Applications of Pr^{3+} Phosphors to Fight the Covid-19 Pandemic

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Outline

1. Pr at Work
2. Some Fundamentals of Pr^{3+} Luminescence
3. UV Disinfection
4. UV Radiation Sources
5. Recent Developments
6. Summary
7. Outlook
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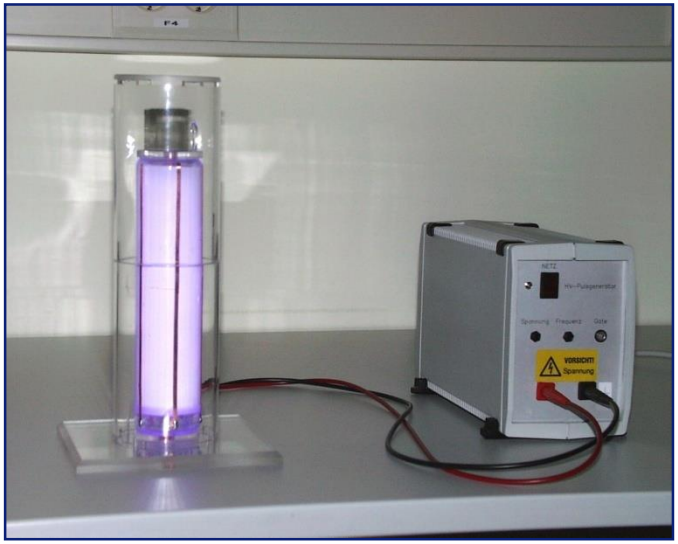
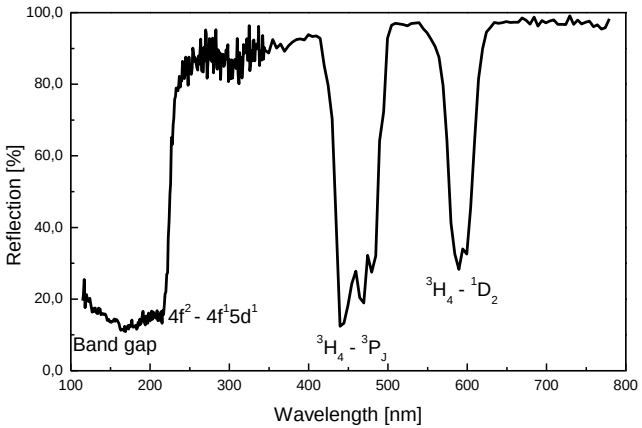


1. Pr at Work

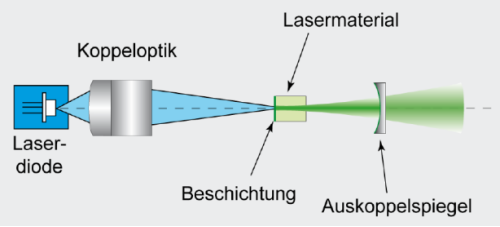
Pr^{3+} Ions in Optical Materials

- Colour filter in goggles for welders and in combination with Nd_2O_3 in goggles for glass makers (absorption of yellow Na lines)
- UV emitting phosphors
- Electroluminescent devices: $(Ca,Sr,Ba)(Ti,Zr)O_3$:Pr,Al
- Photon cascade emission: YF_3:Pr, $NaYF_4$:Pr
- Scintillator crystals/ceramics: Gd_2O_2S:Pr,Ce,F, LuAG:Pr
- Laser gain media: ZBLAN, KY_3F_{10}:Pr, $LiYF_4$:Pr



$PrPO_4$

Pr in other Functional Materials



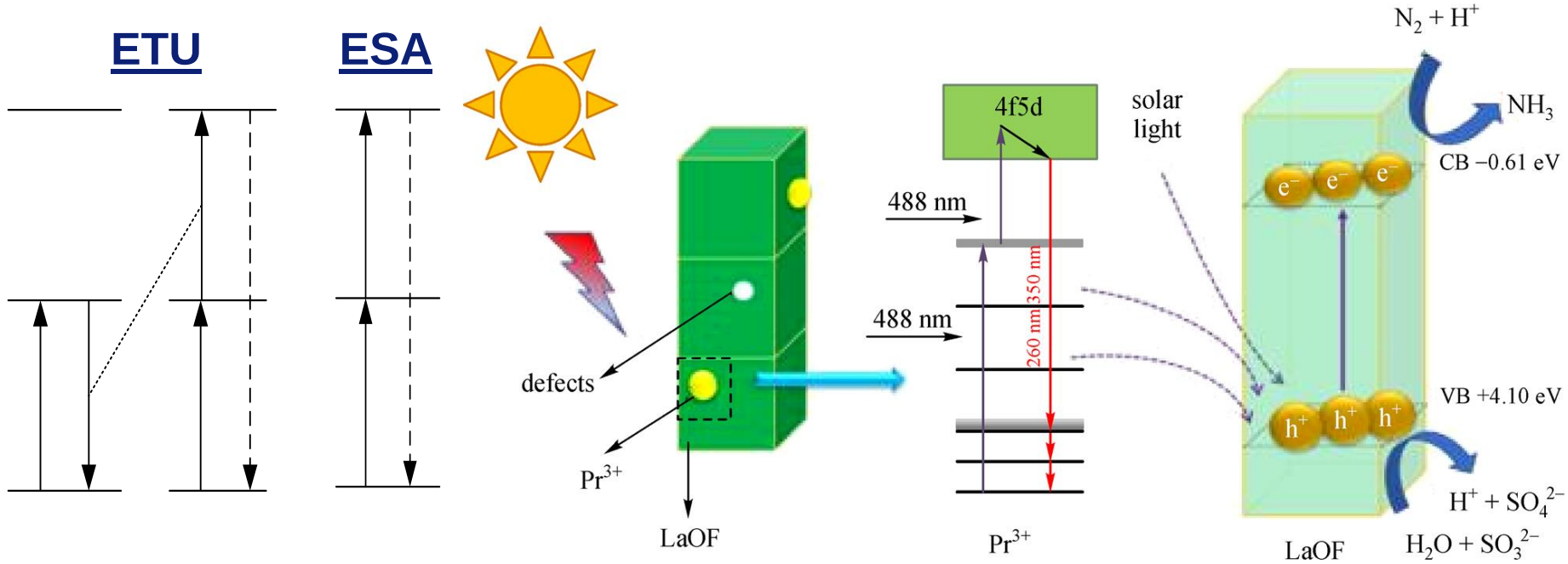
- Corrosion resistant alloys
- Photocatalysts
- Information storage in quantum computing

$Gd_2W_2O_9$:Pr

1. Pr at Work

Novelty: Pr^{3+} for the Photoreduction of Nitrogen N_2

- Pr^{3+} can undergo ESA or Energy Transfer Up-Conversion (ETU)
- LaOF:Pr is an UC Photocatalyst: $N_2 + 6\ H^+ + 6\ e^- \rightarrow 2\ NH_3$
- Activation by blue light is feasible (488 nm laser)



Lit.: Front. Mater. Sci. 14 (2020) 43–51

2. Fundamentals of Pr^{3+} Luminescence

Pr^{3+} ground state configuration

$[Xe]4f^2$ → 13 SLJ-States

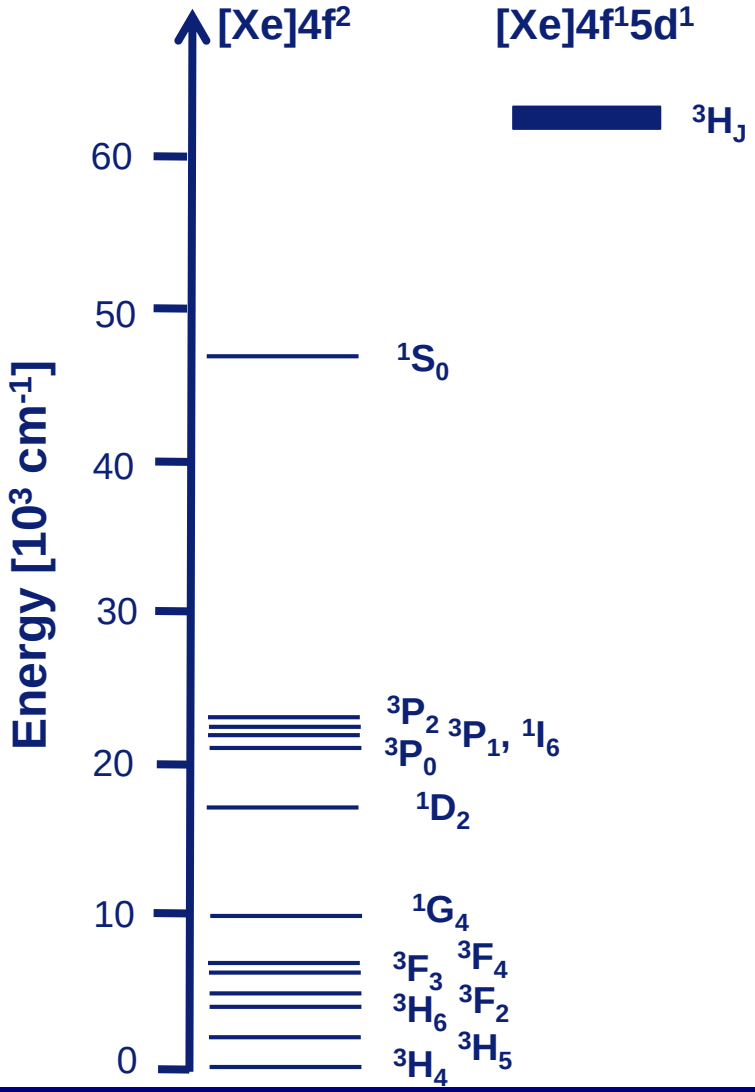
Pr^{3+} excited state configuration

$[Xe]4f^15d^1$

Energy distance between the $[Xe]4f^2$ and $[Xe]4f^15d^1$ configuration is 62000 cm^{-1} (for the free ion)

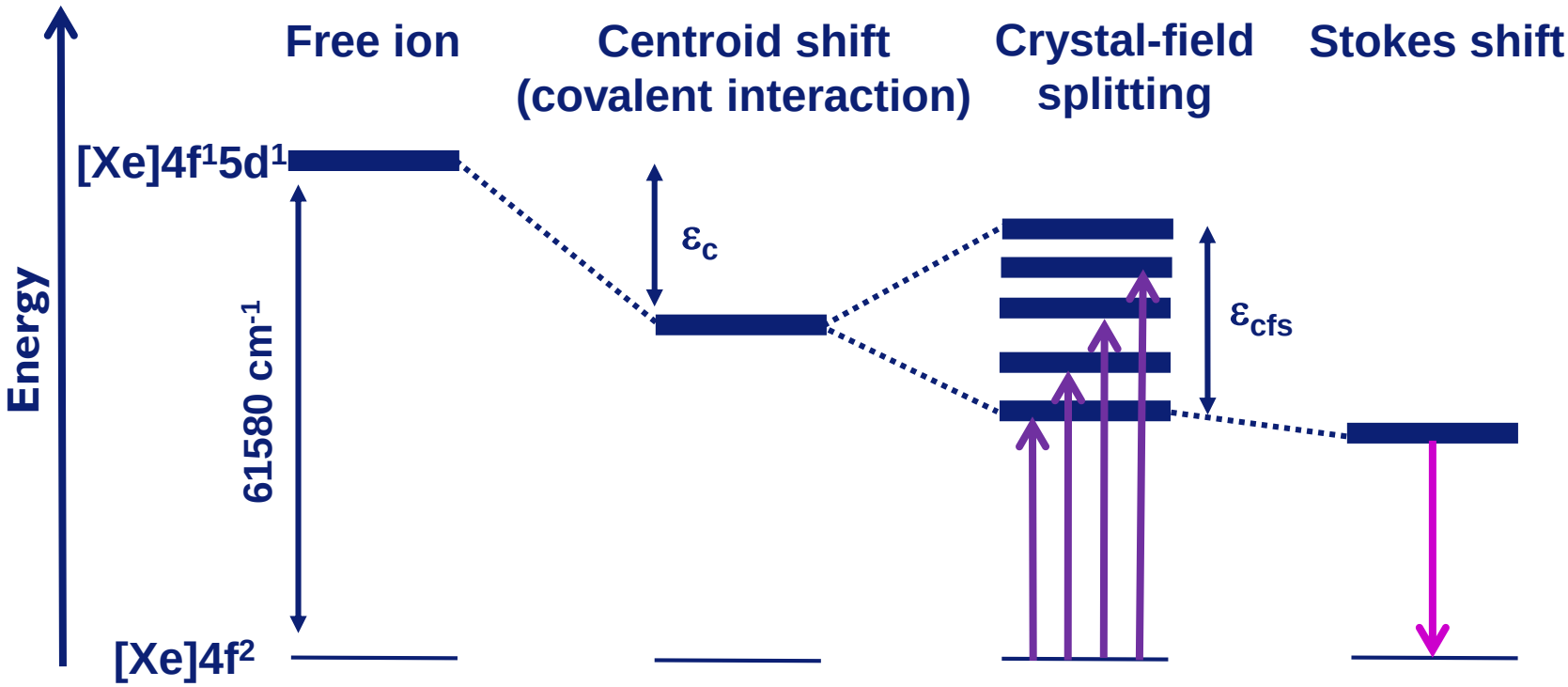
$E^0(Pr^{3+/4+}) = 3.2$ V in $[Pr(H_2O)_9]^{3+}(aq)$

$IE(Pr^{3+/4+}) = 7.8$ eV in $CaF_2(s)$



2. Fundamentals of Pr^{3+} Luminescence

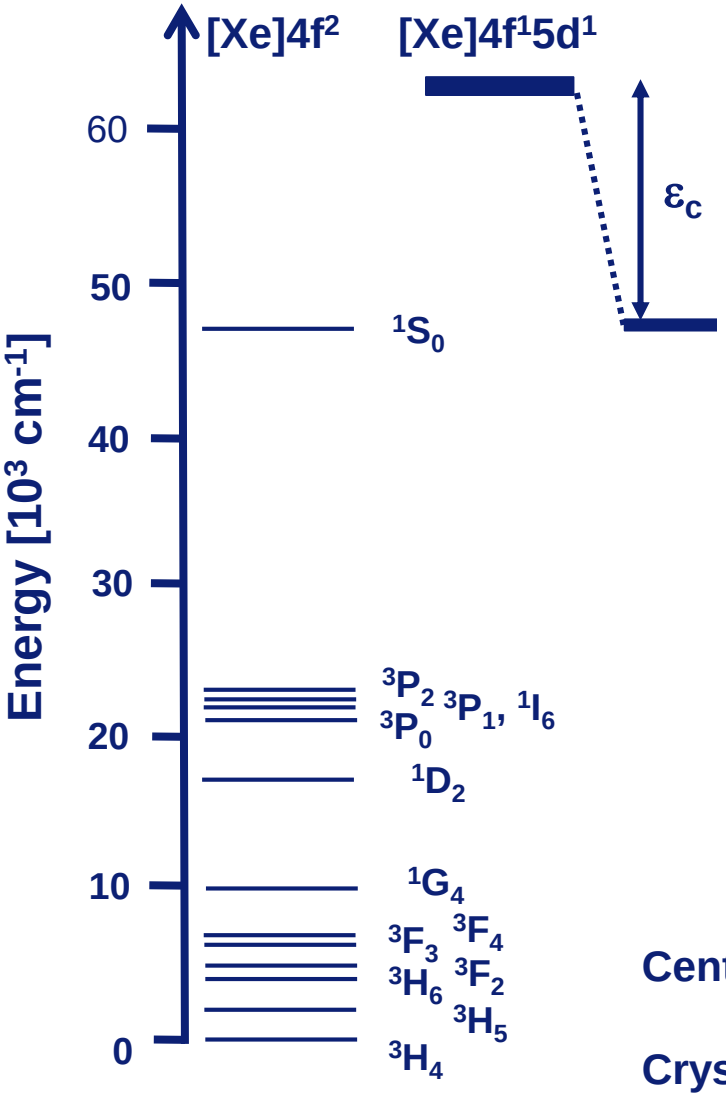
Tuning the energy distance between the $[Xe]4f^2$ and $4f^15d^1$ configuration



Impact factors: (Spectroscopic) polarisibility, ion charge density, site symmetry, coordination number, metal-ligand distance, …

Comment: CFS on energy levels of $4f^n$ configuration typically < 100 cm^{-1}

2. Fundamentals of Pr^{3+} Luminescence



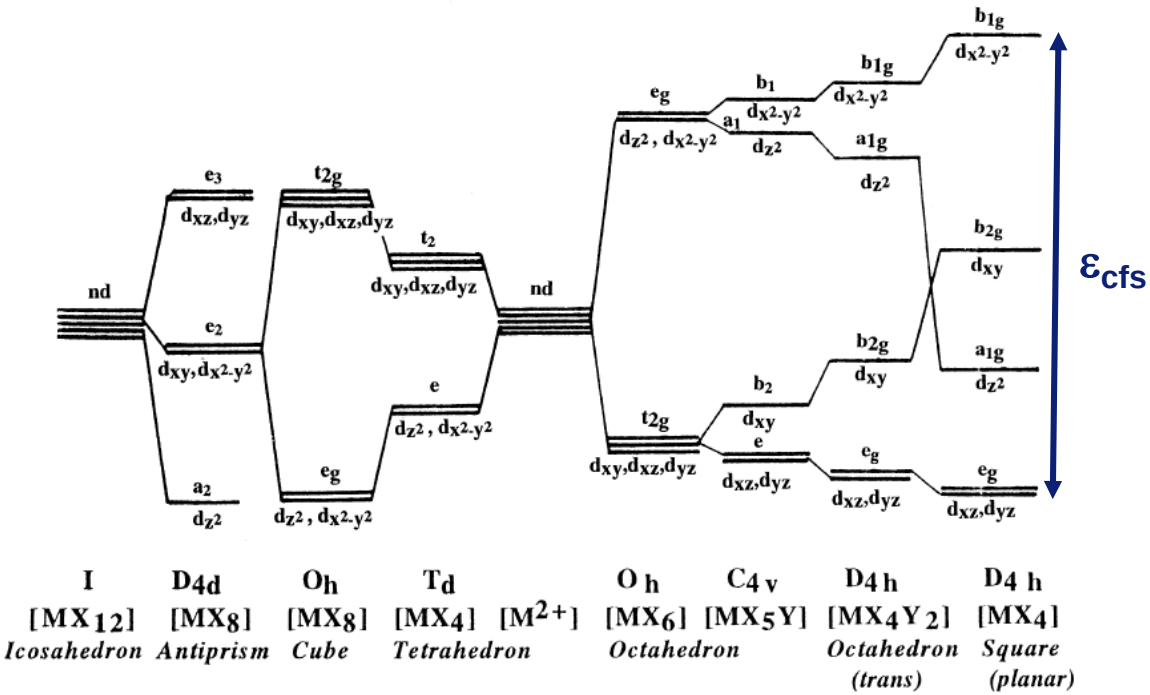


FIGURE 4.5. Splitting of d orbital energy levels in ligand fields of different symmetries. In MX_5Y and MX_4Y_2 complexes the splitting of the T_{2g} and E_g terms can be inverted depending on the ratio of field strengths X/Y. (After Schmidtke [4.12].)

