Fluorescent Lamp Phosphors

Is there still News ?

Thomas Jüstel

tj@fh-muenster.de

thomas.juestel@philips.com

PGS, Seoul, South Korea

March 2007

Outline

1. State-of-the-Art light sources

2. Overview gas discharge lamps

3. Fluorescent lamps – Phosphor issues
   - Energy efficiency and price
   - Lifetime
   - Miniaturisation
   - Hg reduction

4. Phosphors for novel discharges
   - Xe excimer discharge lamps
   - Zn discharge lamps
   - InX discharge lamps

5. Conclusions and outlook

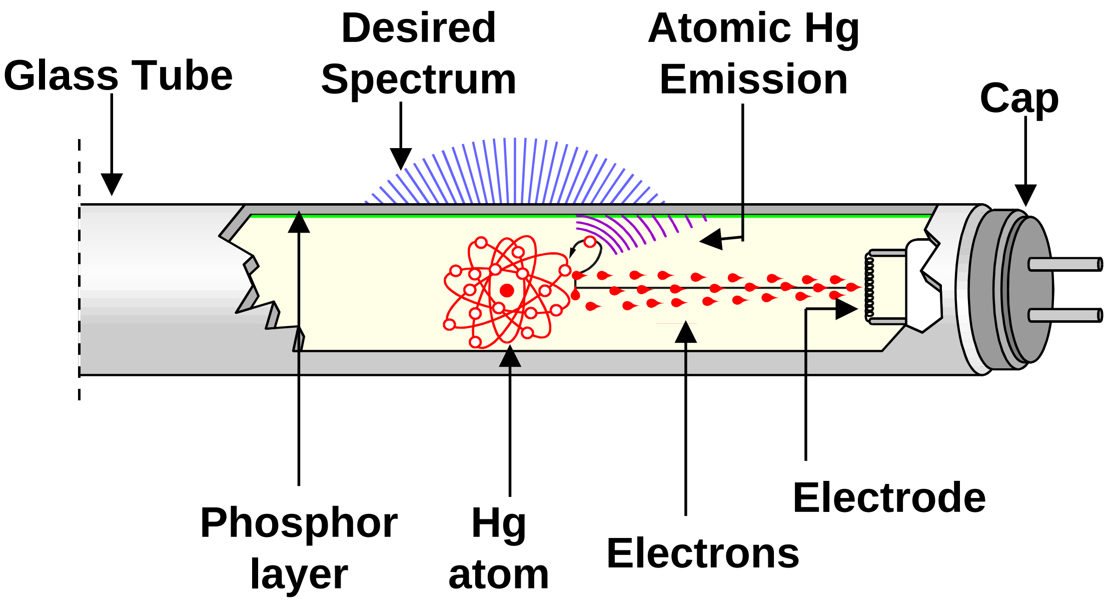
State-of-the-Art Light Sources

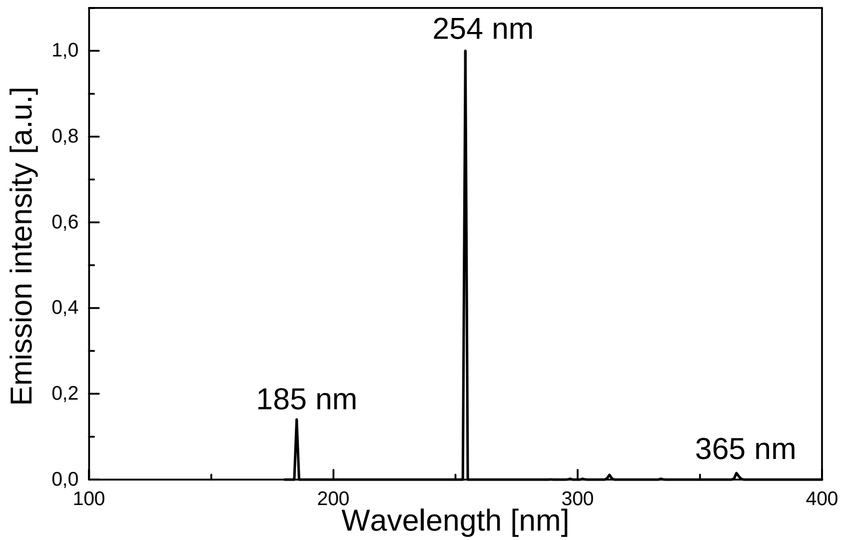
Light source	Electrical input power [W]	Luminous flux [lm]	Luminous efficacy [lm/W]	Color rendering range
Incandescent	10 – 1000	80 – 15000	8 – 15	excellent
Halogen	20 – 2000	300 – 60000	15 – 30	excellent
Low-pressure Hg discharge	7 – 150	350 – 15000	50 – 70 (compact) 100 (straight)	good
High-pressure Hg discharge	50 – 1000	2000 – 60000	40 – 60	good
Metal-halide discharge	20 – 2000	1600 – 24000	80 – 120	good to excellent
Low-pressure Na discharge	20 – 200	2000 – 40000	100 – 200	poor
High-pressure Na discharge	40 – 1000	1600 – 14000	40 – 140	moderate to good
Medium-pressure Xe discharge	up to 1000	up to 40000	35 – 45 (lamps) 4 – 5 (PDPs)	good
White dichromatic Inorganic LED	1 – 5	20 - 150	30 - 50 > 100 (published)	good
White trichromatic inorganic LED	1	20 – 25	20 – 30	excellent
Organic LED (at 1000 cd/m²)	15 mW (per cm²)	0.25 lm (per cm²)	15 - 25 > 50 (published)	good

Overview Gas Discharge Light Sources

Mercury		Sodium	Rare-gas	Other
Low-pressure p < 10 mbar	High-pressure p > 1 bar	Low-pressure	Low-pressure	Low- or high-pressure
Hg/Ar or Hg/Ne	Hg/Ar	Na/Ar/Ne	Ne	S_2
185 + 254 nm	bluish white	589 nm	74 nm	whitish
Compact + tubular FLs	Metal halide lamps • Single line emitter NaX/TlX X = I, Br	High-pressure Na/Hg/Xe whitish yellow	Xe/Ne 147 + 172 nm	Zn InX
Phosphor (blends)	• Multi-line emitter $NaX/TlX/LnX_3$ SnX_2 (X = I, Br and Ln = Dy, Ho, Tm, Sc)		Phosphor (blends)	Phosphor (blends)
Illumination Special lamps			Plasma displ. Special lamps	

Light Generation in Hg Low-pressure Discharges





Hg discharge (185, 254, 365 nm + visible lines)

↓ **phosphor layer**

UV-B / UV-A radiation or white light (CRI ~ 70 – 95)

WPE (trichromatic lamp)

$\eta_{FL} = \eta_{discharge} * \eta_{QD} * \eta_{conversion}$
$= 0.7 * 0.46 * 0.9$
$= 0.29$

Luminous efficiency

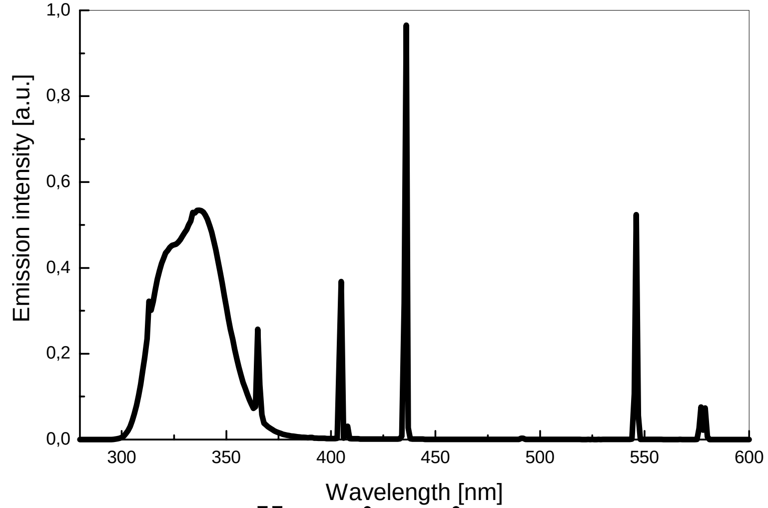
$\eta = \eta_{FL} * LE$
$= 0.29 * (300 – 350\ lm/W_{opt})$
$\sim 90 – 100\ lm/W_{el}$

