vis.)

$Ne^* + Ar \rightarrow Ne + Ar^+ + e^-$
$Ne^* + Xe \rightarrow Ne + Xe^+ + e^-$
(Penning Ionisation)

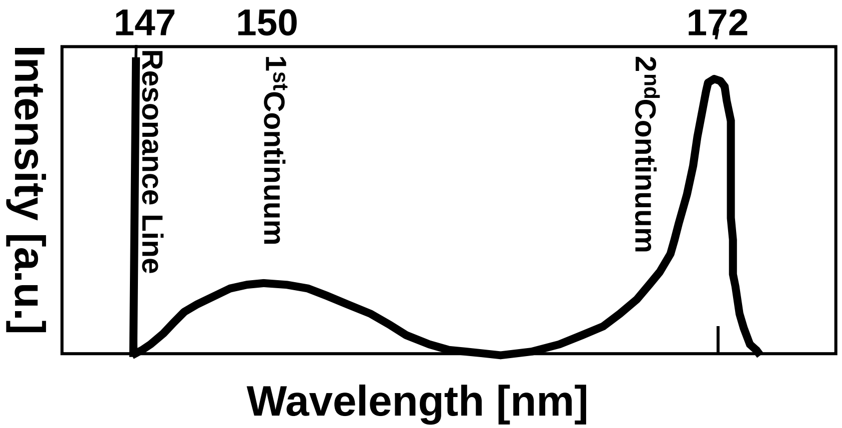
monochrome plasma displays



2. Xe and Xe/Ne Discharges

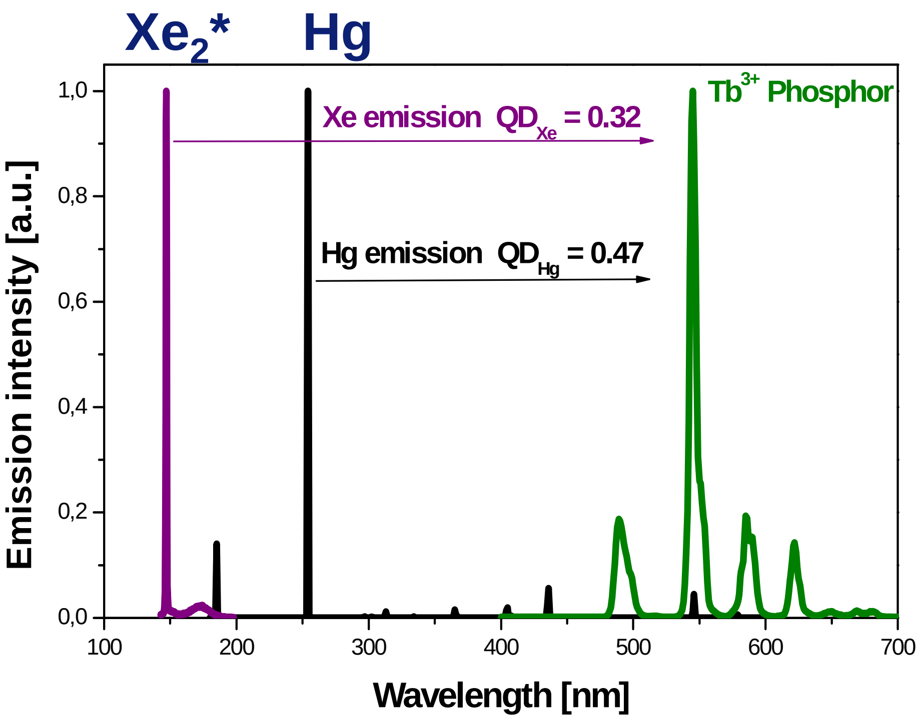
Features

- No Hg (EU legislation issue?)
- Noble gas discharge ⇒ “chemically inert”
- Instant light
- Arbitrary design ⇒ GLS-look-a-like, tubular, flat, co-axial, etc.
- T-independent light output
- Long lifetime even for fast switching cycle scheme
- Emission mainly in the Vacuum Ultraviolet (VUV)



2. Xe and Xe/Ne Discharges

Features



Burner / cell efficiency

$$\varepsilon = \varepsilon_{discharge} * QD * QE * \eta_{escape}$$

QD(Hg) =	0.47
QD(Xe_2*) =	0.32
Hg discharge:	ε = 30%
Xe_2* discharge	ε = 20%

Problem areas of Xe/Ne excimer discharge driven light sources + displays

- Large quantum deficit (QD) ⇒ reduces wall plug efficiency
- VUV radiation ⇒ causes severe photodegradation

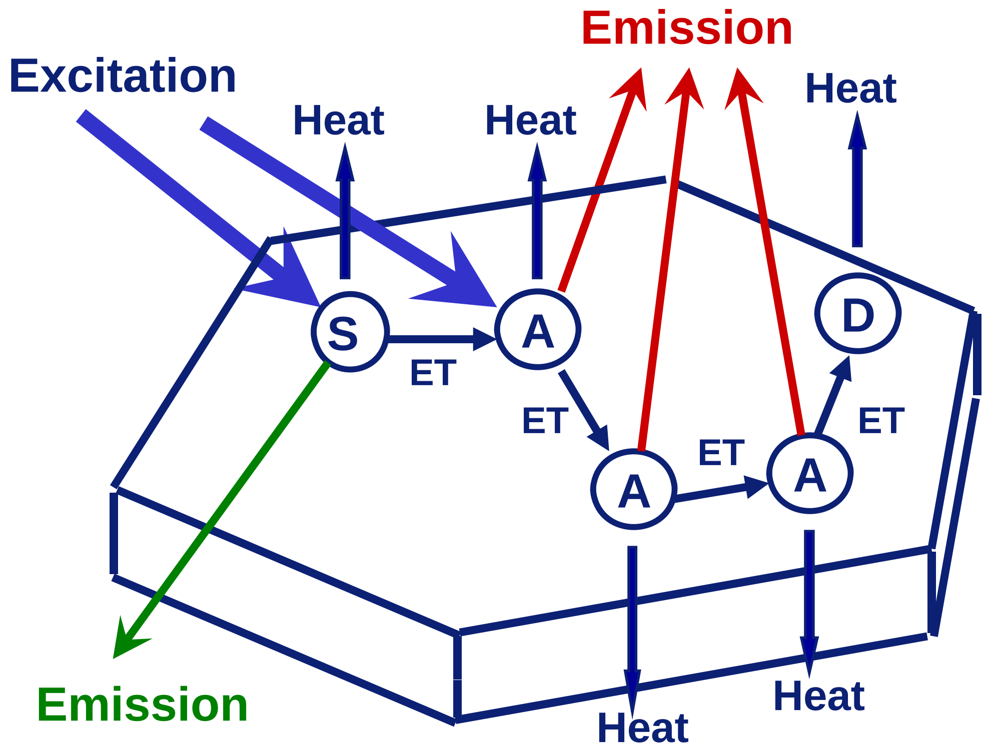
3. Inorganic Luminescent Materials

Requirements on VUV phosphors
- Very good crystallinity
- High purity (99,99% or better)
- Homogeneous distribution of activator and sensitiser ions

Absorption process related to
Optical centres (impurities)
- activators (A)
- sensitisers (S)
- defects (D)

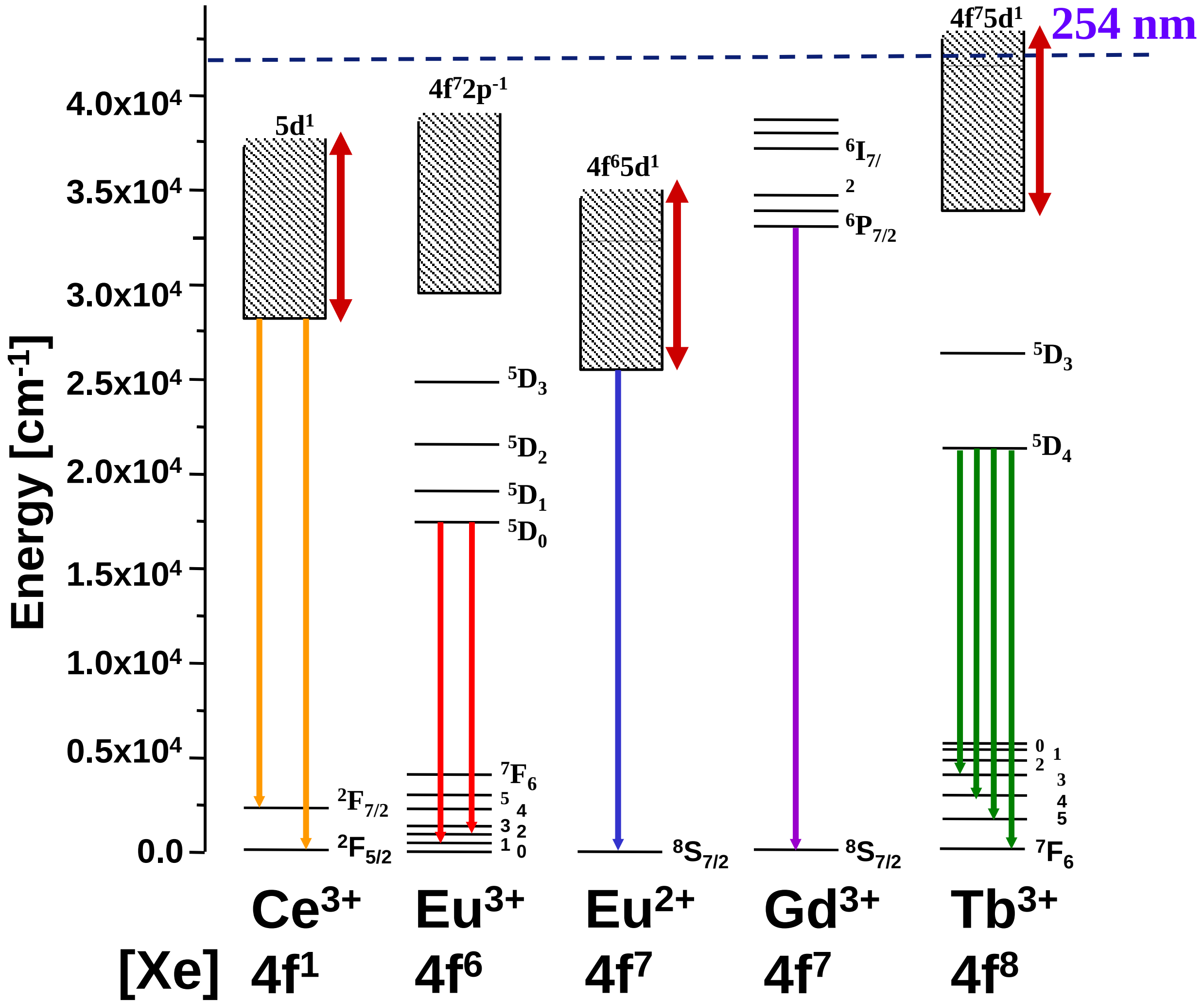
Host lattice (band edge)

Energy transfer often occur prior to emission process!