Centroid shift (ε_c) 3000 – 20000 cm^{-1} (fluorides → garnets)

Crystal-field-splitting (ε_{cfs}) < 23000 cm^{-1} = f(CN, symmetry, …)

2. Fundamentals of Pr^{3+} Luminescence

Photon Cascade Emission (PCE)

First examples (1974)

Sommerdijk et al., J. Lumin. 8 (1974) 341 (Philips)

Piper et al., J. Lumin. 8 (1974) 344 (General Electric)

YF_3:Pr, $NaYF_4$:Pr, $NaLaF_4$:Pr

$^1S_0$ - $^3P_1$,$^1I_6$ transition @ 407 nm

$^3P_0$ - ^3H_J,$^3F_2$ transitions in the red

QE ~ 140% (visible), 166% (total)

Oxidic luminescent materials showing PCE

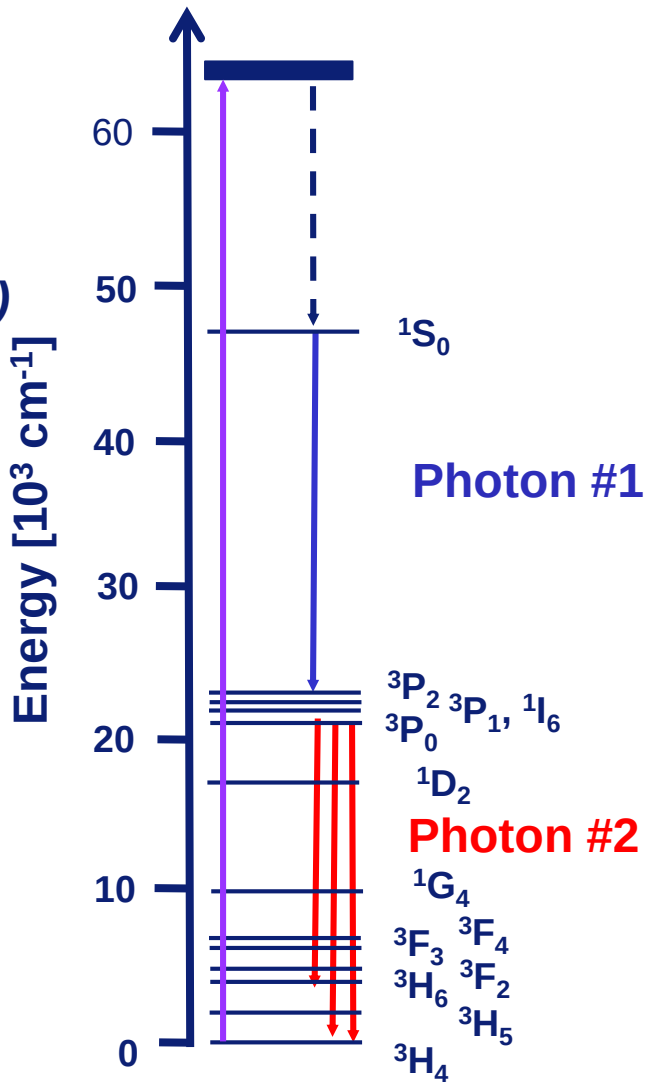
A. Srivastava et al. (General Electric)

Pr^{3+} on host lattice sites with high CN = 9-12

$SrAl_{12}O_{19}$:Pr

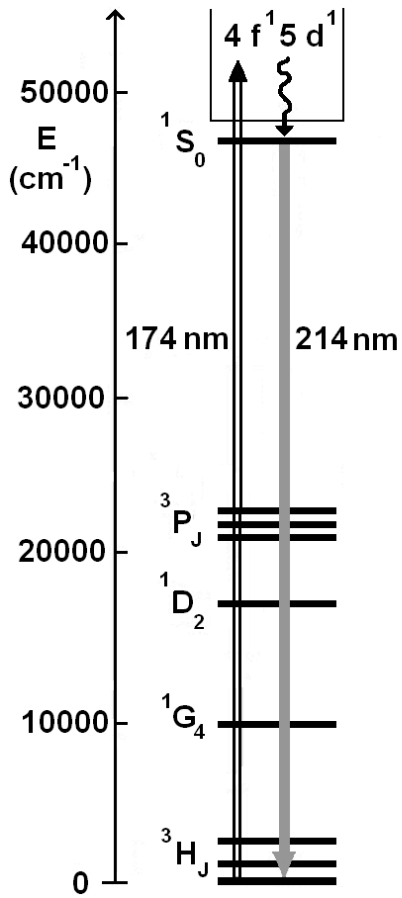
$LaMgB_5O_{10}$:Pr

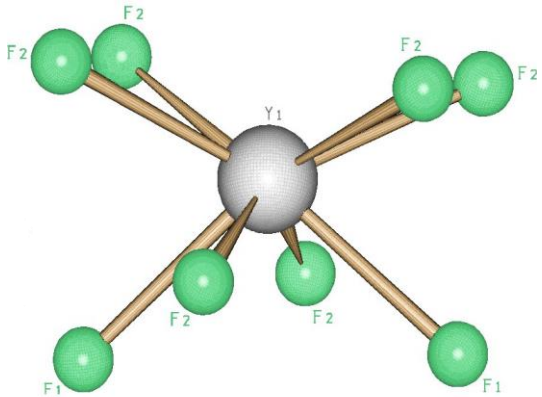
LaB_3O_6:Pr



2. Fundamentals of Pr^{3+} Luminescence

YF_3:Pr - PCE

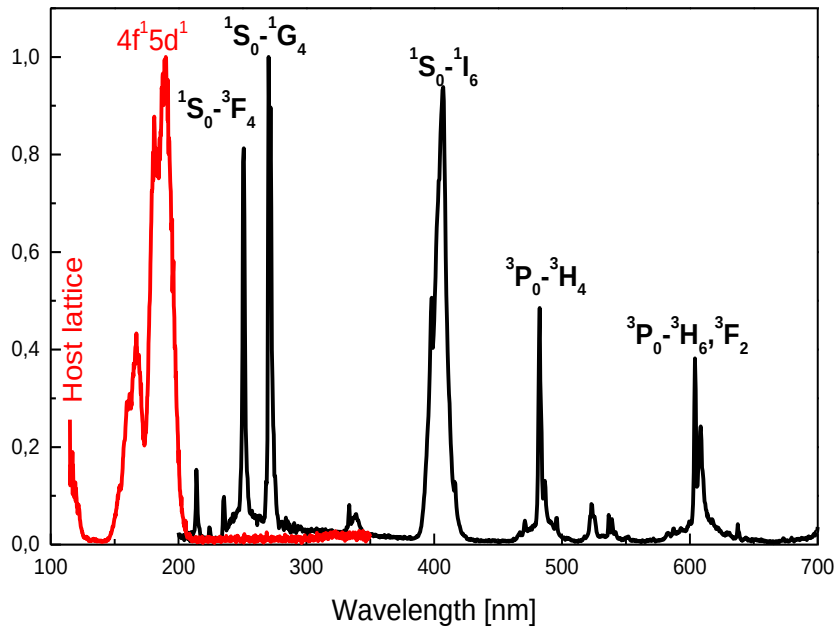




distorted square antiprism (CN = 8)

Y-F distances
4x 2.28 Å
2x 2.30 Å
2x 2.31 Å

CF splitting
~ 8000 cm^{-1}
Centroid shift
~ 5600 cm^{-1}

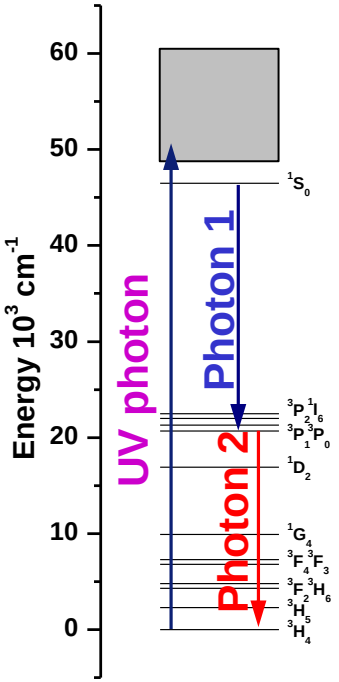


CFS + centroid shift reduces energy of lowest CF component of the $[Xe]4f^15d^1$ configuration by less than 10000 cm^{-1}

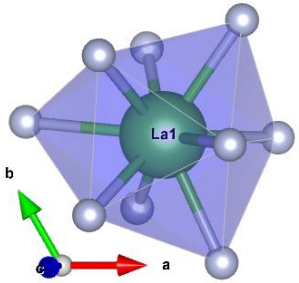
$\Rightarrow$ $E(4f^15d^1) > E(^1S_0)$

$\Rightarrow$ Photon cascade emission

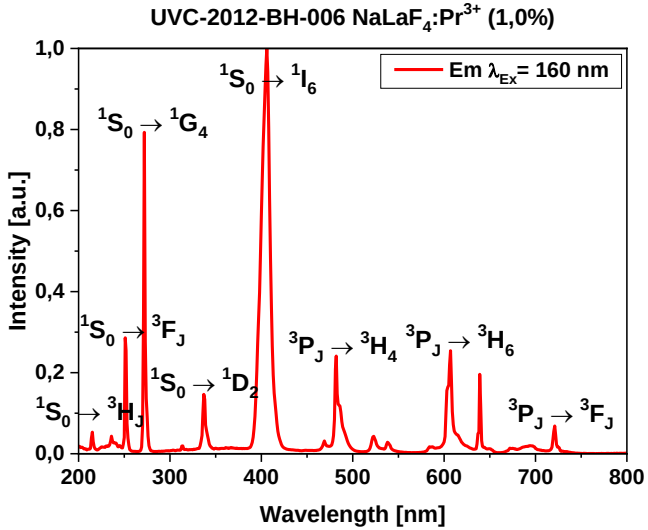
2. Fundamentals of Pr^{3+} Luminescence



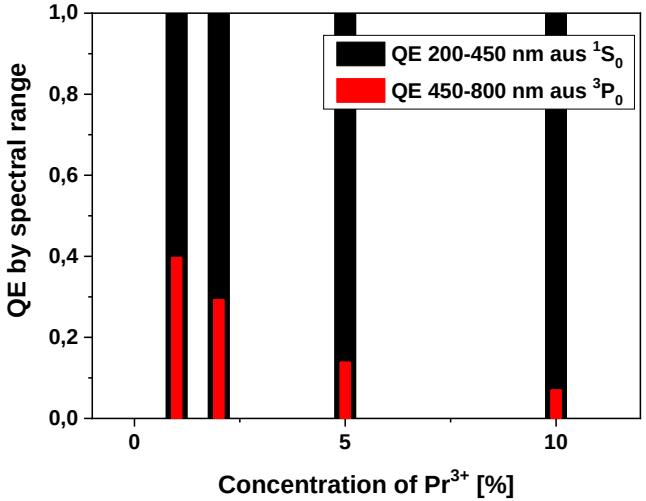
$NaLaF_4$:Pr - PCE



- CN = 9
- IQE up to 140%
- IQE is strongly Pr^{3+} concentration dependent
- Excitation by VUV radiation, i.e. 120 - 190 nm feasible
- Little UV emission, rather low stability and absorption



Pr^{3+} concentration [%]	IQE of $^1S_0$ [%]	IQE of $^3P_0$ [%]	Total IQE [%]
1	100	39.7	139.7
2	100	29.3	129.3
5	100	13.9	113.9
10	100	7.0	107.0

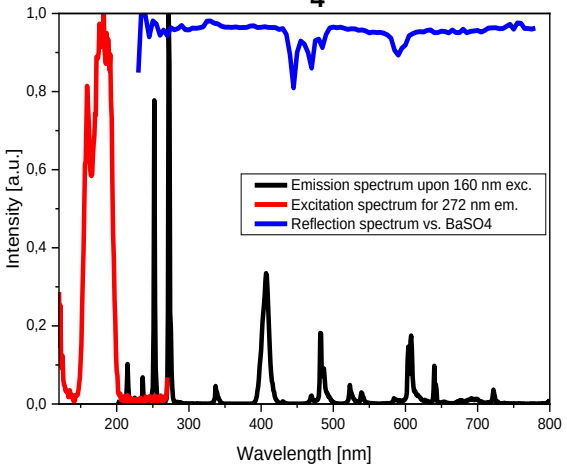


2. Fundamentals of Pr^{3+} Luminescence

Pr^{3+} doped fluorides: $[Xe]4f^15d^1$ – $[Xe]4f^2$ vs. $[Xe]4f^2$ – $[Xe]4f^2$ emission

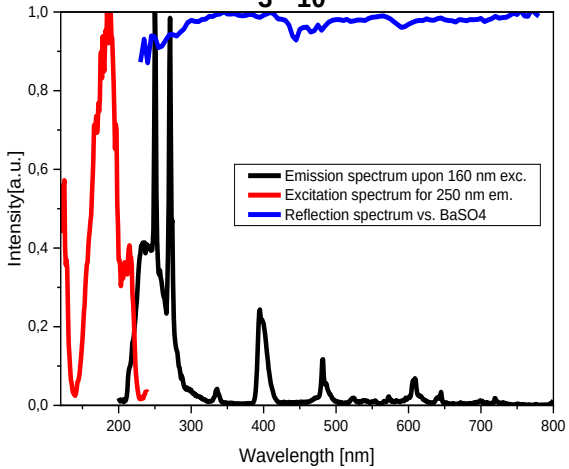
Compound	Emis. max. [nm]	Crystal system	CN	E of lowest CF compon.
$NaYF_4:Pr^{3+}$	213, 236, 405	hexagonal	9	$[Xe]4f^15d^1 > {}^1S_0$
$KY_3F_{10}:Pr^{3+}$	240, 250, 271, 405	cubic	8	$[Xe]4f^15d^1 \sim {}^1S_0$
$KYF_4:Pr^{3+}$	235, 255	hexagonal	7	$[Xe]4f^15d^1 < {}^1S_0$

$NaYF_4:Pr^{3+}$



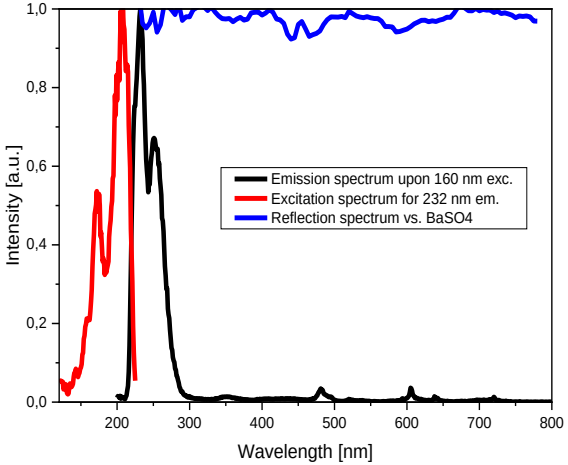
4f-4f emission

$KY_3F_{10}:Pr^{3+}$



4f-4f and 4f-5d emission

$KYF_4:Pr^{3+}$



4f-5d emission

Pr^{3+} phosphors with sole UV-C 4f-5d emission requires hosts enabling large ε_c and ε_{cfs}

