Substitution of critical raw materials in lighting systems

Pier Carlo Ricci
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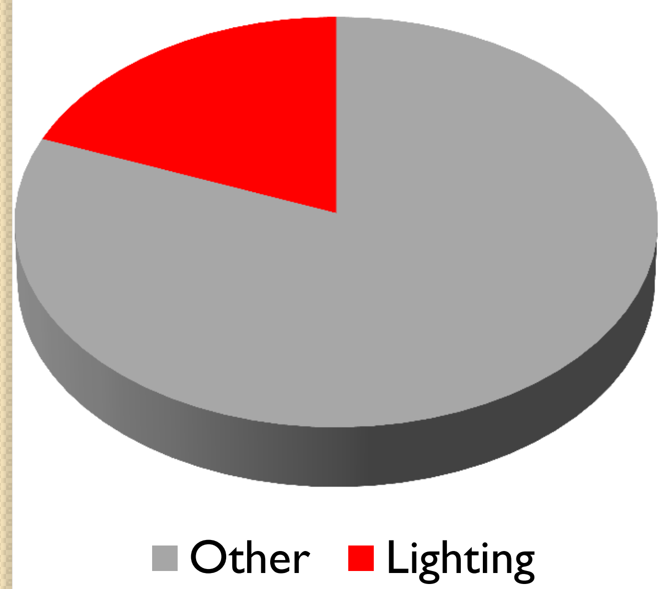
Outlook

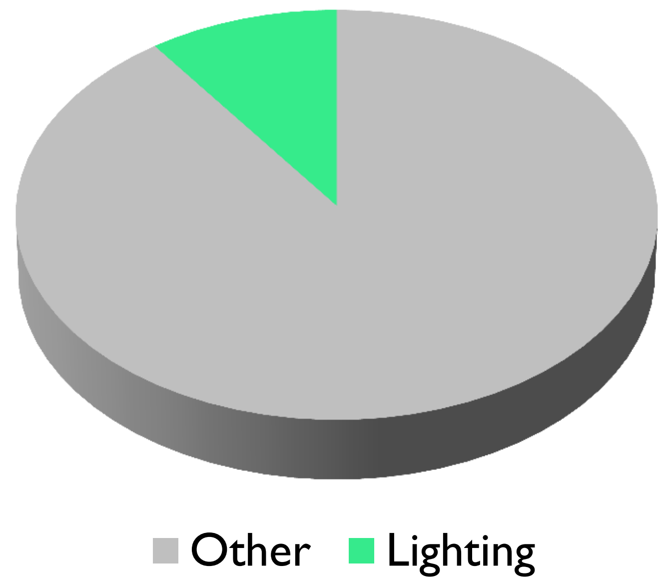
- The importance of the lighting sector
- Fundamentals in SSL
- Criticisms in lighting
- Materials and alternatives

The importance of the lighting sector

Electricity consumption



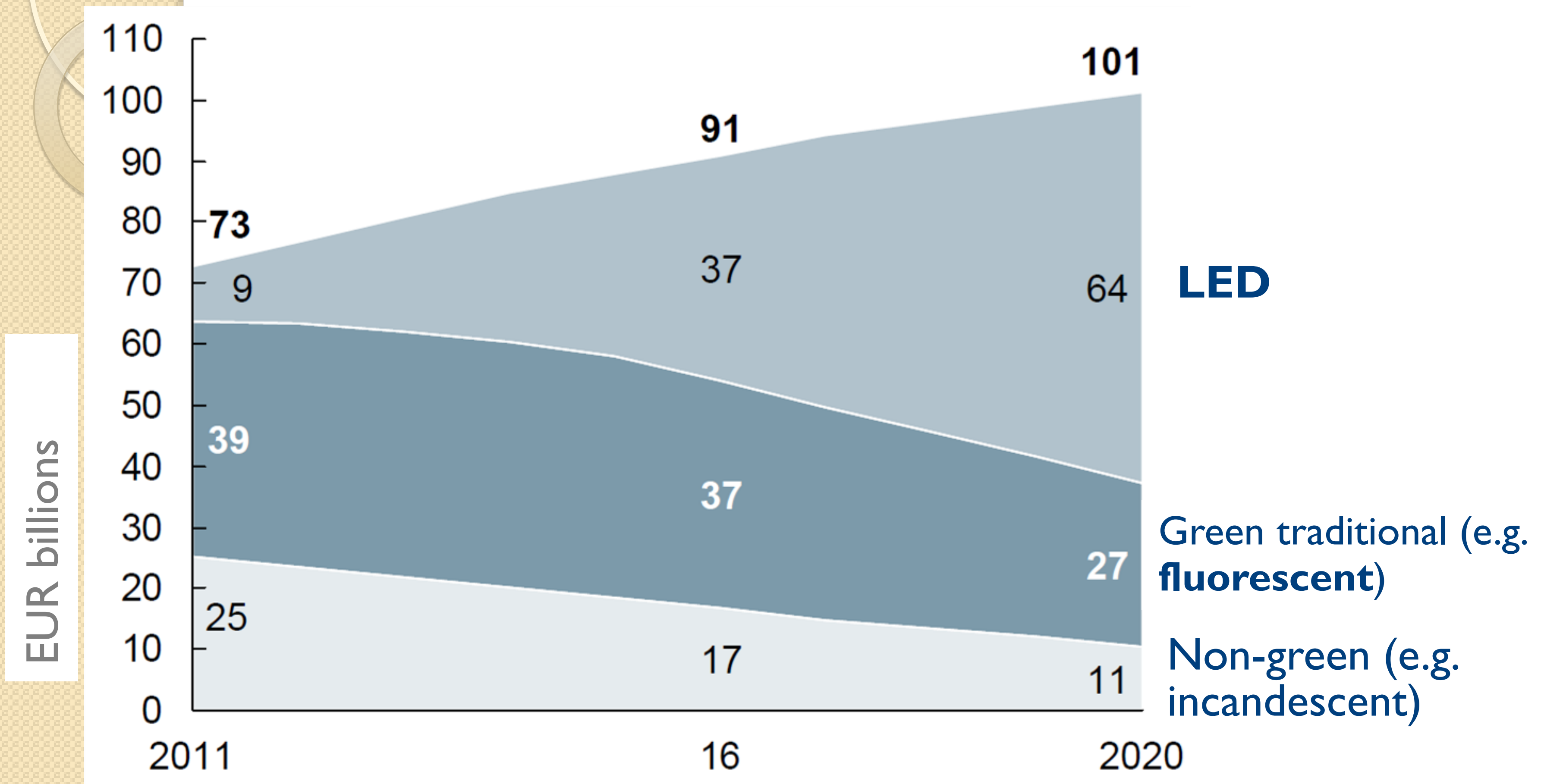
Global CO_2 emission



- Lighting accounts for 19% of electricity consumption world wide and 14% in the EU

