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TOM
Tailored Optical Materials

UV and NIR Emitting Luminescent Materials - Quo Vadis?

Prof. Dr. Thomas Jüstel

FH Münster, FB CIW, RG TOM

MS Teams Online Meeting
February 02nd, 2023

Research Group Tailored Optical Materials

FH Münster University of Applied Sciences
Stegerwaldstr. 39, D-48565 Steinfurt, Germany
Tel: +49-(0)2551-9-62100
Fax: +49-(0)2551-9-62844
E-Mail: tj@fh-muenster.de
Web: http://www.fh-muenster.de/juestel
Skype: thomasjuestel

FH & RG Tailored Optical Materials

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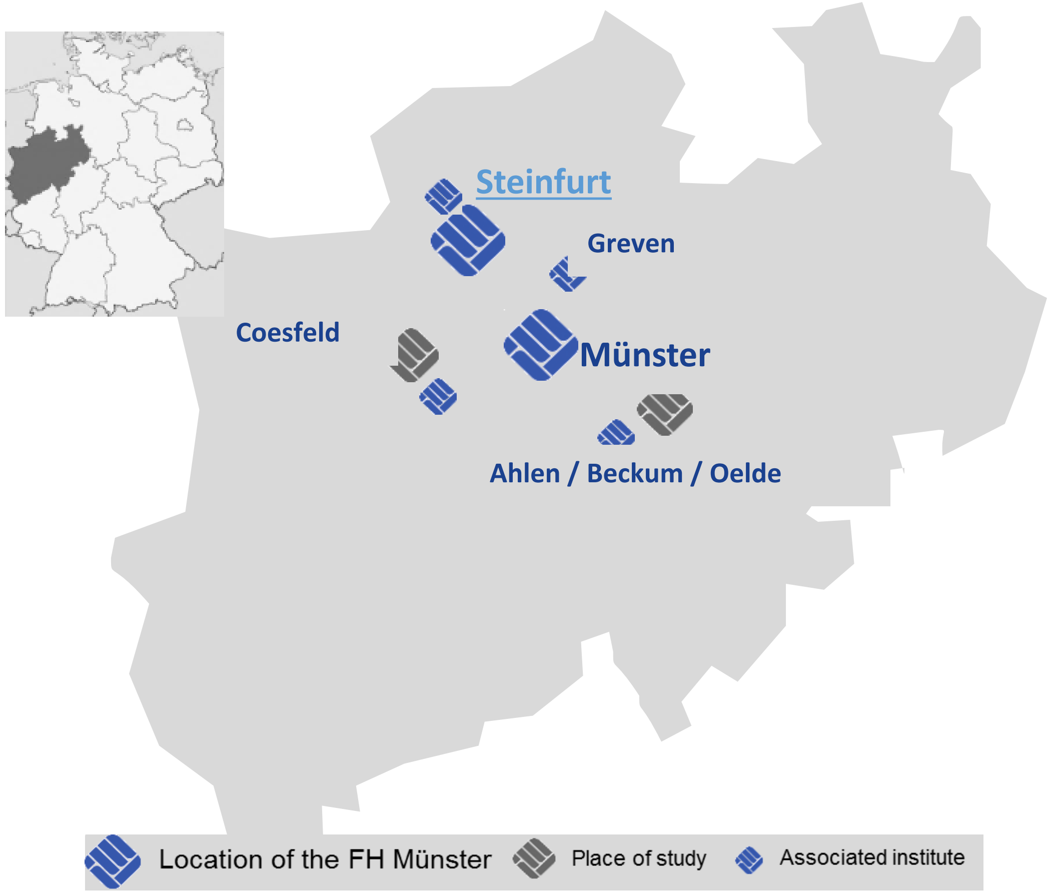


TOM
Tailored Optical Materials

Research areas

- Micro-/Nanoscale Luminescent & Optical Pigments
- Coordination & Solid State Chemistry
- Core-Shell Particles and Coatings
- Photochemistry
- Optical Spectroscopy

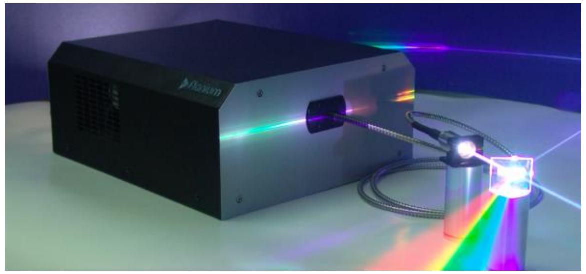
Optical Spectroscopy at RG TOM

Installed EI spectrometers: Temp. & time resolved spectra upon x-ray to NIR excitation

X-Ray Tube Neptune 5200
Voltage Range: 10 - 50 kV
Max. Power: 100 W

Scintillation

Americium source,
α- and γ-Radiation



Up-Conversion

Fianium Supercontinuum SC450-4 White Light Laser, wavelength range 460 nm to 2.4 µm

Down-Conversion

Deuterium bulb, wavelength range 120 to 400 nm

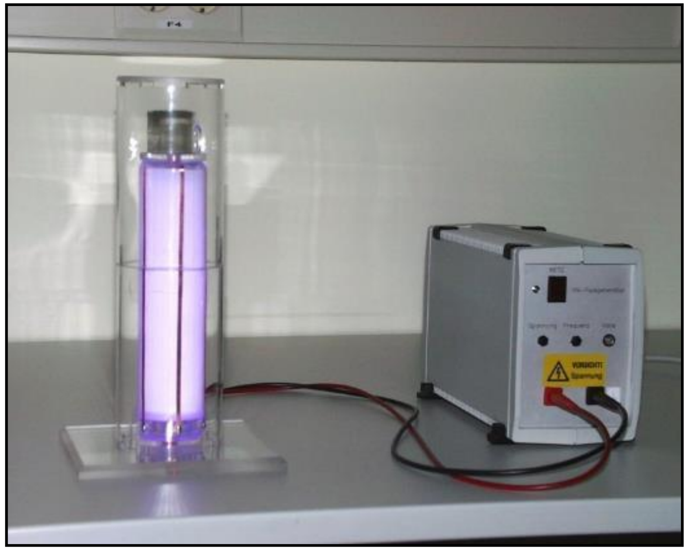
Xenon lamp, wavelength range 200 nm to 900 nm

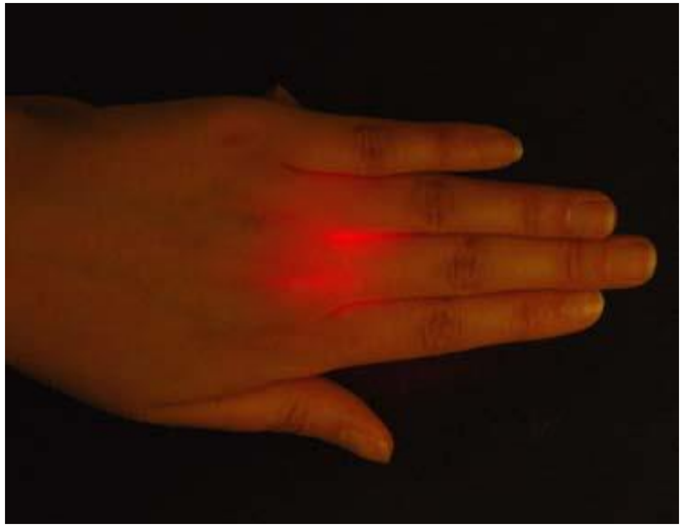
EPL ps Laser, wavelength 265, 375, and 445 nm

Continuous laser, wavelength 375, 405, 445, and 488 nm

Various high power LEDs from 250 to 1100 nm

Contents



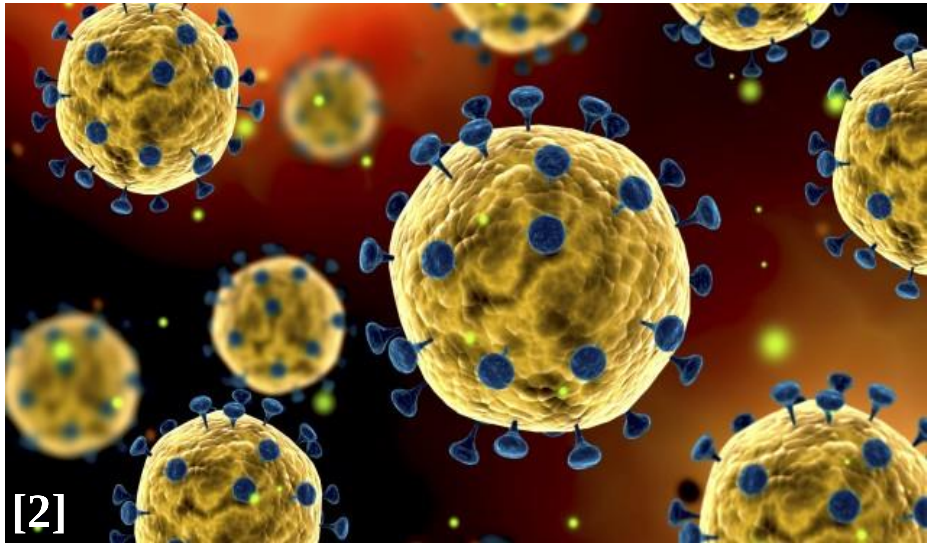


1. Motivation – UV Radiation Sources

Post-antibiotic age, outbreaks, epidemics, and pandemics due to airborne viral diseases

Period	Virus/ -type	Spread	Remarks
1917 - 1920	Spanish flu	Worldwide	Death toll > $1{\cdot}10^{8}$
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 - 2023	SARS-CoV-2	Worldwide	Death toll by 02/23~ $6.8{\cdot}10^{6}$ [3]
Yearly	Influenza	Worldwide	Estimated 290,000 to 645,000 people die each year [1]

Viruses = Volatile nanoparticles often spread by aerosols



Lit.:

[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

[2] Corona-Update: Wie weit ist die Forschung? DAZ.online, 12.03.2020

[3] Worldometer: https://www.worldometers.info/coronavirus/

1. Motivation – NIR Radiation Sources

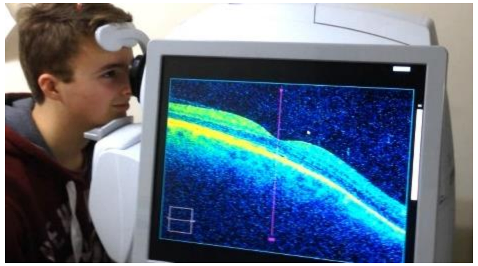
First application of NIR (IUPAC: 780 - 2500 nm) in 1964 by Karl Norris, since then the giant is running strong…..

- **NIR spectroscopy**

Agriculture, astrophysics, food engineering, pharmaceutic science, process monitoring, medical monitoring like pulse oximetry, cancer diagnostic, brain waves interpretation and so on

- **Biosensing & bioimaging**

Optical coherence tomography

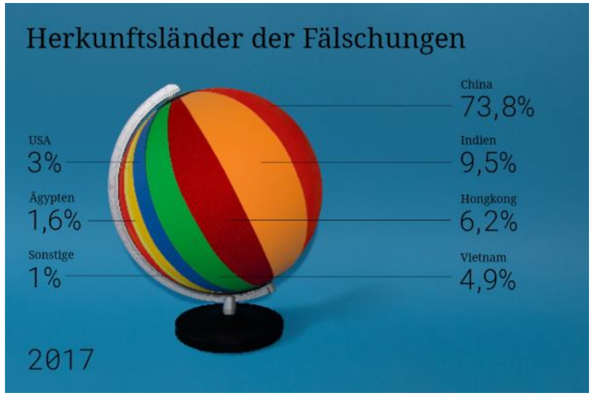


- **NIR illumination**

Active night vision systems, biometric security

1. Motivation – NIR Radiation Sources

Hidden optical markers for anticounter feiting since global product piracy causes more than 50 Bill. USD

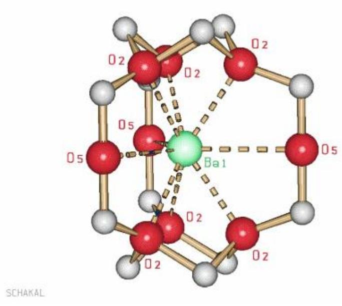


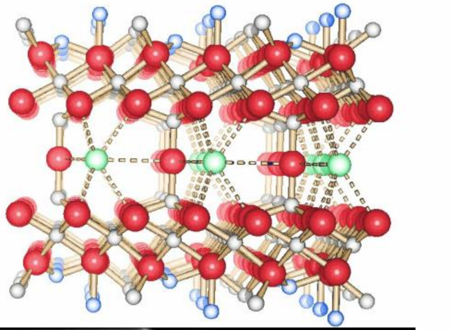
Source: Melina Deschke

Source: www.plagiarius.com

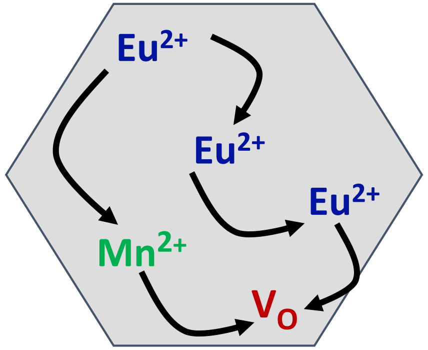
2. Luminescent Materials: Basics

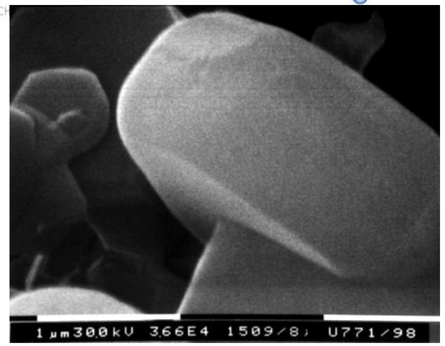
A luminescent material (phosphor) converts absorbed energy into electromagnetic radiation beyond thermal equilibrium





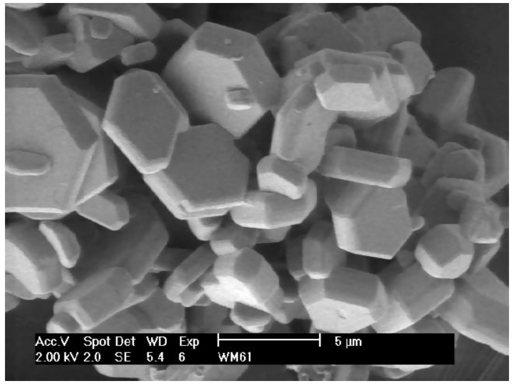
Inorganic host
- Coordination number and geometry
- Symmetry of activator sites
- Optical band gap
- Phonon spectrum

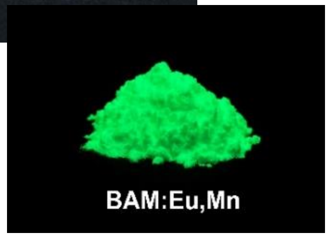




Dopants, co-dopants, and defects → Energy transfer (ET)
- Concentration
- Clustering of activator ions

Particle surface
- Zeta-potential
- Coatings → Light in- and outcoupling



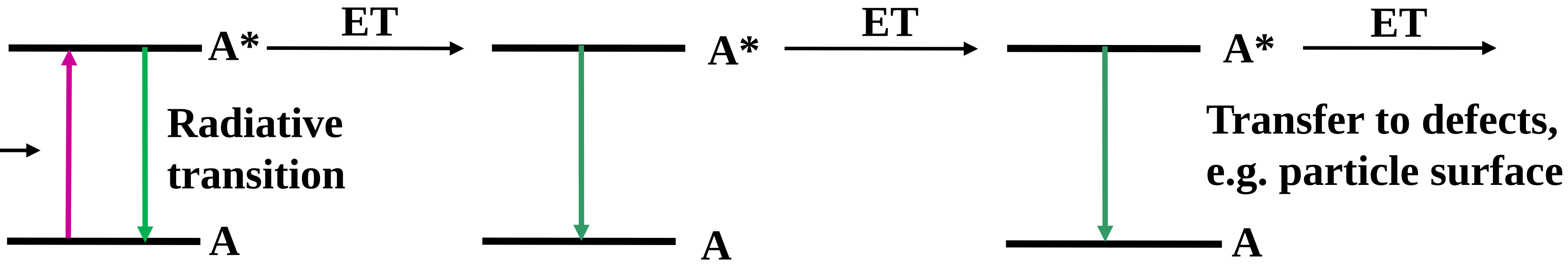


Particle morphology
- Shape & Surface area
- Particle size distribution

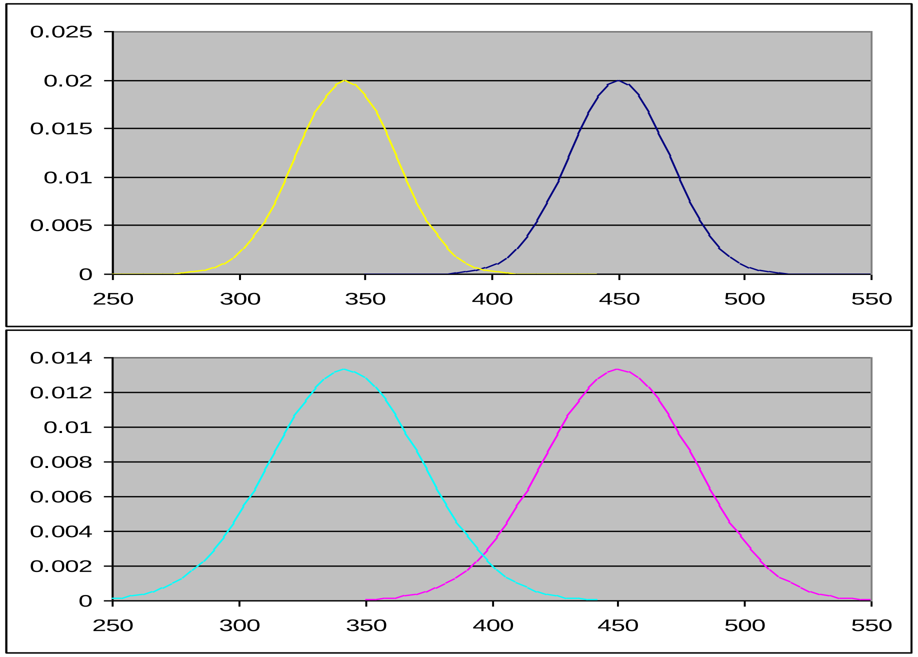
2. Luminescent Materials: Basics

Energy Transfer (ET)

Excitation source & absorption of energy



Typical transfer times ~ $1*10^{-7}$ .... 10^{-8} s



Extent of energy migration depends on

- Distance r(activator – activator)
- Spectral overlap = f(temperature and pressure)
- Radiative decay time of luminescence centres (S or A)

Decay time of radiative transitions

1 - 10 ns	Organic dyes (π-π*), QDots (CB-VB)	
10 - 100 ns	Ce^{3+}, Pr^{3+}, Nd^{3+} (4f-5d)	→ High activator concentration
10 ns - 10 µs	Eu^{2+} (4f-5d), Bi^{3+} (6s-6p)	→ Moderate activator concentration

2. Luminescent Materials: Trends

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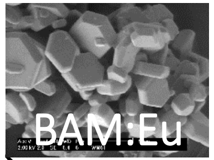
Particle morphology and surface optimization (coatings)

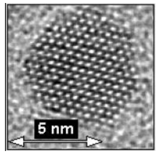
Novel application areas ← → lifetime↑, $T_{1/2}$↑, α↓, λ↑

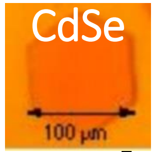
0.1 nm | 1 nm | 10 nm | 100 nm | 1 µm | 10 µm | 100 µm | 1 mm | 10 mm | 100 mm | 1 m

atoms | cluster | nano crystals | micro crystals | single crystals

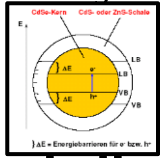


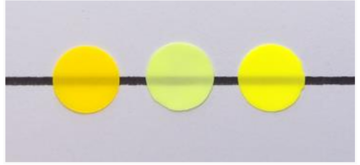
amorphous matter | nano ceramics | ceramics (opaque)



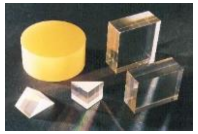


super crystals | ceramics (translucent)





core-shell particles | ceramics (transparent)



Glasses CdSe, $CsPbBr_3$

(bio)marker, µ-LEDs, PV units

$(Y,Tb,Lu)_3Al_5O_{12}$:Ce

$Lu_3Al_5O_{12}$:RE (RE = Ce - Yb)

high power LEDs/laser, scintillators, excimer lamps

2. Luminescent Materials: Trends

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Efficiency: Light sources & displays
→ External quantum yield (EQY)↑
→ µ-particles → ceramics → single crystals

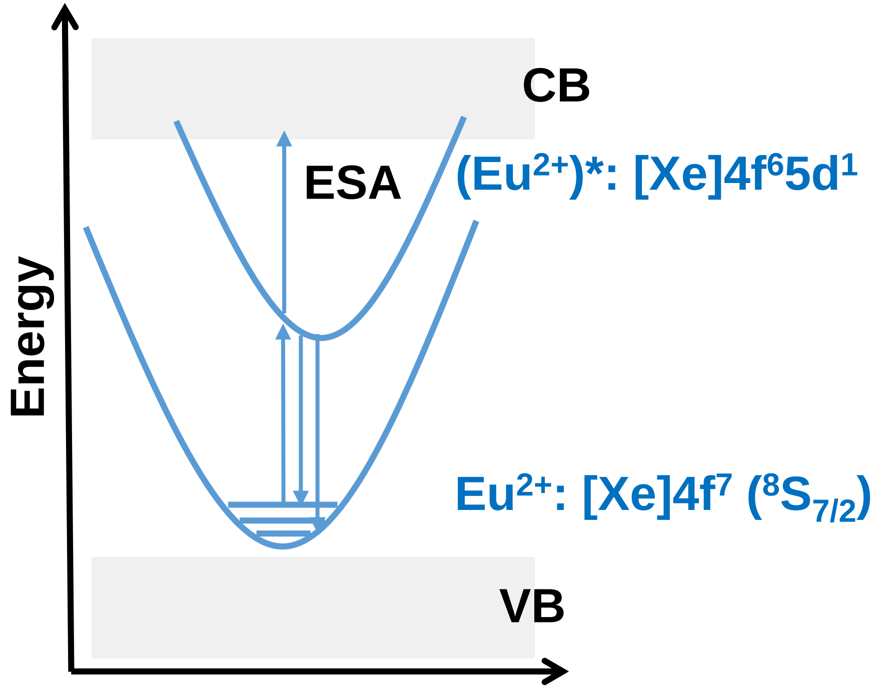
Lifetime: Light sources & displays
→ Defect density↓ and particle coatings

Miniaturisation: µ-LED (displays)
→ PSD↓: Nanocrystals & Quantum Dots
→ Stability↑: Core-shell particles

Power density: High brightness LEDs & laser diodes
→ Decay time & ESA↓ redox stability↑
→ Density of optical center $N_{activator}$ [cm^{-3}]↑

Broad emission spectra: Human centric lighting, NIR sources
→ VIS: (Al,Ga)N LED + cyan, deep red
→ NIR: (In,Ga)N LED + NIR emitter

$$EQY = \frac{\text{Number of emitted photons}}{\text{Number of absorbed photons}}$$



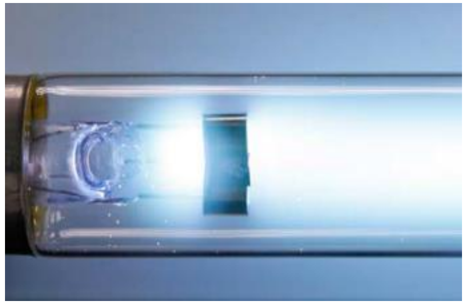
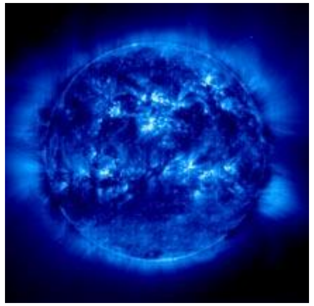
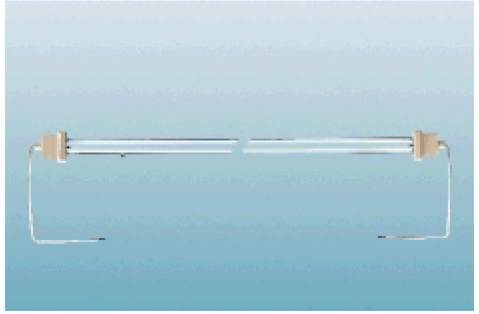
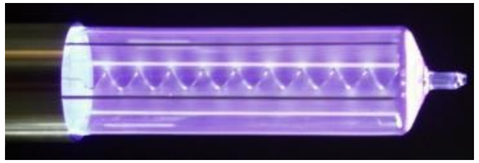
$$P_{em,max} = N_{activator} C_{extraction} R/\tau_r \text{ (R = radius)}$$

