PHILIPS

Efficiency and Thermal Quenching of UV Phosphors

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Outline

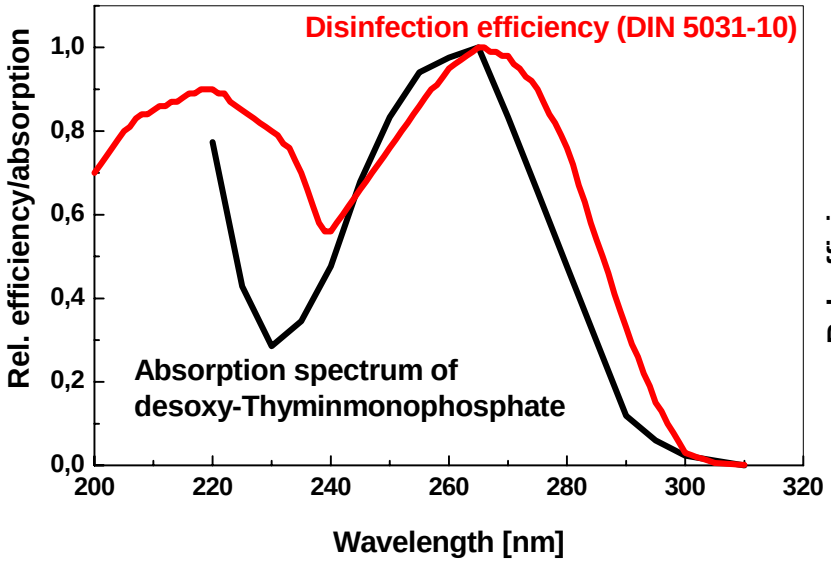
- Application areas of UV-R radiation
- (Fluorescent) UV Light Sources
- Overview UV-R phosphors
- VUV Efficiency of UV-R Phosphors
- Thermal quenching
- From micro to nanoscale materials
- Conclusions

Applications Areas of UV-R Radiation

VUV	UV-C	UV-B	UV-A
100 nm – 200 nm	200 nm – 280 nm	280 nm – 320 nm	320 nm – 400 nm
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
• Waver cleaning • Photochemistry	• Disinfection of air, H_2O and surfaces • Photochemistry	• Treatment of skin diseases, e.g. psoriasis • Tanning	• Water and air purification by means of TiO_2 photocatalyst • Tanning

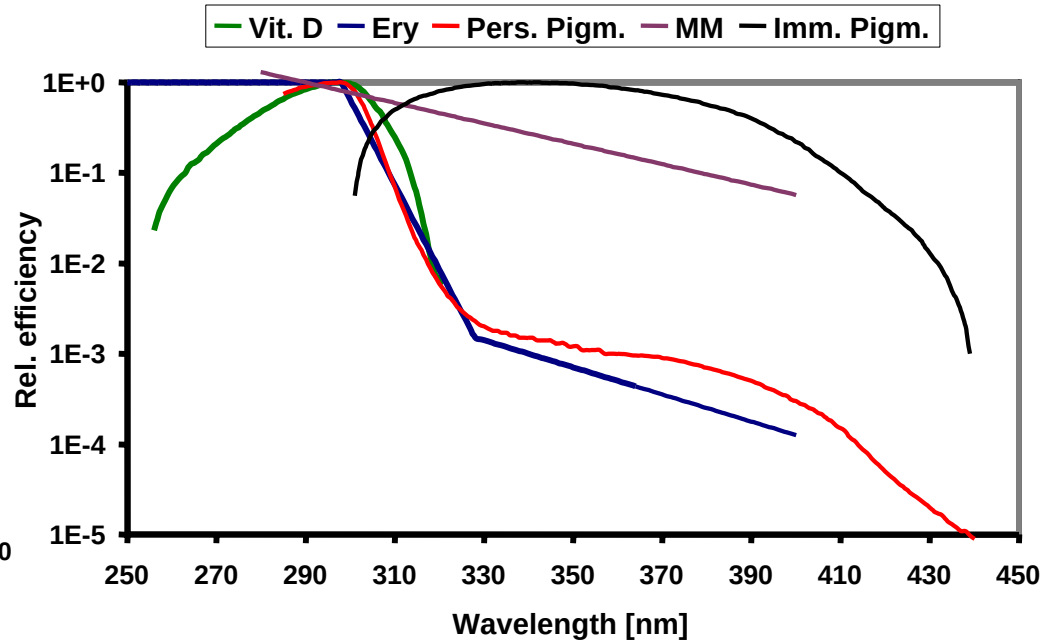
Biological Effects of UV-R Radiation

UV-C



- Excitation of nucleobases (point mutations + cell death)
- Cleavage of O_3, H_2O_2, ClO_2

UV-B and UV-A



- Immediate pigmentation (melanin oxidation)
- Persistent pigmentation (melanosome formation)
- Vitamin D production
- Psoriasis treatment
- Erythema (sunburn)

UV Light Sources

Sunlight > 300 nm

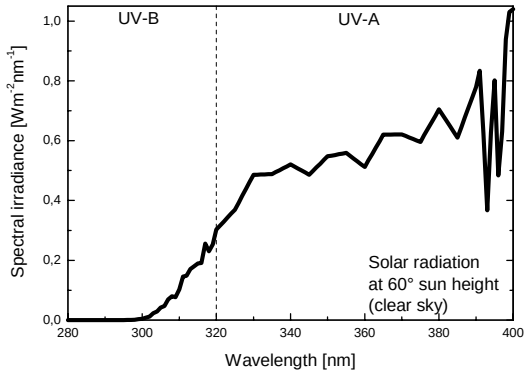
Hg discharge lamps

- low pressure 185, 254 nm
- medium pressure (+ filter) 200 - 400 nm
- low pressure + phosphor 200 - 400 nm

