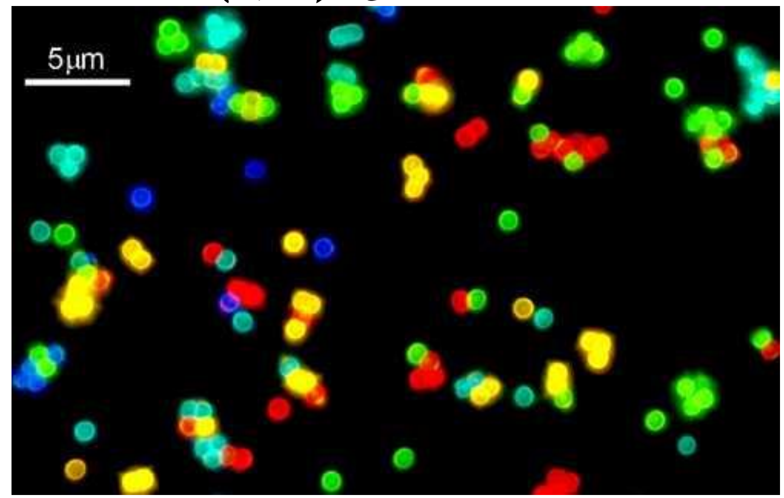
7. Luminescent Materials

Contents

Cd(S,Se) Quantum dots



7.1 History

Some milestones

Credit: Harald Biecker

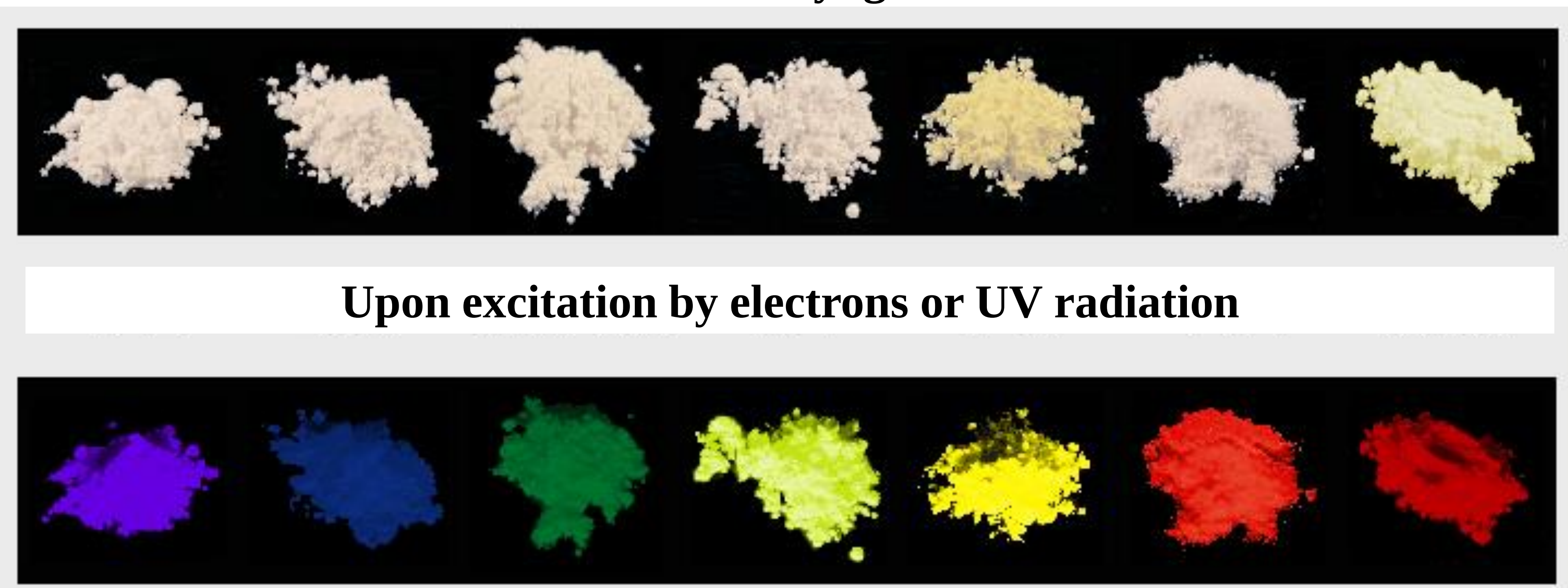
- **Stone of Bologna: Barit (Galilei 1600)**
- **Discovery of phosphors (phosphorescence) (Brand 1669)**
- **First phosphor by reaction of shells with sulfur (Canton 1768)**
- **Application of a phosphor in combination with a Hg-discharge (Becquerel 1859)**
- **Patent on the use of $CaWO_4$ in fluorescent lamps (Edison 1896)**
- **Fluorescent lamps with $MgWO_4$ + $(Zn,Be)_2SiO_4$:Mn (GE 1938)**
- **Development of $Ca_5(PO_4)_3(F,Cl)$:Sb,Mn (McKeag 1942)**
- **ZnS:Ag, $(Zn,Be)_2SiO_4$:Mn and $Zn_3(PO_4)_2$:Mn for first color CRT (1958)**
- **Fluorescent lamps with Eu- and Tb- phosphors (Verstegen 1974)**
- **First oxidic afterglow pigment $SrAl_2O_4$:Eu,Dy (Nemoto 1993)**
- **Nitride phosphors (Schnick 1995)**
- **$K_2SiF_6:Mn^{4+}$ as red line emitter for LEDs (GE 2006)**
- **Transparent ceramics converter for LEDs (Philips 2007)**
- **Narrow band red nitride phosphor $Sr[LiAl_3N_4]$:Eu (Schnick 2014)**

7.2 Definition and Working Principle

Definition

A phosphor is a micro-or nanoscale (in)organic pigment, that after excitation by radiation (NIR-,VIS-, UV-, X-ray-, gamma-), high-energy particles or matter vibrations (phonons), emits electromagnetic radiation beyond thermal equilibrium.

