FH MÜNSTER
University of Applied Sciences

CIW FB Chemieingenieurwesen
Department of Chemical Engineering

United Nations
Educational, Scientific and
Cultural Organization

2019 IYPT
International Year
of the Periodic Table
of Chemical Elements

The Elements: #63

Europium

„Element of the European Union“

$$_{31}\mathrm{Ga} + {}_{32}\mathrm{Ge} \rightarrow {}_{63}\mathrm{Eu}$$

Europa (Εὐρώπη): Consort of Zeus

Background

Discovery and Sources

- Europium was discovered by Eugène-Anatole Demarçay, a French chemist, in 1896. He was able to obtain pure europium in 1901
- The element europium was named after the continent of Europe
- Europium is primarily obtained through an ion exchange process from monazite sand ($(Ce,La,Th,Nd,Y)PO_4$), a material rich in rare earth elements

Properties

- A soft, silvery metal that tarnishes quickly and reacts with water
- Eu^{3+} glows red under UV radiation
- Eu^{2+} doped materials luminesce in the UV or in the whole visible range depending on the crystalline host
- Eu^{2+} and Eu^{3+} are strong paramagnetic ions (6 or 7 unpaired 4f electrons)

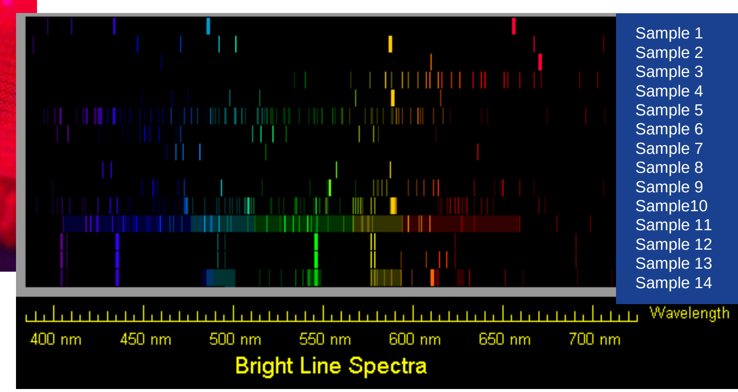
Physical Properties

Relative atomic mass:	151.965 g/mol		
Atomic radius:	204.2 pm		
Density:	5.25 g/cm^3		
Melting point:	822 °C		
Boiling point:	1597 °C		
Electron configuration:	[Xe]$4f^7 6s^2$		
Oxidation states:	+3, +2		
Electronegativity:	1.0		
Cristal structure:	cubic-centered		
Abundance:	2.1 ppm		
1st Ionisation energy:	5.67 eV		
Stable isotopes:	Eu-151:	47.8%	I = 5/2
	Eu-153:	52.2%	I = 5/2

Applications

Eu as a marker for anti counterfeiting (since 1970ties)

- Eu^{3+} show red glow
- Eu^{2+} show blue to yellow/orange glow

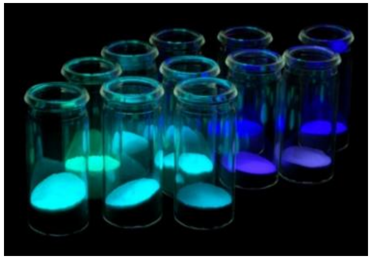


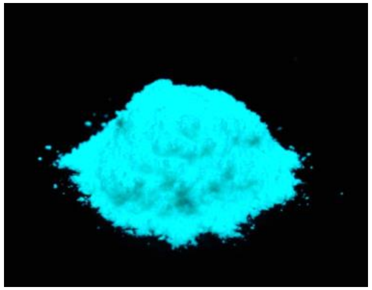
Banknotes and product anticounter feiting with Eu^{2+} and Eu^{3+}

Applications

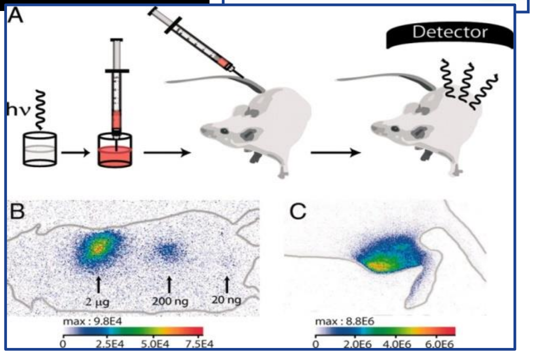
Eu as an activator for afterglow pigments

- $CaAl_2O_4$:Eu,Nd 440 nm
- $Sr_2MgSi_2O_7$:Eu,Dy 469 nm
- $Sr_4Al_{14}O_{25}$:Eu,Dy 490 nm
- $SrAl_2O_4$:Eu,Dy 520 nm
- Sr_2SiO_4:Eu,Dy 570 nm
- Y_2O_2S:Eu,Ti,Mg 620 nm
- $Sr_3Al_2O_5Cl_2$:Eu 630 nm
- CaS:Eu,Tm 655 nm
- $SrSc_2O_4$:Eu 685 nm





N329 in Oss (The Netherlands)