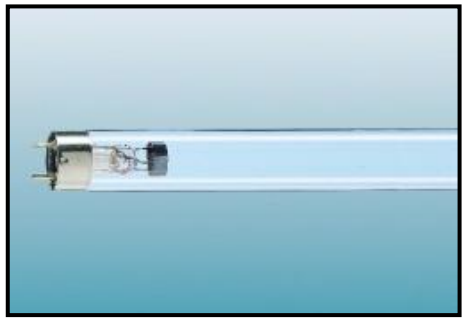
Excimer discharge lamps

- Xe_2* 172 nm
- XeCl* 308 nm
- Xe_2* + phosphor 200 - 400 nm

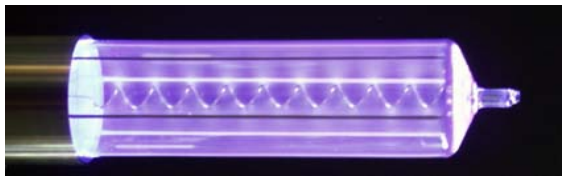
Solar UV spectrum



TUV lamp

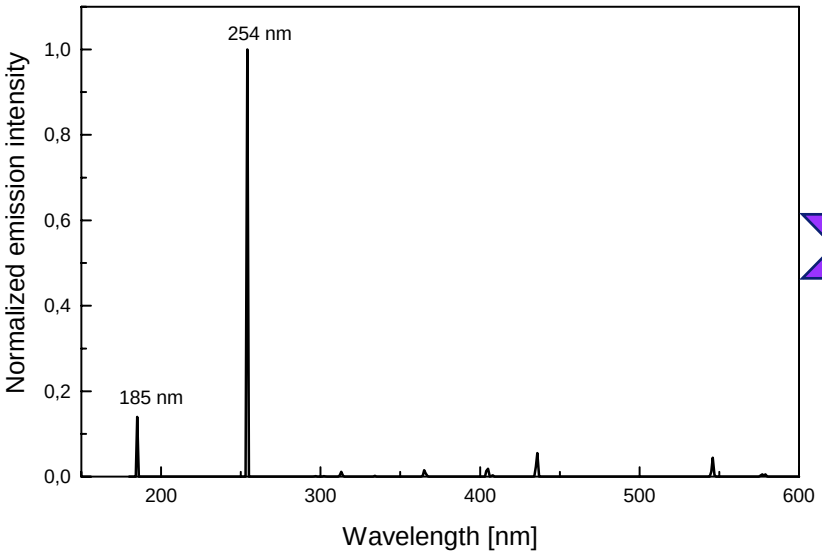


Xeradex lamp



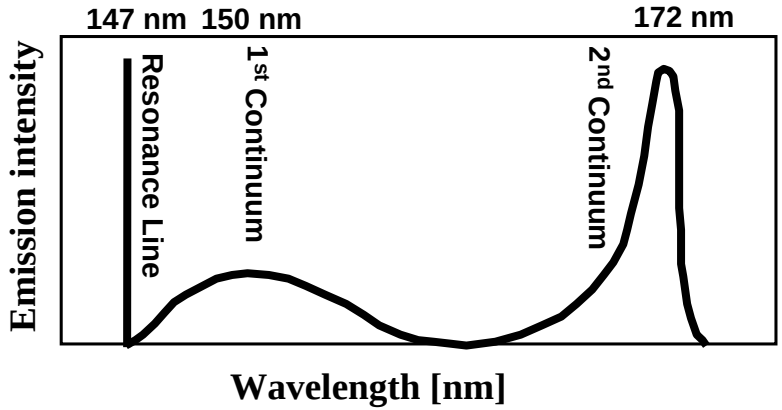
Fluorescent UV Light Sources

Hg low pressure discharge lamp

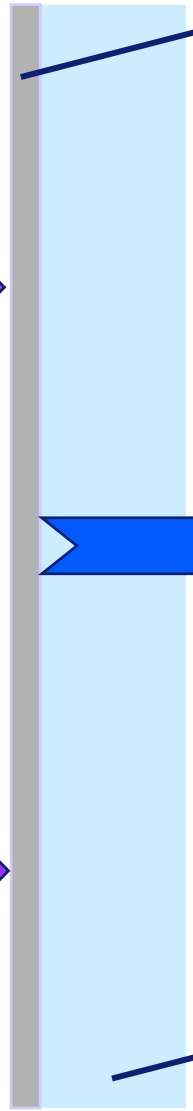


185 nm
254 nm

Xe_2* excimer discharge lamp



150 nm
172 nm



UV Phosphor layer

Desired lamp spectrum

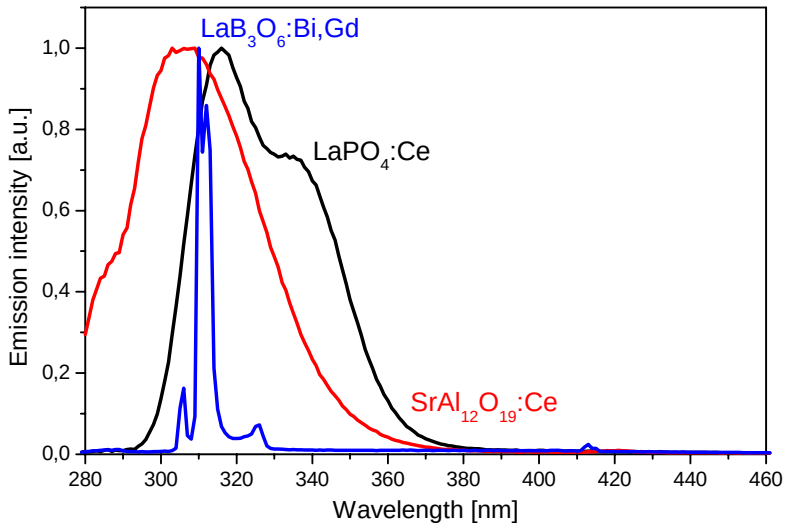
German Patent
DE 199 19 169.7

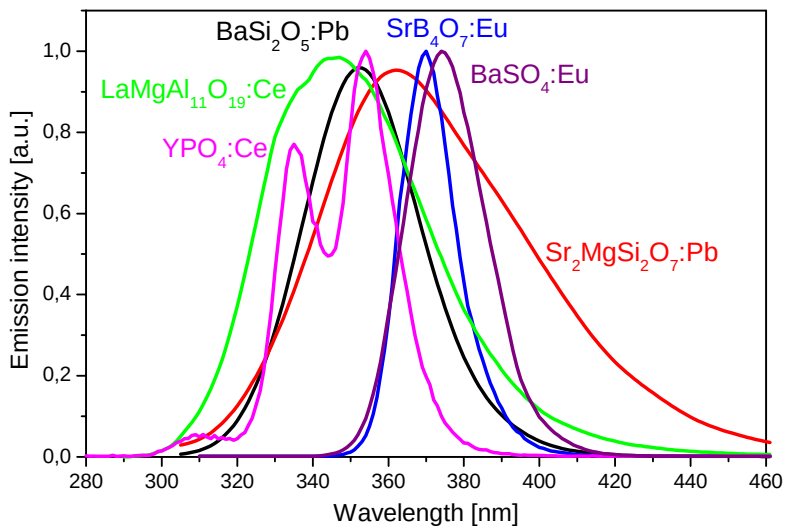
Lamp glass

Overview UV-R Phosphors

Commercial phosphors for fluorescent Hg low pressure lamps

$SrAl_{12}O_{19}:Ce^{3+}$	305 nm
$LaB_3O_6:Bi^{3+},Gd^{3+}$	311 nm
$LaPO_4:Ce^{3+}$	320 nm
$LaMgAl_{11}O_{19}:Ce^{3+}$	340 nm
$(Y,Gd)PO_4:Ce^{3+}$	335, 355 nm
$BaSi_2O_5:Pb^{2+}$	350 nm
$Sr_2MgSi_2O_7:Pb^{2+}$	365 nm
$SrB_4O_7:Eu^{2+}$	370 nm
$BaSO_4:Eu^{2+}$	375 nm

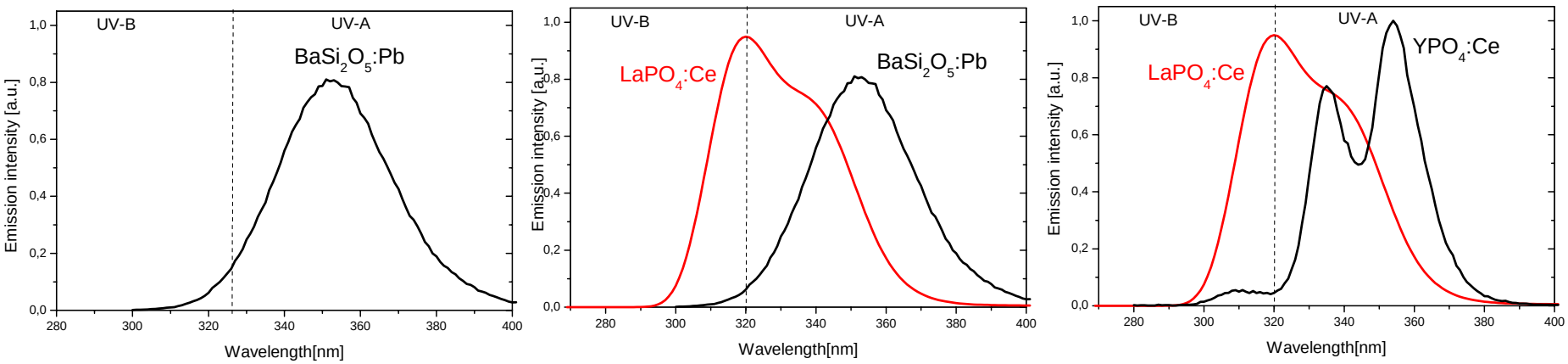




Overview UV-R Phosphors

Fluorescent Hg low pressure lamps for cosmetic purposes

1st Generation	2nd Generation	3rd Generation
$BaSi_2O_5$:Pb or $Sr_2MgSi_2O_7$:Pb	$BaSi_2O_5$:Pb + $LaPO_4$:Ce	YPO_4:Ce + $LaPO_4$:Ce



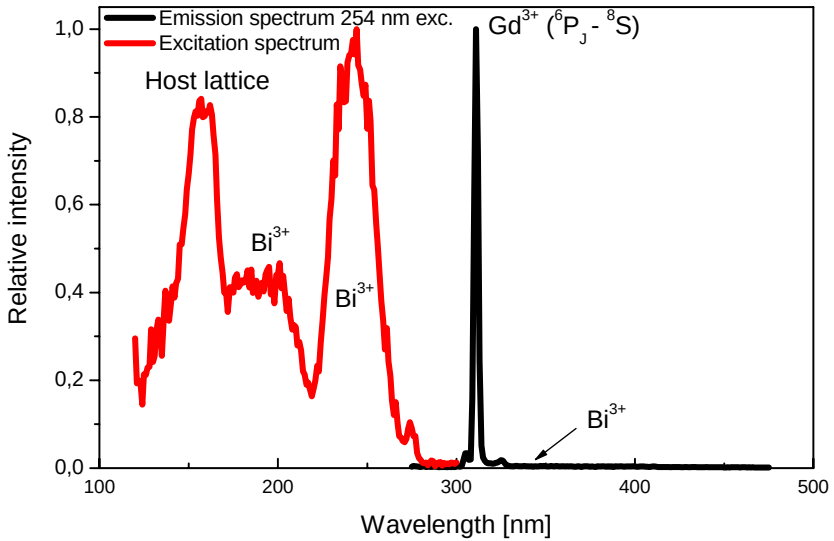
Stability of Pb^{2+} phosphors limits lamp lifetime

