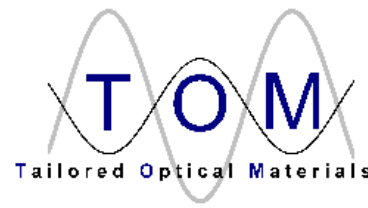




FH MÜNSTER
University of Applied Sciences



Anorganische Konvertermaterialien zur Erzeugung von 200-240 nm Strahlung

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Heike Kätker & Jan-Niklas Keil

27. DAfP-Tagung:
Licht in der Medizin, Biologie und Technik

Quedlinburg, 07. Juli 2023



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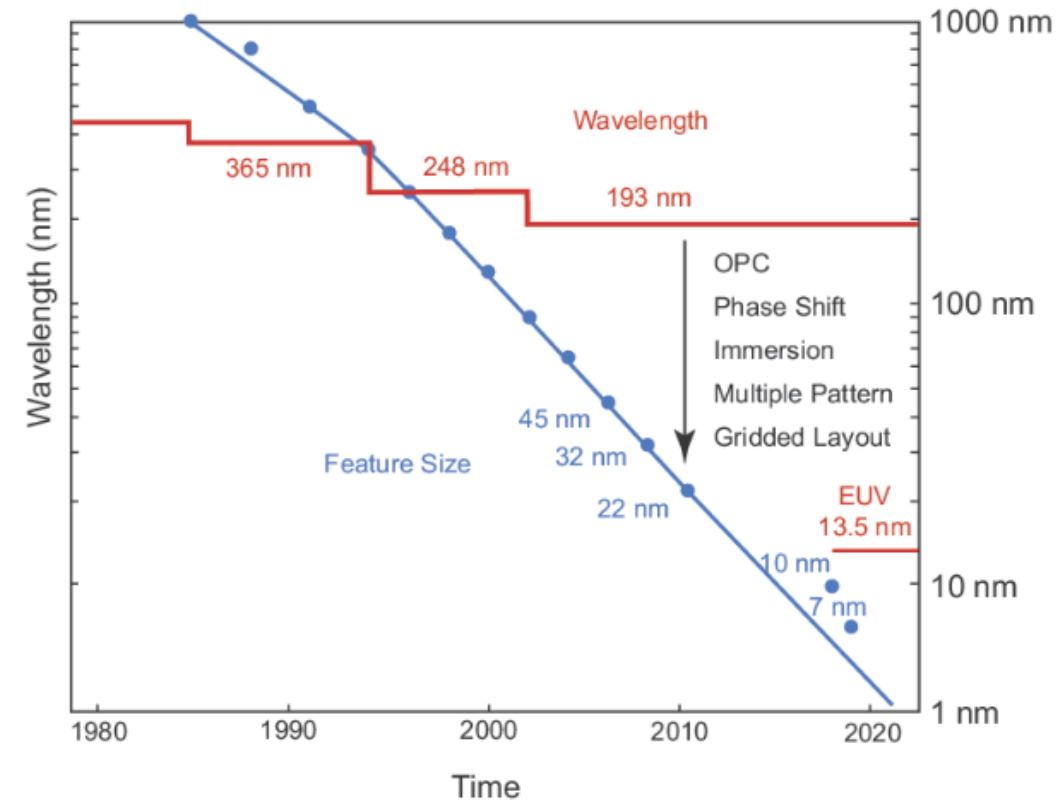
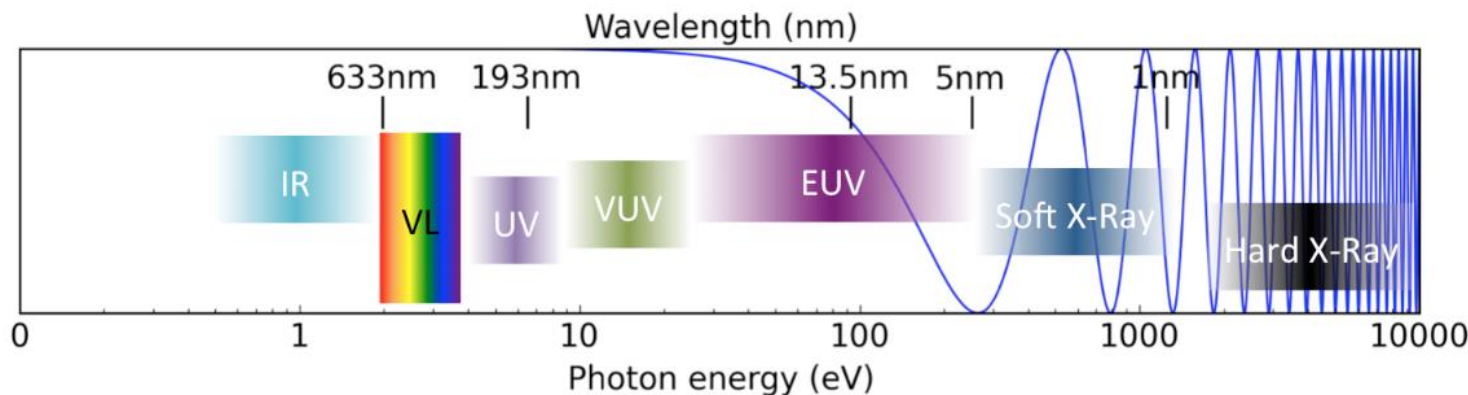
Web: <http://www.fh-muenster.de/juestel>

Skype: thomasjuestel

UV Radiation

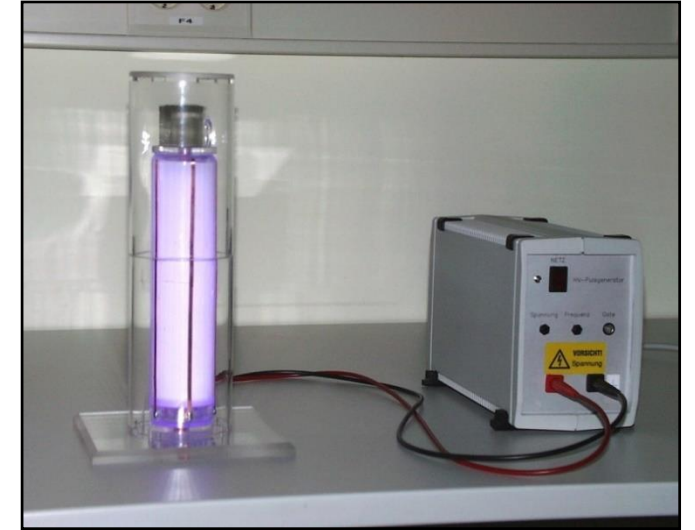
History across the last 222 years....

- 1801** Discovery by Johann W. Ritter due to effect of dispersed solar light on $\text{AgNO}_3 \rightarrow \text{Ag}$ (black)
→ Chemistry as the basis of the photographic process
- 1902** UV radiation kills microorganisms
- 1970** Photolithography by Hg discharge lamps
- Early 70's** g-line (434 nm)
- Early 80's** i-line (365 nm)
- 1990** KrF* laser (248 nm) → Deep UV photolithogr.
- 2000** ArF* laser (193 nm)
- 2017** Sn* plasma (13.5 nm) → EUV lithography
ASML, NL (€6 billion in R&D over 17 years)



Outline

1. Motivation
2. Inorganic Conversion Materials
3. UV Radiation Sources
4. Excimer Discharge Lamps
5. Deep UV-C Emitting Converters
6. UV-C Filter Materials
7. Summary
8. References



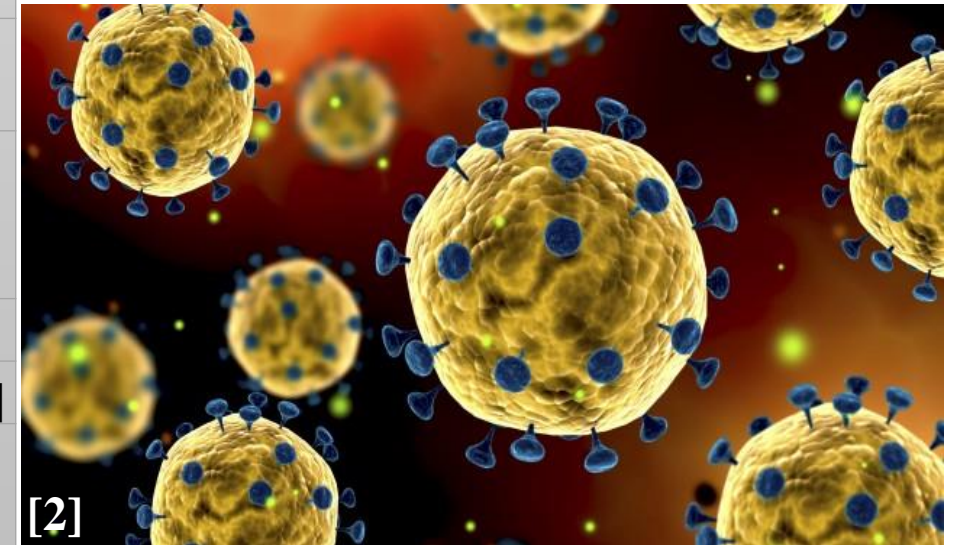
Source: <http://www.instanttrust.com/en/double-blue/>

1. Motivation

Outbreaks, Epidemics and Pandemics of some Airborne Viral Diseases

Period	Virus/ -type	Spread	Remarks
1917 - 1920	Spanish flu	Worldwide	Death toll > 1·10 ⁸
2002 - 2003	SARS-CoV-1	Worldwide	
since 2004	Marburg	Angola and Uganda	Aerosols play a minor role, but are not insignificant
2004 - 2016	A/H5N1	Worldwide	Aerosols hardly play a role, but transmission by aerosol droplets is possible
2009 - 2010	H1N1	Worldwide	
2019 - today	SARS-CoV-2	Worldwide	Death toll by 07/23 ~ 6.9·10 ⁶ [3]
Yearly	Influenza	Worldwide	Estimated 290,000 to 645,000 people die each year [1]

Viruses = Volatile nanoparticles often spread by aerosols



Literature

- [1] A. Danielle Iuliano et al., Estimates of global seasonal influenza-associated respiratory mortality: A modelling study, The Lancet, Volume 391, Issue 10127, P1285-1300, March 31, 2018 [https://doi.org/10.1016/S0140-6736\(17\)33293-2](https://doi.org/10.1016/S0140-6736(17)33293-2)
- [2] Corona-Update: Wie weit ist die Forschung? DAZ.online, 12.03.2020
- [3] Worldometer: <https://www.worldometers.info/coronavirus/>

1. Motivation

Disinfection of Air, Water, and Surfaces

Thermal treatment

Drinking water: $T > 70\text{ °C}$

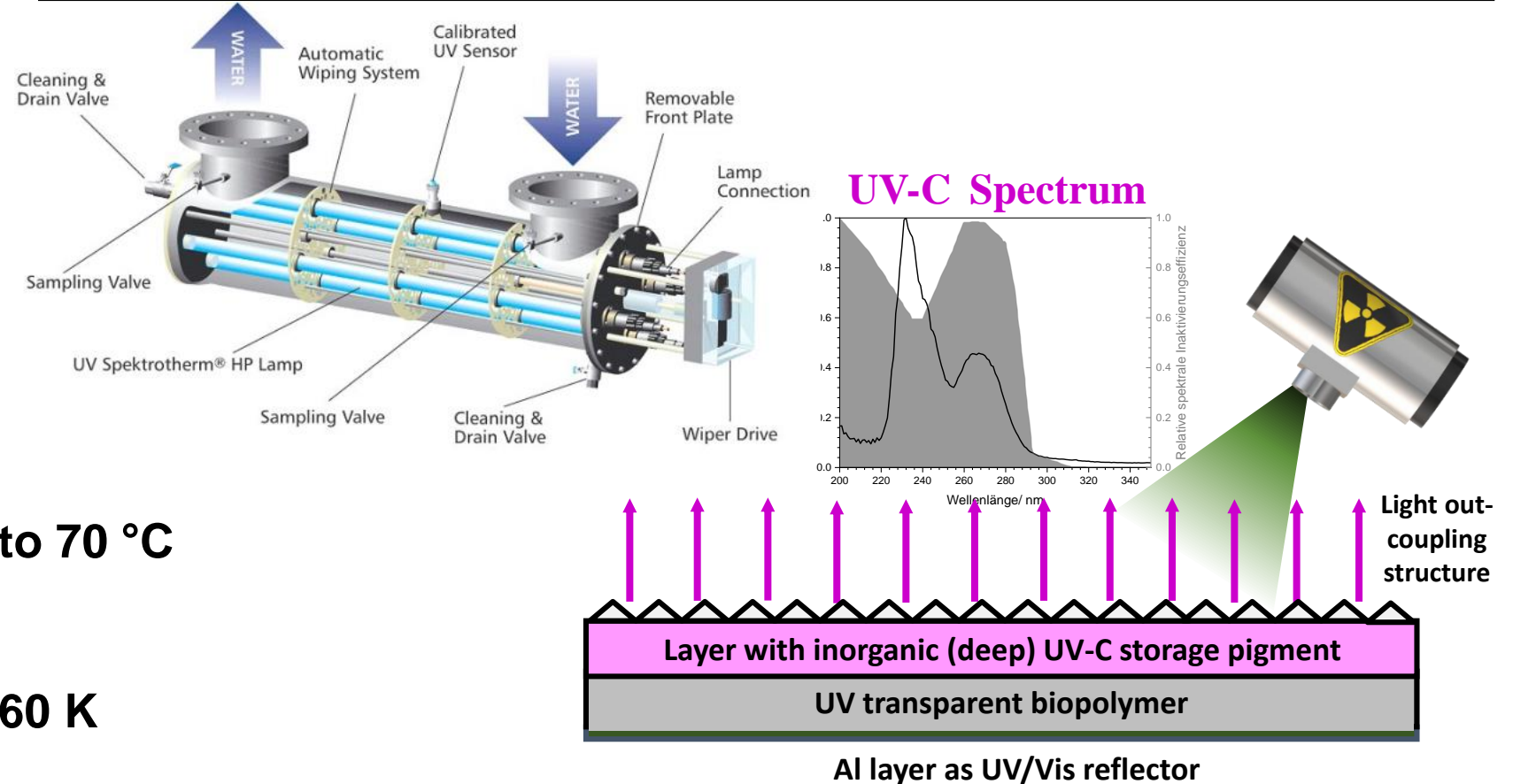
Surfaces: $T > 120\text{ °C}$

Drawback: Energy demand due to high heat capacity of water (and humid air)

Heating of $1\text{ m}^3\text{ H}_2\text{O}$ from 10 to 70 °C

$$\begin{aligned}\Delta Q &= m * c * \Delta T \\ &= 1000\text{ kg} * 4.19\text{ kJ/kgK} * 60\text{ K} \\ &\sim 250000\text{ kJ} \\ &\sim 700\text{ kWh/m}^3\end{aligned}$$

UV-C treatment of air, water, occupied spaces, or surfaces in use

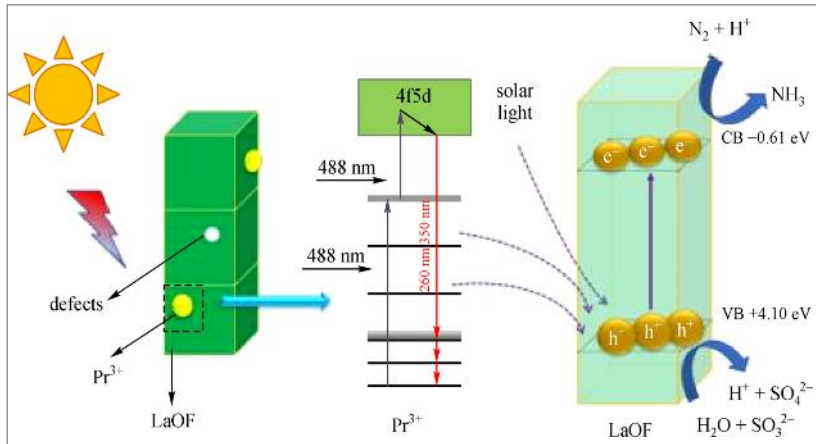


Typical $0.2 - 10\text{ kWh/m}^3$ (Ref.: Dr. M. Salvermoser, Xylem)

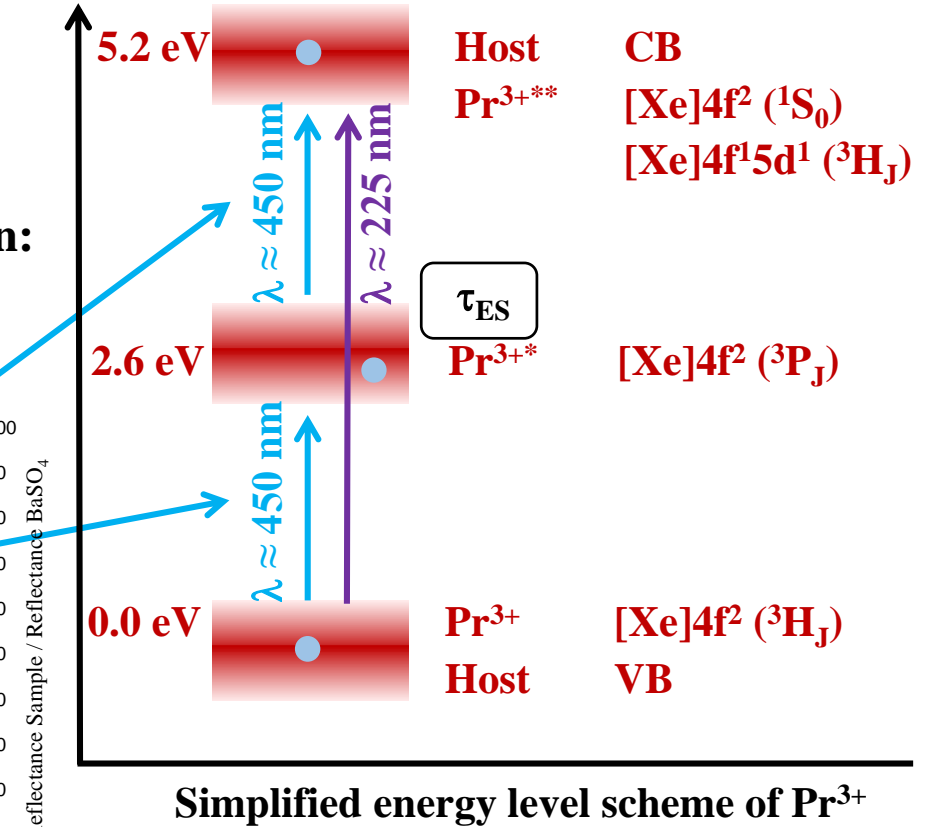
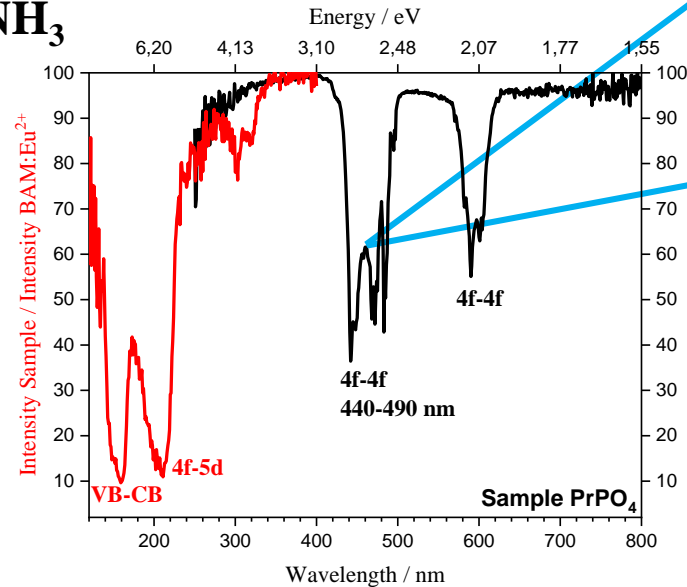
1. Motivation

Photochemistry: New Way to Produce Ammonia?