Lit.: Brils Modell: A. Bril, Physica 15 (1949) 361

3. UV Radiation Sources

Overview

Solar radiation	**> 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 by $Y_2SiO_5:Pr^{3+}$**

3. UV Radiation Sources

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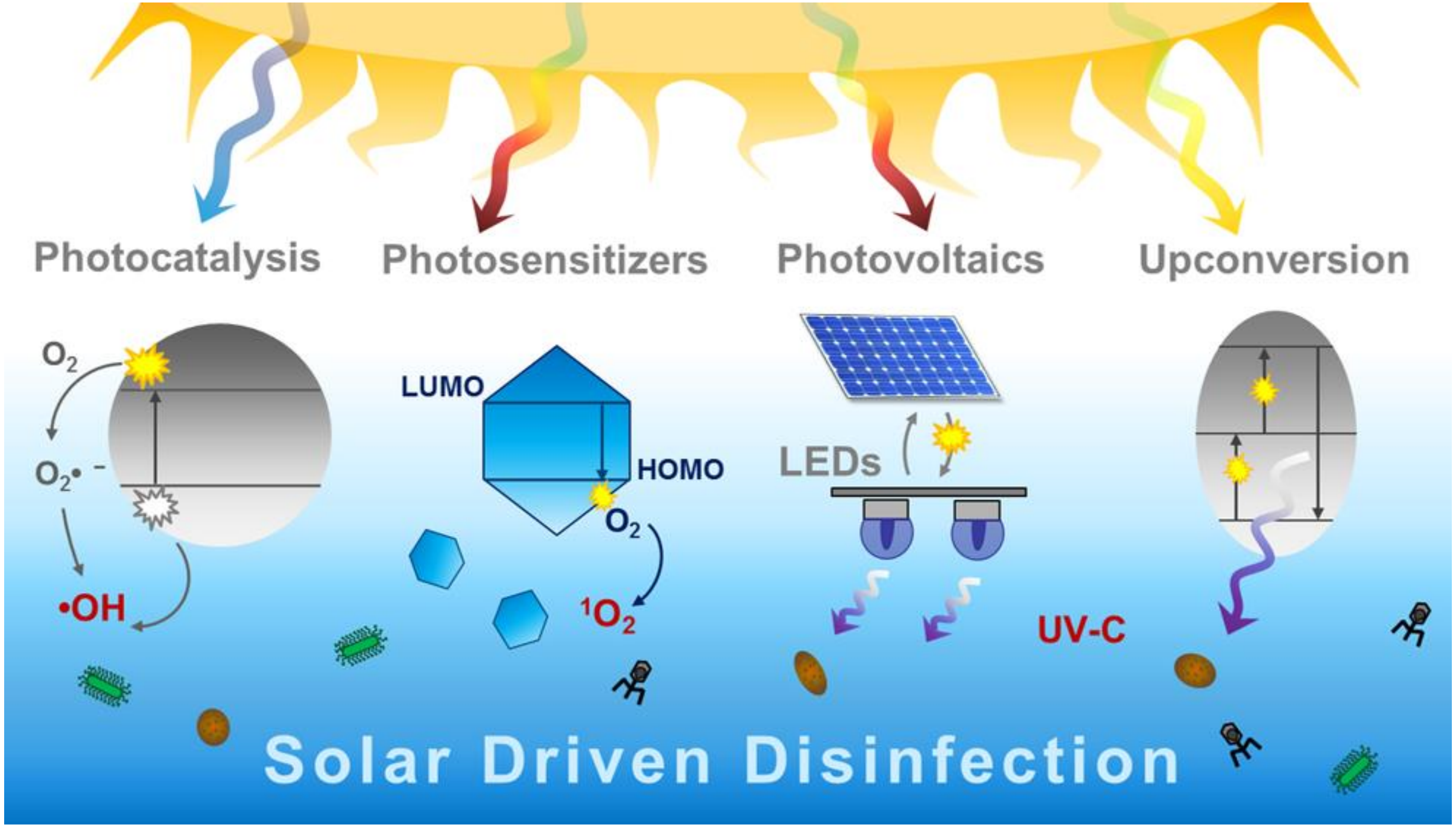
Solar Radiation for Water, Air, and Surface Disinfection

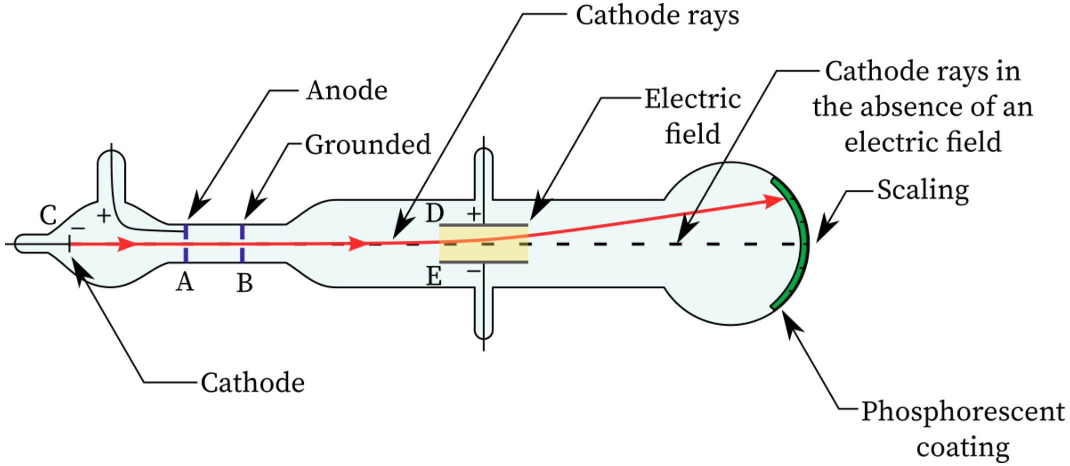


TiO_2 / Titanates W/Mo Cluster* (Al,Ga)N LEDs Pr^{3+} up-converter

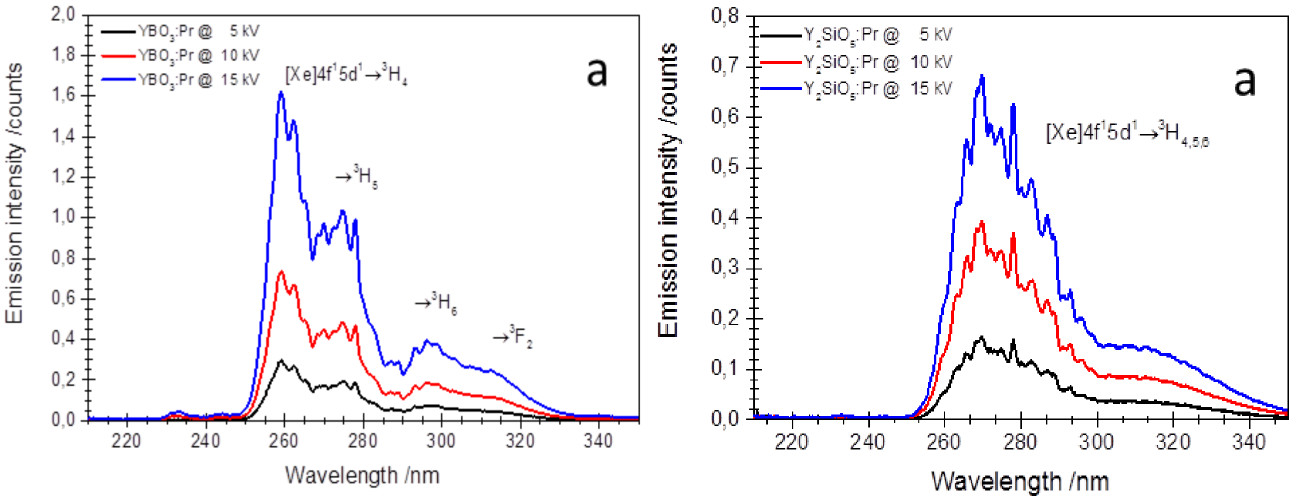
*Lit.: PD properties of tungsten iodide clusters, T. Jüstel, H.-J. Meyer et. al, RSC Advances 10 (2020) 22257

3. UV Radiation Sources

Cathode Ray Tube (CRT) with UV-C Converter YBO_3:Pr or Y_2SiO_5:Pr



YBO_3:Pr and Y_2SiO_5: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.: M. Broxtermann, D. den Engelsen, G.R. Fern, P. Harris, T.G. Ireland, J. Silver, T. Jüstel et al., ECS J. SSST 6 (2017) R47

3. UV Radiation Sources

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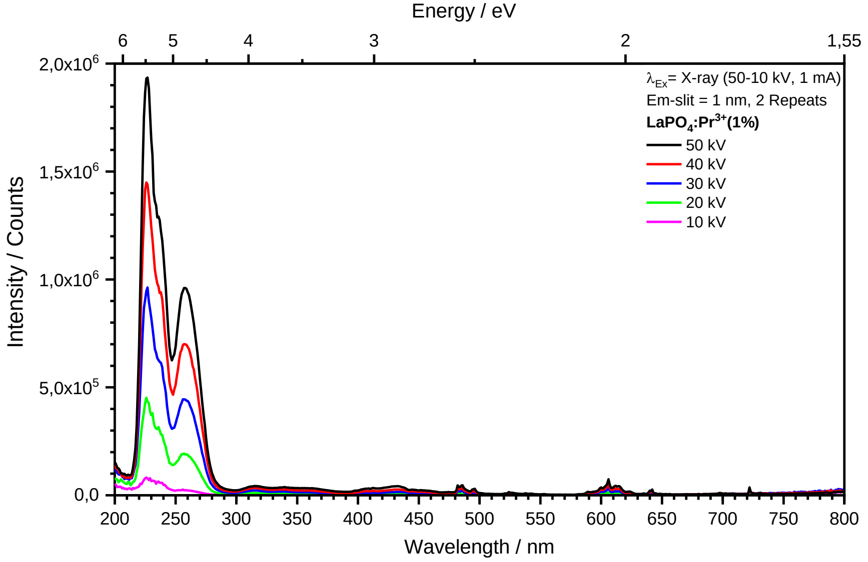
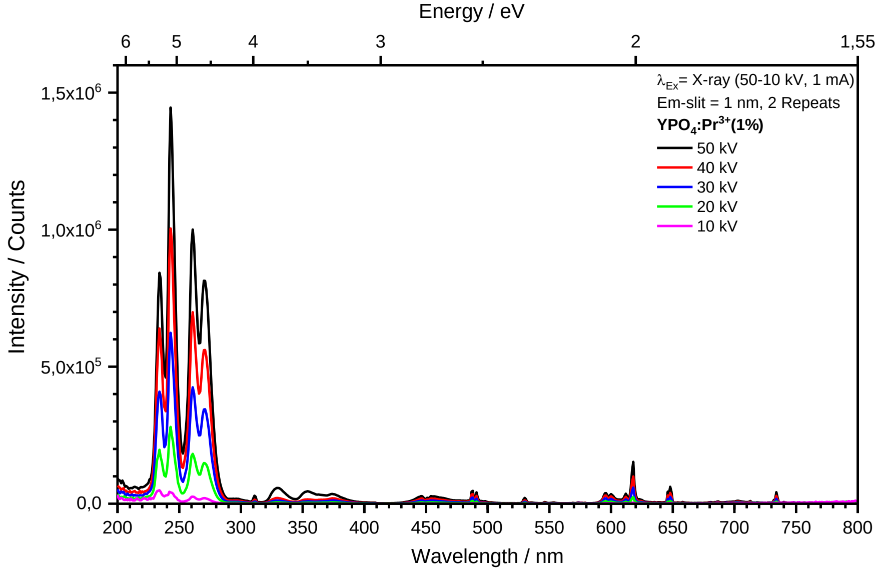
X-ray Tube with UV-C Converter $LaPO_4$:Pr or YPO_4:Pr

$LaPO_4$:Pr upon 10 – 50 keV excitation



YPO_4: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

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

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

3. UV Radiation Sources

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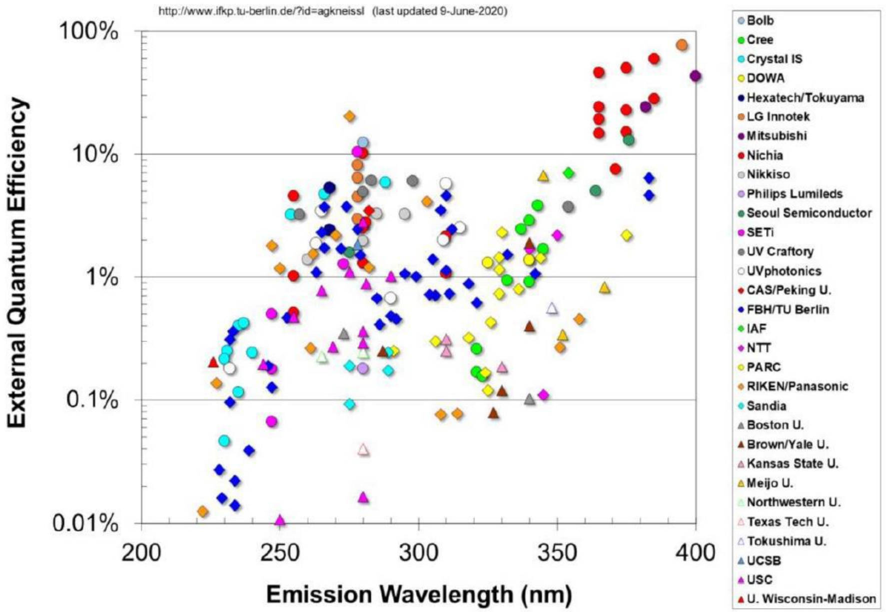
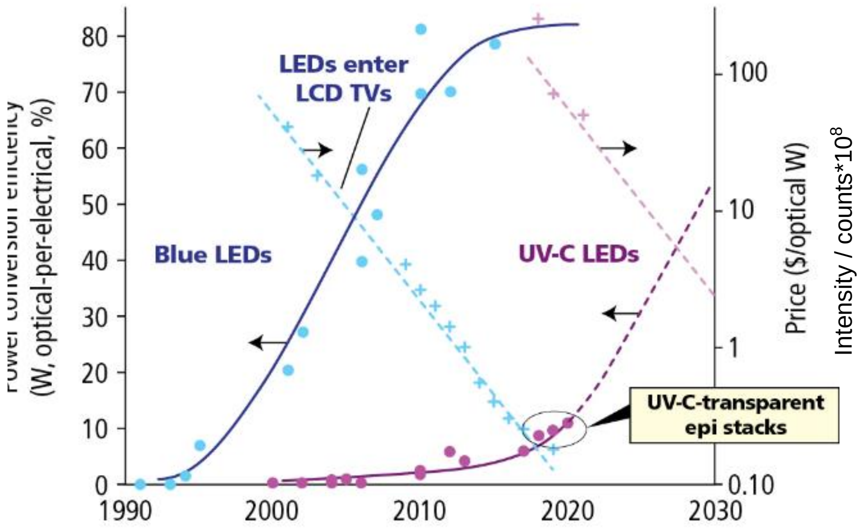
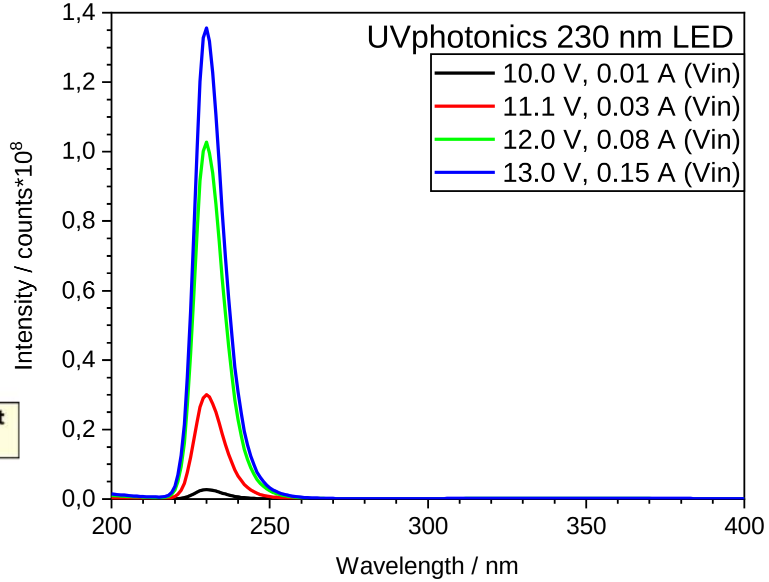
UV Emitting LEDs - Status Quo 2022: WPE ~ 10% at 265 nm[1], WPE ~ 10% at 304 nm[2]







Review of UV LED May 2021

Development goals

- **Internal quantum efficiency ↑**
- **Light outcoupling and WPE ↑**
- **Optical Power ↑**
- **Life time ↑**

UV Photonics, Berlin, 2022

- **230 nm LED**
- **> 100 € LED**

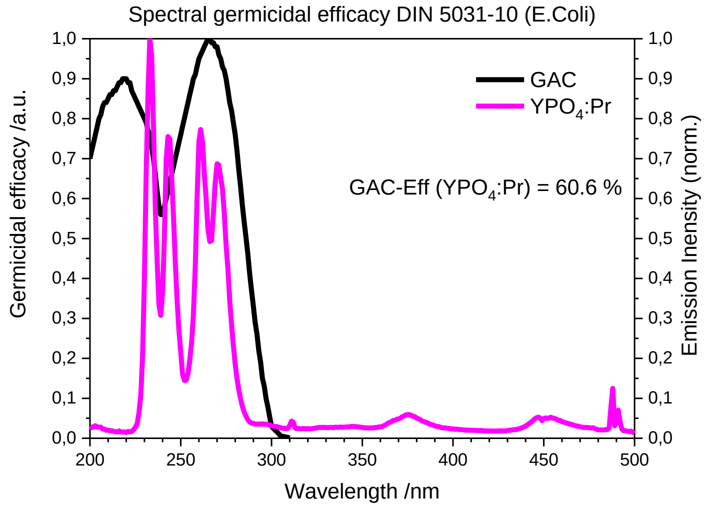
Lit.:
[1] H.-C. Kuo et al., Photonics 8 (2021) 196
[2] H. Hirayama e al., Scientific Reports 12 (2022) 2591

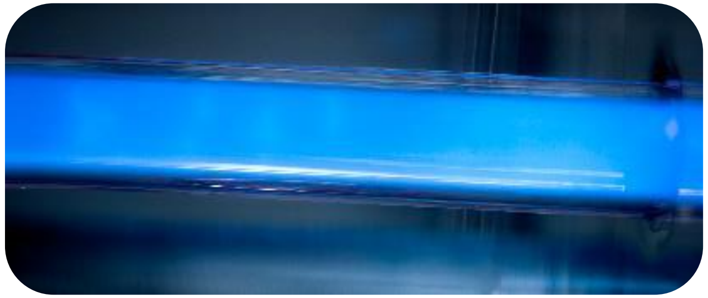
3. UV Radiation Sources

Properties of an „Ideal“ UV Radiation Source

• Highly efficient	η(UV) > 20%	minimal cost of operation
• UV-C spectrum	UV disinfection	λ ~ 260 nm → optimal efficacy according to GAC
	H_2O_2 activation	200 nm < λ < 300 nm
	Human skin safe	λ < 230 nm ?

- Low investment and maintenance costs
- High power (fewer lamps, minimal initial investment)
- Long life time (minimal operation and maintanance costs)
- Mercury free (UNEP Minamata Convention on Mercury 2017)



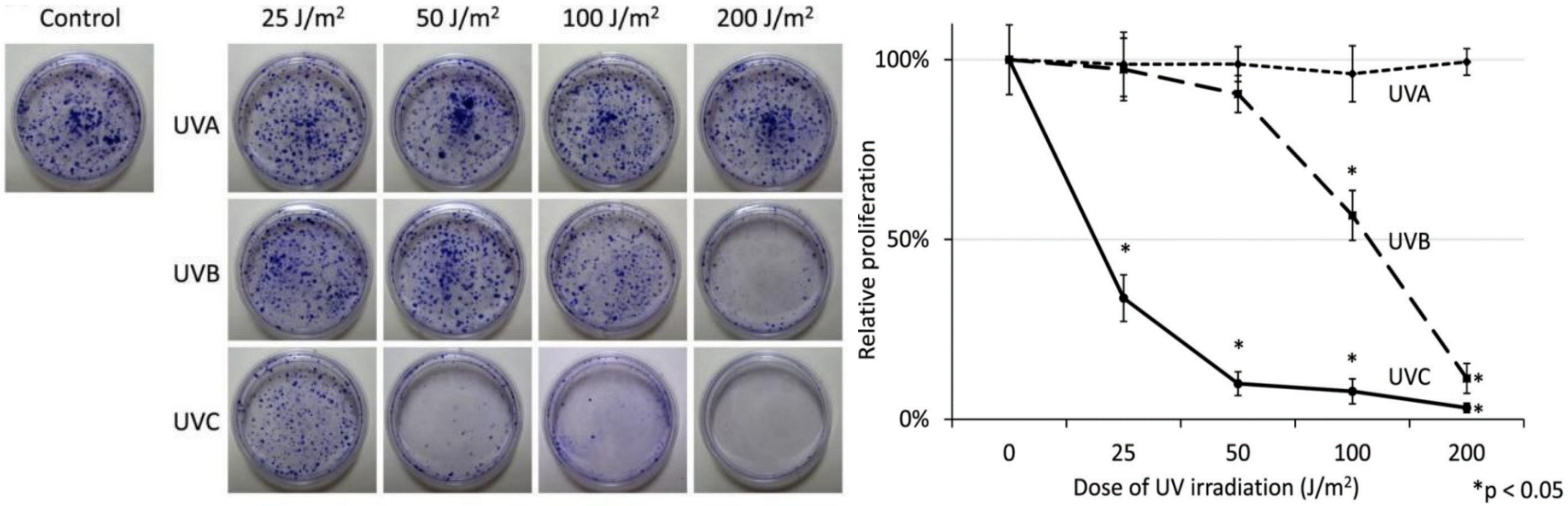


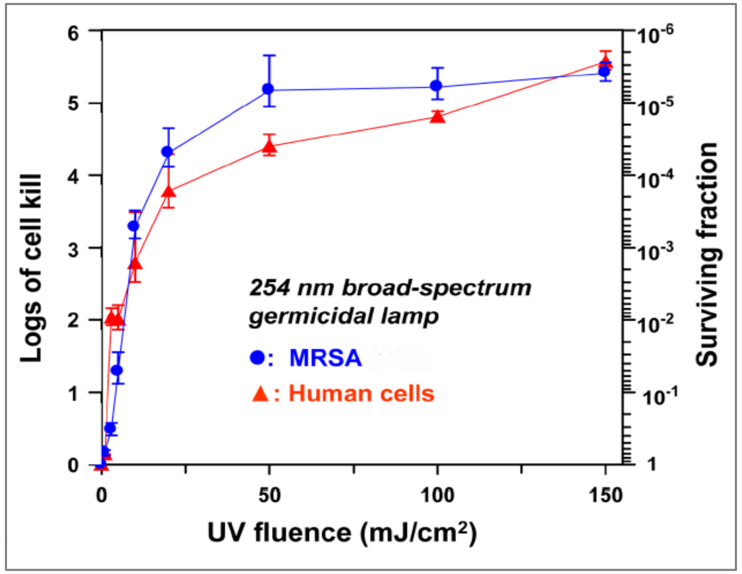
Lit.:

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
M. Broxtermann, T. Dierkes, L.M. Funke, M. Salvermoser, M. Laube, S. Natemeyer, N. Braun, M.R. Hansen, T. Jüstel, J. Lumin. 200 (2018) 1
M. Broxtermann, S. Korte, T. Jüstel, J. Business Chem. 14 (2018) 106

3. UV Radiation Sources

Motivation: Disinfection and medical treatment (cancer & inflammations)