Fluorescent Lamps – Phosphor Issues

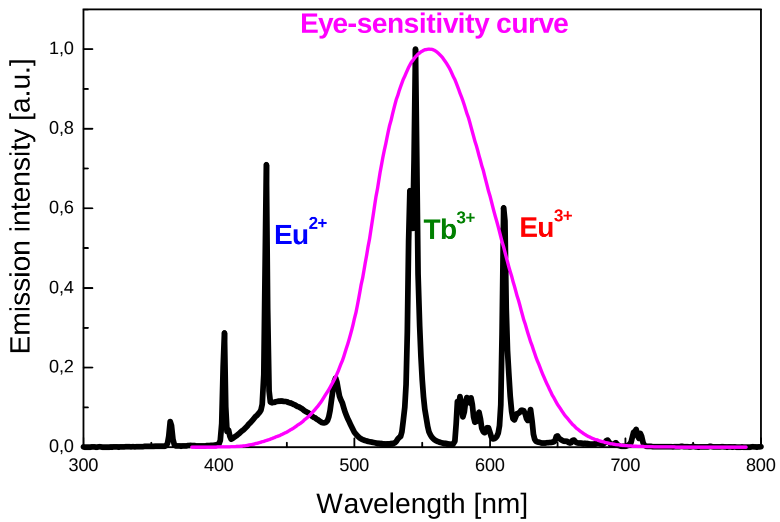
Higher energy efficiency	→ Particle size control of standard phosphors → Ongoing replacement of halo by tricolor blends
Price erosion	→ Cheaper raw materials (activators) → Less phosphor per lamp (layer thickness)
Longer average rated life	→ Particle morphology and coatings
Miniaturization	→ Particle morphology and coatings → Thermal quenching → Hg consumption
Ongoing trend in Hg reduction	→ Particle coatings, additives
Improved color rendering or gamut	→ Novel phosphors or blends → Particle coatings

Fluorescent Lamps – Phosphors

Cosmetic/Medical



Illumination



Rare earth ion

Ce^{3+}
$LaPO_4$:Ce
YPO_4:Ce

Eu^{2+}
$Sr_5(PO_4)_3$(F,Cl):Eu
$BaMgAl_{10}O_{17}$:Eu

Tb^{3+}
$LaPO_4$:Ce,Tb
$CeMgAl_{11}O_{19}$:Tb
$LaMgB_5O_{10}$:Ce,Tb

Eu^{3+}
Y_2O_3:Eu
(Y,Gd)(V,P)O_4:Eu

s^2- or TM ion activated

Pb^{2+}
$Sr_2MgSi_2O_7$:Pb
$BaSi_2O_5$:Pb

Sb^{3+}
$Ca_5(PO_4)_3$(F,Cl):Sb

Mn^{2+}
$BaMgAl_{10}O_{17}$:Eu,Mn
Zn_2SiO_4:Mn
$Ca_5(PO_4)_3$(F,Cl):Sb,Mn
$LaMgB_5O_{10}$:Ce,Tb,Mn

Mn^{4+}
$Mg_4GeO_{5.5}$F:Mn

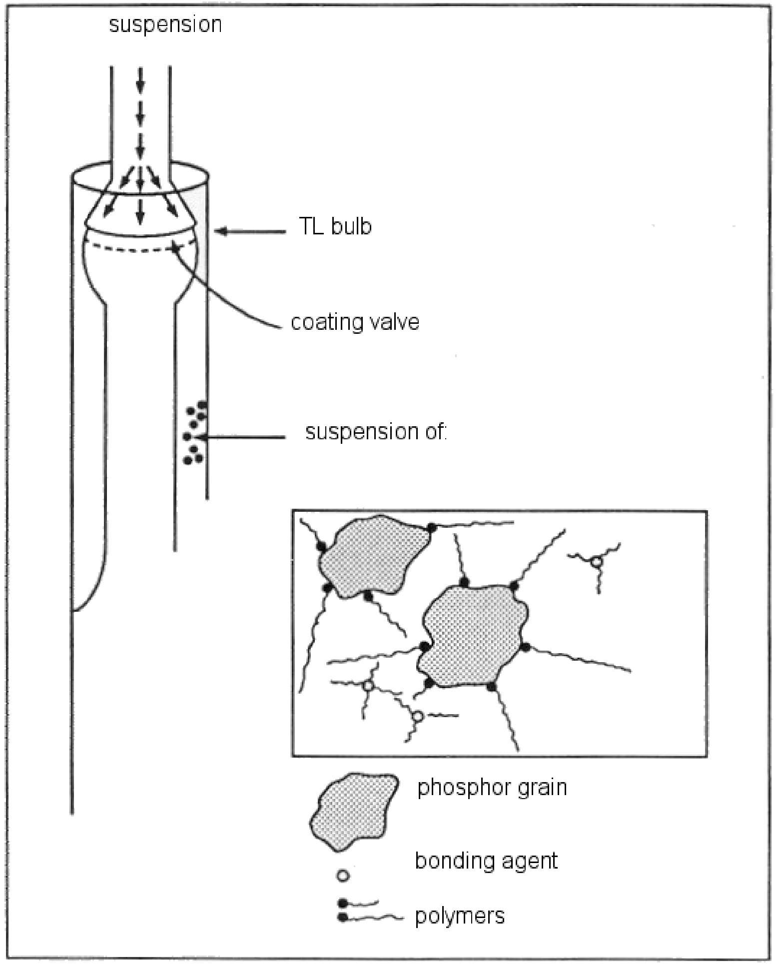
Fluorescent Lamps - Phosphor Issues

Energy efficiency and price

- Selected phosphors operate at physical limit
- RE phosphors are superior to s^{2-} and TM ion phosphors
- Replace expensive by cheap materials
- Further improvements possible by
  - non linear phosphors
  - reduced Hg consumption
  - better adhesion and layer texture
  - Improved incorporation of activators

Consequences

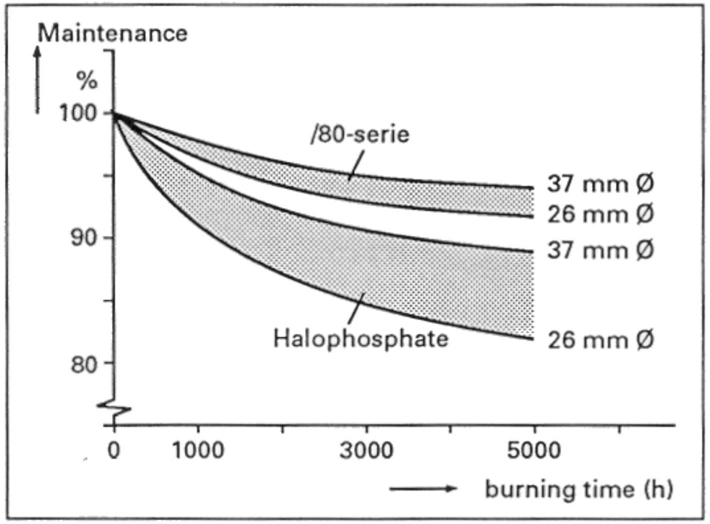
- Improve reactivity of starting materials
  - Reduce particle size
  - Apply sol-gel chemistry
- Improve RE ion distribution by co-precipitates
  - (Y,Eu)-oxides
  - (Ce,Gd,Tb)-oxides
  - (Ce,Gd,Tb)-phosphates
- Replace Tb^{3+} by Mn^{2+} phosphors
- Apply host lattices with an alkaline PZC
- Apply particle coatings



Fluorescent Lamps - Phosphor Issues

Lifetime

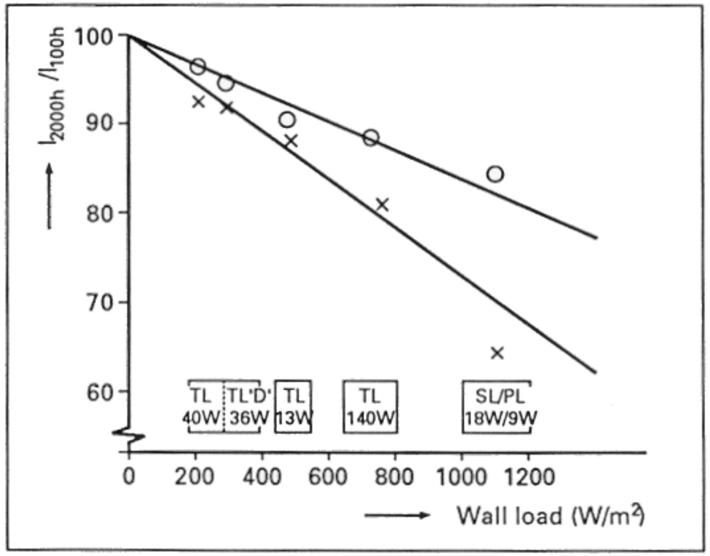
- Sb, Pb, Bi, Zn have affinity to mercury
  → blackening of phosphor layer
- RE ions are relatively stable
  → enable compact fluorescent lamps
- Trend towards higher wall loads ~ 2500 W/m^2
  due to decreasing tube diameter