- Haber-Bosch (α -Fe) $\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3$ (400 - 500 °C)
- Nitrogenases ($\text{Fe}^{\text{n+}}$) $2 \text{N}_2 + 10 \text{H}^+ + 8 \text{e}^- \rightleftharpoons 2 \text{NH}_4^+ + \text{H}_2$ (RT)
- Heterogenous photocatalysis by up-conversion induced photoionisation:
Semiconductor (SC) + blue laser $\rightarrow \text{SC}^* \rightarrow \text{SC}^{**}$ ($\text{e}^-_{\text{CB}} + \text{h}^+_{\text{VB}}$)
 $\text{e}^-_{\text{CB}} + \text{N}_2 \rightarrow (\text{N}_2)^-$
 $6 (\text{N}_2)^- + 6 \text{H}_2\text{O} \rightarrow 6 \text{OH}^- + 5 \text{N}_2 + 2 \text{NH}_3$



Photocatalytic NH_3 synthesis at LaOF:Pr



Simplified energy level scheme of Pr^{3+}

Need: 225 nm radiation source for photocatalytic N_2 activation

Lit.: LaOF-Pr MW hydrothermal synthesis for photocatalytic N fixation, Front Mater Sci. 14 (2020) 43

2. Inorganic Conversion Materials

Working Principle

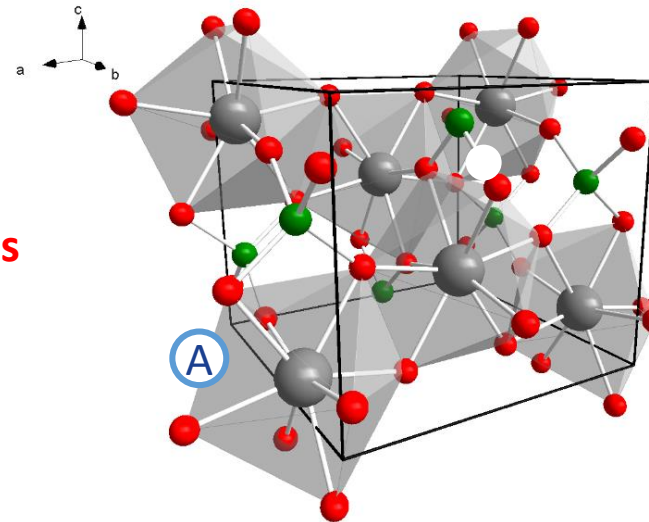
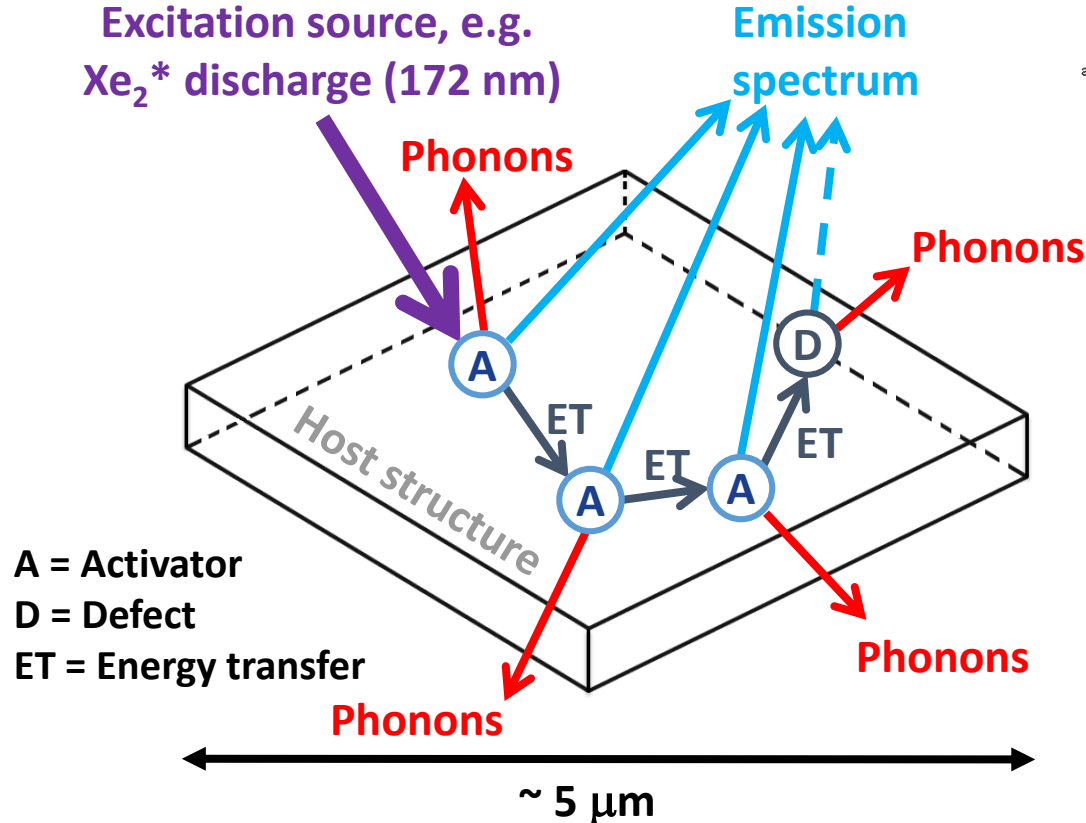
1. Excitation
2. Energy transfer (ET)
3. Relaxation

Absorption of energy from external source ($h\nu$, e^- , x-rays, E-field)

To activator ions or defects (storage and afterglow)

Radiative: Emission (luminescence) → Luminescent pigments

Non-radiative: Heat (phonons) → Absorption pigments (filter)

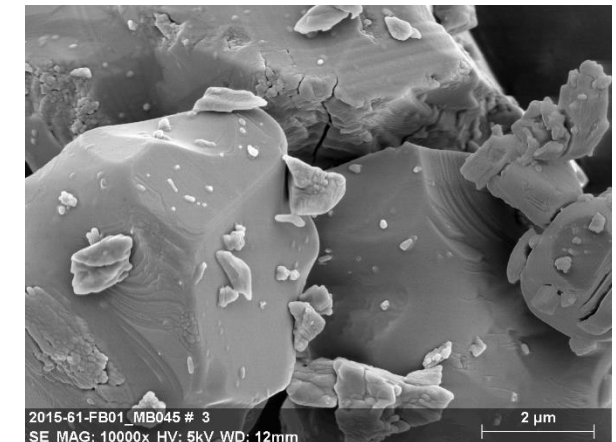


Host structure, e.g. YPO_4 or $LuPO_4$

Activator ion (A): Sc^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Gd^{3+} , Bi^{3+}

Lit.: W.O. Milligan, Inorg. Chim. Acta 60 (1982) 39

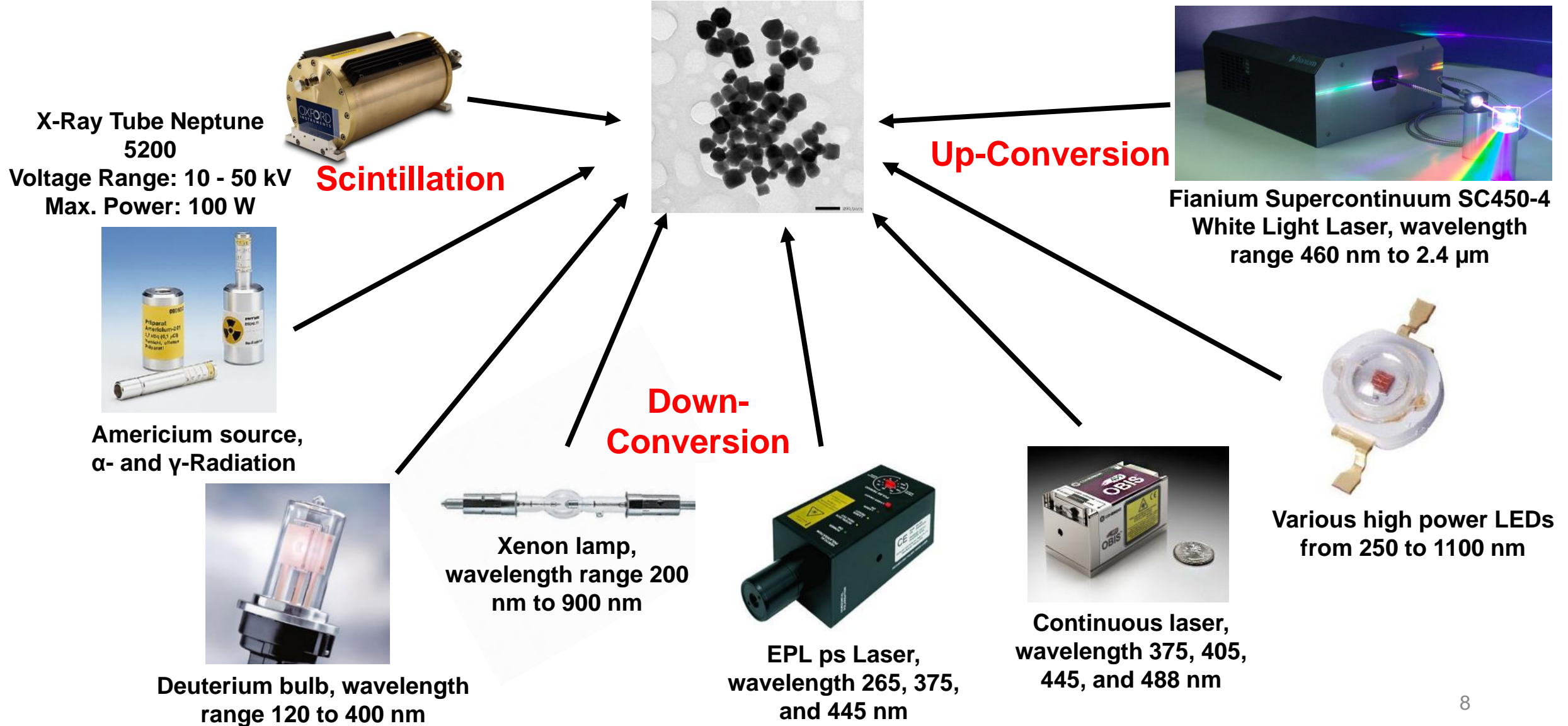
SEM image of $YPO_4:Bi^{3+}$



Typical particle size 1 - 10 μm

2. Inorganic Conversion Materials

Excitation Sources for Deep UV Emission by Micro- or Nanoscale Conversion Materials



2. Inorganic Conversion Materials

Relevant Properties of Deep UV Emission by Micro- or Nanoscale Conversion Materials

Exc. and emission spectra

Quantum yield (QY)

Germicidal efficacy (%)

Spectral consistency

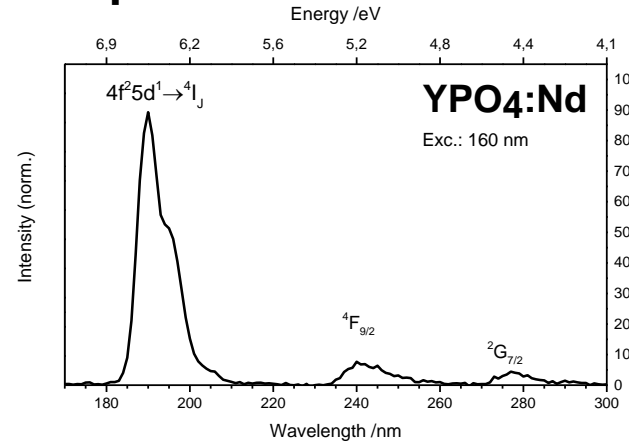
Decay curve

Thermal quenching

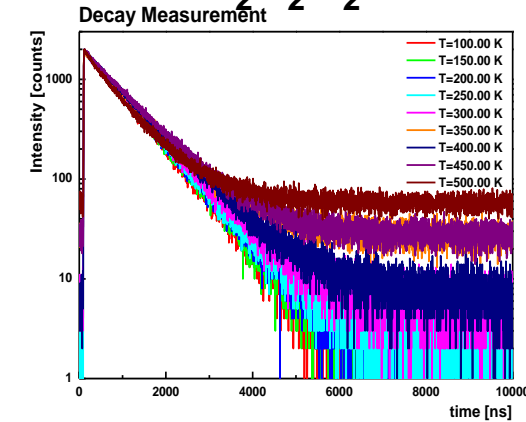
Linearity

Stability in manufacturing process and in operation

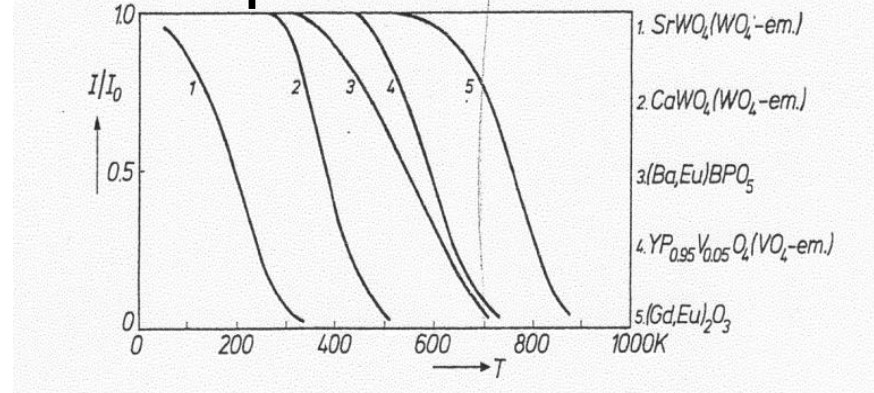
Emission spectrum of $\text{YPO}_4:\text{Nd}$ upon 160 nm excitation



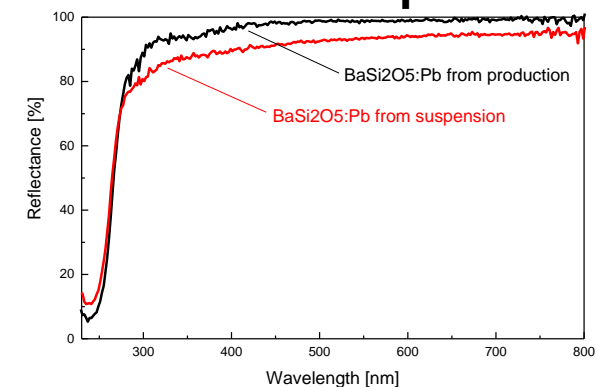
Decay curves of $\text{SrSi}_2\text{N}_2\text{O}_2:\text{Eu}$



Temp. dependent PL of conversion materials upon 254 nm excitation



Reflection spectrum of $\text{BaSi}_2\text{O}_5:\text{Pb}$ before and after processing



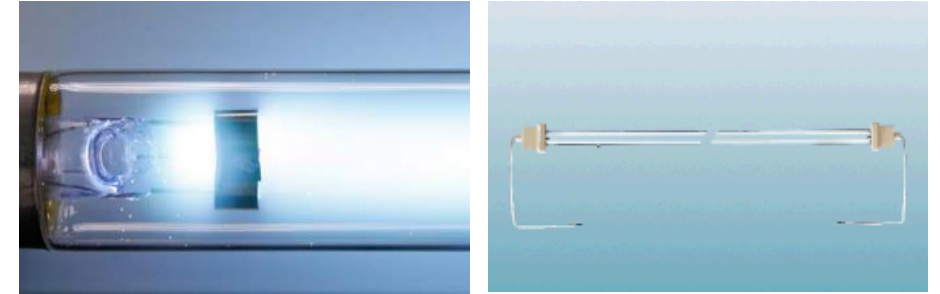
3. UV Radiation Sources

For the Deep UV-C Range

Hg discharge lamps

- low pressure
- amalgam
- medium pressure

185, 254 nm
185, 254 nm
200 – 400 nm



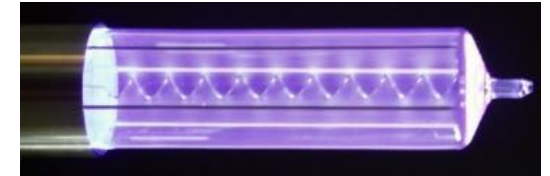
D₂ discharge lamps

110 – 400 nm

Excimer laser

- ArF*

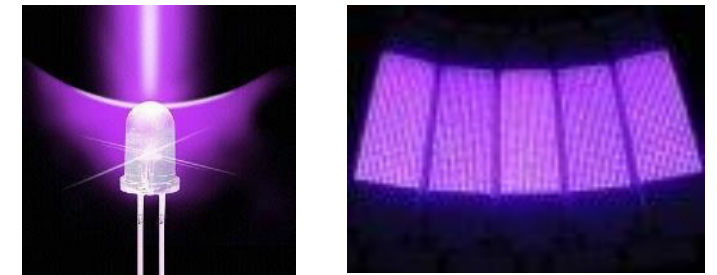
193 nm



Excimer discharge lamps, e.g. Dielectric Barrier Discharge (DBD) lamps

- KrBr*
- KrCl*
- Xe₂* + UV phosphor (fluorescent DBD)

207 nm
222 nm
190 – 400 nm



(Al,Ga)N UV LEDs

210 – 365 nm

X-ray tube + UV phosphor

190 – 400 nm

Cathode ray tube + UV phosphor

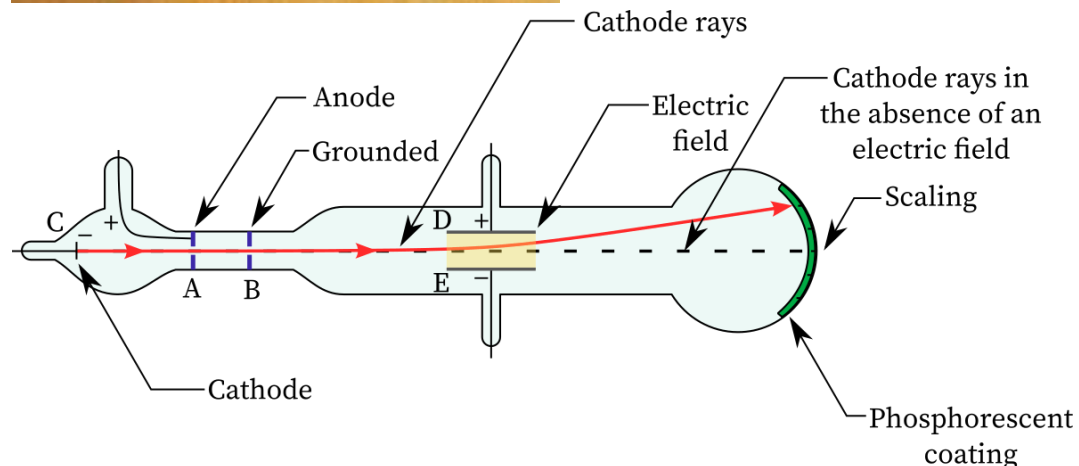
190 – 400 nm

Blue laser or blue LED + up-converter

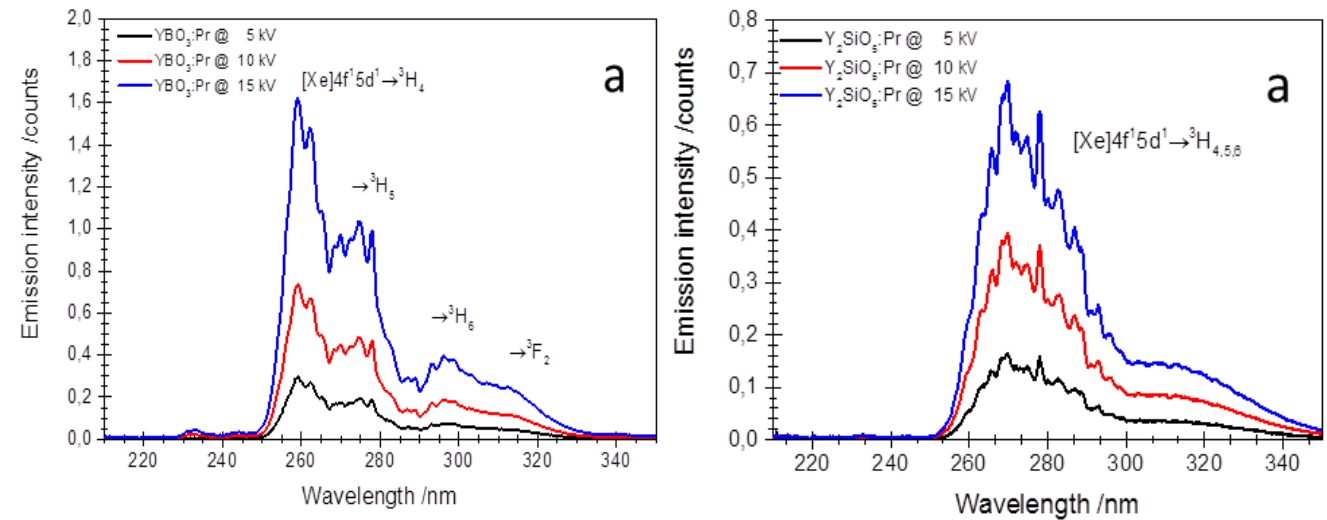
200 – 250 nm

3. UV Radiation Sources

Cathode Ray Tube (CRT) with UV-C Converter $\text{YBO}_3:\text{Pr}$ or $\text{Y}_2\text{SiO}_5:\text{Pr}$



$\text{YBO}_3:\text{Pr}$ and $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$ spectra upon e^- excitation