	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

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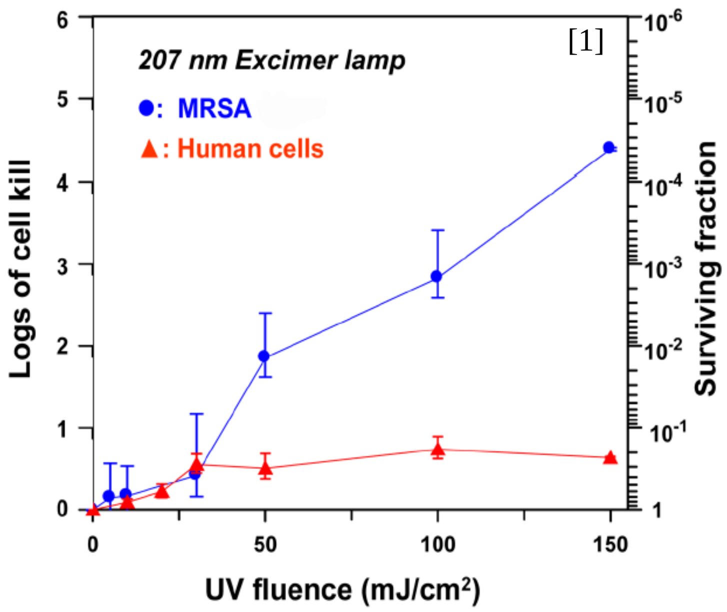
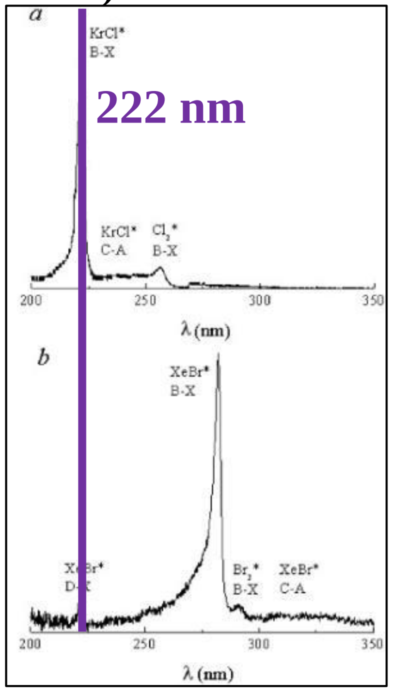
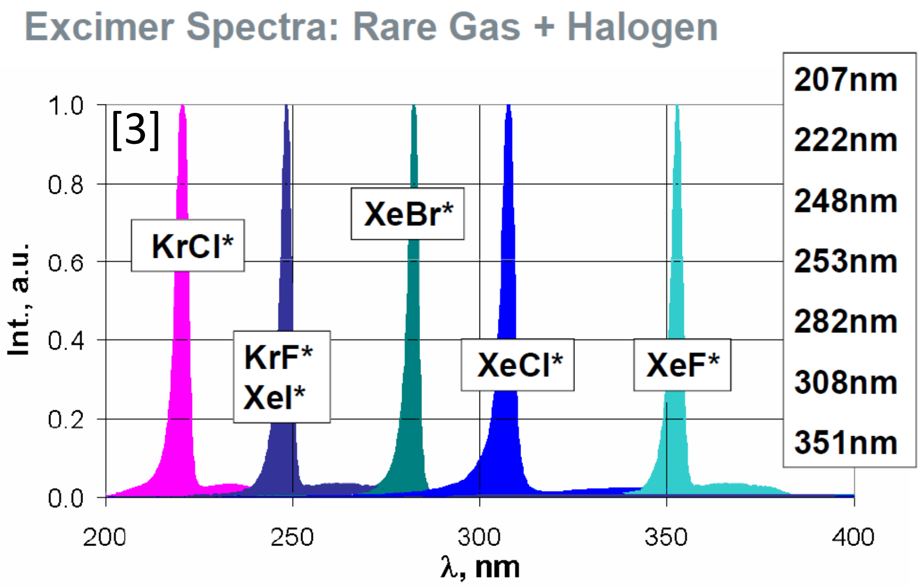
Indoor Air Disinfection with Deep UV-C

- 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 [2]
- Alternative: KrCl* excimer discharge (222 nm) shows undesired spectral features" above 230 nm (Cl_2*)





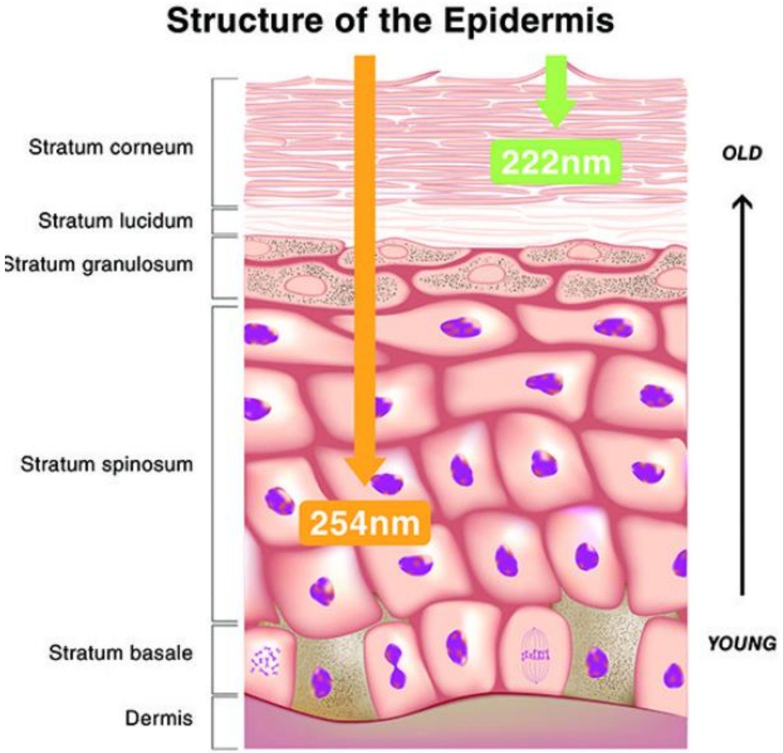


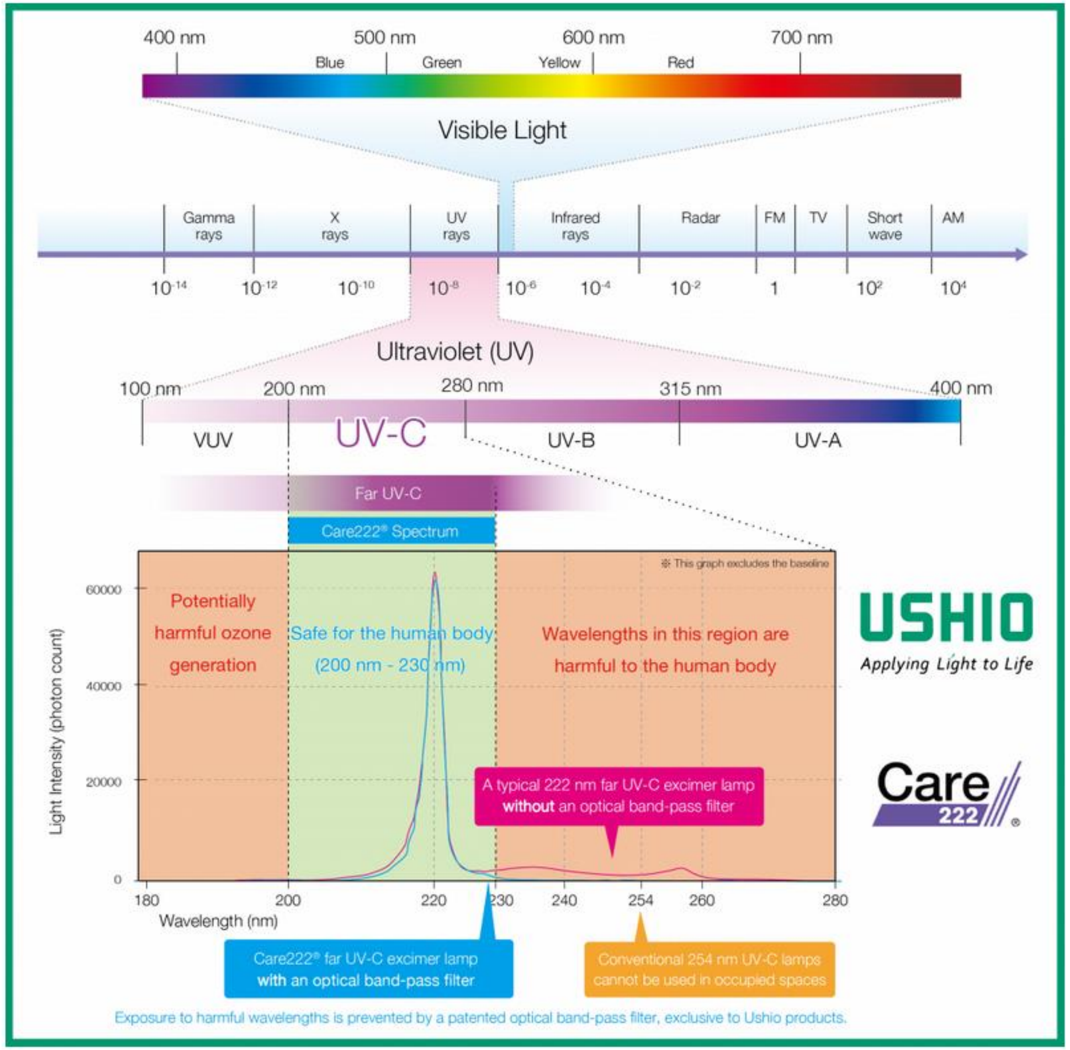
Lit.: [1] D.J. Brenner et al., Radiat. Res. 187 (2017) 483
[2] M. Erofeev, V.F. Tarasenko, Quantum Electronics, 2008, 38, 401-403
[3] A. Voronov, Heraeus, Übersicht der UV-Lampen und ihre Einsatzgebiete, Darmstadt Oktober 2009

3. UV Radiation Sources

Care222® Ushio: KrCl* excimer discharge

Commercial product of Ushio which was introduced to the market as eye and skin safe disinfection lamp





Source: Ushio Homepage

3. UV Radiation Sources

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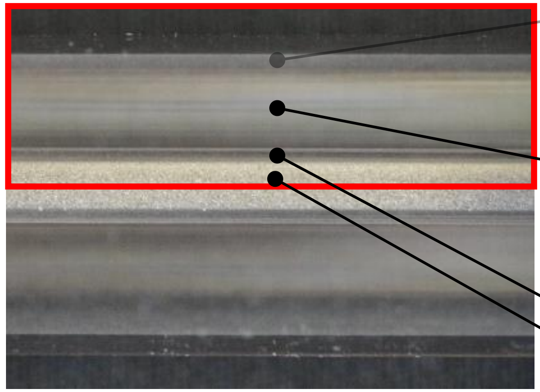
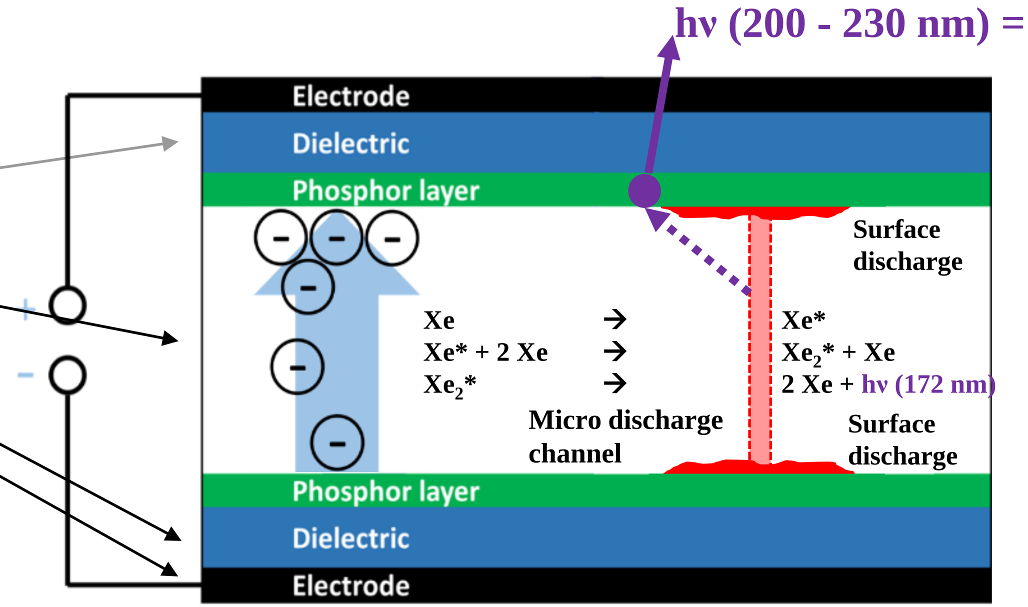
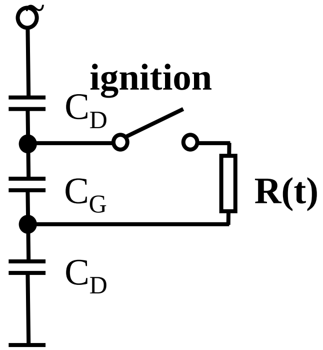
Indoor Air Disinfection with Deep UV-C (200-230 nm) emitting Xe_2^* lamp?

Xe_2^* excimer discharge (η > 30%) with suitable radiation converter screen (172 → 222 nm) is most efficient

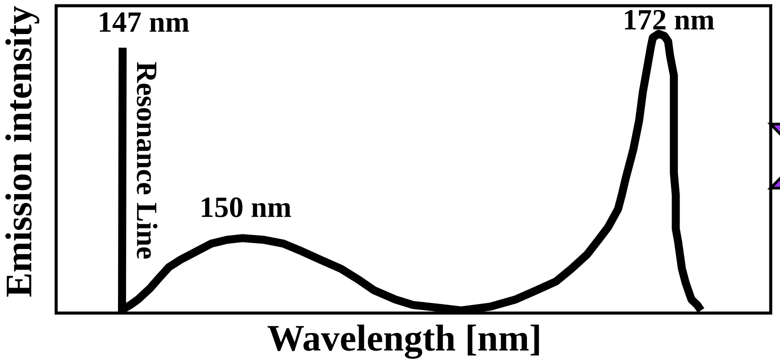


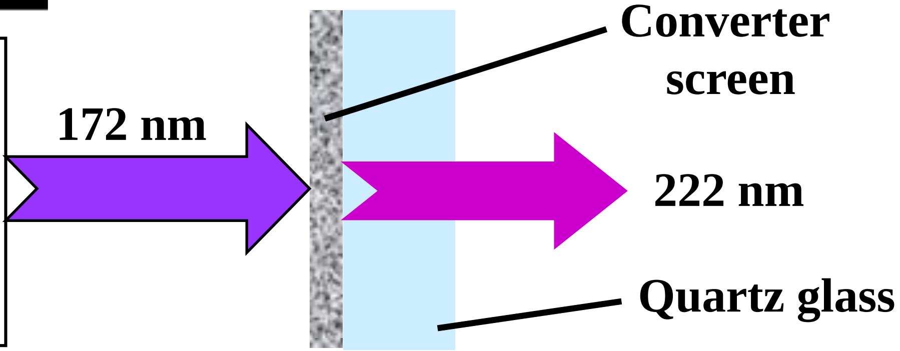




Typical lamp parameter

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





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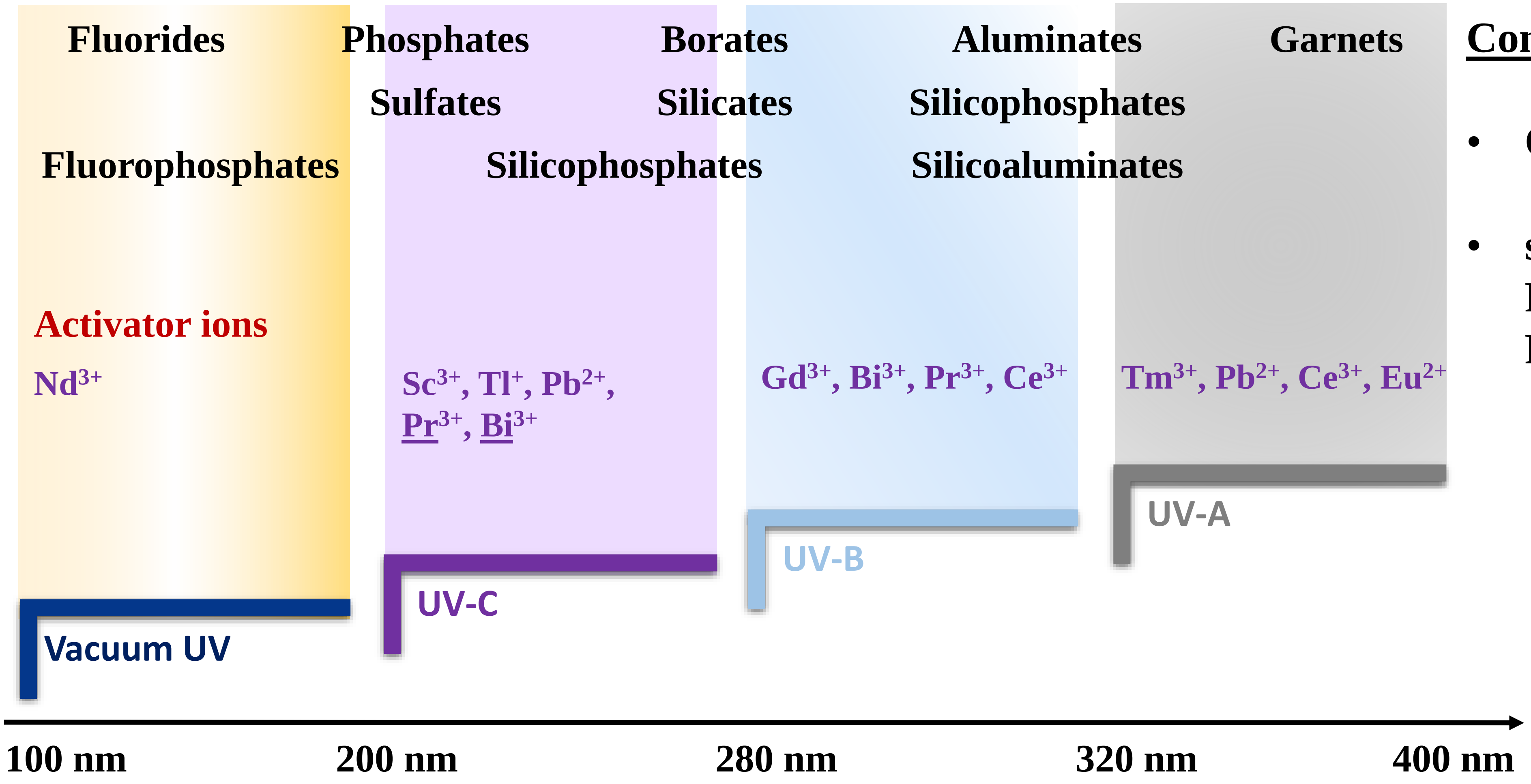
Suitable Hosts and Activators (for deep UV-C emission)

Host matrices



Conclusions

- Oxidic hosts solely
- s^2-ions or trivalent RE ions required
  RE = Sc^{3+}, Pr^{3+}, Nd^{3+}

4. UV Emitting Phosphors

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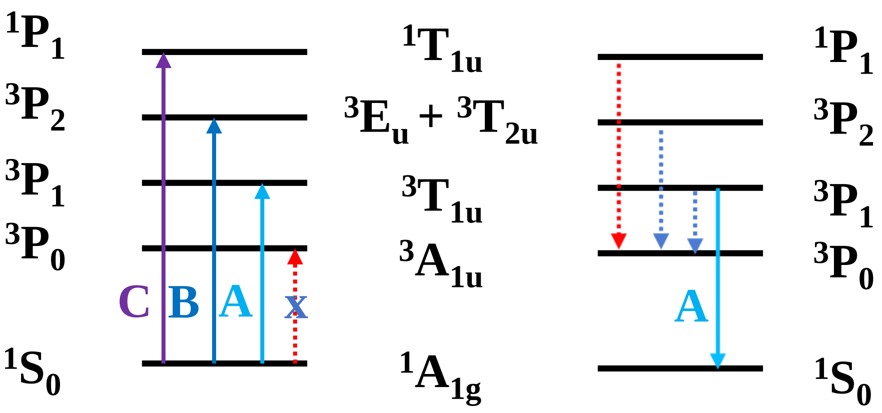
Phosphors Activated by Ions with s^2 Configuration

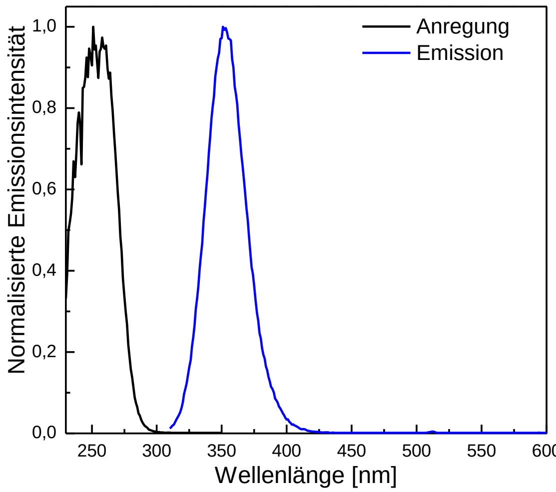
$[Ar]3d^{10}4s^2$	Ga^+, Ge^{2+}, As^{3+}
$[Kr]4d^{10}5s^2$	In^+, Sn^{2+}, Sb^{3+}
$[Xe]4f^{14}5d^{10}6s^2$	Tl^+, Pb^{2+}, Bi^{3+}

Excitation Mulliken (cubic) Emission

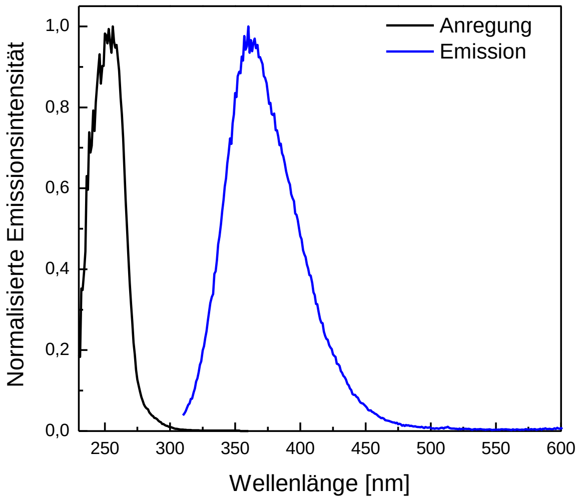


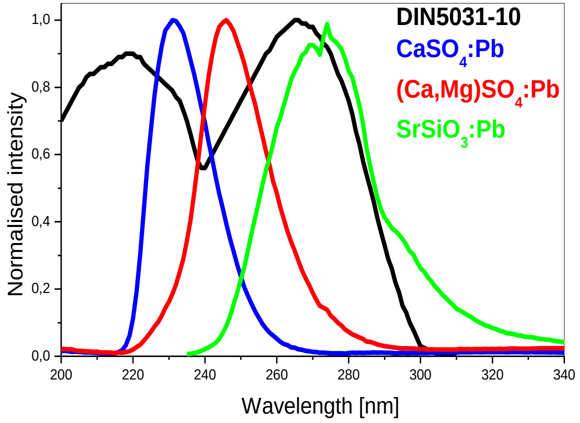
Efficient broad band emission, but strongly dependent on temperature