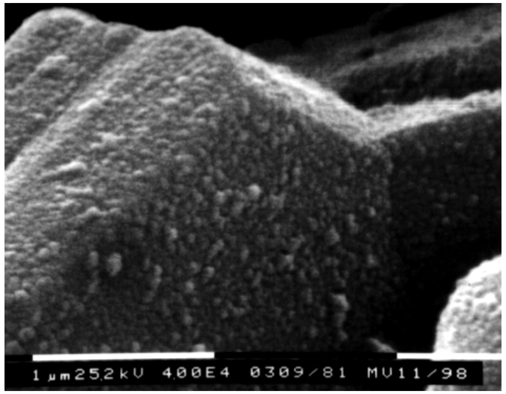


Consequences

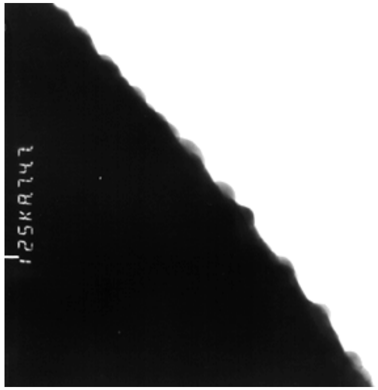
- Glass protection by thin Al_2O_3 layer
  reduction of Hg/Na exchange
- Particle coatings of Pb^{2+} and TM phosphors
- RE phosphors are relatively stable but upon
  even higher wall loads coatings might be necessary

Lifetime decreases by increasing wall load





Me_2O_3 coated $BaMgAl_{10}O_{17}$:Eu (left image) and $BaSi_2O_5$:Pb (right image)



Fluorescent Lamps - Phosphor Issues

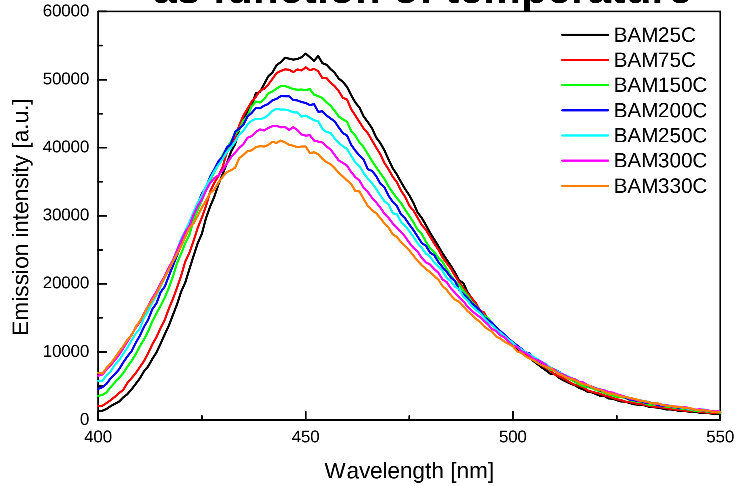
Miniaturisation

- Lamp temperature depends on lamp diameter
  - TL 36 mm 40°C
  - TL 26 mm 50°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 efficiency decreases with increasing temp.
- Excitation and emission spectra broadens with increasing temp.

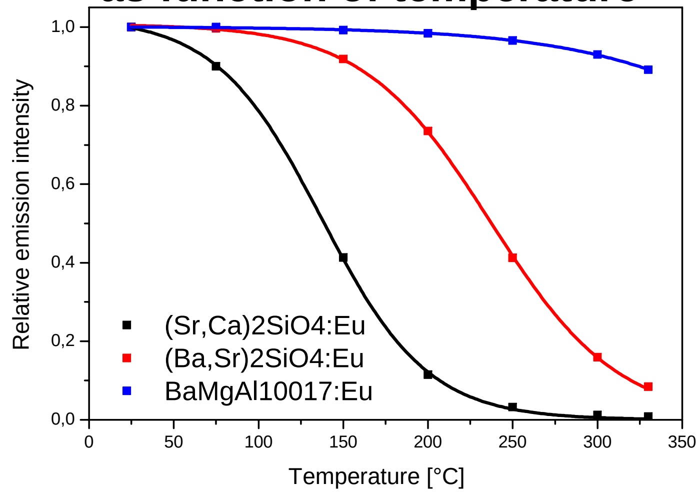
Consequences

- Phosphors with little thermal quenching
- Reduce spectral overlap and Stokes Shift
- Adjust activator concentration

Emission band of $BaMgAl_{10}O_{17}$:Eu as function of temperature



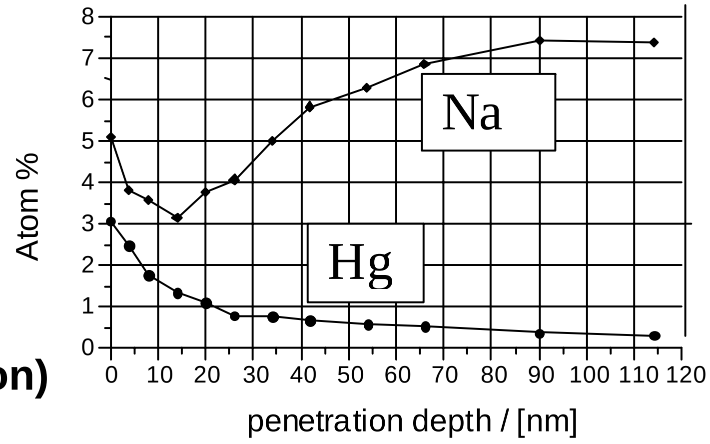
Rel. QE of Eu^{2+} phosphors as function of temperature



Fluorescent Lamps - Phosphor Issues

Hg consumption

- **Phosphor coated glass consumes up to 5 mg at 10000 h by Na/Hg exchange**
- **Bare glass even up to 250 mg at 10000 h**
- **Phosphors up to 50 µg at 10000 h (HgO formation)**
  - **In particular $BaMgAl_{10}O_{17}$:Eu is a strong Hg consumer**
  - **Incorporation of HgO into BaO conduction layers?**
- **Electrode region > 100 µg at 10000 h (Ba-amalgam formation)**



D.A. Doughty, R.H. Wilson and E.G. Thaler, J. Electrochem. Soc. 142 (1995) 3542

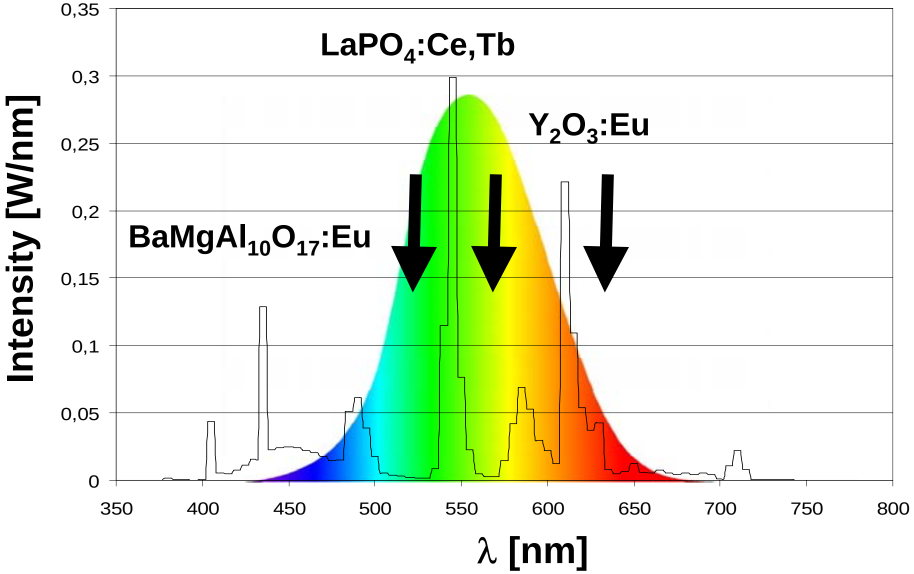
Consequences

- **Since $Hg^{+/2+}$ adheres to phosphor surface and no neutralisation of Hg ions takes place as phosphor surface is too electronegative (low PZC, e.g. silicates)**
- **Use phosphors with PZC > 8 or apply phosphor coatings to adjust PZC > 8**
- **Correlation between electronegativity and PZC experimentally proven (Tamatani et al., Toshiba)**
- **PZC in suspension can be measured easily by ESA equipment**
- **Approach has been proven in single component BAM lamps and lamps with different kinds of $LaPO_4$:Ce,Tb *(B. Smets, ECS 2000)***