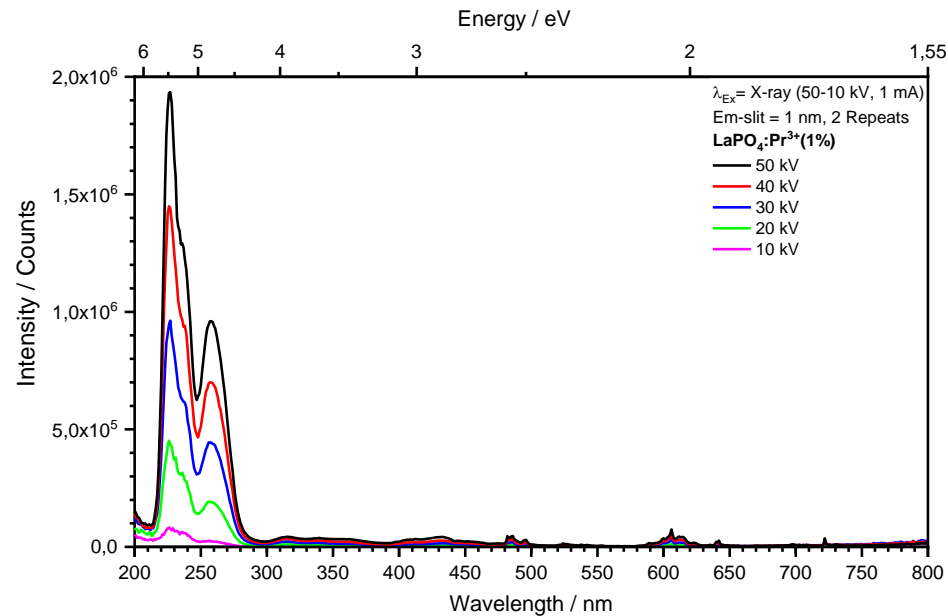
Accelerated electrons hit a phosphor screen to yield cathodoluminescence (CL): The principle is similar to that of a cathode ray tube for TV sets/monitors

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

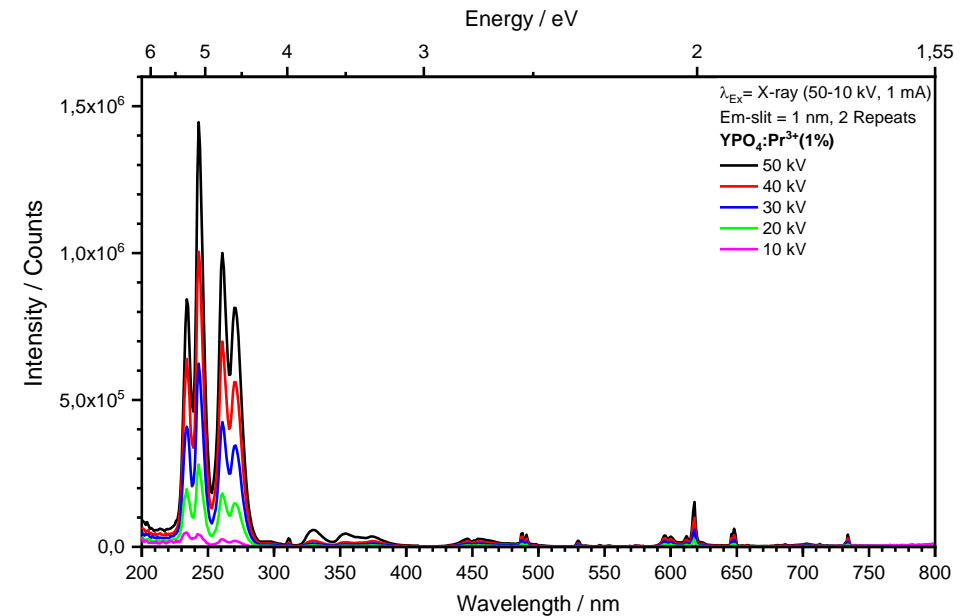
3. UV Radiation Sources

X-ray Tube with UV-C Converter $\text{LaPO}_4:\text{Pr}$ or $\text{YPO}_4:\text{Pr}$

$\text{LaPO}_4:\text{Pr}$ upon 10 – 50 keV excitation



$\text{YPO}_4:\text{Pr}$ upon 10 – 50 keV excitation



Pr^{3+} doped ortho-phosphates (LuPO_4) and ortho-silicates (Lu_2SiO_5) are efficient UV-C emitting scintillators

Spin-off: Cancer treatment by $\text{LnPO}_4:\text{Pr,Nd}$ (Ln = Y, La, Lu)

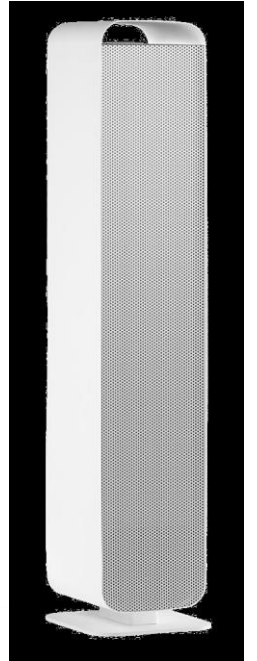
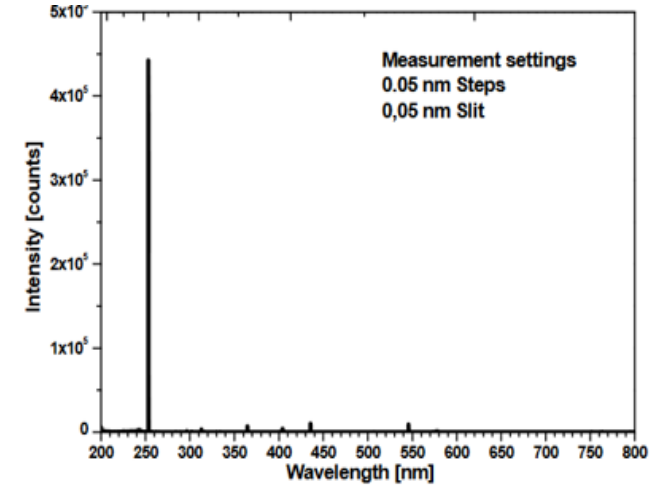
Lit.: J. Kappelhoff, J.N. Keil, M. Kirm, V. Makhov, K. Chernenko, S. Möller, T. Jüstel, J. Chem. Phys. 562 (2022) 111646

3. UV Radiation Sources

Main Application Areas: Water and Indoor Air or Surface Disinfection

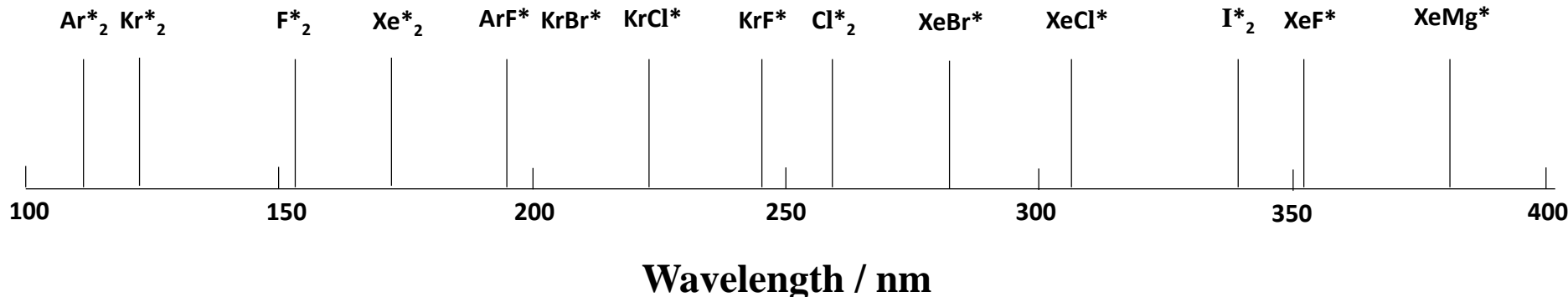
Standard: Hg discharge lamps (LP, MP, HP)

- 253.7 nm (Hg*) radiation is very effective
- Hazardous towards skin and eyes → closed device required
- 185.0 nm Hg line is filtered off to prevent O₃ formation



Excimer discharge lamps

- Excimer lamps emit in the VUV or UV range with high power density
- Lamp filling, e.g. Xe or Kr and X₂, govern emission spectrum & efficiency



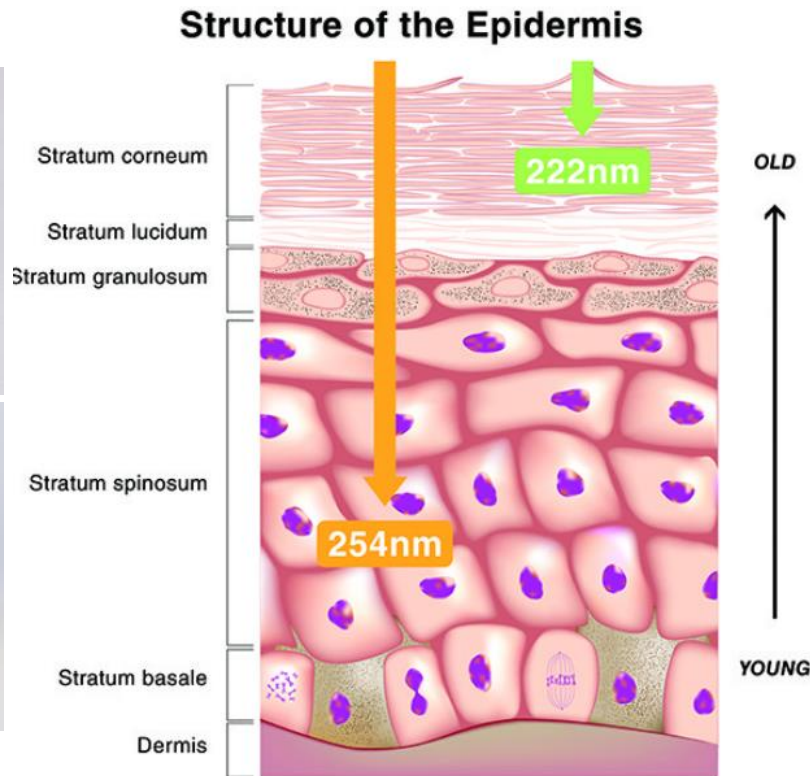
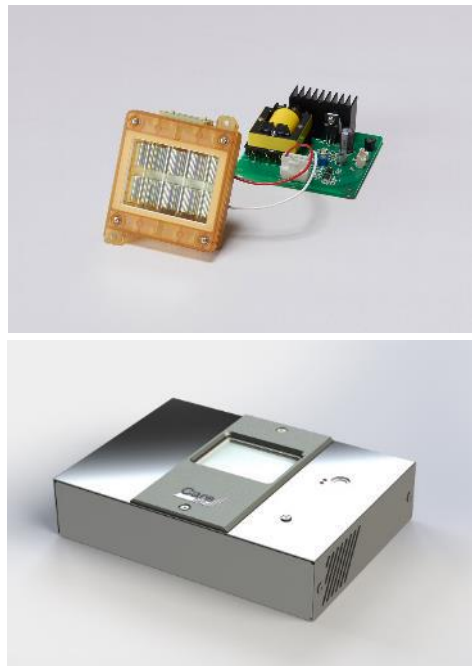
STAMBOLI Air Purifier

- Air flow: 160 m³ h⁻¹
- Light sources: Hg LP UV-C lamp (253.7 nm), ozone free
 - Voltage: 220 - 240 V
- Input power: 72 W
- UVC output: ~ 30 W
- Lifetime of UV-C lamps ~ 9000 hours

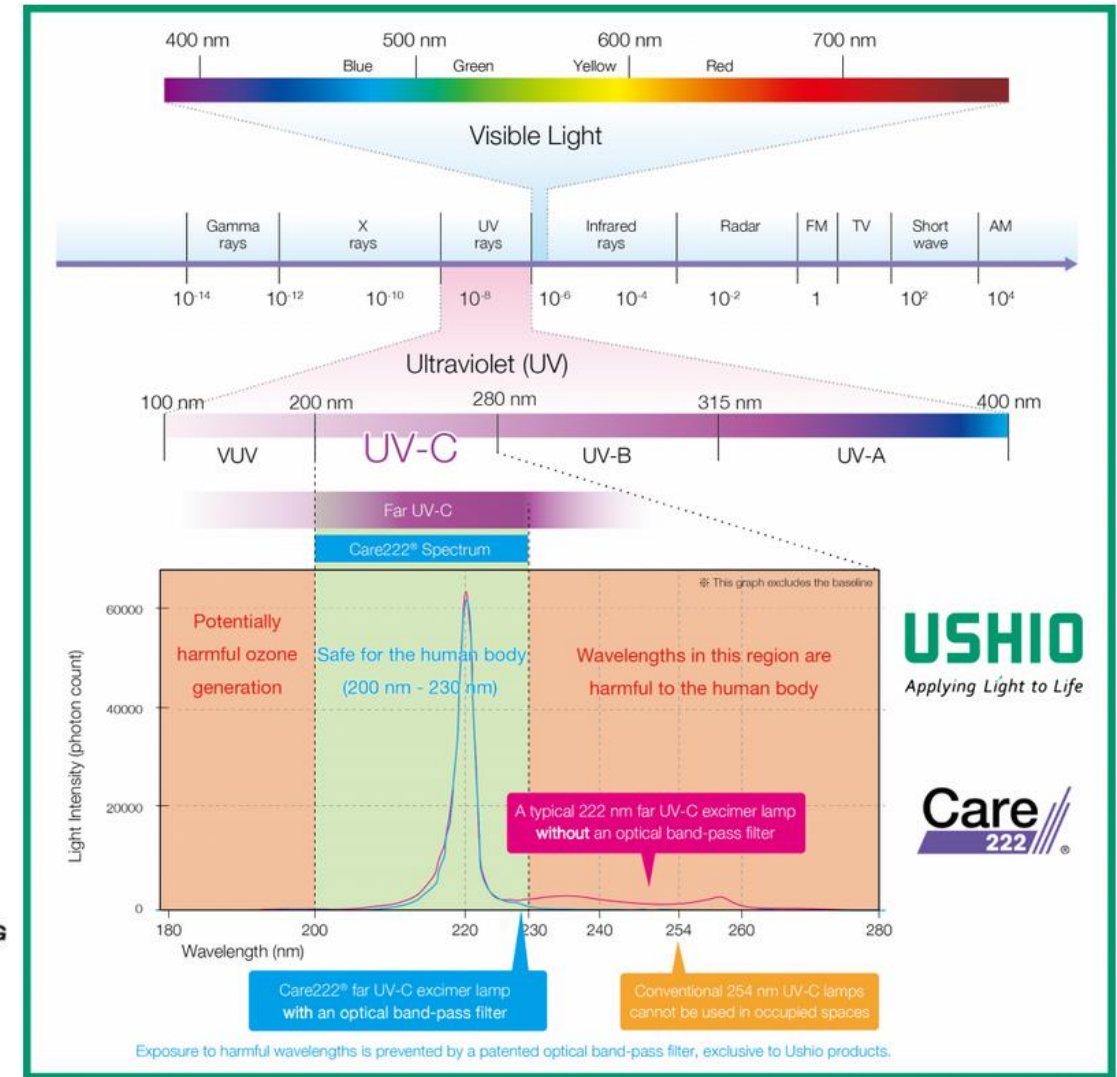
4. Excimer Discharge Lamps

Care222® Ushio

Commercial product of Ushio
“for eye and skin safe indoor disinfection”



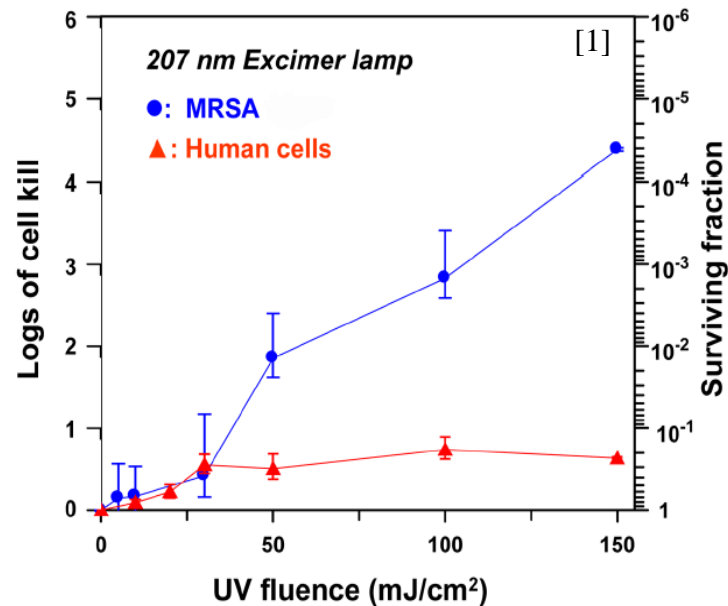
Source: Ushio Homepage



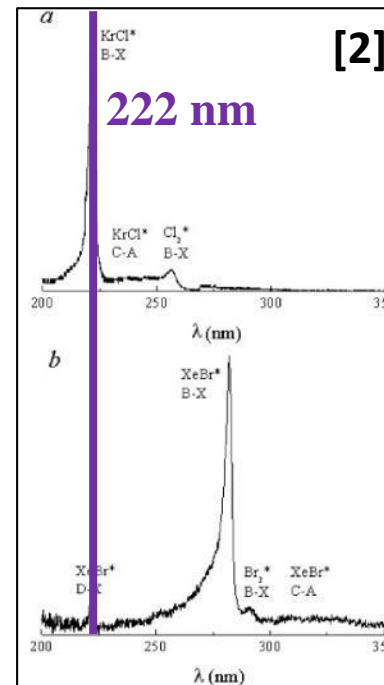
4. Excimer Discharge Lamps

Novel Application – Indoor Air Disinfection with Deep UV-C

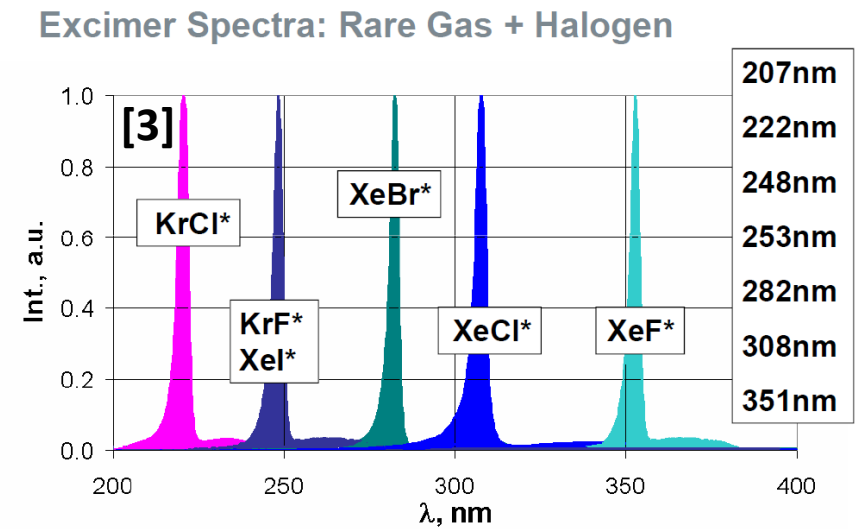
- Recent publications on the influence of deep UV-C radiation on human skin and eye cells showed, that radiation between 207 and 222 nm efficiently kills pathogens potentially without harm to exposed human tissues [1]
- KrBr* excimer discharge lamps (207 nm) have been successfully tested
- Alternative: KrCl* excimer discharge (222 nm) shows undesired spectral features above 230 nm (Cl₂*)