- It is responsible for 6-8% of global greenhouse emissions

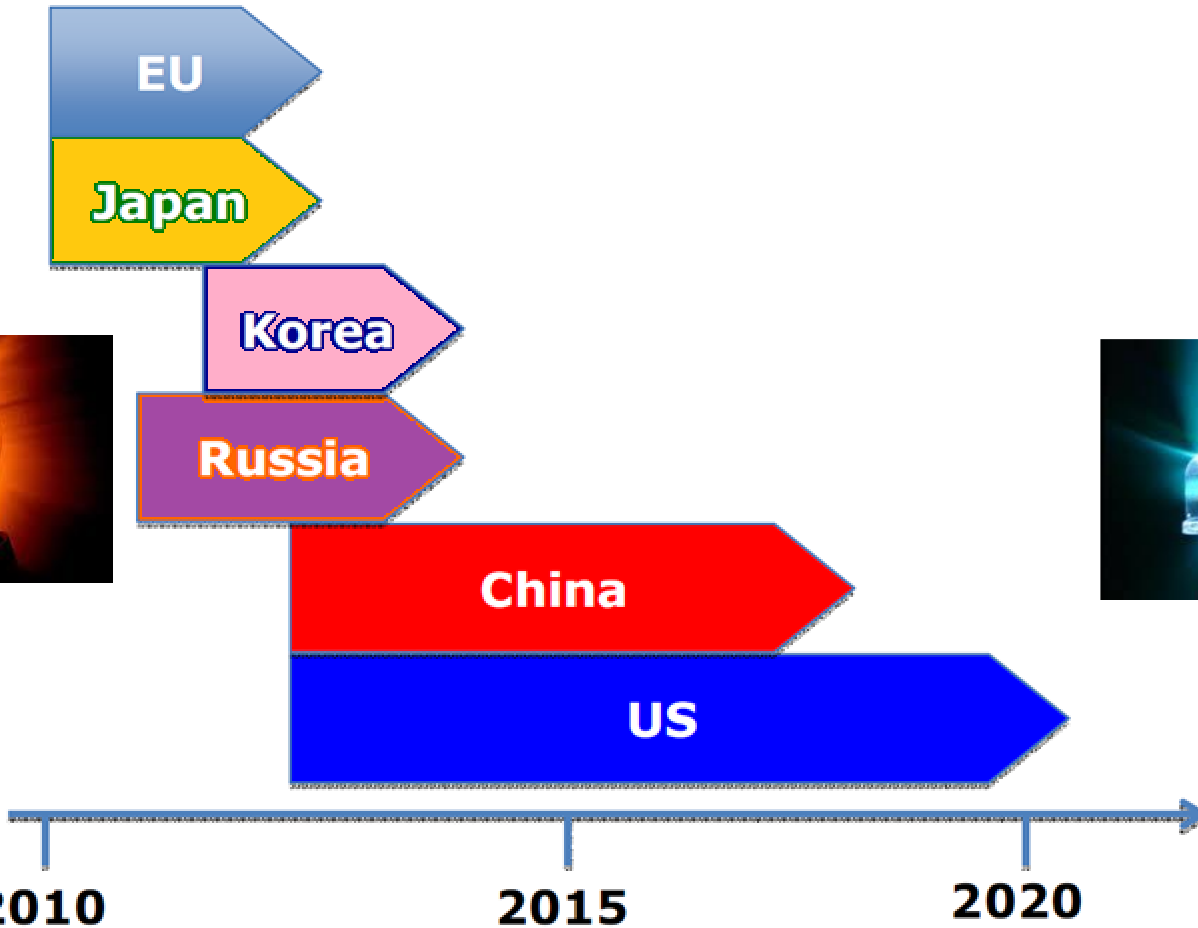
Global lighting products market trends



- LED technology is forecasted to be the leading technology on global lighting products by 2020

SOURCE: McKinsey's 2012 report

Towards the LED technology



Why LED?

LOW-COST

Long life up to and beyond 20,000 hours.
lifetime –

The energy consumed by one LED is the equivalent of 50 halogen bulbs.

PERFORMANCE

LEDs offer greater color mixing.

Combined with compact size, offers wide range of design options.

TECHNICAL

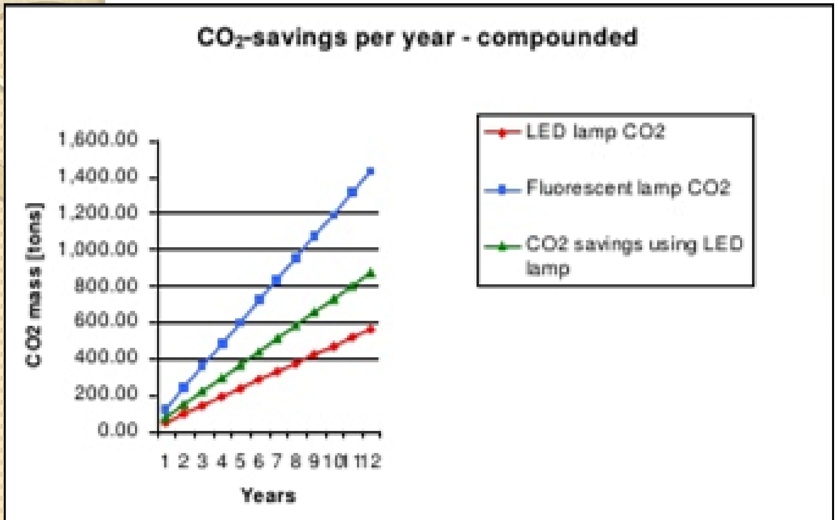
Compact size
Long life
Shock resistant
Instant on/off

ENVIRONMENTAL

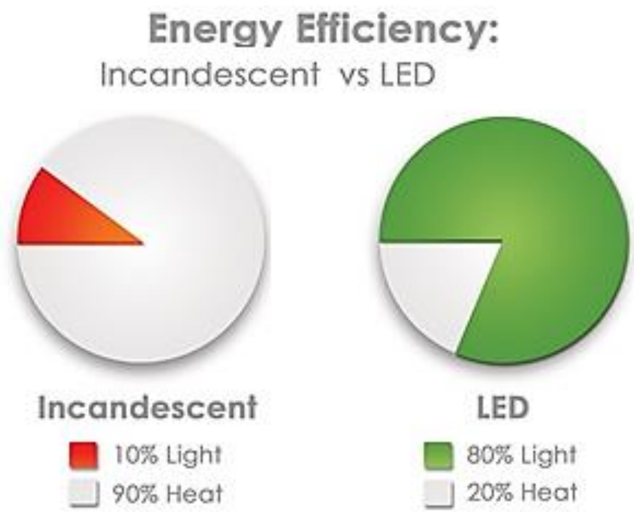
LEDs are more energy efficient.

Coupled with longevity, LED bulbs = fewer lamps required to be disposed of.

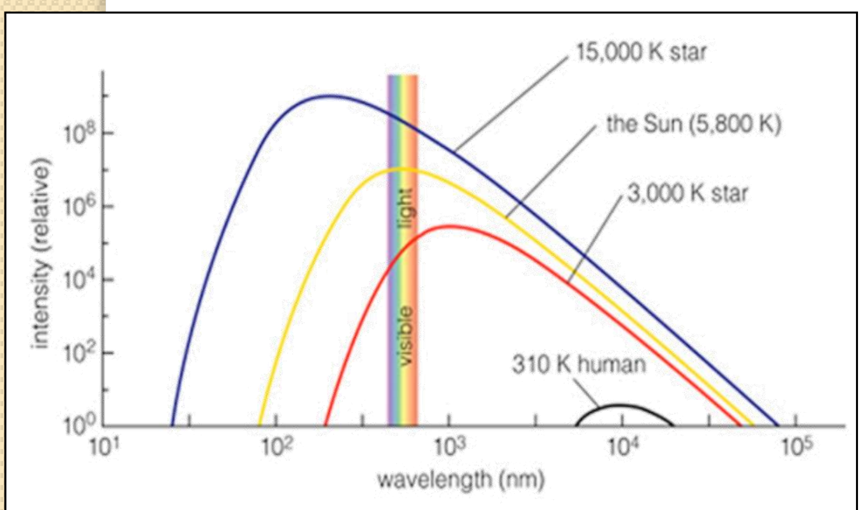
Why LED?



CO_2-savings per year - compounded
LED lamp CO2
Fluorescent lamp CO2
CO2 savings using LED lamp
CO2 mass [tons]
1,600.00
1,400.00
1,200.00
1,000.00
800.00
600.00
400.00
200.00
0.00
1 2 3 4 5 6 7 8 9 10 11 12
Years

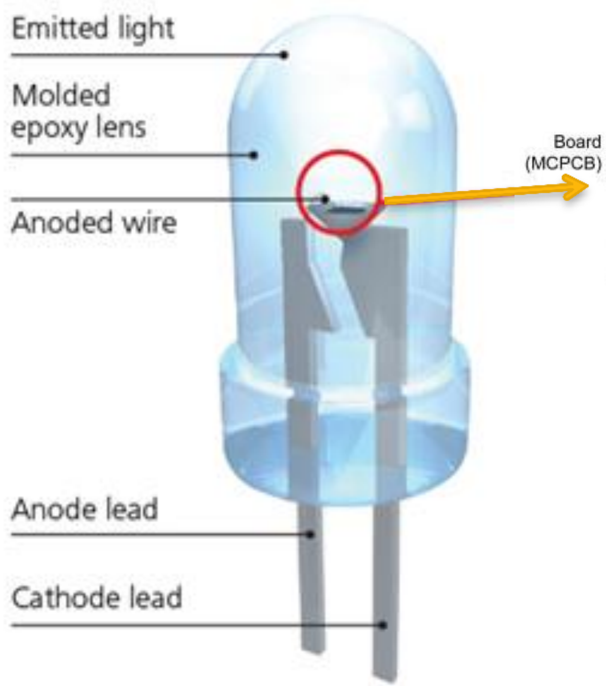


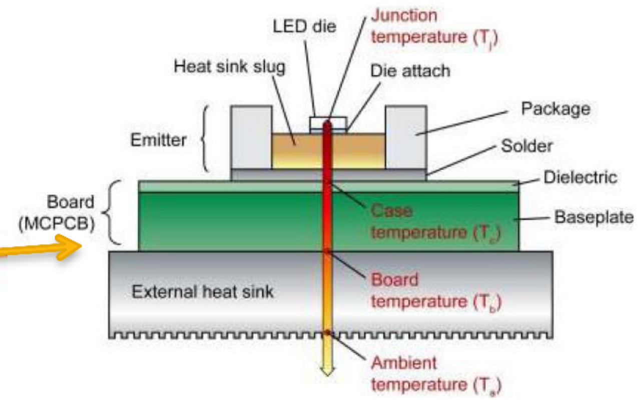
Energy Efficiency:
Incandescent vs LED
Incandescent
10% Light
90% Heat
LED
80% Light
20% Heat