Quantum efficiency upon 254 nm excitation of these phosphors is larger than 90%

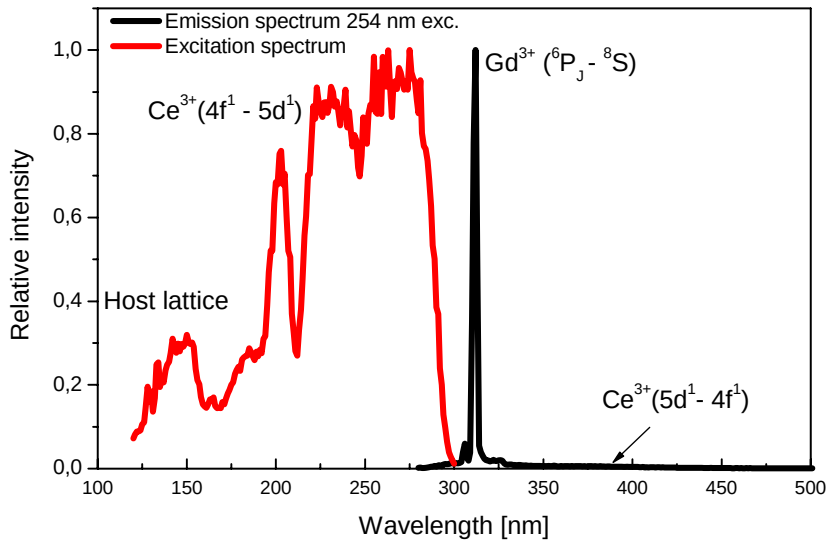
Overview UV-R Phosphors

Fluorescent Hg low pressure lamps for medical purposes

Standard phosphor
$LaB_3O_6:Bi^{3+},Gd^{3+}$



Novel material
Ce^{3+} sensitised Gd^{3+} phosphor



Shortcomings:
- Long-term stability due to photochemistry of Bi^{3+}
- Hg consumption

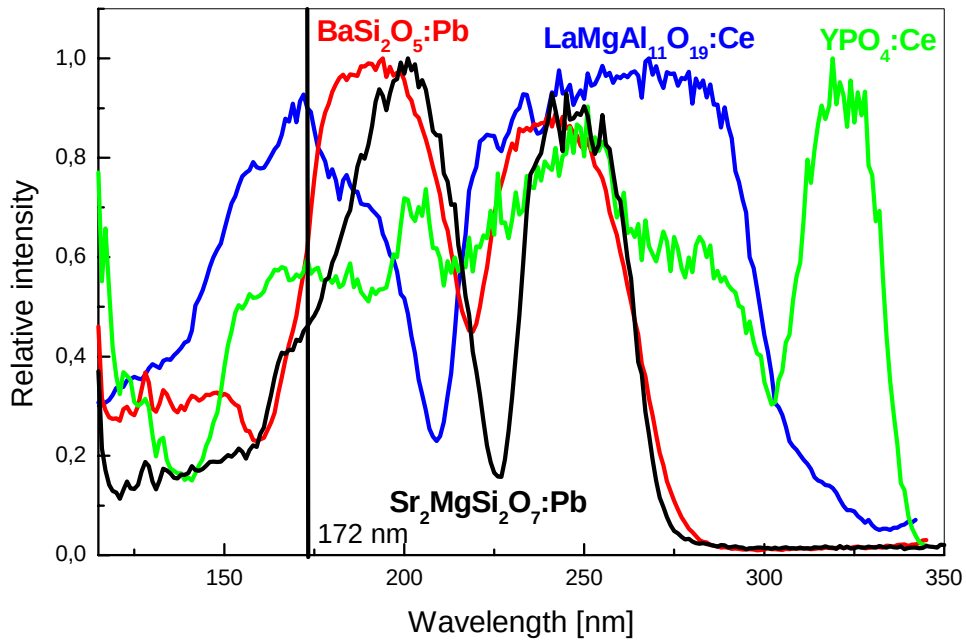
Advantages:
- Efficient ET to Gd^{3+}
- Broad and intense Ce^{3+} absorption
- Higher efficiency

VUV Efficiency of UV-R Phosphors

High VUV efficiency

⇒ potential application in fluorescent Xe_2* excimer discharge lamps

UV-A phosphors (Ce^{3+} and Pb^{2+} activated)



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

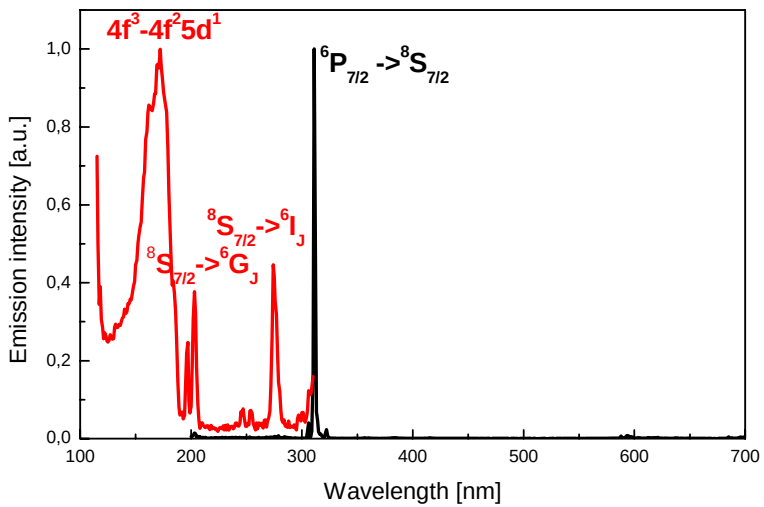
VUV Efficiency of UV-R Phosphors

UV-B phosphors (Gd^{3+} activated)

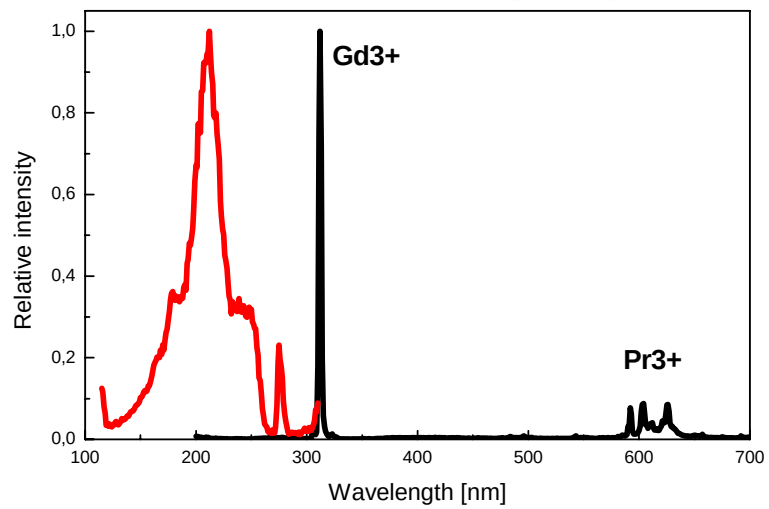
Sensitisation of Gd^{3+} for 172 nm excitation by

- **Host lattice** — suitable band edge required
- **Bi^{3+}** — large lattice position (e.g. La^{3+}) required
- **Ce^{3+}** — suitable 4f5d states required
- **Nd^{3+}** — suitable 4f5d states required
- **Pr^{3+}** — suitable 4f5d states required

Nd^{3+} sensitised Gd^{3+} phosphor



Pr^{3+} sensitised Gd^{3+} phosphor

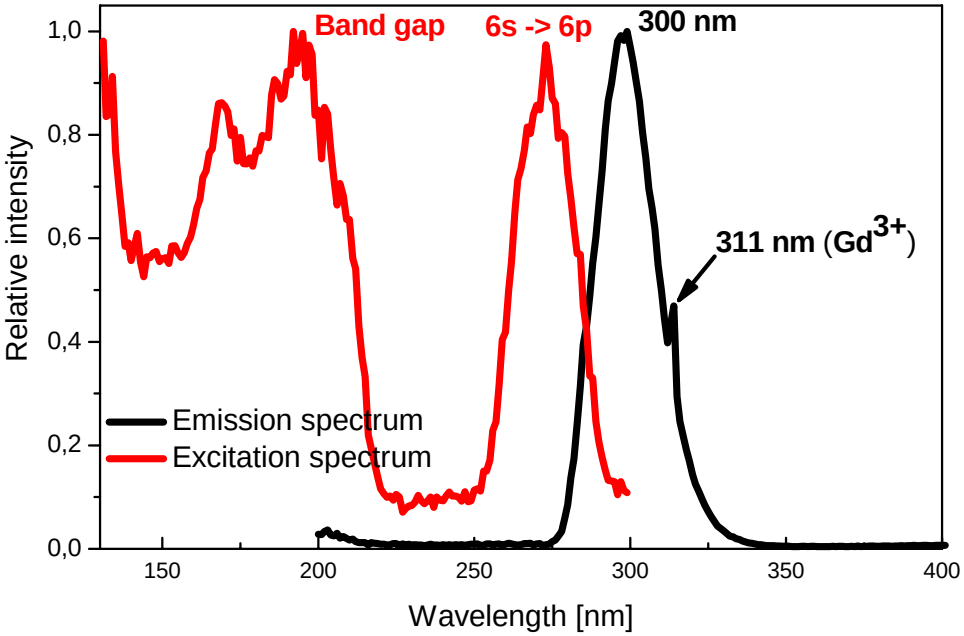


VUV Efficiency of UV-R Phosphors

UV-B phosphors (Gd^{3+} activated)