Lit.: [1] D.J. Brenner et al., Radiat. Res. 187 (2017) 483



[2] M. Erofeev, V.F. Tarasenko, Quantum Electronics, 2008, 38, 401-403

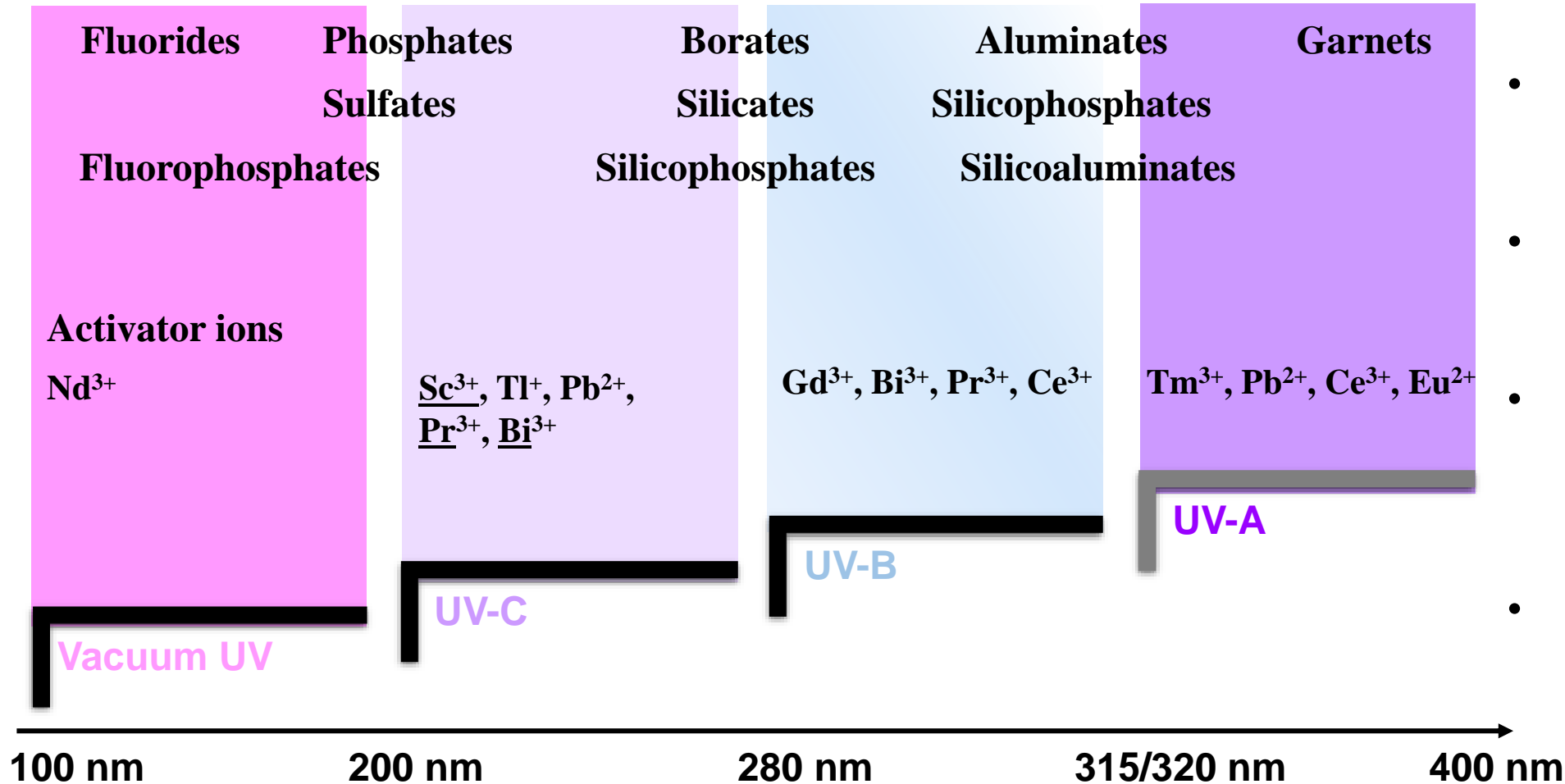


[3] A. Voronov, Heraeus, Übersicht der UV-Lampen und ihre Einsatzgebiete, Darmstadt Oktober 2009

5. Deep UV-C Emitting Converters

Suitable Host Matrices and Activator Ions

Host matrices



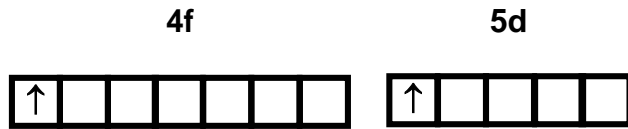
Conclusions due to requirements from the application:

- Oxidic or fluoridic hosts only
- s^2 or trivalent RE ions required
- Pr^{3+} , Bi^{3+} , and Sc^{3+} are ROHs compliable
- $\text{YPO}_4:\text{Bi}$ emitting at 241 nm is used a reference converter

5. Deep UV-C Emitting Converters

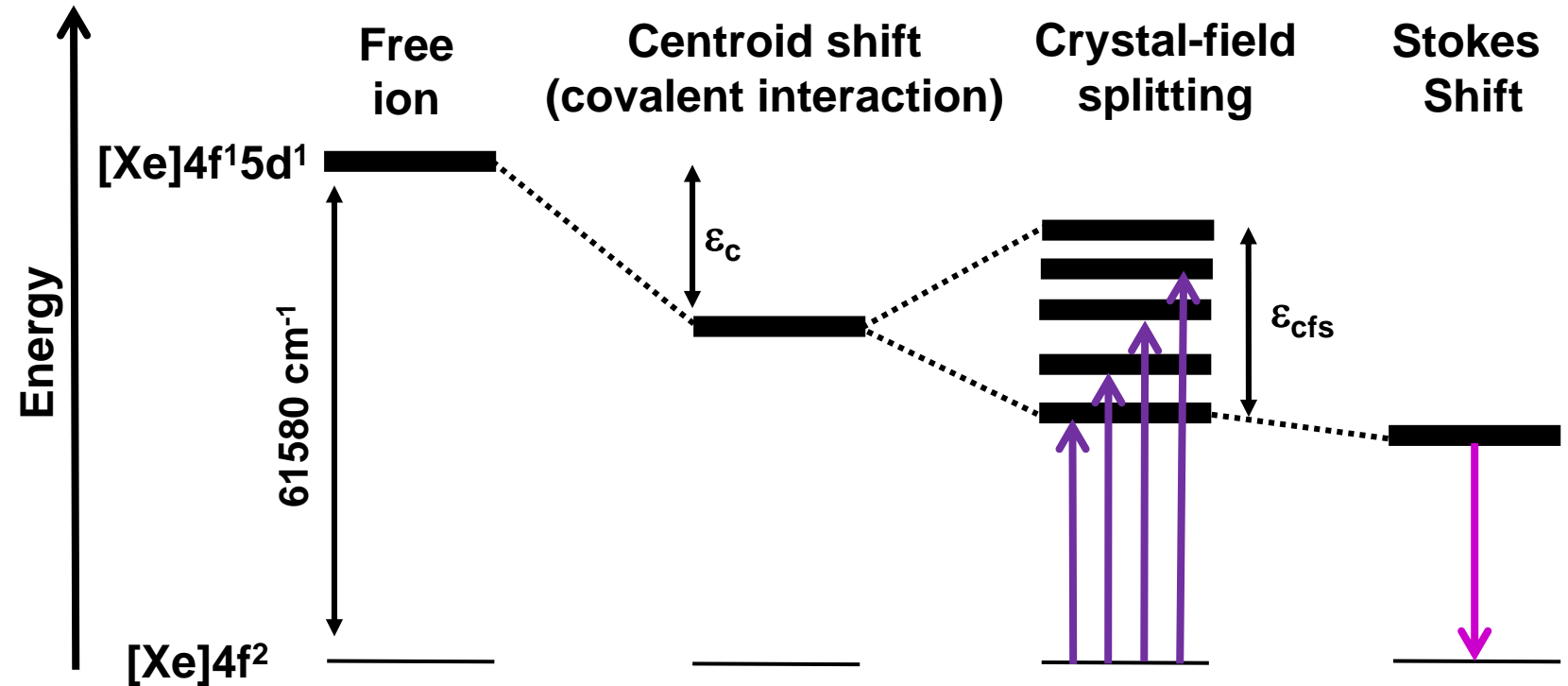
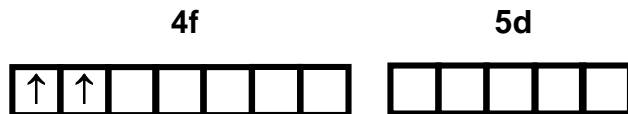
Suitable Host Matrices and Activator Ions

Pr³⁺ excited state



Pr³⁺ ground state

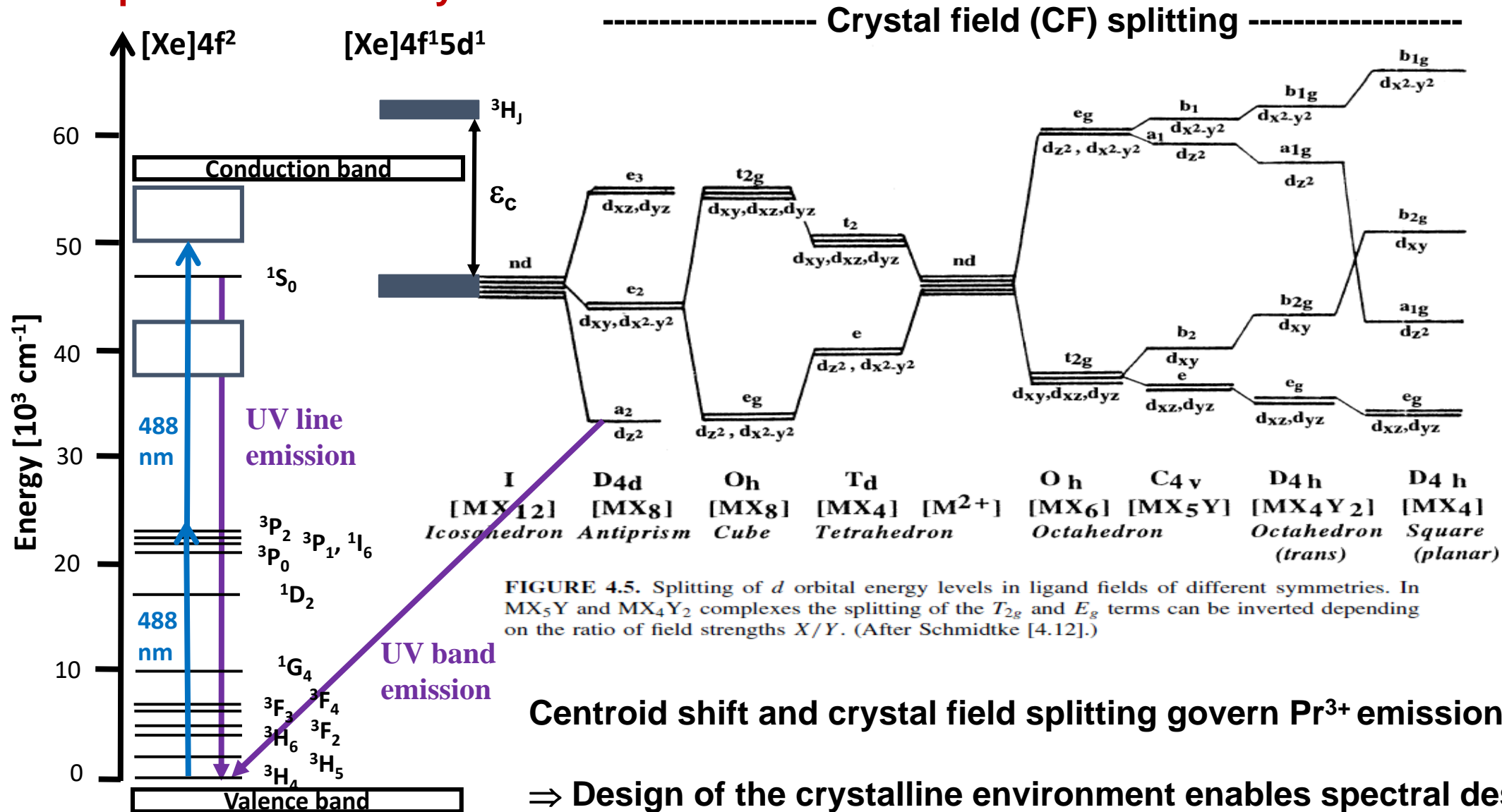
[Xe]4f² → 13 SLJ-States



Ion	Eu ²⁺	Ce ³⁺	Pr ³⁺	Nd ³⁺
Energy distance between [Xe]4f ² and [Xe]4f ¹ 5d ¹ conf.	34000 cm ⁻¹ 295 nm	50000 cm ⁻¹ 200 nm	61580 cm ⁻¹ 160 nm	72000 cm ⁻¹ 140 nm

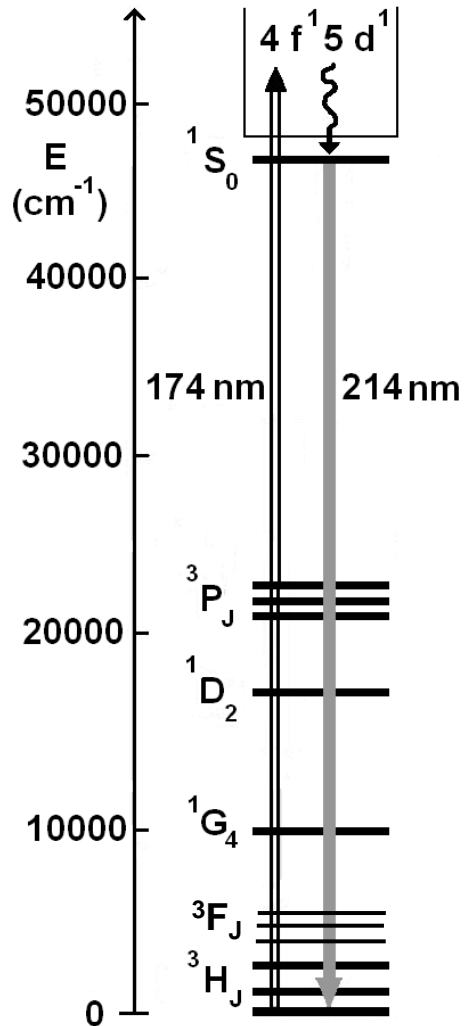
5. Deep UV-C Emitting Converters

Phosphors Activated by Pr^{3+}



5. Deep UV-C Emitting Converters

Fluoride Phosphors Activated by Pr³⁺

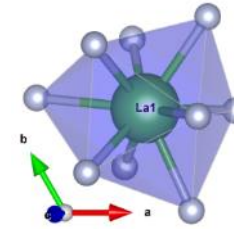


NaYF₄:Pr³⁺

CN 9 (2 sites)

UV Lines

214 nm + Vis

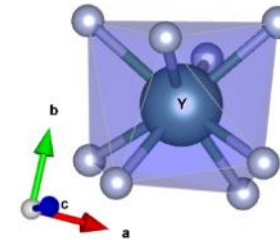


LiYF₄:Pr³⁺

CN 8 (1 site)

UV Bands

218 nm + Vis

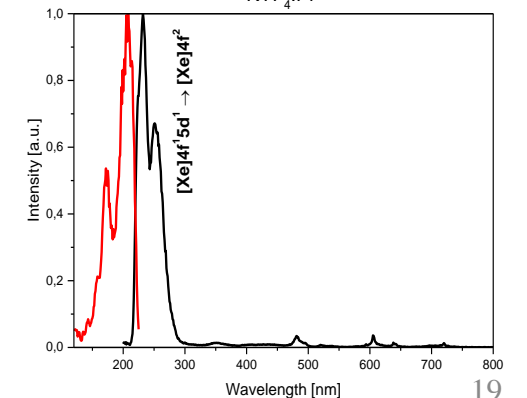
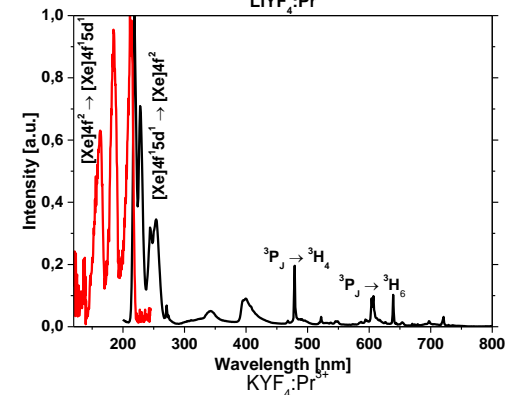
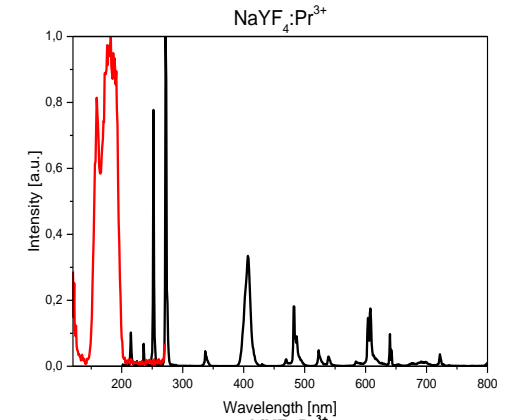
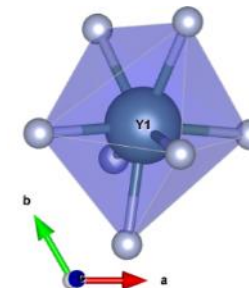


KYF₄:Pr³⁺

CN 7 (6 sites)

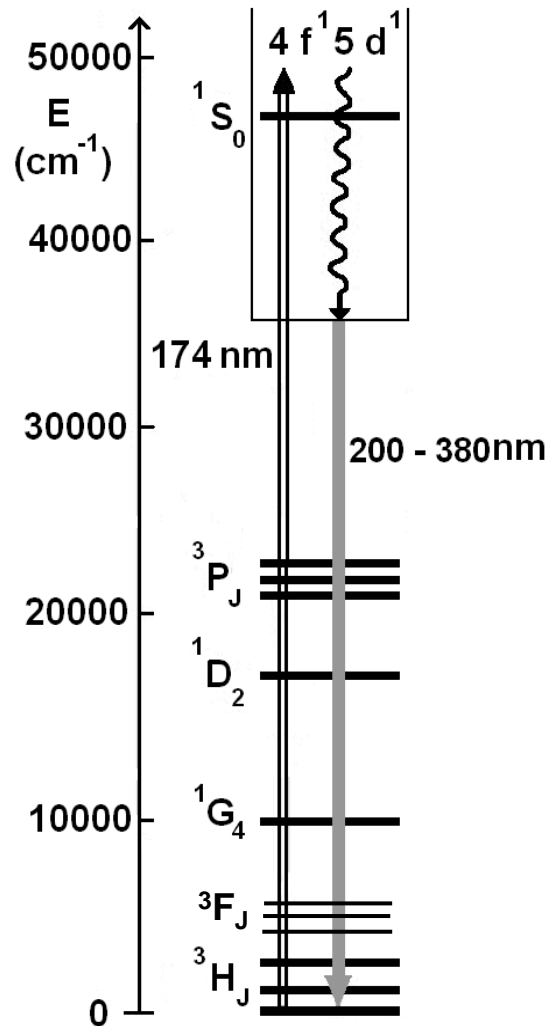
UV Bands

232 nm

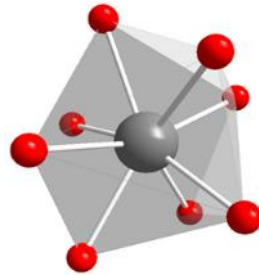


5. Deep UV-C Emitting Converters

Oxidic Phosphors Activated by Pr^{3+}



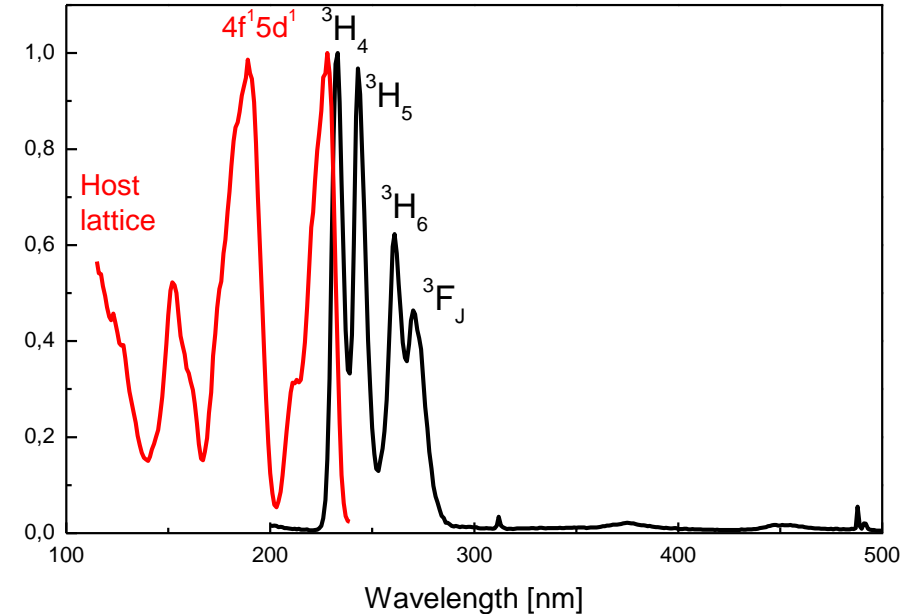
$(\text{Y,Lu})\text{PO}_4$
Band gap $E_g = 9.0 \text{ eV}$
Single crystallographic site



Distorted dodecahedra CN = 8

Y-O Distances
 $4 \times 2.24 \text{ \AA}$
 $4 \times 2.24 \text{ \AA}$

CF Splitting $\sim 12000 \text{ cm}^{-1}$
Centroid shift $\sim 9600 \text{ cm}^{-1}$