Fluorescent Lamps - Phosphor Issues

Color rendering (trichromatic phosphor blends)

- Fairly good color rendering $\rightarrow$ $R_a = 80 - 85$
- Lack of radiation in the
  - cyan 500 – 535 nm
  - yellow 560 – 580 nm
  - deep red > 610 nm



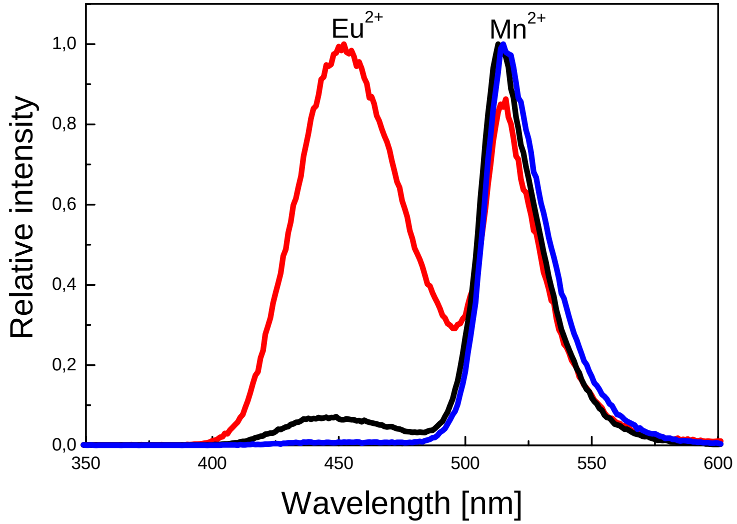
Consequences

- Additional broad band phosphors
  - $Sr_4Al_{14}O_{25}$:Eu
  - $Ca_5(PO_4)_3(F,Cl)$:Sb,Mn
- Modification of applied trichromatic phosphors
  - $BaMgAl_{10}O_{17}$:Eu $\rightarrow$ $BaMgAl_{10}O_{17}$:Eu,Mn
  - $GdMgB_5O_{10}$:Gd,Tb $\rightarrow$ $GdMgB_5O_{10}$:Ce,Tb,Mn

$\rightarrow$ R_a ~ 88 – 98, but luminous efficiency ~ 60 – 80 lm/W

Typical blend *(Osram Patent EP1306885)*	
$Sr_4Al_{14}O_{25}$:Eu	28.5 wt-%
$(Ce,Gd)(Zn,Mg)B_5O_{10}$:Mn	28.5 wt-%
$Ca_5(PO_4)_3(F,Cl)$:Sb,Mn	26.9 wt-%
$BaMgAl_{10}O_{17}$:Eu	6.1wt-%
$CeMgAl_{11}O_{19}$:Tb	10.0 wt-%

Emission spectra of $BaMgAl_{10}O_{17}$:Eu,Mn

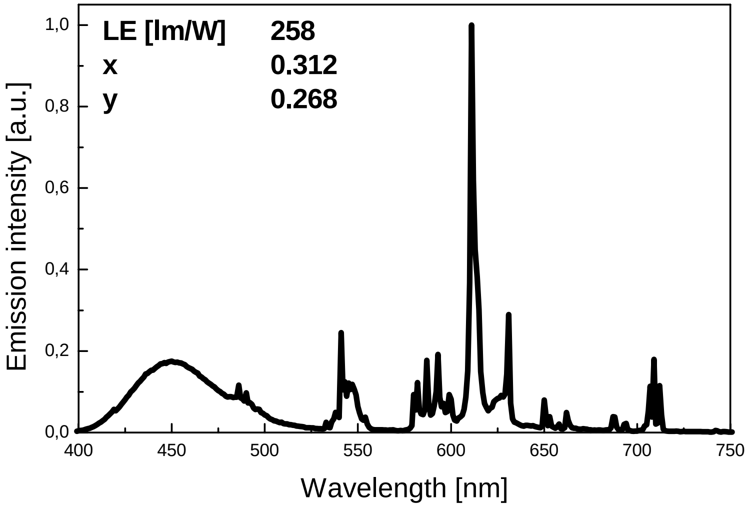


Fluorescent Lamps - Phosphor Issues

Color rendering (trichromatic phosphor blends)

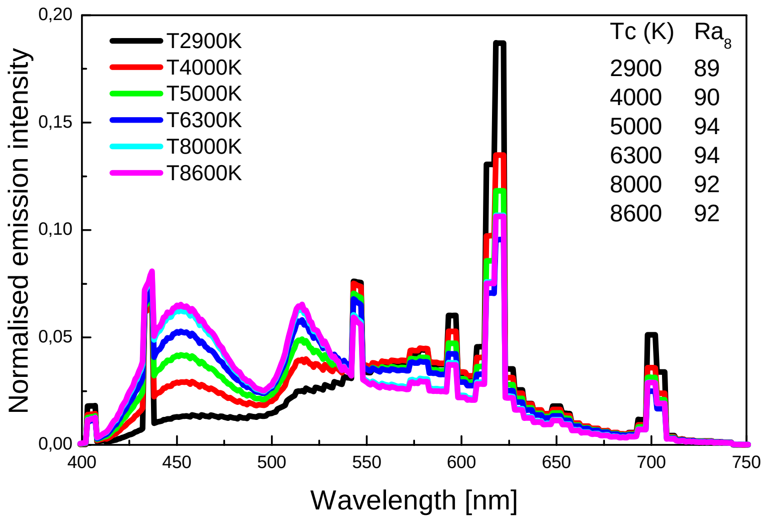
Application of $BaMgAl_{10}O_{17}$:Eu,Mn (Philips Lighting Maarheeze)

Emission spectrum of a blend of $BaMgAl_{10}O_{17}$:Eu,Mn + $LaPO_4$:Ce,Tb + Y_2O_3:Eu under 254 nm excitation



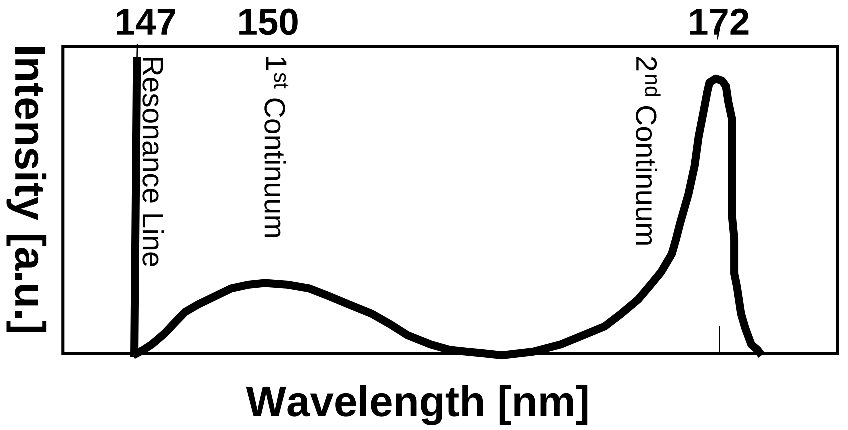
Ra ~ 88

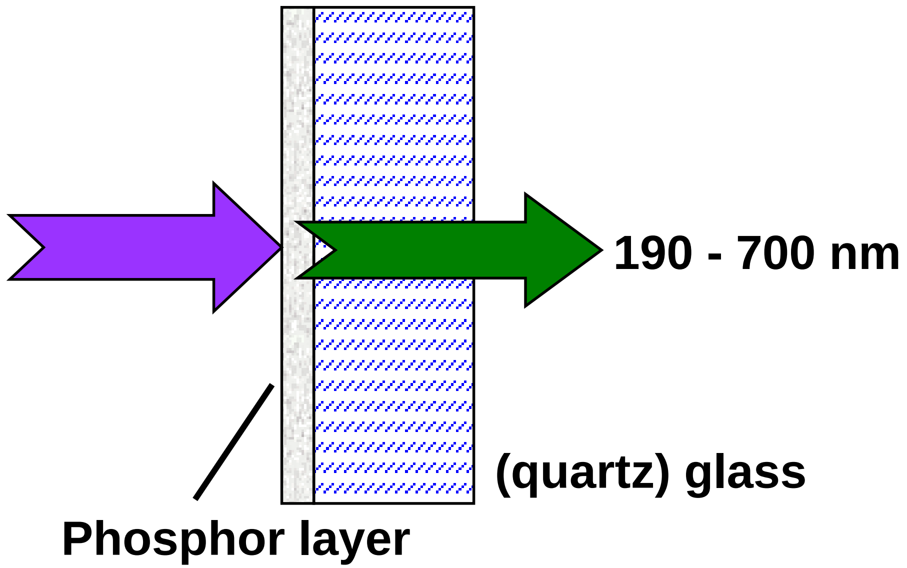
Calculated emission spectra of fluorescent lamps comprising $BaMgAl_{10}O_{17}$:Eu,Mn + Yellow + YVO_4:Eu