Applications

Eu as an essential emitter for modern displays and light sources

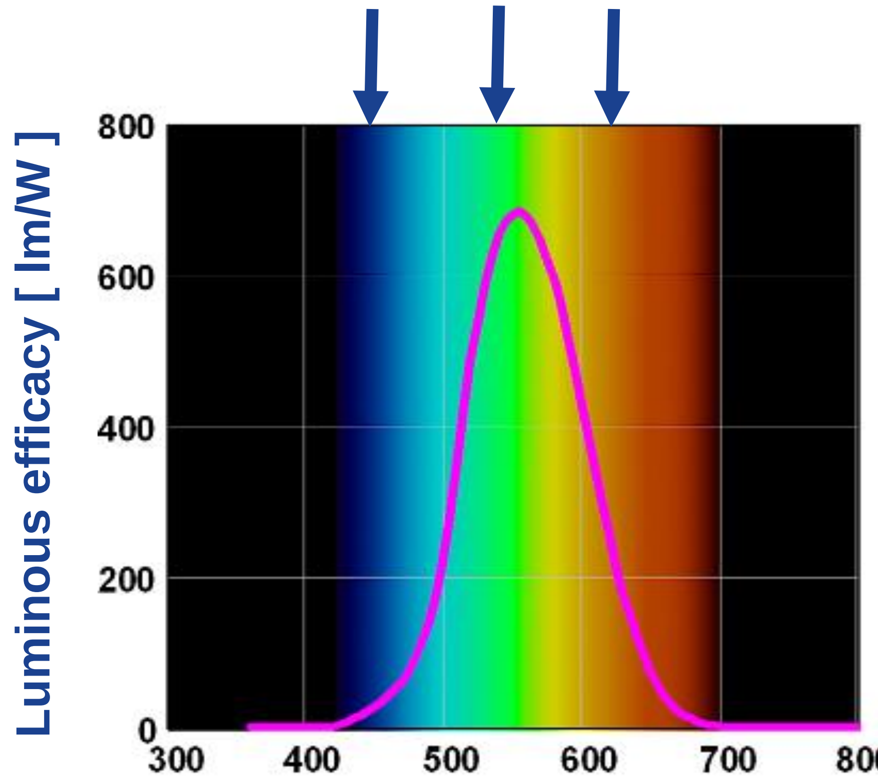
Light yield of a light source

Strongly dependent on emission spectrum

Optimum is at 555 nm
$V(\lambda)$ = 683 lm/W (η_v = 100%)

Emission of lines or narrow bands by

Eu^{2+} Tb^{3+} Eu^{3+}/Mn^{4+}



Evolution of Light Sources

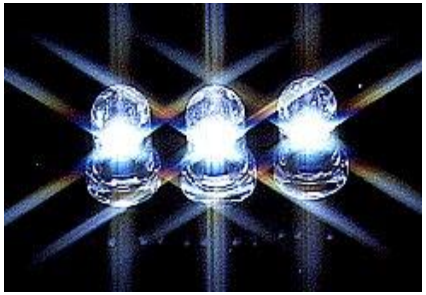
1st Revolution	2nd Revolution	3rd Revolution (Eu^{2+} and Eu^{3+})	4th Revolution (Eu^{2+})

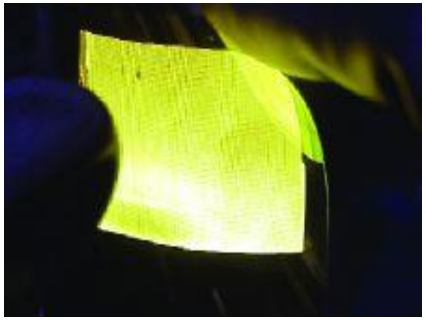
First there was open fire...

...then the fire was tamed...

...put into a glass bulb...