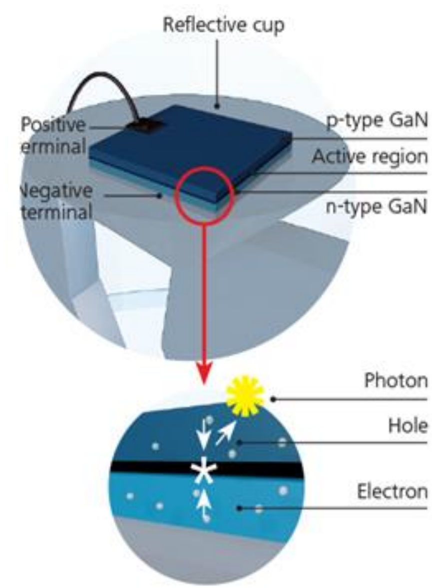


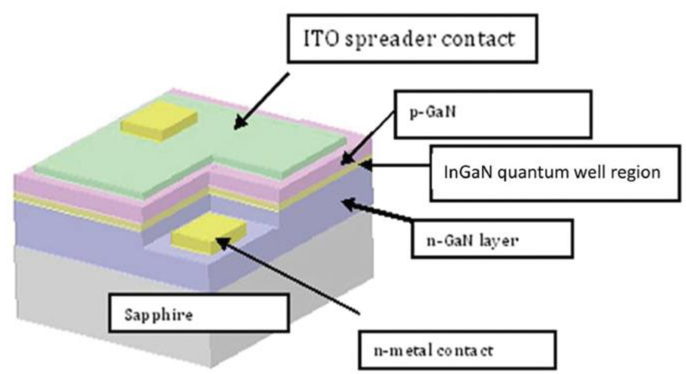
15,000 K star
the Sun (5,800 K)
3,000 K star
310 K human
visible light
intensity (relative)
10^8
10^6
10^4
10^2
10^0
10^1
10^2
10^3
10^4
10^5
wavelength (nm)

Inside the LED

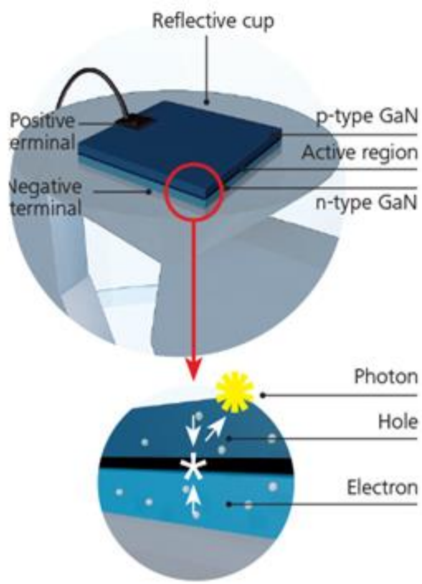


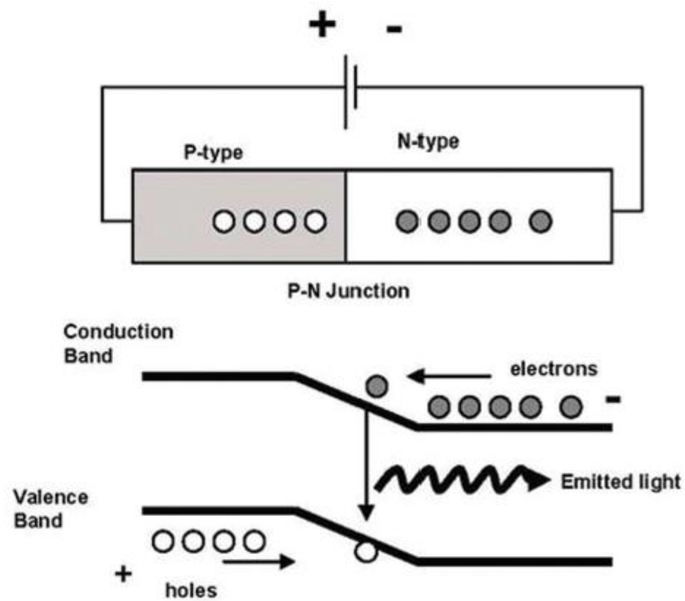




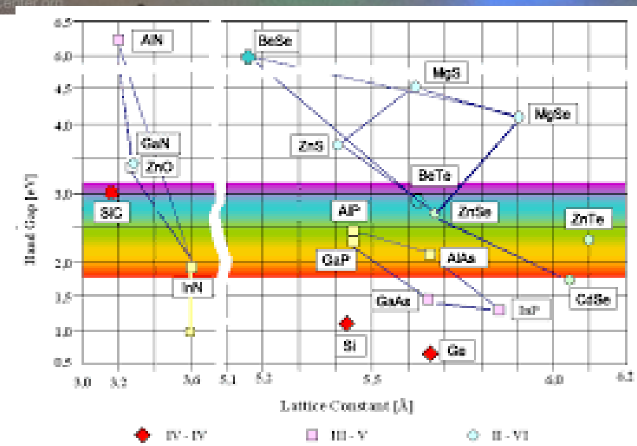


Inside the LED

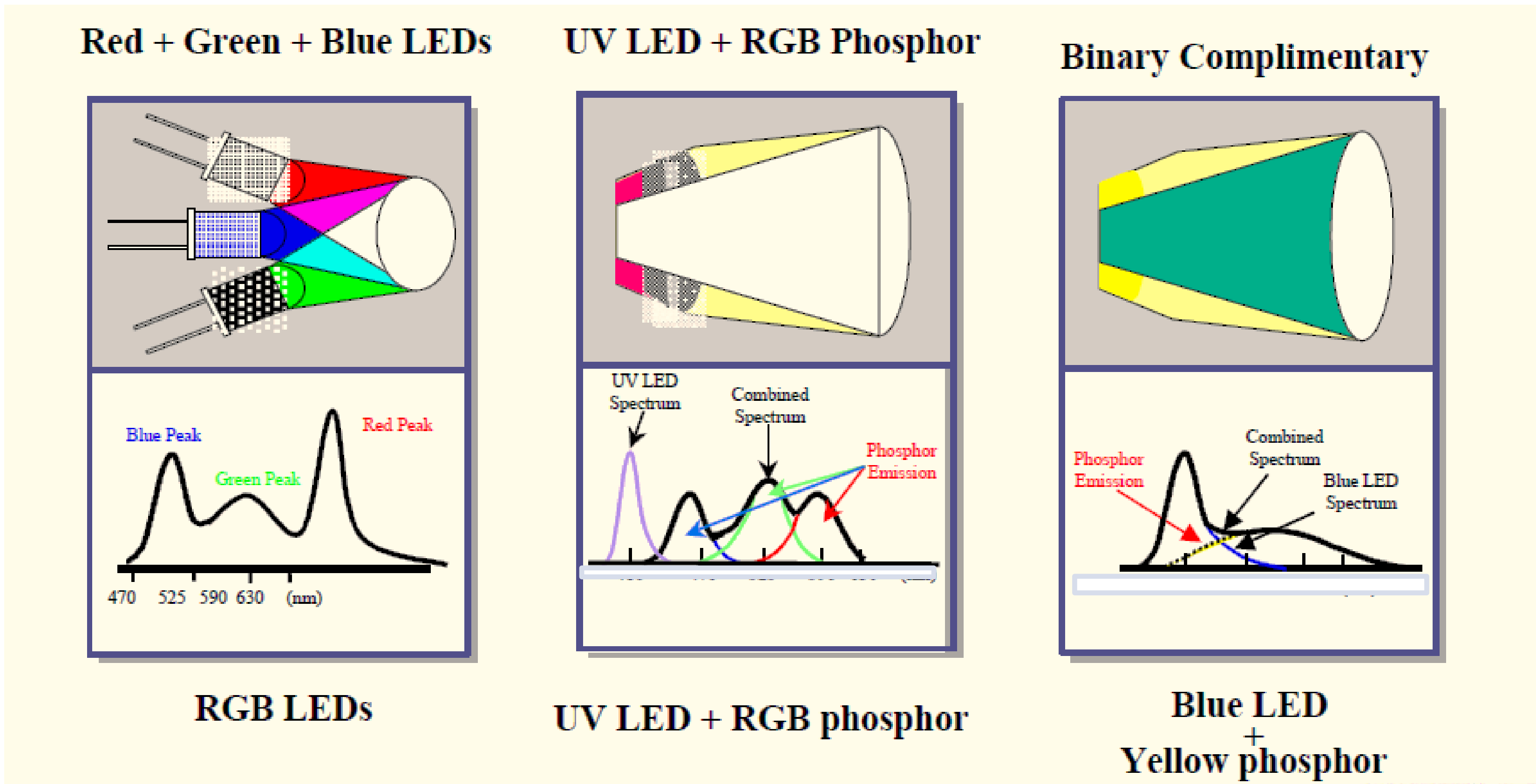




Semiconductor Material	Wavelength
GaAs	850-940nm
GaAsP	630-660nm
GaAsP	605-620nm
GaAsP:N	585-595nm
AlGaP	550-570nm
SiC	430-505nm
GaInN	450nm



How do we obtain the white emission?