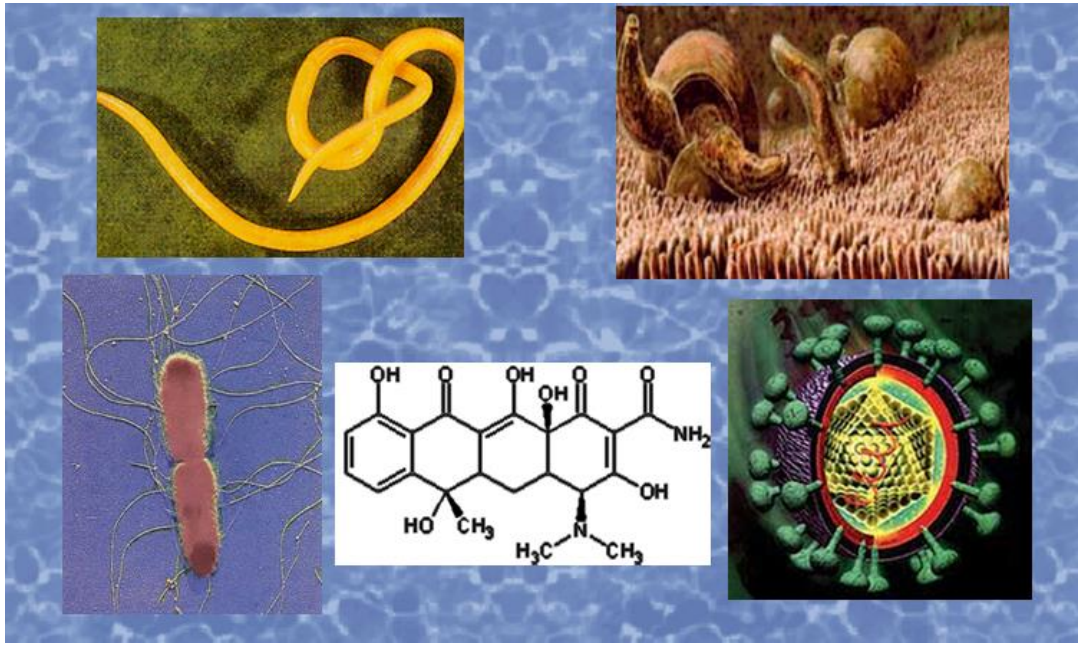
3. UV Disinfection

Application areas

→ Drinking, process, and waste water, air, exhaust gas, and surfaces

By inactivation of microorganisms

By mineralisation of organic matter



UV-C

Vacuum UV

UV-C/B and ozone

UV-C and H_2O_2

UV-A/B and photocatalyst

→ Formation of oxidative ROS

Singlet oxygen	$^1O_2$
Ozone	O_3
Hydroxy radicals	$HO^{\cdot}$
Hyperoxide radicals	$O_2^{-\cdot}$

3. UV Disinfection

By mineralisation of organic matter (microorganisms and µ-pollutants)

Energy of chemical bonds

10 – 1100 kJ mol^{-1}

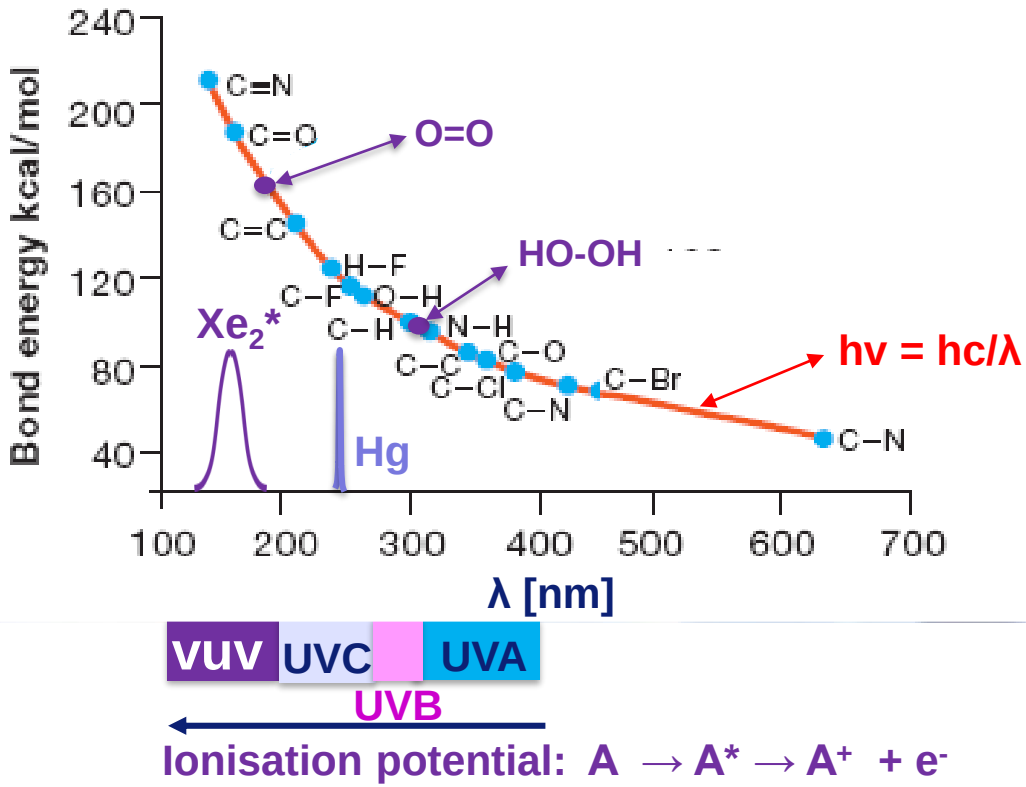
2.4 – 263 kcal mol^{-1}

Energy of optical radiation

$E = N_A hc/\lambda = 119226/\lambda$ kJ mol^{-1}

1 eV = 8065 cm^{-1}
= 96.2 kJ mol^{-1}
= 23 kcal mol^{-1}

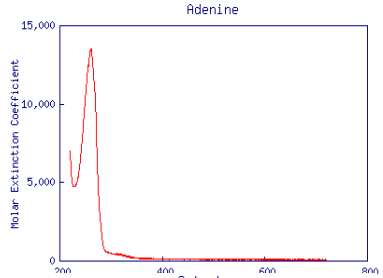
Bond energy

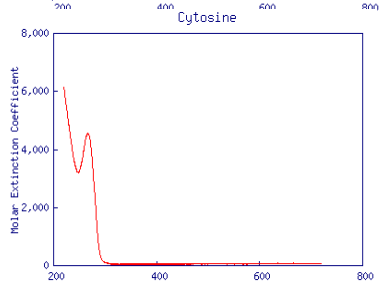


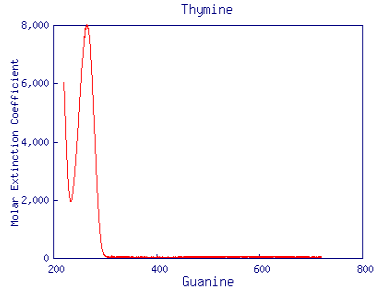
Ionisation potential: $A \rightarrow A^* \rightarrow A^+ + e^-$

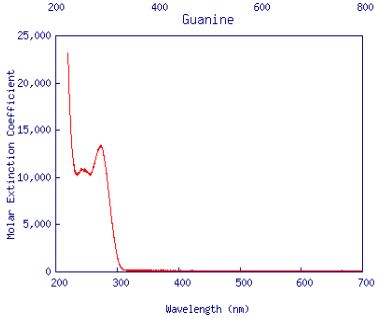
Thus vacuum UV radiation is able to cleave all kind of covalent chemical bonds

3. UV Disinfection





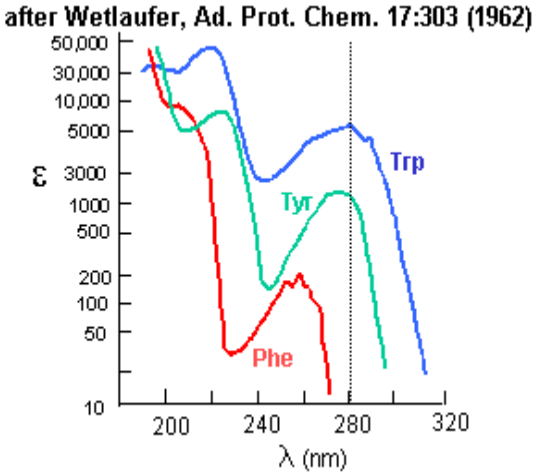


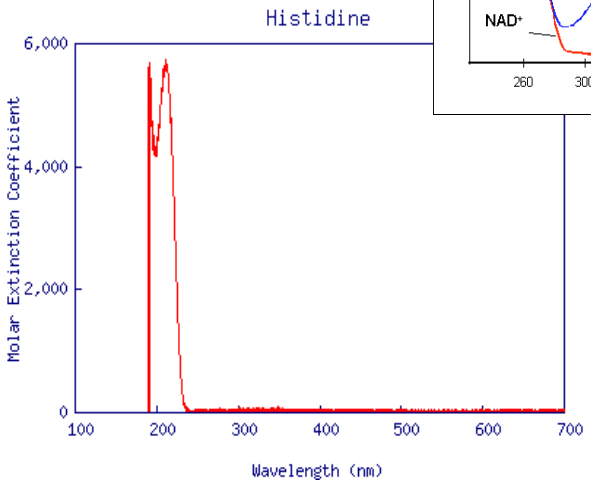


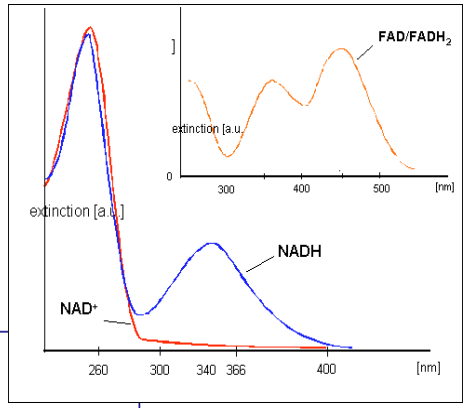
Nucleotides show intense absorption bands at 265 nm (A, C, T, G) and additionally at 240 nm (G)

Aromatic amino acids show absorption bands at 280 nm (Trp, Tyr), at 250 nm (Phe), or at 210 nm (His)

Other biomolecules absorb even in the near-UV or blue spectral range, e.g. NAD(P)H or $FADH_2$

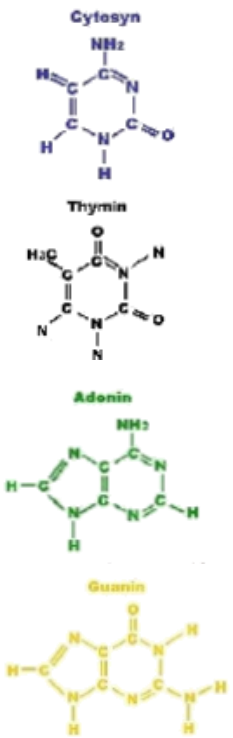




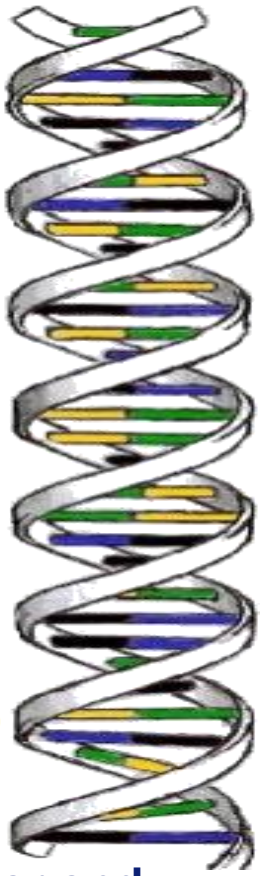


3. UV Disinfection

Bases

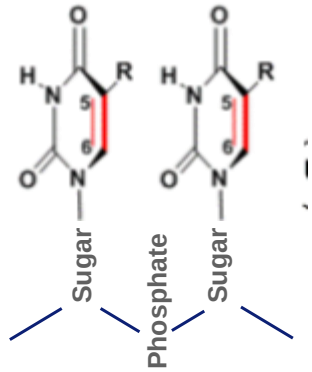


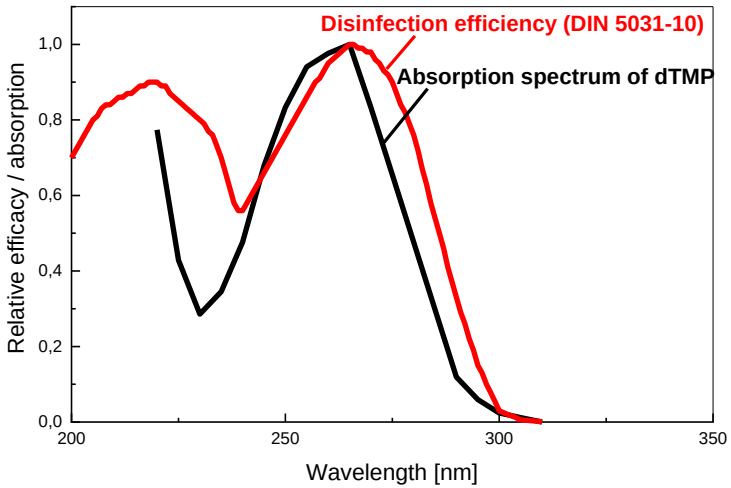
DNA double helix



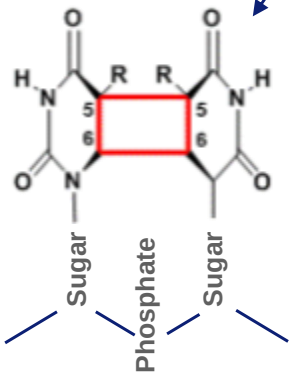
+ sugar and phosphate units

adjacent Thymin bases

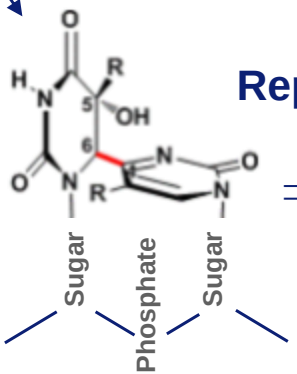




UV radiation



Cyclobutan-Pyrimidindimer (CPD) 70-80%



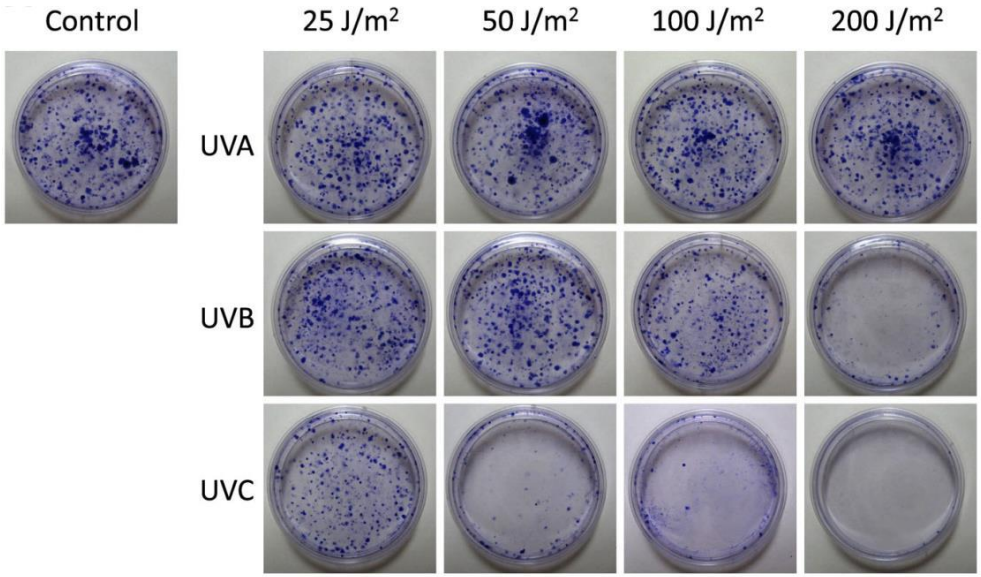
Pyrimidin-Pyrimidon-Photoproduct (64PP) 20-30%