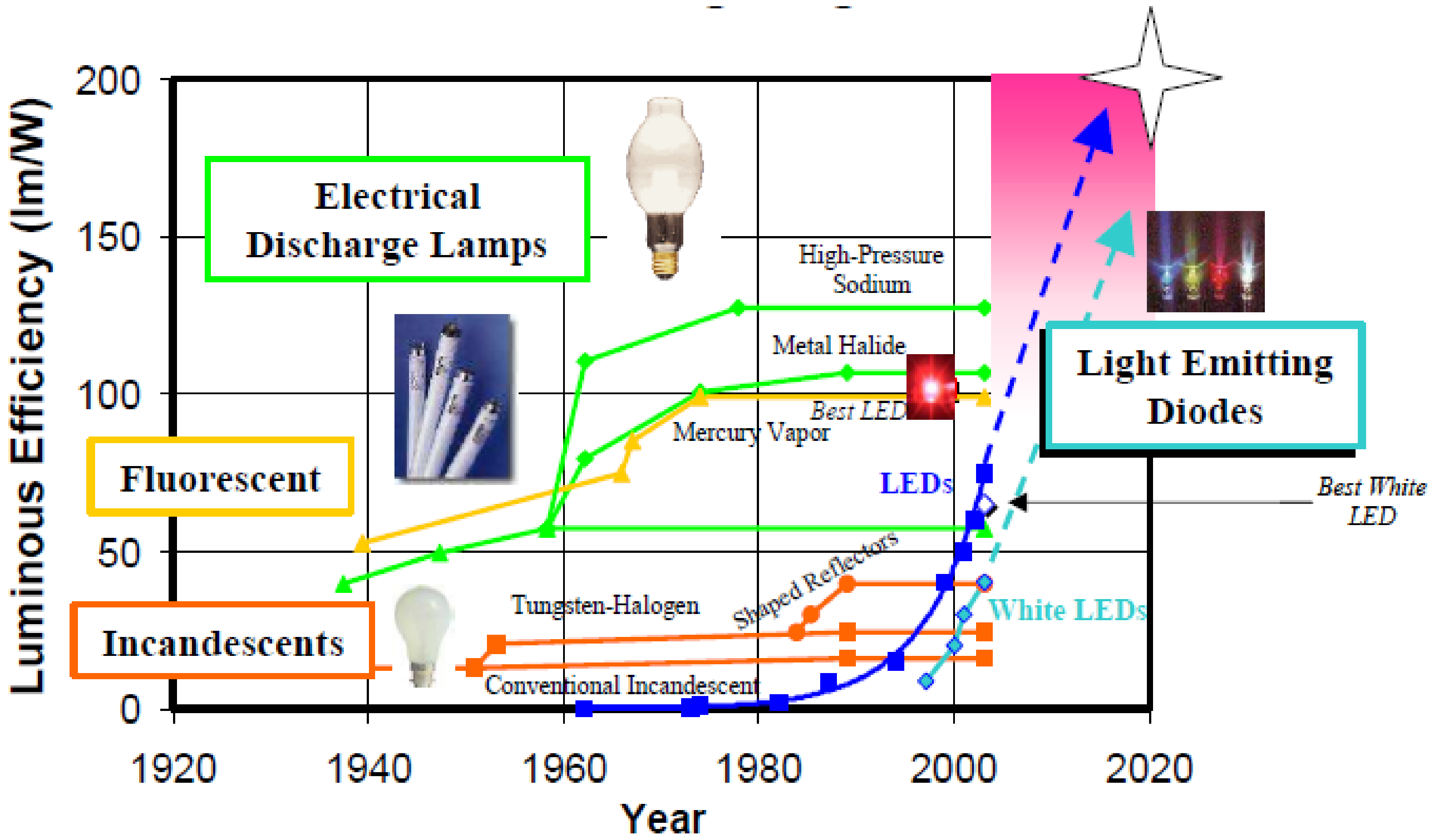
...and made more efficient...





...then the fire vanished and light only prevailed !