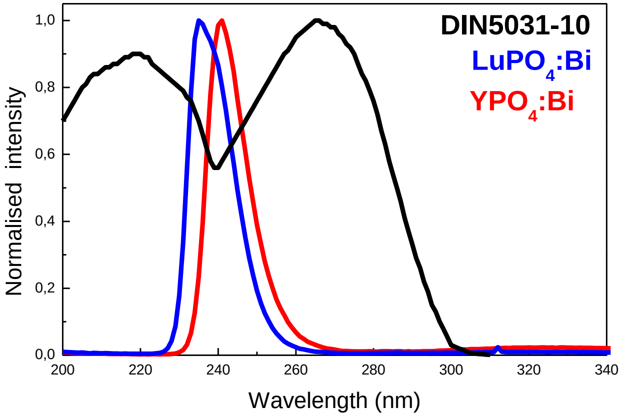
$BaSi_2O_5:Pb$



$Sr_2MgSi_2O_7:Pb$



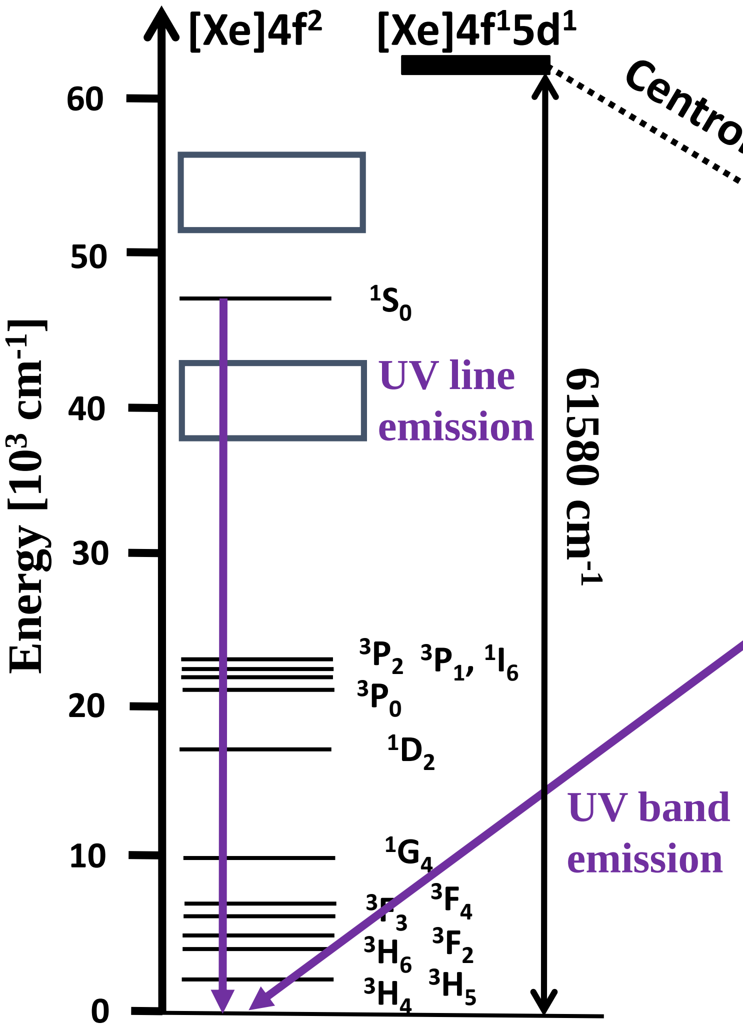




4. UV Emitting Phosphors

Phosphors Activated by Pr^{3+}

------------------ Crystal field (CF) splitting ------------------



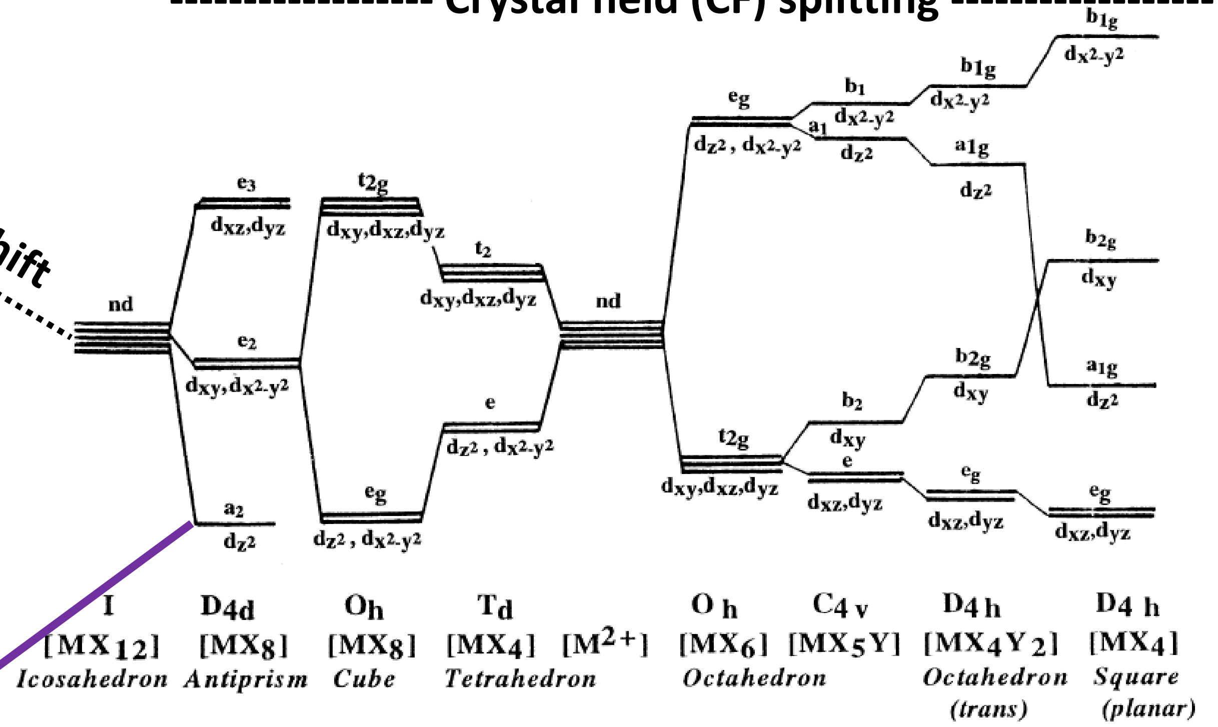


FIGURE 4.5. Splitting of *d* orbital energy levels in ligand fields of different symmetries. In MX_5Y and MX_4Y_2 complexes the splitting of the T_{2g} and E_g terms can be inverted depending on the ratio of field strengths X/Y. (After Schmidtke [4.12].)

Centroid shift and crystal field splitting determine Pr^{3+} luminescence spectra

Source: H.H. Schmidtke, Univ. Düsseldorf

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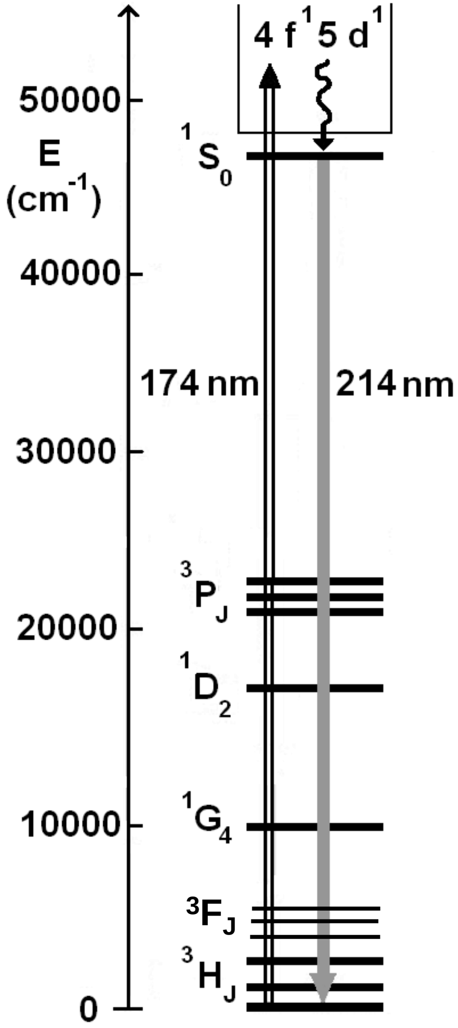
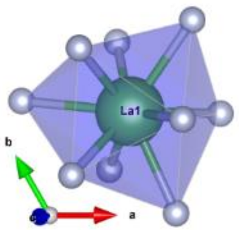
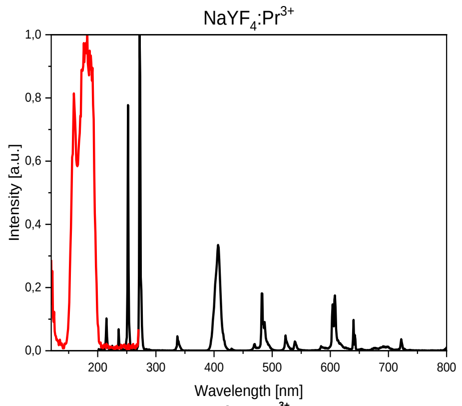
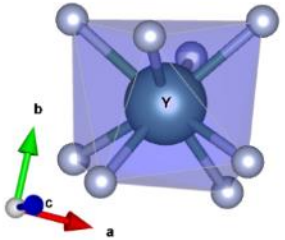
Fluoride Phosphors Activated by Pr^{3+}

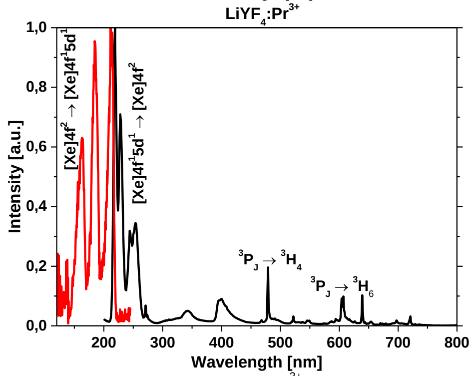


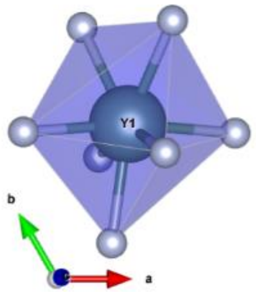
$NaYF_4:Pr^{3+}$	CN 9 (2 sites)
UV Lines	214 nm + Vis lines
$LiYF_4:Pr^{3+}$	CN 8 (1 site)
UV Bands	218 nm + Vis lines
$KYF_4:Pr^{3+}$	CN 7 (6 sites)
UV Bands	232 nm

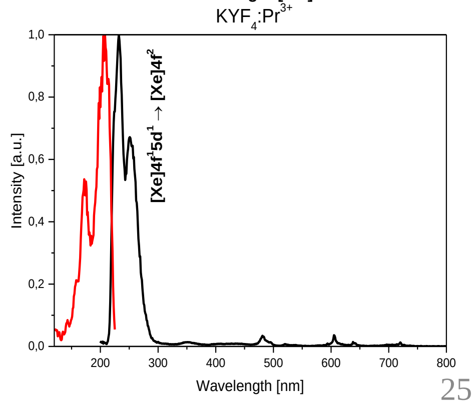












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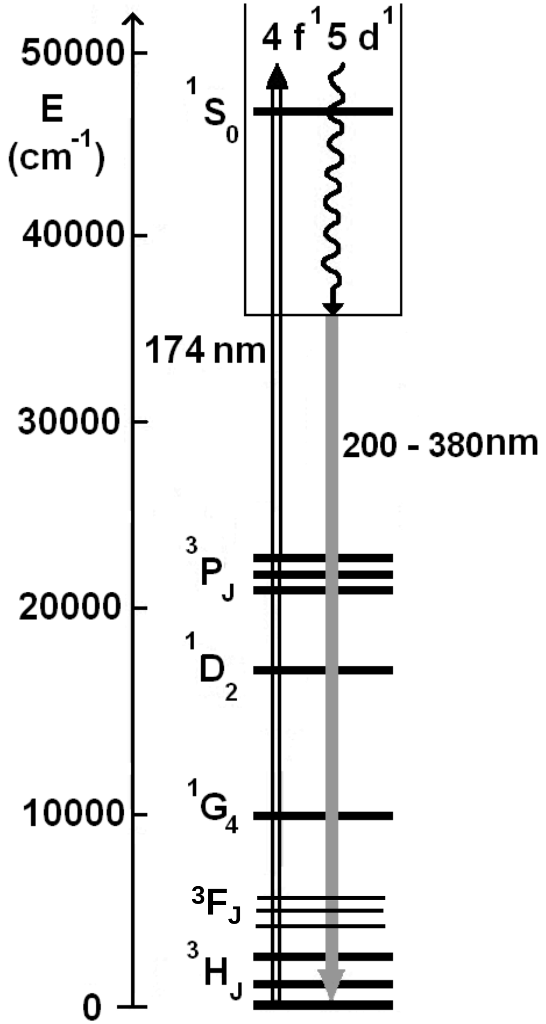
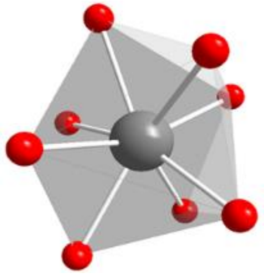
Oxidic Phosphors Activated by Pr^{3+}



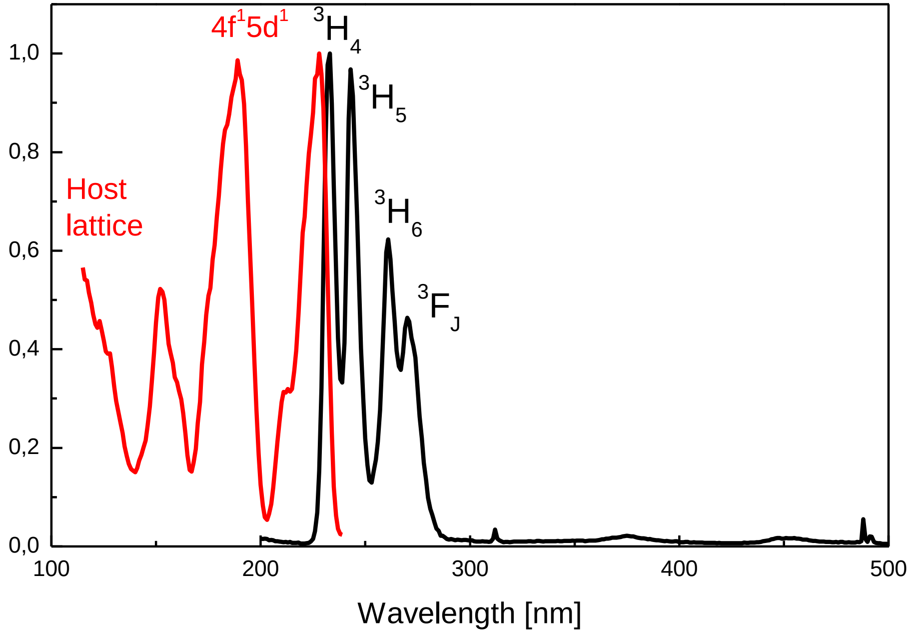
$(Y,Lu)PO_4$
Band gap E_g = 9.0 eV
1 crystallographic site



Distorted dodecahedra CN = 8

Y-O Distances
4 x 2.24 Å
4 x 2.24 Å

CF Splitting ~ 12000 cm^{-1}
Centroid shift ~ 9600 cm^{-1}



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

4. UV Emitting Phosphors

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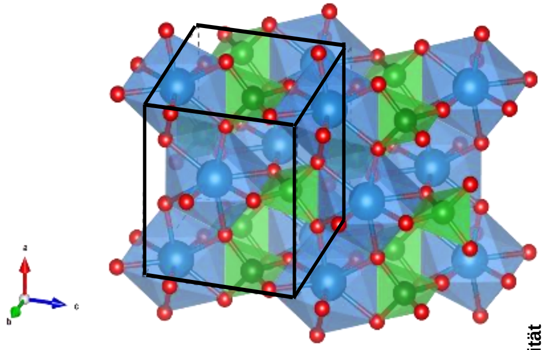
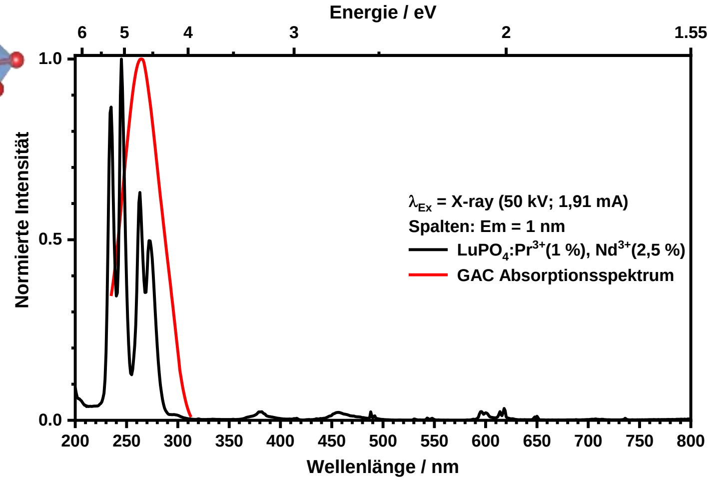
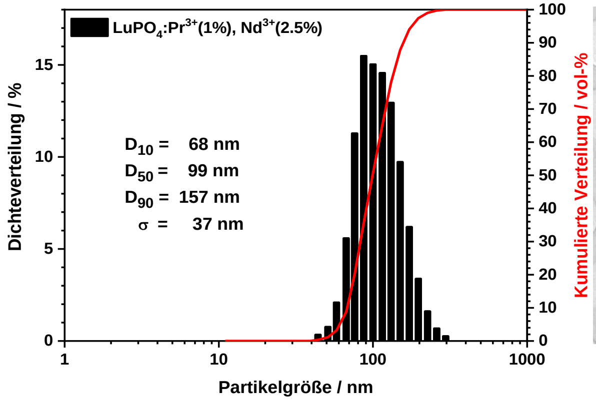
Summary: Phosphors Activated by Pr^{3+}

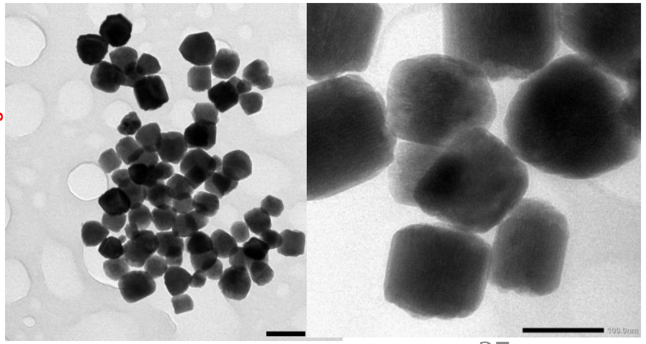
1. VUV: Cleavage of water and oxygen species
   - $(Y,Lu)PO_4$:Nd(,Pr) 193 nm
2. Deep UV-C: Removal of µ-pollutants & skin safe UV
   - $LiYF_4$:Pr 218 nm
   - $CaSO_4$:Pr 222 nm
   - $LuPO_4$:Pr 232 nm
   - YPO_4:Pr 235 nm
3. UV-C: Disinfection
   - $CaLi_2SiO_4$:Pr 252 nm
   - YBO_3:Pr 265 nm
   - Y_2SiO_5:Pr 270 nm
   - $Y_2Si_2O_7$:Pr 275 nm
4. UV-B: Photocatalysis e.g. Vitamin D formation
   - $Lu_3Ga_2Al_3O_{12}$: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 (FH MS)









4. UV Emitting Phosphors

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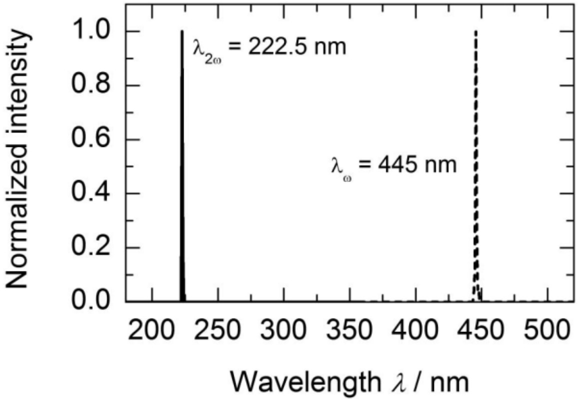
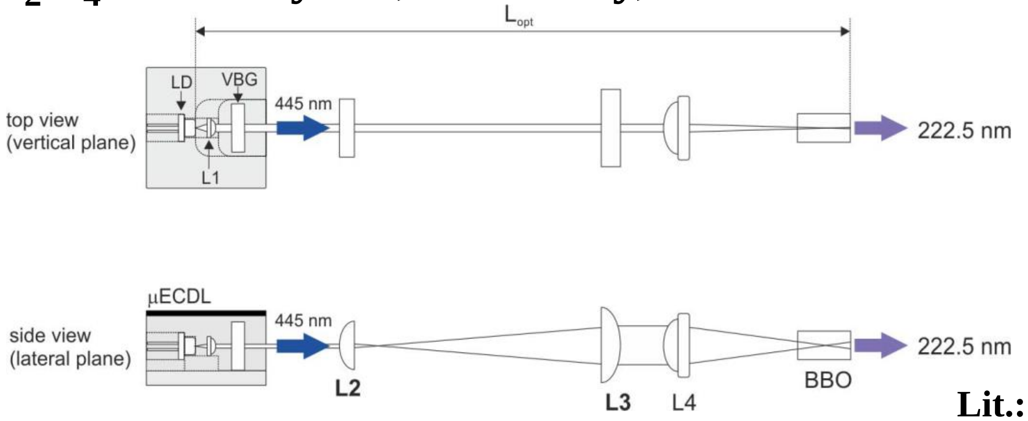
Surface Disinfection Claimed by Blue LED or Laser Diode + Blue-to-UV up-Converter

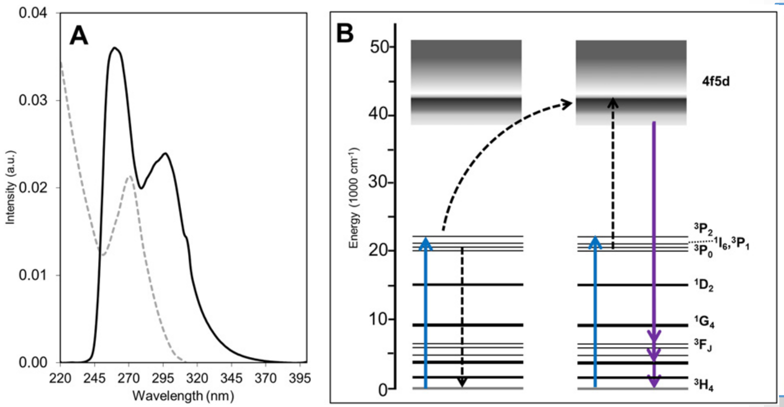
1. SHG: 445 nm laser diode + ß-BaB_2O_4 NLO crystal, Germany, Berlin

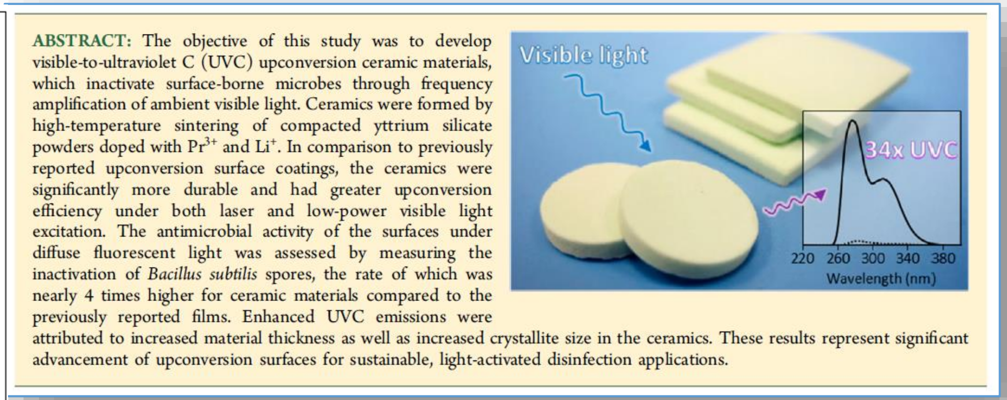




Lit.: G. Tränkle et al., IEEE Phot. Tech. Lett. 30 (2018) 289

2. ETU: 445 nm laser diode + Y_2SiO_5: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 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.

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

4. UV Emitting Phosphors

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

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

Zhiqian Yin, Peng Yuan, Zheng Zhu, Tianyi Li, Yanmin Yang *

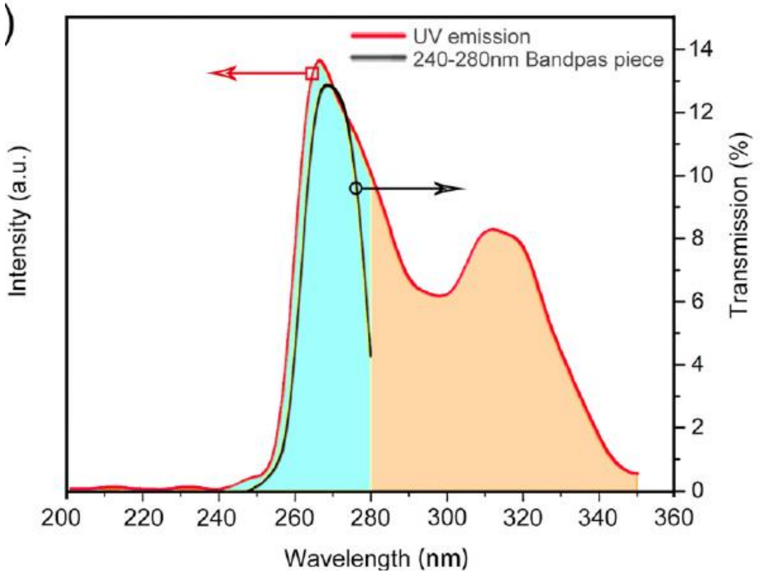
College of Physics Science and Technology, Institute of Life Science and Green Development, Hebei Key Lab of Optic-electronic Information and Materials, Hebei University, Baoding, 071002, PR China

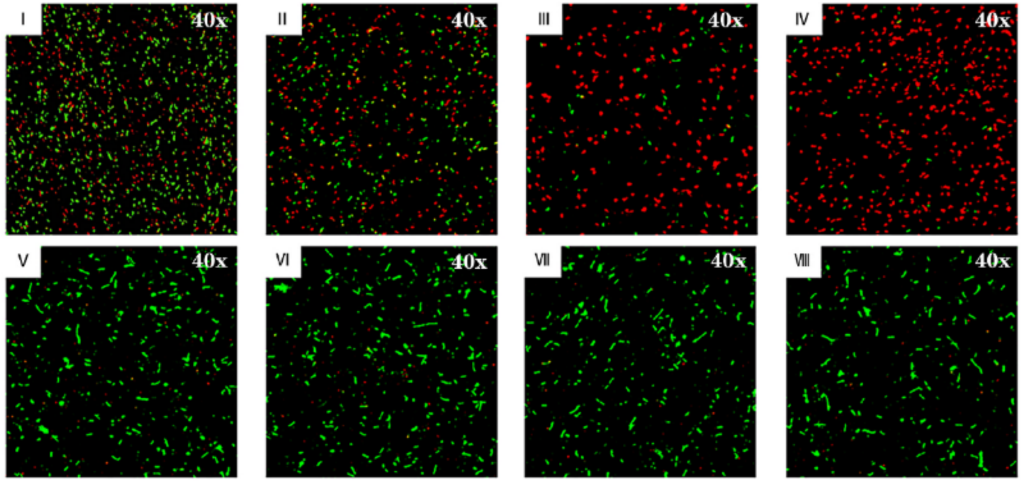
A R T I C L E I N F O

Keywords:
Up-conversion emission
Ultraviolet C
Optical properties
Silicate

A B S T R A C T

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.