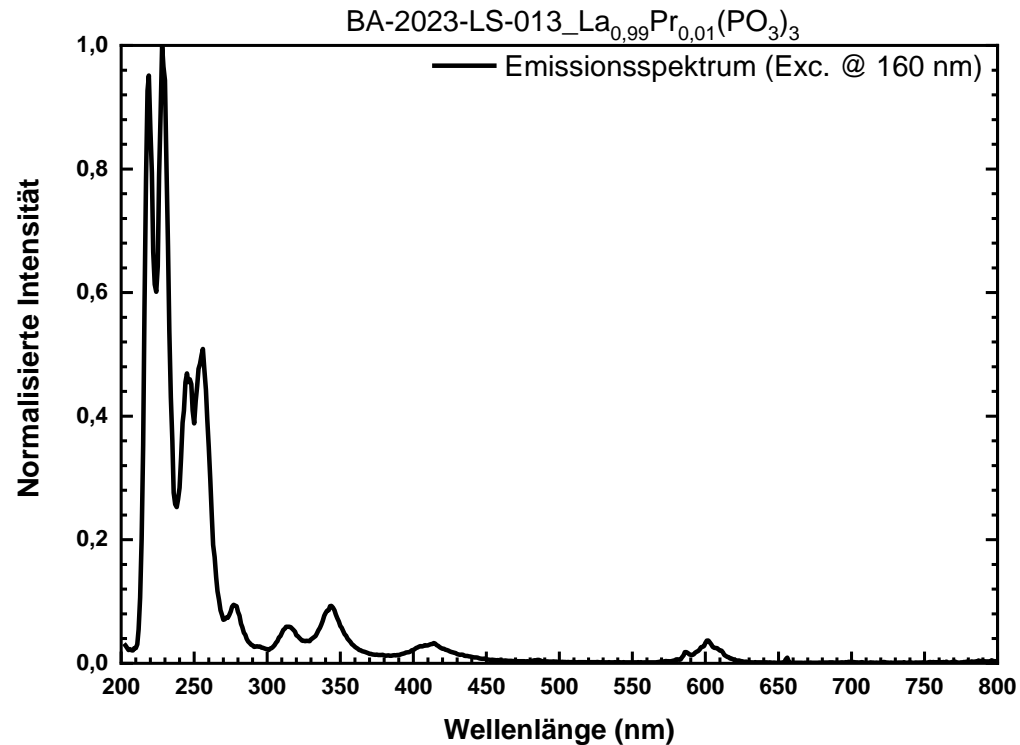


- \Rightarrow CF Splitting and centroid shift reduces lowest CF component of the $[\text{Xe}]4f^{15}d^1$ configuration by around 22000 cm^{-1}
- $\Rightarrow E(4f^{15}d^1) < E(1S_0)$
- $\Rightarrow [\text{Xe}]4f^{15}d^1 - [\text{Xe}]4f^2$ band emission

5. Deep UV-C Emitting Converters

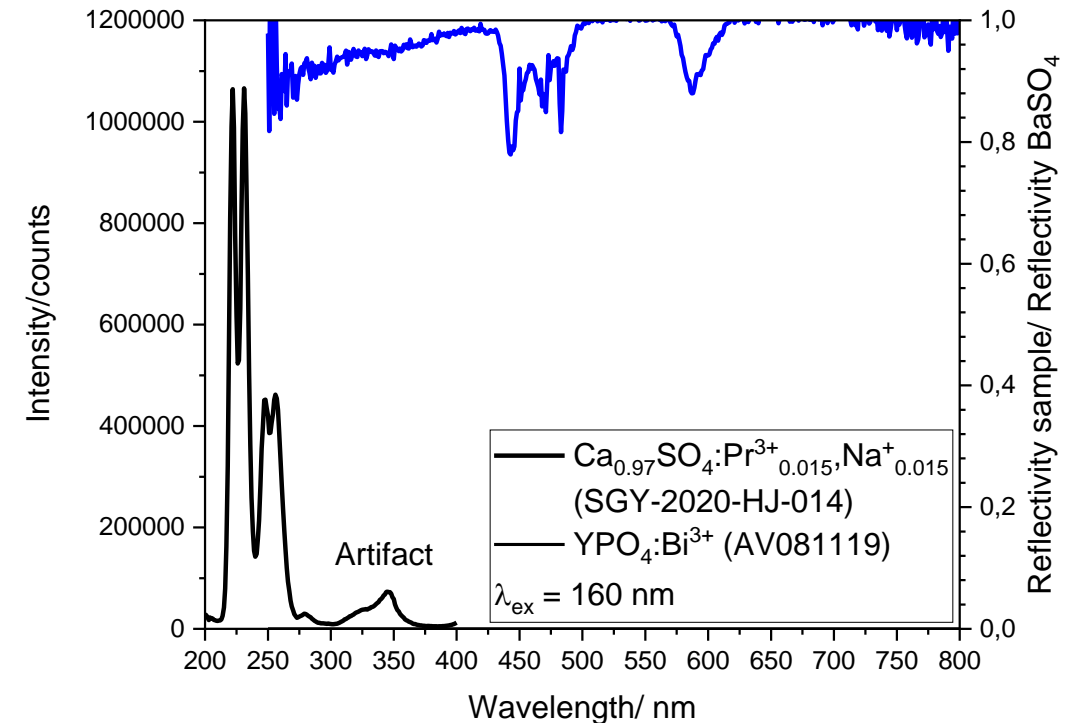
Oxidic Phosphors Activated by Pr^{3+} with Deep UV-C Emission: Enhance Host Acidity!

$\text{La}(\text{PO}_3)_3:\text{Pr}^{3+}$



First emission maxima at 218 nm

$\text{CaSO}_4:\text{Pr}^{3+}\text{Na}^+$



First emission maximum at 222 nm

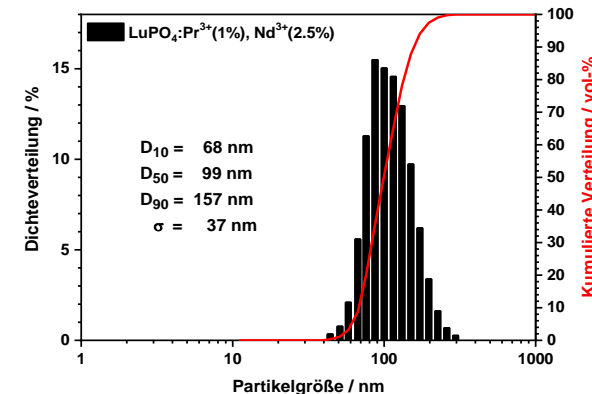
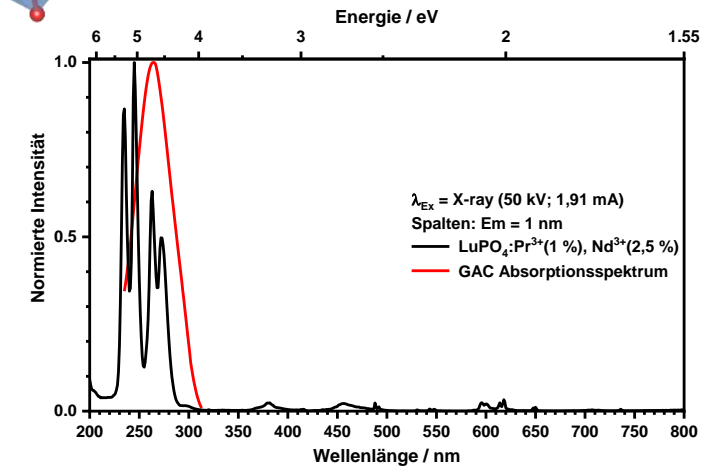
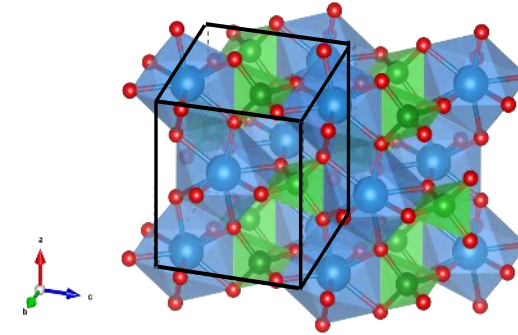
5. Deep UV-C Emitting Converters

Deep UV-C Phosphors Activated by Pr³⁺

Accessible UV wavelength range 218 – 320 nm

• LiYF ₄ :Pr	218 nm
• La(PO ₃) ₃ :Pr	218 nm
• CaSO ₄ :Pr	222 nm
• LuPO ₄ :Pr	232 nm
• YPO ₄ :Pr	235 nm
• YAIO ₃ :Pr	241 nm
• CaLi ₂ SiO ₄ :Pr	252 nm
• YBO ₃ :Pr	265 nm
• LiYSiO ₄ :Pr	267 nm
• Y ₂ SiO ₅ :Pr	270 nm
• Y ₂ Si ₂ O ₇ :Pr	275 nm
• Lu ₃ Ga ₂ Al ₃ O ₁₂ :Pr	300 nm
• Lu ₃ Al ₅ O ₁₂ :Pr	310 nm
• Y ₃ Al ₅ O ₁₂ :Pr	320 nm

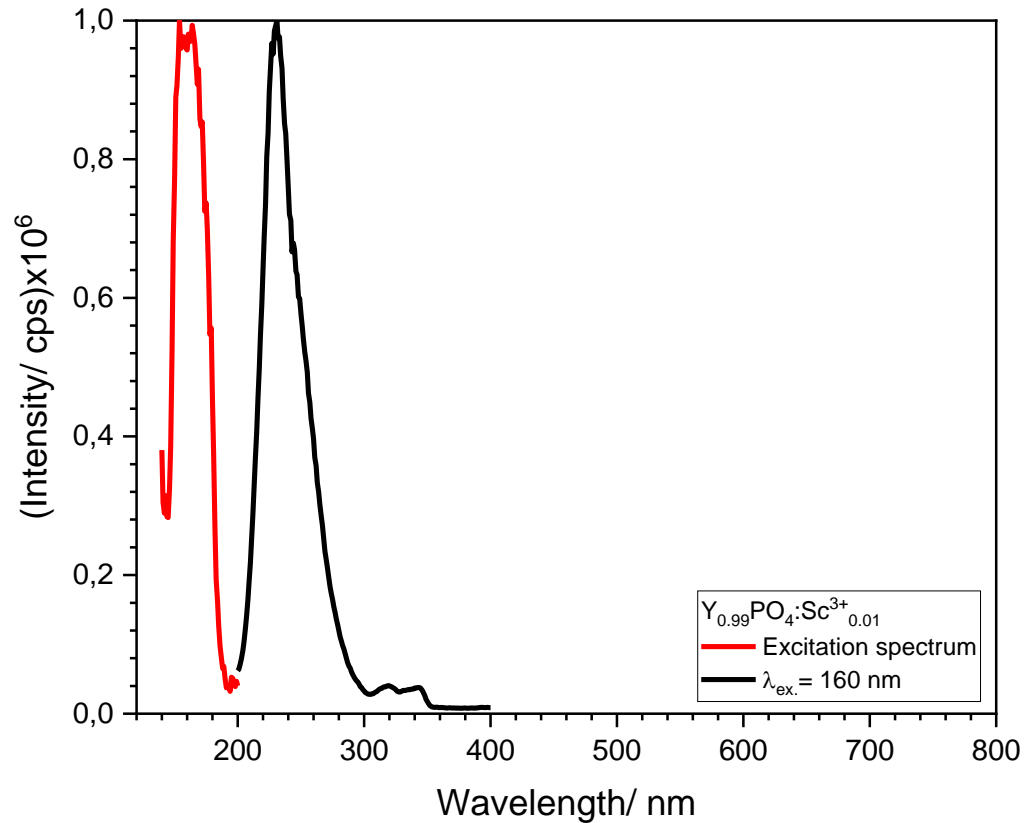
Structure, emission, and PSD of LuPO₄:Pr



5. Deep UV-C Emitting Converters

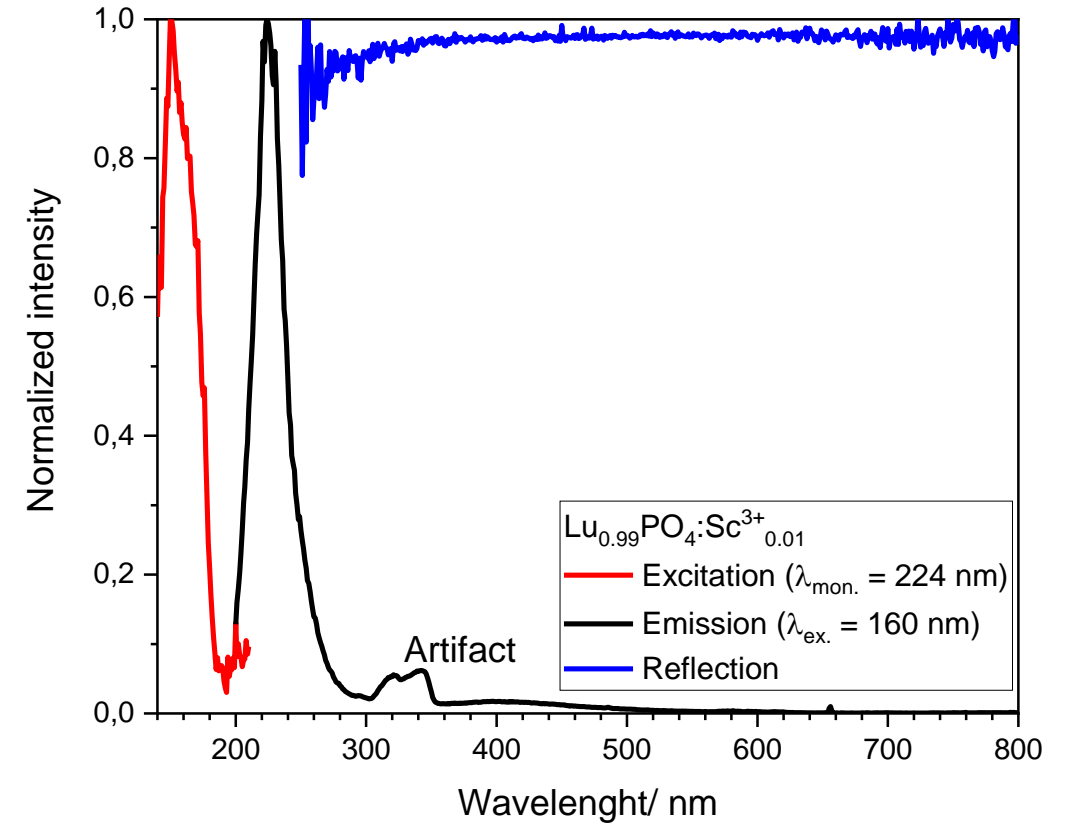
Deep UV-C Emitting Phosphate Phosphors Activated by Sc^{3+}

$\text{YPO}_4:\text{Sc}^{3+}$



Emission maximum at 230 nm

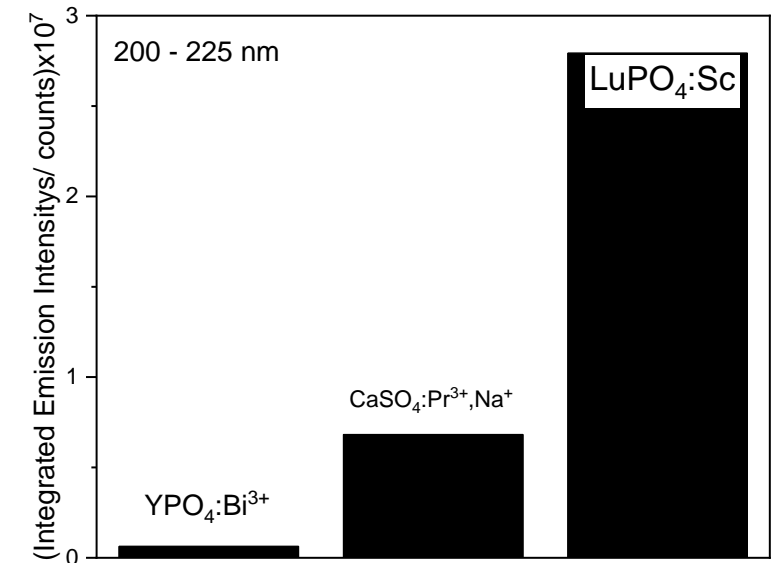
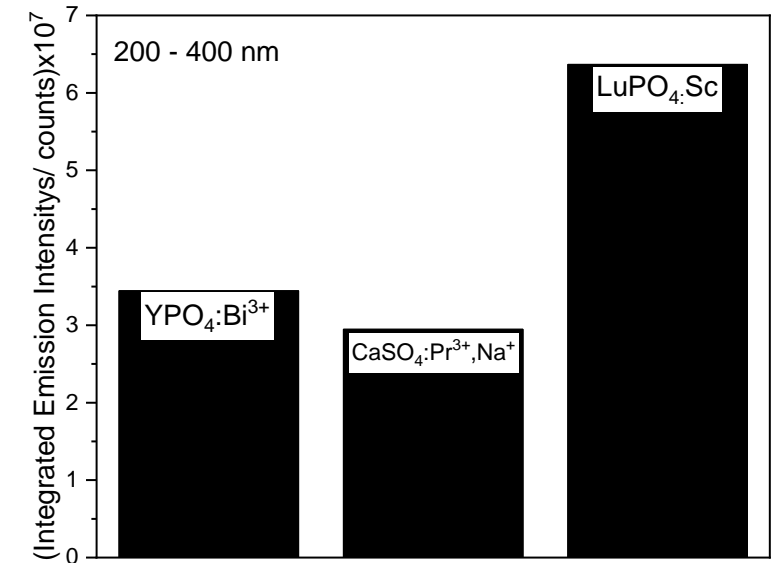
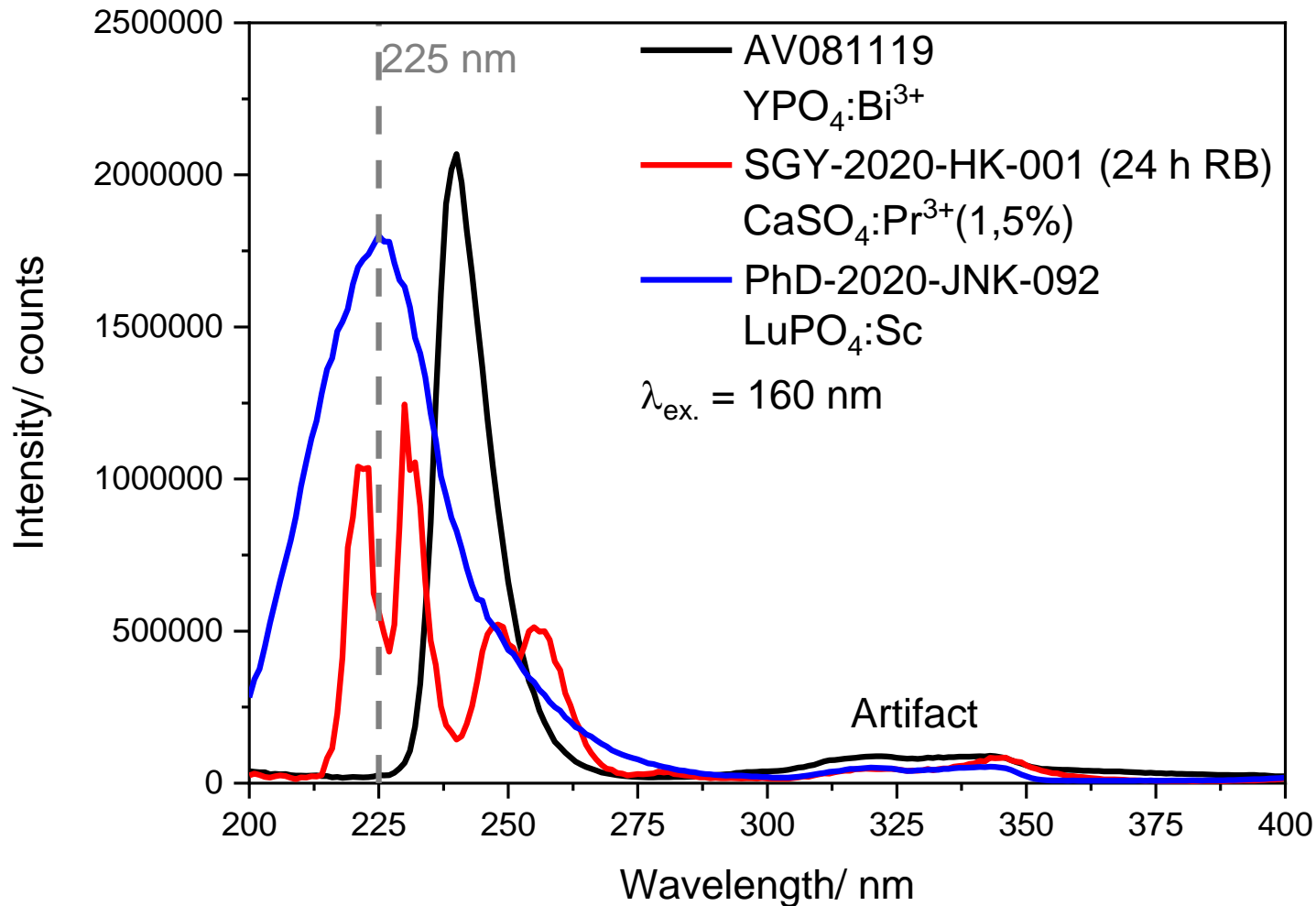
$\text{LuPO}_4:\text{Sc}^{3+}$