Evolution of Light Sources



Source: Philips

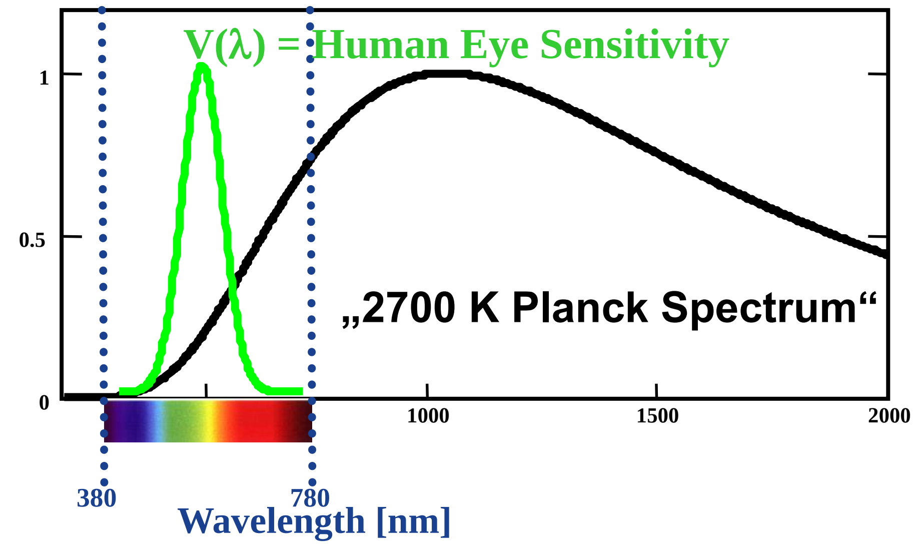
Evolution of Light Sources

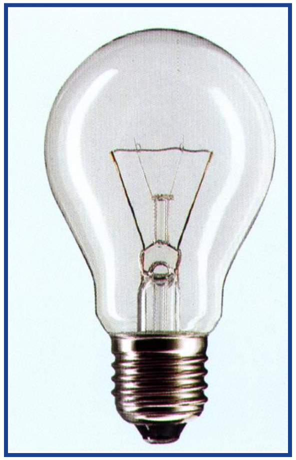
19th century – „Solid State Lighting“

Emission from solids in thermal equilibrium „Black body radiation“

Materials: C, Os, W

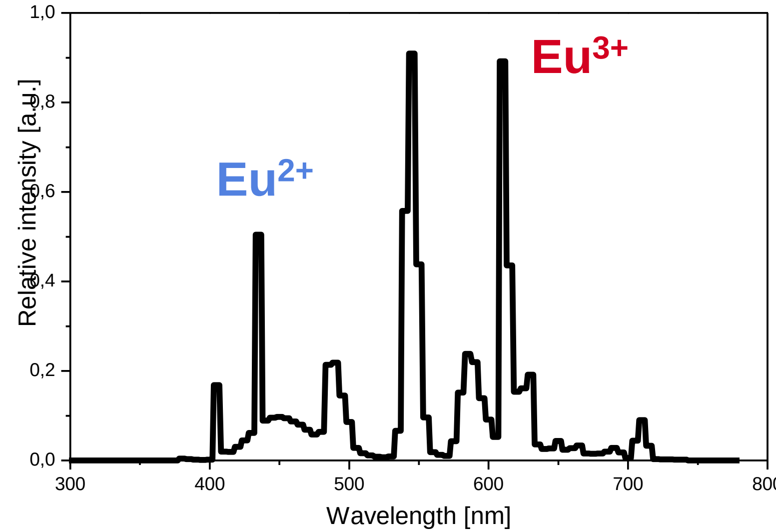
Incandescent + halogen lamps





Evolution of Light Sources

20th century – „Gas Discharge Lighting“



Emission from excited atoms/ions

Gas fillings: Hg, Na, Ne, Ar, Kr, Xe,
+ Luminescent materials

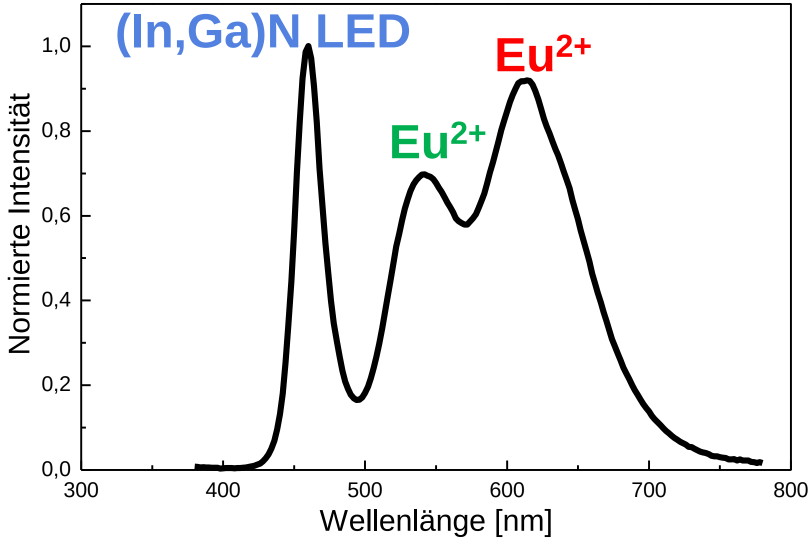
Fluorescent lamps + plasma displays



Source: Philips

Evolution of Light Sources

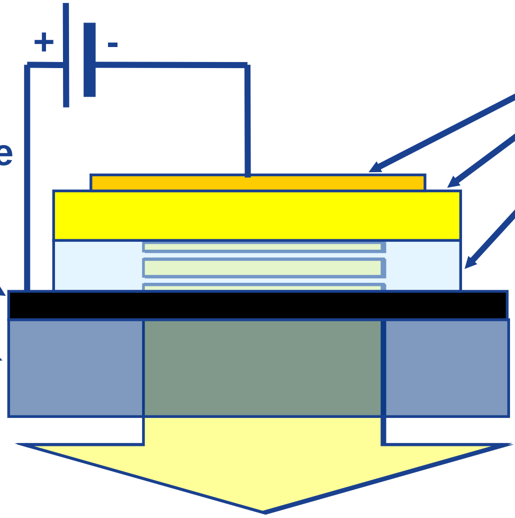
21st century – „Solid State Lighting“



Emission from solids due to recombination of charge carriers

Materials: (Al,In,Ga)P, (Al,In,Ga)N, polymers, Ir^{3+}-complexes

Inorganic and Organic LEDs



Indium-Tin-Oxide anode

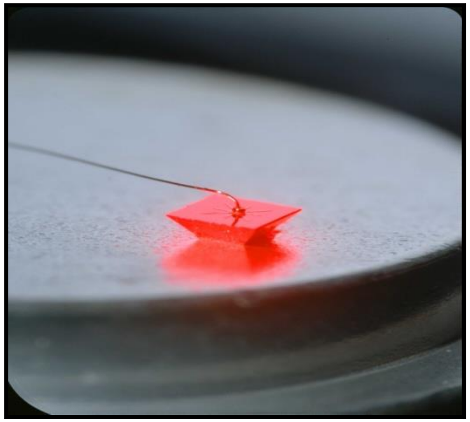
Glass

Metal cathode

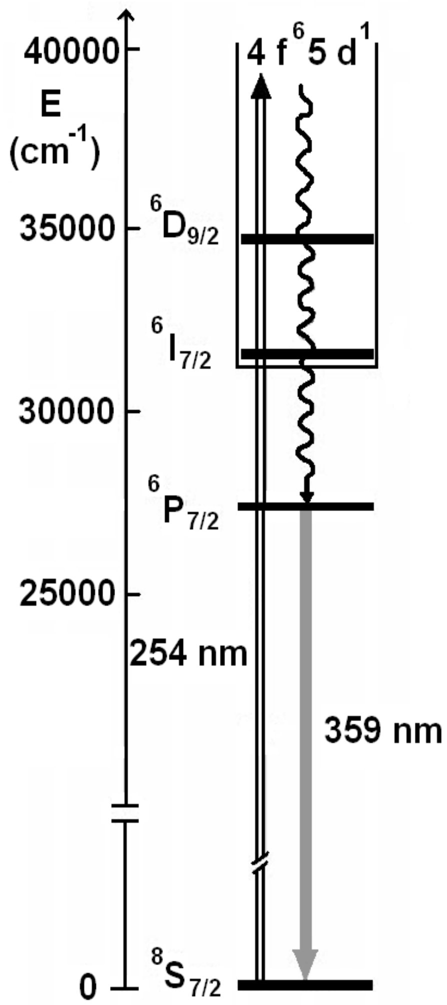