Ra > 90

Xe Excimer Discharge Lamps – Light Generation





Features

– Discharge efficiency ~ 65% (elaborated driving scheme)
– Hg free
– Fast switching cycles
– Temperature independent
– Dimmable
– High lifetime
– Main emission band at 172 nm (VUV)

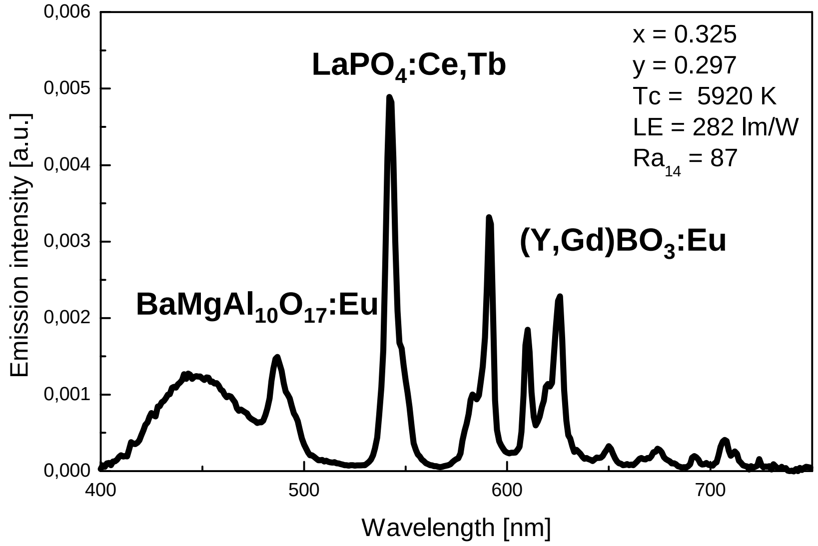
Application areas	Phosphor layer
– Plasma displays	RGB
– Copier lamps	RGB or B/W
– LCD Backlighting	RGB
– Medical skin treatment	UV-A/B
– Disinfection	UV-C
– Ultra pure water	-
– Surface/wafer cleaning	-

Xe Excimer Discharge Lamps – Phosphor Issues

Presently applied VUV phosphors

PDPs	Excimer lamps
$BaMgAl_{10}O_{17}$:Eu	$BaMgAl_{10}O_{17}$:Eu
$Y(V,P)O_4$	
Zn_2SiO_4:Mn	$LaPO_4$:Ce,Tb
$BaAl_{12}O_{19}$:Mn	$(Y,Gd)BO_3$:Tb
$BaMgAl_{10}O_{17}$:Eu,Mn	
$(Y,Gd)BO_3$:Eu	$(Y,Gd)BO_3$:Eu
Y_2O_3:Eu	
$(Y,Gd)(V,P)O_4$:Eu	
5 – 10 lm/W	< 50 lm/W

Spectrum of Osram Planon

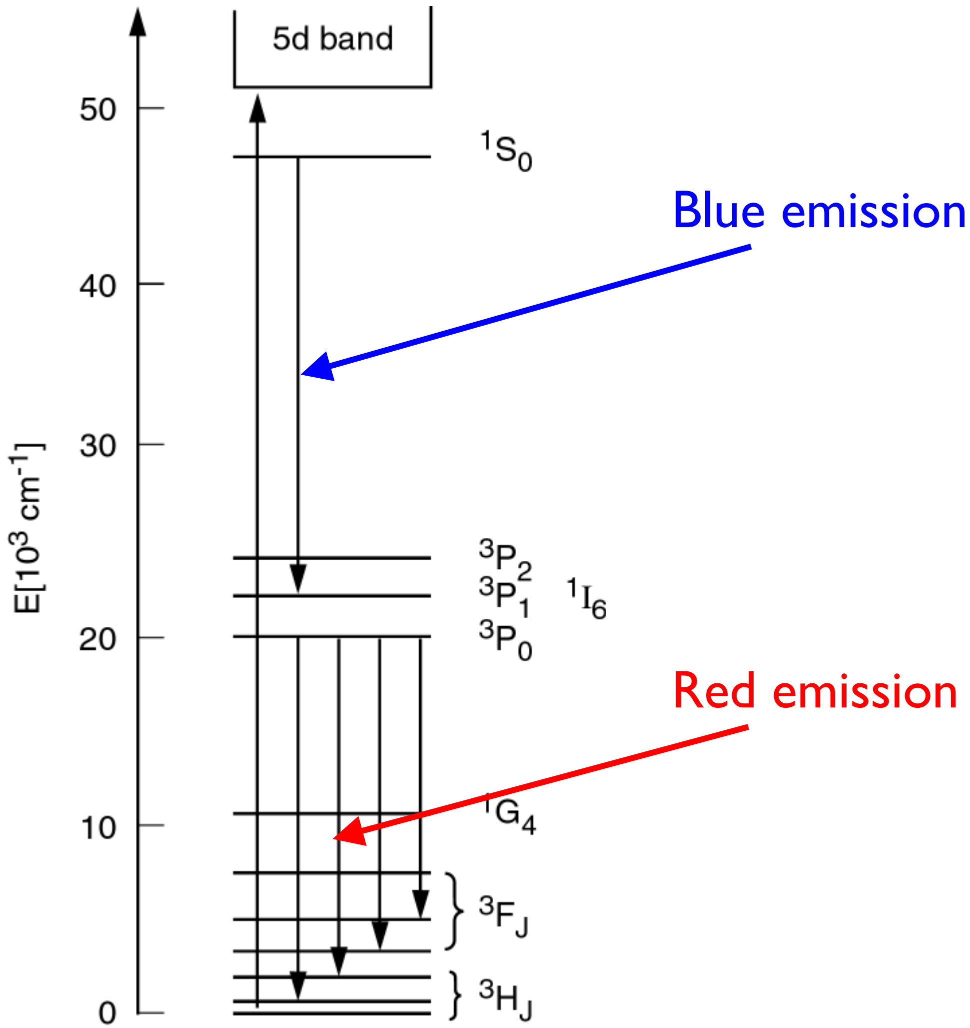


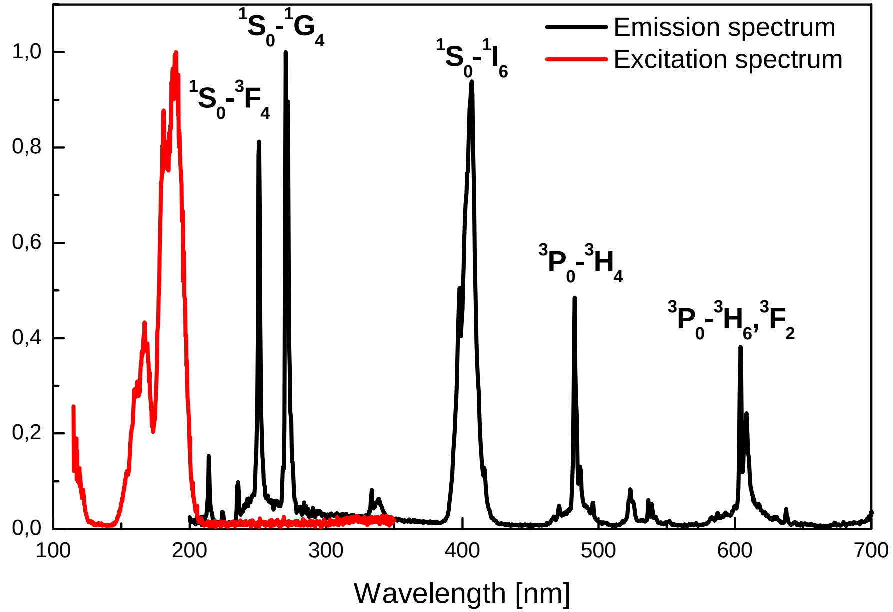
Problem areas

Efficiency	→ Down conversion phosphors
VUV Stability	→ Particle coatings (MgO or Al_2O_3)
Color point	→ Improved red x, y ~ Y_2O_2S:Eu
Novel application areas	→ UV phosphors