3. Inorganic Luminescent Materials

Fundamental aspects: Simplified energy level schemes of selected RE ions

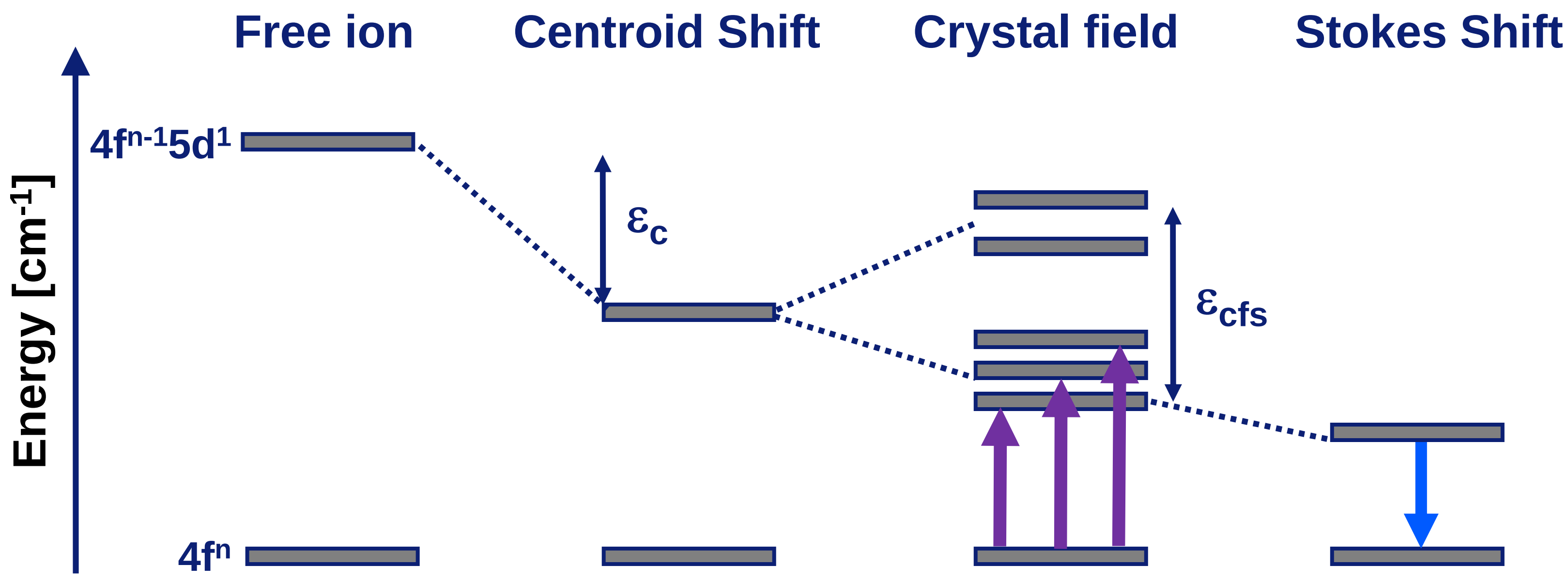


Line emission from
Pr^{3+}
Nd^{3+}
Sm^{3+}
Eu^{3+} (Eu^{2+})
Gd^{3+}
Tb^{3+}
Dy^{3+}
Ho^{3+}
Er^{3+}
Tm^{3+}
Yb^{3+}

Band emission from
Ce^{3+}
Pr^{3+}
Nd^{3+}
Eu^{2+}
Yb^{2+}
(Tl^{+}, Pb^{2+}, Sb^{3+}, Bi^{3+})

3. Inorganic Luminescent Materials

Fundamental aspects: Energy distance between the $4f^n$ and $4f^{n-1}5d^1$ configuration



Free ion: $4f^{n-1}5d^1$ level @	Eu^{2+}	Ce^{3+}	Pr^{3+}	Nd^{3+}
	34000 cm^{-1}	50000 cm^{-1}	62000 cm^{-1}	70000 cm^{-1}

Only RE ions and some main group element ions are applicable in luminescent materials showing UV emission

4. Phosphors for Plasma Display Panels

Quality Issues

Production compatibility

Temperature stability	Sensitivity towards oxidation
Suspension stability	Solubility, surface potential

Performance

Brightness	QE, particle morphology, saturation
Color point stability	VUV Stability

Image quality

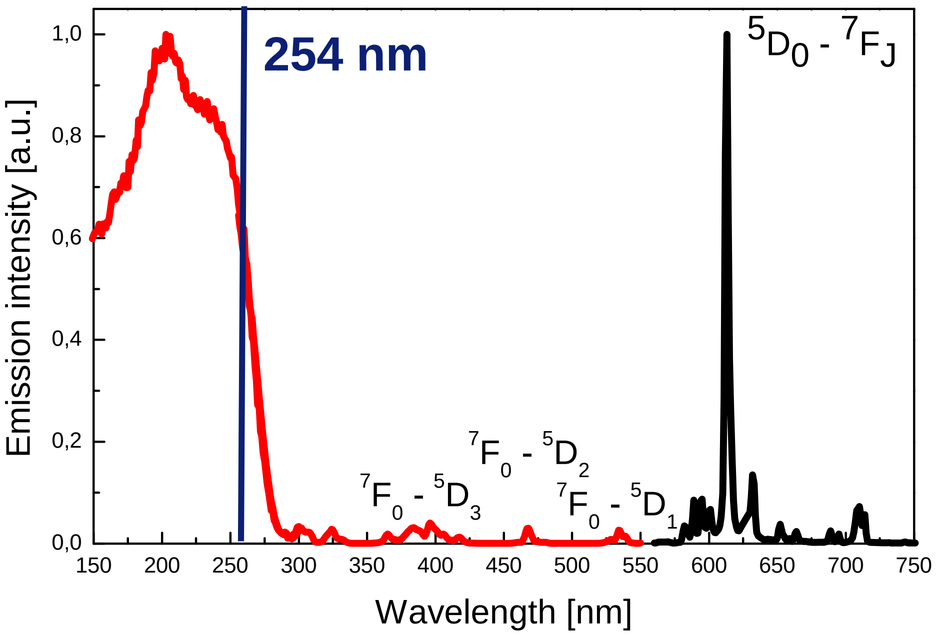
Motion artefacts	Decay time
Color gamut	Color point (stability)

Environment

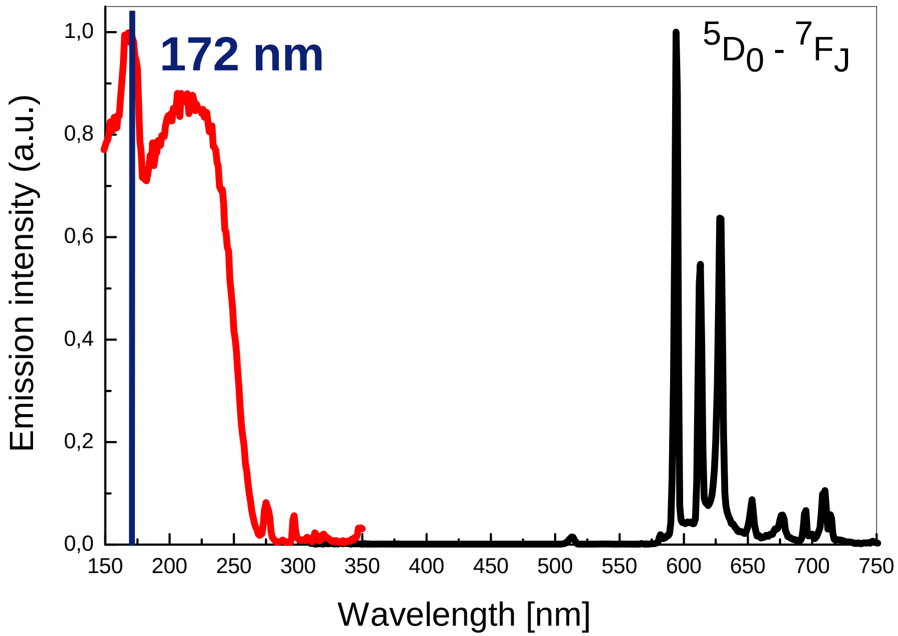
Energy efficiency	QE, particle morphology
Toxicity	Chemical composition

4. Phosphors for Plasma Display Panels
- Efficient Red Emitting Phosphor -

$Y_2O_3:Eu^{3+}$
Low-pressure Hg discharges



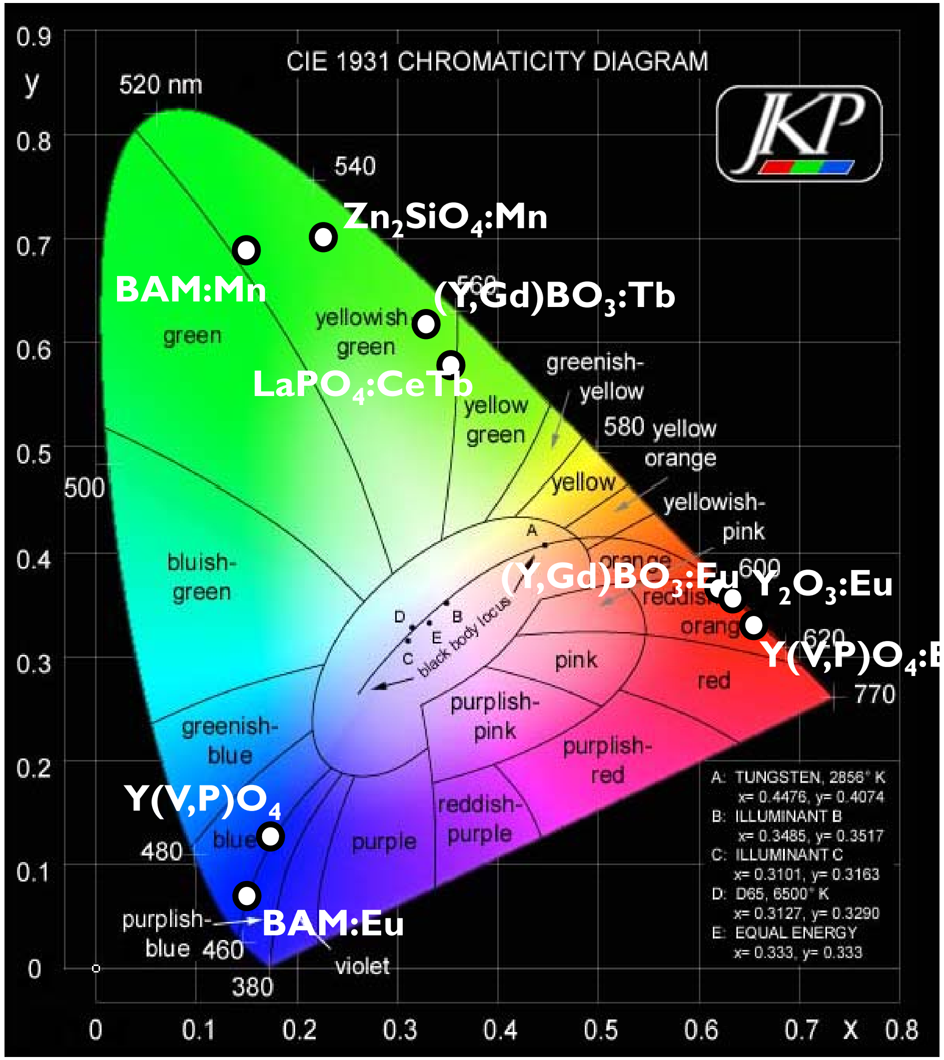
$(Y,Gd)BO_3:Eu^{3+}$
Xe excimer discharges