Lit.: 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, Ceramics International 47 (2021) 4858

4. UV Emitting Phosphors

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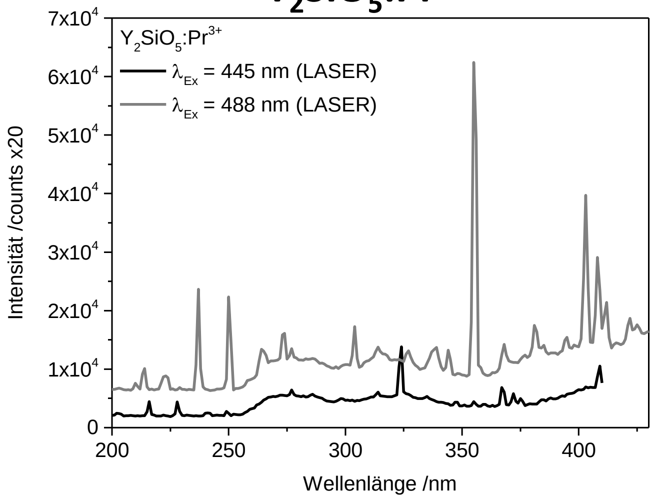
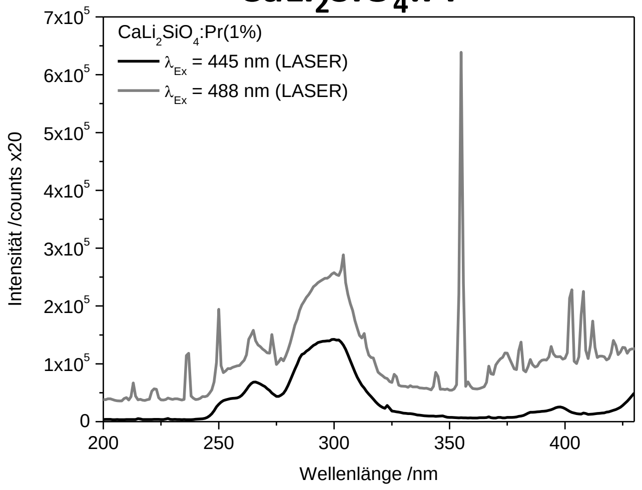
Issues with Published Pr^{3+} Doped ortho-Silicates

- **Low stability results in hydrolysis in humid air** → **hydroxides → carbonates**
- **Low efficiency of the up-conversion process** **Y_2SiO_5:Pr: QE ~ 0.01% (literature value)**
- **Up-conversion spectroscopy** **Artifacts and reproducibility**
  Determination of absorption strength

Y_2SiO_5:Pr



$CaLi_2SiO_4$:Pr



$QE = N_{(h\nu\ emitted)}/N_{(h\nu\ absorbed)}$

488 nm laser diode excitation:

Y_2SiO_5:Pr I ~ $1.5 \cdot 10^4$ cts

$CaLi_2SiO_4$:Pr I ~ $3 \cdot 10^5$ cts

4. UV Emitting Phosphors

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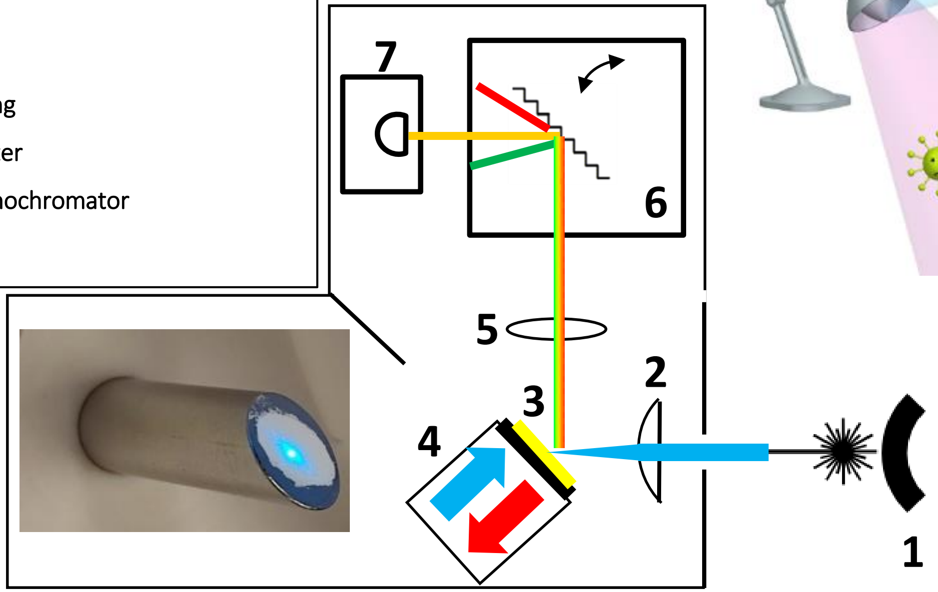
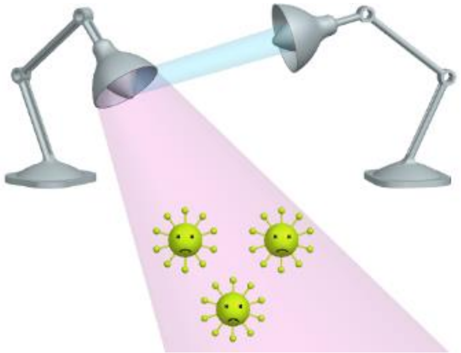
Pr^{3+} up-Conversion Spectroscopy at FH MS

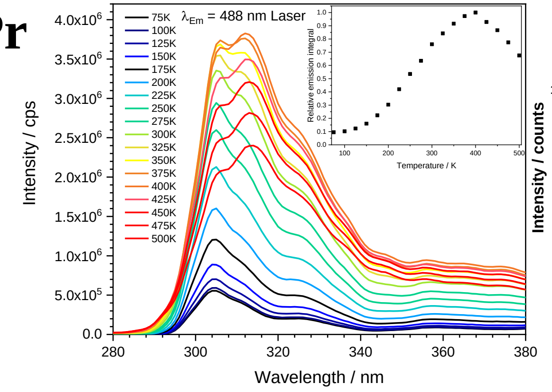
1 - Laser diode (445 nm / 488 nm)
2 - Focusing lens
3 - Sample
4 - Passive cooling
5 - Short pass filter
6 - Emission monochromator
7 - Detector

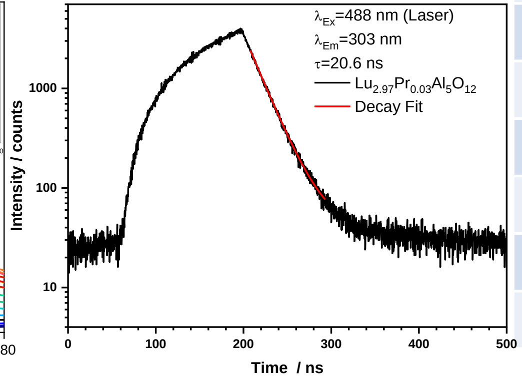




Host Material for Pr^{3+}	Emission / nm	Excitation / nm
Ba_2SiO_4	250-360	488 nm
$BaY_2Si_3O_{10}$	255-360	488 nm
$Ca_2LuSc_2GaSi_2O_{12}$	280-400	488 nm
$Ca_2Al_2SiO_7$	255-360	488 nm
$CaLi_2SiO_4$	245-350	488 nm
$Ca_2Sc_2Si_3O_{12}$	298-400	488 nm
$KYSiO_4$	265-400	488 nm
$LiYSiO_4$	255-400	488 nm
$Lu_3Al_5O_{12}$	280-400	488 nm
$Lu_3(Al,Ga)_5O_{12}$	280-400	488 nm
$Lu_3Al_3Sc_2O_{12}$	280-400	488 nm
$Lu_2CaAl_4SiO_{12}$	280-400	488 nm
$Lu_2Si_2O_7$	250-360	488 nm
Lu_2SiO_5	250-360	488 nm
$NaYSiO_4$	255-320	488 nm
$Sr_2MgSi_2O_7$	260-410	488 nm
$Sr_3MgSi_2O_6$	280-410	488 nm
Y_2SiO_5	255-355	488 nm

Example: LuAG:Pr
I ~ $4 \cdot 10^6$ cts
QE ~ 0.1-1.0%
T_{opt} ~ 400 K
Mechanism: ETU





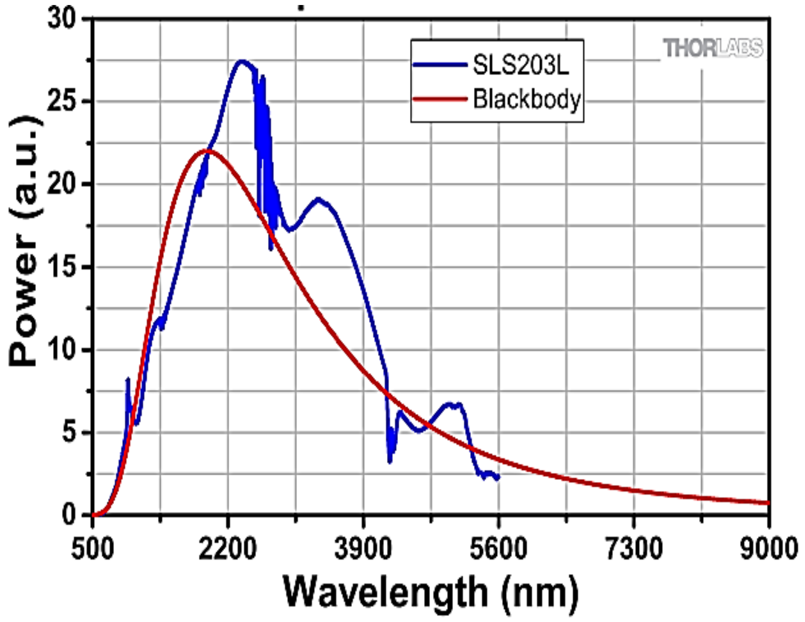
5. NIR Radiation Sources

Types

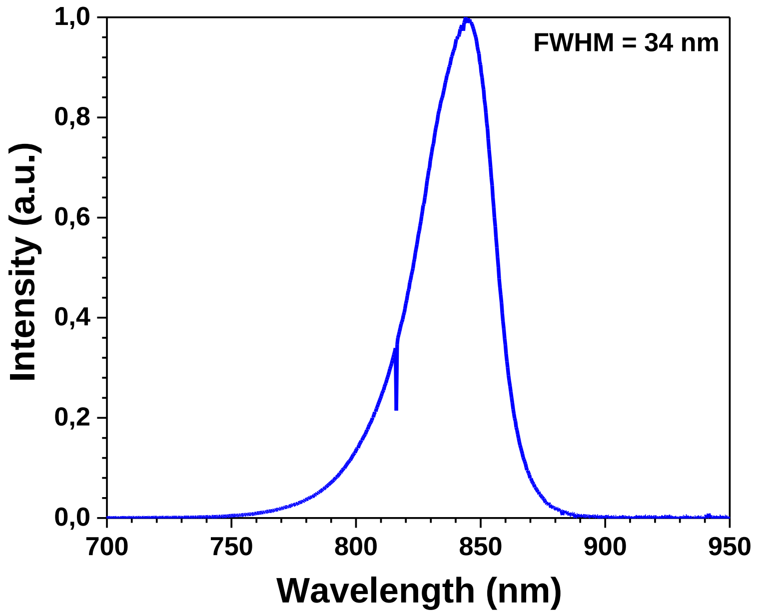
- Incandescent bulbs
- Silicon carbide heating elements (Globar®)
- Nernst Glowers
- GaAs or (Al,Ga)As LEDs

low efficiency
large size
high energy consumption

Spectral power distribution of a Globar® SLS203L in comparison to black body radiation at 1500 K



Emission spectrum of a 3 W 850 nm LED



5. NIR Radiation Sources

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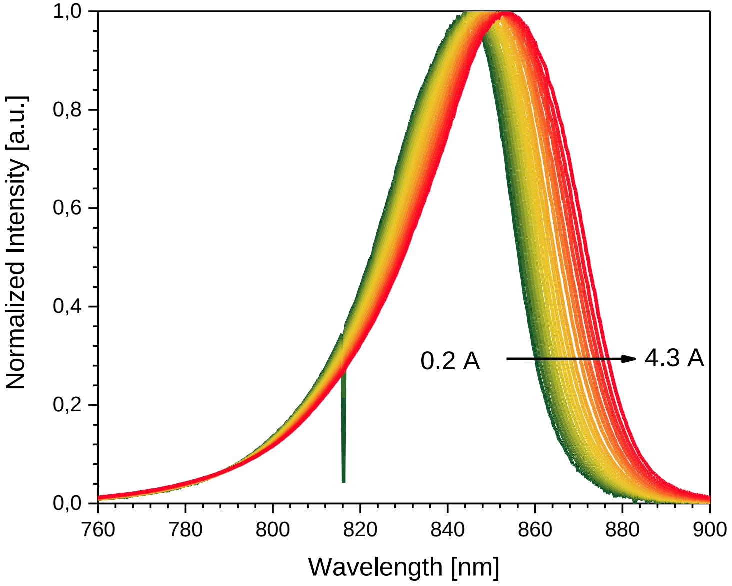
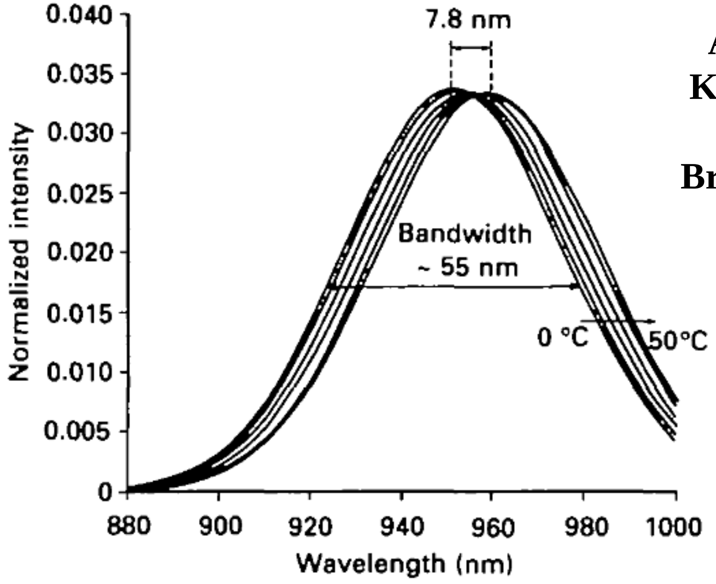
Limitations of NIR emitting LEDs

- **Narrow emission spectrum**
- **Poor thermal stability**
- **Sensitivity towards humidity**
- **Shift of EL spectrum with drive, lifetime, and temperature**

Emission spectra of an LED array comprising 10 x 3 W 850 nm LEDs measured upon increasing drive current



Shift in emission spectrum of infrared LED with an increase of ambient temperature from 0 °C to 50 °C



Adapted from K.J. Reynolds et al., Br. J. Anaesth. 67 (1991) 638

5. NIR Radiation Sources

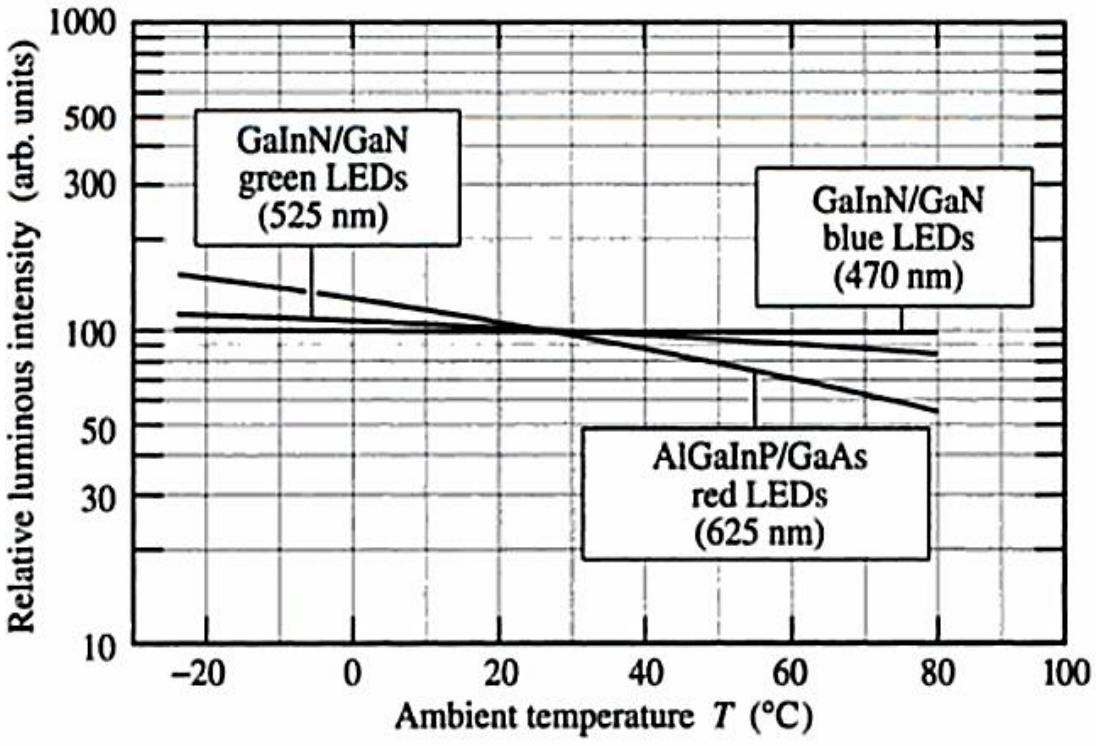
Phosphor Converted NIR emitting LEDs

Advantages of blue or UV emitting (In,Ga)N semiconductor chips

- Good thermal stability
- High wall-plug efficiency (WPE)
- Small spectral shift upon temperature increase
- Very high lifetime

Requirements for NIR emitting phosphors

- High quenching temperature ($T_{1/2} > 450$ K)
- Spectral consistent
- Strong absorption in the spectral range of the LED chip emission
- High internal and external quantum yield



Typical output intensity of blue (Ga,In)N/GaN, green (Ga,In)N/GaN, and red (Al,Ga,In)P/GaAs LEDs as a function of ambient temperature

Adapted from: E.F. Schubert, Light-Emitting Diodes, Cambridge University Press, 2003

6. NIR Emitting Phosphors

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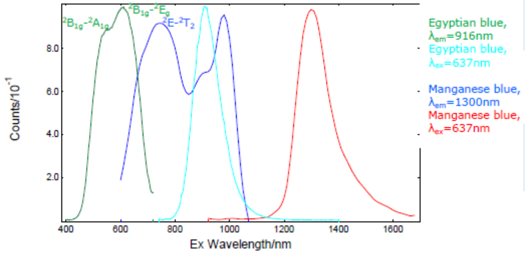
Potential activators

Transition metal ions

- V^{n+}, Cr^{n+}, Mn^{n+}, Fe^{n+}, Co^{2+}, Ni^{2+}, Cu^{2+}
- Mostly broad band emission (lines for Cr^{3+}, Mn^{4+})
- Strong absorption due to spin allowed 3d-3d transitions or LMCT transitions
- Strong thermal quenching

Source: Edinburgh Instruments



Lanthanide ions

- Nd^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}
- Line emission
- Weak absorption due to 4f-4f transitions
- Mostly rather high quenching temperature

Activator	$\lambda_{em,max}$	Typical inorganic host materials
Mn^{4+}	730 nm	$SrLaAlO_4$, $CaLaMgSbO_6$
Mn^{5+}	1150 nm	Na_2CaSiO_4
Mn^{6+}	1100 nm	$BaSO_4$
Cr^{3+}	850 nm	$Sr_8MgLa(PO_4)_7$
Cr^{4+}	1250 nm	Mg_2SiO_4
Cu^{2+}	910-960 nm	$(Ca,Sr,Ba)CuSi_4O_{10}$
Ni^{2+}	1600 nm	$KMgF_3$
Co^{2+}	3200 nm	ZnSe
Eu^{2+}	840 nm	$Ca_3Sc_2Si_3O_{12}$
Nd^{3+}	1060 nm	$(Y,Gd,Lu)_3(Al,Sc,Ga)_2Al_3O_{12}$
Ho^{3+}	2280 nm	$(Y,Gd,Lu)_3(Al,Sc,Ga)_2Al_3O_{12}$
Er^{3+}	1550 nm	$(Y,Gd,Lu)_3(Al,Sc,Ga)_2Al_3O_{12}$
Yb^{3+}	980 nm	$(Y,Gd,Lu)_3(Al,Sc,Ga)_2Al_3O_{12}$

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Example: [Ar]3d³ Ions

V^{2+}, Cr^{3+}, Mn^{4+}, Fe^{5+}

Crystal field splitting in Al_2O_3

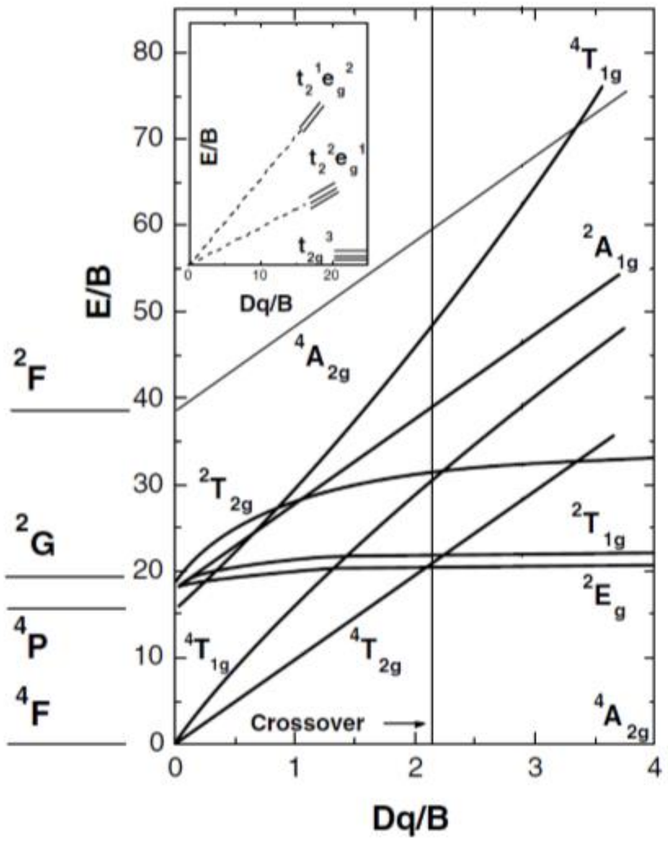
V^{2+}	15240 cm^{-1}
Cr^{3+}	18145 cm^{-1}
Mn^{4+}	21290 cm^{-1}
Fe^{5+}	(> 22000 cm^{-1})