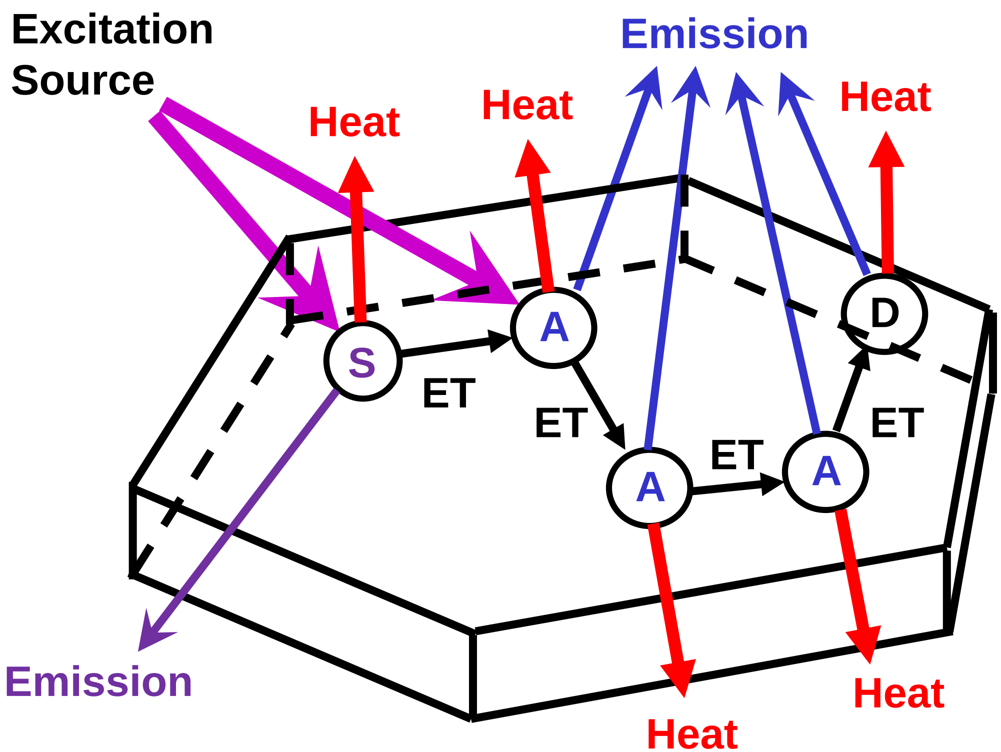
Under daylight



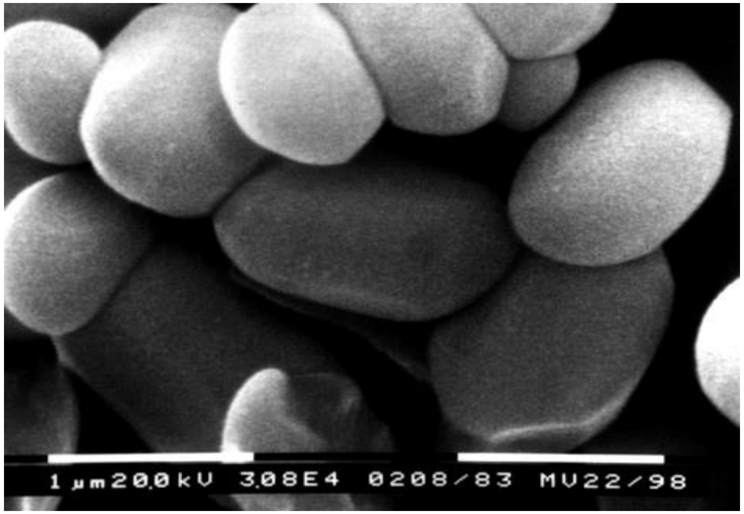
7.2 Definition and Working Principle

Working principle

1. **Excitation:** Absorption of energy from an external source
2. **Energy transfer (ET):** To activator ions (luminescence) or defects (storage)
3. **Relaxation :** Radiative: Emission (luminescence) → Luminescent pigm.
   Non-radiative: Heat (phonons) → Pigment



SEM image of (Y,Gd)BO_3:Eu



Typical particle size 1 - 10 µm

7.3 Luminescence Mechanisms

Type	Physical process (time scale)
Fluorescence	Spin-allowed transition (ns - µs)
Phosphorescence	Spin-forbidden transition (ms)
Afterglow (pers. luminescence)	Thermal activation of charge carriers (s)

Type	Excitation source	Applications
Photoluminescence	UV photons	Fluorescent lamps
Radioluminescence	x- and γ-rays, e^-, e^+, α	x-ray imaging, CT, PET
Cathodoluminescence	Electrons	TVs, monitors
Electroluminescence	Electric field	LEDs, EL displays
Thermoluminescence	Heat	Age determination
Chemiluminescence	Chemical reaction	Emergency signals
Bioluminescence	Biochemical reaction	Fireflies, jellyfish
Sonoluminescence	Ultrasound	-
Mechanoluminescence	Mechanical energy	-
Lyoluminescence	Free radicals	-

7.4 Chemical Composition

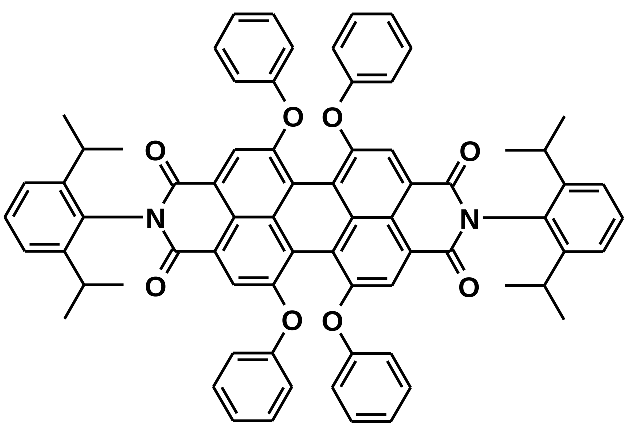
Organic phosphors (dyes or pigments)

Requirements and properties

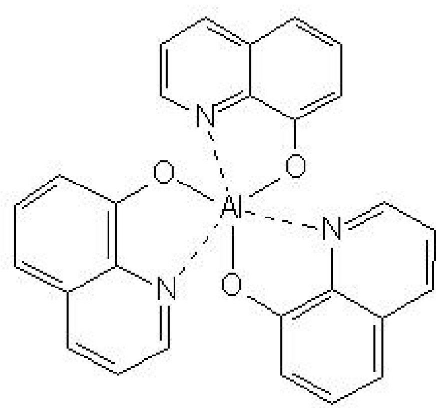
- **usually aromatic compounds: No C-H, N-H, or O-H bonds as ν > 2900 cm^{-1} yields MPR**
- **low energy $\pi \rightarrow \pi^*$ transitions**
- **quantum yield increases with number of aromatic rings and degree of condensation**
- **fluorescence especially favored for rigid structures**
- **fluorescence increase for bounding to a metal $\rightarrow$ complex formation**

Examples of selected efficient fluorescent compounds

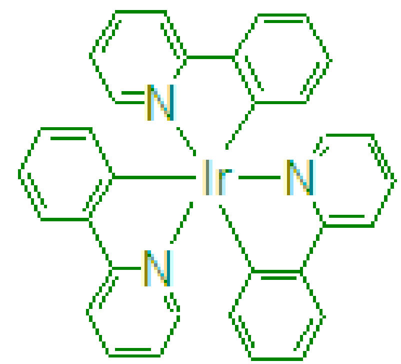
Perylenes



[Al(8-hydroxyquinolinate)$_3$



[Ir(phenylpyridine)$_3$]

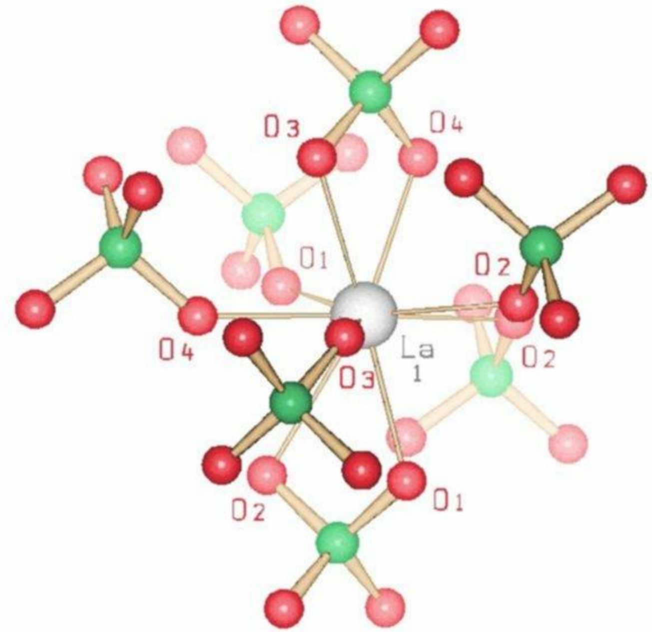


7.4 Chemical Composition

Inorganic phosphors (Luminescent pigments)