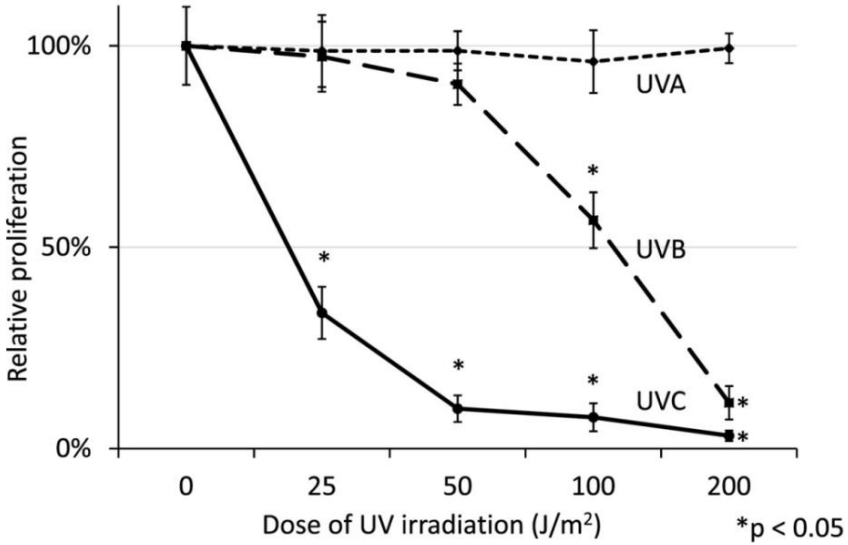
<u>Result</u>

Replication of DNA hampered
⇒ cell mitosis inhibited
⇒ no infectious potential

3. UV Disinfection

Effect of UV-C/B/A Radiation





	Penetration characteristic	Damage conferred
UV-C	Penetrates cell membranes/cell walls	mainly DNA damage
UV-B	Most responsible for sunburns. Penetrates deeper than UV-C, but is typically adsorbed by the skin's stratum corneum (dead cell layer)	DNA and other cell components by generation of free radicals
UV-A	Long wavelengths that reach inner strata of skin causing premature aging in humans	Shown to cause membrane damage

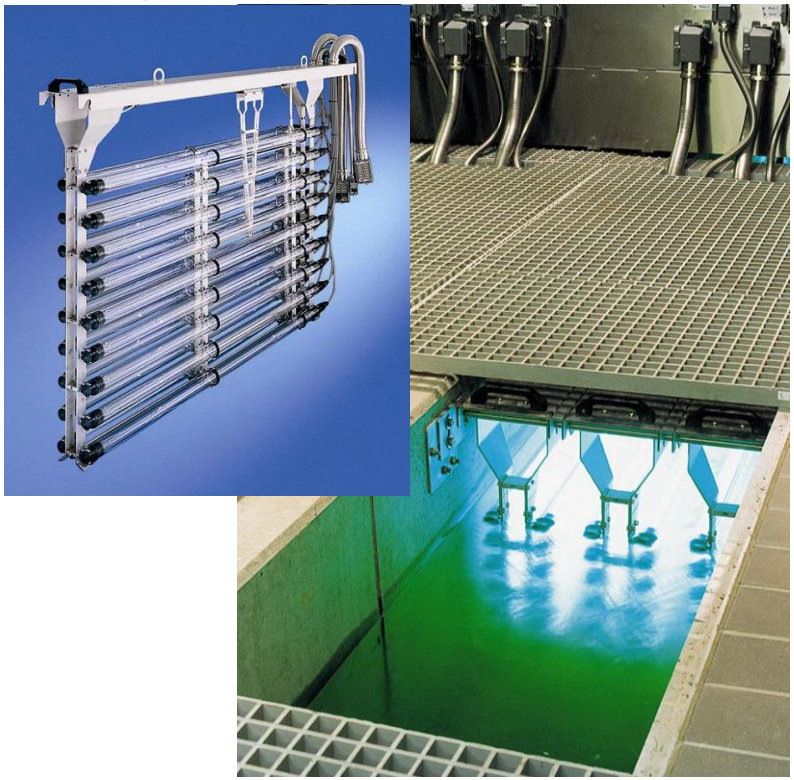
increasing penetration

Typical penetration depth of UV-C radiation into tissue ~ 40 µm!

Lit.: S. Miwa et al., J. Cellular Biochemistry 114 (2013) 2493

3. UV Disinfection

Drinking water: Examples of industrial and municipal appliances

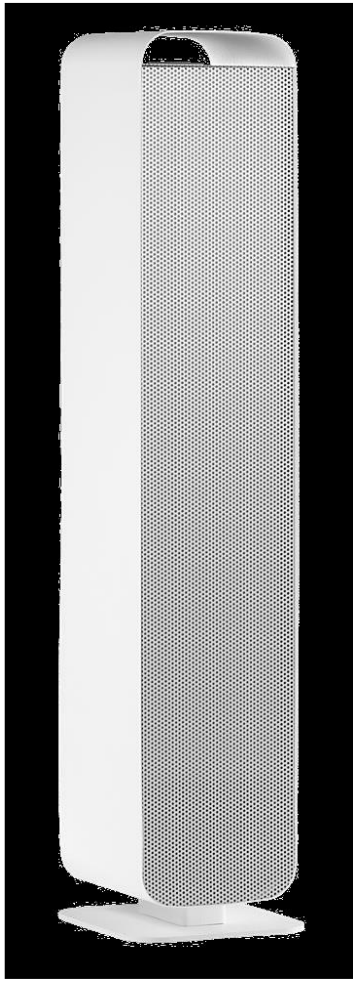


Location: Bad Toelz, Germany
Flow rate: 200 … 2000 $m^3 h^{-1}$
UV Power: 18 kW
Number of lamps: 144

Location: Manukau, New Zealand
Flow rate: 50.400 $m^3 h^{-1}$
UV power: min. ~ 320 kW
Number of lamps: ~ 2500

3. UV Disinfection

Indoor ambient air and exhaust gas treatment



Example: STAMBOLI air purifier

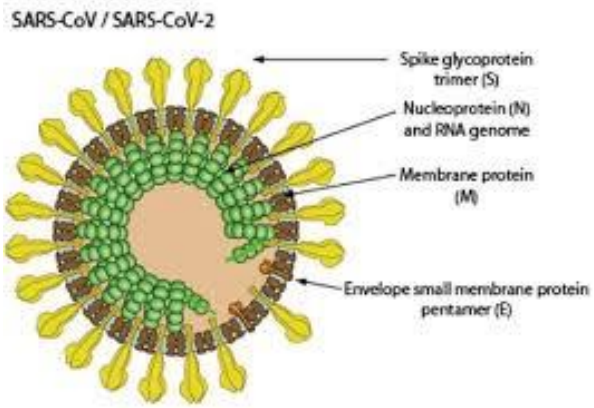
- Air flow: 160 $m^3\ h^{-1}$
- Light sources: Hg LP UV-C lamp (253.7 nm), ozone free
- Voltage: 220 - 240 V
- Input power: 72 W (output ~ 30 W UV-C)
- Lifetime of UV-C lamps: 9000 hours

Alternative approaches

- Photo-Fenton-reaction: $Fe^{2+} + H_2O_2 + hv \rightarrow Fe^{3+} + OH^- + OH^{\cdot}$
- UV-A/B LED + TiO_2 photocatalyst: $O_2^{-\cdot} + OH^{\cdot}$
- O_3 at alkaline surfaces: $Mg(OH)_2 + O_3 \rightarrow MgO + O_2 + H_2O_2$
- O_3 and humidity + UV-C lamp: $O_3 + H_2O + hv \rightarrow O_2 + H_2O_2$
- Atmospheric plasms: O_3
- Xe excimer lamp (172 nm): $3\ O_2$ cleavage $\rightarrow 2\ O_3$
  H_2O cleavage $\rightarrow OH^{\cdot} + H^{\cdot}$

3. UV Disinfection

Pr^{3+} for fighting the Covid-19 Pandemic



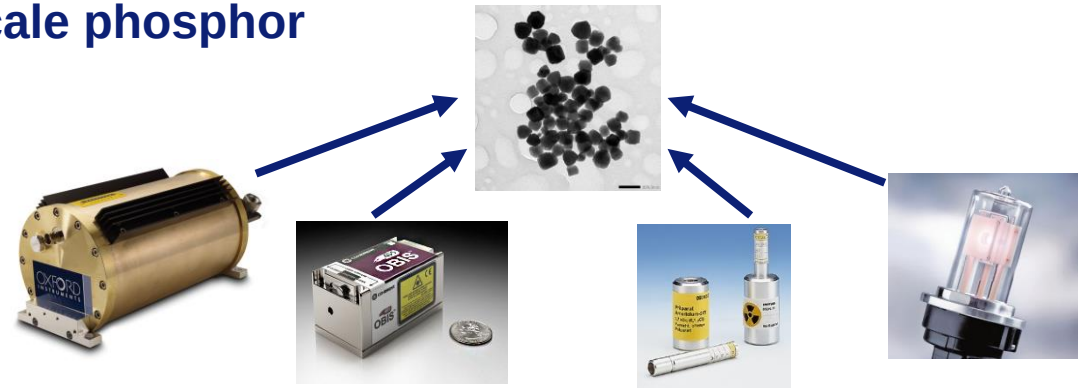
SARS-CoV-2 Virus Base Data

- RNA Virus!
- 80 – 140 nm (Lit.: Kaniyala Melanthota et al., 2020)
- Single strand RNA with positive polarity
- Four structural proteins (S, E, M, N)
- 30 kBases
- Photochemistry unknown yet

Goal: Inactivation of the virus by photochemical damage, e.g. by strand break

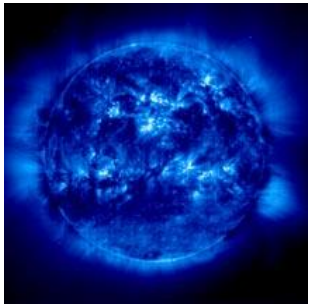
→ Far UV emitting microscale phosphor excited by

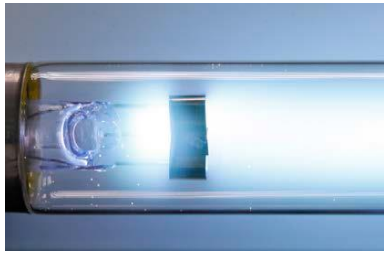
- X-rays
- Blue laser
- High energy particles
- VUV radiation

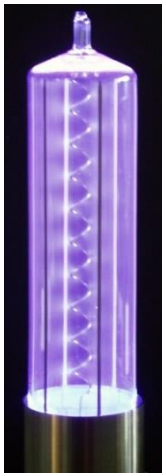


4. UV Radiation Sources

Sun	**> 300 nm**
Hg discharge lamps	
• low pressure	185, 254 nm
• amalgam	185, 254 nm
• medium pressure	200 – 400 nm
Xe/(Hg) discharge lamps	**230 – 800 nm**
D_2 discharge lamps	**110 – 400 nm**
Excimer laser	
• ArF*	193 nm
Excimer discharge lamps, e.g. Dielectric Barrier Discharge (DBD) lamps	
• XeCl*	308 nm
• XeBr*	282 nm
• KrCl*	222 nm
• Xe_2*	172 nm
• Xe_2* + UV phosphor(fluorescent DBD)	190 – 400 nm
(Al,Ga)N UV LEDs	**210 – 365 nm**
X-ray or cathode ray tube + UV phosphor	**190 – 400 nm, e.g. $Y_2SiO_5:Pr^3$**

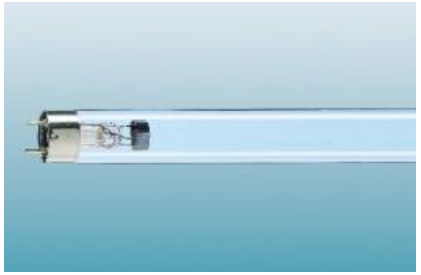
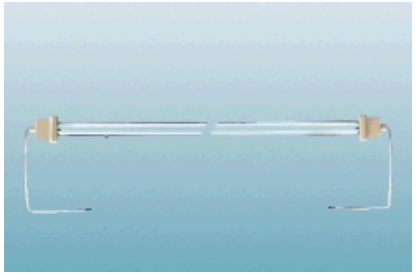






4. UV Radiation Sources

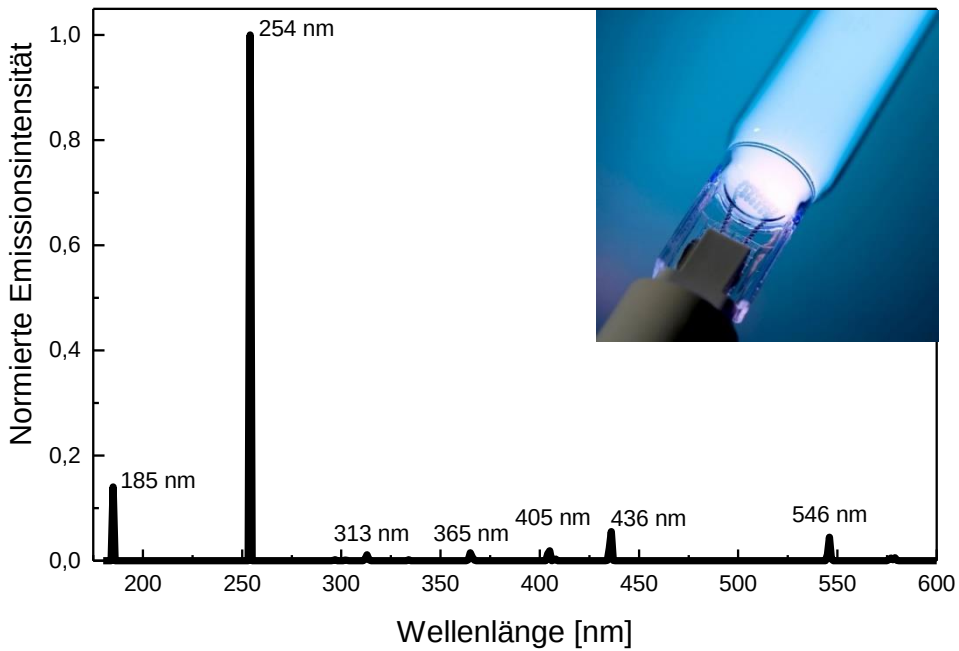
Hg discharge lamps: Overview

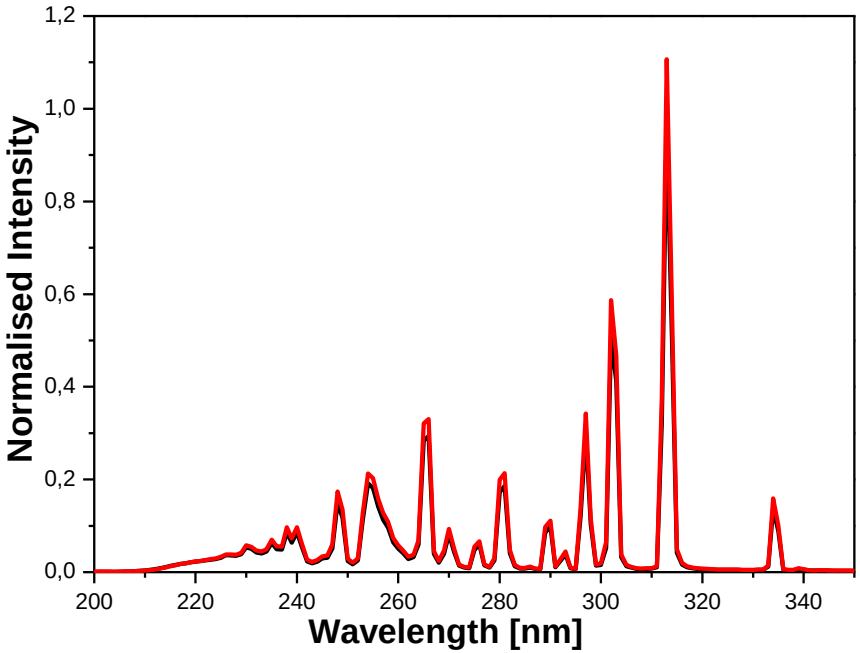
	Low pressure Hg	Amalgam	Medium pressure Hg
			
UV-C spectrum	254 nm	254 nm	200 - 280 nm
Typical lamp power	4 ... 100 W	100 ... 300 W	1 ... 17 kW
Lamp efficiency	< 40%	30 ... 35%	10 ... 15%
GAC factor	85%	85%	80%
UV-C power per length	0.2 W / cm	0.7 W / cm	15 W / cm
Wall temperature	40 °C	100 °C	600 - 800 °C

⇒ **Selection depends on application and operation costs**

4. UV Radiation Sources

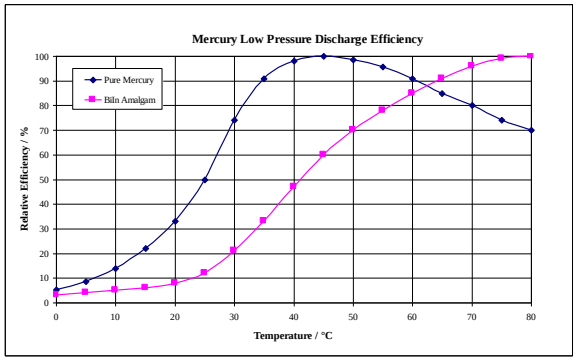
Hg discharge lamps: Low-pressure/amalgam vs. medium pressure