4. Phosphors for Plasma Display Panels

Colour points and decay times

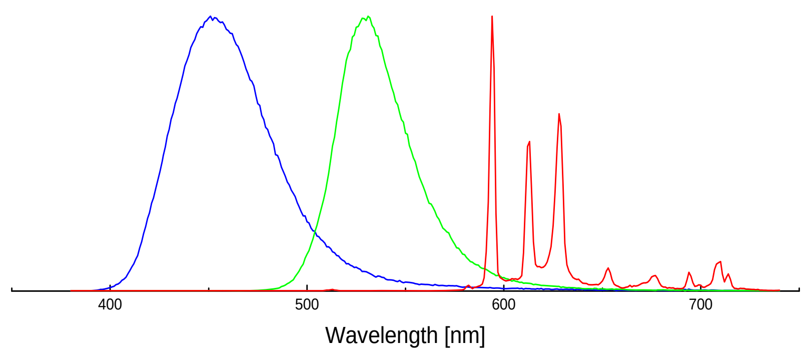
Phosphor	x	y	τ [ms]
$BaMgAl_{10}O_{17}:Eu$	0.148	0.068	< 1
$Y(V,P)O_4$	0.161	0.133	< 1
$BaMgAl_{10}O_{17}:Mn$	0.140	0.695	12
$Zn_2SiO_4:Mn$	0.233	0.702	10
$(Y,Gd)BO_3:Tb$	0.324	0.615	8
$LaPO_4:Ce,Tb$	0.350	0.582	3
$(Y,Gd)BO_3:Eu$	0.636	0.357	8
$Y_2O_3:Eu$	0.640	0.346	2.5
$Y(Y,P)O_4:Eu$	0.657	0.330	1



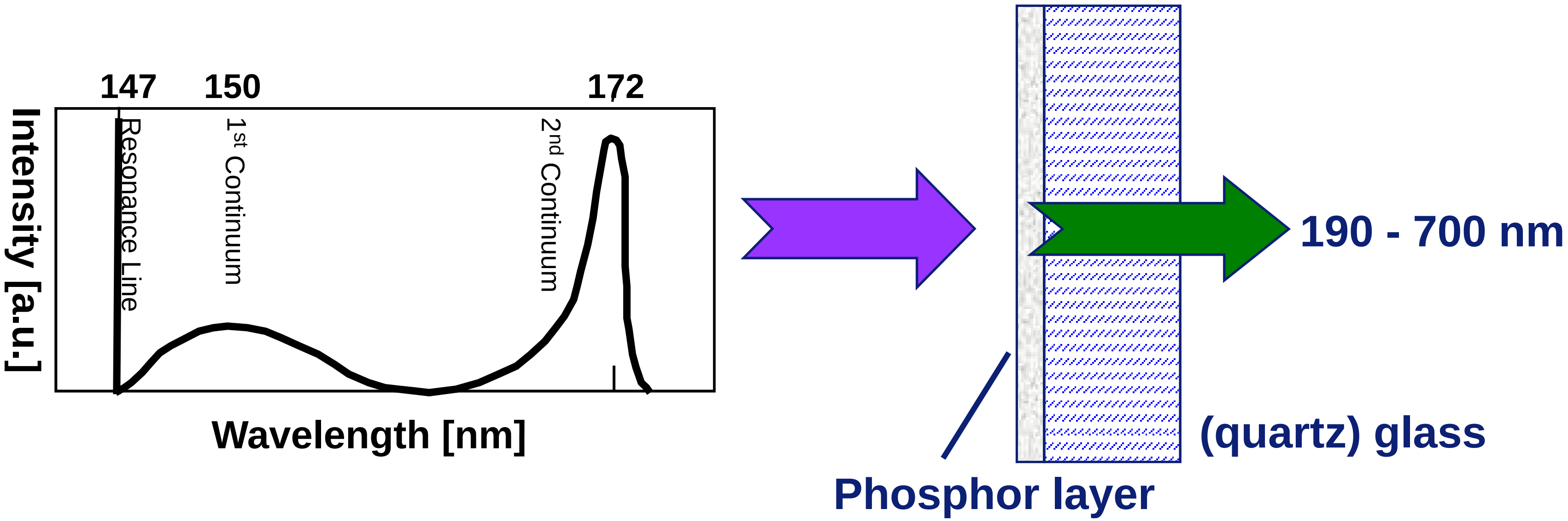
4. Phosphors for Plasma Display Panels

VUV phosphors

Presently applied	shortcoming	Novel materials based on host lattices with suitable band edge
$BaMgAl_{10}O_{17}$:Eu	stability	$BaMg_3Al_{14}O_{25}$:Eu $Sr_6BP_5O_{20}$:Eu $BaAl_2Si_2O_8$:Eu $CaAl_2O_4$:Eu $LaPO_4$:Tm
Zn_2SiO_4:Mn	decay time	$BaAl_{12}O_{19}$:Mn $BaMg_3Al_{14}O_{25}$:Mn
$(Y,Gd)BO_3$:Eu	color point	$(Y,Gd)_2SiO_5$:Eu



5. Phosphors for Xe_2^* Discharge Lamps



Features
- Discharge efficiency ~ 65%
- Hg free
- Fast switching cycles
- Temperature independent
- Dimmable
- High lifetime
- Mainly VUV emission

Potential application areas	Phosphor layer
– Photocopier lamps	RGB or B/W
– LCD Backlighting	RGB
– Medical skin treatment	UV-A/B
– Photochemistry	UV-A/B/C
– Disinfection	UV-C
– Ultra pure water	-
– Surface/wafer cleaning	-

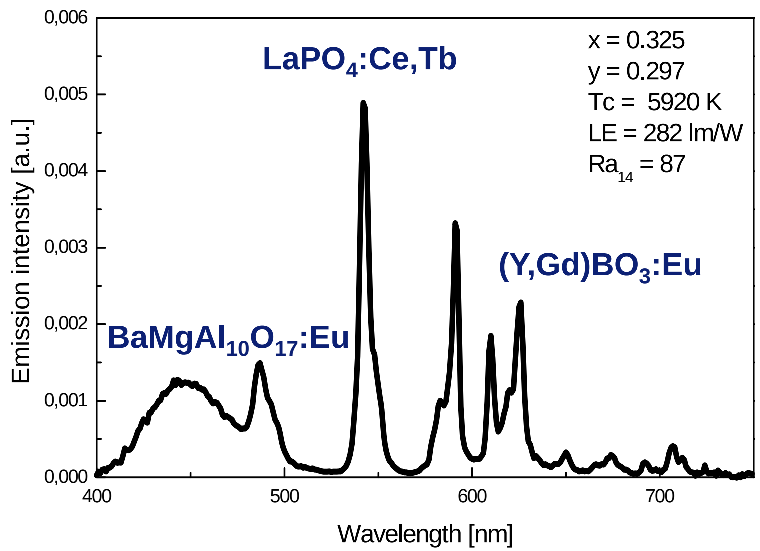
5. Phosphors for Xe_2^* Discharge Lamps

VUV phosphors for white Xe_2^* discharge lamps

$BaMgAl_{10}O_{17}$:Eu	80 $lm/W_{opt.}$
$LaPO_4$:Ce,Tb	500 $lm/W_{opt.}$
$(Y,Gd)BO_3$:Tb	530 $lm/W_{opt.}$
$(Y,Gd)BO_3$:Eu	275 $lm/W_{opt.}$
$(Y,Gd)_2O_3$:Eu	290 $lm/W_{opt.}$