- Host material + Dopants + Defects
- Dopants = Activators + Sensitizers + Impurities
- Defects = 0-D (vacancies), 1-D (dislocations), 2-D (boundaries, surfaces), 3-D (pores)

Example, writings: $La_{1-x-y}Ce_xTb_y(PO_4)$ = $(La,Ce,Tb)PO_4$ = $LaPO_4$:Ce,Tb = Ce,Tb:$LaPO_4$



7.4 Chemical Composition

Composition ⇒ Inorganic host + Dopants + Impurities + Defects

Dopants = Activator/Sensitizers (Impurities) = RE-, TM-, and s^2-ions

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn						

6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

7.4 Chemical Composition

Luminescent pigment = Inorganic host + Dopants (Impurities) + Defects

Inorganic Host

- **Selection in accordance to requirements defined by the application area:**
  Excitation energy, absorption strength, chemical environment, temperature, pressure and so on

Dopants (Impurities)

- **Selection and concentration depends on host lattice and application:**
  Solubility, mobility, oxidation state stability, CT state location
- **Co-dopants to enhance absorption**

Defects

- **Afterglow (persistent luminescence)**
- **Luminescence quenching (conc. and temperature dependent)**
- **Stability reduction**

7.4 Chemical Composition

Luminescent pigment = Inorganic host + Dopants (s^{2-}, TM, or RE ions) + Defects

Inorganic host

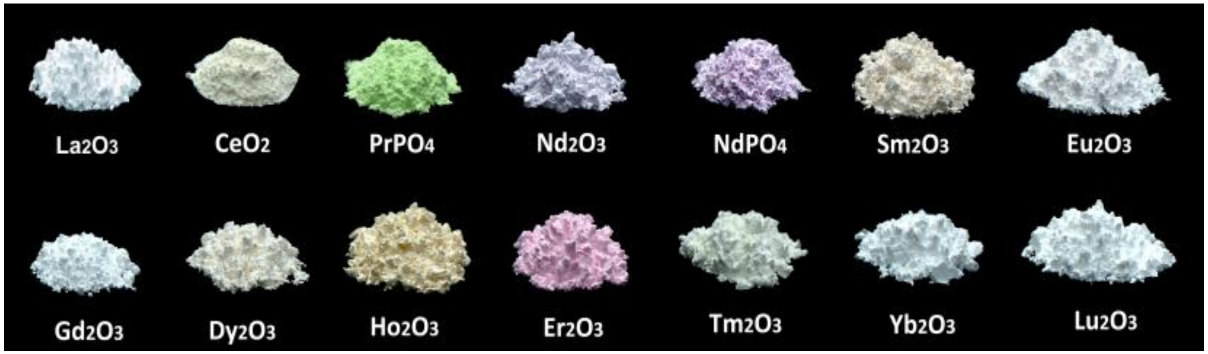
- **Oxides** Y_2O_3, $Y_3Al_5O_{12}$, YBO_3, YVO_4, YPO_4, $LaPO_4$, $BaMgAl_{10}O_{17}$, …
- **Sulfides** ZnS, MgS, CaS, SrS, $SrGa_2S_4$, $SrIn_2S_4$, Y_2O_2S, Gd_2O_2S, …
- **Fluorides** CaF_2, $LiYF_4$, K_2SiF_6, KYF_4, KY_3F_{10}, YOF, K_2NbF_7, …
- **Nitrides** $CaSiN_2$, $CaAlSiN_3$, $Sr_2Si_5N_8$, $La_3Si_6N_{11}$, $SrSi_2N_2O_2$, $SrLiAl_3N_4$, …

Dopants (impurities)

- **s^2 Ions** Sn^{2+}, Sb^{3+}, Tl^{+}, Pb^{2+}, Bi^{3+}
- **TM Ions** Ti^{3+}, $V^{2+/3+}$, $Cr^{3+/4+}$, $Mn^{2+/4+}$, Fe^{3+}, Co^{2+}, Ni^{2+}, $Cu^{+/2+}$, Ag^{+}, Au^{+}
- **RE Ions** Ce^{3+}, Pr^{3+}, Nd^{3+}, $Sm^{2+/3+}$, $Eu^{2+/3+}$, Gd^{3+}, Tb^{3+}, Dy^{3+}, Er^{3+}, Tm^{3+}, $Yb^{2+/3+}$

Defects

- **Cation vacancy** V_C
- **Anion vacancy** V_A
- **Interstitials** I
- **Colour centers** F



7.4 Chemical Composition

Luminescent pigment = Inorganic host + Dopants (impurities) + Defects

Inorganic Host

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

Dopants (impurities) and defects

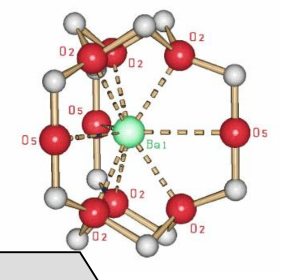
- Concentration
- Phase diagram and miscibility gaps

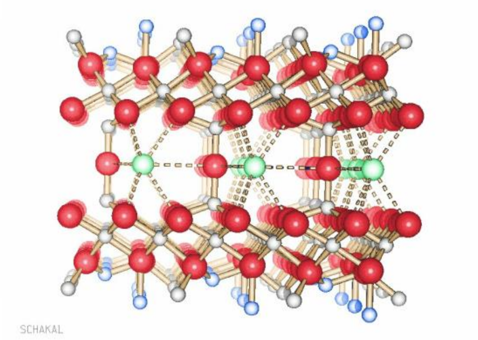
Particle surface

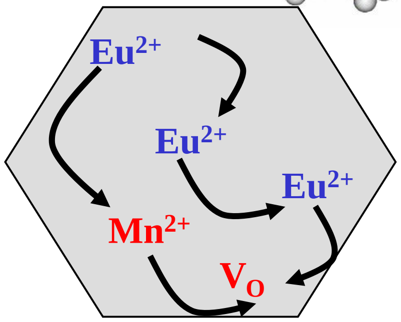
- Zeta-potential
- Surface area, defects, and energy
- Coatings → Light in- and outcoupling