Organic luminescent layer

Transparent organic

Hole transport layer



Europium – The Magic of Colour

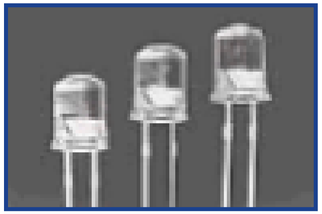


Eu^{2+} Phosphor	Emission band bei [nm]
$KMgF_3$:Eu	359 (Line)
SrB_4O_7:Eu	368
$BaSO_4$:Eu	374
$Sr_2P_2O_7$:Eu	420
$BaMgAl_{10}O_{17}$:Eu	453
$SrSiAl_2O_3N$:Eu	480
$Sr_4Al_{14}O_{25}$:Eu	490
$BaSi_2N_2O_2$:Eu	490
Ba_2SiO_4:Eu	505
$SrAl_2O_4$:Eu	520
$SrGa_2S_4$:Eu	535
$SrSi_2N_2O_2$:Eu	541
Sr_2SiO_4:Eu	575
$Ba_2Si_5N_8$:Eu	585
SrS:Eu	610
$Sr_2Si_5N_8$:Eu	615
$CaAlSiN_3$:Eu	650
CaS:Eu	655
$SrSiN_2$:Eu	700

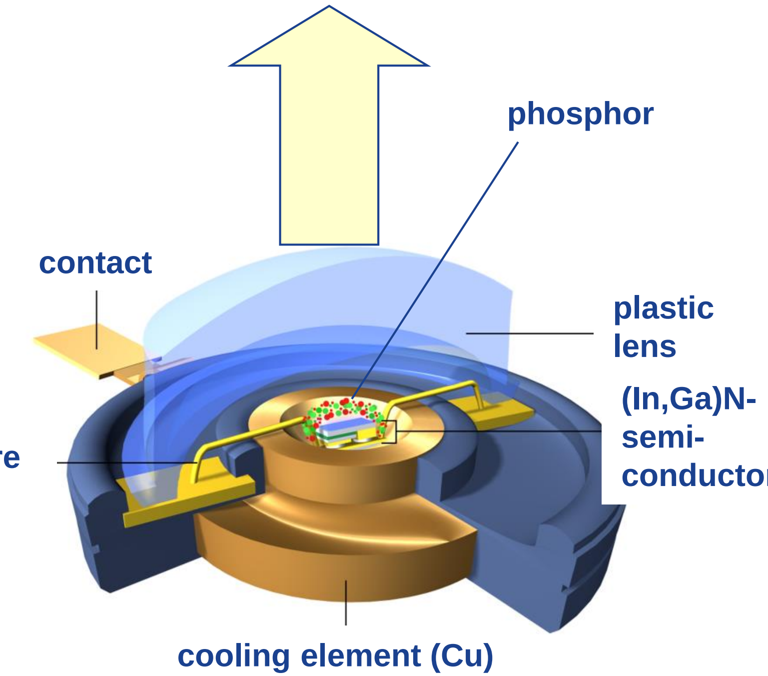
Trend for ΔE: Fluorides < Oxides < Oxynitrides < Nitrides ~ Sulfides

Phosphor Converted White LEDs

Principle of operation



< 1.0 lm	10 – 500 lm
< 0.1 W	0.6 – 5 W
< 120 °C	120 – 200 °C
< 100 W/cm²	100 – 200 W/cm²
> 120 K/Wm	2 – 12 K/W



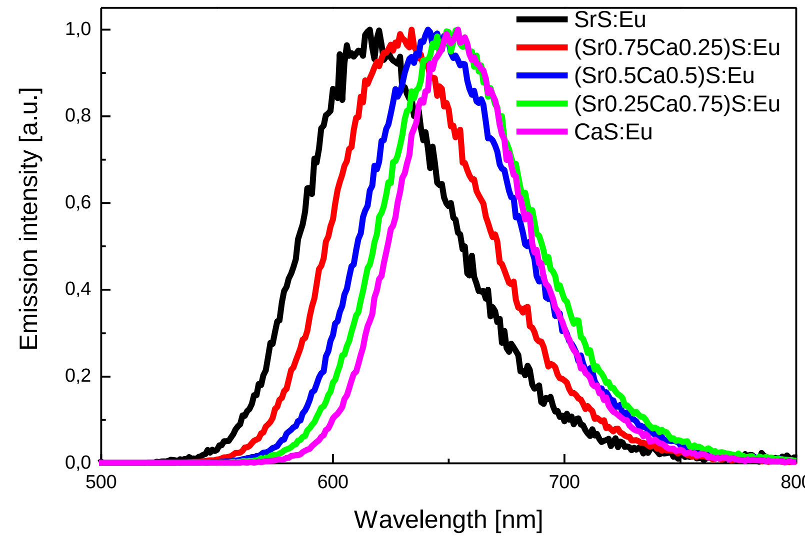
(In,Ga)N semiconductor +	phosphor (converter)	→ LED colour
Blue 420 – 480 nm	Yellow	cool white
	Yellow + Red	warm white
	Green + Red	cool & warm white