Luminous efficiency < 50 $lm/W_{el.}$

Spectrum of Osram Planon

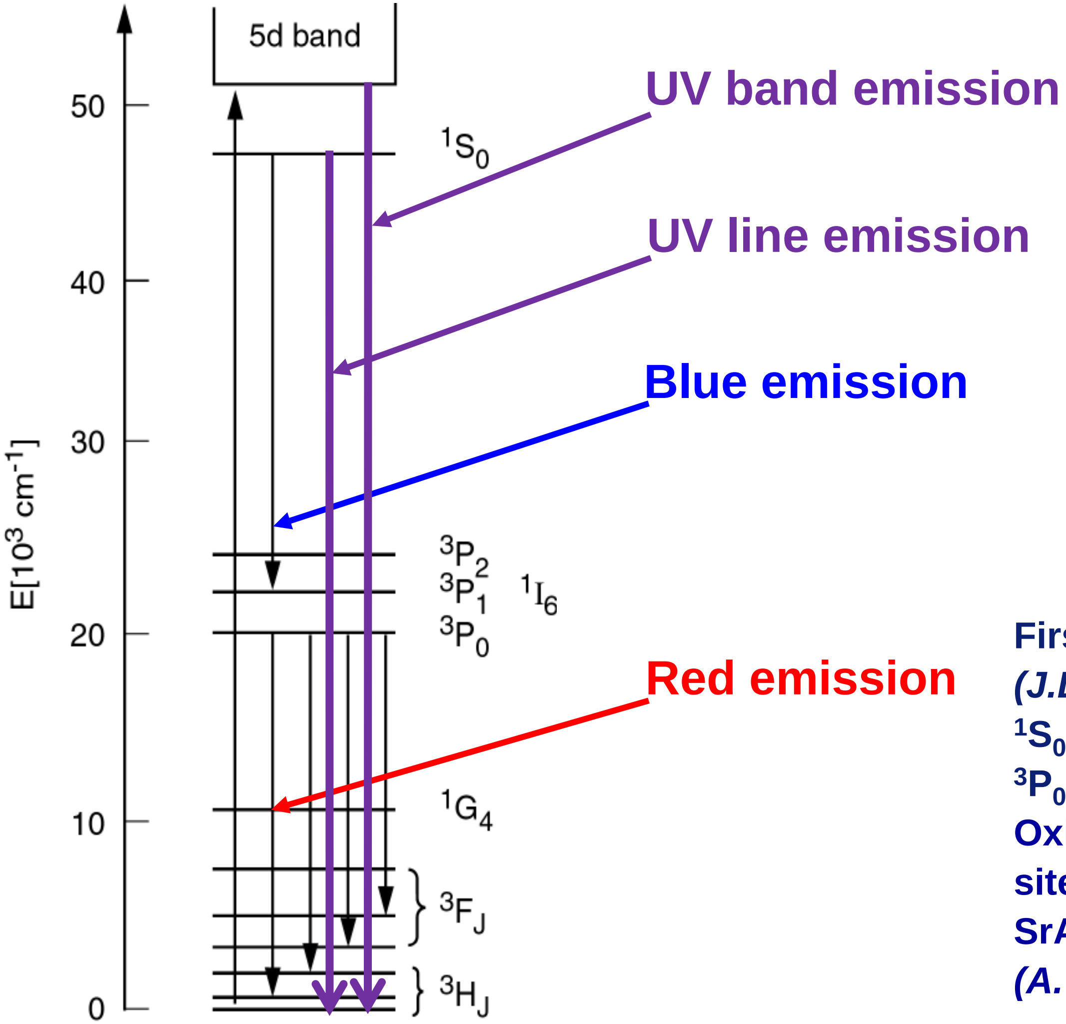


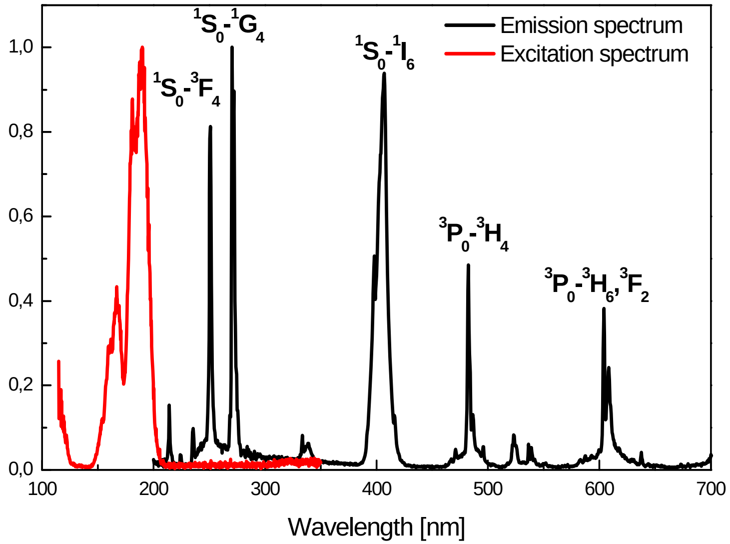
Challenges related to VUV phosphors for Xe_2^* discharge lamps

a) Lamp efficacy	→ Down conversion phosphors
b) VUV stability	→ Particle coatings (MgO or Al_2O_3)
c) Color point stability	→ Optimised blue phosphor
d) Novel application areas	→ UV phosphors

5. Phosphors for Xe_2* Discharge Lamps

Down conversion phosphors: Single ion mechanism on Pr^{3+}



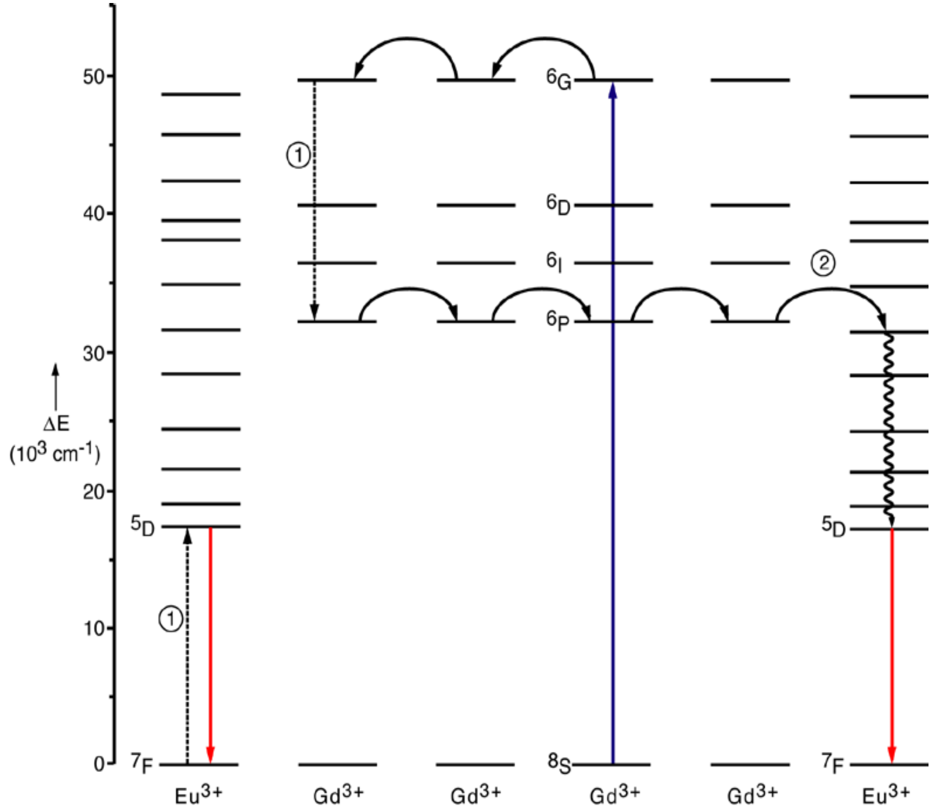


First fluorides: YF_3:Pr und $NaYF_4$:Pr
(J.L. Sommerdijk et al., J. Lumin. 8 (1974) 341)
$^1S_0$ - $^3P_1$,$^1I_6$ at 407 nm
$^3P_0$ - $^3H_6$,$^3F_2$ at 615 nm
Oxidic phosphors: Host lattices with Ln^{3+} sites having high coordination number
$SrAl_{12}O_{19}$:Pr, $LaMgB_5O_{10}$:Pr, and LaB_3O_6:Pr
(A. Srivastava et al., GE)

5. Phosphors for Xe_2^* Discharge Lamps

Down conversion phosphors: Pair mechanism in Gd^{3+}-Eu^{3+} or Gd^{3+}-Er^{3+}

- **Discovered by A. Meijerink et al. in 2000**
- **Internal quantum efficiency about 195% in $LiGdF_4$**
- **External quantum efficiency about 30 – 35% at 202 nm due to competitive host lattice absorption, which does not result in luminescence (low transfer efficiency!)**



Gd —202 nm→ Gd**

Gd + Eu —CR→ Eu* + Gd***

Eu* → Eu + hν

Gd* + Eu —ET→ Gd + Eu*

Eu* → Eu + hν

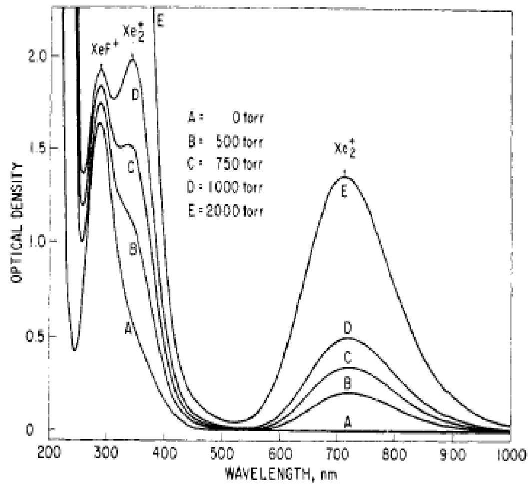
5. Phosphors for Xe_2* Discharge Lamps

VUV Stability

Sample	C 1s	O 1s	Si 2p	Y 3p3/2	Xe 3d5/2
Y-phosphor (as made) SiO_2 coated	1.1	70.2	28.7	< 0.05	< 0.1
Y-phosphor after 100 h lamp operation	0.3	68.7	28.4	< 0.05	2.6

(all values in atom-%)

- Phosphor degrades due to
  - VUV radiation
  - Direct contact to the discharge
- Low penetration depth of VUV radiation
- $Xe_2^{*/+}$ adheres to phosphor surface, electron take-up is difficult as phosphor surface is too electronegative (low PZC, e.g. silicates or SiO_2)
- Xe_2^+ is stabilised by strong Lewis acids (SbF_5, SiO_2) and absorbs in the UV-A/B and red spectral range



a)JACS 102 (1980) 2856
b) E. Riedel, Modern Inorganic chemistry

Consequences

- No silicate phosphors!
- Coating by alkaline materials
  - Al_2O_3 or MgO as protective coating

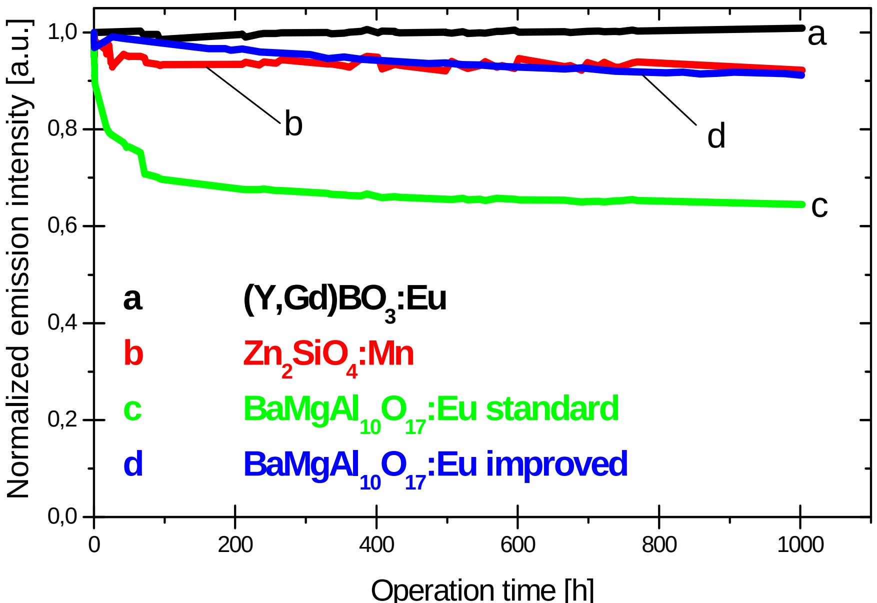
5. Phosphors for Xe_2^* Discharge Lamps

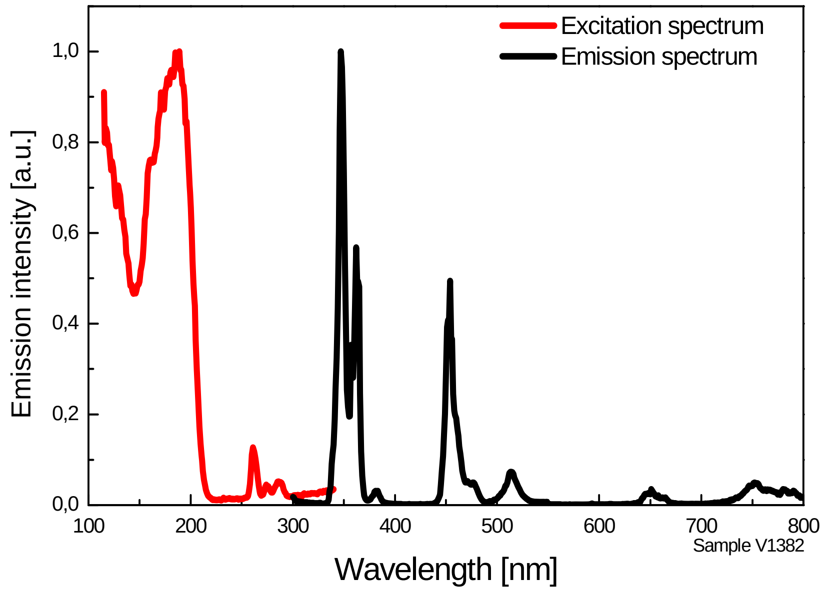
Color point stability (blue phosphor)