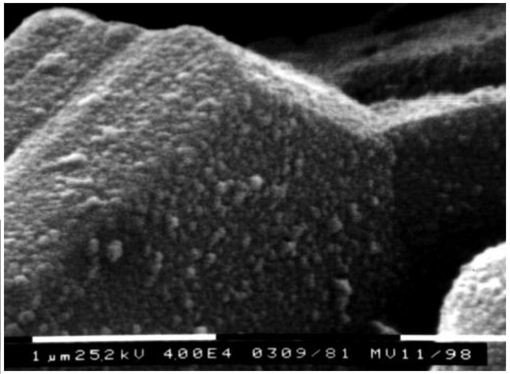
Particle morphology

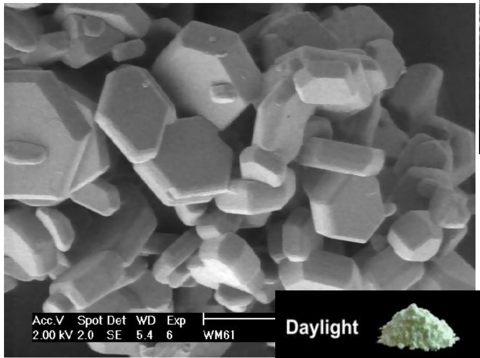
- Shape
- Particle size distribution
- Agglomeration

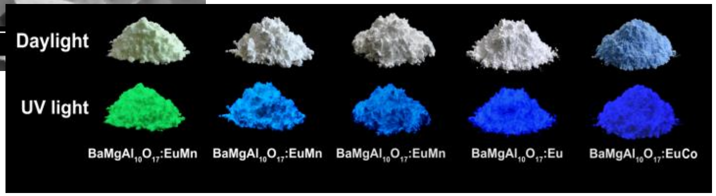












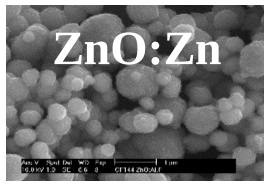
7.4 Chemical Composition

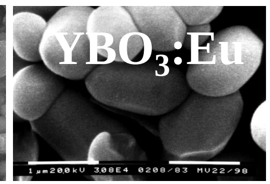
Luminescent pigments – Particle Morphology and Surface Optimisation

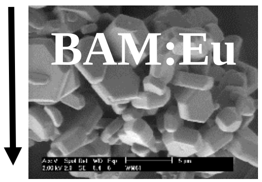
Novel application areas ⟵ ⟶ lifetime↑, $T_{1/2}$↑, α↓, λ↑

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

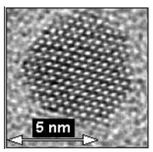
atoms | cluster | nano crystals | micro crystals | single crystals

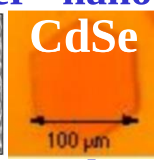


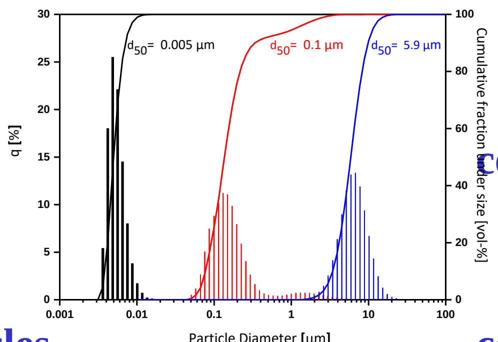




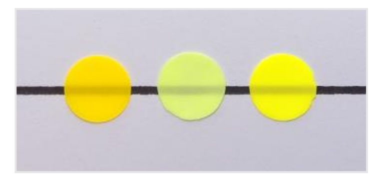
amorphous matter | nano ceramics | ceramics (opaque)

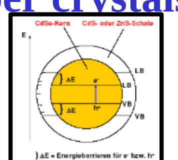




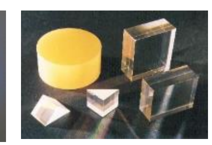


super crystals | ceramics (translucent)





core-shell particles | ceramics (transparent)



Glasses CdSe, $CsPbBr_3$ | $(Y,Tb,Lu)_3Al_5O_{12}$:Ce $Lu_3Al_5O_{12}$:SE (SE = Ce - Yb)

(bio)marker, µ-LEDs, PV units | high power LEDs/laser, scintillators, excimer lamps

7.5 Composition and Function

Most relevant physical properties

Photoluminescence (PL) spectra

Absorption and reflection spectra

Quantum yield (QY) (internal and external)

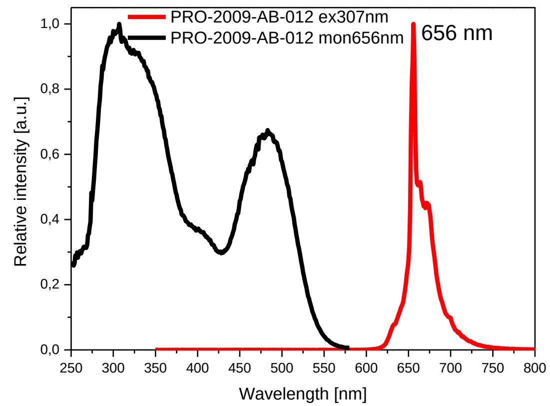
Stability and colour point consistency

Decay curves and afterglow (T-dependent)

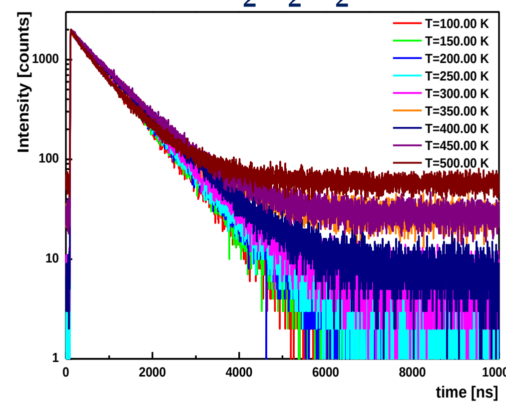
Thermal quenching

Linearity (saturation)

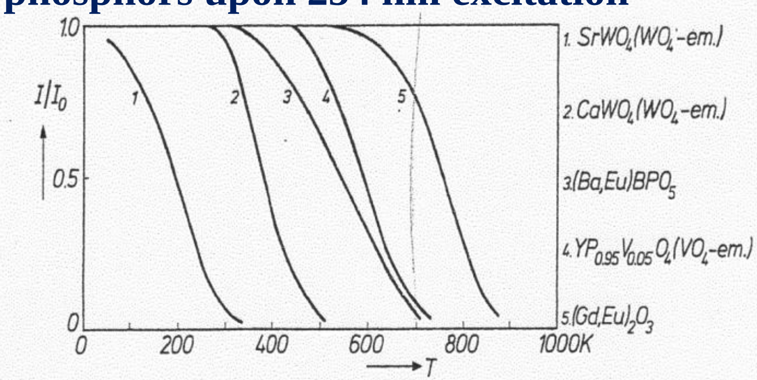
PL (excitation and emission) spectrum of Mg_2TiO_4:Mn



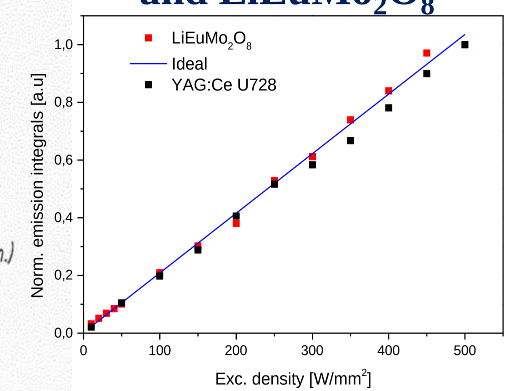
Decay curves of $SrSi_2N_2O_2$:Eu



Temperature dependent PL of some phosphors upon 254 nm excitation



Linearity of YAG:Ce and $LiEuMo_2O_8$



7.5 Composition and Function

Composition: Listed by the activator (transition metal ions and s^2-ions)