Phosphor Converted White LEDs

Sulphide phosphors $(Sr_{1-x}Ca_x)S:Eu$

SrS:Eu — crystal field strength → **CaS:Eu**

stability + color saturation

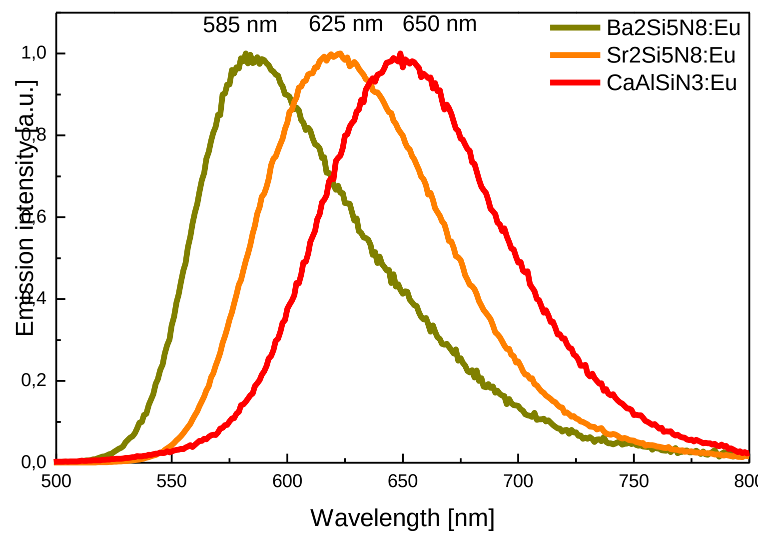


Nitride phosphors

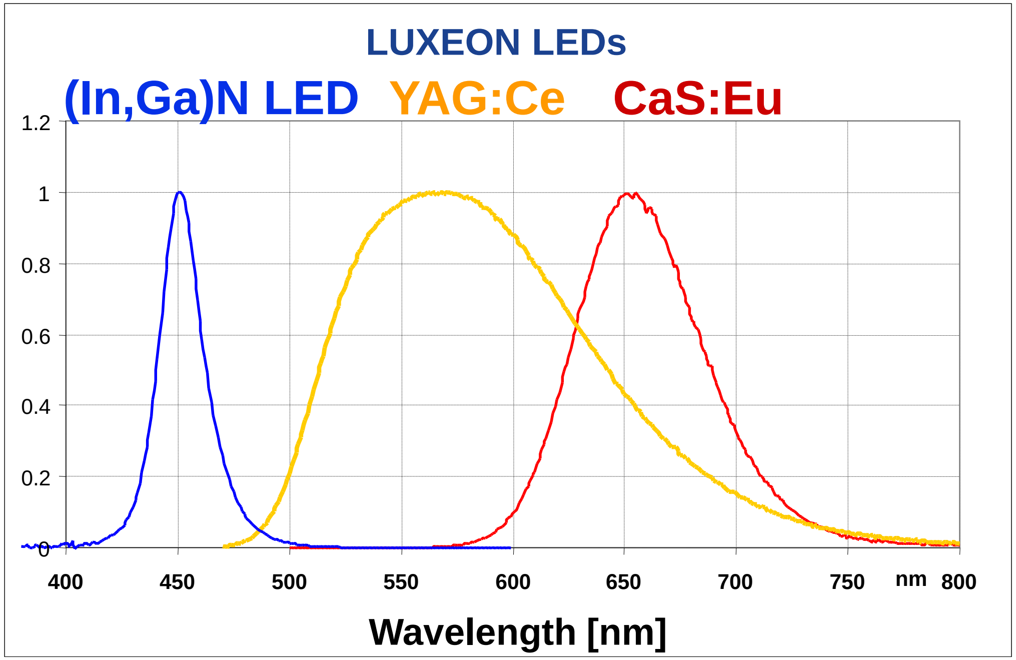
$Ba_2Si_5N_8:Eu$

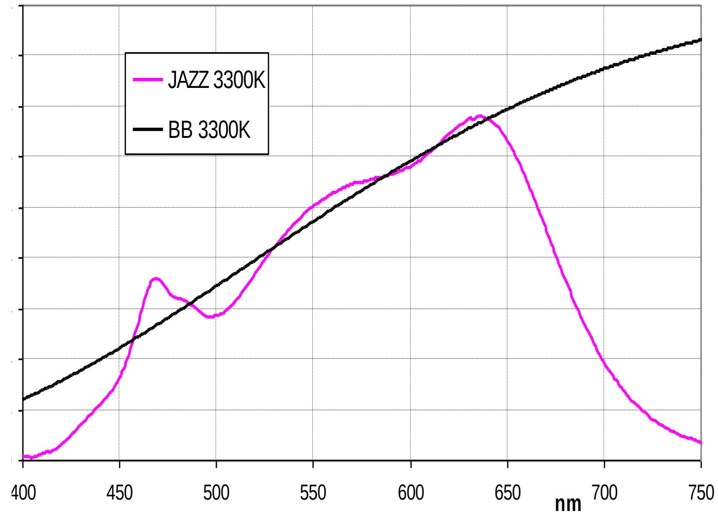
$Sr_2Si_5N_8:Eu$

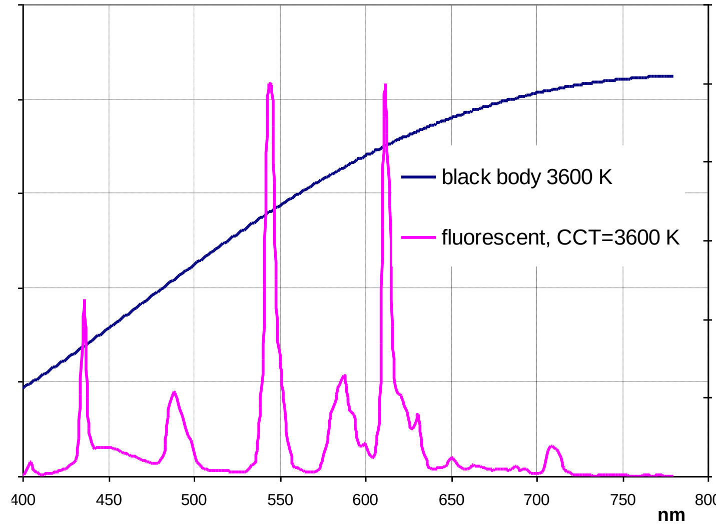
$CaAlSiN_3:Eu$



Phosphor Converted White LEDs





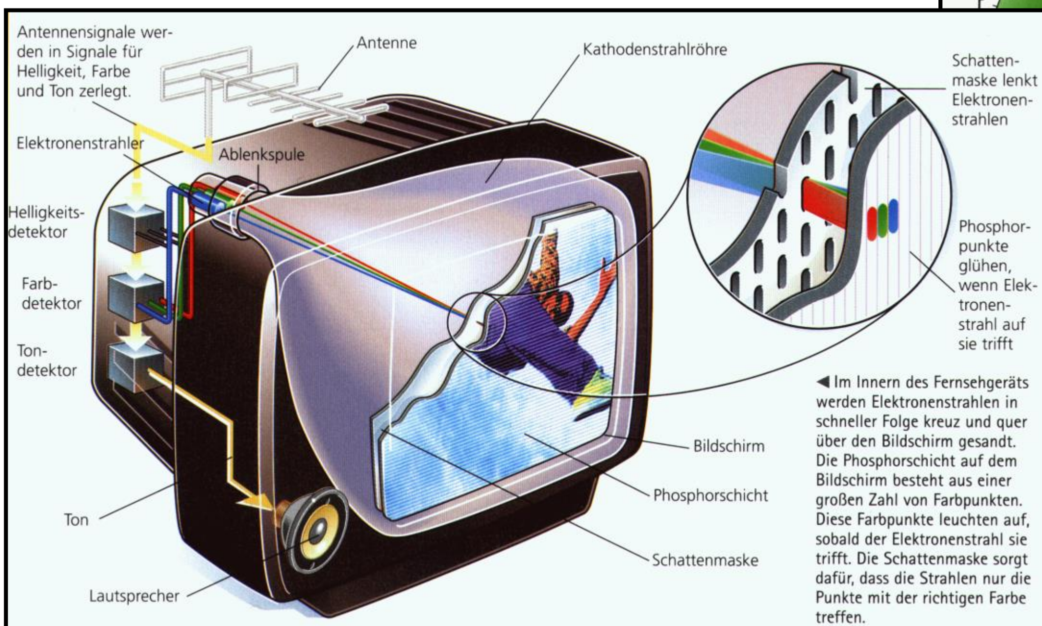


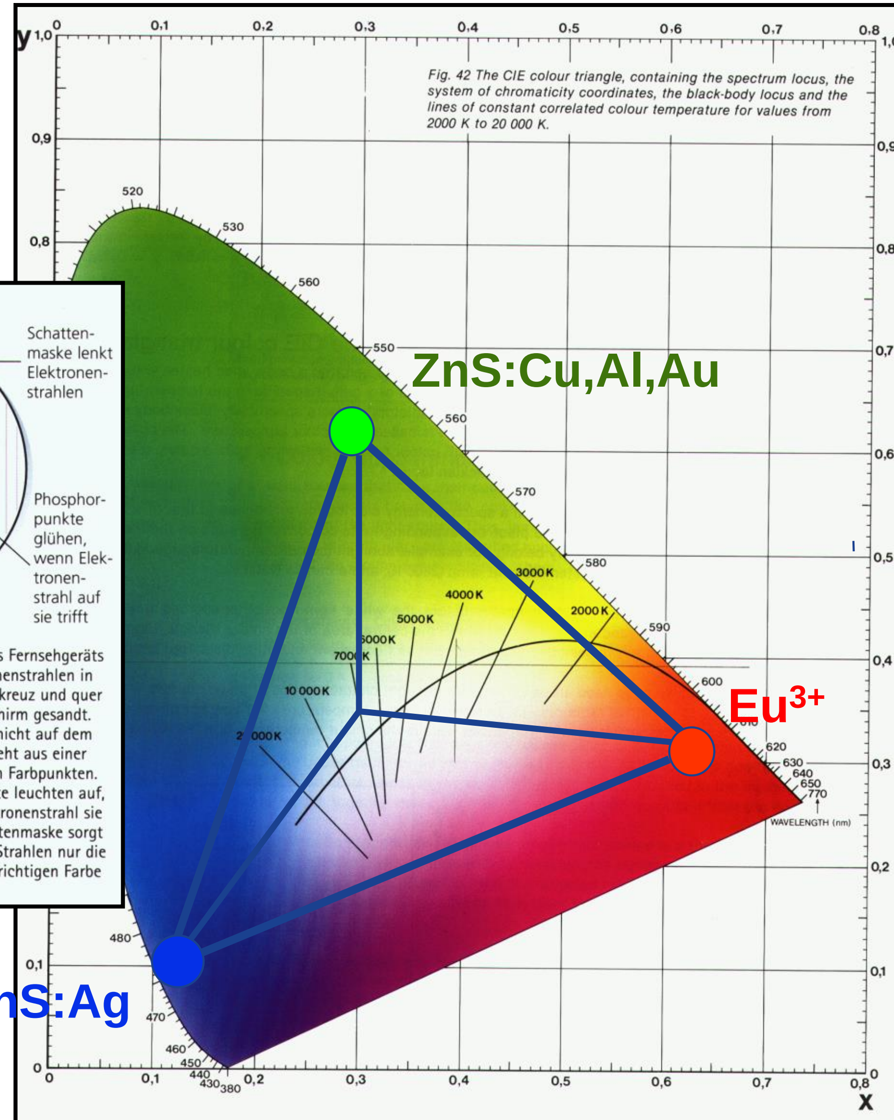