Emission maximum at 225 nm

5. Deep UV-C Emitting Converters

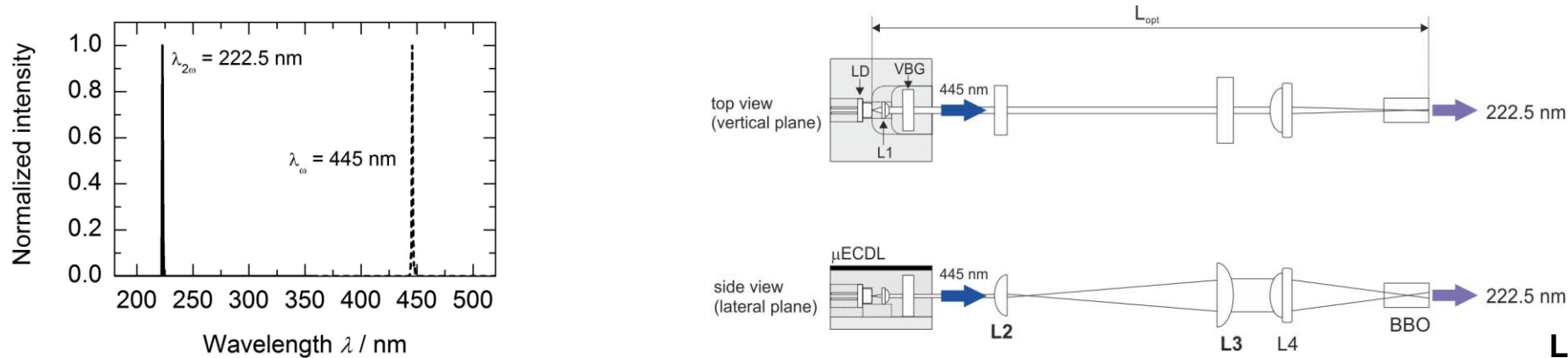
Deep UV-C Emitting Phosphate Phosphors Activated by Sc^{3+}



5. Deep UV-C Emitting up-Converters

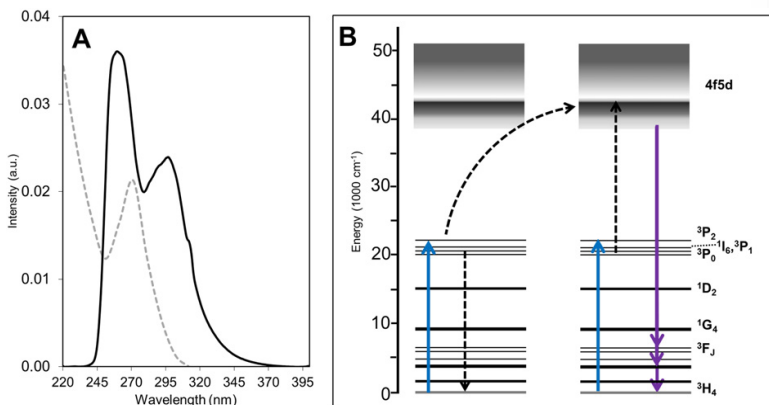
Surface Disinfection Claimed by Blue LED or Laser Diode + Blue-to-UV up-Converter

1. SHG: 445 nm laser diode + β -BaB₂O₄ NLO crystal, Germany, Berlin



Lit.: G. Tränkle et al., IEEE Phot. Tech. Lett. 30 (2018) 289

2. ETU: 445 nm laser diode + Y₂SiO₅:Pr,Li ceramic, Georgia, Atlanta



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 Pr³⁺ 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.

The image shows several yellow ceramic samples. A graph inset shows a peak at approximately 270 nm, labeled '34x UVC', with a wavelength range from 220 to 380 nm.

Lit.:
1. E.L. Cates, A.P. Wilkinson, J.-H. Kim, J. Luminescence 160 (2015) 202
2. E.L. Cates, J.-H. Kim, J. Photochemistry & Photobiology, B: Biology 153 (2015) 405

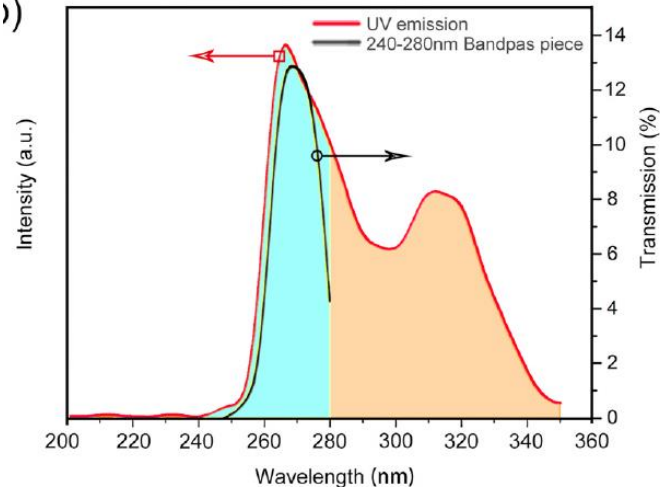
5. Deep UV-C Emitting up-Converters

Surface Disinfection by Blue LED or Laser Diode + Blue-to-UV up-Converter

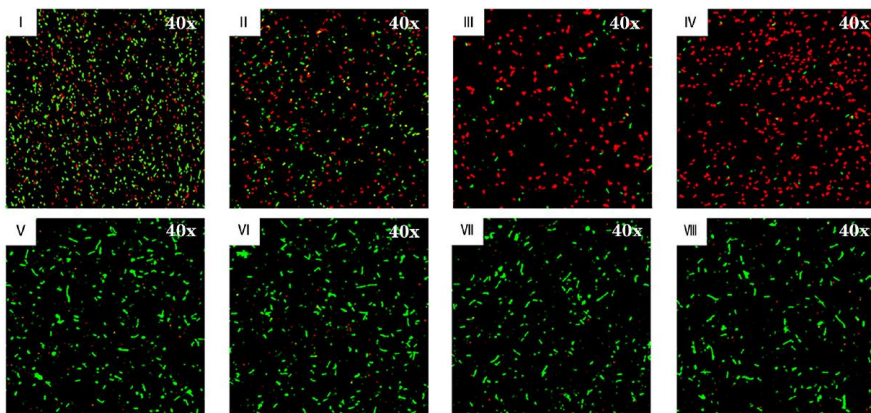
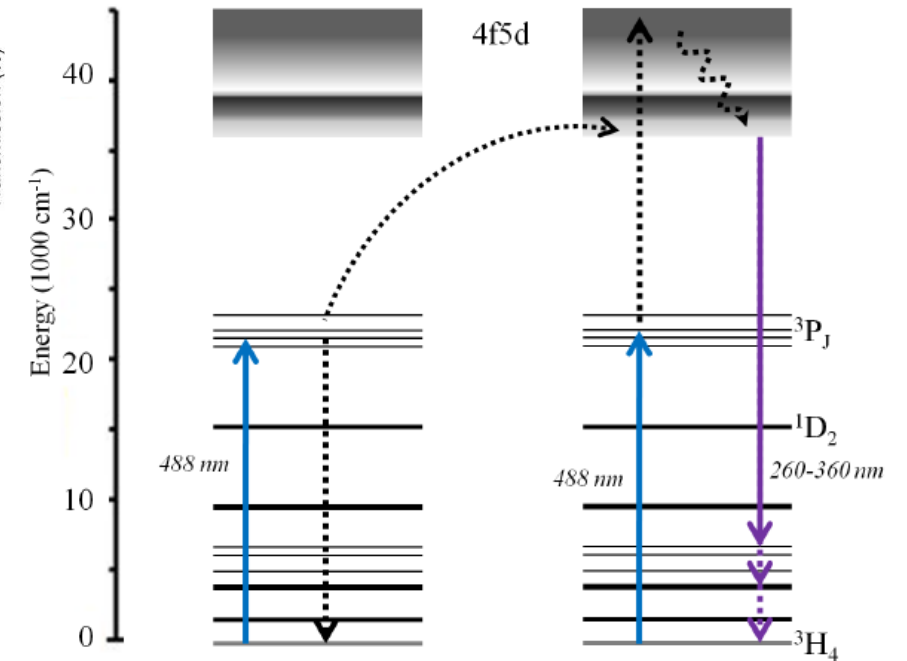
Some published UV up-Converter)

- $\text{Y}_2\text{SiO}_5:\text{Pr},\text{Li}$
- $\text{SrLi}_2\text{SiO}_4:\text{Pr}$
- $\text{CaLi}_2\text{SiO}_4:\text{Pr}$
- $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Pr}$

Sole working activator: Pr^{3+}



Energy Transfer Up-Conversion



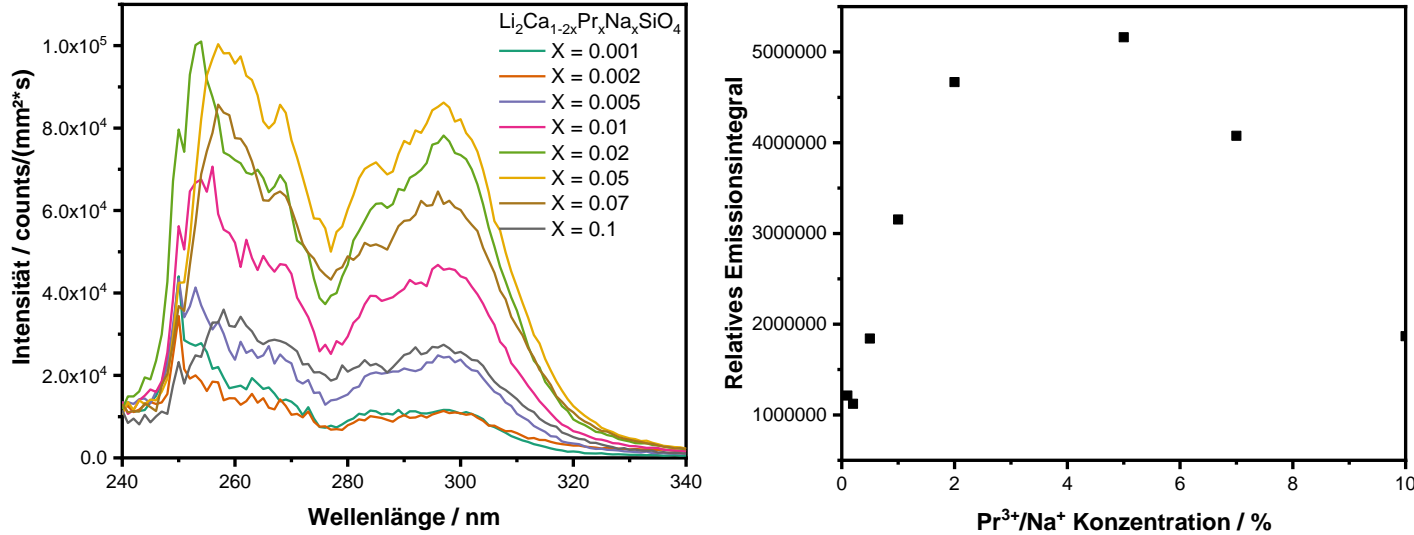
Lit.:

a) Z. Yin, P. Yuan, Z. Zhu, T. Li, Y. Yang, Pr^{3+} doped $\text{Li}_2\text{SrSiO}_4$: an efficient visible-ultraviolet C up-conversion phosphor, *Ceramics International* (2020)

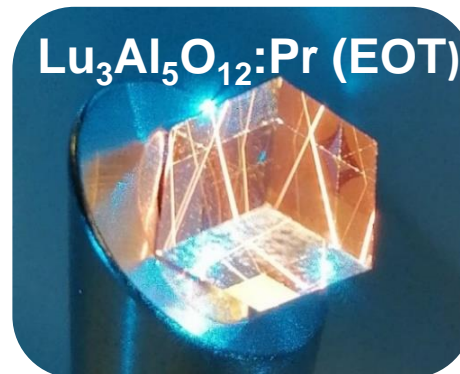
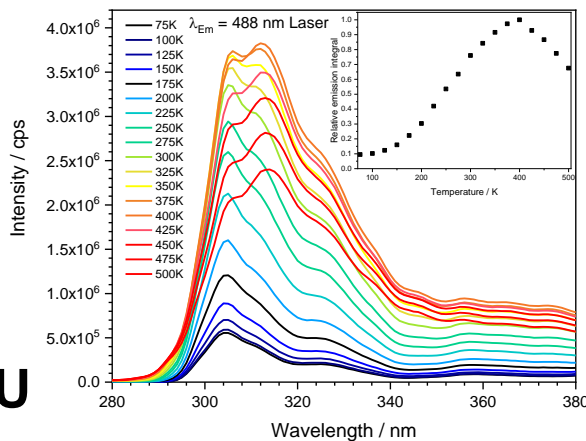
b) T. Jüstel et al. WO002021073914 A1, WO002021073915 A1

5. Deep UV-C Emitting up-Converters

Up-Converter $\text{CaLi}_2\text{SiO}_4:\text{Pr}^{3+}(\%)\text{Na}^+(5\%)$



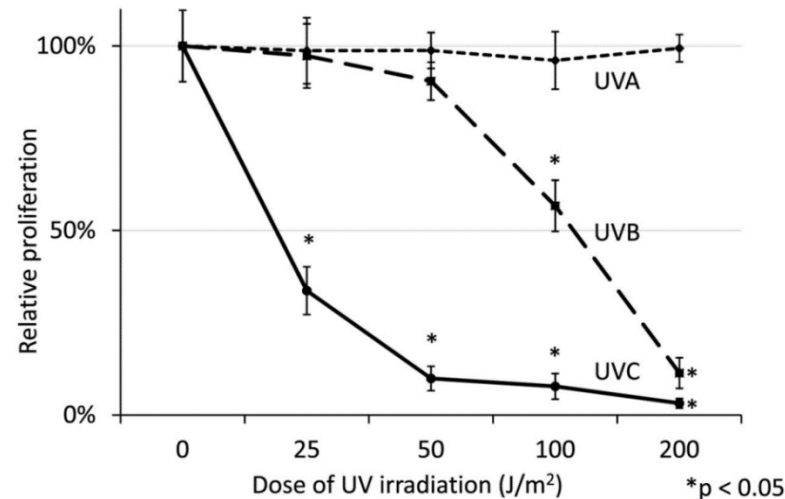
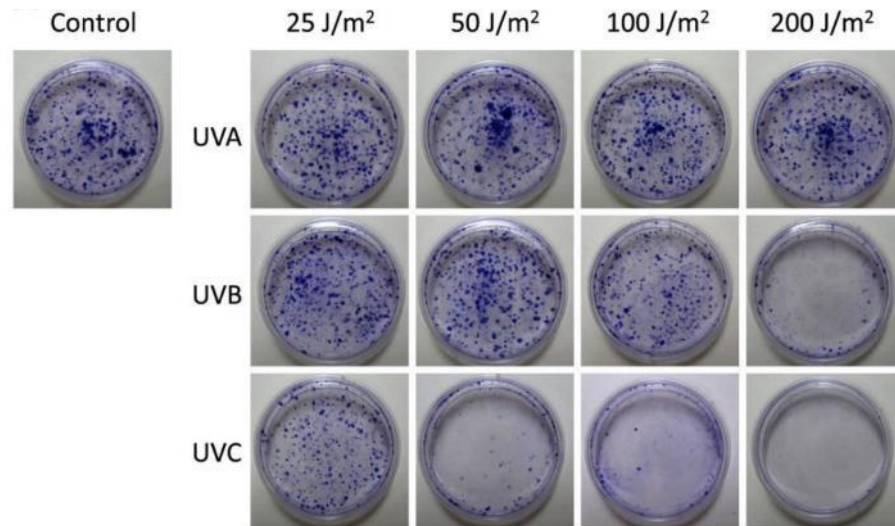
Reference
 $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Pr}$
 $I \sim 4 \cdot 10^6$ cts
QE $\sim 0.2\%$
 $T_{\text{opt}} \sim 400$ K
Mechanism: ETU



Host Material for Pr^{3+}	Emission / nm	Excitation / nm
Ba_2SiO_4	250-360	488 nm
$\text{BaY}_2\text{Si}_3\text{O}_{10}$	255-360	488 nm
$\text{Ca}_2\text{LuSc}_2\text{GaSi}_2\text{O}_{12}$	280-400	488 nm
$\text{Ca}_2\text{Al}_2\text{SiO}_7$	255-360	488 nm
$\text{CaLi}_2\text{SiO}_4$	240-350	488 nm
$\text{Ca}_2\text{Sc}_2\text{Si}_3\text{O}_{12}$	298-400	488 nm
KYSiO_4	265-400	488 nm
LiYSiO_4	255-400	488 nm
$\text{Lu}_3\text{Al}_5\text{O}_{12}$	280-400	488 nm
$\text{Lu}_3(\text{Al,Ga})_5\text{O}_{12}$	280-400	488 nm
$\text{Lu}_3\text{Al}_3\text{Sc}_2\text{O}_{12}$	280-400	488 nm
$\text{Lu}_2\text{CaAl}_4\text{SiO}_{12}$	280-400	488 nm
$\text{Lu}_2\text{Si}_2\text{O}_7$	250-360	488 nm
Lu_2SiO_5	250-360	488 nm
NaYSiO_4	255-320	488 nm
$\text{Sr}_2\text{MgSi}_2\text{O}_7$	260-410	488 nm
$\text{Sr}_3\text{MgSi}_2\text{O}_6$	280-410	488 nm
Y_2SiO_5	255-355	488 nm

6. UV-C Filter Materials

For Indoor Illumination Involving UV-C Radiation

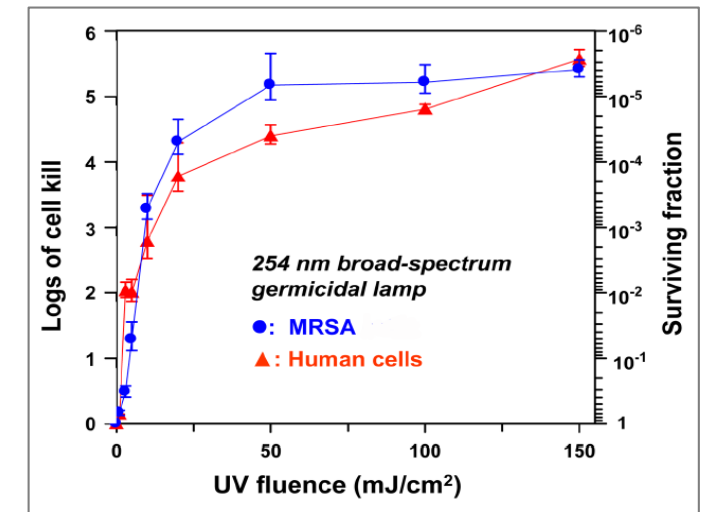
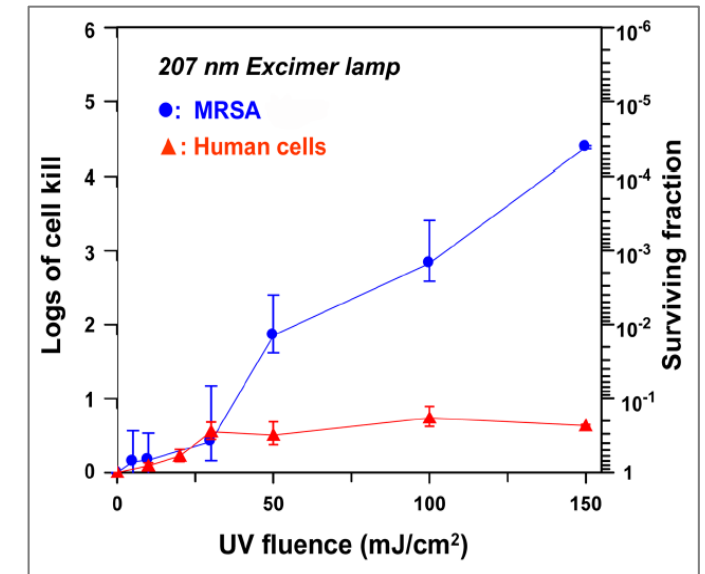