Activator	Host material	Emission at [nm]	Color	Applications
Cr^{3+}	Al_2O_3 (Ruby) $Ga_3Ga_5O_{12}$ (Garnet)	694	Red IR-A	Solid State Laser NIR LEDs
Mn^{2+}	Zn_2SiO_4 (Willemite) $BaMgAl_{10}O_{17}$ (ß-Alumina)	525 515	Green Green	PDPs, CRTs PDPs, FLs
Mn^{4+}	$Mg_4GeO_{5.5}F$ K_2SiF_6	655 630	Deep Red Red	Hg high-pressure lamps LEDs
Fe^{3+}	$LiAlO_2$	735	Red	FLs
Cu^+	ZnS	530	Green	CRTs
Ag^+	ZnS	450	Blue	CRTs
Sn^{2+}	$(Sr,Mg)_3(PO_4)_2$	630	Red	Hg high-pressure lamps
Sb^{3+}	$(Sr,Ca)_5(PO_4)_3(Cl,F)$	480	Blue-Green	FLs
Tl^+	NaI CsI	415 560	Blue Yellow	x/γ-ray detectors x/γ-ray detectors
Pb^{2+}	$BaSi_2O_5$ (Sanbornite) $Sr_2MgSi_2O_7$ (Akermanite)	350 365	UV-A UV-A	FLs for tanning
Bi^{3+}	$Bi_4Ge_3O_{12}$	480	Blue-Green	x/γ-ray detectors

7.5 Composition and Function

Composition: Listed by the activator (rare earth ions: Ce … Yb)

Activator	Host material	Emission at (nm)	Color	Applications
Ce^{3+}	$LaPO_4$ YPO_4 $Y_3Al_5O_{12}$ (Garnet)	320 335, 355 560	UV-B UV-A Yellow	FLs for tanning FLs for tanning FLs, LEDs
Pr^{3+}	Gd_2O_2S $CaTiO_3$	510 610	Green Red	Computer Tomography (CT) Field Emission Displays (FEDs)
Nd^{3+}	$Y_3Al_5O_{12}$ (Garnet)	1064	IR-A	Solid State Laser
Eu^{2+}	SrB_4O_7 $BaMgAl_{10}O_{17}$ $Sr_4Al_{14}O_{25}$	368 453 490	UV-A Blue Blue-green	FLs for tanning FLs, PDPs FLs, LEDs
Eu^{3+}	Y_2O_3 YVO_4	611 615	Red Red	FLs Hg high-pressure lamps
Gd^{3+}	$(La,Bi)B_3O_6$ $Lu_3Al_5O_{12}$ (Garnet)	311 314	UV-B UV-B	FLs for photochemistry and photomedicine
Tb^{3+}	$LaPO_4$ $CeMgAl_{11}O_{19}$ $(Gd,Ce)MgB_5O_{10}$	544 544 544	Green Green Green	FLs FLs FLs
Yb^{3+}	$Y_3Al_5O_{12}$ (Garnet)	980	IR-A	Solid State Laser

7.6 Application Areas

$Lu_3Al_5O_{12}$:Pr (EOT)

Application in	Excitation source
Scintillator crystals	γ-rays, particles
X-rays intensifier	X-rays
Cathode ray tubes	electrons
Plasma screens	147, 172 nm
Xe-discharge lamps	172 nm
Hg-high pressure discharge lamps	200 – 350 nm
Hg-low pressure discharge lamps (FLs)	185, 254 nm
Emissive LCDs	370 – 400 nm
Phosphor converted light emitting diodes (pcLEDs)	370 – 480 nm
Solid State Laser (SSL)	300 – 1000 nm

Host material (above dashed line) / Activator (below dashed line)

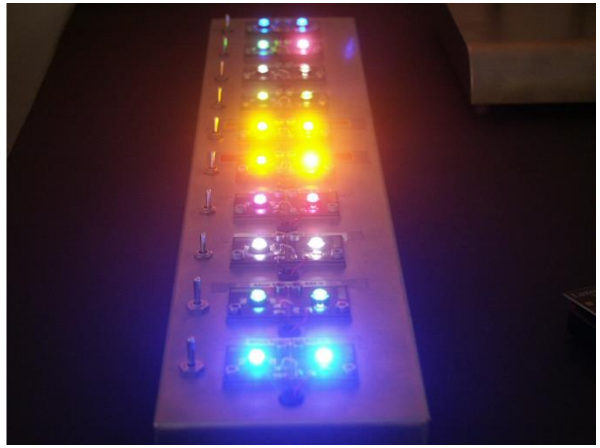
↑ Excitation energy

Main application areas: Lighting, imaging, projection, detection, and sensing

7.6 Application Areas

TV

LEDs



Plasma TVs

Fluorescent lamps

Tomography

Electroluminescent screens

7.6 Application Areas

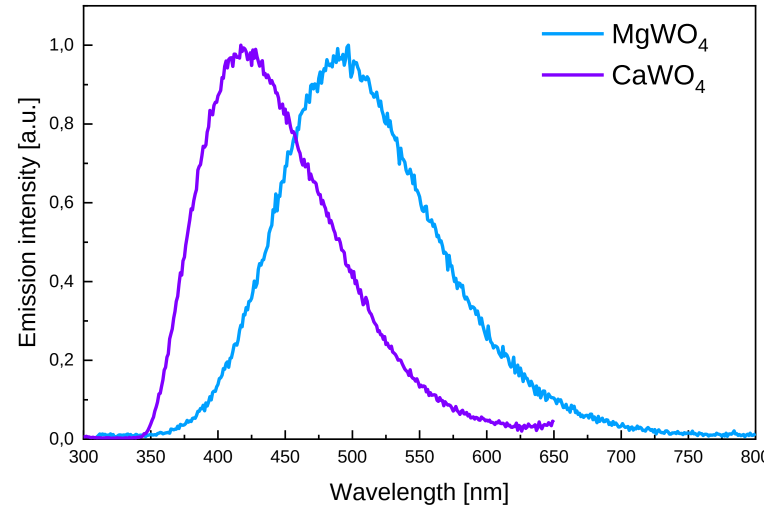
Function	Application field
Optical brighteners	Paint, paper, pulp, clothing, detergent
Copy protection	Banknotes, stamps, credit cards, certificates, tickets
Product protection	Pharmaceuticals, plastics
Security labeling	Emergency exit lighting, emergency exits
Advertising / visualization	Decoration, advertisement, logos
Conversion of high-energy radiation or particles	X-ray films, CT, SPECT, positron emission tomography, EUV-amplifier
Cosmetics	Dental ceramics, tanning lamps
Marker for the analysis	Detection of nucleic acids + proteins
Lithographie	Photocopier
Photochemistry and biology	Water purification, disinfection, breeding boxes and cabinets, air pollution control
Medicine	Diagnostics, photodynamic therapy