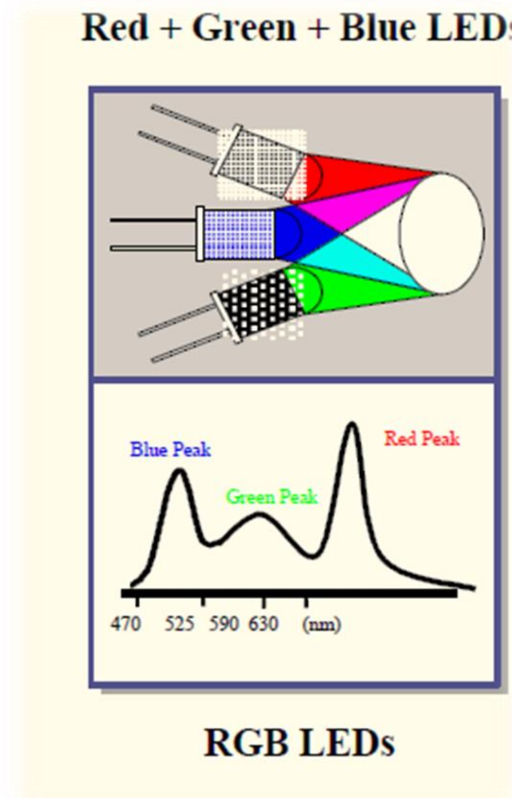


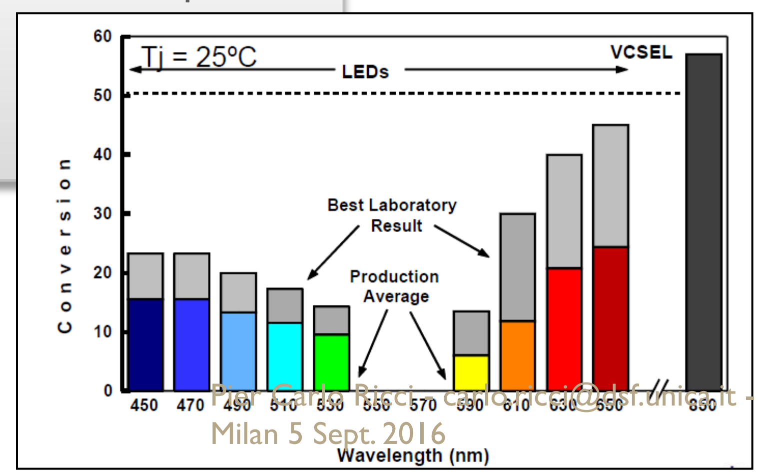
Red + Green + Blue LEDs
UV LED + RGB Phosphor
Binary Complimentary
Blue Peak
Green Peak
Red Peak
470 525 590 630 (nm)
UV LED Spectrum
Combined Spectrum
Phosphor Emission
Phosphor Emission
Combined Spectrum
Blue LED Spectrum
RGB LEDs
UV LED + RGB phosphor
Blue LED + Yellow phosphor

R+G+B LED

- Dynamic tuning of color temperature
- Excellent color rendering!
- Very large color Gamut available!

- High costs
- Color mixing tricky!
- Yellow-Green Gap!

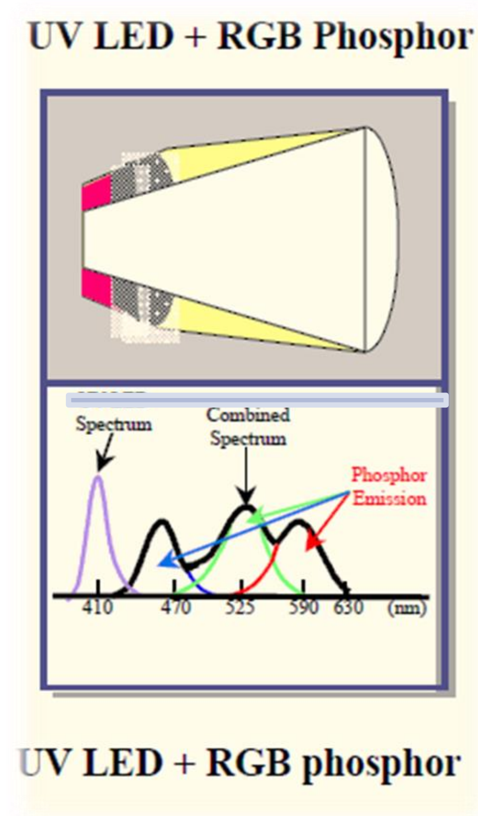




UV LED + RGB phosphors

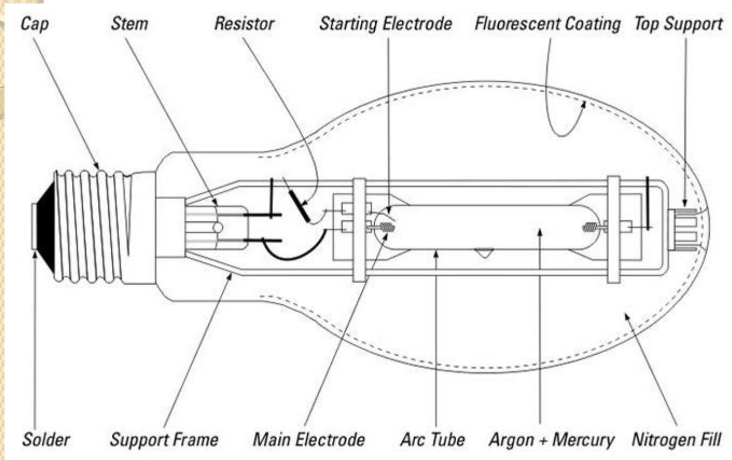
- White point determined by phosphors ONLY!
- Excellent color rendering possible!
- “Simple to manufacture!”
- Temperature stability of phosphors.

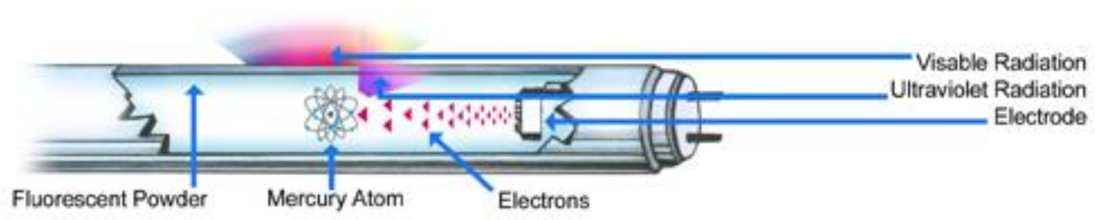
- Potential for damaging UV light leakage!
- Efficient UV LED pumped phosphor not available yet! → high costs



CFL work in this configuration!

CFL working principle

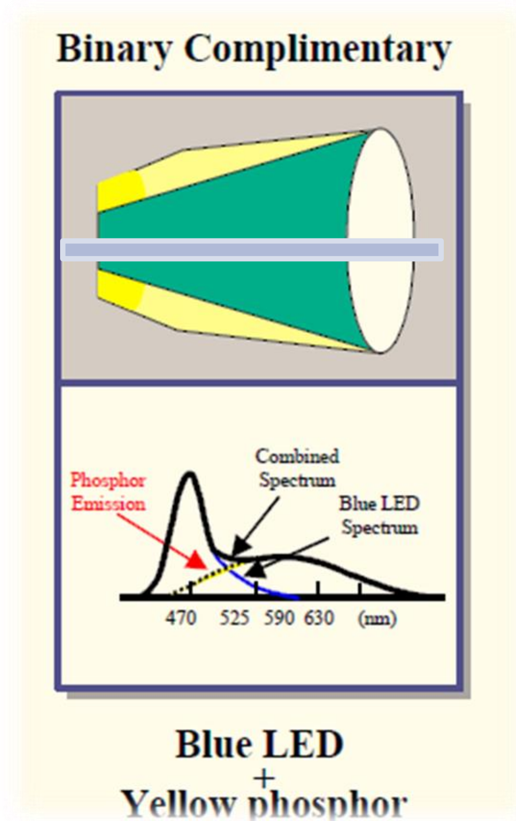




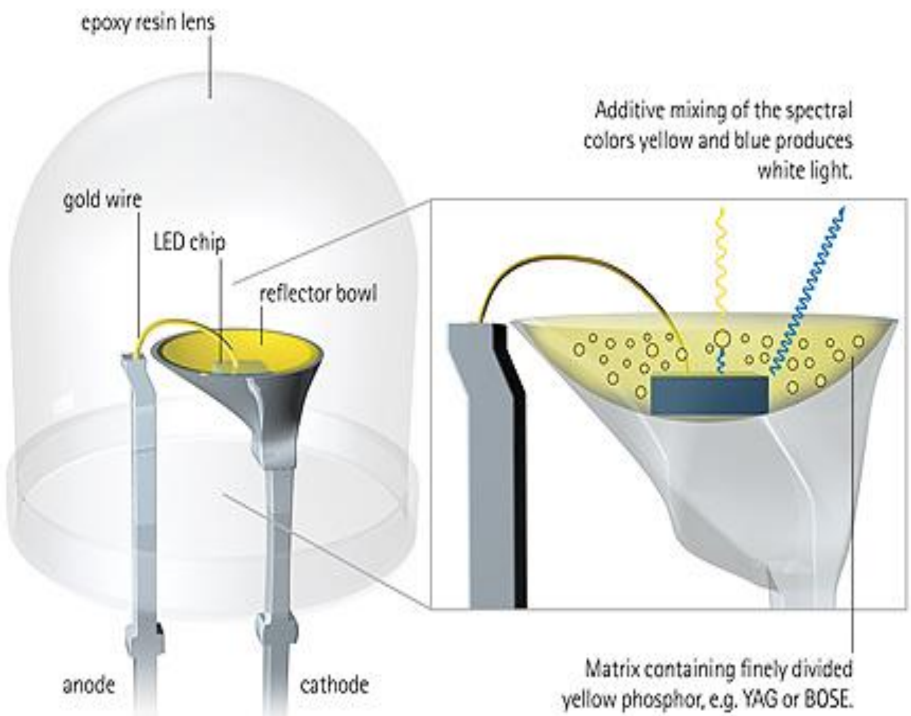
Blue LED + Y phosphor

• Simple and single Yellow phosphor
• Decent color rendering
• "Simple to manufacture!"
• Temperature stability of phosphors.