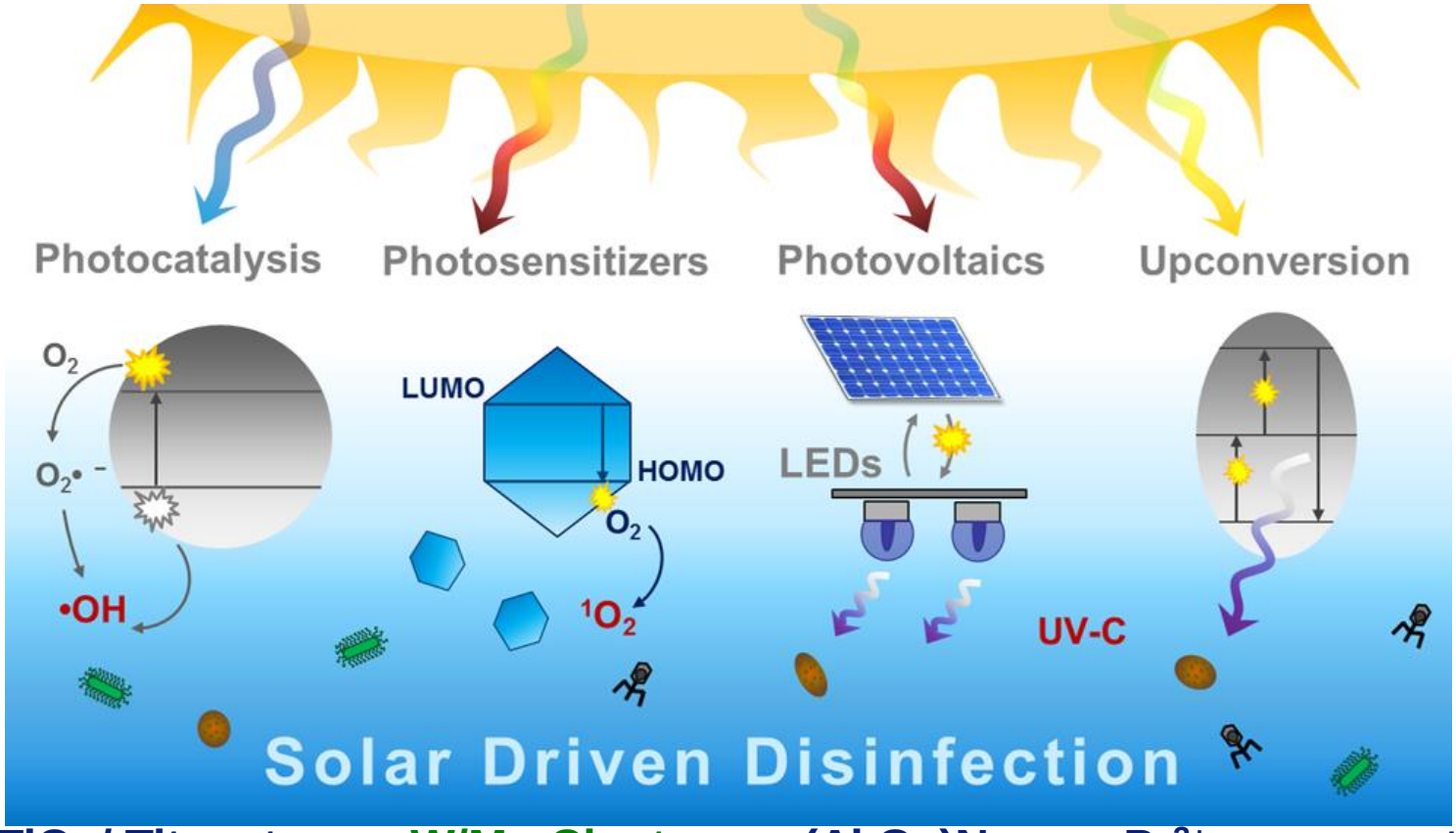
Main application issues

- Hg content
- Spectrum cannot be modulated
- Limitations on design, dimming, and switching
- Cooling reduces efficiency
- Power density ⇔ Wall plug efficiency



5. Recent Developments

Use of solar radiation / combined with artificial radiation sources for air, water, and surface disinfection or purification

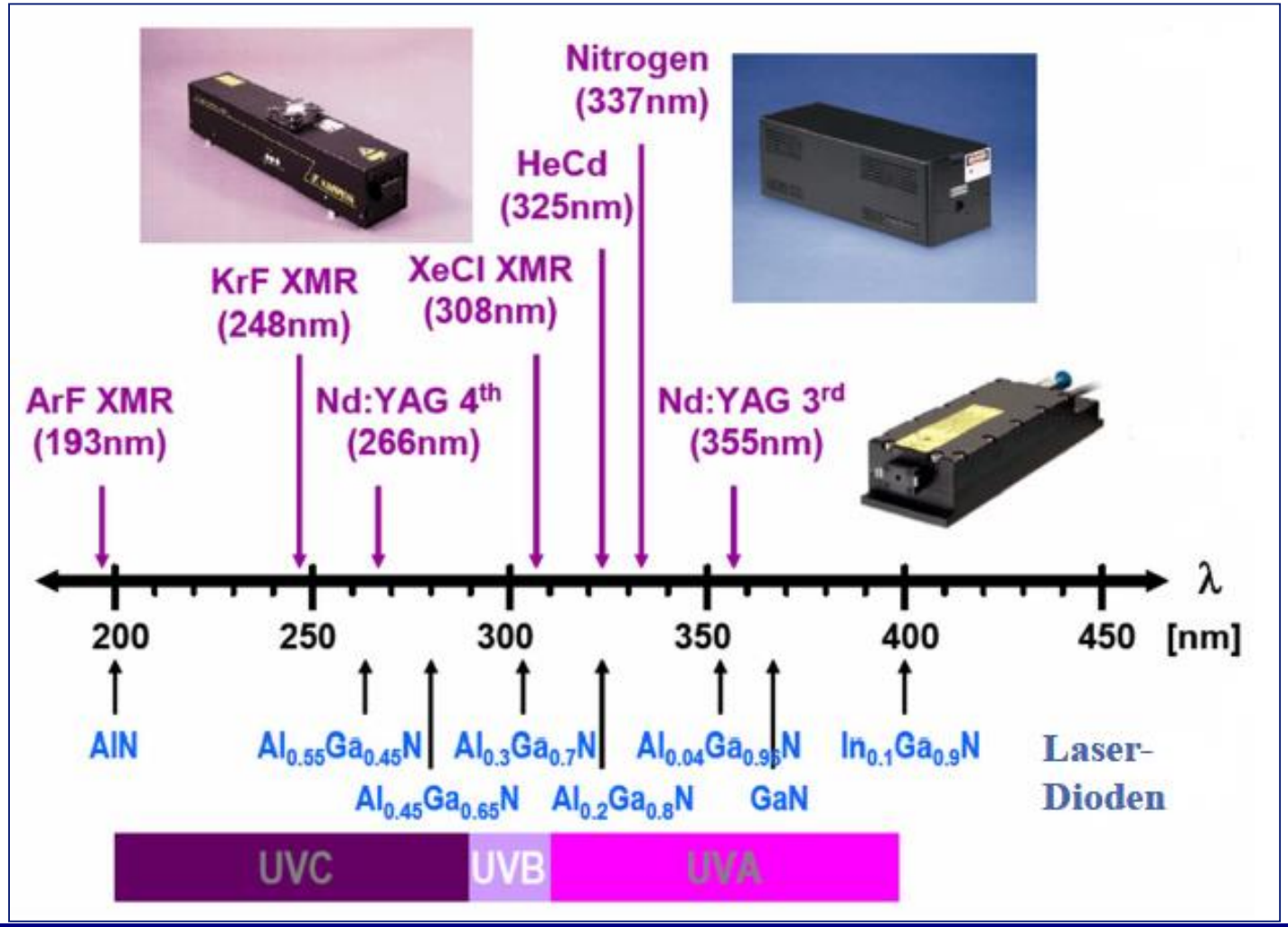


TiO_2 / Titanates **W/Mo Cluster** **(Al,Ga)N** **Pr^{3+} up-converter**

Lit.: PD properties of tungsten iodide clusters, T. Jüstel, H.-J. Meyer et. al, RSC Advances 10 (2020) 22257

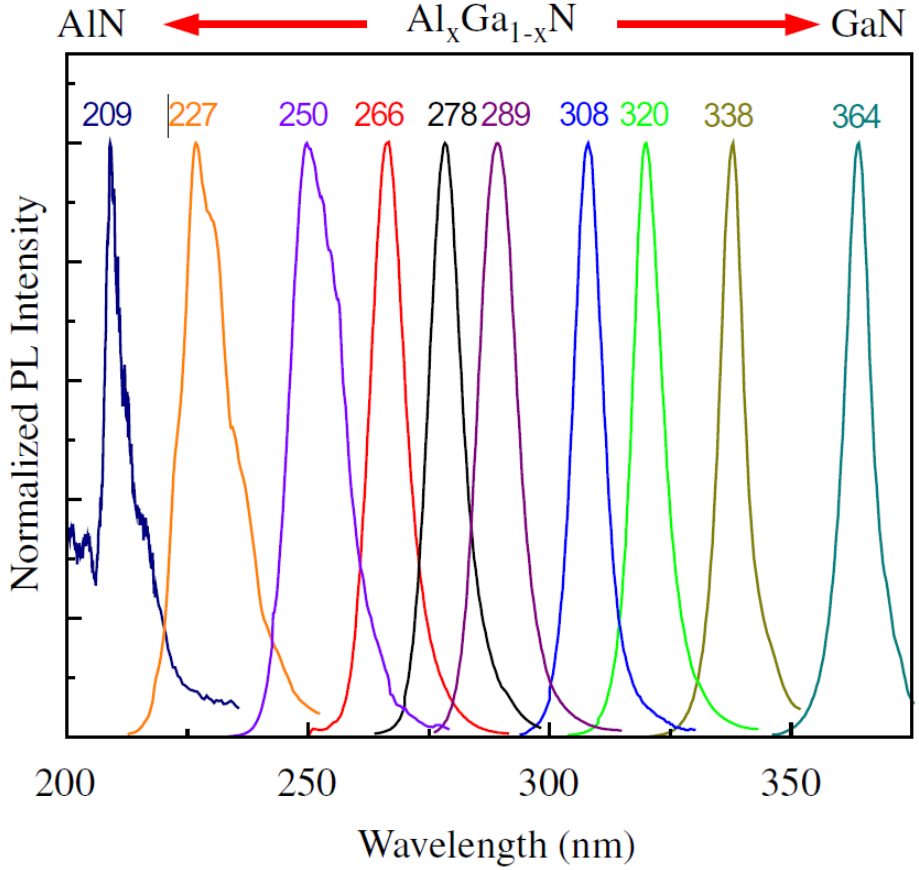
5. Recent Developments

UV Emitting LEDs and Laser Diodes



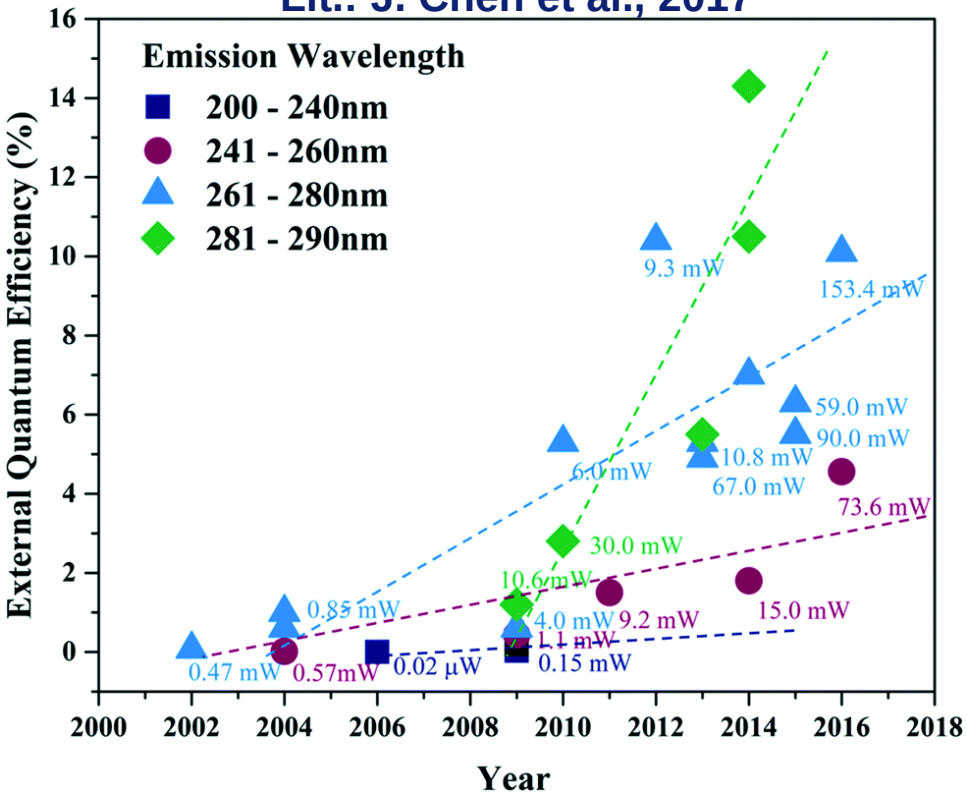
5. Recent Developments

UV Emitting LEDs - (Al,Ga)N Semiconductors



UV spectra of (Al,Ga)N semiconductors

Lit.: J. Chen et al., 2017



Development of external quantum efficiency and UV power of (Al,Ga)N LEDs from 2000 to 2018

5. Recent Developments

UV Emitting LEDs – Status Quo 2020: WPE ~ 10%, 265 nm

External quantum efficiency

$$\eta_{\mathrm{EQE}} = \eta_{\mathrm{inj}} * \eta_{\mathrm{rad}} * \eta_{\mathrm{exit}} = \eta_{\mathrm{IQE}} * \eta_{\mathrm{exit}}$$

„Wall-plug efficiency (WPE)“:

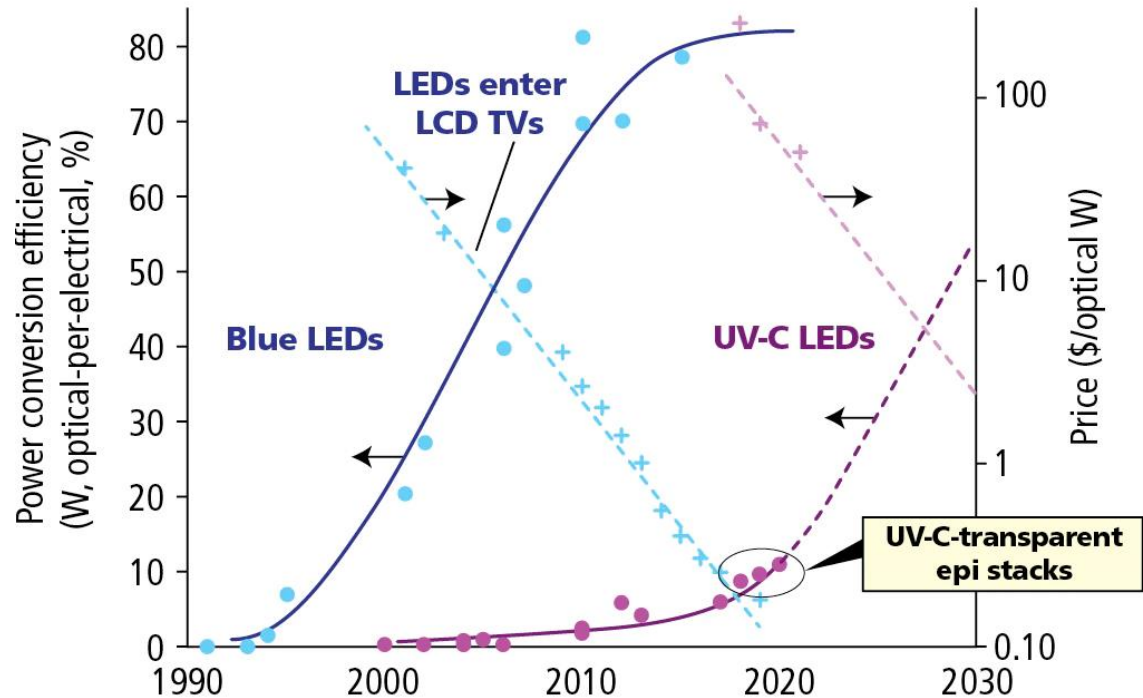
$$WPE = \frac{P_{out}}{I_{op} * V} = \eta_{EQE} \frac{\hbar\omega}{e * V} = \eta_{EQE} * \eta_{elect}$$

Optical power:

$$P_{\mathrm{out}} = \eta_{\mathrm{EQE}} \frac{\hbar\omega}{e} I_{\mathrm{op}} = I_{\mathrm{op}} * V * \mathrm{WPE}$$

Maximum electrical power:

$$P_{\mathrm{el,max}} = I_{\mathrm{op}} * V = \frac{T_{\mathrm{jmax}} - T_{\mathrm{h\alpha}}}{R_{\mathrm{th}} * (1 - WPE)}$$



Current development goals

- Internal quantum efficiency ↑
- Light outcoupling ↑
- Power density ↑
- Life time ↑

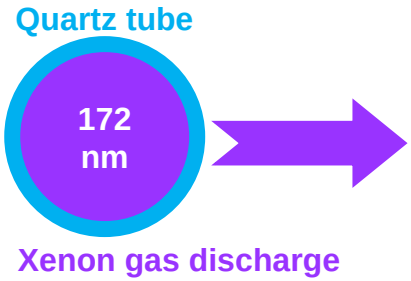
Lit.:

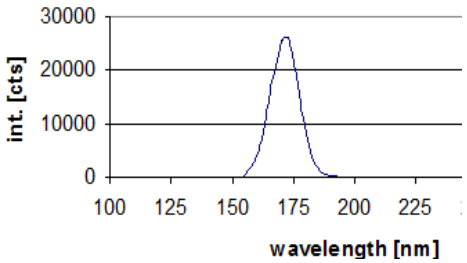
a) M. Kneissl et al., Nature Photonics 13 (2019) 233
b) LED Magazine, July 24th, 2020

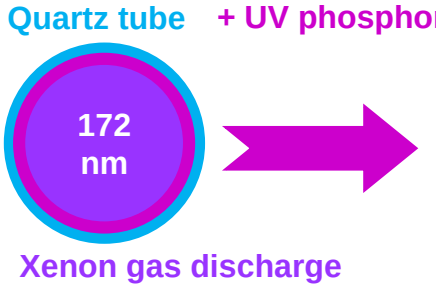
5. Recent Developments

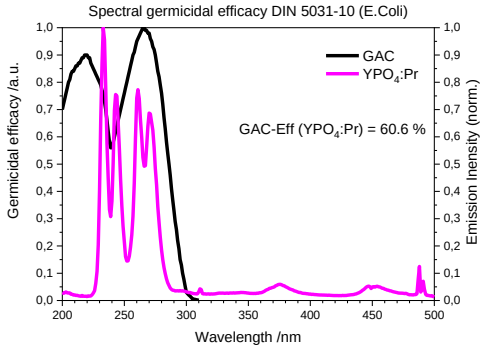
Properties of the ideal UV radiation source

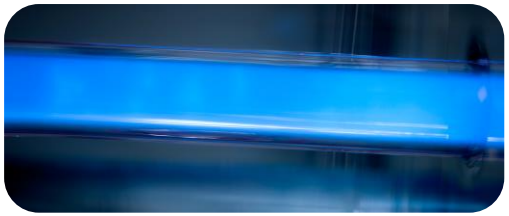
- Highly efficient: η(UV) > 20% (minimal cost of operation)
- UV-C radiation: UV disinfection: λ ~ 260 nm (max. GAC)
  H_2O_2 activation: 200 nm < λ < 300 nm
  Ozone formation: λ < 240 nm
- Inexpensive
- High power (fewer lamps, minimal initial investment)
- Long life time (minimal operation and maintanance costs)
- Free of mercury (UNEP Minamata Convention on Mercury 2017) → Xenon







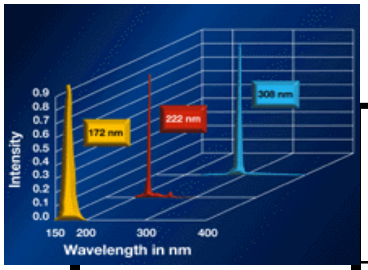


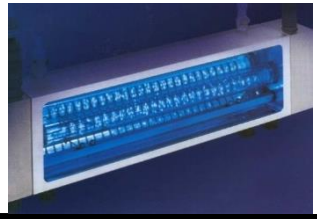


Lit.:
T. Jüstel, J. Dirscherl, H. Nikol, D.U. Wiechert, Device for Disinfection of Water with UV-C Discharge
T. Jüstel, H. Nikol, J. Dirscherl, W. Busselt, EP00201427, US 6398970 B1
T. Jüstel, H. von Busch, G. Heussler, W. Mayr, US 7298077 B2
G.F. Gärtner, G. Greuel, T. Jüstel, W. Schiene, US 7687997 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
T. Jüstel. G. Greuel, J.M. Kuc, US 9334442 B2
T. Jüstel et al., J. Lumin. 200 (2018) 1

5. Recent Developments

Excimer forming gases and gas blends

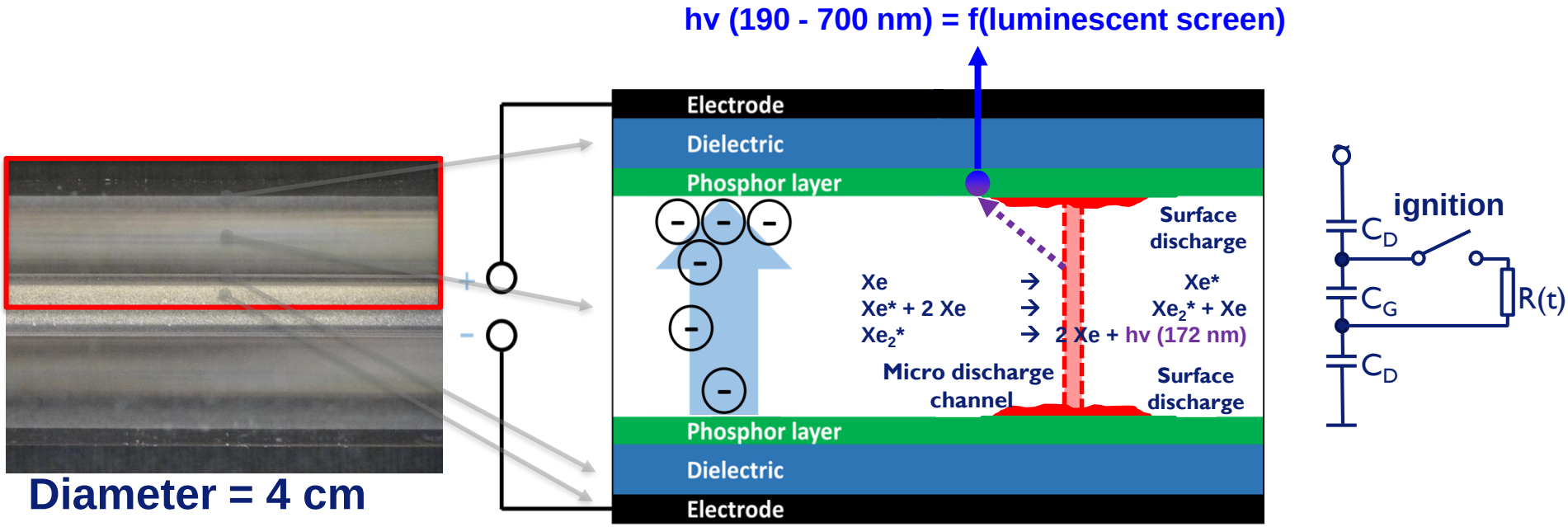




	F	Cl	Br	I	Pure noble gases
Pure halides	158 nm	258 nm	293 nm	342 nm	-
Ar	> 10% 193 nm	ca. 5% 175 nm	< 0.1% 161 nm	-	Ar^*_2 ~10% 126 nm
Kr	> 10% 248 nm	18% 222 nm	ca. 5% 207 nm	< 0.1% 185 nm	Kr^*_2 ~15% 146 nm
Xe	> 10% 351 nm	14% 308 nm	15% 282 nm	ca. 5% 253 nm	Xe^*_2 30% 172 nm

5. Recent Developments

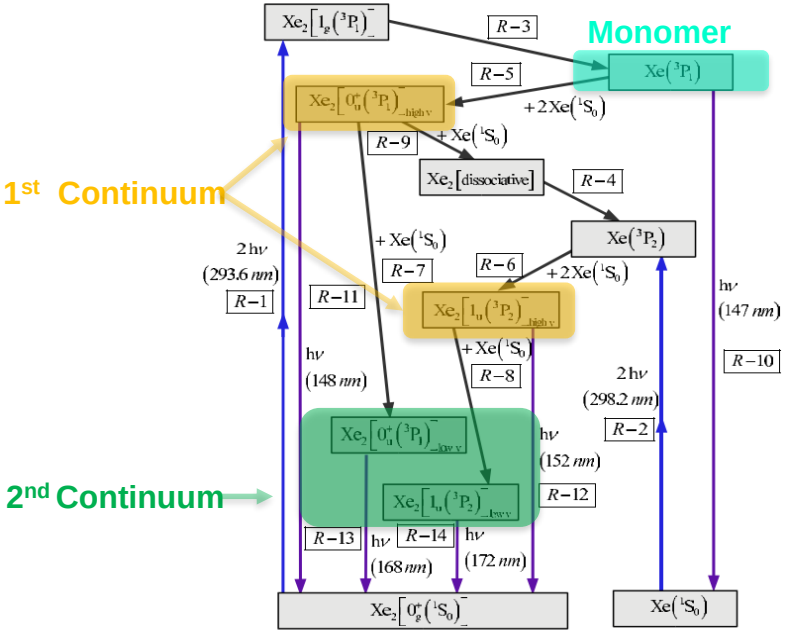
Lamp sketch and working principle



Diameter = 4 cm
Length = 12 cm
Wall load ~ 0.1 – 1.0 W cm^{-2}
p(Xe) = 300 mbar
P = 10 - 100 W
U = 3 - 5 kV
f = 10 - 50 kHz

5. Recent Developments

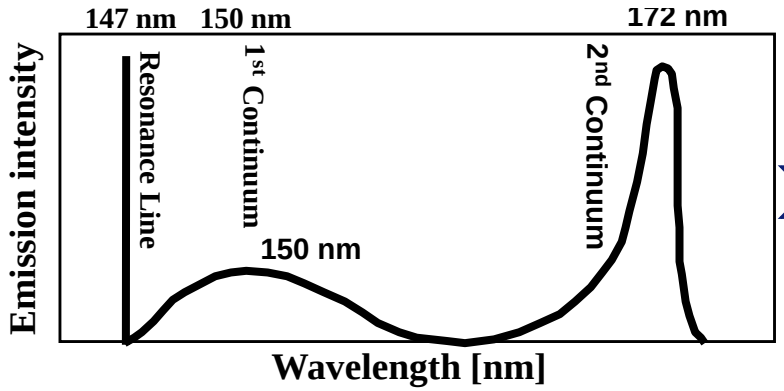
Xe discharge spectrum

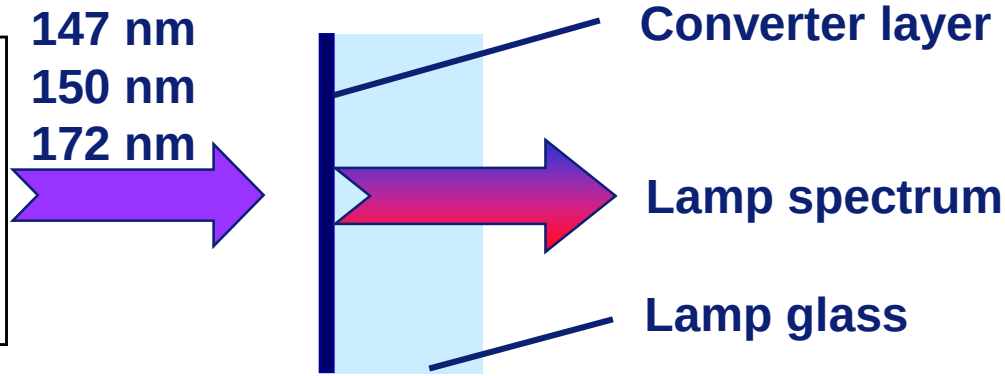


Excited monomeric Xe species emits at 147 nm (8.44 eV)
Xe resonance line

1st Emission continuum
148 nm (8.38 eV)
$Xe_2[0^+_U(^3P_1)_{high\ n}] \rightarrow Xe_2[0^+_g(^1S_0)]$
152 nm (8.16 eV)
$Xe_2[1_U(^3P_2)_{high\ n}] \rightarrow Xe_2[0^+_g(^1S_0)]$

2nd Emission continuum
186 nm (7.38 eV)
$Xe_2[0^+_U(^3P_1)_{low\ n}] \rightarrow Xe_2[0^+_g(^1S_0)]$
172 nm (7.21 eV)
$Xe_2[1_U(^3P_2)_{low\ n}] \rightarrow Xe_2[0^+_g(^1S_0)]$





5. Recent Developments

UV Phosphors – Hosts and Activators

VUV	UV-C	UV-B	UV-A

100 nm — 200 nm — 280 nm — 320 nm — 400 nm

Host: E_g > 6.0 eV

Fluorides Phosphates Borates Silicate Aluminates

Activator ion: Good redox stability

Nd^{3+}

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

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

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

5. Recent Developments

UV Phosphors for Xe excimer discharge lamps

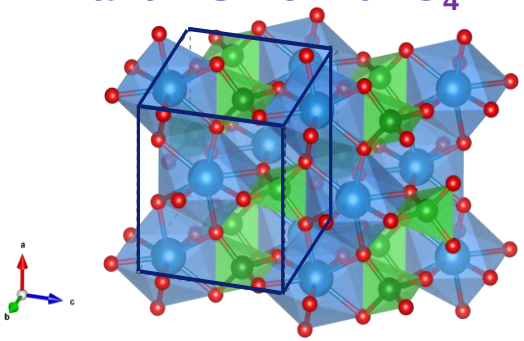
1. **Water and oxygen cleavage**
   - $(Y,Lu)PO_4$:Nd,Pr — 193 nm

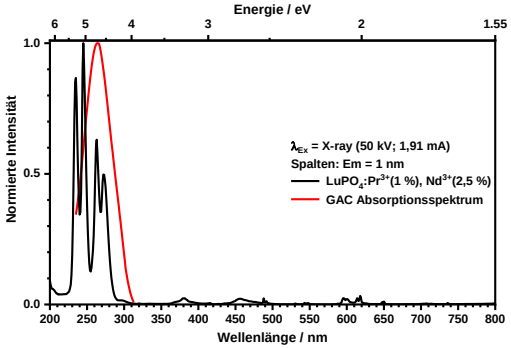
2. **Mineralisation of µ-pollutants**
   - $CaSO_4$:Pr — 218 nm
   - $LaPO_4$:Pr — 225 nm
   - *$(Y,Lu)PO_4$:Pr* — 235 nm

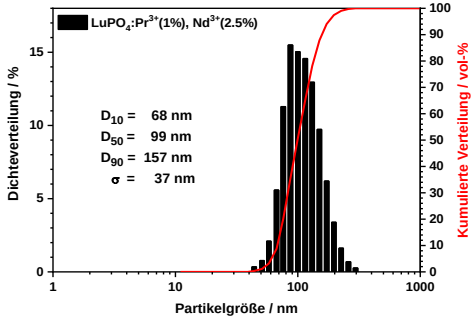
3. **Disinfection of air and surfaces**
   - $CaLi_2SiO_4$:Pr — 252 nm
   - YBO_3:Pr — 265 nm
   - Y_2SiO_5:Pr — 270 nm
   - $Y_2Si_2O_7$:Pr — 275 nm

4. **Photocatalysis**
   - $Lu_3Ga_2Al_3O_{12}$:Pr — 300 nm
   - $Lu_3Al_5O_{12}$:Pr — 310 nm
   - $Y_3Al_5O_{12}$:Pr — 320 nm