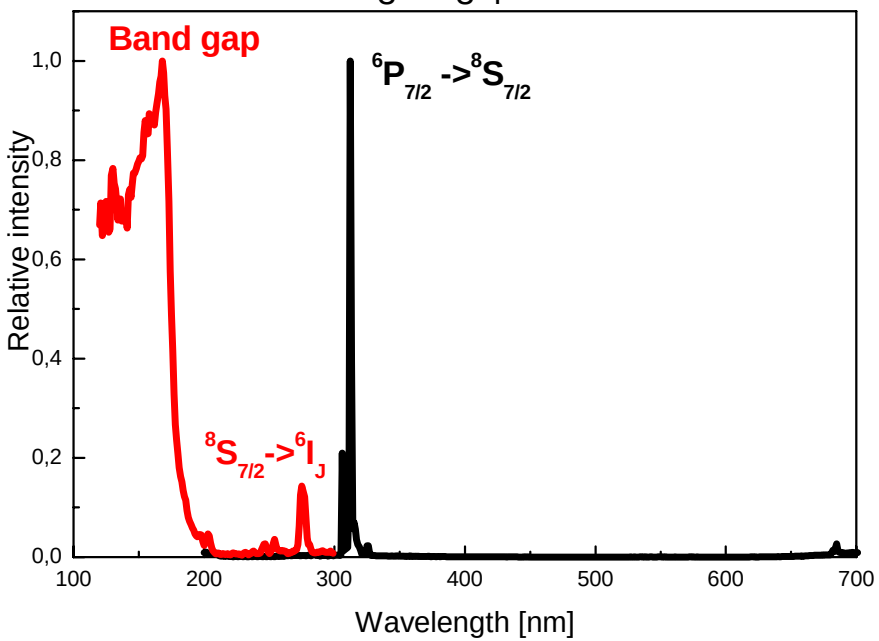
Bi^{3+} sensitised Gd^{3+} phosphor

$Lu_3Al_5O_{12}$:1%Bi, 0.1%Gd



HL sensitised Gd^{3+} phosphor

$YAl_3(BO_3)_4$:50%Gd



Co-doping by Gd^{3+} results in 311 nm emission

Efficient ET from the host lattice to Gd^{3+}

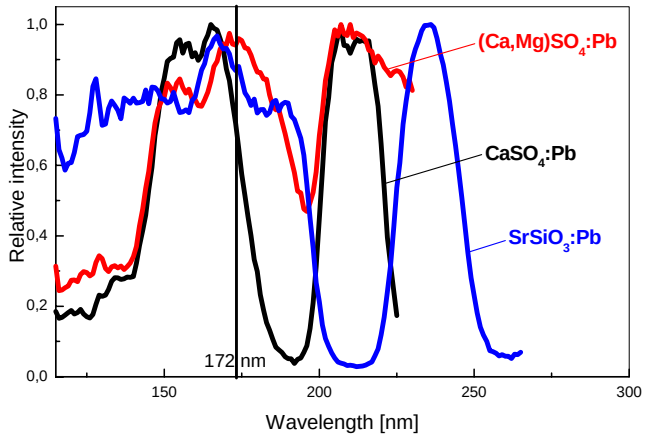
VUV Efficiency of UV-R Phosphors

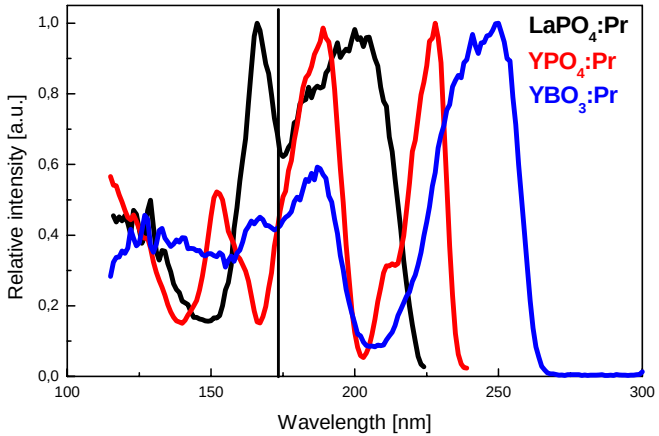
UV-C phosphors ⇒ Fluorescent Xe_2^* excimer lamps for disinfection purposes