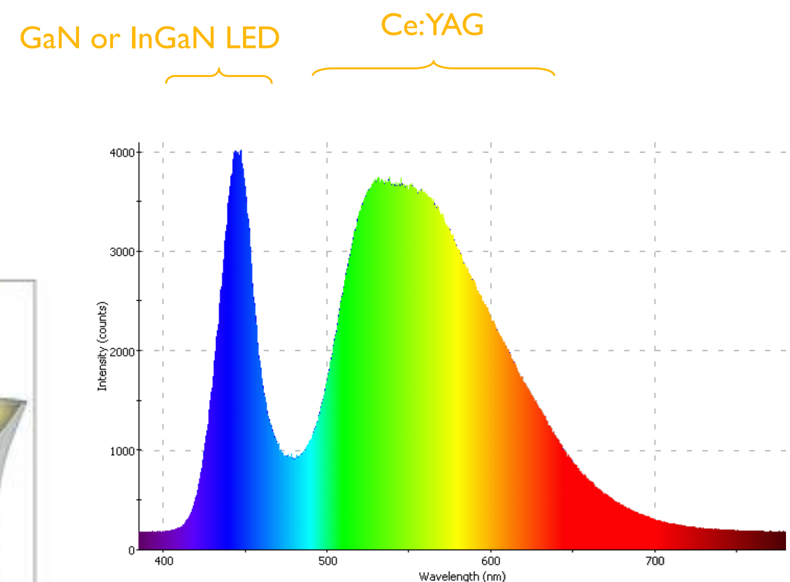
• Limits on efficiency due to phosphor conversion efficiency
• Better color rendering
• Ubiquity of Ce:YAG



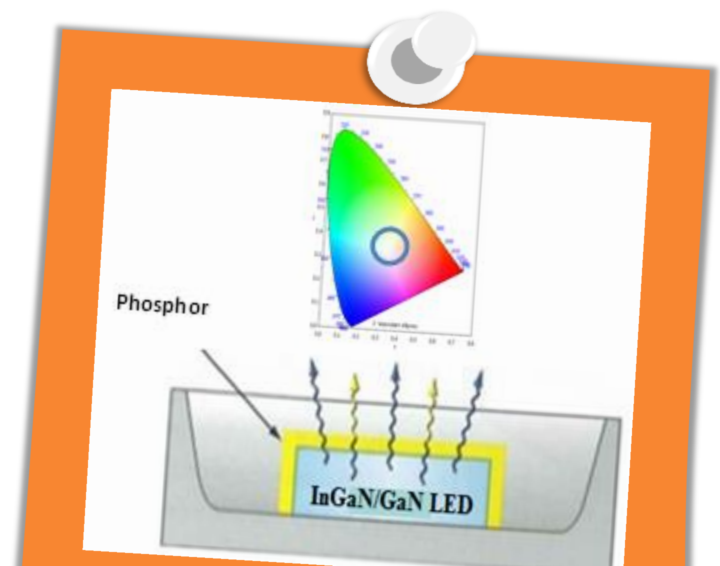
White LED



epoxy resin lens
gold wire
LED chip
reflector bowl
anode
cathode
Additive mixing of the spectral colors yellow and blue produces white light.
Matrix containing finely divided yellow phosphor, e.g. YAG or BOSE.



GaN or InGaN LED
Ce:YAG
Intensity (counts)
4000
3000
2000
1000
0
400
500
600
700
Wavelength (nm)

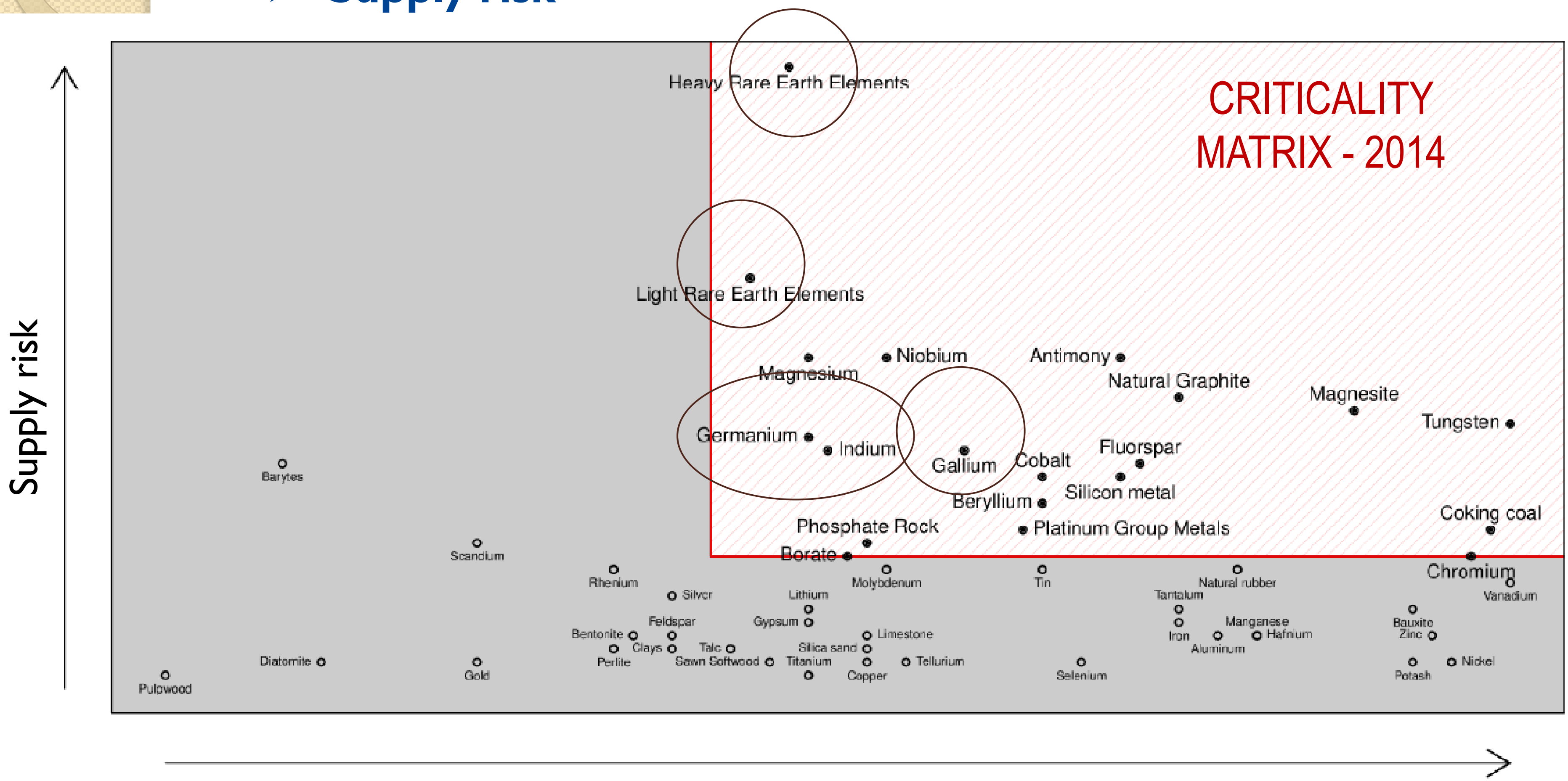


Phosphor
InGaN/GaN LED

Criticisms

Critical raw materials list

- **20 'critical raw materials'** for the whole EU economy based on:
  - **Economic importance**
  - **Supply risk**