Improved $BaMgAl_{10}O_{17}$:Eu,(Mn) by application Mg^{2+} excess during synthesis
(J.-P. Cuif, Rhodia, PGS 2005)

Alternative materials

- $BaAl_2Si_2O_8$:Eu 435 nm
  (Chem. Mater. 2006)
- $LaPO_4$:Tm 454 nm
  blended with $BaMgAl_{10}O_{17}$:Eu
  (J. Luminescence 2005)





5. Phosphors for Xe_2^* Discharge Lamps

UV Phosphors – Host lattices and activators

VUV	UV-C	UV-B	UV-A
100 nm – 200 nm	200 nm – 280 nm	280 nm – 320 nm	320 nm – 400 nm

100 nm 200 nm 280 nm 320 nm 400 nm

Host lattices

Fluorides Phosphates Borates Silicates Aluminates

Suitable activators

Nd^{3+}, Tl^{+}

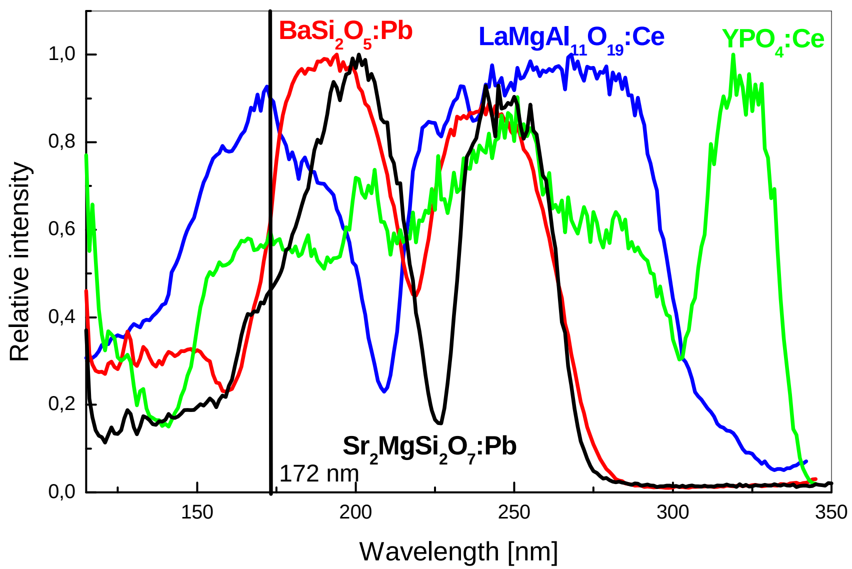
Pb^{2+}, Pr^{3+}, Bi^{3+}

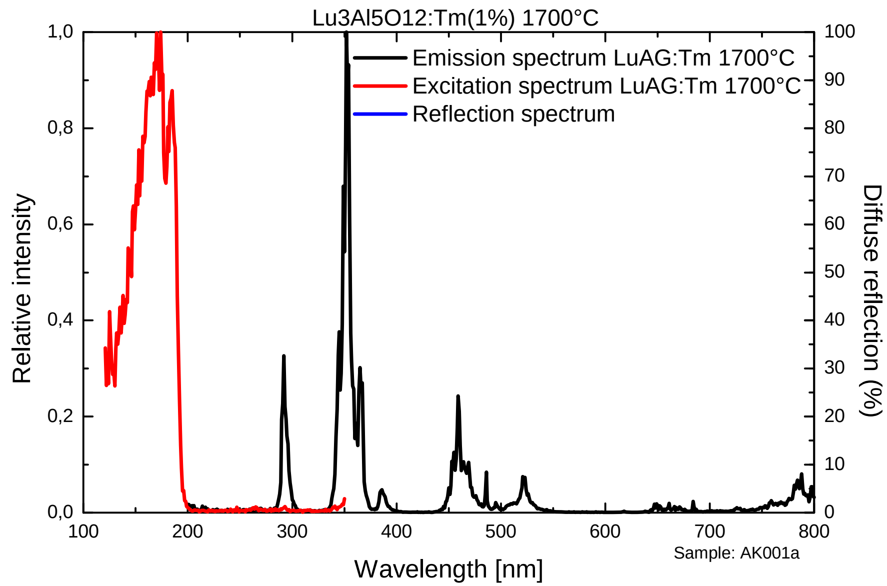
Gd^{3+}, Bi^{3+}, Pr^{3+}, Ce^{3+}

Tm^{3+} , Pb^{2+}, Ce^{3+}

5. Phosphors for Xe_2* Discharge Lamps

UV-A Phosphors





UV-A emitting phosphors for UV-C excitation (LP Hg discharge lamps)

VUV Efficiency: $LaMgAl_{11}O_{19}$:Ce > YPO_4:Ce ~ $BaSi_2O_5$:Pb > $Sr_2MgSi_2O_7$:Pb

UV-A emitting phosphor for VUV excitation

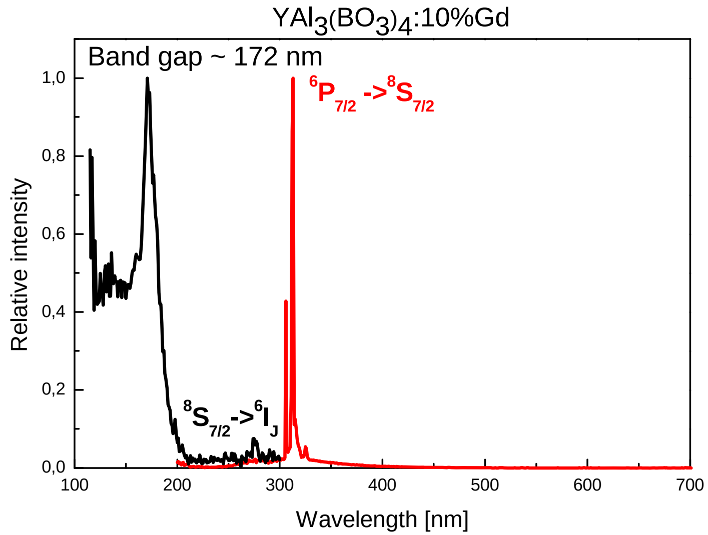
$Lu_3Al_5O_{12}$:Tm Emission @ 292 and 352 nm, exc. max. at 170 nm

5. Phosphors for Xe_2* Discharge Lamps

UV-B Phosphors – Gd^{3+} emitter

Sensitisation by the host lattice (suitable band gap!)

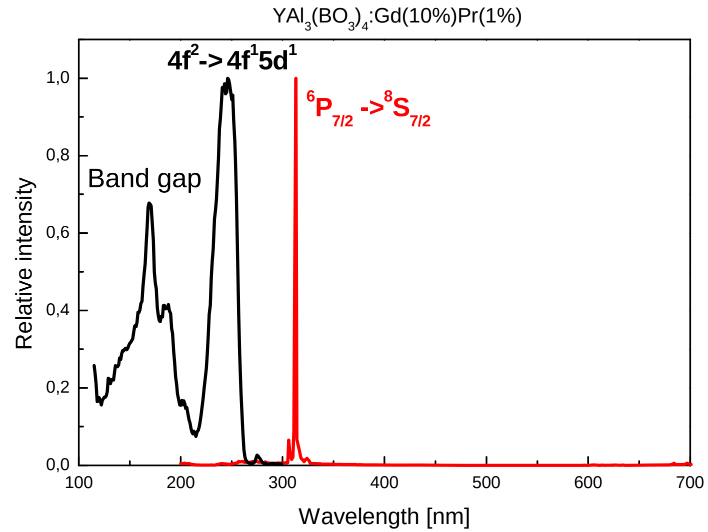
Example: $YAl_3(BO_3)_4$:Gd
(NEC patent US2005/001024)



Sensitisation by co-dopants

Bi^{3+} → large lattice position (e.g. La^{3+}) required
Ce^{3+} → suitable 4f5d state pos. required
Pr^{3+} → suitable 4f5d state pos. required
Nd^{3+} → suitable 4f5d state pos. required

Example: $GdPO_4$:Nd
(Philips patent EP06112503)