Pb^{2+} sensitised

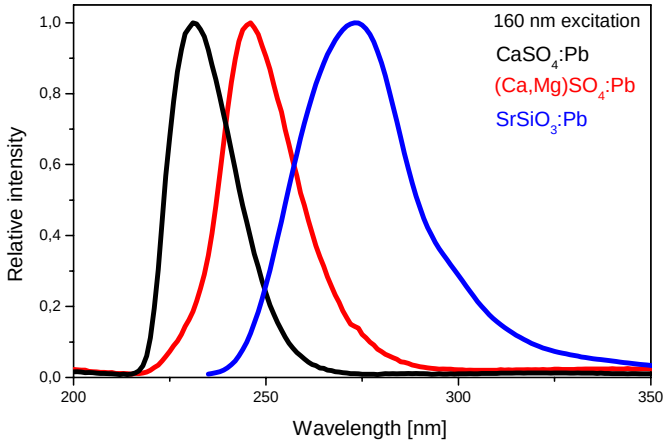
Pr^{3+} sensitised

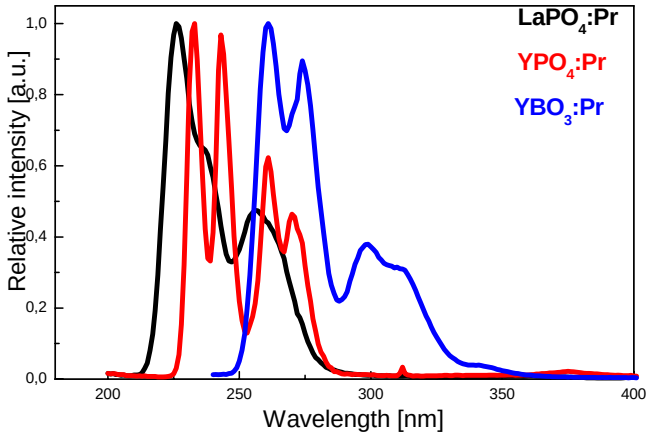
Excitation Spectra



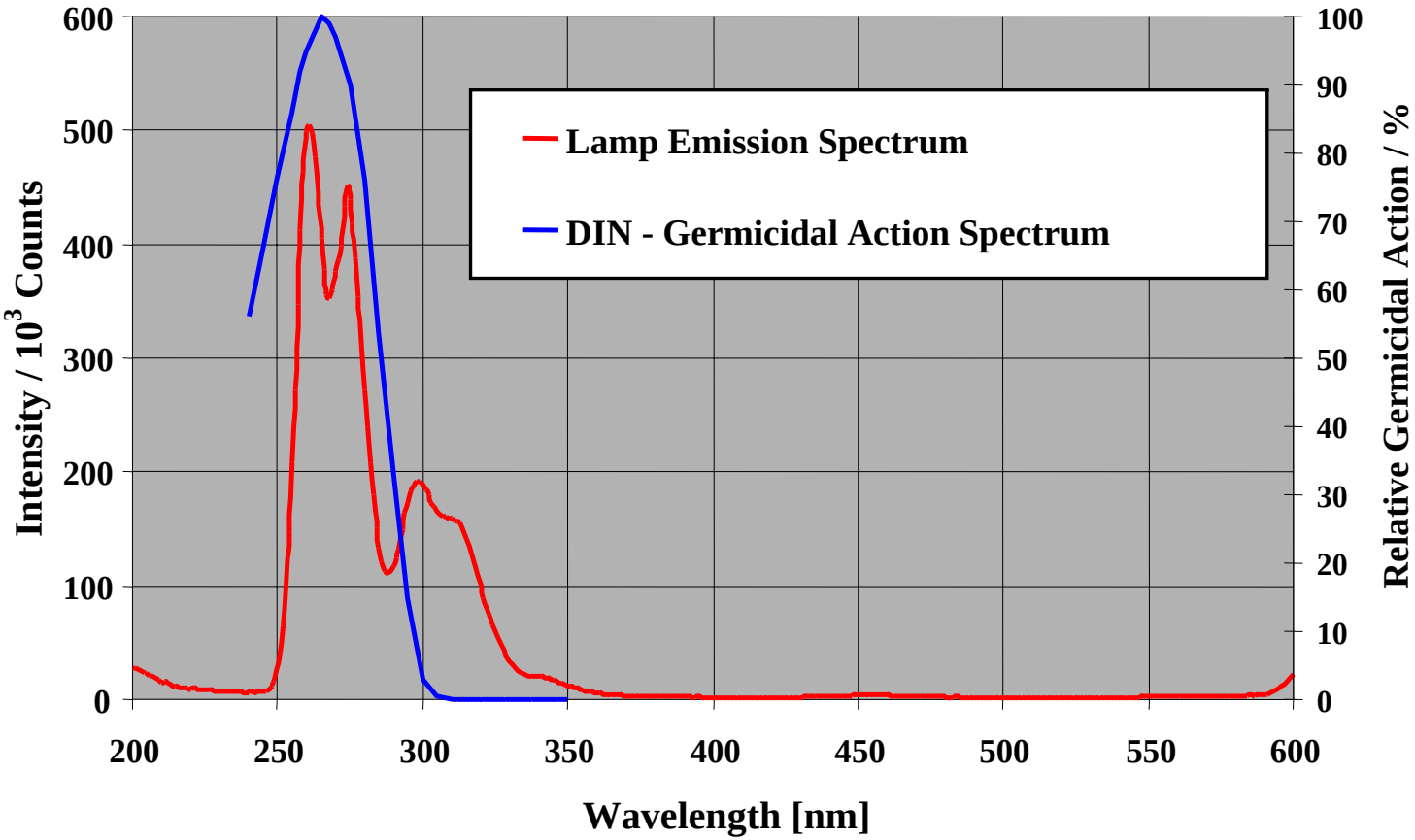


Emission Spectra





Xe_2^*- Excimer Lamp with YBO_3:Pr

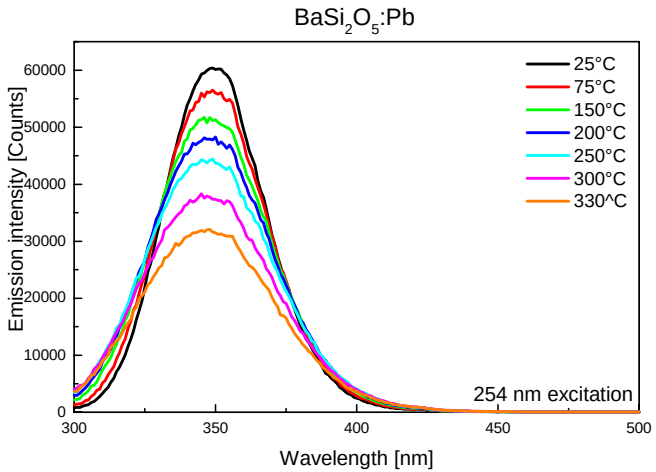


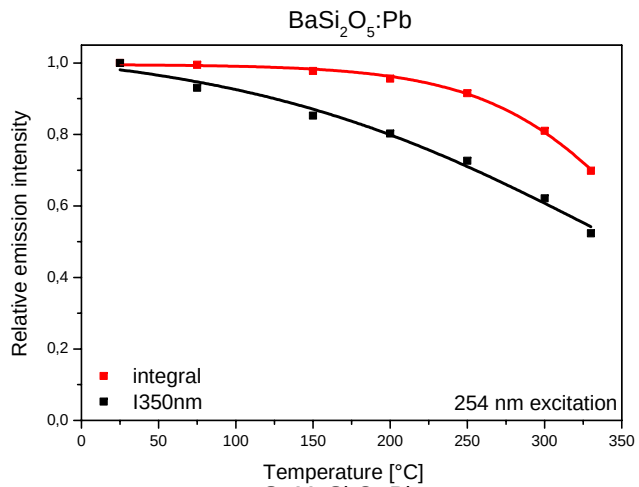
Lamp spectrum shows strong overlap with the germicidal action spectrum

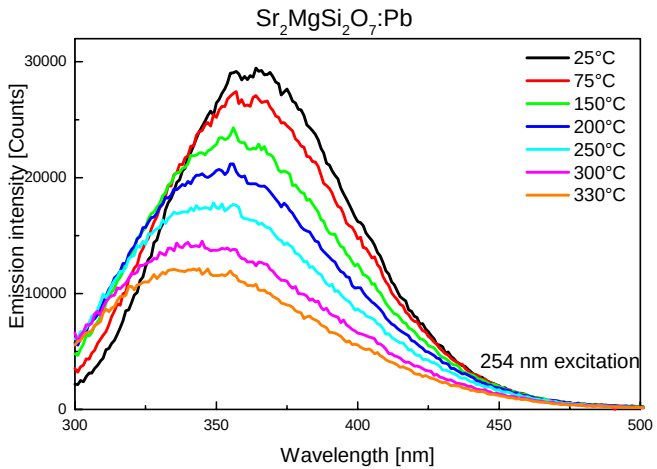
VUV Efficiency of UV-R Phosphors

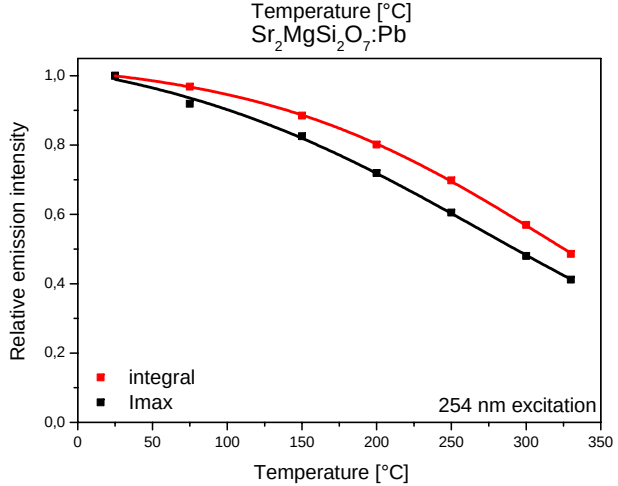
Phosphor	exc. band max.	em. band max.	light output 172 nm
$LaPO_4$:Pr	165, 200 nm	225 nm	70%
YPO_4:Pr	160, 190 nm	233 nm	70%
Best practice	170 nm	241 nm	90%
$(Ca,Mg)SO_4$:Pb	170 nm	245 nm	80%
$LuBO_3$:Pr	240 nm	257 nm	50%
YBO_3:Pr	240 nm	261 nm	50%
Y_2SiO_5:Pr	170, 245 nm	270 nm	20%
$SrSiO_3$:Pb	170, 235 nm	275 nm	80%
$LaPO_4$:Ce	170, 270 nm	320 nm	90%
YPO_4:Ce	170, 270 nm	335, 355 nm	55%
$LaMgAl_{11}O_{19}$:Ce	170, 275 nm	340 nm	90%