Economic importance

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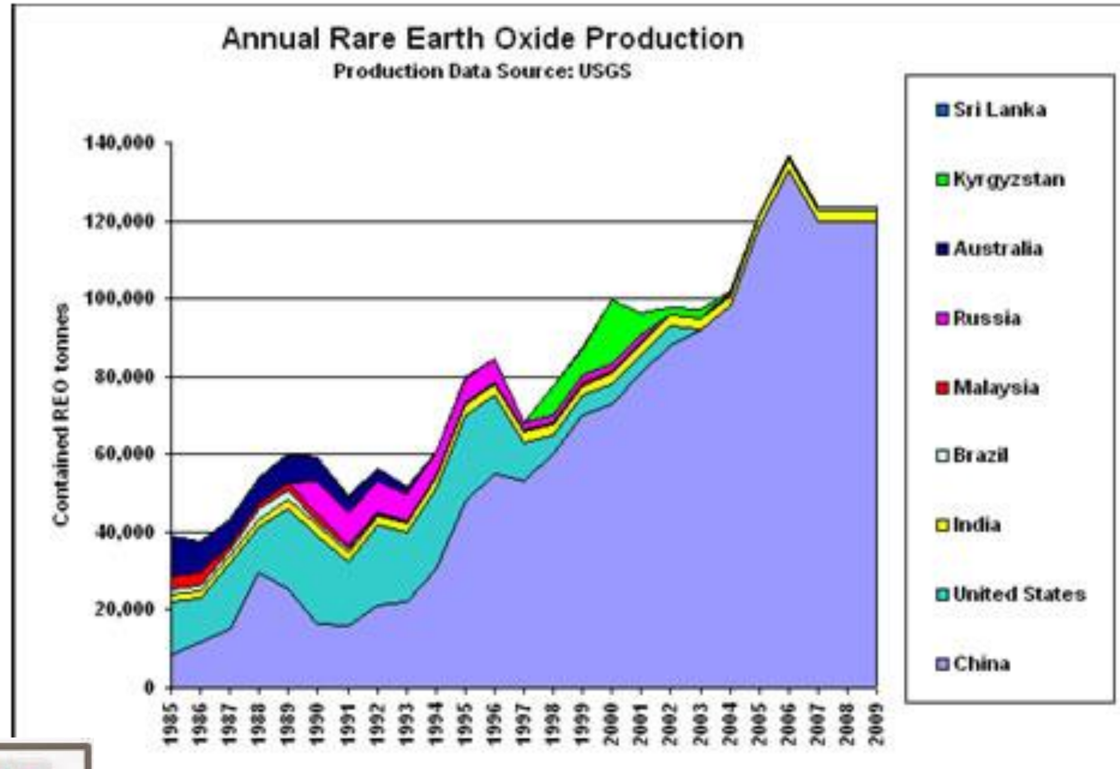
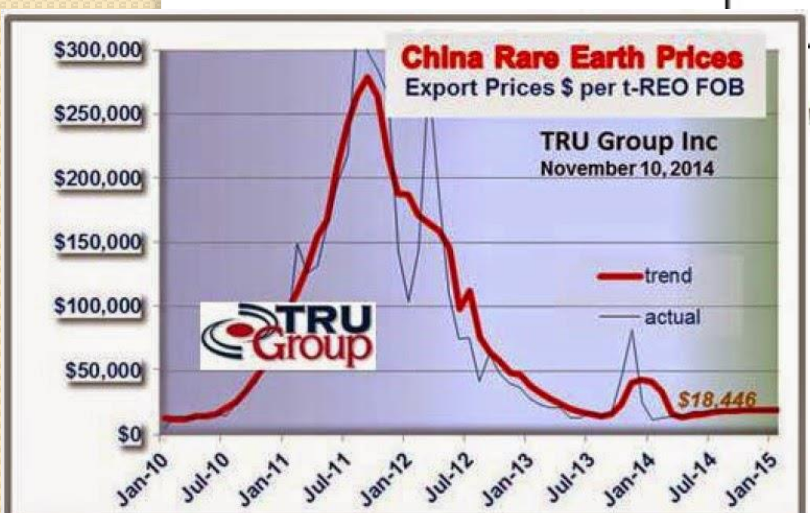
Criticisms





www.kaiserbottomfish.com

China

99 % Heavy Rare Earths

87 % Light Rare Earths

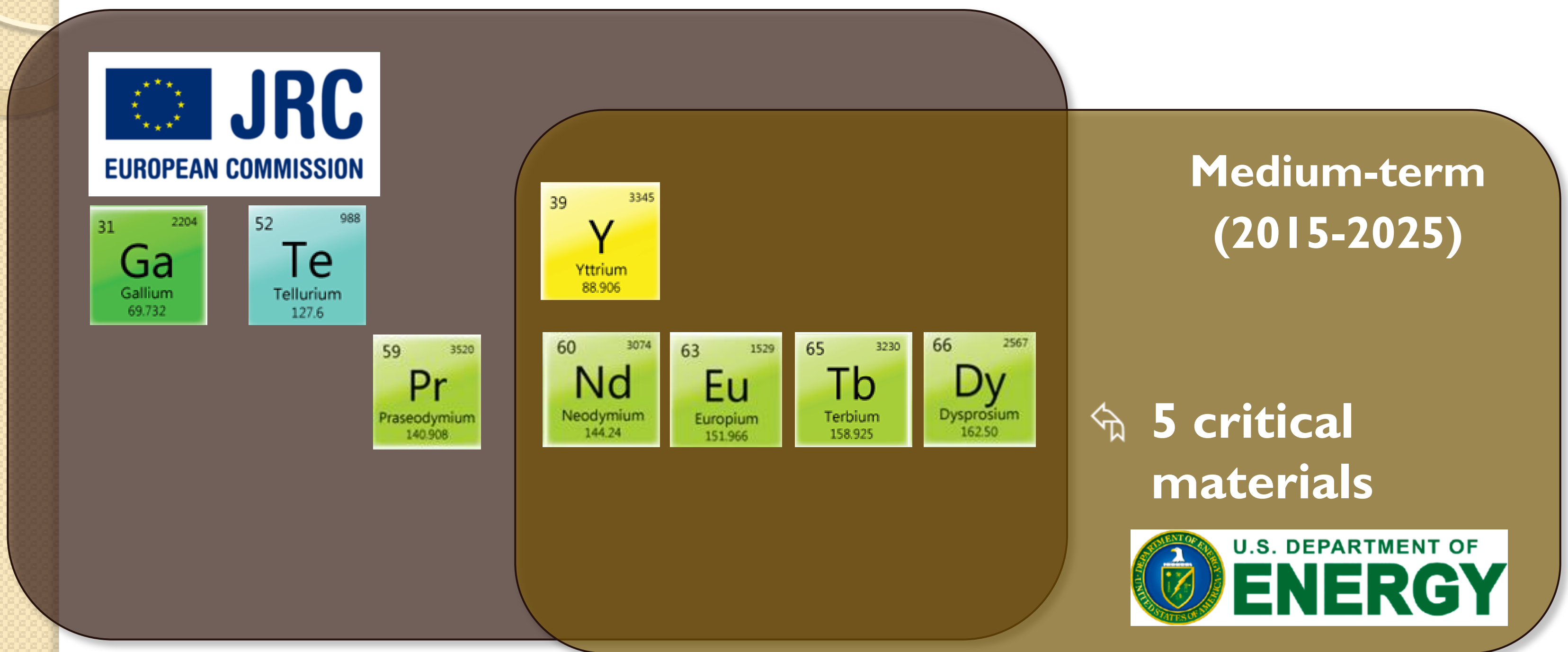
Criticisms

Main actors in LED lighting supply chain.[1]			
	Europe	North America	Asia
REE Production	- - -	- - -	95–99% China
LED Manufacturing	OSRAM,Optogan, Valtavalo	Philips LumiLed	75- 80 % Asia Nichia, Edison Opto, Epistar
LED Assembly	OSRAM Philips Lighting Havells-Sylvania	Ge Lighting	Samsung LED,Nichia, Epistar, Toshiba, Sharp, LG electronics

Toxic Lake in Baotou (China)
About 75 % world production of rare earths




Critical materials for low-carbon technologies



- **Five materials (rare earths)** are assessed critical in both EU and US economies
- *Several other materials are assessed medium-high critical (e.g. graphite, Re, Hf, Ge, Pt, In)*

How can we tailor new suitable phosphors?

Phosphor requirements

1. The emission spectrum, in combination with the emission of the other components (LED, other phosphors), leads to a white emission with a specific color rendering (CRI) and color temperature (CCT).

2. The excitation spectrum matches the pumping LED emission.

3. The quantum efficiency approaches unity, thus maximizing the overall electrical-to-optical conversion efficiency of the entire LED-phosphor package.

4. The emission does not saturate at high pumping fluxes (meaning PL decay times of much faster than 1ms).

5. The emission spectrum, excitation spectrum and high quantum efficiency do not vary and degrade at elevated working temperature, humid conditions, high current or luminous density.