	Penetration characteristic	Damage conferred
UV-C	Penetrates cell membranes/cell walls	mainly DNA damage
UV-B	Most responsible for sunburns. Penetrates deeper than UV-C, but is typically adsorbed by the skin's stratum corneum (dead cell layer)	DNA and other cell components by generation of free radicals
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



6. UV-C Filter Materials

Motivation: Indoor Illumination Involving UV-C Radiation

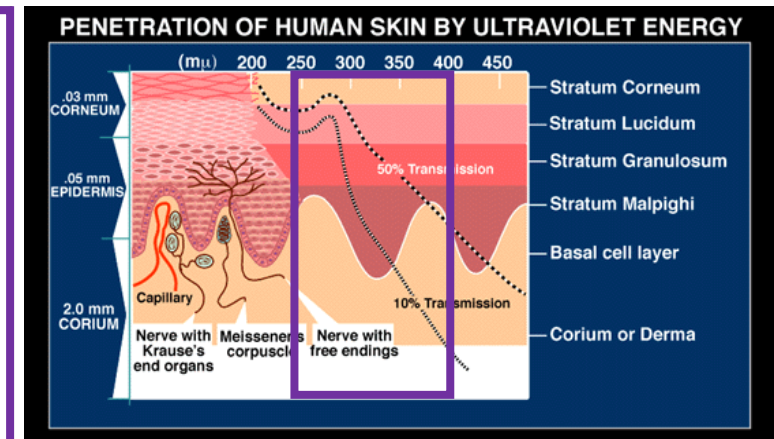
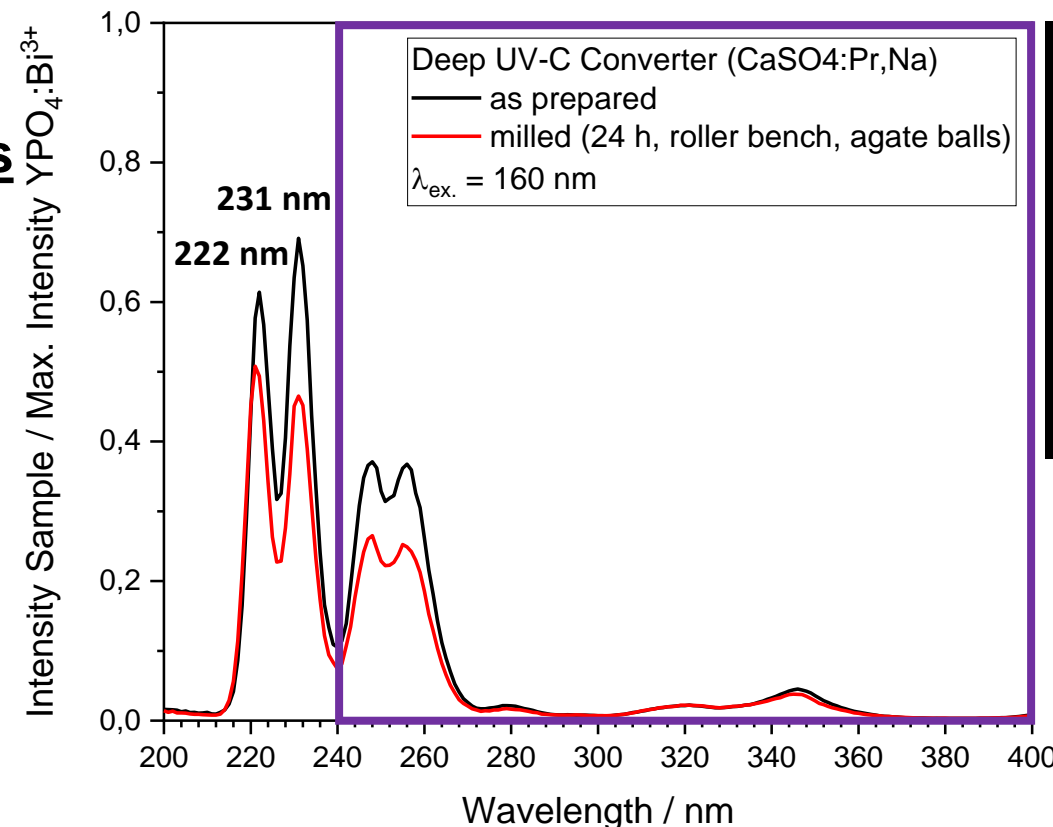
Idea: Use of Xe_2^* excimer discharge lamps with suitable radiation converter screen (172 nm \rightarrow 222 nm)

Best practice phosphors

$\text{LiYF}_4:\text{Pr}$ 218 nm

$\text{CaSO}_4:\text{Pr}$ 222 nm

$\text{LuPO}_4:\text{Pr}$ 232 nm

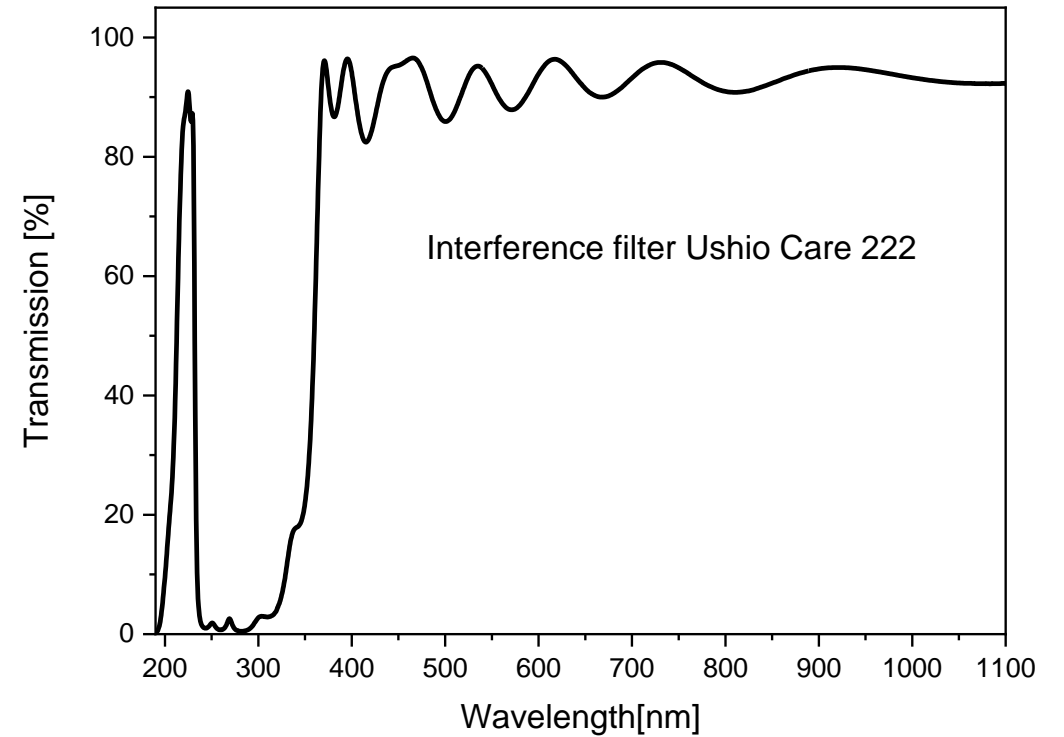
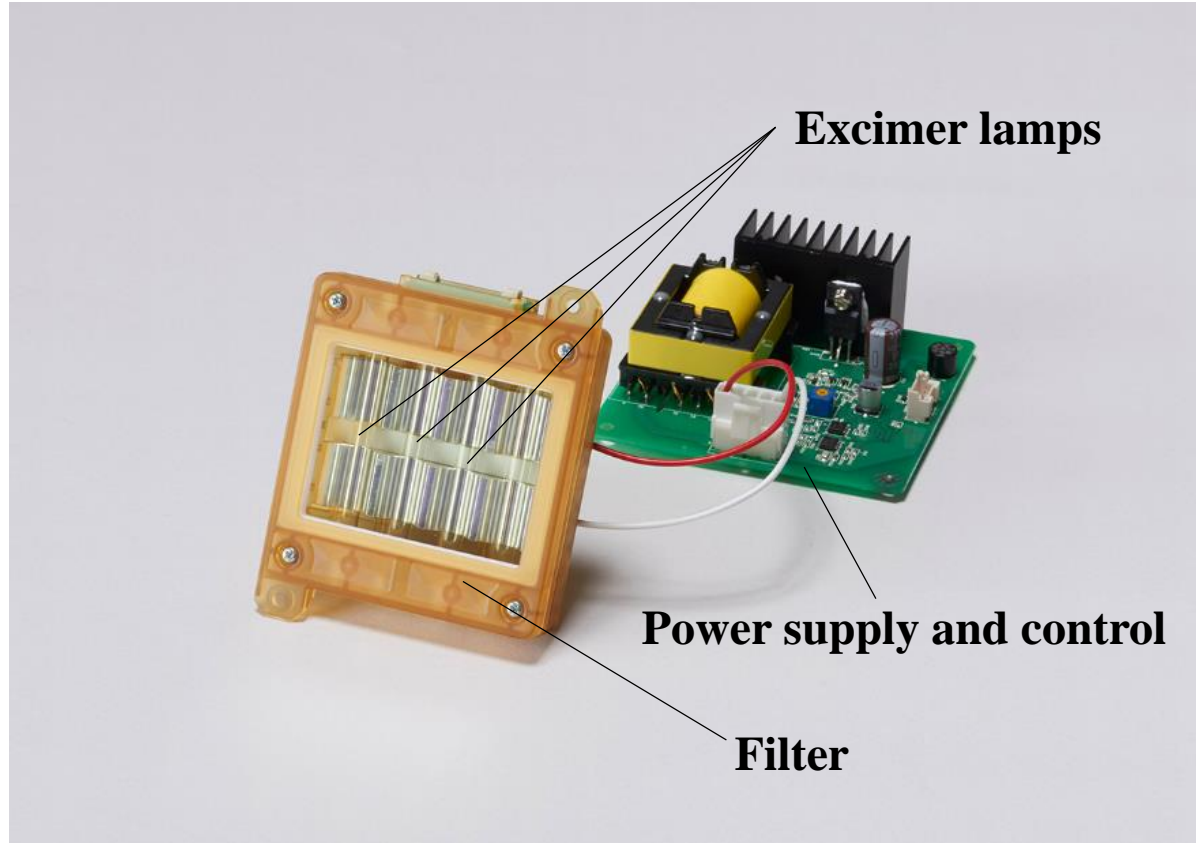


Desired UV filter

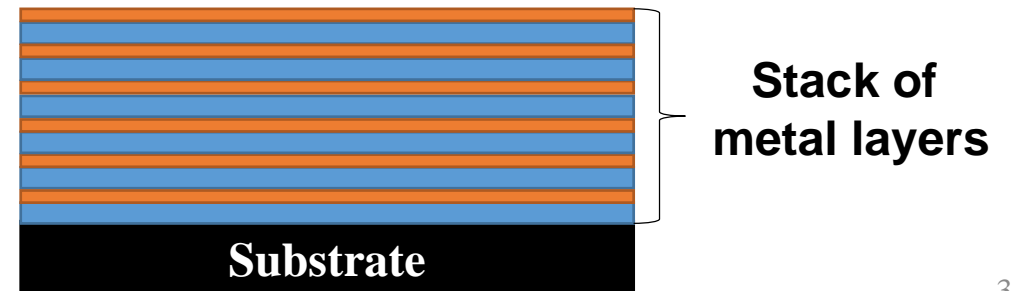
Challenge: A filter for 240 – 400 nm radiation is required

6. UV-C Filter Materials

Components of Care222® Ushio



Sketch of the applied interference filter

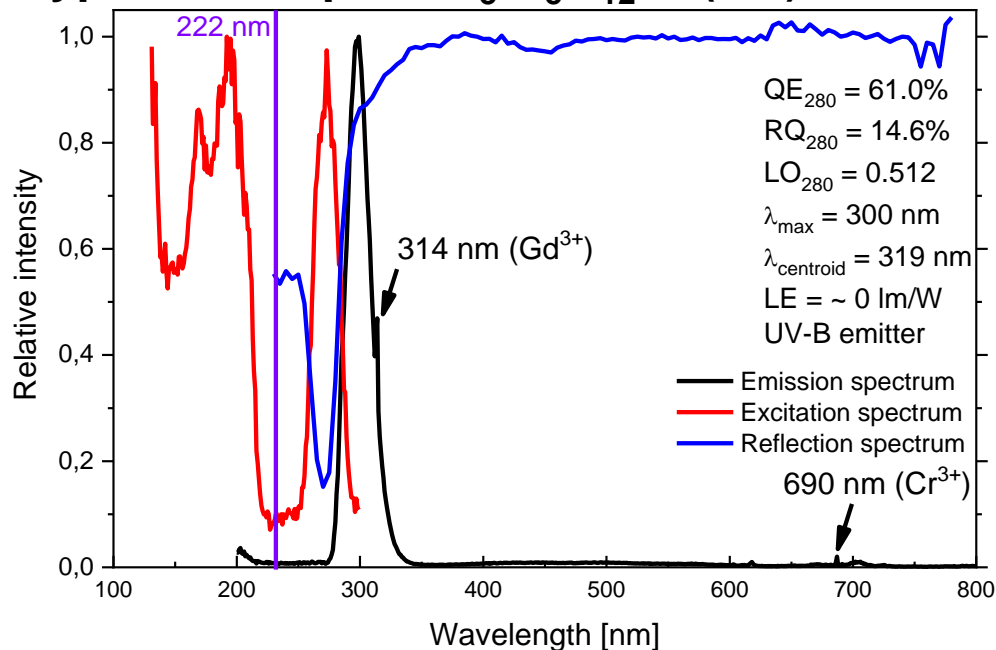


6. UV-C Filter Materials

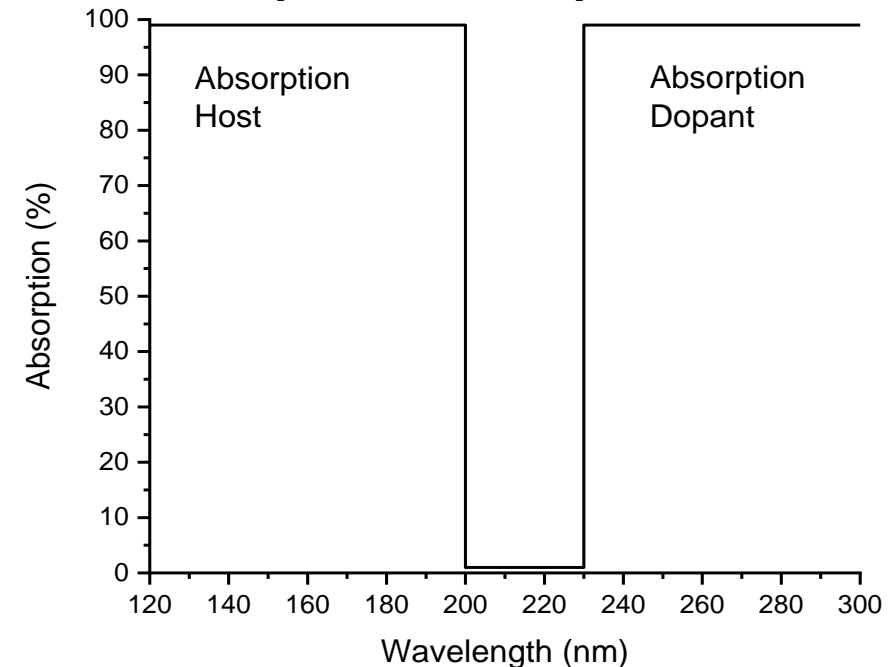
Alternative filter: Absorption pigment with suitable band gap and long edge absorbing dopant

- Host material with absorption edge at 190 to 200 nm (6.2 - 6.4 eV)
- Activator with high absorption cross section between 250 and 300 nm
- s²-Ion Bi³⁺: [Xe]4f¹⁴5d¹⁰6s² → [Xe]4f¹⁴5d¹⁰6s¹6p¹ interconfigurational transition

Typical example: Lu₃Al₅O₁₂:Bi(1%) “LuAG:Bi”



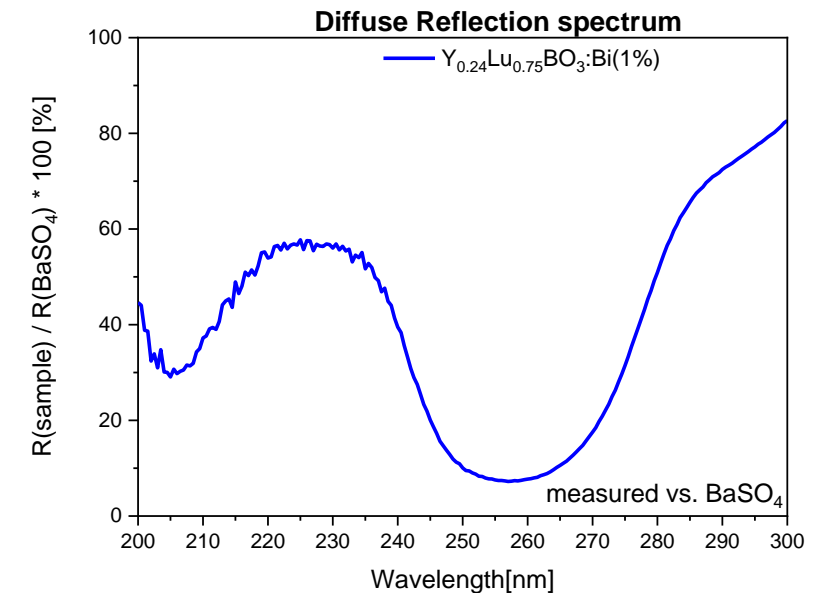
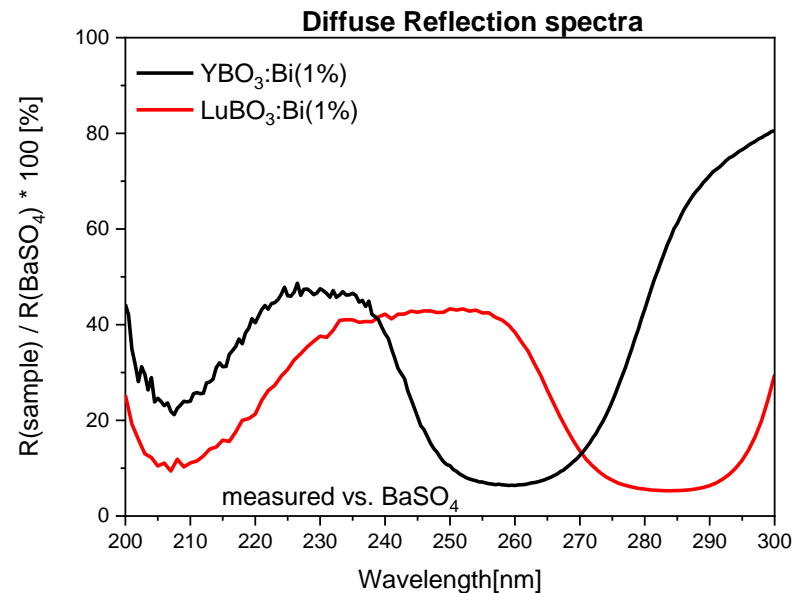
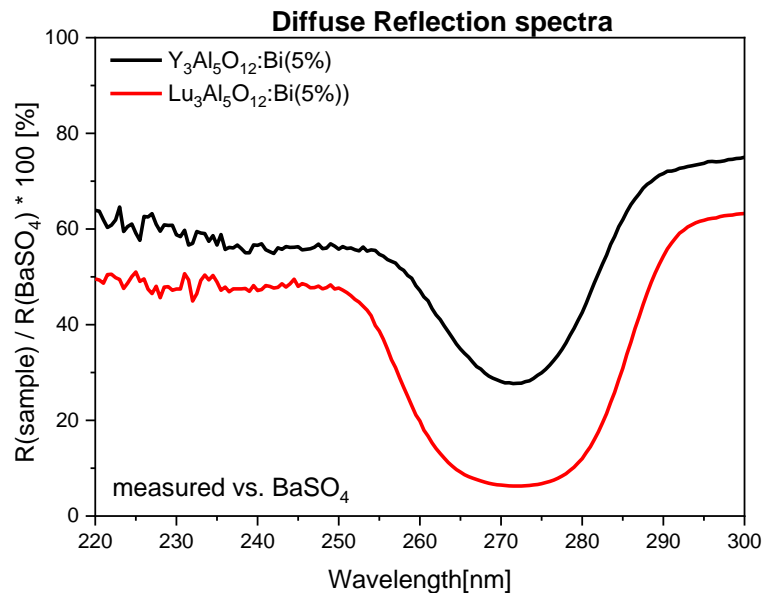
Optimal filter spectrum