Xe Excimer Discharge Lamps – Phosphor Issues

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



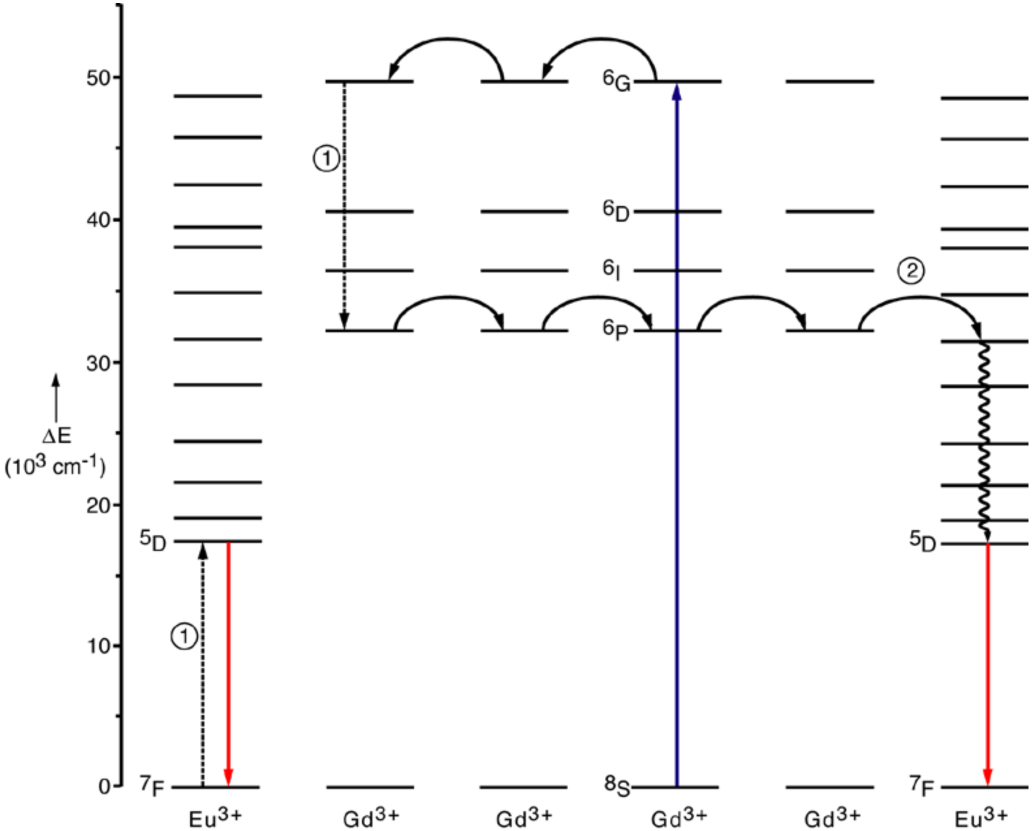


First fluorides: YF_3:Pr und $NaYF_4$:Pr
(J.L. Sommerdijk et al., J. Lumin. 8 (1974) 341)
$^1S_0$ - $^3P_1$,$^1I_6$ at 407 nm
$^3P_0$ - $^3H_6$,$^3F_2$ at 615 nm
Oxidic phosphors: Host lattices with Ln^{3+} sites having high coordination number
$SrAl_{12}O_{19}$:Pr, $LaMgB_5O_{10}$:Pr, and LaB_3O_6:Pr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

Xe Excimer Discharge Lamps – Phosphor Issues

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

- **Discovered by A. Meijerink et al.**
- **Internal quantum efficiency about 195% in $LiGdF_4$**
- **Measured quantum efficiency about 30 – 35 % at 202 nm due to competitive defect absorption**



Gd —(202 nm)→ Gd**

Gd** + Eu —(CR)→ Eu* + Gd*

Eu* → Eu + hν

Gd* + Eu —(ET)→ Gd + Eu*

Eu* → Eu + hν

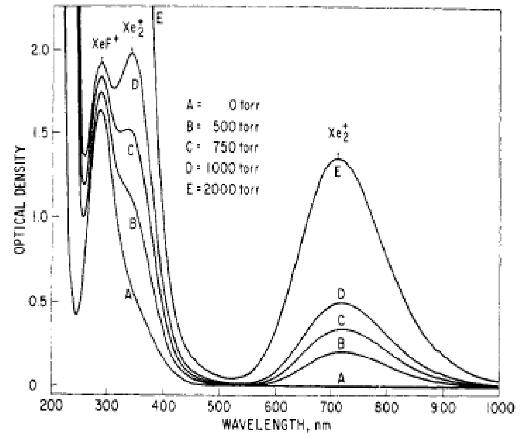
Xe Excimer Discharge Lamps – Phosphor Issues

VUV Stability

- Fairly good, but blue phosphor degrades
  - VUV radiation
  - Direct contact to the discharge
- Low penetration depth of VUV radiation
- $Xe_2^{*/+}$ adheres to phosphor surface and no neutralisation of Xe_2^+ ions 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

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

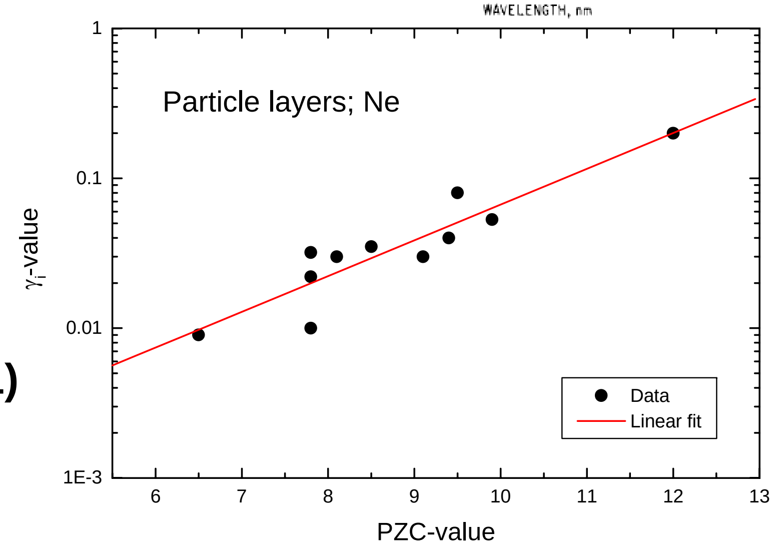
(all values in atom-%)



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

Consequences

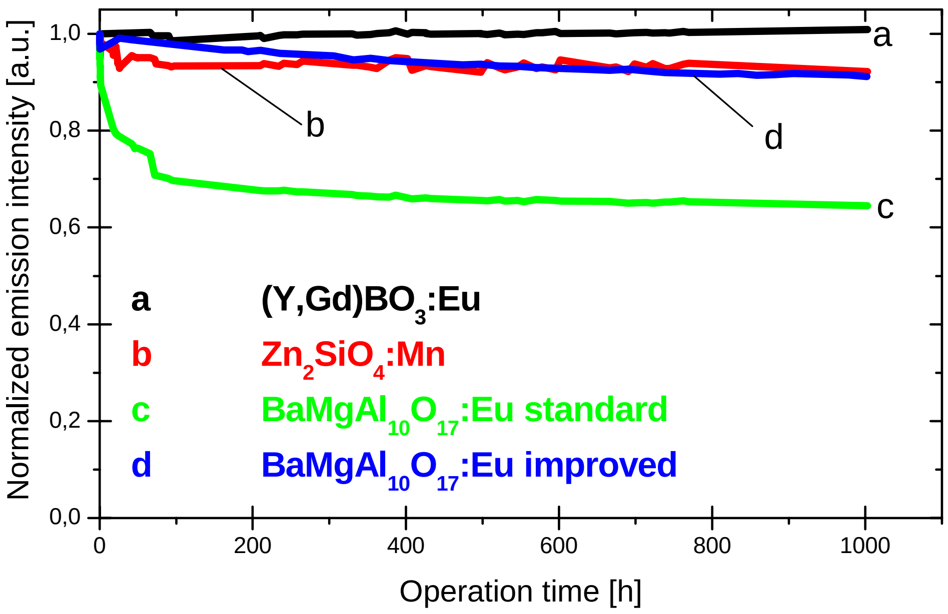
- Optimisation of the composition
- Alternative blue phosphor
- No silicate phosphors
- Coating by alkaline materials
  - Al_2O_3 as protective coating
  - MgO as high γ-material (T. Jüstel, Phosphor SID 2001)
  - La_2O_3 possible but narrow band gap