Thermal Quenching - UV-A Phosphors





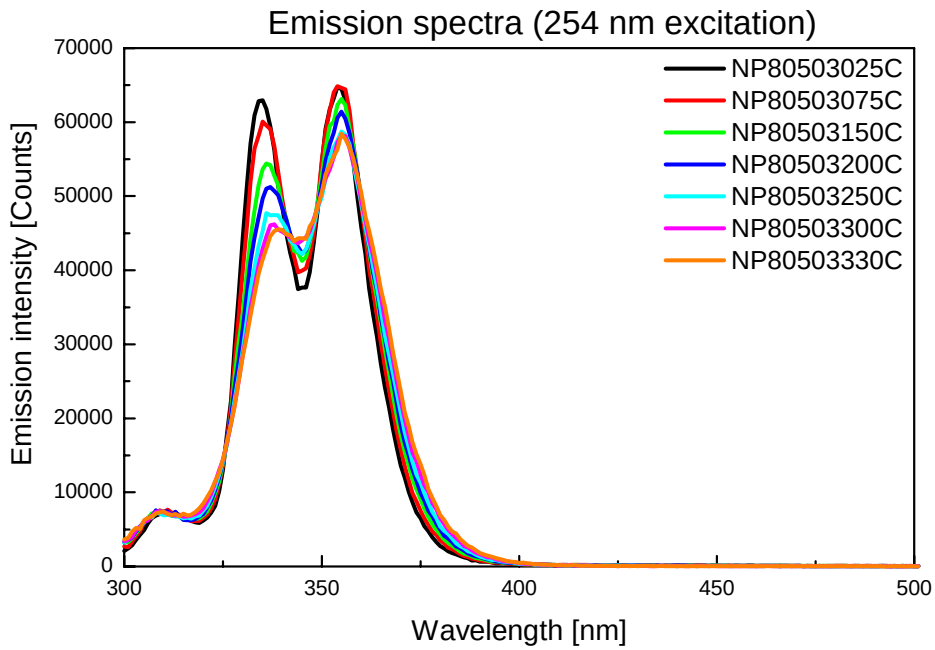


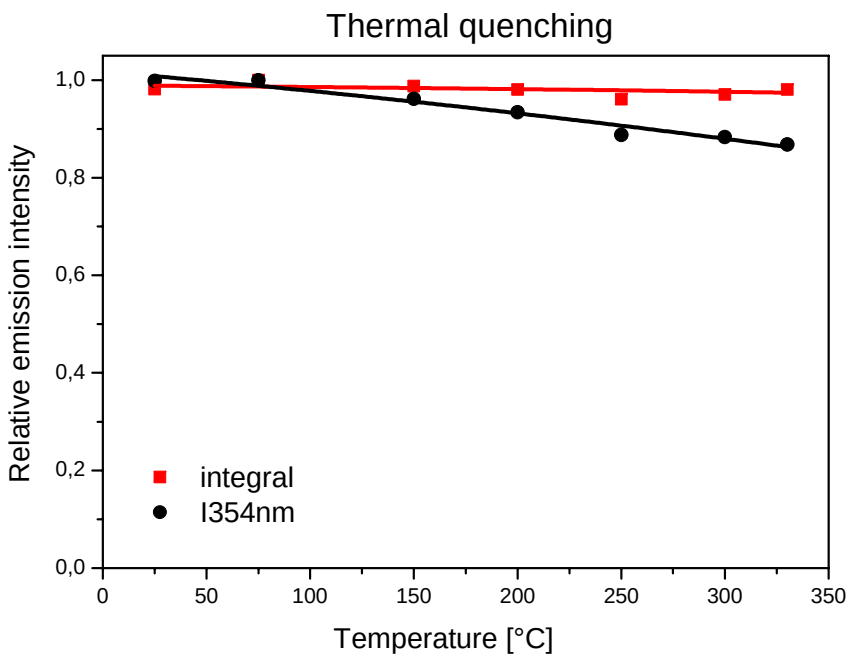


Phosphor	Stokes Shift [cm^{-1}]	FWHM [cm^{-1}]	QE_{254} RT [%]	$TQ_{1/2}$ [°C]
$BaSi_2O_5$:Pb	10600	2700	95	375
$Sr_2MgSi_2O_7$:Pb	12000	4300	80	316

Thermal Quenching - UV-A Phosphors

YPO_4:Ce



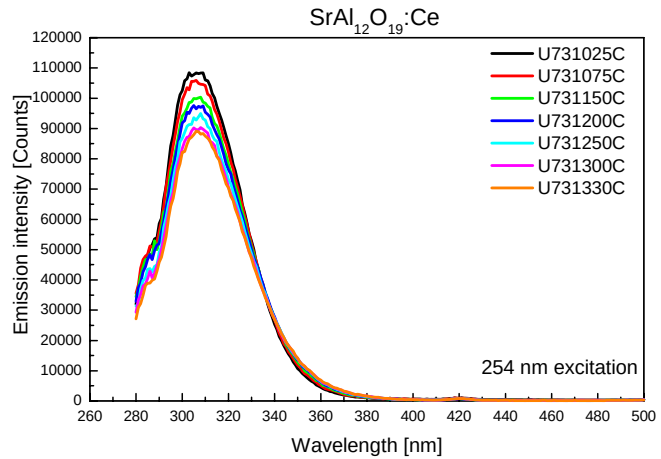


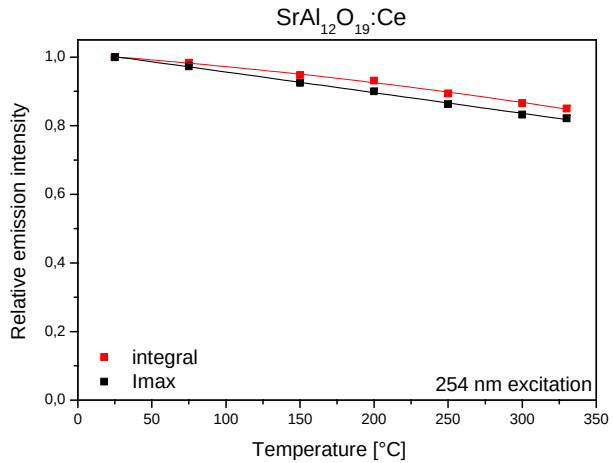
$TQ_{1/2}$ is estimated to be above 700°C!

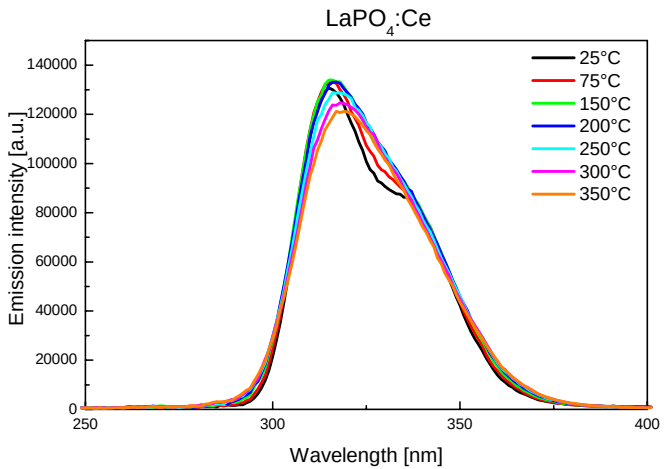
UV-B to UV-A ratio remains constant between RT and 330°C

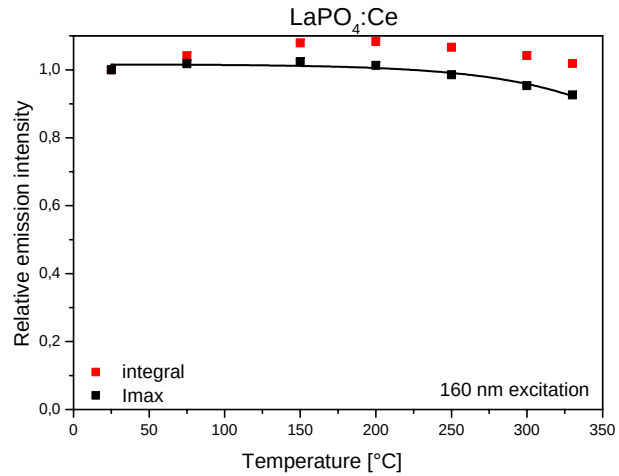
355 nm band increases at the cost of the 335 nm band with increasing temp.

Thermal Quenching - UV-B Phosphors







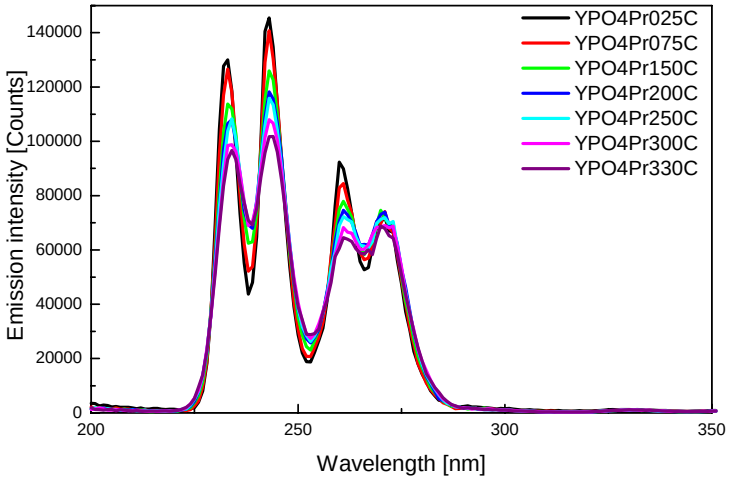


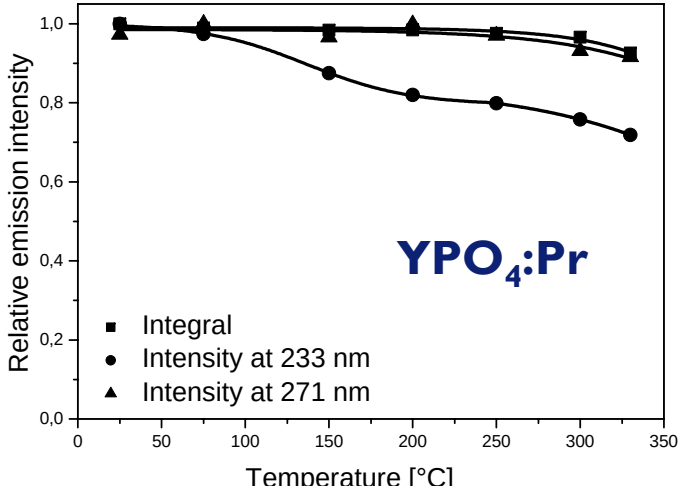
$TQ_{1/2}$ of commercially available UV-B phosphors is above 400°C