7.7 Band Emitting Phosphors

Optical transitions (mostly interconfigurational)

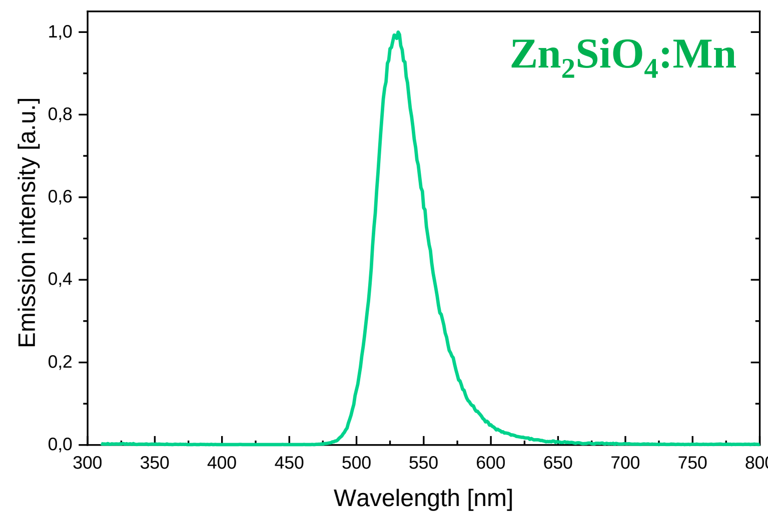
- Charge-Transfer (LMCT or MLCT)
- $5s^2$-$5s^15p^1$, $6s^2$-$6s^16p^1$
- $4f^n$-$4f^{n-1}5d^1$
- $3d^n$-$3d^n$

FWHM



Suitable activator ions/moieties

- VO_4^{3-}, WO_4^{2-}
- Sn^{2+}, Sb^{3+}, Tl^+, Pb^{2+}, Bi^{3+}
- Ce^{3+}, Eu^{2+}, Yb^{2+}
- Mn^{2+}, Cu^{2+}

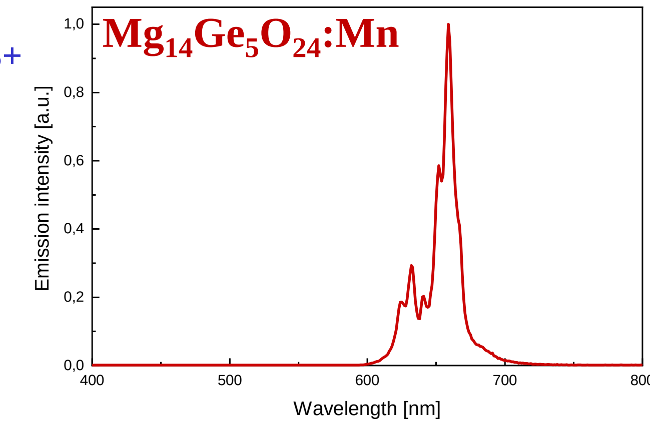


Examples	Mineral type
• $(Zn,Be)_2SiO_4$:Mn	Willemite
• $CaWO_4$	Scheelite
• $MgWO_4$	Wolframite
• $Ca_5(PO_4)_3(F,Cl)$:Sb,Mn	Apatite

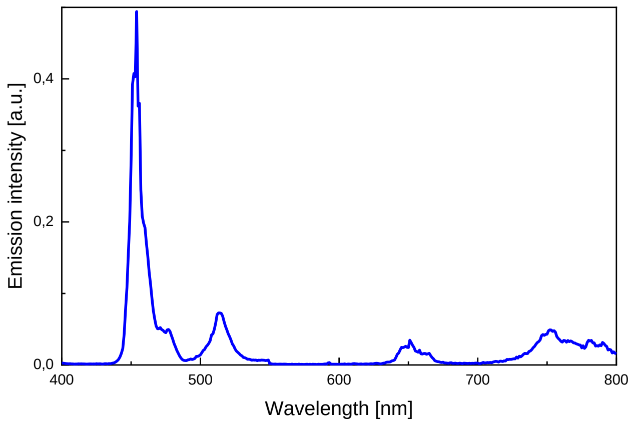
7.8 Line Emitting Phosphors

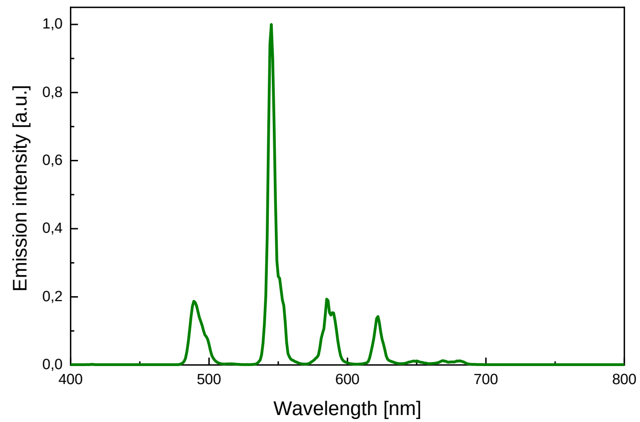
Optical transitions (intraconfigurational)

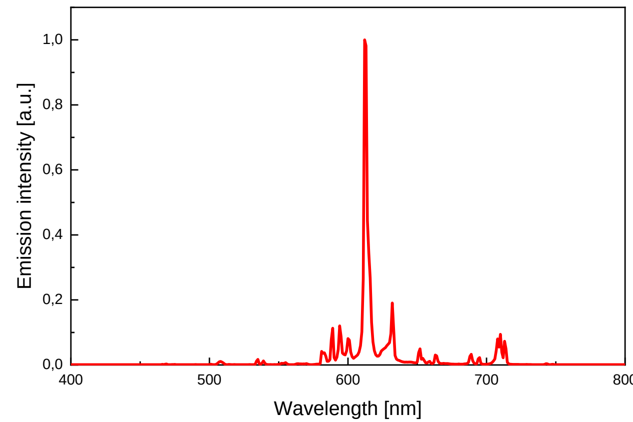
- $4f^n$-$4f^n$ Pr^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+}, Er^{3+}, Dy^{3+}, Tm^{3+}
- $3d^n$-$3d^n$ Mn^{4+}, Cr^{3+}