Lit.: J. Phys. Soc. Jpn. 81 (2012) 104709

→ Mn^{4+} show solely line emission (^2E-$^4A_2$): 620 - 750 nm

→ Band emission ($^4T_2$-$^4A_2$) only expected for Cr^{3+} and V^{2+}

→ V^{2+} and Fe^{5+} stabilization in solids is difficult



Tanabe-Sugano diagram for d³-ions

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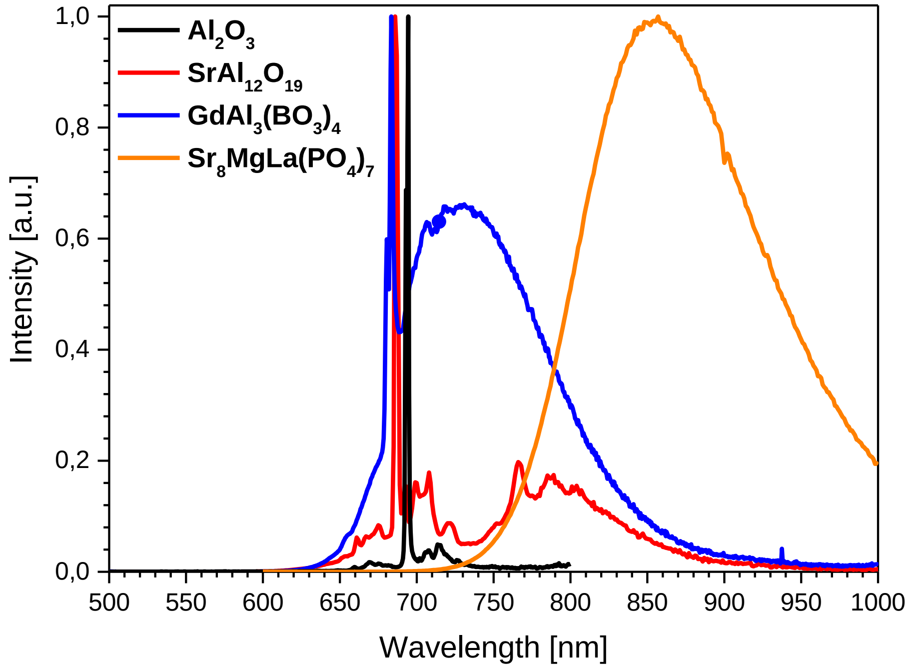
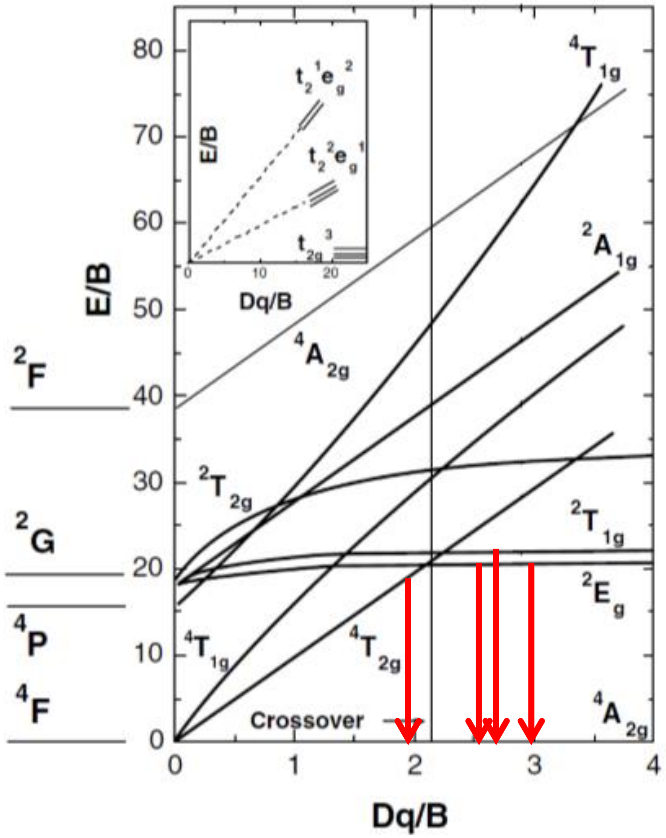
Cr^{3+} activated phosphors





Host	Dq /cm^{-1}	B /cm^{-1}	E(^{2}E) /cm^{-1}	Dq/B
α-Al_2O_3	1795	630	14399	2,85
$SrAl_{12}O_{19}$	1707	636	14575	2,68
$GdAl_3(BO_3)_4$	1672	677	14633	2,47
$Sr_8MgLa(PO_4)_7$	1421	686	-	2,07

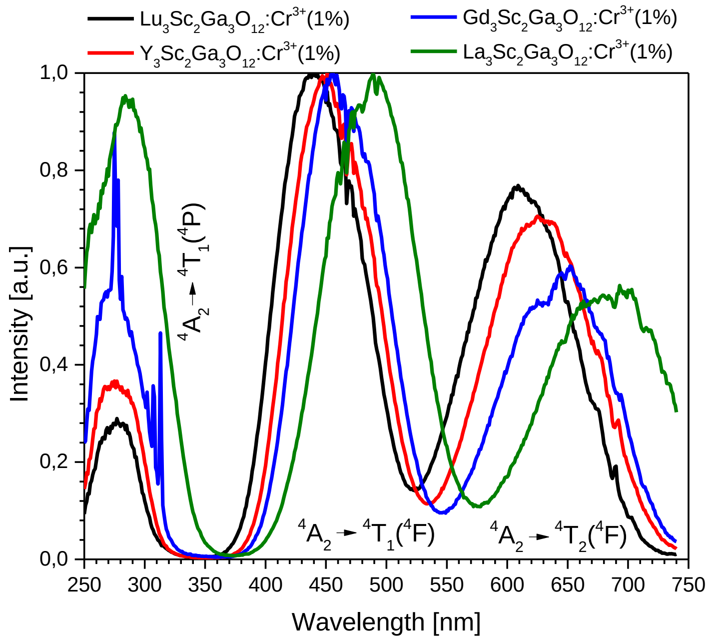
B↓ **increased covalency of Cr-O bonds**

B↑ **decreased covalency of Cr-O bonds**

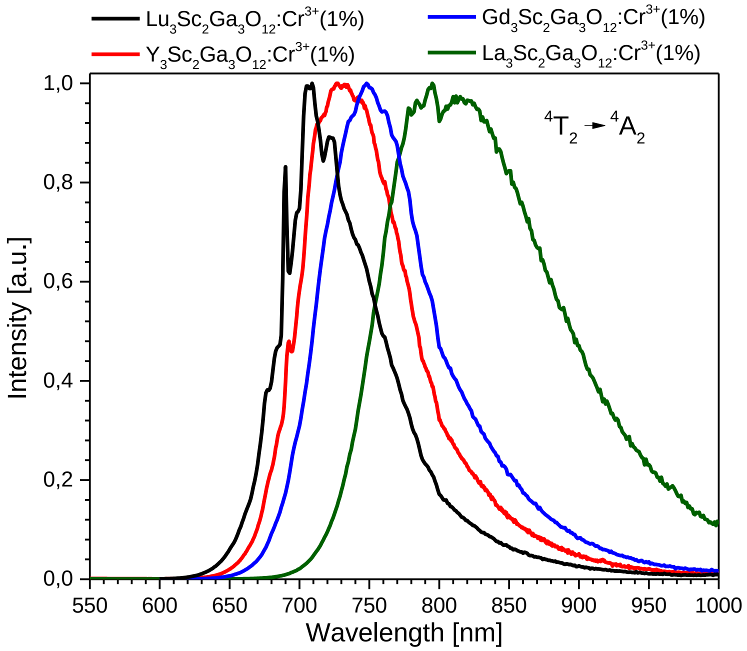
6. NIR Emitting Phosphors

Garnets $X_3Sc_2Ga_3O_{12}:Cr^{3+}$ (X = Lu, Y, Gd, La)

Excitation spectra of XSGG:Cr^{3+} with X = Lu, Y, Gd, La



Emission spectra of XSGG:Cr^{3+} with X = Lu, Y, Gd, La



Host	Ionic radius X^{3+} /Å	Sc-O distance /Å	X-O distance /Å
LuSGG	1.12	1.993	2.490
YSGG	1.16	2.018	2.522
GSGG	1.19	2.041	2.550
LaSGG	1.30	2.086	2.607

Host	Dq [cm^{-1}]	Em. max	FWHM	Stokes Shift
LuSGG	1626	722 nm	73 nm	2585 cm^{-1}
YSGG	1587	740 nm	90 nm	2445 cm^{-1}
GSGG	1563	754 nm	90 nm	2354 cm^{-1}
LaSGG	1458	818 nm	145 nm	2392 cm^{-1}

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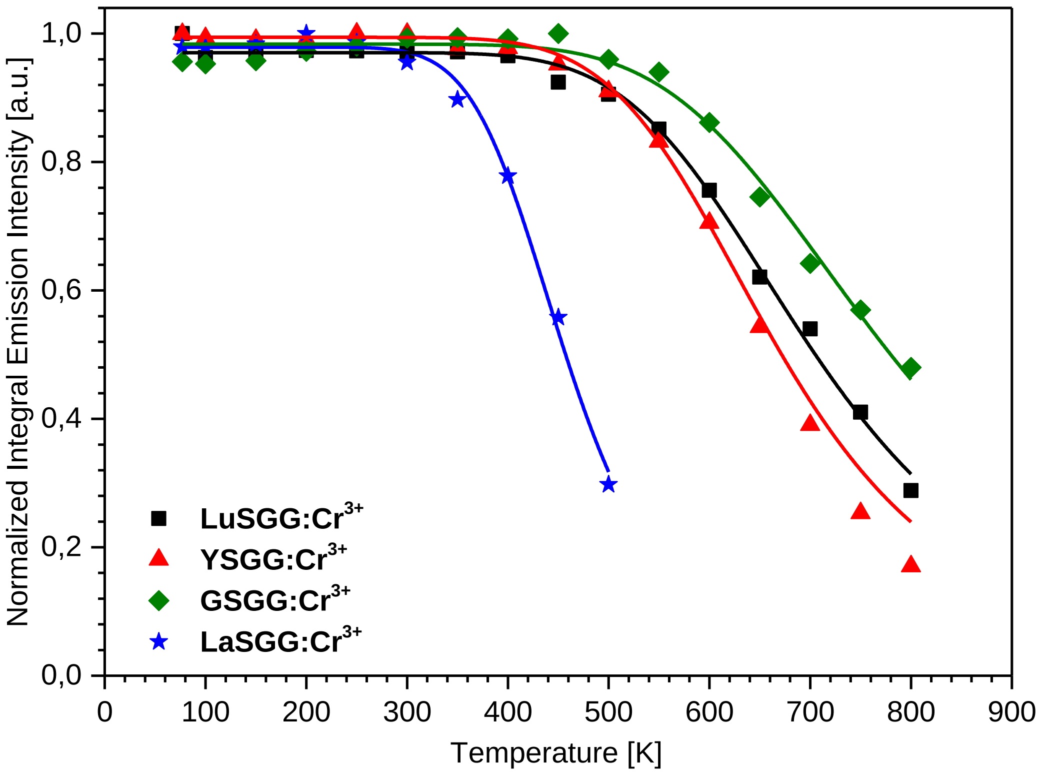
Garnets $X_3Sc_2Ga_3O_{12}:Cr^{3+}$ (X = Lu, Y, Gd, La)

X = Gd
- **Superior quenching behavior**

X = La
- **Strong thermal quenching of LaSGG compared to other XSGG**
- **Small Dq, i.e. low energetic position of $^4T_2$ level**
- **Large Stoke‘sche Shift (Huang-Rhys-Parameter: S = 6)**
- **Large FWHM of $^4T_2$ band**



Host / Decay	τ_{3K}	τ_{RT}
LuSGG	2,2 ms	314 µs
YSGG	1,2 ms	125 µs
GSGG	425 µs	102 µs
LaSGG	178 µs	104 µs

Host	Dq [cm^{-1}]	Em. max	FWHM	Stokes Shift	$T_{1/2}$
LuSGG	1626	722 nm	73 nm	2585 cm^{-1}	714 K
YSGG	1587	740 nm	90 nm	2445 cm^{-1}	660 K
GSGG	1563	754 nm	90 nm	2354 cm^{-1}	780 K
LaSGG	1458	818 nm	145 nm	2392 cm^{-1}	450 K

6. NIR Emitting Phosphors

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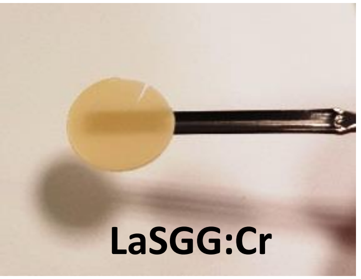
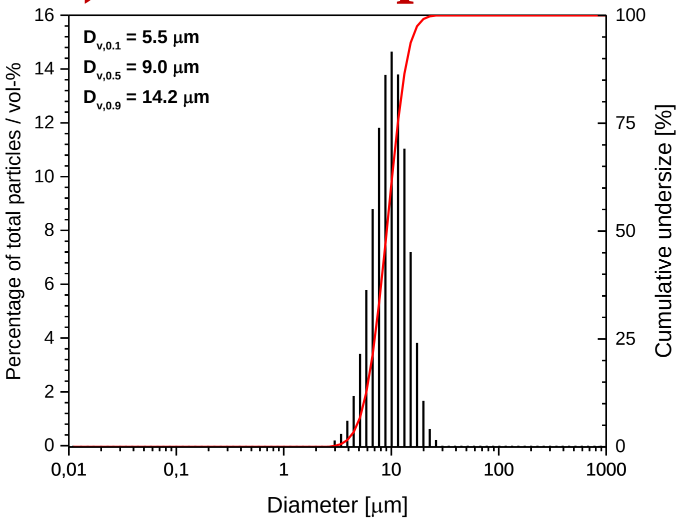
Garnets $X_3Sc_2Ga_3O_{12}:Cr^{3+}$ for application in silicone onto (In,Ga)N LED chips

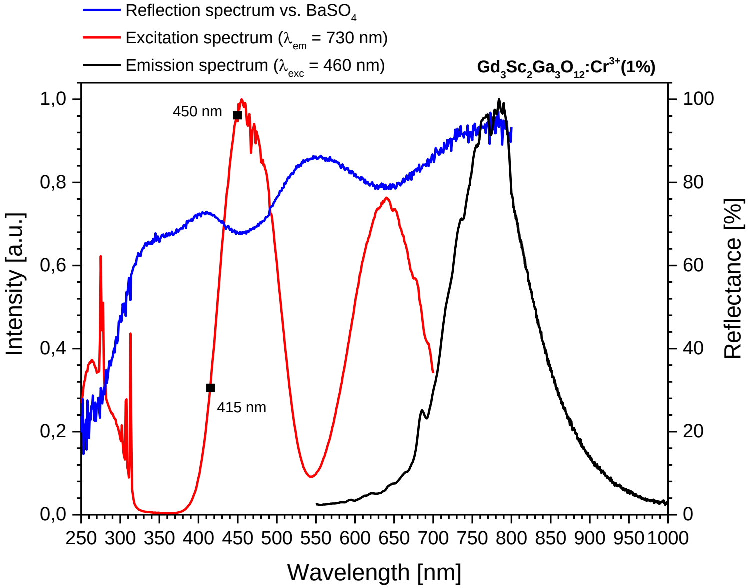
d_{50} = 9.0 µm for GSGG:Cr^{3+}

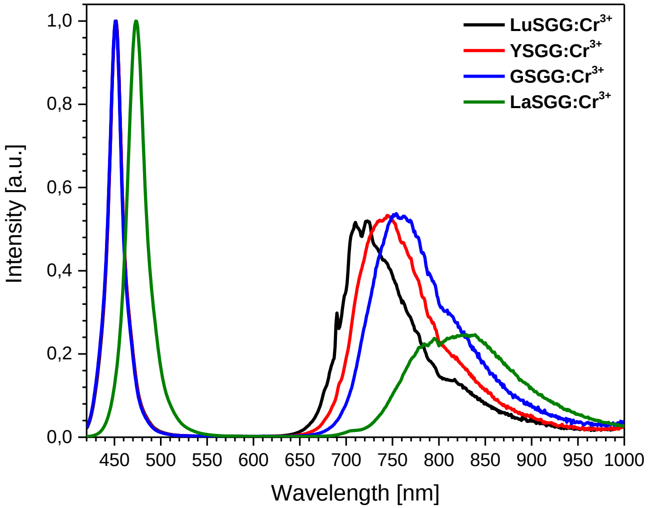
Broad emission between 650 and 900 nm

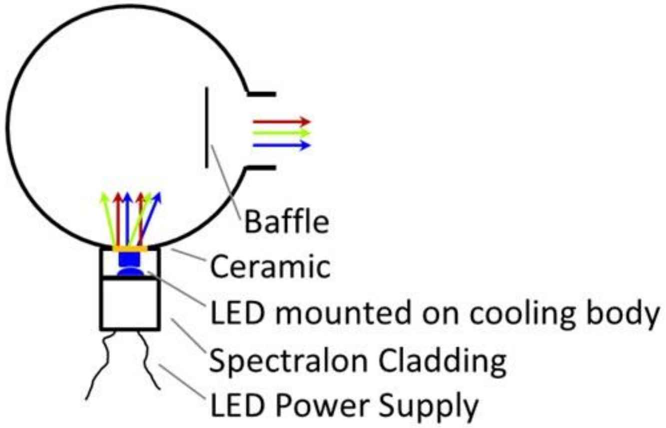
Highest conversion efficiency for GSGG ~ 5%











Lit.: B. Malysa, A. Meijerink, T. Jüstel, J. Luminescence 202 (2018) 523

6. NIR Emitting Phosphors

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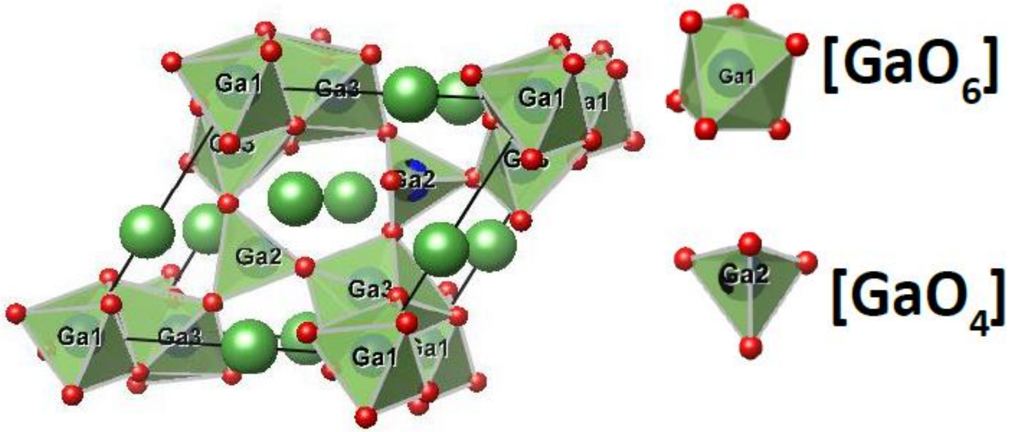
Cr^{3+} Phosphors for NIR emitting sources based on (In,Ga)N LED chips

- Thermal NIR sources show very broad emission spectra
- NIR emitting LEDs are very efficient, but show problems concerning lifetime, thermal quenching, and spectral consistency
- Phosphor converted LEDs could combine efficiency and stability of blue emitting LEDs with broad band NIR-Emission of Cr^{3+}

Host	Dq	Emission max. at RT	FWHM	Stokes Shift	$T_{1/2}$
$CaSc_2O_4$	1471 cm^{-1}	820 nm	164 nm	3042 cm^{-1}	< 240 K
$SrSc_2O_4$	1389 cm^{-1}	860 nm	168 nm	2939 cm^{-1}	< 240 K
$Sr_8MgLa(PO_4)_7$	1421 cm^{-1}	848 nm	141 nm	2487 cm^{-1}	300 K
$GdAl_3(BO_4)_3$	1672 cm^{-1}	730 nm	116 nm	3136 cm^{-1}	650 K
LuSGG	1626 cm^{-1}	722 nm	73 nm	2585 cm^{-1}	714 K
YSGG	1587 cm^{-1}	740 nm	90 nm	2445 cm^{-1}	660 K
GSGG	1563 cm^{-1}	754 nm	90 nm	2354 cm^{-1}	780 K
LaSGG	1458 cm^{-1}	818 nm	145 nm	2392 cm^{-1}	450 K

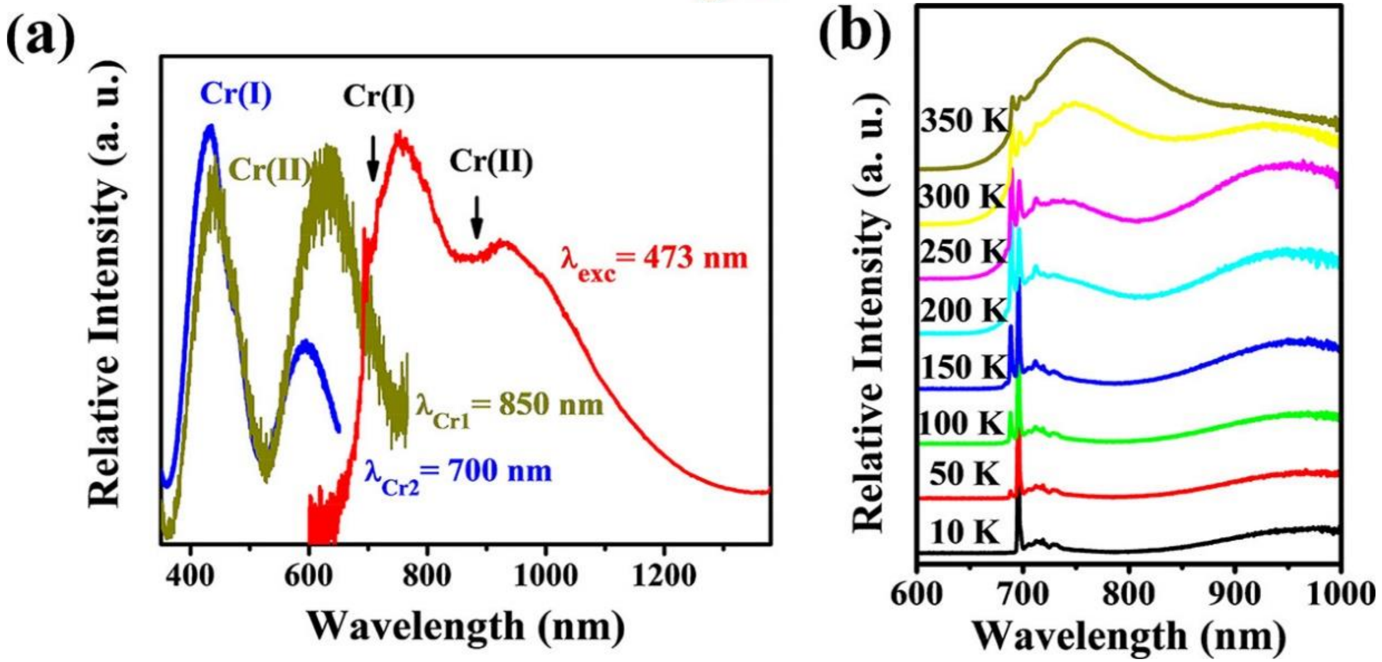
6. NIR Emitting Phosphors

Cr^{3+}/Cr^{4+} Co-activated phosphors



Example: $La_3Ga_5GeO_{14}:Cr^{3+/4+}$ exhibits broad emission from deep red to NIR range

- Cr^{3+} onto octahedral Ga^{3+} site Cr(I)
- Cr^{4+} onto tetrahedral Ga^{3+} site Cr(II)



Cr^{4+} photoluminescence suffers from strong thermal quenching

Lit.: ACS Energy Lett. 3 (2018) 2679

6. NIR Emitting Phosphors

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Sensitized NIR emitting phosphors

$Cr^{3+} \rightarrow Cr^{4+}$				900 – 1400 nm
$Cr^{3+} \rightarrow Yb^{3+}$	$Cr^{3+} \rightarrow Nd^{3+} \rightarrow Yb^{3+}$	$Ce^{3+} \rightarrow Yb^{3+}$	$Ce^{3+} \rightarrow Tb^{3+} \rightarrow Yb^{3+}$	980 – 1040 nm
$Cr^{3+} \rightarrow Nd^{3+}$	$Ce^{3+} \rightarrow (Cr^{3+}) \rightarrow Nd^{3+}$	$Eu^{2+} \rightarrow Nd^{3+}$	$Eu^{2+} \rightarrow Mn^{2+} \rightarrow Nd^{3+}$	1050 – 1080 nm
$Cr^{3+} \rightarrow Ni^{2+}$				1200 – 1600 nm
$Cr^{3+} \rightarrow Tm^{3+}$				1400 – 1550 nm
$Cr^{3+} \rightarrow Er^{3+}$				1540 – 1560 nm
$Cr^{3+} \rightarrow Ho^{3+}$				1900 – 2100 nm