6. UV-C Filter Materials

State-of-the-Art: Bi³⁺ Doped ortho-Borates

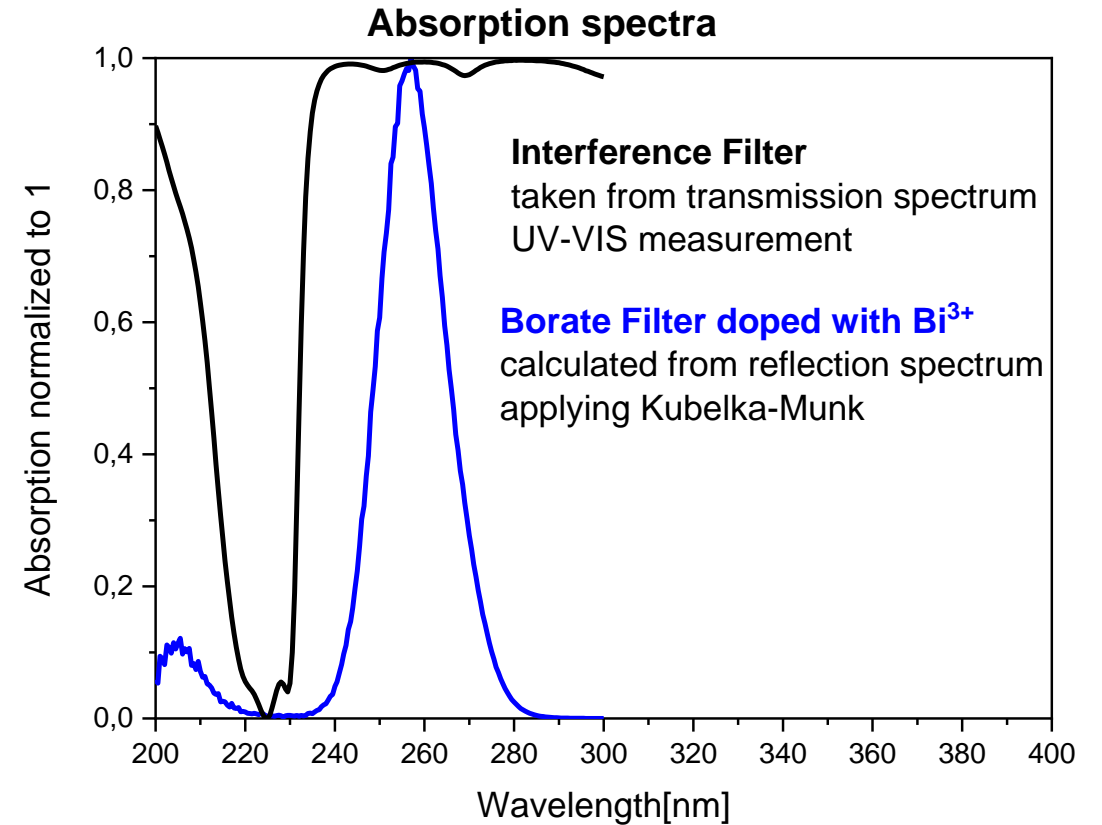
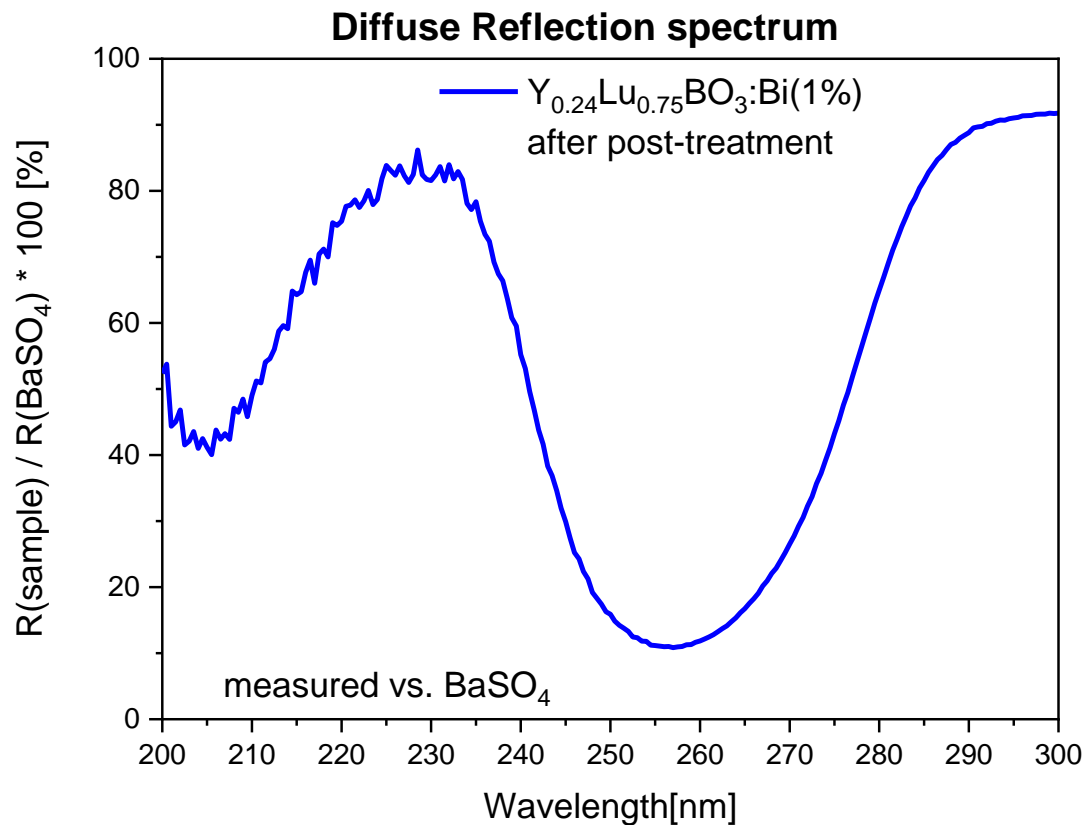
- Garnets absorption is too red-shifted and thus not suitable
- (Y,Ln)BO₃:Bi³⁺ crystallising in the pseudo-vaterite structure (Ln = Sc, Nd – Lu)
- (Lu,Ln)BO₃:Bi³⁺ crystallising in the calcite structure are not suitable



6. UV-C Filter Materials

Optimisation of $(Y,Lu)BO_3$ Doped with Bi^{3+}

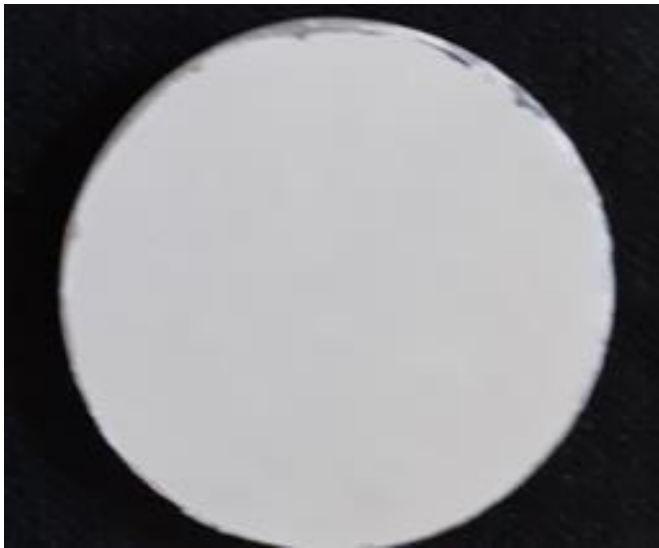
Reflectance could be increased by the application of a post-treatment, viz. a washing process



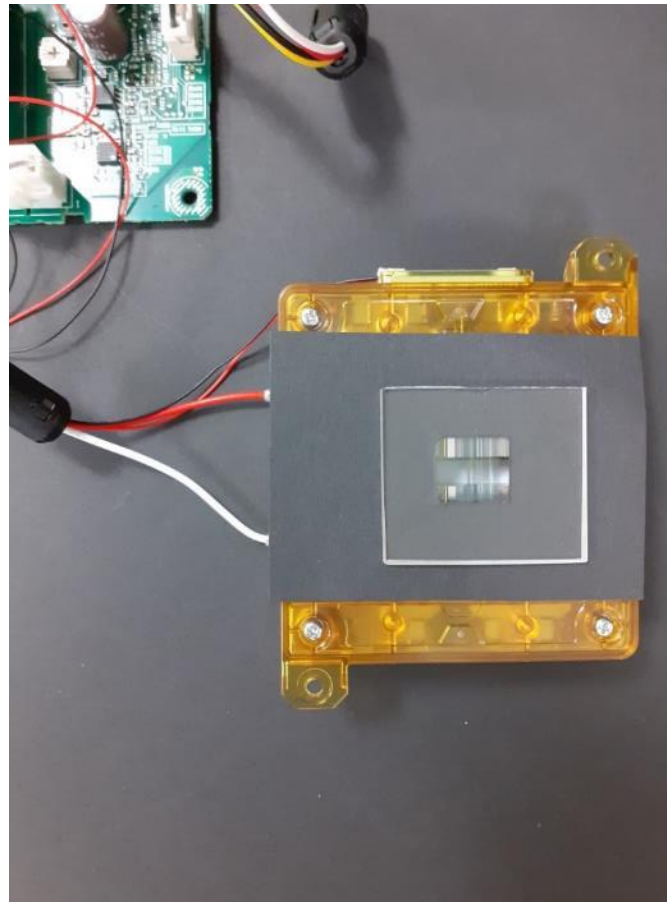
6. UV-C Filter Materials

Application of $(Y,Lu)BO_3$ Doped with Bi^{3+}

Coated quartz slides were used for spectroscopic characterisation



Finished Coating



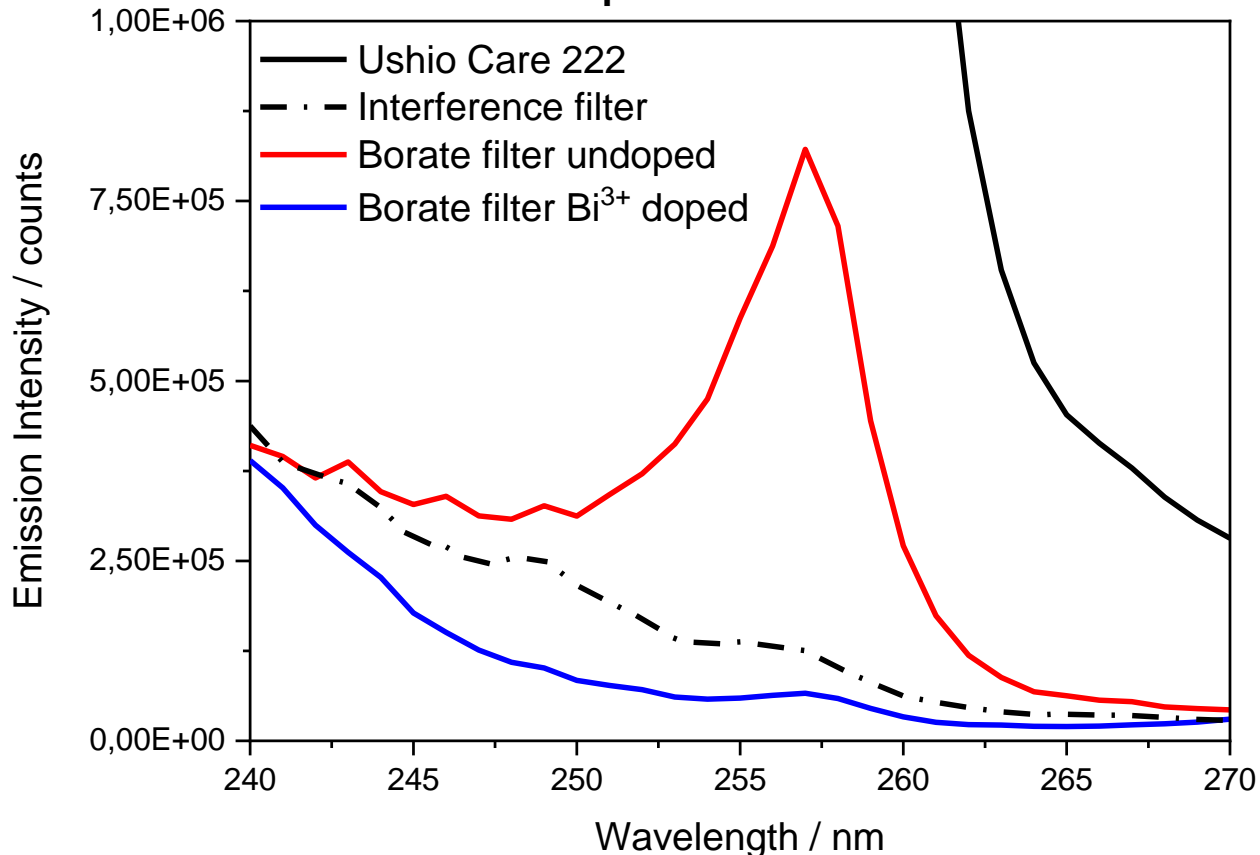
- For transmission spectroscopy, the interference filter was removed from a Ushio Care 222 lamp
- The lamp was covered by a black piece of polycarbonate (PC)
- The sample was placed on top of the PC

6. UV-C Filter Materials

Application of (Y,Lu)BO₃ Doped with Bi³⁺

Coated quartz slides were used for spectroscopic characterisation

Emission spectra Ex Care 222

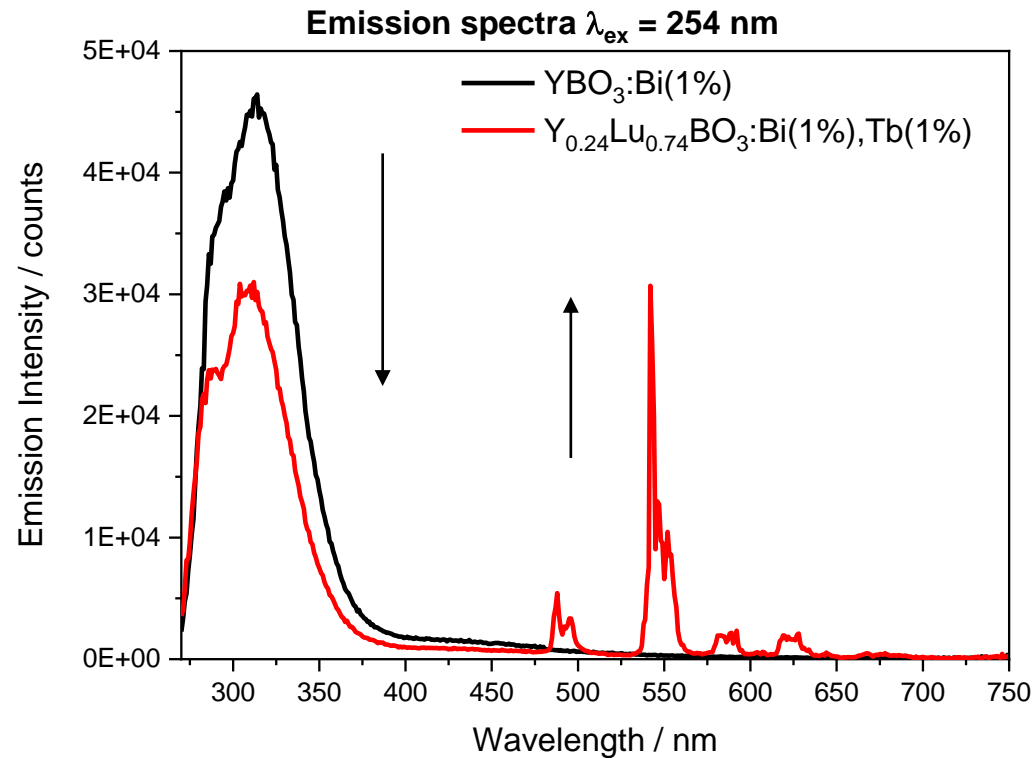


Results

- The Bi³⁺ doped (Y,Lu)BO₃ filter shows the strongest reduction of the undesired emission between 240 and 270 nm
- Strong scattering also reduces the overall 222 nm intensity

6. UV-C Filter Materials

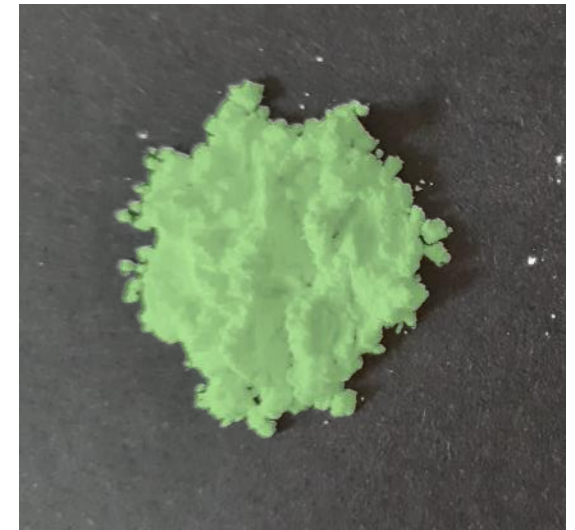
Energy Transfer to Shift Harmful Bi^{3+} UV-B Emission to Lower Energy (VIS or NIR)



The $\text{Bi}^{3+} \rightarrow \text{Tb}^{3+}$ energy transfer reduces the UV-B emission of Bi^{3+} and yields green Tb^{3+} emission



$\text{Y}_{0.24}\text{Lu}_{0.74}\text{BO}_3:\text{Bi}^{3+}$
under 254 nm excitation



$\text{Y}_{0.24}\text{Lu}_{0.74}\text{BO}_3:\text{Bi}^{3+},\text{Tb}^{3+}$
under 254 nm excitation

Other ET schemes

$\text{Bi}^{3+} \rightarrow \text{Eu}^{3+}$ red emission, ET efficient but CT band of Eu^{3+} in the UV-C

$\text{Bi}^{3+} \rightarrow \text{Nd}^{3+}$ NIR emission, but ET not efficient

$\text{Bi}^{3+} \rightarrow \text{Ho}^{3+}$ NIR emission, ET efficient

7. Summary

Deep UV-C Emitting Radiation Sources

- | | | | |
|---|--------------|-------------|------------|
| · LEDs or laser diodes | 230 - 240 nm | lifetime? | |
| · 450 nm LEDs or laser diodes + deep UV-C up-converter | 225 nm | efficiency? | |
| · Excimer discharge lamp | KrBr* | 207 nm | side bands |
| | KrCl* | 222 nm | side bands |
| · Xe ₂ * Excimer discharge lamp + deep UV-C phosphor | 200 - 240 nm | side bands | |
| · x-ray tube + deep UV-C phosphor | 200 - 240 nm | | |
| · Cathode-ray tube + deep UV-C phosphor | 200 - 240 nm | | |

7. Summary

Deep UV-C Emitting Conversion Materials / Filter for KrCl* discharge lamps

Conversion materials

- Suitable activator ions are Pr^{3+} , Bi^{3+} , and Sc^{3+} , however, broad band emission is not limited to 200 – 240 nm, thus a filter is required yet
- Phosphor must be long-term stable upon VUV, x-ray, or electron excitation

Filter for KrCl* excimer discharge lamps

- Wide band gap and radiation hard host material required
- Absorption at the low energy edge cannot be achieved by the band edge
→ dopant is required
- Most suitable dopant is Bi^{3+} in borates, which emits in the UV-B/A range
- UV-B/A emission can be suppressed by energy transfer due to a co-dopant, e.g. Tb^{3+} or other NIR emitting RE ions

Application areas

- | | |
|---|--------------|
| • TOC removal (herbizides, hormones, pharmaceuticals, PFAS) | < 250 nm |
| • Indoor air disinfection | 200 – 240 nm |
| • Nitrate decomposition | < 240 nm |
| • Photocatalytical synthesis at RT | 200 – 240 nm |



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 $\text{LaB}_3\text{O}_6:\text{Gd,Bi}$, $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Pr}$, $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Gd}$, $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Pr}$, and $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Gd}$, *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 $\text{Li}_2\text{SrSiO}_4$: An efficient visible-ultraviolet C up-conversion phosphor, *Ceramics International* 47 (2021) 4858
- F. Schröder, S. Fischer, T. Jüstel, On the concentration dependency of Pr doped $\text{Li}_2\text{CaSiO}_4$, *Austr. J. Chem.* 75 (2022) 760
- J.-N. Keil, H. Kätker, R.T. Wegh, M.P.J. Peeters, T. Jüstel, Novel Bandpass Filter for Far UV-C Emitting Radiation Sources *Optical Materials* 140 (2023) 113866

Internet Links

- Homepage T. Jüstel www.fh-muenster.de/juestel
- Ushio www.ushio.com
- Signify www.signify.com

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