6. The chemical and temperature stability are excellent.

Excitation wavelength (nm)	Phosphor(s)	CRI
460	$Y_3Al_5O_{12}:Ce^{3+}$	71
460	$Y_3Al_5O_{12}:Ce^{3+}$, $Sr_2Si_5N_8:Eu^{2+}$	80
460	$Y_3Al_5O_{12}:Ce^{3+}$, $Sr[LiAl_3N_4]:Eu^{2+}$	90
455	$SrSi_2O_2N_2:Eu^{2+}$, $CaSiN_2:Ce^{3+}$	91
455	$BaSi_2O_2N_2:Eu^{2+}$,β-SiAlON:Eu^{2+},Ca-α-SiAlON:Eu^{2+}, $CaAlSiN_3:Eu^{2+}$	96
365	$BaMgAl_{10}O_{17}:Eu^{2+}$, $Ca_9La(PO_4)_7:Eu^{2+},Mn^{2+}$	92
350-450	$Ba_{1-x}Sr_xSiO_4$:Eu2+	80
495	SrGa2S4:Eu2+	80

Main drawbacks

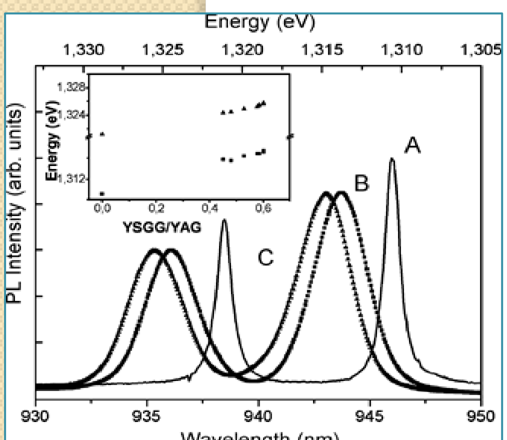
- Nitride phosphors require extreme and expensive preparation conditions, including high temperature and high nitrogen pressures.
- Fluorescence reabsorption and non-uniformity of luminescent properties.

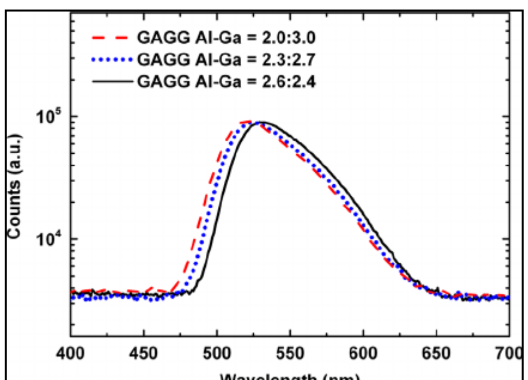
- Sulfide phosphors present strong emission quenching with temperature
- hydrophobicity, hydrolysis
- toxicity of the hydrolysis products (H2S gas) hinders commercial application

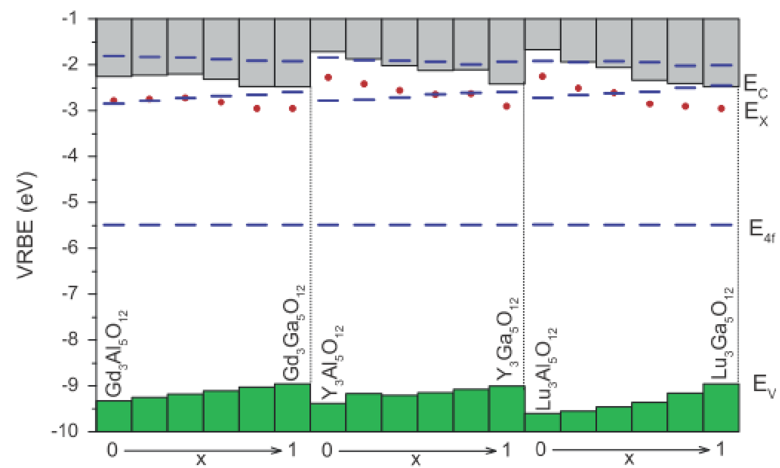
New matrices with reduced content of REE

- The emission of rare earth ions is generally due to optical transitions within the f-manifold.
- In case of Eu2+ and Ce3+the recombination is related to 5d–4f optical transitions the emission bands are relatively broad.

The unique electronic configuration of REE allows to retain their spectral properties irrespective of the host matrix



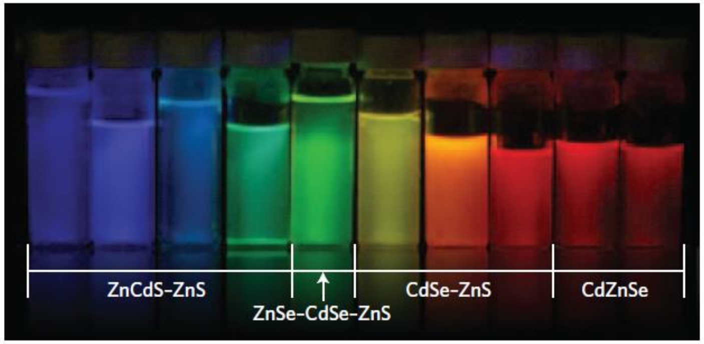




P. Dorenbos, J. Lumin. **134** (2012) 310

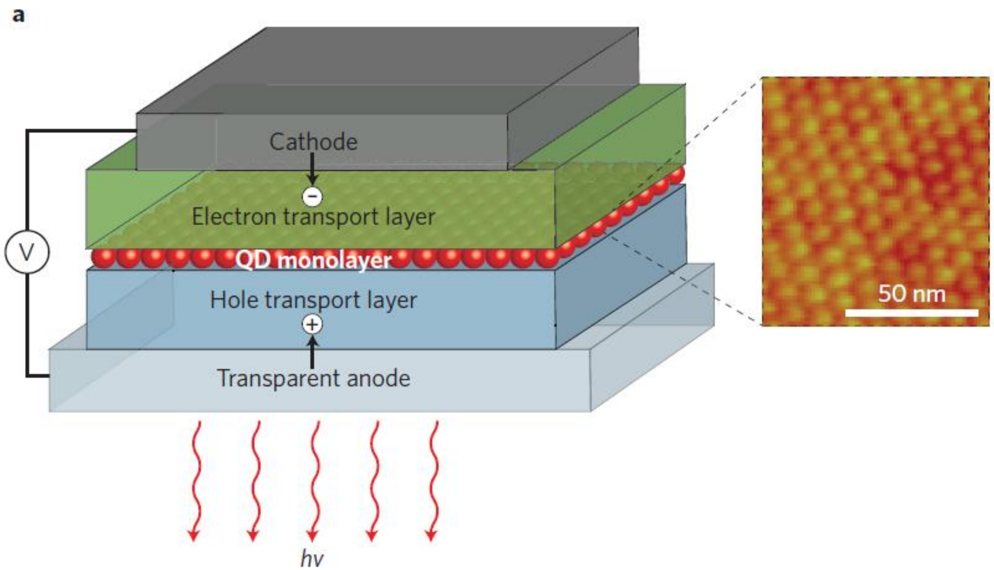
Alternatives

- Nanosized inorganic
  - Colloidal quantum dot
  - Nano carbon emitters
  - Perovskite Crystals

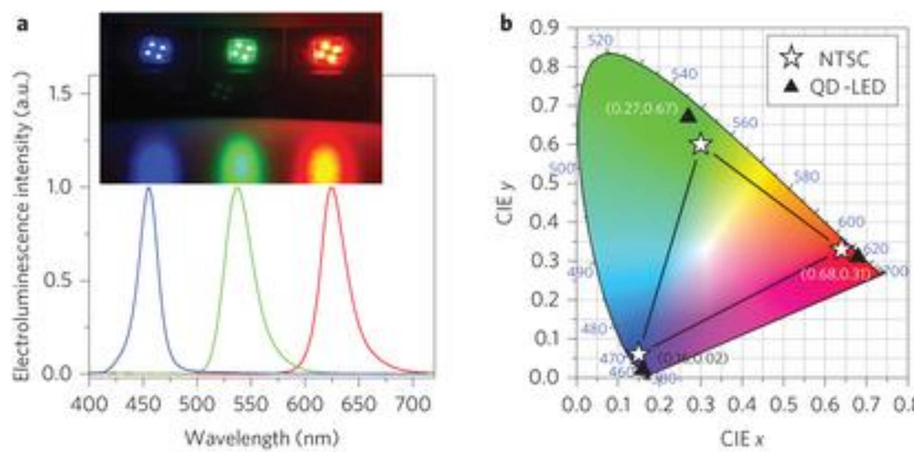


- Organic phosphors

QD-based LED



- High tunability
- High CRI
- Good efficiency



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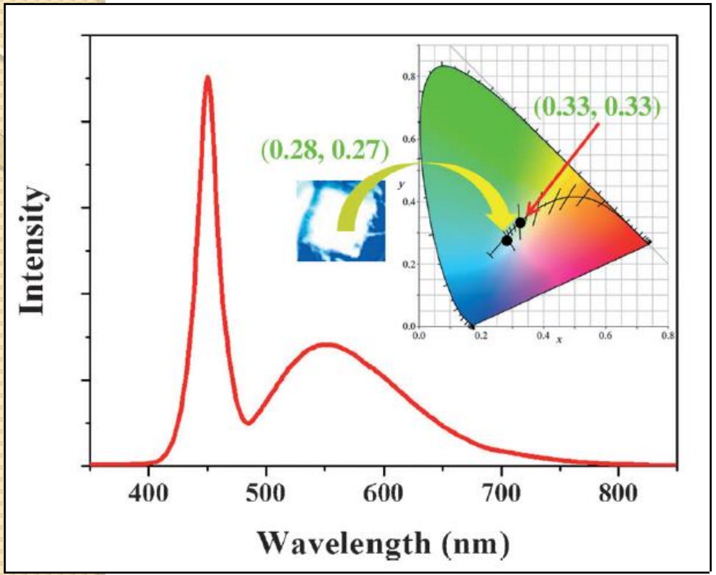
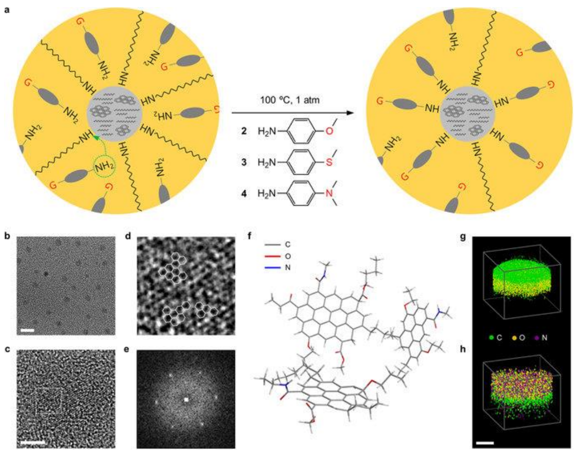
Drawbacks