Structure, emission, and PSD of $LuPO_4$:Pr

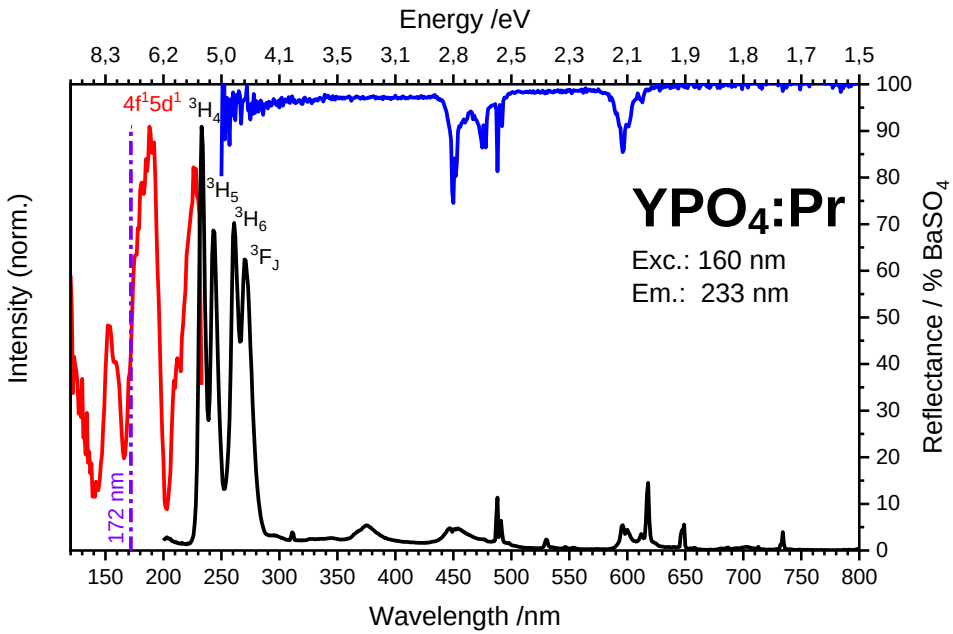


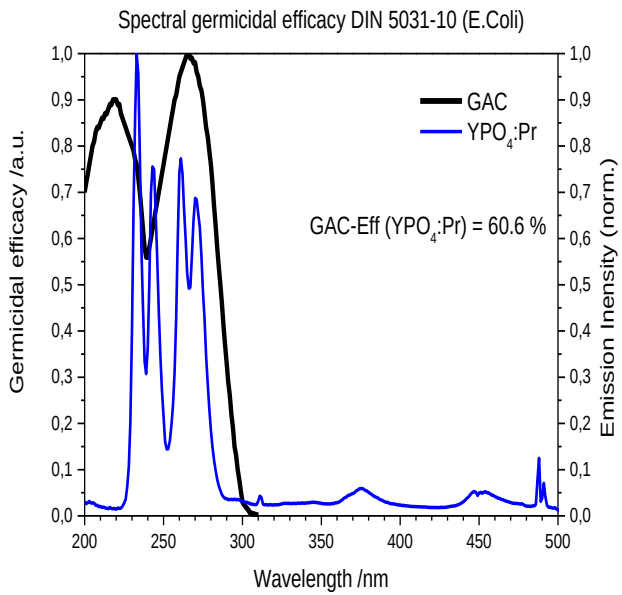




5. Recent Developments

UV Phosphors for Xe excimer discharge lamps: ortho-phosphates





$\lambda_{max}(YPO_4:Pr) = 233$ nm

QE ~ 90%

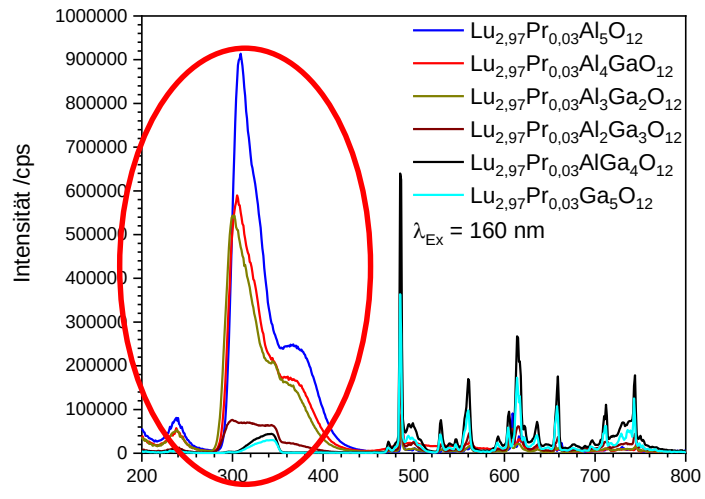
GAC: Efficacy of inactivation of E. coli according to DIN 5031-10

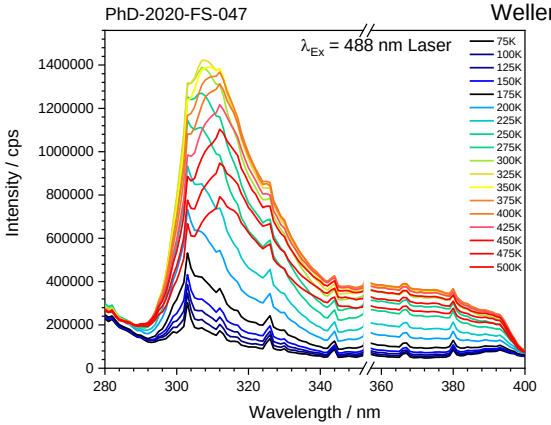
$$E_{GAC}(Phosphor) = \frac{\int (Em_{Phosphor} \times GAC)}{\int Em_{Phosphor}}$$

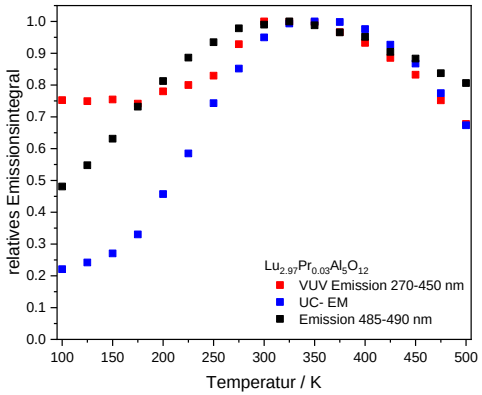
5. Recent Developments

Emission and GAC overlap of selected UV-C emitters, Pr^{3+} doped garnets

Material	$\lambda_{max.}$(Em.) [nm]	GAC-Efficacy [%]
$(Y,Lu)PO_4$:Nd,Pr	193	57
$CaSO_4$:Pr	218	68
$LaPO_4$:Pr	225	69
YPO_4:Pr	233	61
$LuPO_4$:Pr	234	61
$YAlO_3$:Pr	245	41
$La_2Si_2O_7$:Pr	247	33
$CaLi_2SiO_4$:Pr	253	44
$CaMgSi_2O_6$:Pr	260	n. a.
YBO_3:Pr	265	46
$Lu_2Si_2O_7$:Pr	266	48
Y_2SiO_5:Pr	270	22
$BaZrSi_3O_9$	275	48
Lu_2SiO_5:Pr	277	16
$Lu_3Ga_2Al_3O_{12}$:Pr	*300*	*5*
$Lu_3Al_5O_{12}$:Pr	*310*	*2*
$Lu_2YAl_5O_{12}$:Pr	312	~ 0
$LuY_2Al_5O_{12}$:Pr	316	~ 0
$Y_3Al_5O_{12}$:Pr	320	~ 0







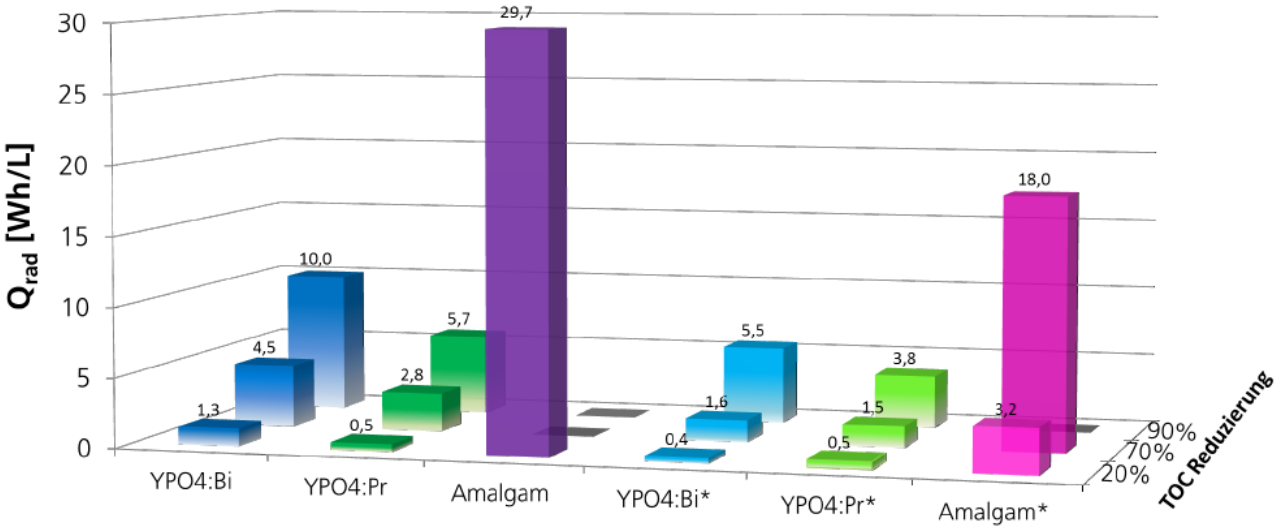
Lit.: F. Schröder, T. Jüstel, J. Luminescence (2021) under review

5. Recent Developments

YPO_4:Pr coated Xe excimer discharge lamps compared to YPO_4:Bi coated ones and to amalgam low-pressure discharge lamps

Source: N. Braun, GVB

Goal: Degradation of sulfamethoxazole (antibiotic)



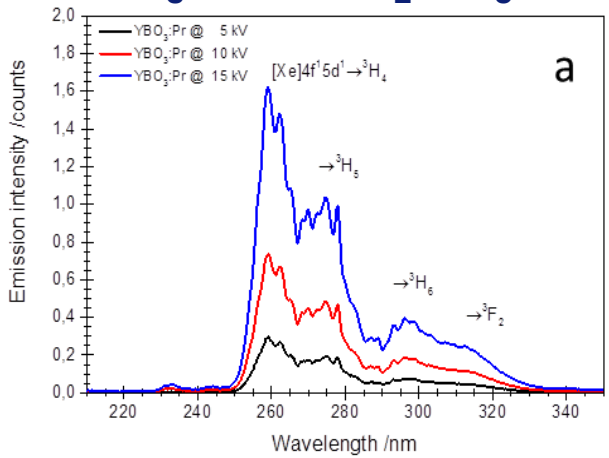
Source: A. Nietzsch, DLR

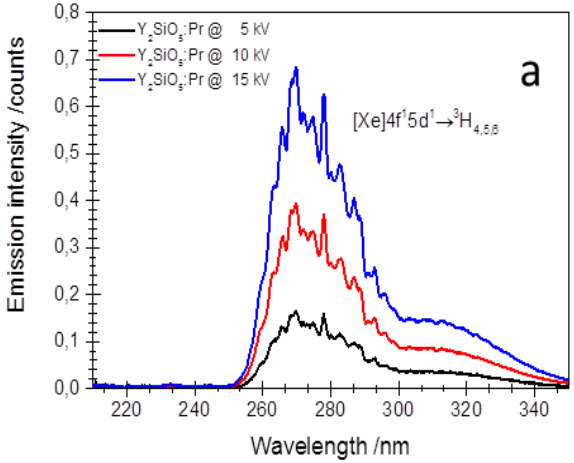
Photolytical degradation by use of a YPO_4:Pr converted Xe excimer lamp allows a reduction of the required dose by 95% compared to an amalgam lamp

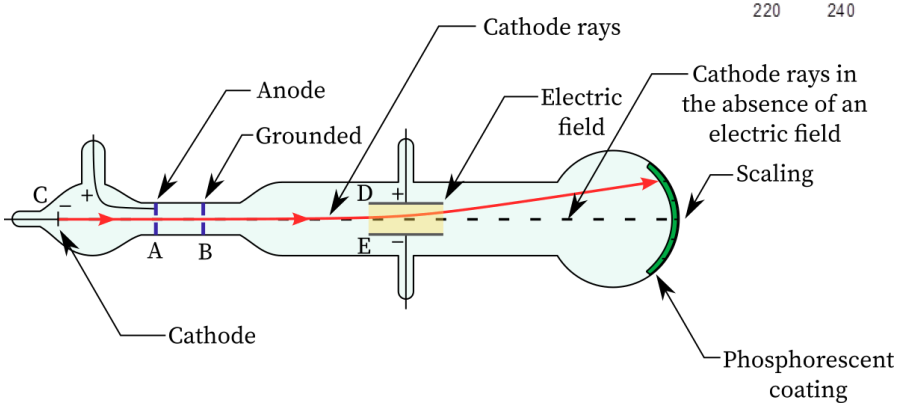
5. Recent Developments

Cathode ray tube with UV-C converter

YBO_3:Pr and Y_2SiO_5:Pr^{3+} spectra upon e^- excitation







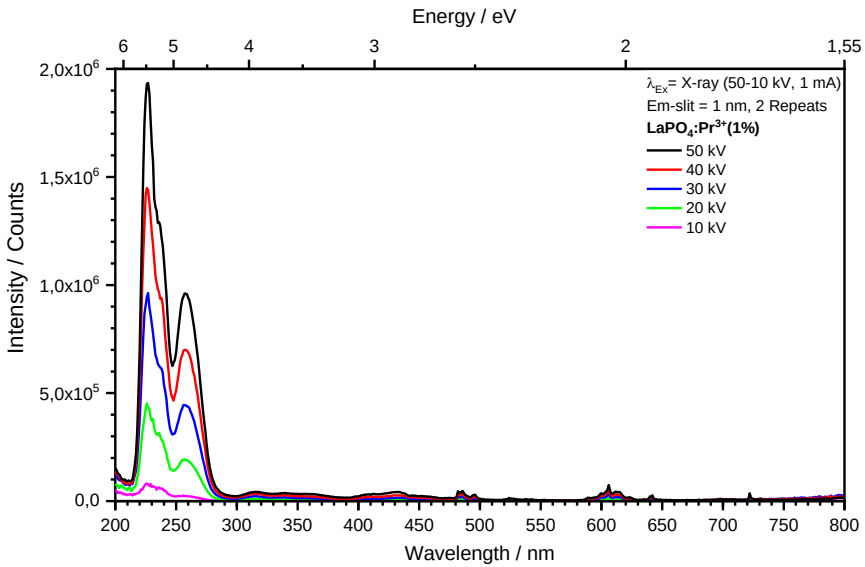
Lit.: J. Silver, M. Broxtermann, T. Jüstel et al., ECS J. SSST 6 (2017) R47

Accelerated electrons hit a phosphor layer to yield cathodoluminescence: The principle is similar to that of a cathode ray tube for TV sets/monitors

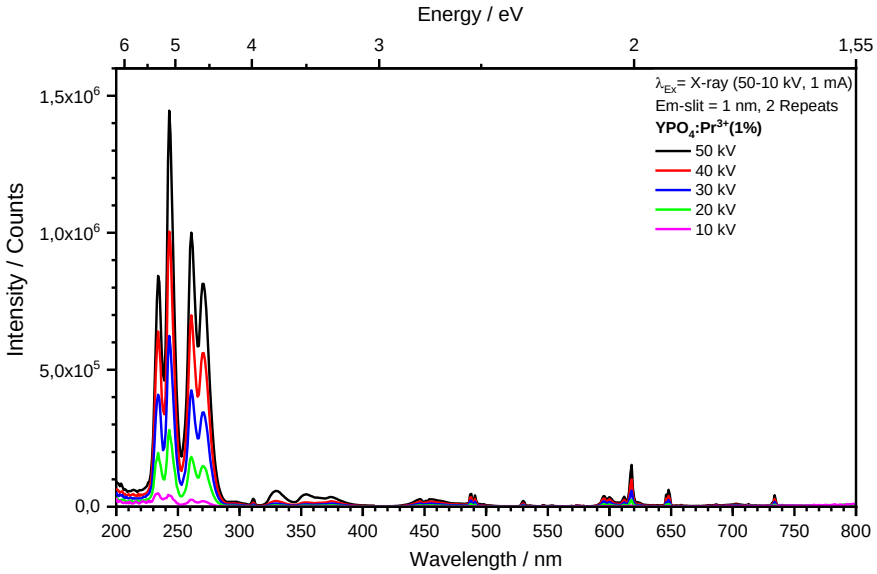
5. Recent Developments

X-ray tube with UV-C converter $LaPO_4$:Pr and YPO_4:Pr

$LaPO_4$:Pr 10 – 50 keV excitation



YPO_4:Pr 10 – 50 keV excitation



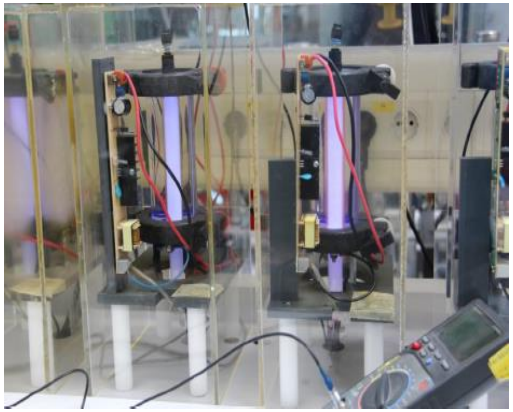
Source: Jan Kappelhoff

Almost solely UV-C emitting scintillators….