- **Very weak electron-phonon coupling**
- **Lines or line multiplets**







$LaPO_4$:Tm
YBO_3:Tm
$Y_3Al_5O_{12}$:Tm

$LaPO_4$:Ce,Tb
$LaMgB_5O_{10}$:Ce,Tb
$LaMgAl_{11}O_{19}$:Ce,Tb

Y_2O_3:Eu
$(Y,Gd)BO_3$:Eu
YVO_4:Eu

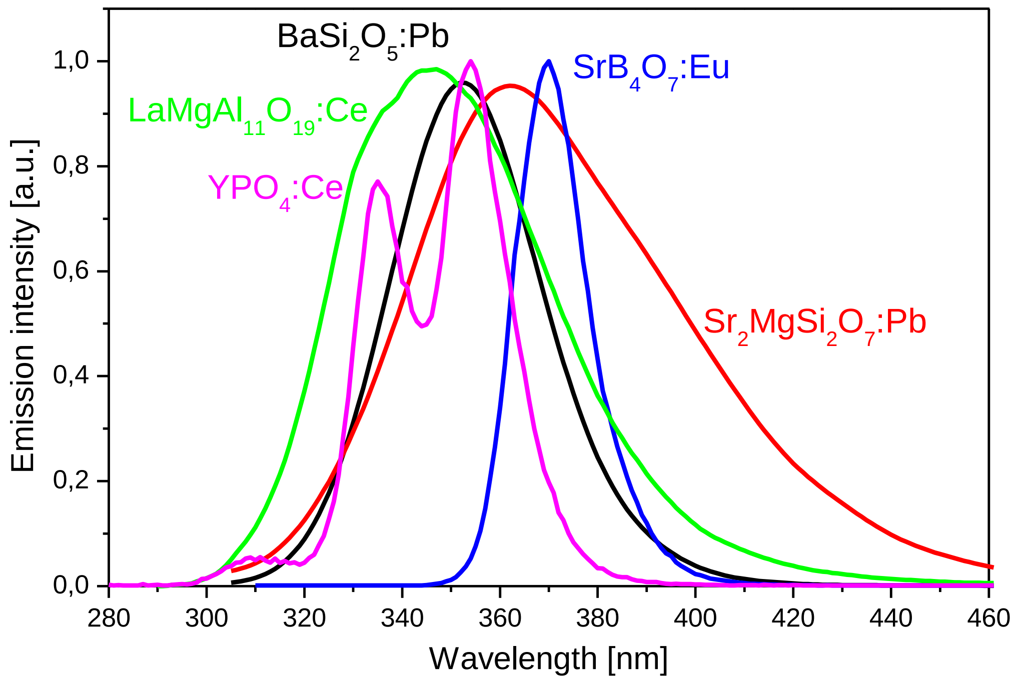
7.9 UV-A Phosphors

Optical transitions

- $4f^n$-$4f^{n-1}5d^1$
- $6s^2$-$6s^16p^1$

Suitable activators

- Eu^{2+} >365 nm, 1 band
- Ce^{3+} 2 overlapping bands
- Pb^{2+} 1 very broad band



Commercial materials	Emission at	Mineral type	Application area
• $LaMgAl_{11}O_{19}$:Ce	345 nm	Magnetoplumbite	Tanning lamps
• YPO_4:Ce	335, 355 nm	Xenotime	Tanning lamps
• $BaSi_2O_5$:Pb	350 nm	Sanbornit	Tanning lamps
• $Sr_2MgSi_2O_7$:Pb	365 nm	Akermanite	Tanning lamps
• SrB_4O_7:Eu	368 nm	Borax	Black light lamps

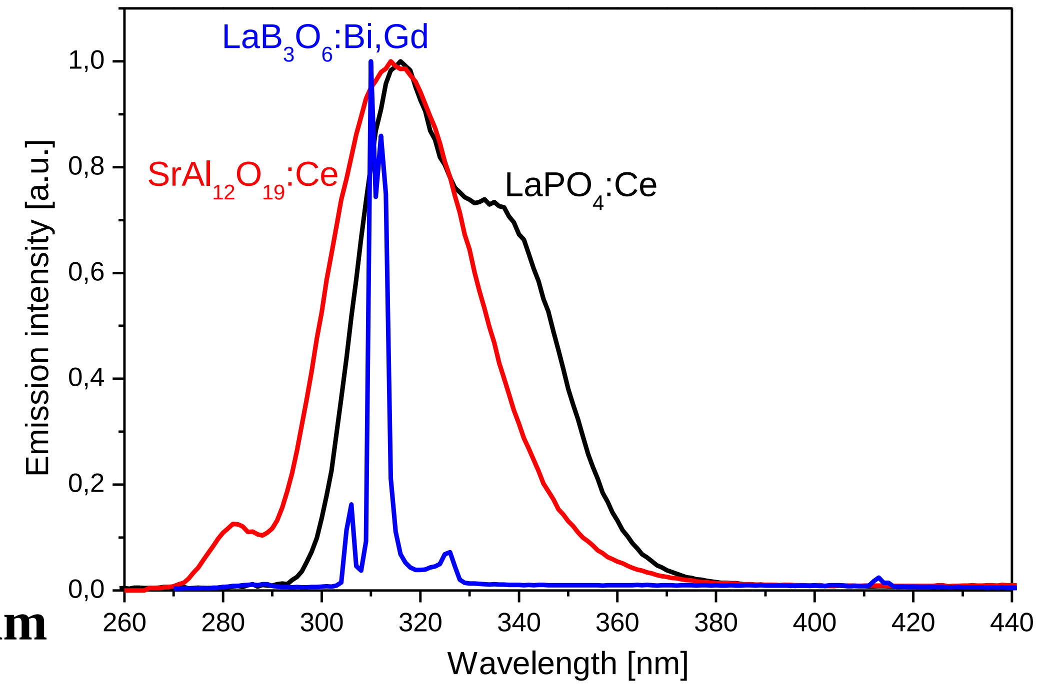
7.10 UV-B Phosphors

Optical transitions

- $4f^n$-$4f^{n-1}5d^1$
- $4f^n$-$4f^n$
- $6s^2$-$6s^16p^1$

Suitable activators

- Ce^{3+} 2 overlapping bands
- Bi^{3+} 1 band
- Gd^{3+} few lines around 312 nm



Commercial materials	Emission at	Mineral type	Application area
• $SrAl_{12}O_{19}$:Ce	300 nm	Magnetoplumbite	Tanning lamps
• LaB_3O_6:Bi,Gd	311 nm	-	Medical lamps
• $LaPO_4$:Ce	320 nm	Monazite	Tanning lamps