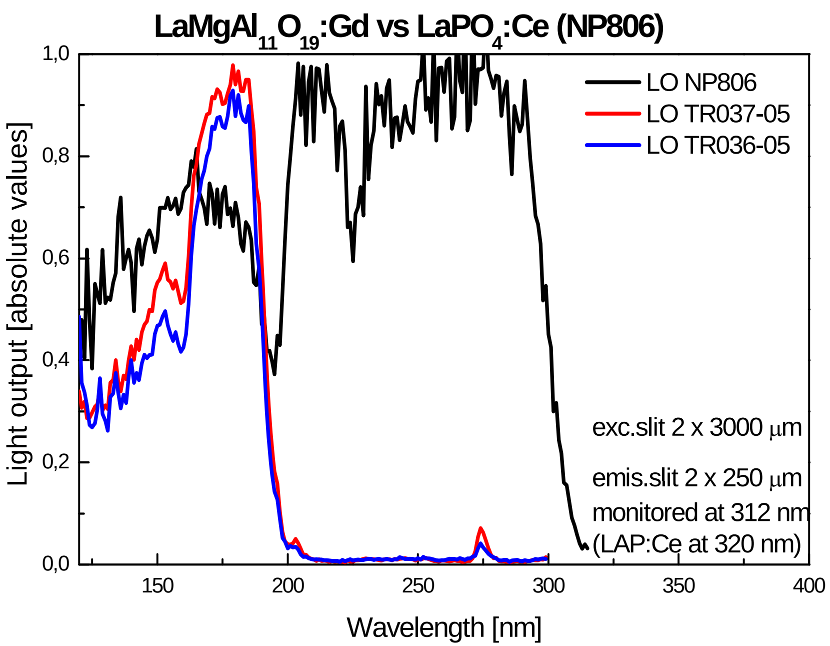


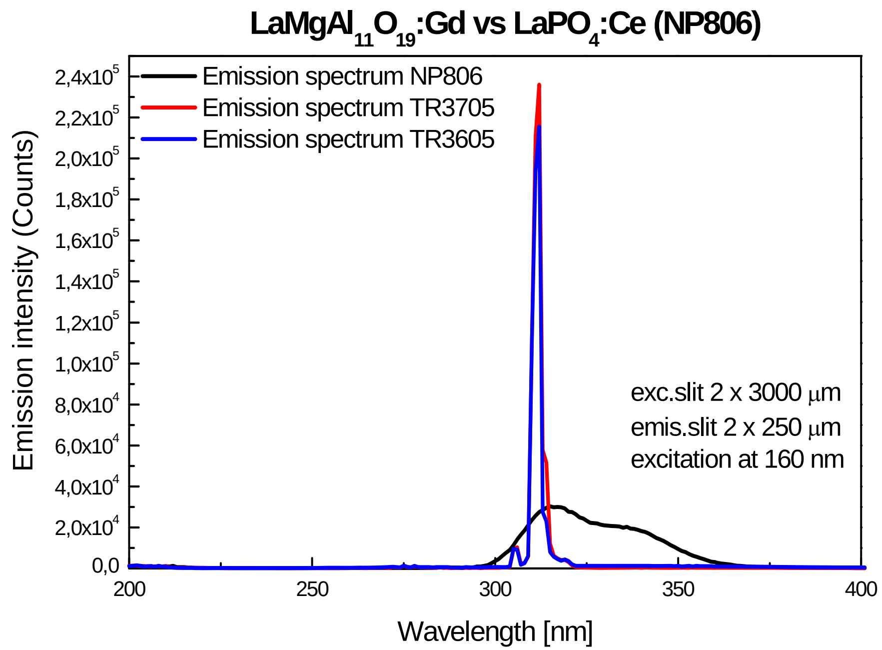
5. Phosphors for Xe_2^* Discharge Lamps

UV-B Phosphors – Gd^{3+} emitter

$LaMgAl_{11}O_{19}$:30%Gd^{3+}

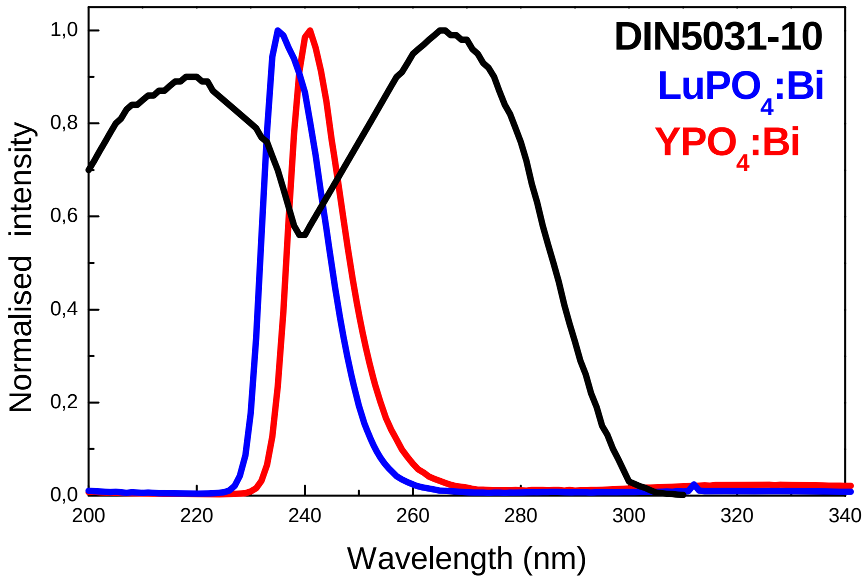
QE(172 nm) close to 100%!

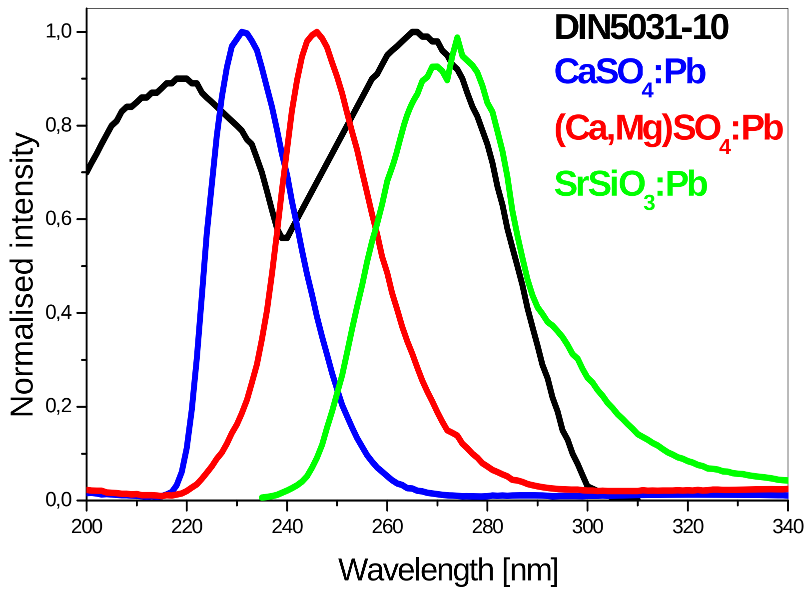




5. Phosphors for Xe_2* Discharge Lamps

UV-C Phosphors - Bi^{3+} and Pb^{2+} emitter



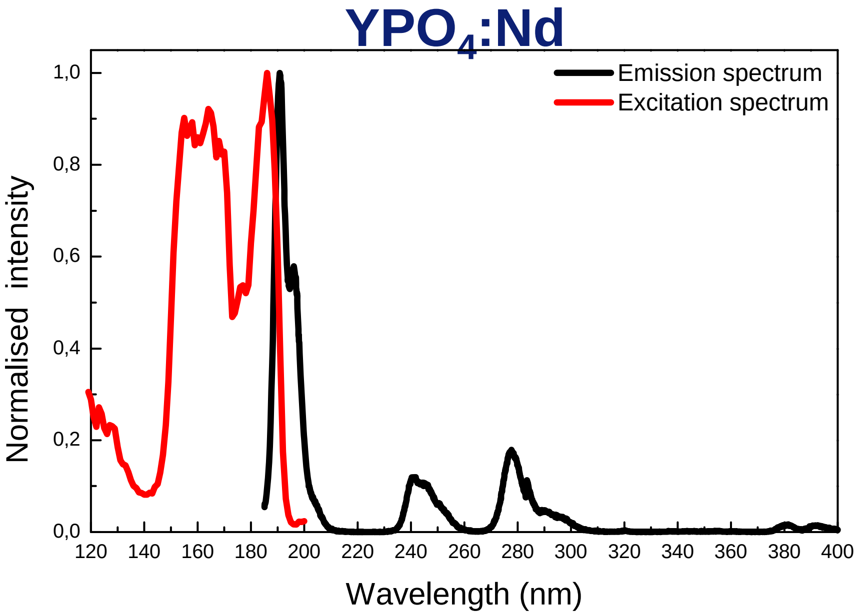


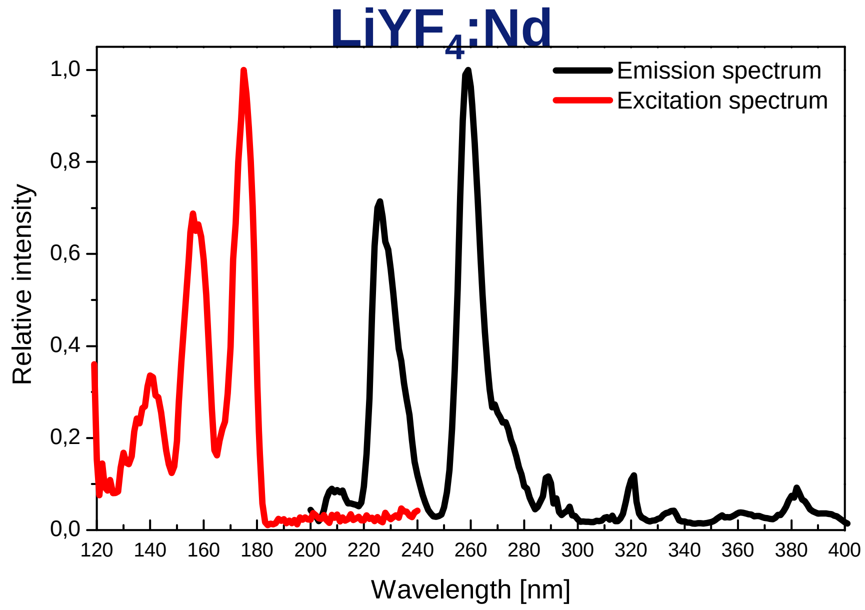
(Ca,Mg)SO_4:Pb, $SrSiO_3$:Pb $\Rightarrow$ sensitivity towards water, Xe up-take

(Y,Lu)PO_4:Bi $\Rightarrow$ good chemical stability + high VUV efficiency

5. Phosphors for Xe_2* Discharge Lamps

VUV to VUV down converting phosphors - Nd^{3+} emitter





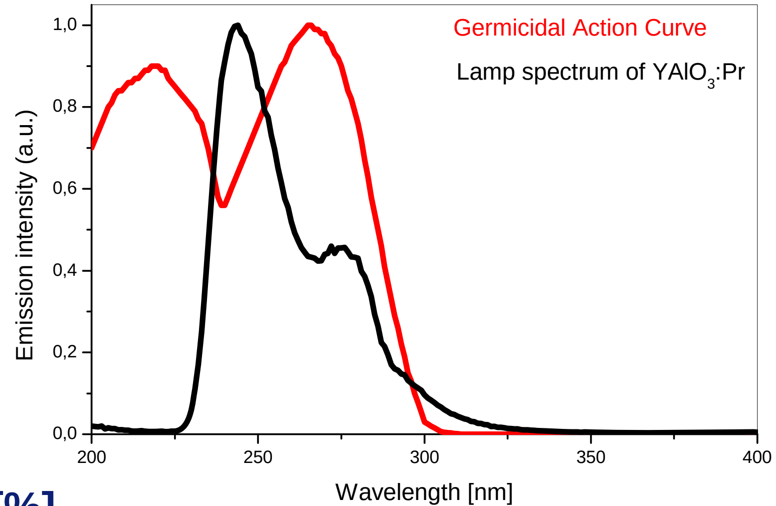
Emission maxima at 190 + 240 + 278 nm

5. Phosphors for Xe_2* Discharge Lamps

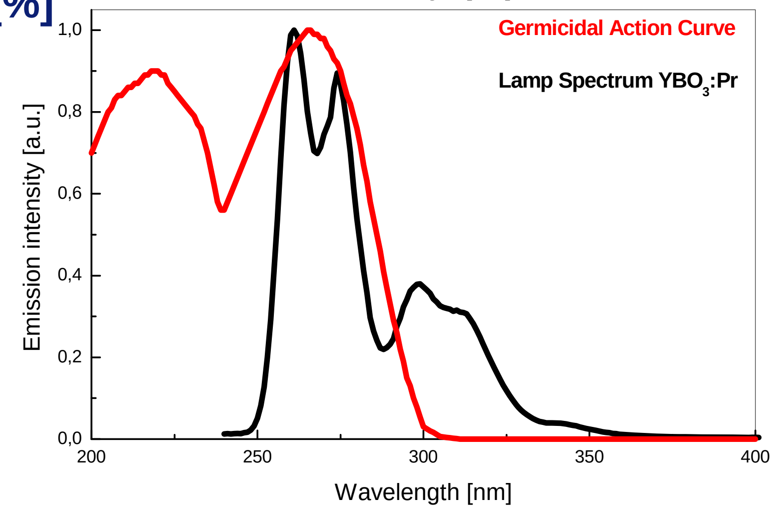
Phosphor converted Xe_2* excimer discharge lamp for disinfection