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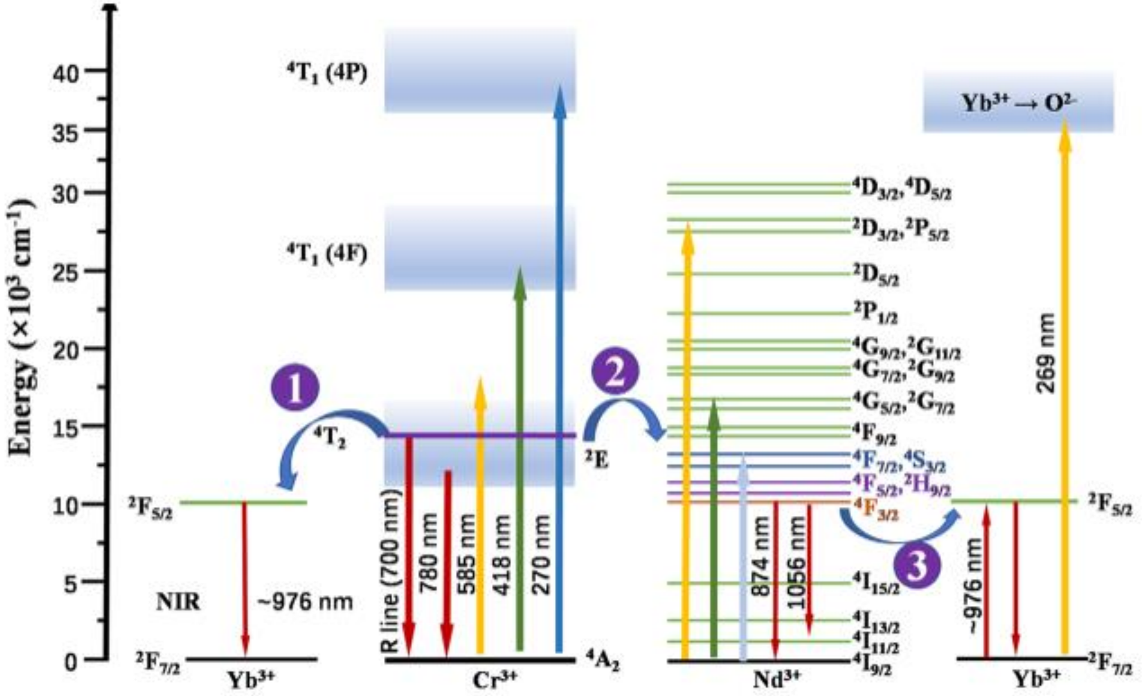
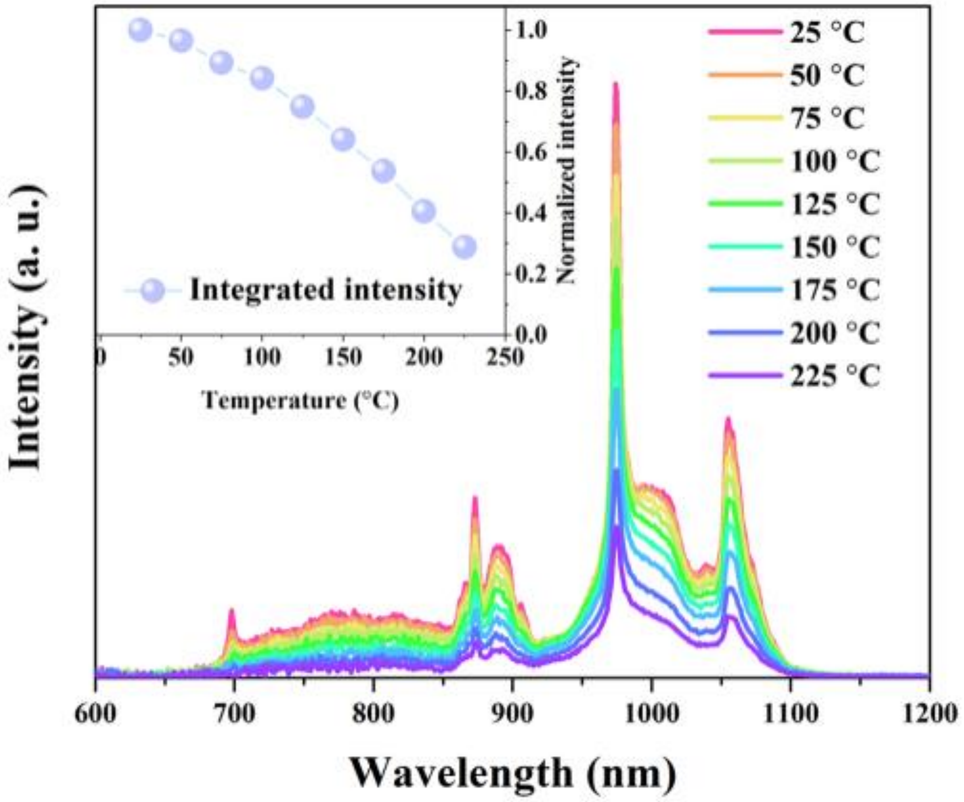
Cr^{3+}/Yb^{3+} Co-activated phosphors

Example: $La_3GaGe_5O_{16}:Cr^{3+},Yb^{3+}$ improvement of ET to NIR range by incorporation of additional Nd^{3+}





Problems: Thermal quenching and spectral consistency

Lit.: L. Zhao et al., Inorg. Chem. 61 (2022) 13618

6. NIR Emitting Phosphors

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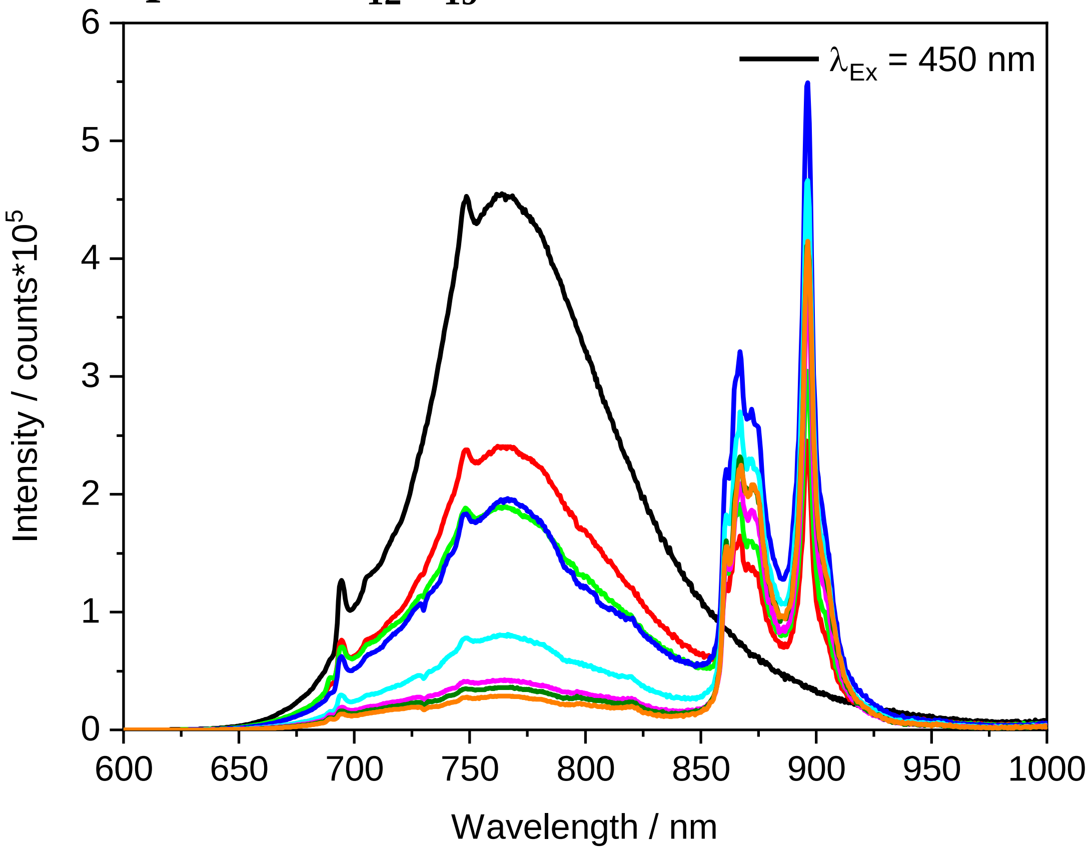
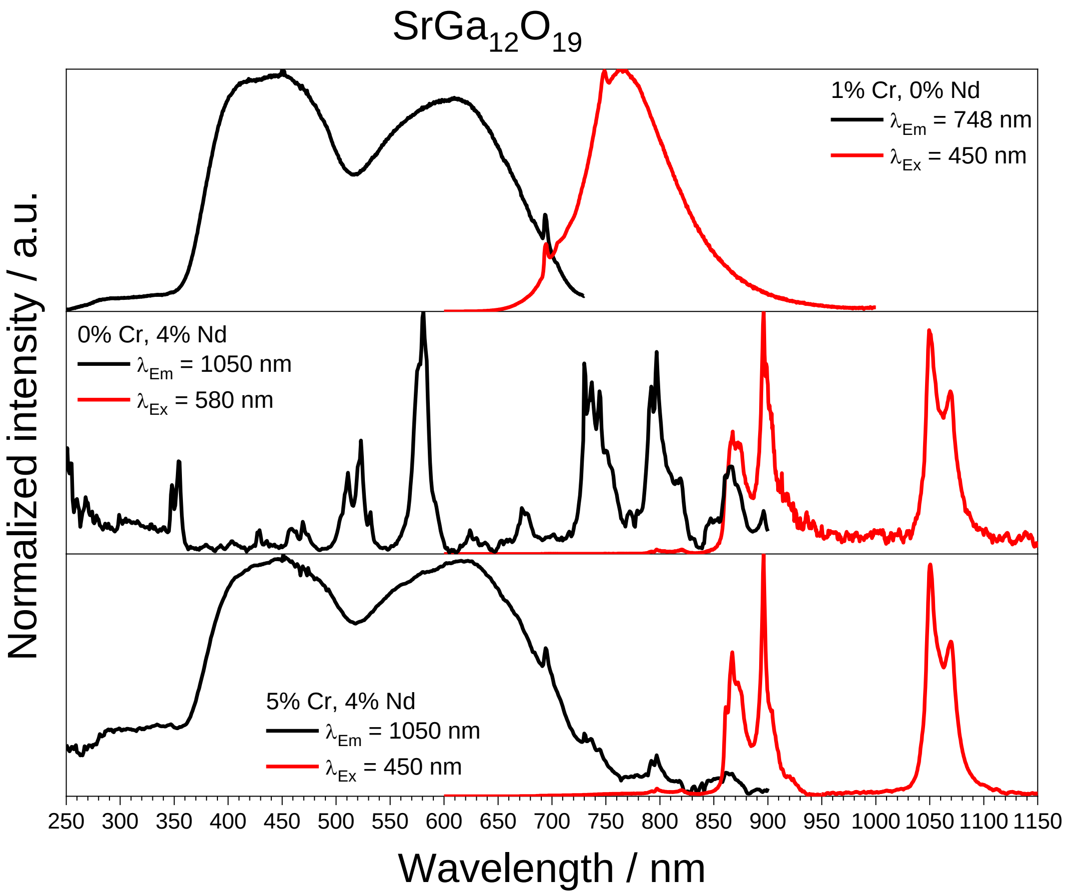
Cr^{3+}/Nd^{3+} Co-activated phosphors

Example: $SrGa_{12}O_{19}:Cr^{3+},Nd^{3+}$





Lit.: V. Anselm, T. Jüstel, J. Mater. Res. 11 (2021) 785

6. NIR Emitting Phosphors

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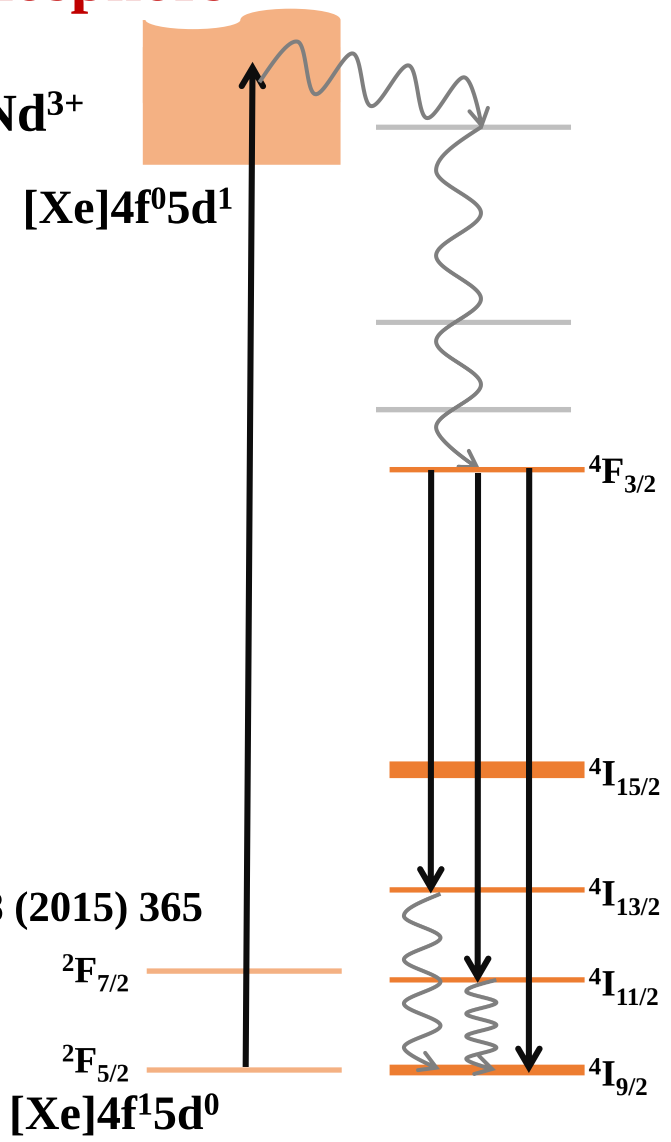
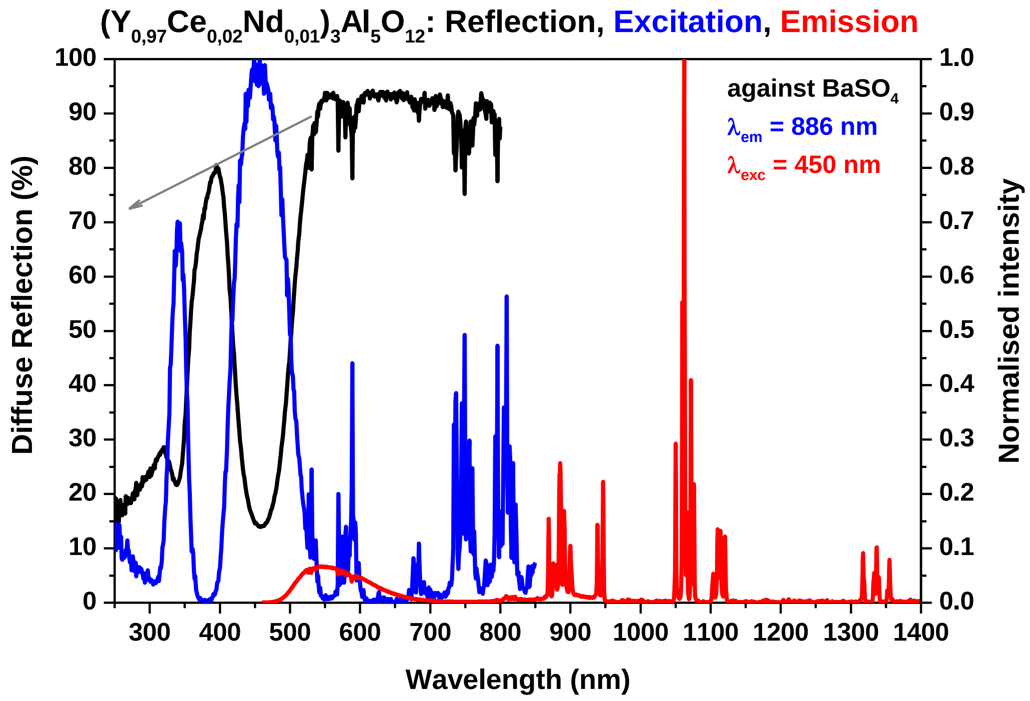
Ce^{3+}/Nd^{3+} Co-activated phosphors

Example: $(Y,Lu)_3Al_5O_{12}:Ce^{3+},Nd^{3+}$



Lit.: S. Möller, T. Jüstel, J. Lumin. 158 (2015) 365

Energy transfer from Ce^{3+} to Nd^{3+} is working, though not completely



6. NIR Emitting Phosphors

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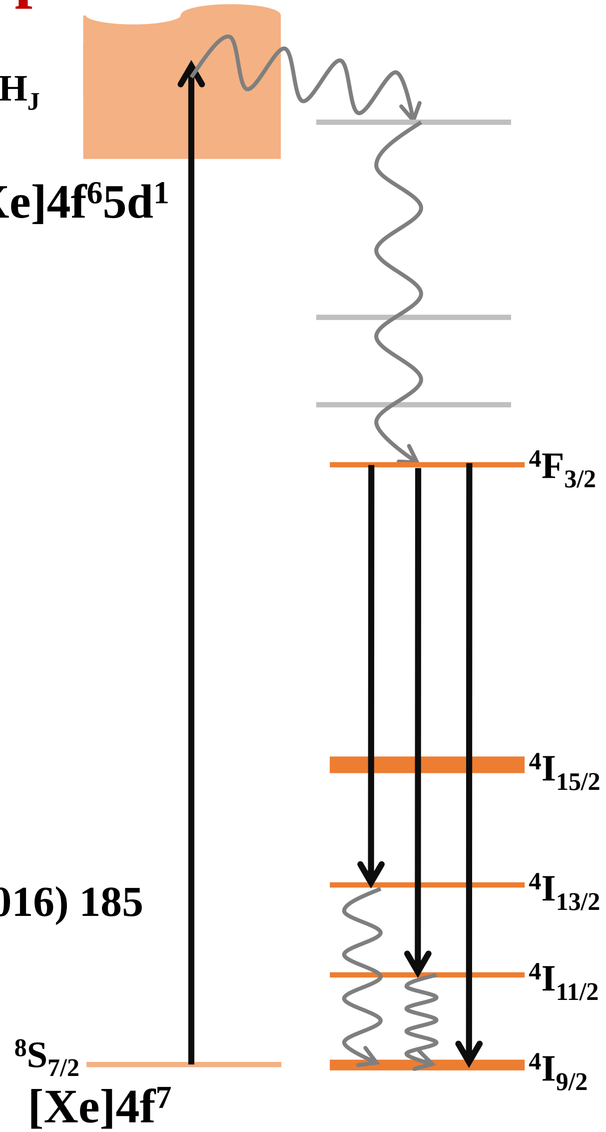
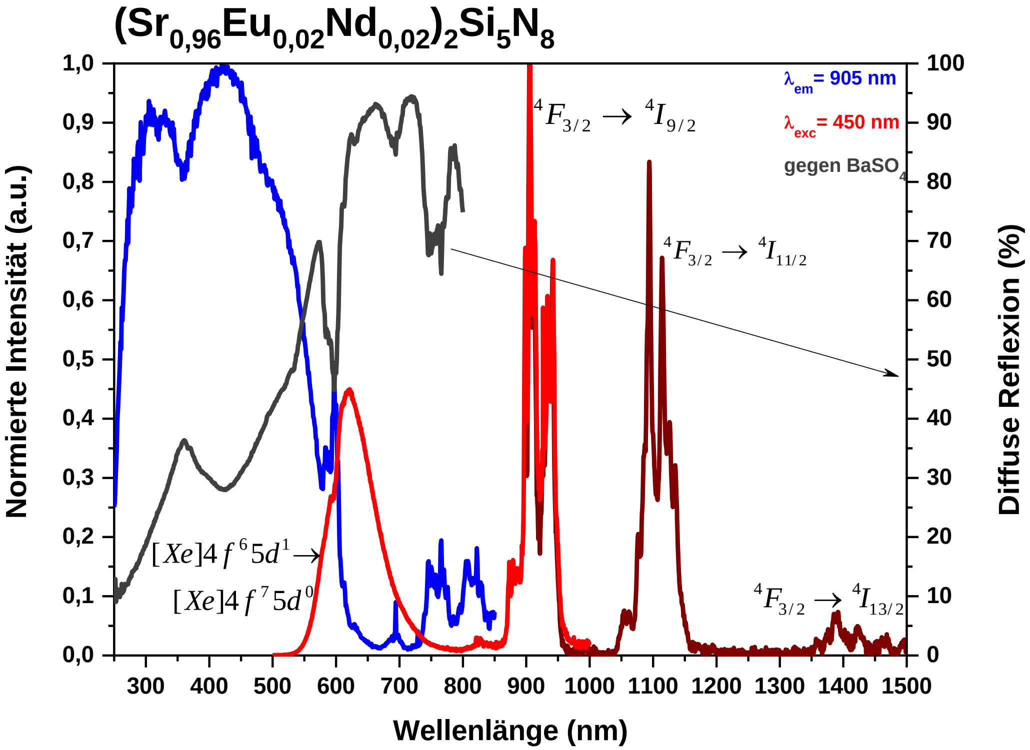
Eu^{2+}/Nd^{3+} Co-activated phosphors

Example: $Sr_2Si_5N_8:Eu^{2+},Nd^{3+}$



Energy transfer from Eu^{2+} to Nd^{3+} is working, though not completely

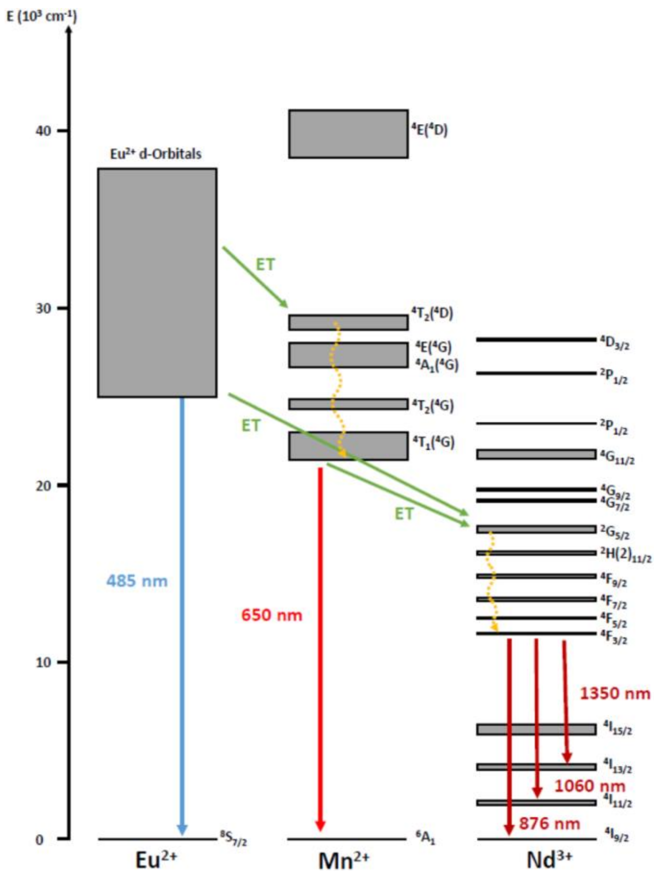


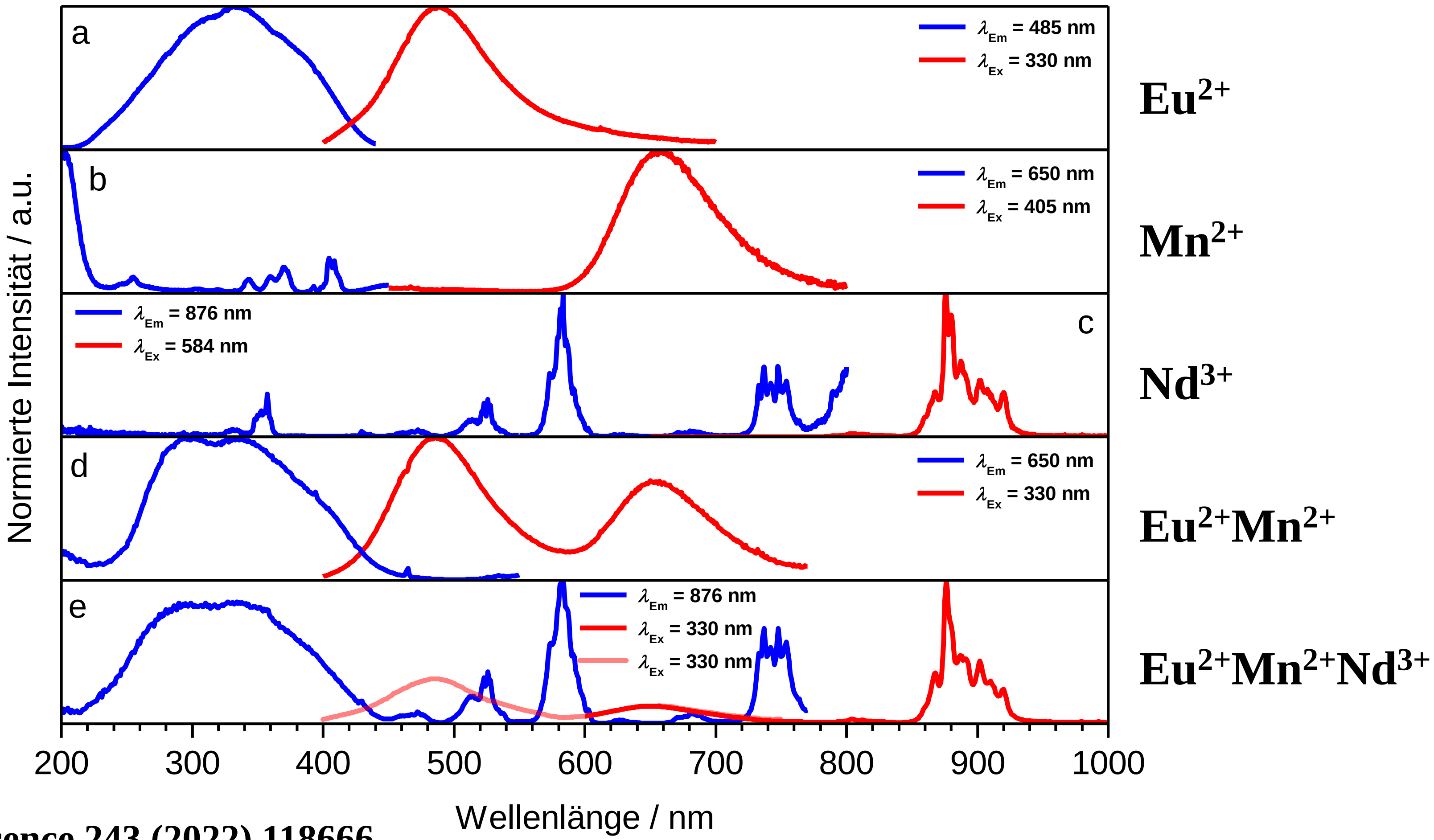
Lit.: S. Möller, T. Jüstel, J. Lumin. 172 (2016) 185