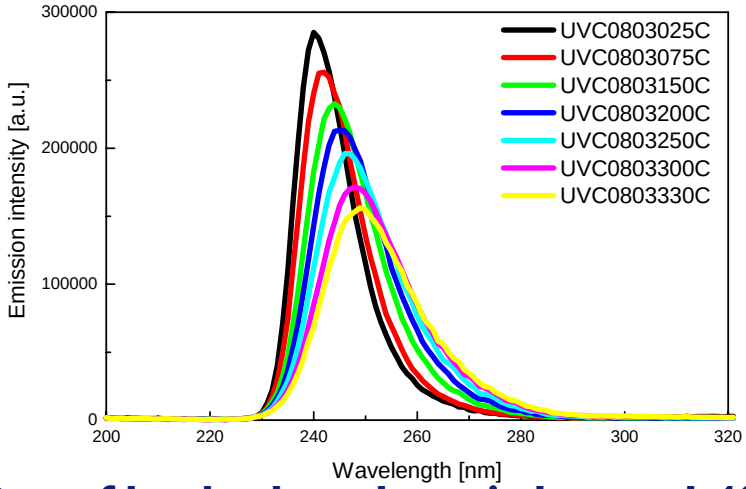
VUV efficiency of $LaPO_4$:Ce increases from RT to 200°C

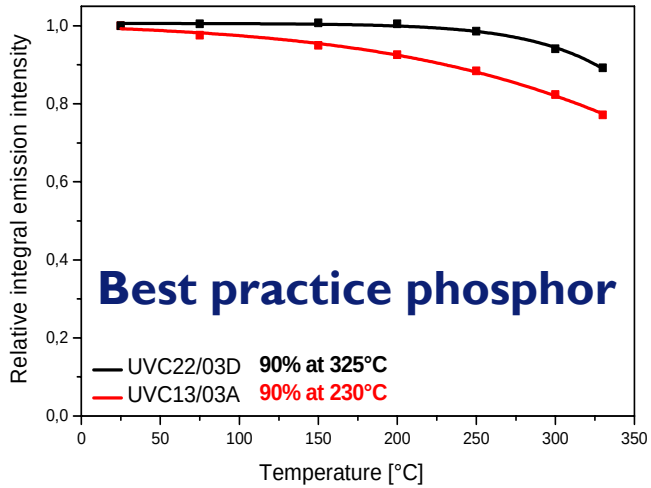
(more efficient ET from host lattice to Ce^{3+}?)

Thermal Quenching - UV-C Phosphors









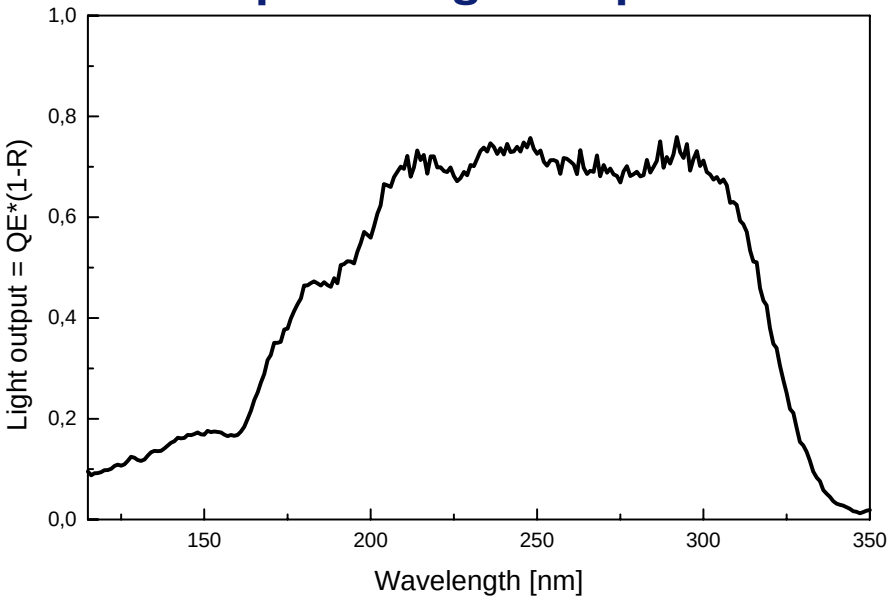
$TQ_{1/2}$ of both phosphors is beyond 400°C

Emission band of best practice phosphor shifts towards 250 nm upon heating

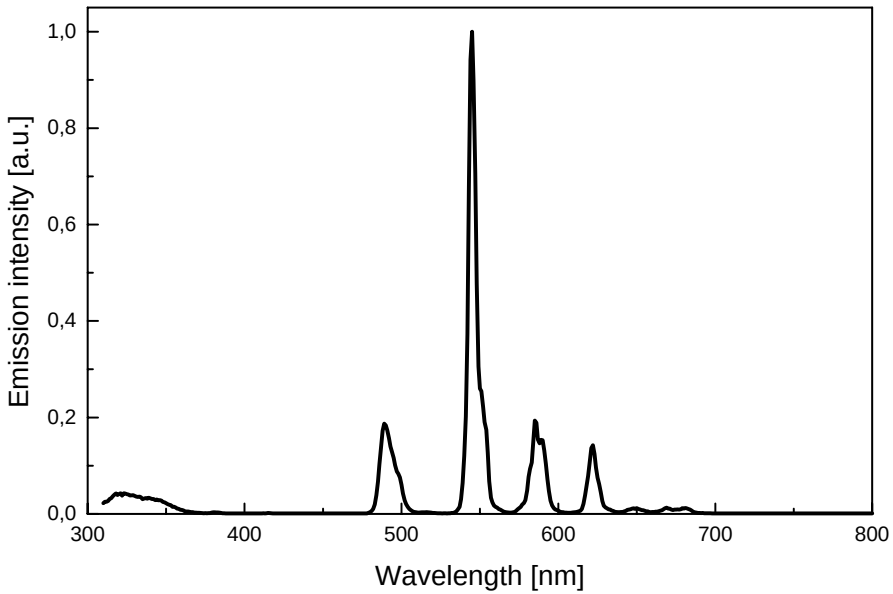
From Micro to Nanoscale Materials

$LnPO_4$ is a stable host for many activators: Ce, Pr, Gd, Tb, ...
Synthesis in organic solvents with a high boiling point

Spectral light output



Emission spectrum



$LaPO_4$:Ce,Tb from M. Haase et al.
Quantum efficiency ~ 60 % (40 % Tb^{3+} + 20 % Ce^{3+})
Microscale $LaPO_4$:Ce,Tb ~ 95%

From Micro to Nanoscale Materials

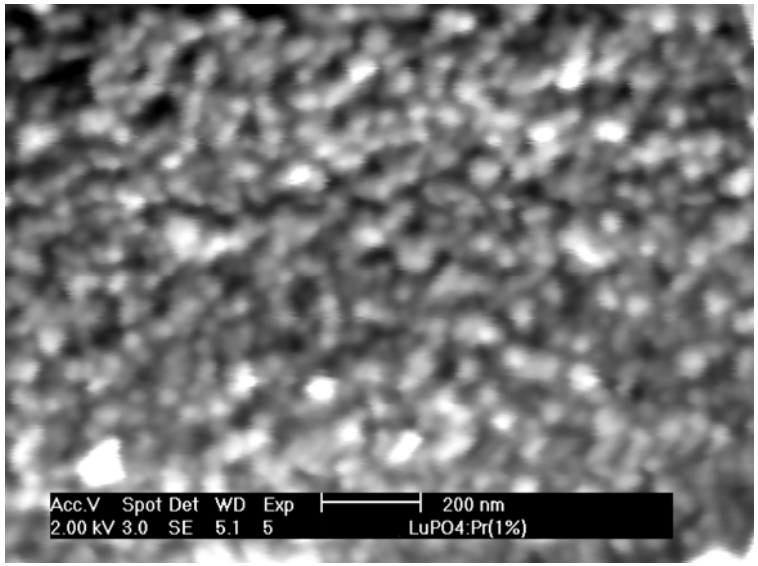
Alternative $LnPO_4$ synthesis approach

1. **Complexation of Ln^{3+}**
2. **Destabilisation of Ln-complex**
3. **Precipitation of the phosphate**

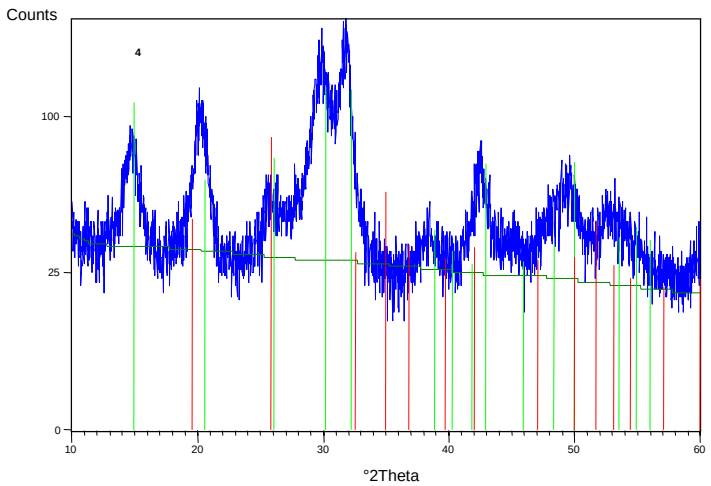
SEM: particle size < 50 nm

XRD: crystalline particles, particle size ~ 10 nm (Debye-Scherrer)