Requires UV-C emitting phosphor with a high conversion efficiency <u>and</u> a large integral overlap with germicidal action curve

⇒ e.g. Pr^{3+} or Bi^{3+} activated materials



Phosphor	λ_{max} [nm]	GAC overlap [%]
YPO_4:Pr	233	78
YPO_4:Bi	241	71
$YAlO_3$:Pr	245	71
YBO_3:Pr	263	61
Line @	265	100
Line @	311	0

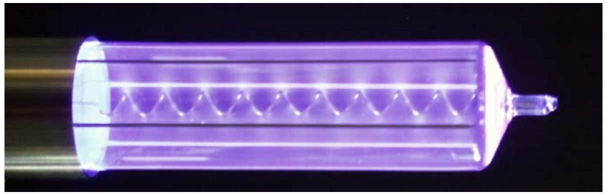


6. Application Areas

Lamps without phosphor ⇒ **solely 172 nm radiation**

Lamps with VUV phosphors ⇒ **spectrum can be defined by the phosphor in accordance to application area**

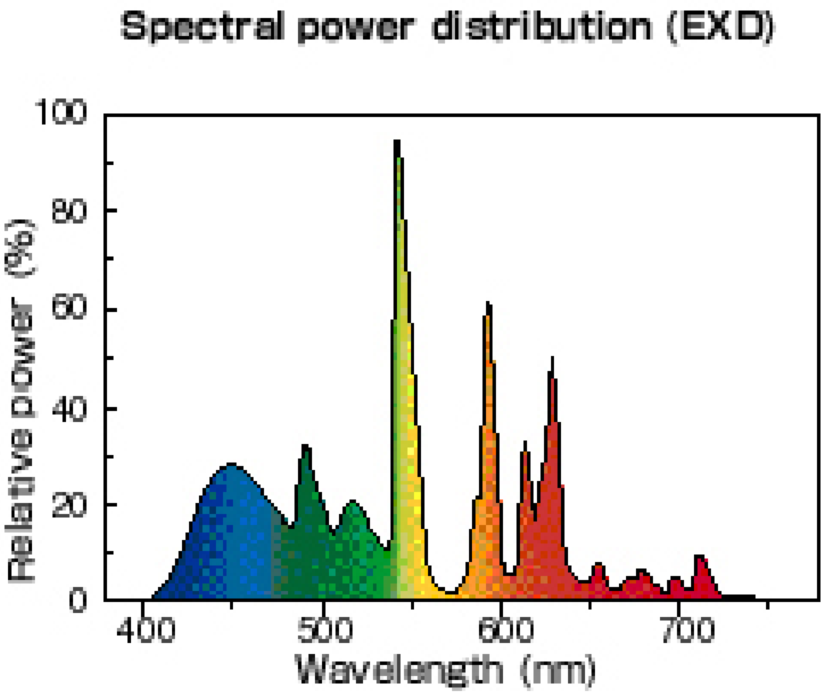
Application area	Required emission	Embodiments from
• Hg-free CFL-i	White (tricolour blend)	-
• Backlighting of LCDs	White or UV-A	Osram, Hitachi, Stanley
• Photocopier / scanner	White or UV-A	NEC, Ushio
• Purification	VUV	Heraeus, Ushio, Radium
• Disinfection	UV-C	-
• Tanning	UV-A	-
• Photochemistry	UV-B or UV-A	-

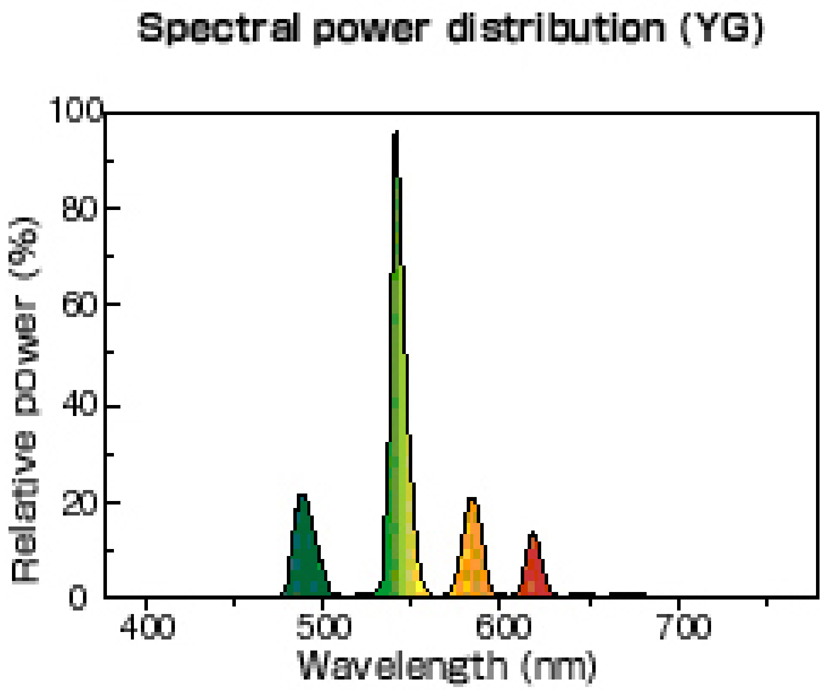


XERADEX (Radium)

6. Application Areas

Xe Discharge lamps - Copiers and scanners





Color ⇒ Tetrachromatic phosphor blend

$BaMgAl_{10}O_{17}$:Eu

Zn_2SiO_4:Mn

$LaPO_4$:Ce,Tb

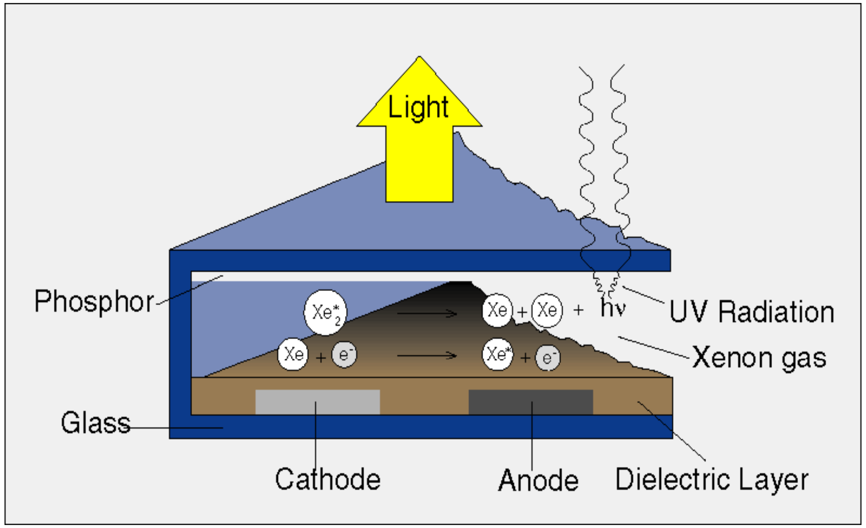
(Y,Gd)BO_3:Eu

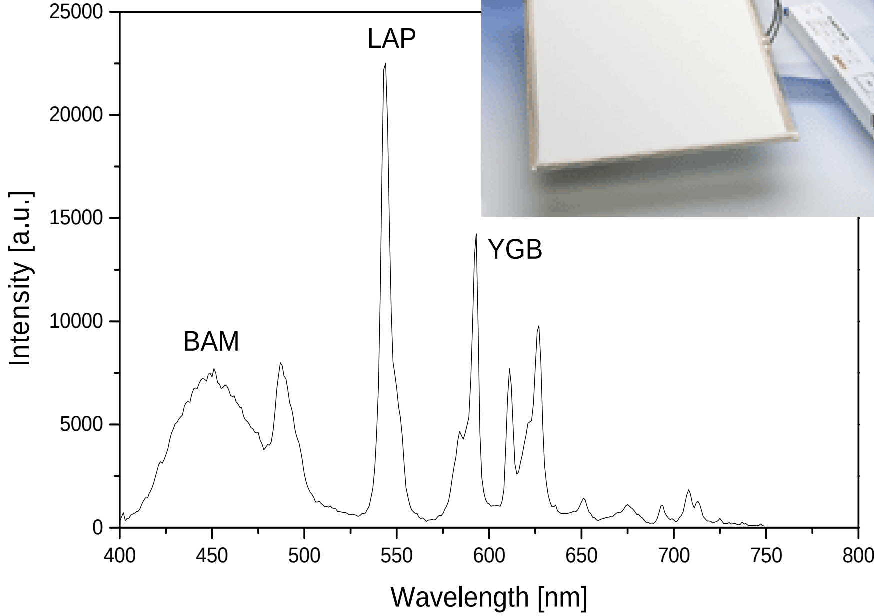
B/W ⇒ single phosphor

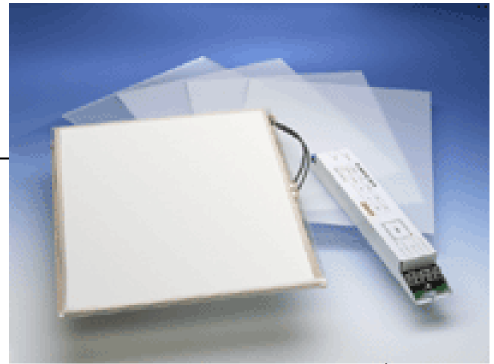
$LaPO_4$:Ce,Tb

6. Application Areas

Xe Discharge lamps - LCD Backlighting







Tricolor blend

- $BaMgAl_{10}O_{17}$:Eu 38 %
- $LaPO_4$:Ce,Tb 38 %
- $(Y,Gd)BO_3$:Eu 24 %

Lamp specifications

Color point x = 0.290, y = 0.276

CCT = 9570 K

R_a = 89

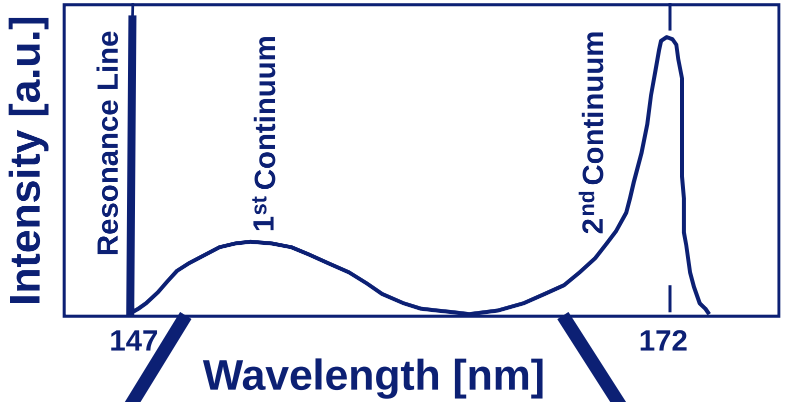
6. Applications Areas - UV Radiation

100 nm | 200 nm | 280 nm | 320 nm | 400 nm

VUV	UV-C	UV-B	UV-A
12.5 - 6.9 eV	6.2 – 4.5 eV	4.5 - 3.9 eV	3.9 – 3.1 eV
Cleavage of H_2O and O_2 into radicals Ozone formation Cleavage of C-C, C-H, C-O bonds	Excitation of C=C bonds Excitation of nucleobases Cleavage of O_3, ClO_2 and H_2O_2	Vitamine D production Transcription of repair enzymes Melanosome formation (skin)	Photocatalytic reactions Melanine oxidation (skin) Decomposition of organic pigments Activation of photocatalytical pigments
• Waver cleaning •Photochemistry	• Disinfection of air, H_2O and surfaces • Photochemistry	• Treatment of skin diseases, e.g. psoriasis • Tanning • Photochemistry	• Water and air purification @ TiO_2 photocatalyst, form. of $OH^{\cdot}$ and $O_2^{\cdot}$ radicals • Tanning • H_2O_2 production in-situ