6. NIR Emitting Phosphors

$Eu^{2+}/Mn^{2+}/Nd^{3+}$ Co-activated phosphors

Example: $Ca_9Lu(PO_4)_7:Eu^{2+},Mn^{2+},Nd^{3+}$





Lit.: V. Anselm, T. Pier, T. Jüstel, J. Luminescence 243 (2022) 118666

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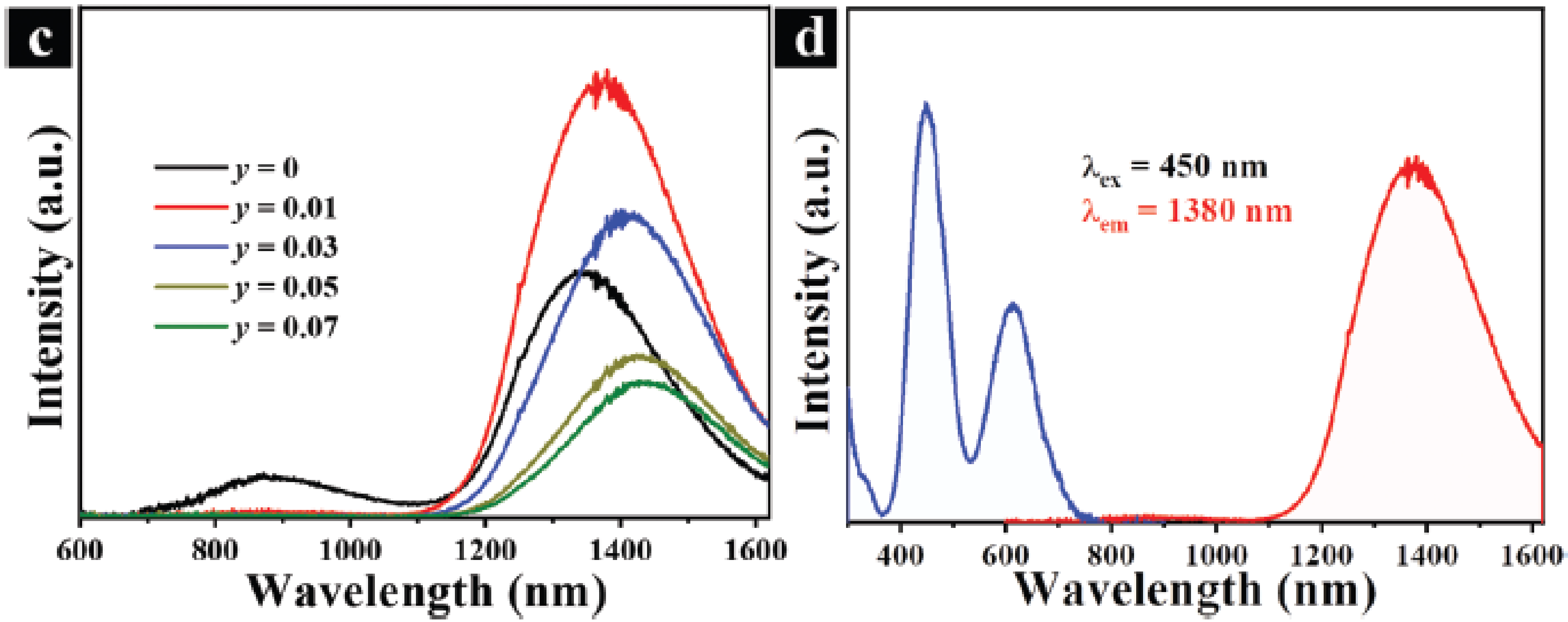
Cr^{3+}/Ni^{2+} Co-activated phosphors

Example: $LiMgPO_4:Cr^{3+},Ni^{2+}$

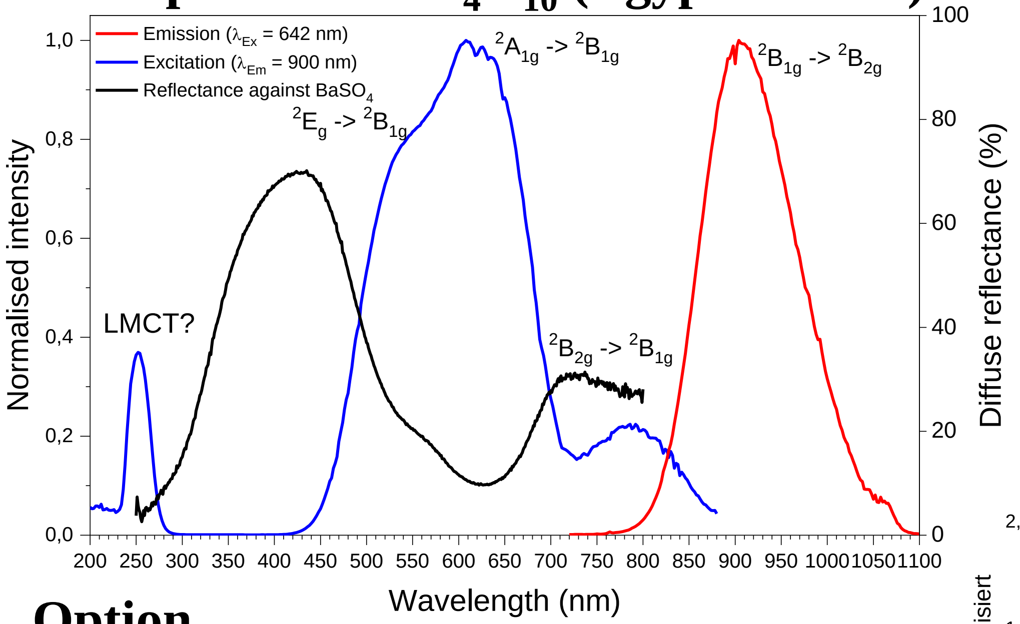


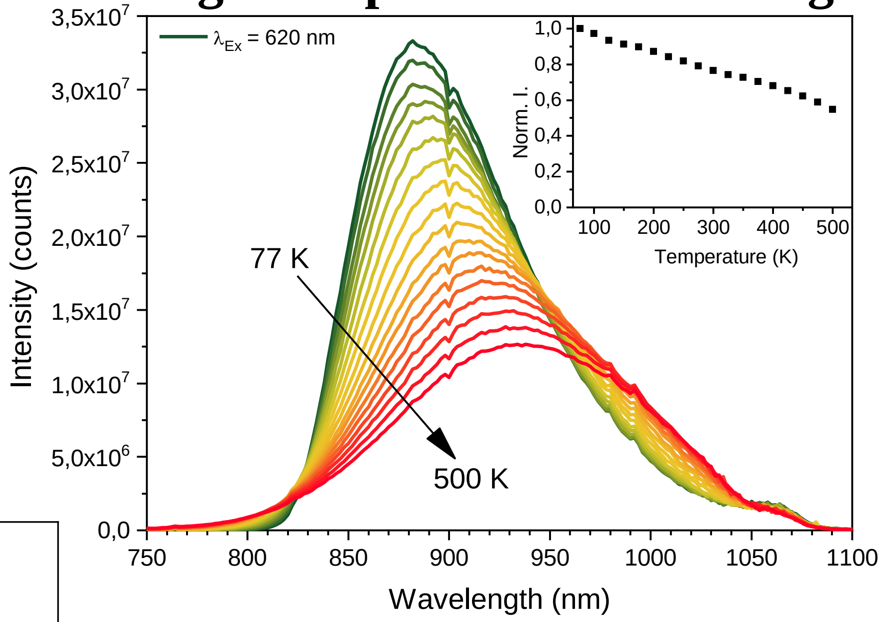
Lit.: Adv. Mater. Technol. 7 (2022) 2200320

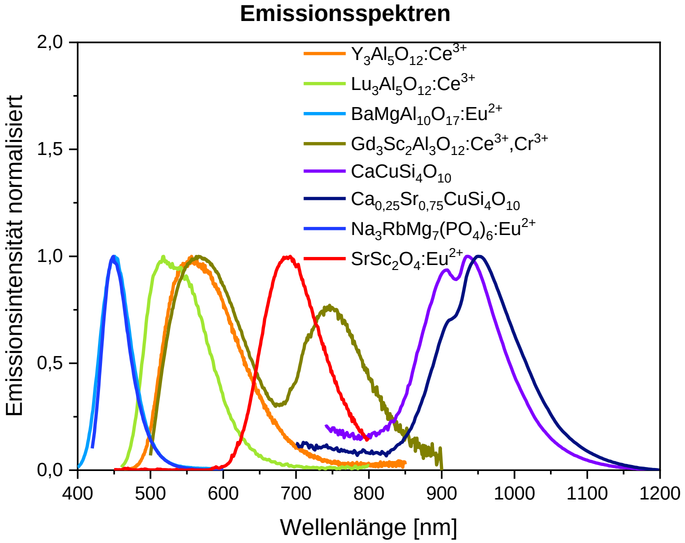
6. NIR Emitting Phosphors

Cu^{2+} activated phosphors

Examples: $CaCuSi_4O_{10}$ (Egyptian blue) & $BaCuSi_4O_{10}$ (Han blue) with strong absorption in the red range







Option

- **LED with full VIS to NIR spectrum**

Challenges

- **Absorption in the blue range**
- **Spectral consistency**

6. NIR Emitting Phosphors

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Cu^{2+} activated phosphors

Optimisation of Egyptian blue

Source: Australian Museum

Composition	λ (Ex,max) / nm	λ (Em,max) / nm	Thermal stability	Crystal system	Space group
$CaCuSi_4O_{10}$	620	935	> 1000 °C decomposition to tridymit, cuprit	tetragonal	P4/ncc (# 130)
$(Ca_{0,25}Sr_{0,75})CuSi_4O_{10}$	620	950	> 1000 °C decomposition to tridymit, cuprit	tetragonal	P4/ncc (# 130)
$(Ca_{0,25}Sr_{0,75})CuGeSi_3O_{10}$	620	960	> 1000 °C decomposition to tridymit, cuprit	tetragonal	P4/ncc (# 130)

7. Outlook

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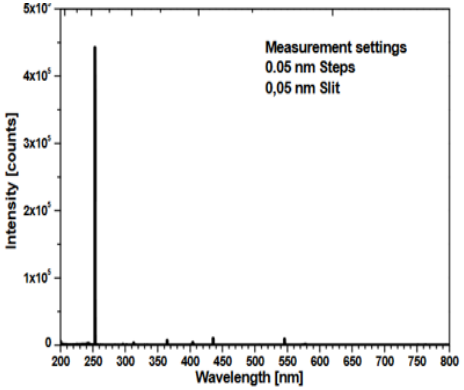
UV Radiation sources for water, air, surface disinfection/purification & photochem./-med.

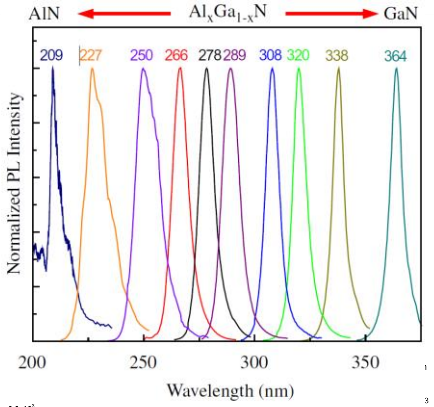
Today: Hg discharge lamps → phosphors for UV-A/B conversion required

- 253.7 nm main Hg* line, discharge is highly efficient and effective
- Hazardous towards skin and eyes → closed devices required
- 185.0 nm Hg line causes ozone formation
- Mature technology



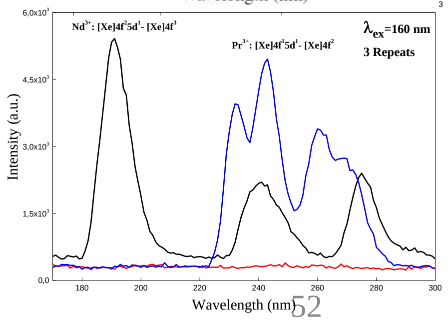
Future: LEDs! → LED phosphors for broad band UV spectra?

- Flexible, low-voltage, Efficiency: UV-A up to 50%, UV-B/C ~ 10%
- Band gap of (Al,Ga)N solid solution ~ 210 – 365 nm, practical limit ~ 230 nm
- Challenges: Stability and efficiency below 250 nm



Future: Excimer lamps? → VUV phosphors available from 193 – 380 nm

- Most common: Xe_2* 172 nm, KrCl* 222 nm, XeBr* 282 nm, XeCl* 308 nm
- Emission from 147 – 380 nm possible, potential for high power density
- Challenges: Stability and price → Quartz & phosphor degradation, driver, Xe



7. Outlook

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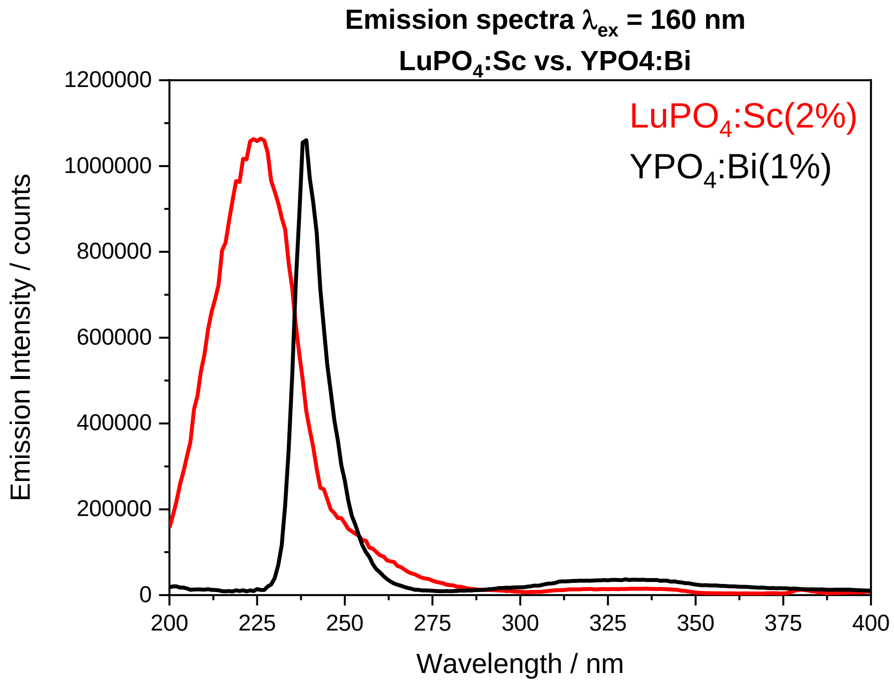
UV Radiation sources - Other options

- **450 nm LEDs or laser diodes + UV-C up-converter** — **220 – 230 nm**
- **Excimer discharge lamp with KrBr*** — **207 nm**
- **Xe_2* Excimer discharge lamp + deep UV-C emitting Sc^{3+} phosphor** — **200 – 220 nm**
- **x-ray tube + UV-C phosphor** — **200 – 280 nm**
- **Cathode-ray tube + UV-C phosphor** — **200 – 280 nm**



7. Outlook

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NIR Radiation sources for curing of coatings & biomedicine, NIR spectroscopy

- **(In,Ga)N LED comprising NIR phosphor with high quantum yield, little thermal quenching and high spectral consistency**
- **Search for Cr^{3+} activated materials with a small Stokes Shift**
- **Results from energy transfer studies**

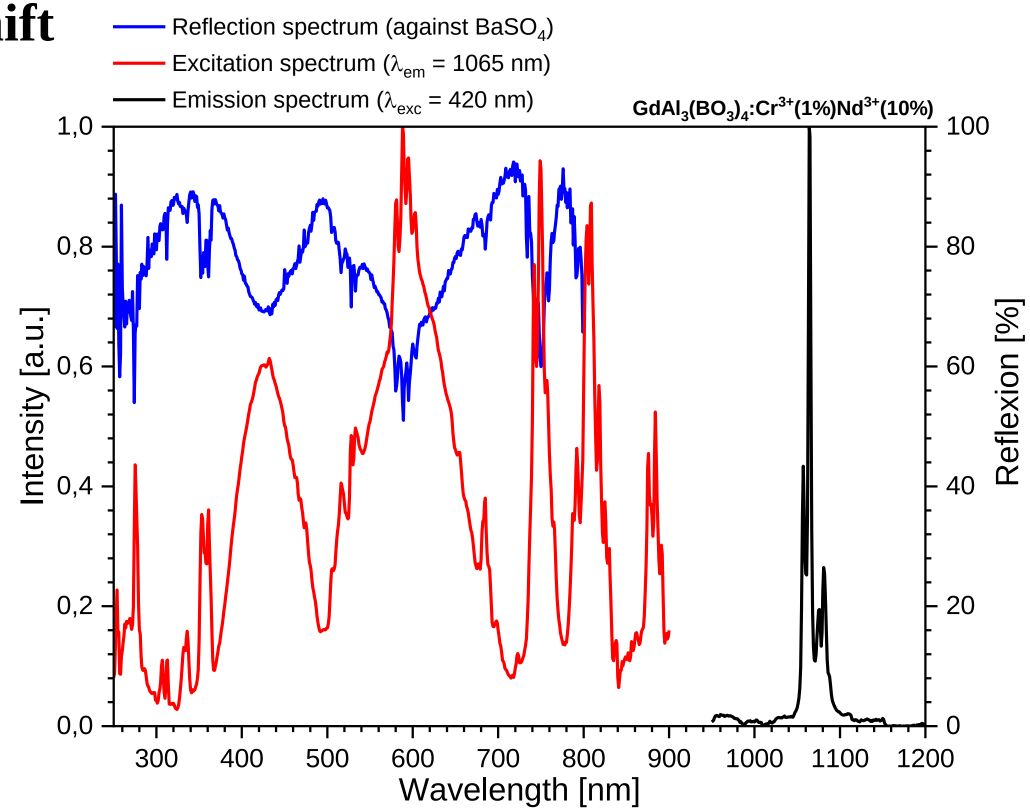
Cr^{3+} useful sensitiser for Cr^{4+}

Cr^{3+} useful sensitiser for RE activated NIR phosphors

Ce^{3+} useful sensitiser for RE activated NIR phosphors

Eu^{2+} useful sensitiser for RE activated NIR phosphors

Improvement of ET by Mn^{2+} or Nd^{3+} addition feasible



7. Outlook

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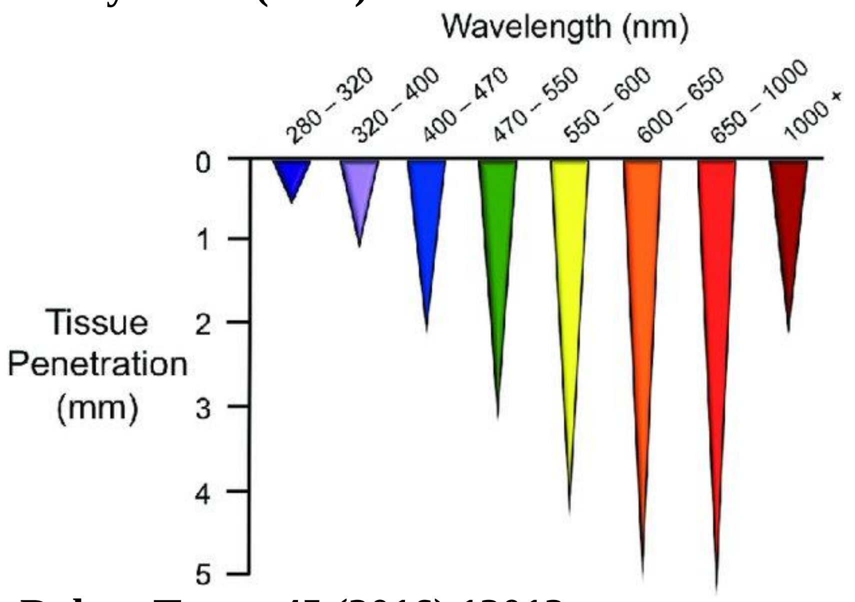
NIR Radiation sources for curing of coatings & biomedicine, NIR spectroscopy

- **Transition metals can cover the spectral range from 700 to 1600 nm**
  - **The couple $Cr^{3+/4+}$ can generate very broad NIR (700 - 1200 nm) emission spectra**
  - **Control of oxidation states will be challenging, i.e. host must have octahedral and tetrahedral sites as e.g. in $K_2Ge_4O_9$**
  - **Ni^{2+} emits from 1200 nm ($ZnGa_2O_4:Ni^{2+}$) to 1600 nm, while $KMgF_3:Ni^{2+}$ show high thermal stability according to literature**
  - **Ni^{2+} is rather redox-stable and synthesis of respective materials thus rather simple**
  - **Cu^{2+} is an efficient NIR emitter in some silicates**

- **Trivalent lanthanide ions to fill up spectral gaps, but absorption remains a tremendous problem: Sensitisation required as for Eu^{3+}**

NIR Range (nm)	Approximate penetration depth in Polystyrene (mm)
1100 – 1500	~ 5
1500 – 2000	~ 3
2000 - 2500	~ 1 - 2

Ref.: Analyst. 140 (2015) 2093



Ref.: Dalton Trans. 45 (2016) 13012

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- Homepage T. Jüstel — www.fh-muenster.de/juestel
- Research Gate — www.researchgate.com
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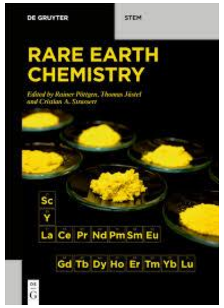

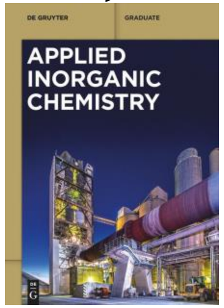

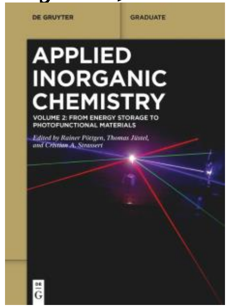

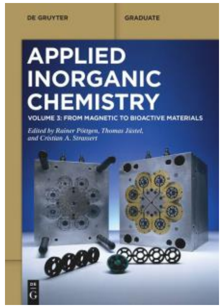

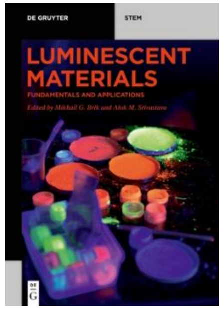

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