Xe Excimer Discharge Lamps – Phosphor Issues

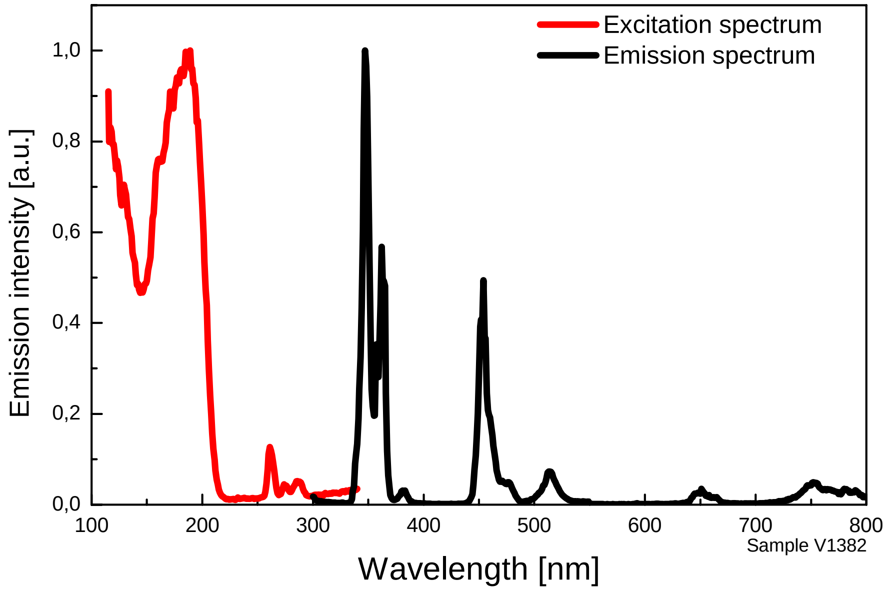
Blue VUV phosphors

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



Alternative materials

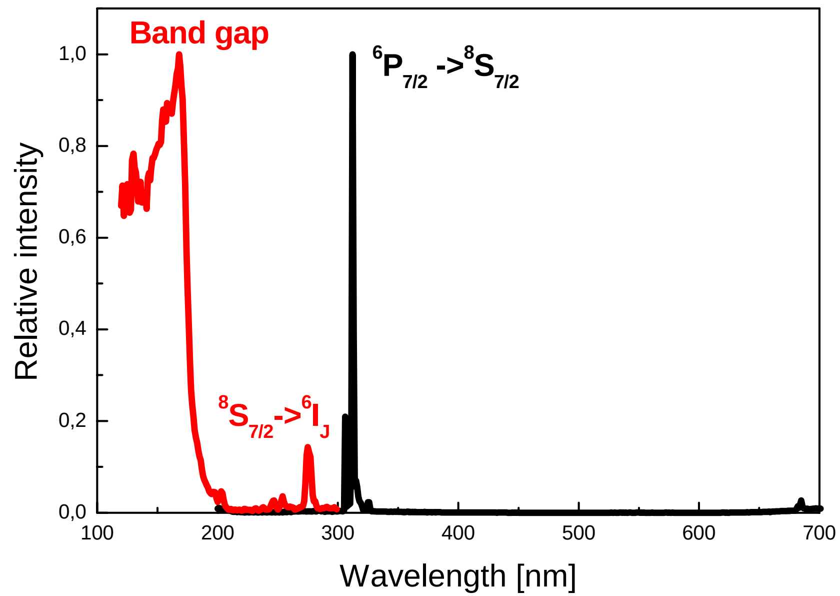
- **$BaAl_2Si_2O_8$:Eu 435 nm**
  (Chem. Mater. 2006)
- **$LaPO_4$:Tm 454 nm**
  blended with $BaMgAl_{10}O_{17}$:Eu
  (J. Luminescence 2005)



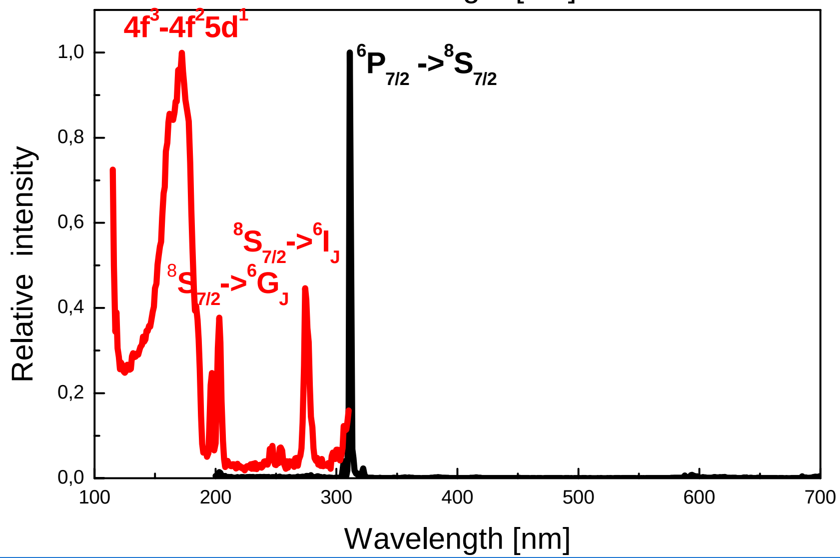
Xe Excimer Discharge Lamps – Phosphor Issues

Novel application areas → UV phosphors

- **UV-B phosphors**
  - **Host lattice sensitisation**
    $YAl_3(BO_3)_4$:Gd
    (NEC patent US2005/001024)
  - **Nd^{3+} as a sensitiser**
    $GdPO_4$:Nd
    (Philips patent EP06112503)



- **UV-C phosphors (T. Jüstel, PGS 2005)**
  - **Wide band gap host lattices, e.g. phosphates**
  - **s^2-ion activated: Tl^+, Pb^{2+}, Bi^{3+}**
  - **RE ion activated: Pr^{3+}**
    (several Philips patents)



Novel Gas Discharges

Goals

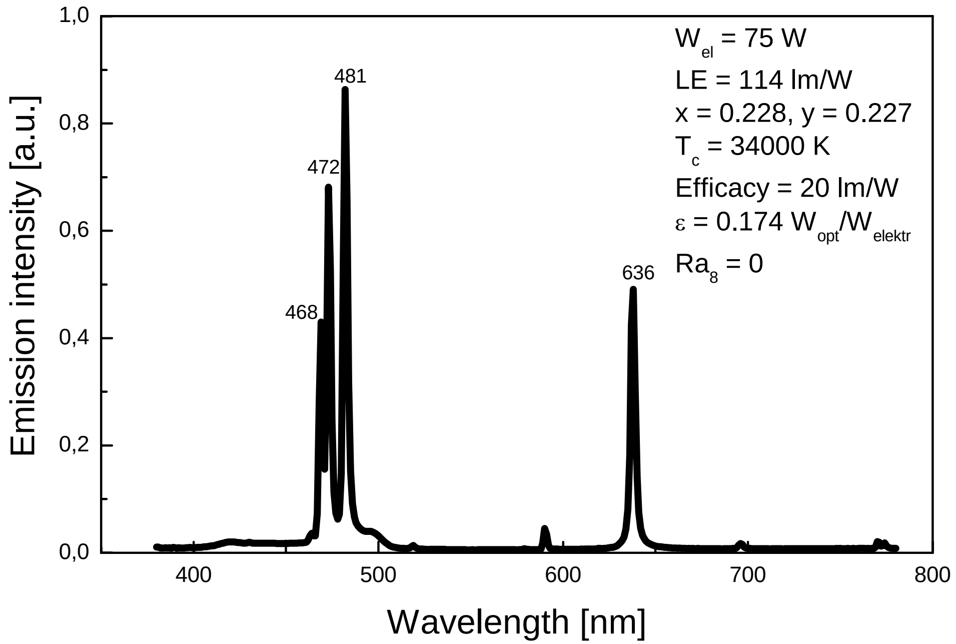
- **White emission** → **high-pressure (+ metal halides)**
- **Blue emission** → **phosphor conversion required as in LEDs**

What has been recently invented?