6. Application Areas

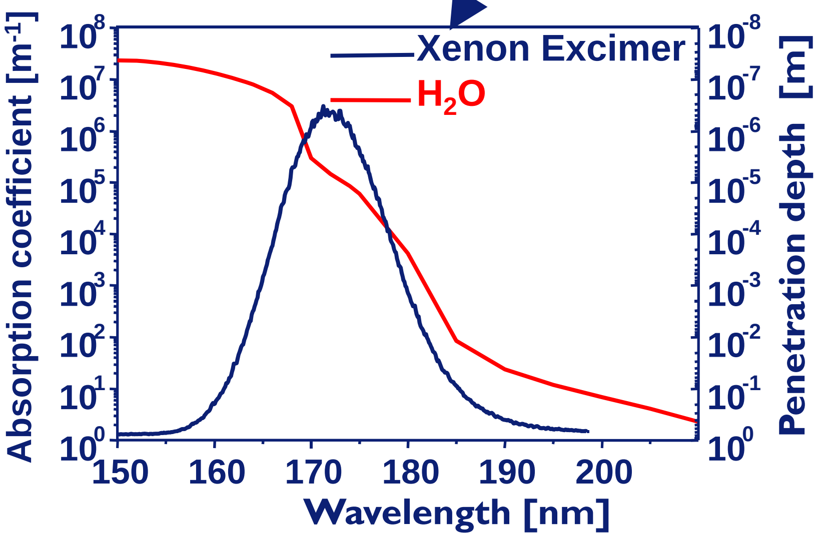
Xe_2* Discharge lamps for disinfection and Purification purposes

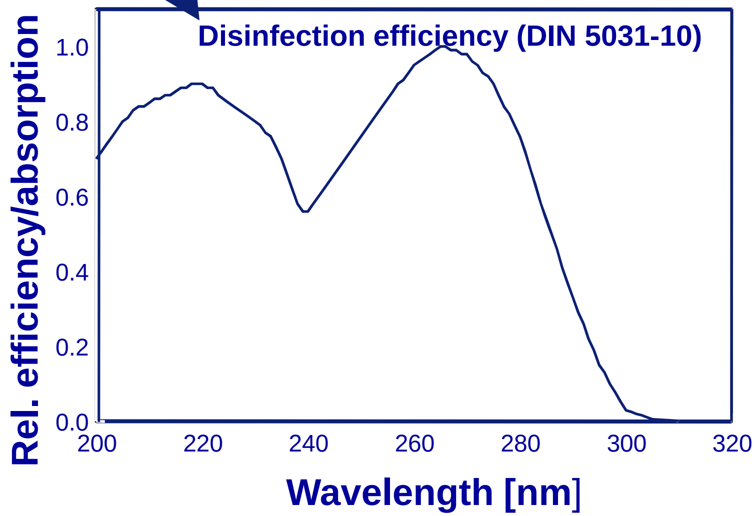


Xe excimer emission spectrum

convert to 190 - 200 nm

convert to 200 - 280 nm



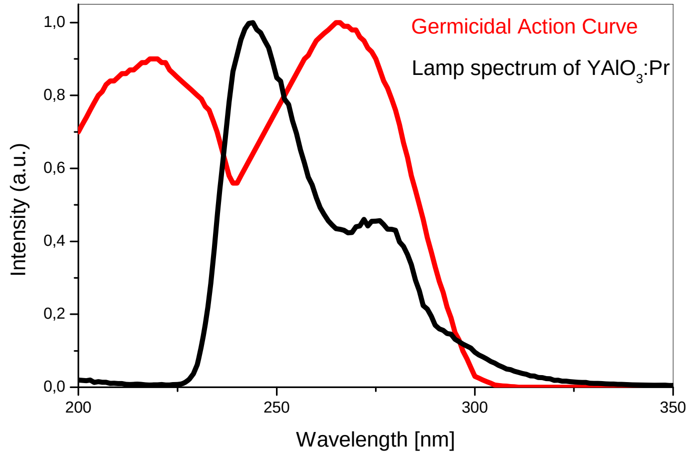


to improve penetration depth

to improve GAC overlap

6. Application Areas

Phosphor converted Xe_2^* excimer discharge lamp

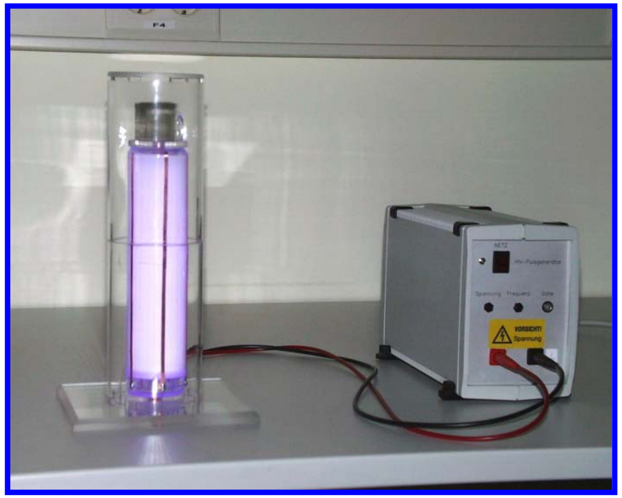


Requires development and optimization

of UV-C phosphors with a large GAC overlap

⇒ e.g. Pr^{3+} or Bi^{3+} activated phosphors

$LaPO_4$:Pr	**225 nm**
KYF_4:Pr	**232 nm**
YPO_4:Pr	**233 nm**
YPO_4:Bi	**241 nm**
$YAlO_3$:Pr	**245 nm**
KY_3F_{10}:Pr	**249 nm**
$LuBO_3$:Pr	**257 nm**
YBO_3:Pr	**261 nm**
Y_2SiO_5:Pr	**270 nm**



Best practice UV-C phosphor so far **YPO_4:Bi**
Lamp efficiency **30%**

7. Conclusions

VUV phosphors as luminescent converters for Xe(Ne) discharges

• UV	Ce^{3+}, Pr^{3+}, Nd^{3+}, Gd^{3+}, Tm^{3+}	Tl^{+}, Pb^{2+}, Bi^{3+}
• Blue	Eu^{2+}, Ce^{3+}	Bi^{3+}
• Green	Tb^{3+}	Mn^{2+}
• Red	Eu^{3+}	Mn^{2+}, Mn^{4+}

Plasma display panels

- Long-term stability of phosphors with redox active activators is an issue
- Phosphor blends as a trade-off between color point and efficiency
- Red phosphor with a deep red color point is still required (Mn^{4+}?)

Xe Excimer discharge lamps

- Luminous efficiency limited to 40 – 50 lm/W
- Down conversion phosphors are not within immediate reach
- Niche products: Photocopying, surface cleaning, backlighting, etc.
- Novel UV phosphors might open attractive application areas for Xe_2* lamps
- UV-A phosphor with a high VUV efficiency is $LaMgAl_{11}O_{19}$:Ce
- Gd^{3+} activated UV-B phosphors can be sensitised via host lattice or Nd^{3+}, Bi^{3+}
- LuAG as a host lattice yields stable and efficient UV phosphors (Gd^{3+}, Tm^{3+})
- YPO_4:Bi and YPO_4:Nd are the most efficient UV-C and VUV phosphors so far

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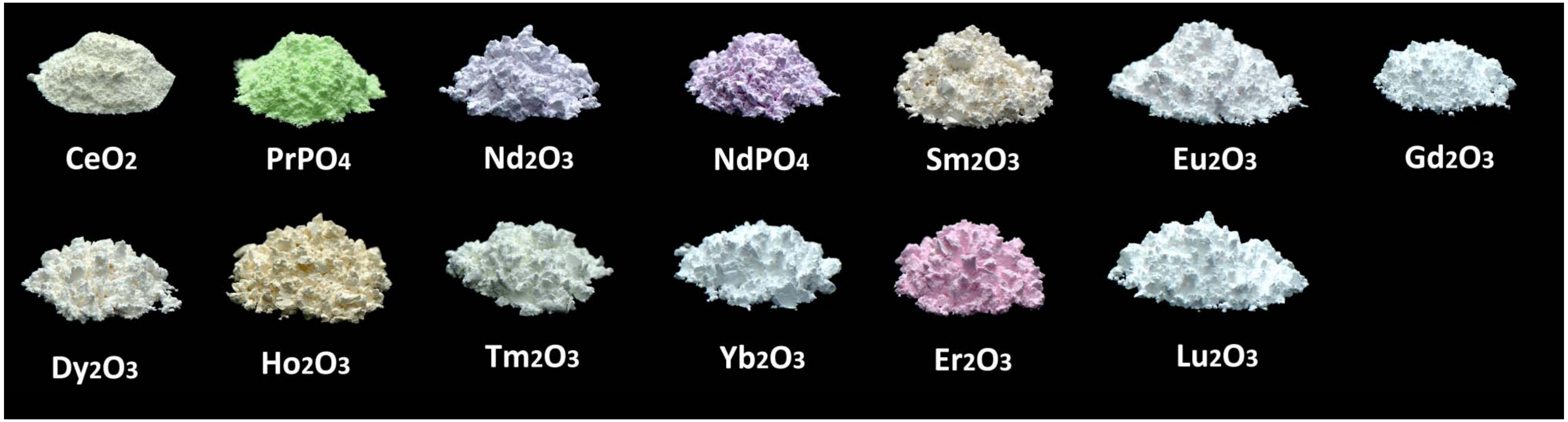
Suppliers of high puritiy Rare Earth Compounds



Thanks to you for your kind attention…..