Many spin-offs: Cancer & inflammation treatment by $LnPO_4$:Pr,Nd (Ln = Y, La, Lu)

6. Summary

Xe_2^* Excimer discharge lamps



- Discharge spectrum: 147, 150, 172 nm
- Fluorescence: 190 – 380 nm
- Hg-free, fast switching, large form factor
- Problems: Driver, lifetime, price, market access
- Gas discharge and converter determines lamp spectrum

Goal: Hg free UV radiation source with spectrum adapted to application

Lamps for special applications: Pr^{3+} phosphors

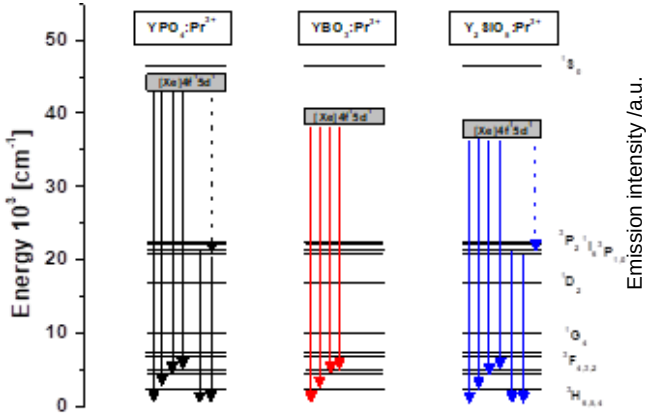
- 222 nm Air disinfection / Virus inactivation (eye and skin safe?)
- 235 nm Mineralisation of organic µ-pollutants
- 241 nm Disinfection & mineralisation of organic µ-pollutants
- 310 nm Photochemistry/-medicine

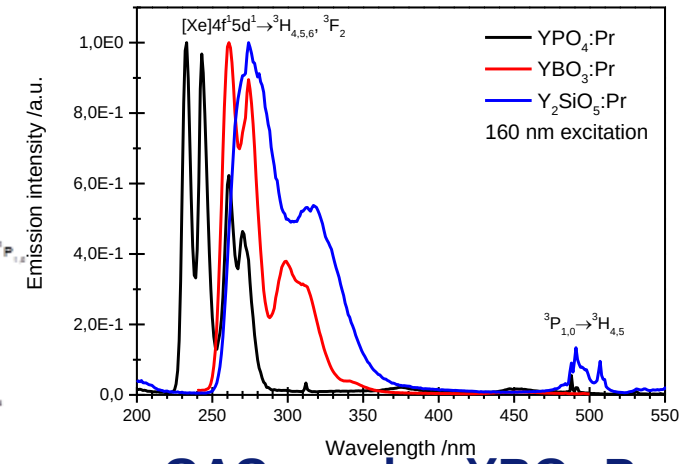
6. Summary

Pr^{3+} Phosphors for fluorescent Xe excimer discharge lamps

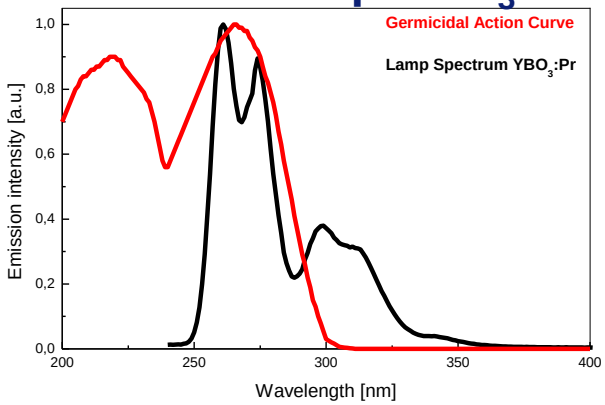
VUV → UV converter: Emission between 190 and 380 nm

- $(Y,Lu)PO_4$:Nd,Pr
- $CaSO_4$:Pr
- YPO_4:Pr
- $LaPO_4$:Pr
- $(Y,Lu)PO_4$:Pr
- YBO_3:Pr
- Y_2SiO_5:Pr
- $Lu_3Al_5O_{12}$:Pr





GAC overlap YBO_3:Pr

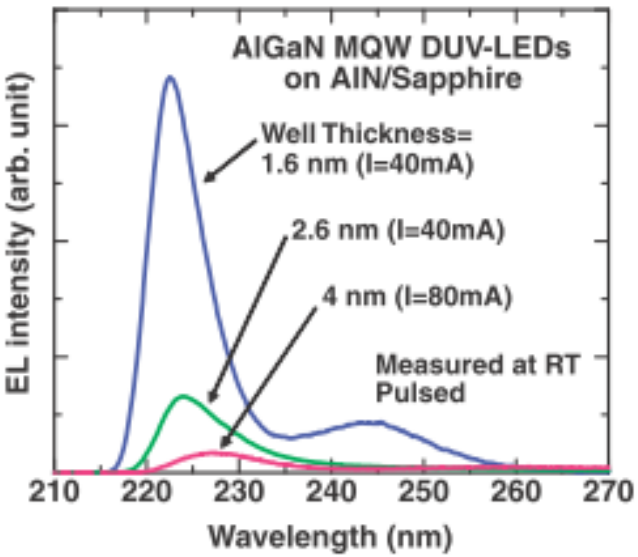


Remaining challenges

- Operational lifetime of lamps < 10000 h
- Phosphor damaged by VUV and exc. Xe species
- Coating by α-Al_2O_3 (sapphire)
- Industrialisation

6. Summary

UV Emitting LEDs / Laser Diodes



- Theoretical limit: 205 nm
  Experimental limit ~ 220 nm
  Practical limit ~ 250 nm
- Thus far UV-LED are challenging!
- Heat dissipation determines yield and life time
- Refractive index increases with increasing energy

Problems to be solved

- UV flux: EL quantum yield, thermal quenching, saturation
- Energy efficiency: light outcoupling, reabsorption
- Spectral consistency: encapsulation, stability of semiconductor
- Mass production: cost & reliability

7. Outlook

(Al,Ga)N / (In,Ga)N LEDs or laser diodes: UV up-conversion

Pr3+ doped Li2SrSiO4: an efficient visible-ultraviolet C up-conversion phosphor

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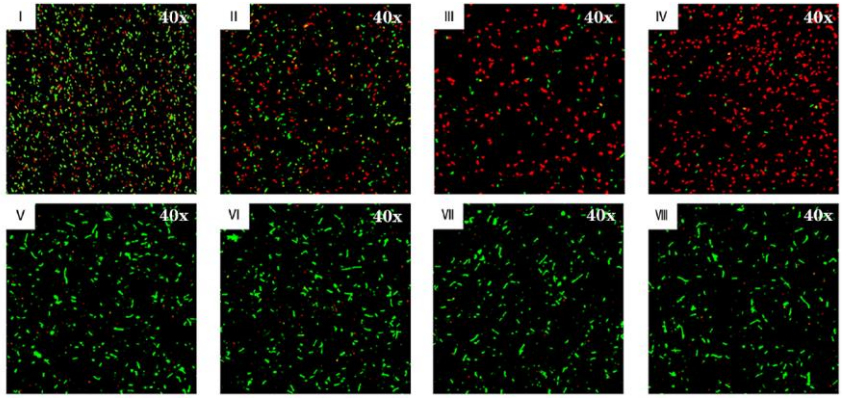
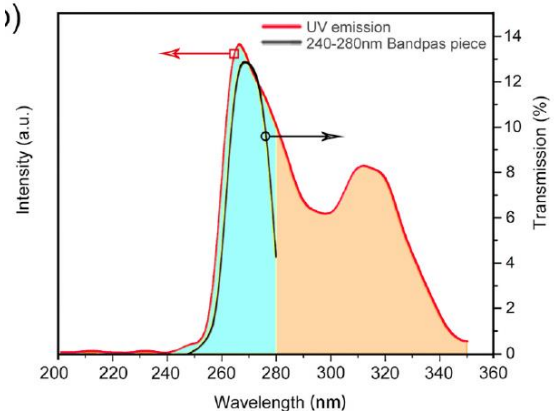
ABSTRACT

Up-conversion (UC) phosphor converting visible light into ultraviolet C light (UVC) has potential application in many fields. However, the lower energy conversion efficiency limits its practical application. Here, we proven that the synthesized $Li_2SrSiO_4:Pr^{3+}$ phosphor is an efficient UV phosphor with the emission power of 0.25 mW/cm^2 (0.1 mW/cm^2 for UVC band), which can effectively inactivate bacteria within 10 min. Based on the different propagation properties of visible light and UVC in ordinary glass, we proposed a scheme to coat this phosphor inside the slide and cover glass of a confocal microscope to realize the real-time observation of the response of microorganisms under UVC irradiation, thereby providing a new effective method for microbial research.

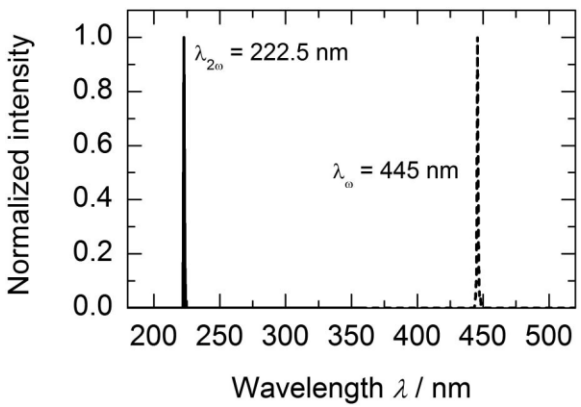


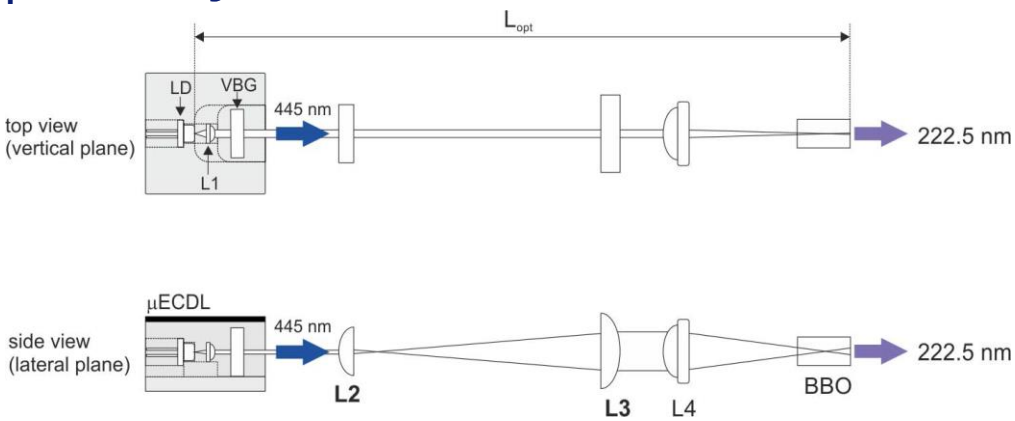


7. Outlook

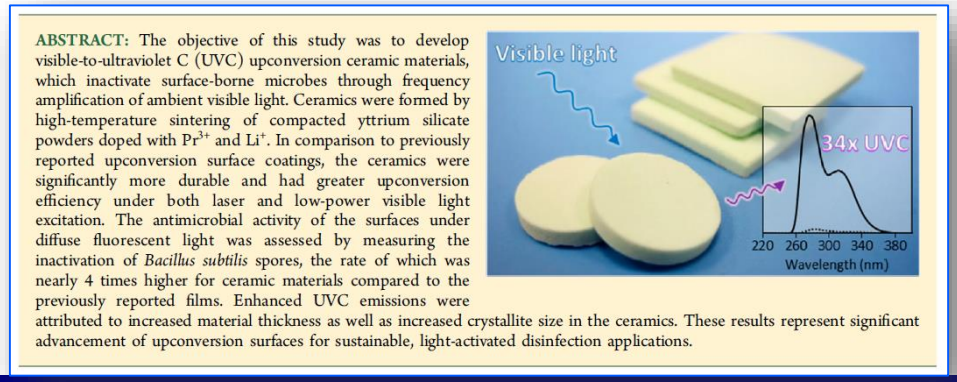
(Al,Ga)N / (In,Ga)N LEDs or laser diodes: UV up-conversion

1. 445 nm laser diode + ß-BaB_2O_4 NLO crystal





2. 445 nm laser diode + up-converter Y_2SiO_5:Pr,Li ceramic

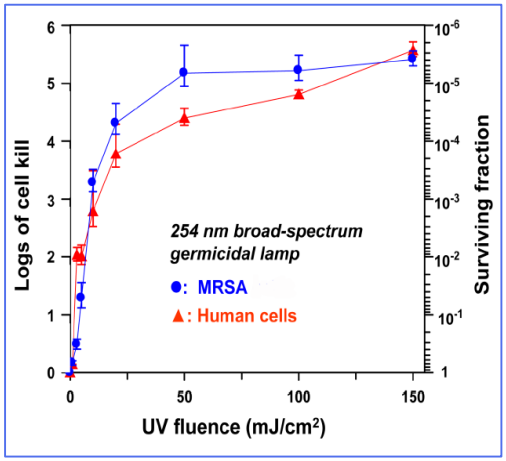


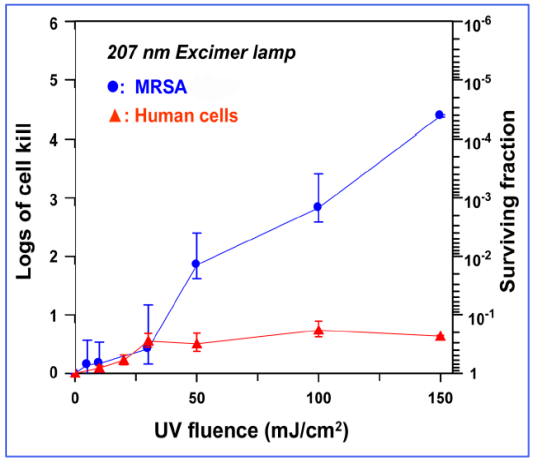
ABSTRACT: The objective of this study was to develop visible-to-ultraviolet C (UVC) upconversion ceramic materials, which inactivate surface-borne microbes through frequency amplification of ambient visible light. Ceramics were formed by high-temperature sintering of compacted yttrium silicate powders doped with Pr^{3+} and Li^{+}. In comparison to previously reported upconversion surface coatings, the ceramics were significantly more durable and had greater upconversion efficiency under both laser and low-power visible light excitation. The antimicrobial activity of the surfaces under diffuse fluorescent light was assessed by measuring the inactivation of *Bacillus subtilis* spores, the rate of which was nearly 4 times higher for ceramic materials compared to the previously reported films. Enhanced UVC emissions were attributed to increased material thickness as well as increased crystallite size in the ceramics. These results represent significant advancement of upconversion surfaces for sustainable, light-activated disinfection applications.

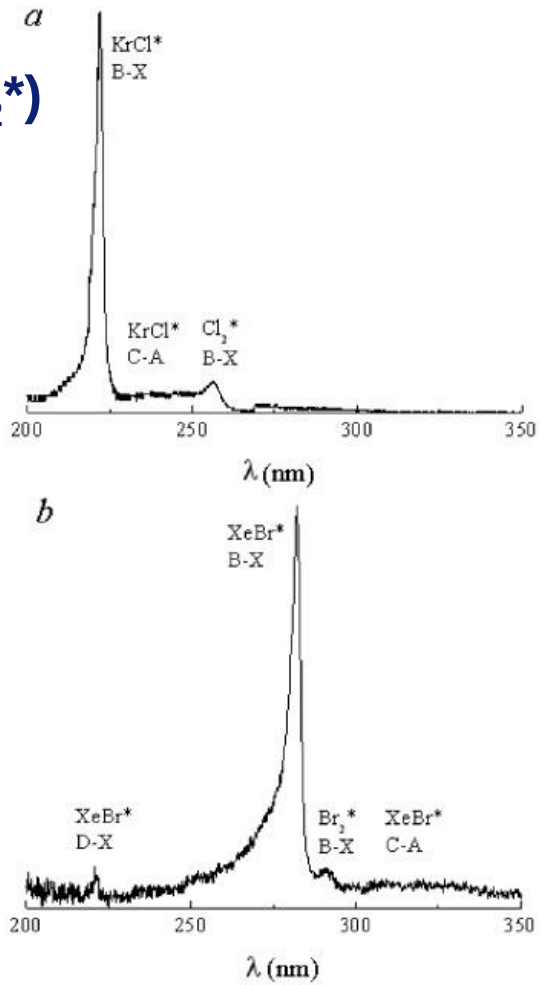
7. Outlook

KrCl*-excimer emitter: Skin and eye-proof radiation?

- Primary emission: 222 nm (KrCl*) + 258 nm (Cl_2*)
- Bandpass filter 200 – 230 nm required
- Problems?: Driver, life time, cost, safety







Lit.: D.J. Brenner et al., Radiat. Res. 187 (2017) 483

Ushio Homepage: Care222 UV disinfection solutions

8. Literature and Internet Links

Literature

- M. Broxtermann, T. Jüstel, Photochemically Induced Deposition of Protective Alumina Coatings onto UV Emitting Phosphors for Xe Excimer Discharge Lamps, Mat. Res. Bull. 80 (2016) 249
- J. Chen, S. Loeb, J-H. Kim, LED Revolution: Fundamentals and Prospects for UV Disinfection Applications, Envir. Sci.: Water Res. Technol. 3 (2017) 188
- M. Laube, T. Jüstel, On the Photo- and Cathodoluminescence of LaB_3O_6:Gd,Bi, $Y_3Al_5O_{12}$:Pr, $Y_3Al_5O_{12}$:Gd, $Lu_3Al_5O_{12}$:Pr, and $Lu_3Al_5O_{12}$:Gd, ECS J. SSST 7 (2018) R206
- M. Laube, T. Jüstel, Novel UV-A and -B Emitting Device for Medical Treatment, Photo-chemistry, and Tanning Purposes, ECS J. SSST 9 (2020) 065012
- Z. Yin, P.Yuan, Z. Zhu, T. Li, Y. Yang, Pr^{3+} doped Li_2SrSiO_4: an efficient visible-ultraviolet C up-conversion phosphor, Ceramics International 2020

Internet Links

- Homepage T. Jüstel — www.fh-muenster.de/juestel
- EnviroChemie — www.envirochemie.com/de/home
- JW Holding — www.jw-holding.de
- Nichia — www.nichia.co.jp/about_nichia/index.html
- Osram Opto — www.osram.de/
- Robert Koch Institute — www.rki.de
- Ushio — www.ushio.com
- Signify — www.signify.com
- Xylem Water Solutions — www.xylem.com

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