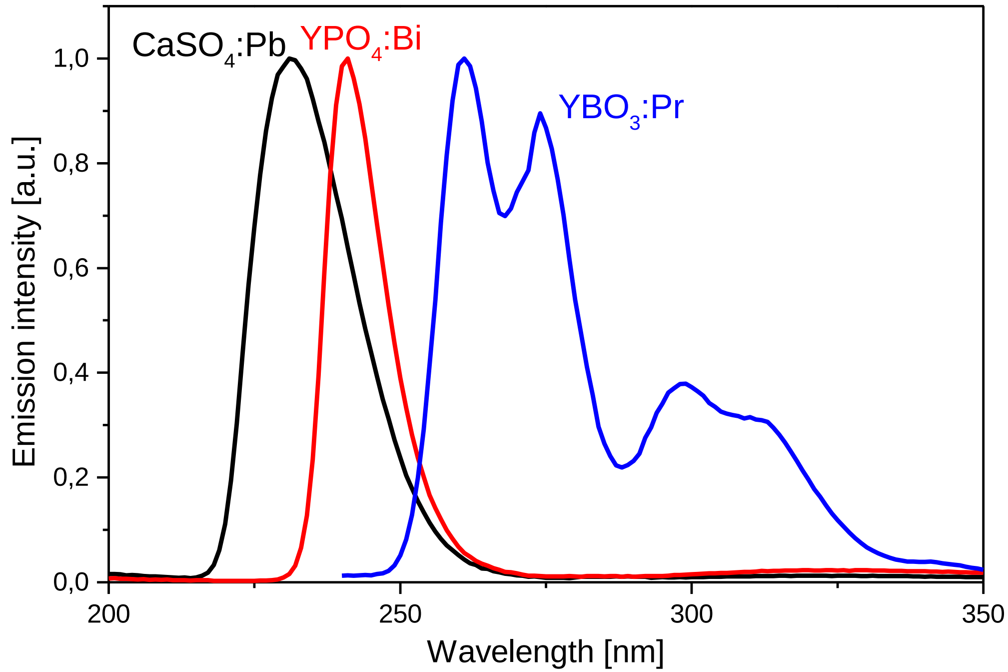
7.11 UV-C Phosphors

Optical transitions

- $4f^n$-$4f^{n-1}5d^1$
- $6s^2$-$6s^16p^1$

Suitable activators

- Pr^{3+} 4 overlapping bands
- Tl^+ 1 band
- Pb^{2+} 1 band
- Bi^{3+} 1 band



Examples	Emission at	Mineral type	Application area
• YBO_3:Pr	265 nm	Vaterite	Disinfection
• $YAlO_3$:Pr	245 nm	Perovskite	Disinfection
• YPO_4:Bi	240 nm	Xenotime	Disinfection
• $CaSO_4$:Pb	230 nm	Anhydrite	Disinfection

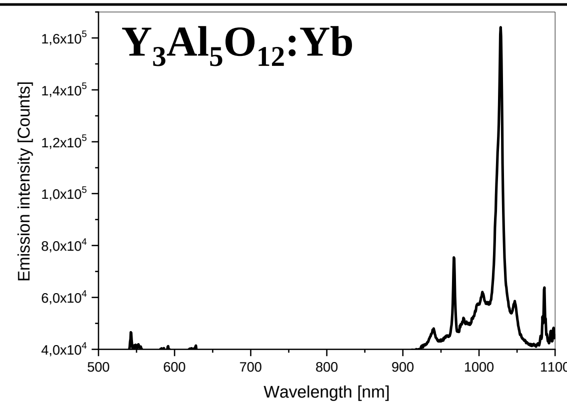
7.12 NIR Phosphors

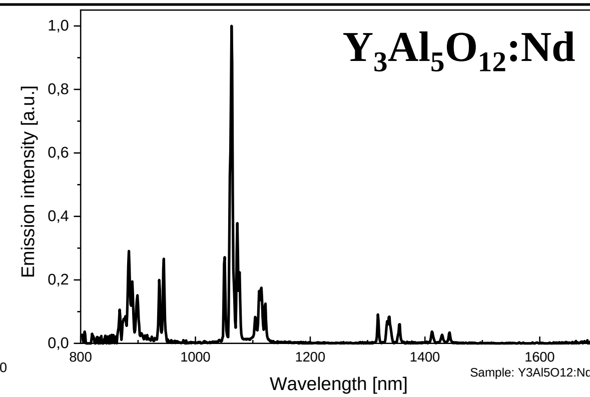
Optical transitions

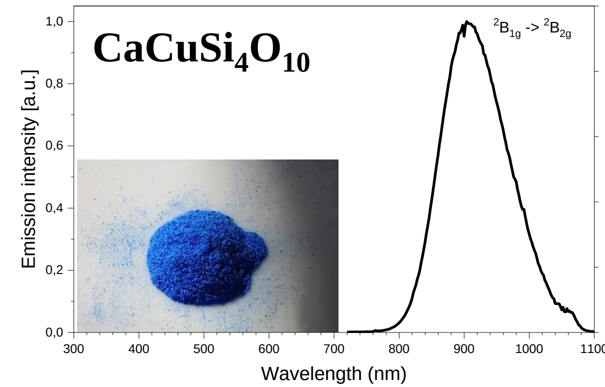
- $3d^n$-$3d^n$
- $4f^n$-$4f^n$

Suitable activators

- Cr^{3+} lines, 680 - 800 nm
- Cu^{2+} 1 band, 800 - 1000 nm
- Nd^{3+} lines, 1050 - 1100 nm
- Yb^{3+} lines, 950 - 1050 nm







Examples	Emission at	Mineral type	Application area
• Al_2O_3:Cr	694 nm	Corundum	Ruby laser
• $CaCuSi_4O_{10}$	910 nm	Cuprorivaite	NIR Marker
• $Y_3Al_5O_{12}$:Yb	1028 nm	Garnet	Solid state laser
• $Y_3Al_5O_{12}$:Nd	1064 nm	Garnet	Solid state laser

7.13 Future Trends

Efficiency: Light sources & displays

→ External quantum yield (EQY)↑

→ µ-particles → ceramics → single crystals

Lifetime/stability: Light sources & displays

→ Defect density↓ and particle coatings

Miniaturisation: µ-LED (displays)

→ PSD↓: Nanocrystals & Quantum Dots

→ Stability↑: Core-shell particles

Power density: HP LEDs & laser diodes

→ Decay time & ESA↓ redox stability↑

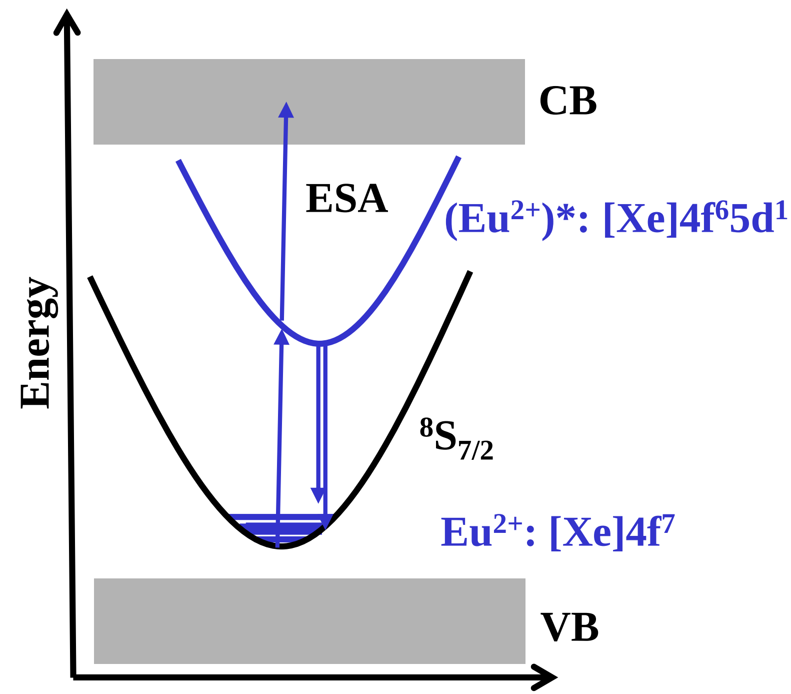
→ Density of optical center $N_{activator}$ [cm^{-3}]↑

Novel spectra: NUV, NIR, human centric lighting

→ UV: (Al,Ga)N LED / Xe excimer lamps

→ NIR: (In,Ga)N LED + deep red/NIR emitter

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



$P_{em,max} = Na_{ctivator}C_{extraction}\, R/\tau_r$ (R = radius)

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