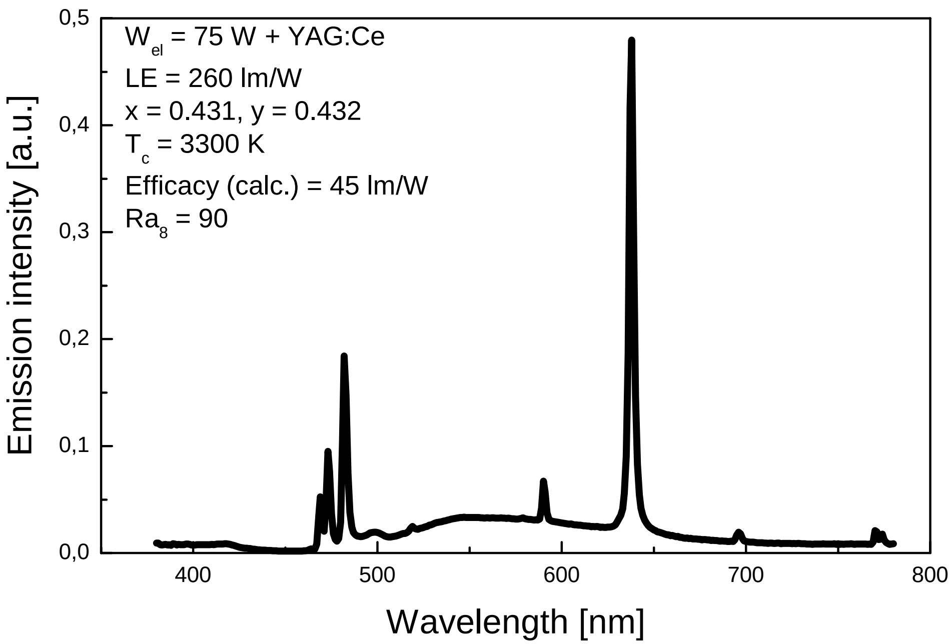
- **Zn gas discharge lamps**
  - **Low-pressure** **Line emitters *(M. Born, Plasma Sources Sci. Technol. 2002*)**
  - **High-pressure** **Automotive head lamps *(Osram Patent EP1465237)***

- **InX gas discharge lamps**
  - **Low-pressure** ***(Philips Patent EP1540703)***

Zn/Ar low-pressure discharge



Zn/Ar discharge lamp + YAG:Ce coated envelope

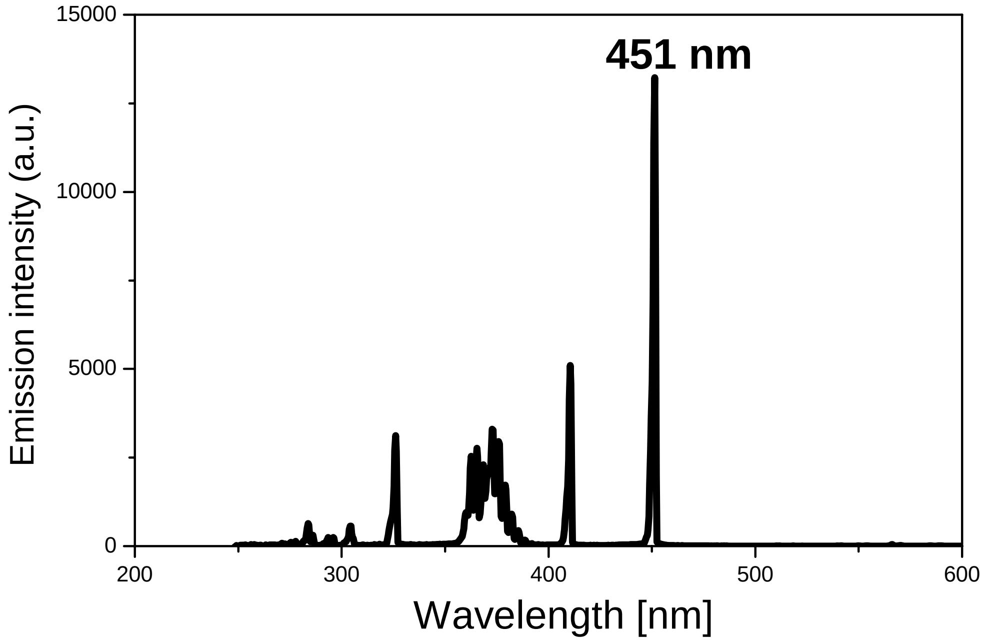


Luminous efficiency ~ 45 lm/W

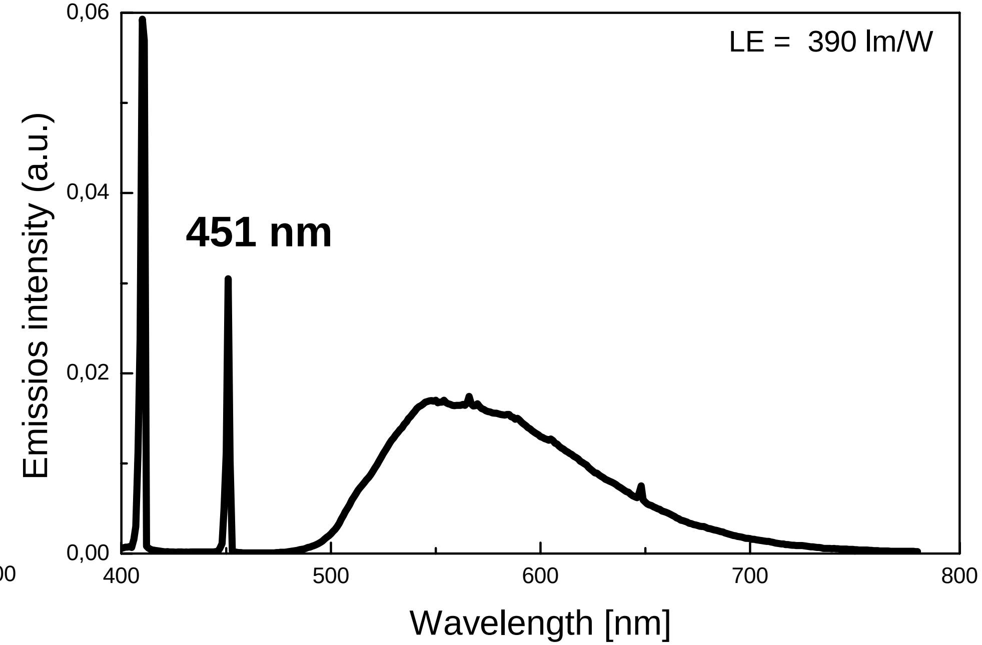
High colour rendering CRI ~ 90 at T_c = 3300 K

Phosphors for InX Discharge Lamps

InX low-pressure discharge



InX discharge lamp + envelope coated by YAG:Ce phosphor



Luminous efficiency ~ 100 lm/W
High colour rendering CRI ~ 80 at T_c = 4000 K
(Philips patent US2004/0169456)

Conclusions and Outlook

Fluorescent lamp phosphors - Is there still news?
Yes there is, but breakthroughs cannot be expected in the area of phosphors for gas discharge lamps anymore

Hg low-pressure lamps

- **Phosphors and blends are well optimised**
- **Further developments are driven by price erosion and environmental aspects (energy efficiency, lifetime, Hg content)**
- **Hg consumption in fluorescent lamps is well understood and countermeasures are identified and implemented**

Xe excimer discharge lamps

- **Efficiency limited to 40 – 50 lm/W**
- **Down conversion phosphors are not within immediate reach**
- **Novel UV phosphors might open attractive application areas for Xe_2* lamps**

Blue emitting low-pressure gas discharges

- **Ideal concept to optimise wall plug efficiency due to small Stokes Shift**
- **LED phosphors might be applicable**
- **Present discharge efficiency and technological bottlenecks might not justify further development in view of advances in LED technology**

Thanks for your attention!