Warm white LEDs for indoor lighting

- Electric power consumption ~ 1 W
- Luminous efficacy ~ 100 lm/W
- Wall plug efficiency ~ 30 %
- Colour rendering index = 85 – 95
- Colour temperature 2700 – 4000 K

Emissive Displays

Colour mixing in the Braun‘s tube





1st generation $YVO_4:Eu^{3+}$

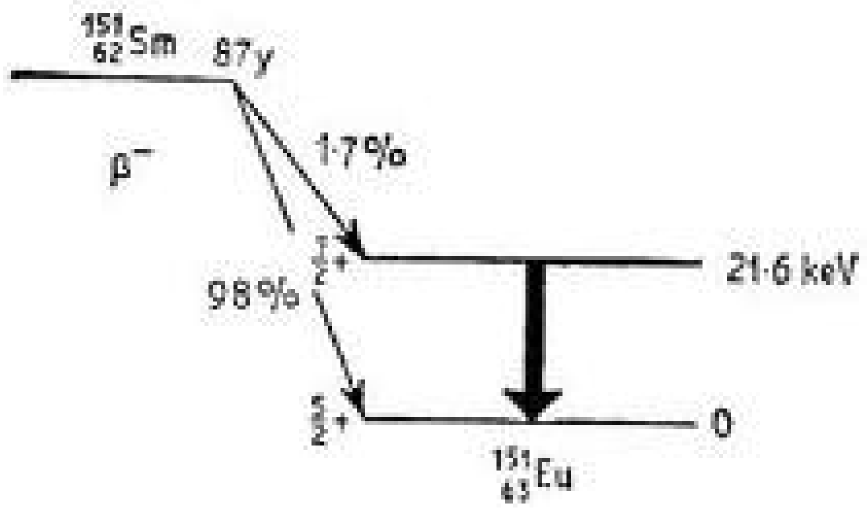
2nd generation $Y_2O_2S:Eu^{3+}$

Europium – Further Applications

- MRT Contrast enhancement
- ^{151}Eu Mößbauer spectroscopy
- Alloys
- Neutron absorber
- Scintillators
- Storage phosphors, e.g. for the imaging plate: Ba(F,Br):Eu^{2+}

^{151}Eu Mößbauer Spectroscopy

- Source: ^{151}Sm τ ~ 90 a (SmF_3); reference to EuF_3
- ^{151}Eu – 21.54 keV Mößbauer transition
- ^{153}Eu – has 3 Mößbauer transitions (83.37, 97.43, and 103.18 keV); complex nuclear levels and source have short half-lives (^{153}Sm ~ 46.7 h)



Velocity range: -30 to +30 mm/s

Eu^{2+} Isomer shifts are in the range of -13 to -8 mm/s

Eu^{3+} Isomer shifts are in the range of 0.0 to 5 mm/s