SEM Image

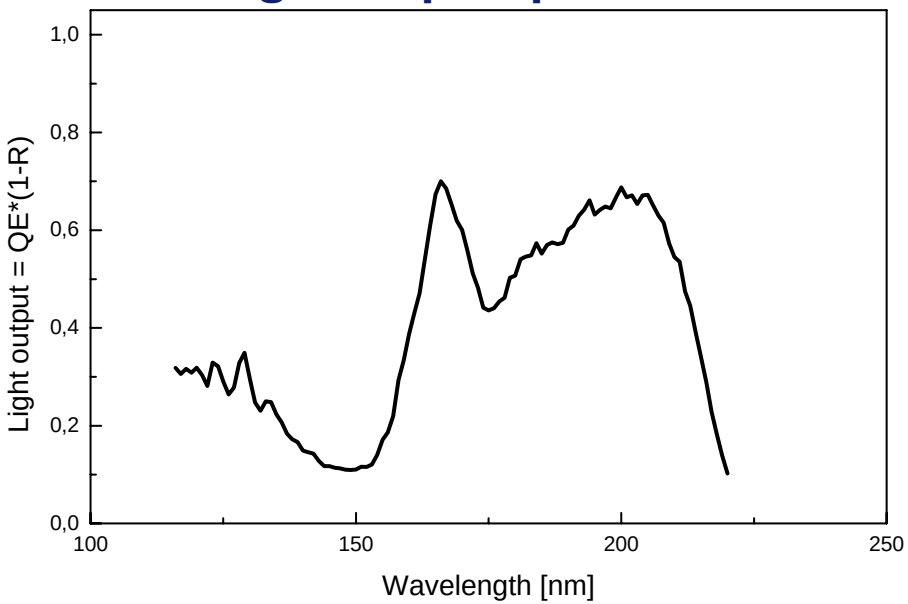


XRD Diagram

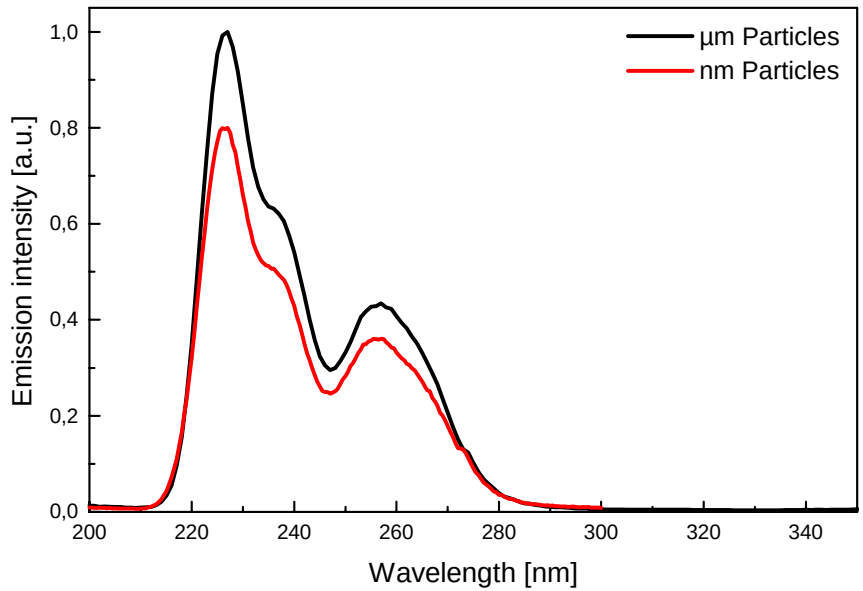


From Micro to Nanoscale Materials

Light output spectrum



Emission spectrum



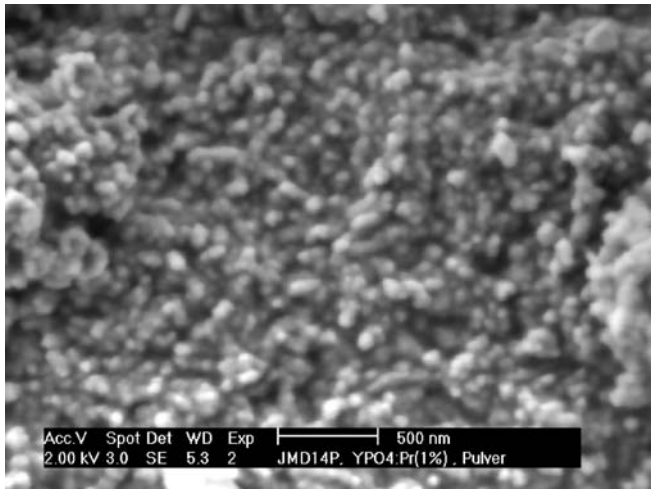
Quantum efficiency of $LaPO_4$:Pr

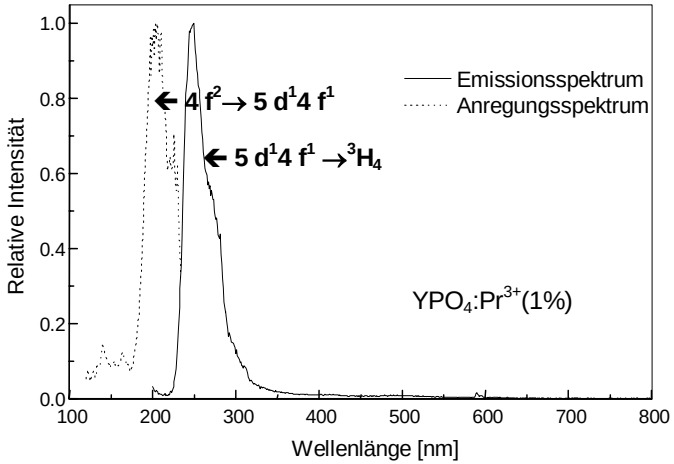
- **µm particles: ~ 70 %**
- **nm particles: ~ 55 %**

Further materials synthesised: YPO_4:Pr, $LuPO_4$:Pr, YPO_4:Ce, $LaPO_4$:Ce

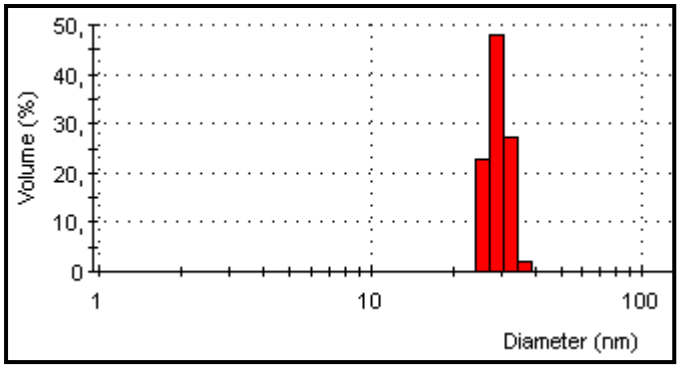
From Micro to Nanoscale Materials

YPO_4:Pr and $LuPO_4$:Pr as 235 nm Emitter

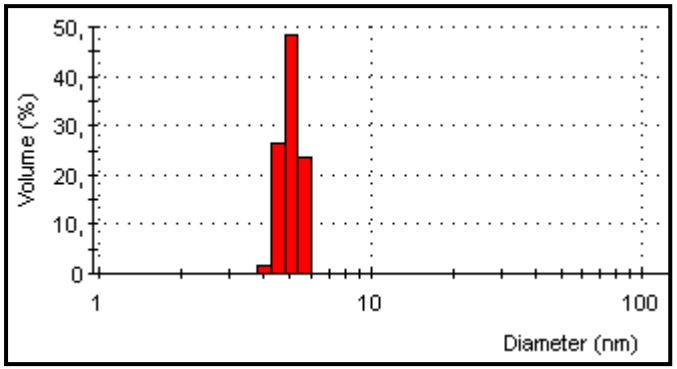




YPO_4:Pr (30 nm particles)



$LuPO_4$:Pr (5 nm particles)



Conclusions

UV Phosphors for Hg discharge lamps

- very efficient materials known, in particular $LnPO_4$:Ce (Ln = Y, La)
- wall load and lamp temperature increase results in stability problems $\Rightarrow$ use coatings + avoid Pb^{2+} phosphors
- thermal quenching is not a matter of concern

UV Phosphors for Xe_2* excimer discharge lamps

- UV-A phosphor with a high VUV efficiency is $LaMgAl_{11}O_{19}$:Ce
- Gd^{3+} activated UV-B phosphors have to be sensitised
- efficient UV-C phosphors have been identified
- thermal quenching is not a matter of concern

Nanoscale Phosphors

- nanoscale ortho-phosphates (monazite and xenotime structure) can be synthesised via hydrolysis of RE-complexes
- efficiency is about 60 – 70% of microscale phosphors