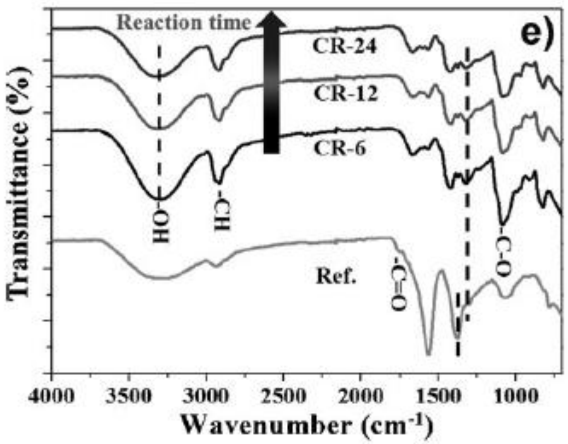
- Short term stability
- The best performance were obtained in

  Cd-based QD

Carbon nanodots



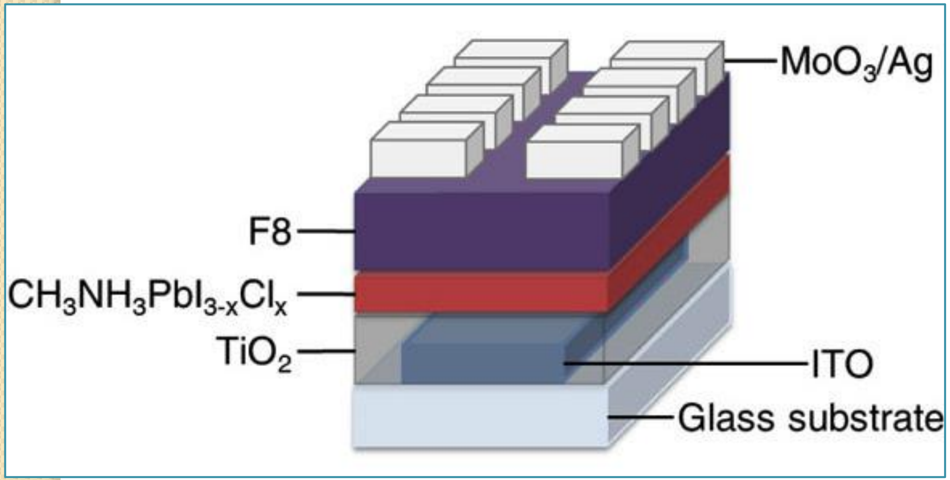


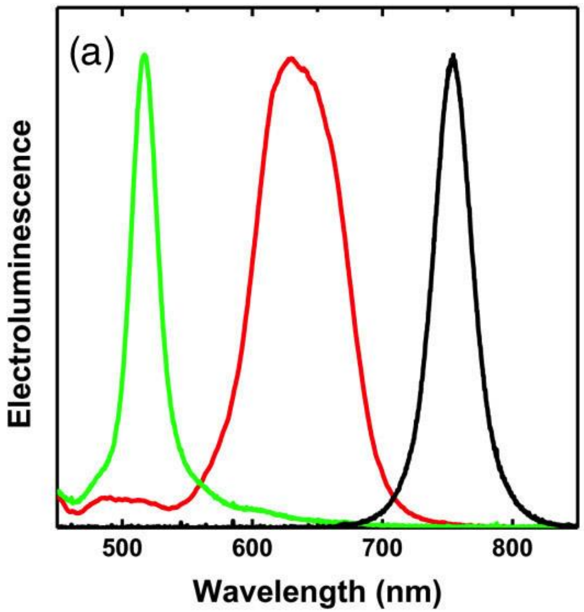


Cost effective

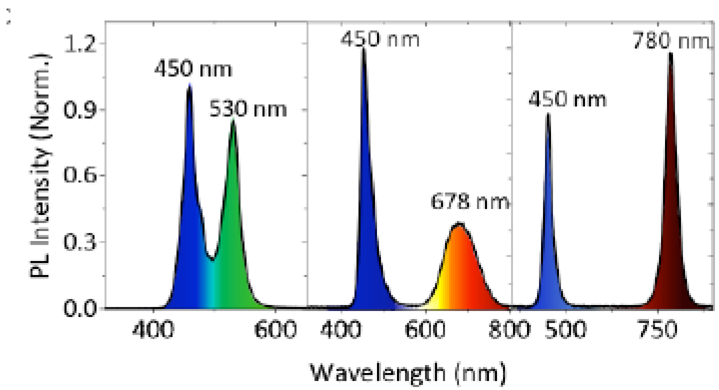
Low stability

Organometal halide perovskite Pe-LED

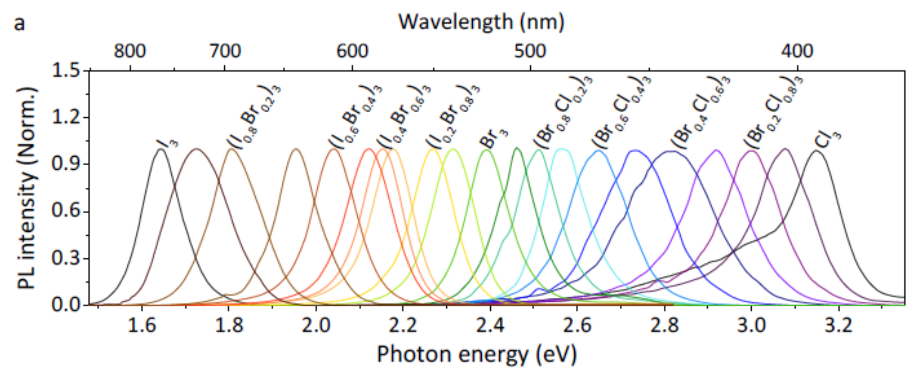




Perovskite as phosphors in InGaN based white LED



$CH_3NH_3PbX_3$
(X=Cl, Br and I)



Drawbacks

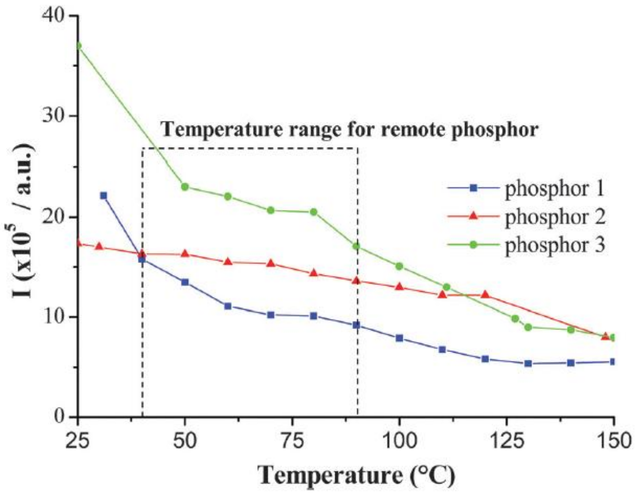
- Short term stability
- Quantum efficiency
- Large use of Lead

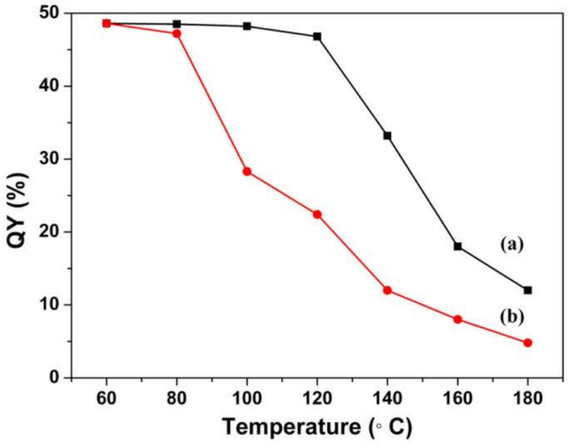
Organic Phosphors

- High Efficiency
- Free from CRM
- Relative Low growth temperature (<500 °C)

- Low Thermal Stability
- Generally working in solution (quenching effect)

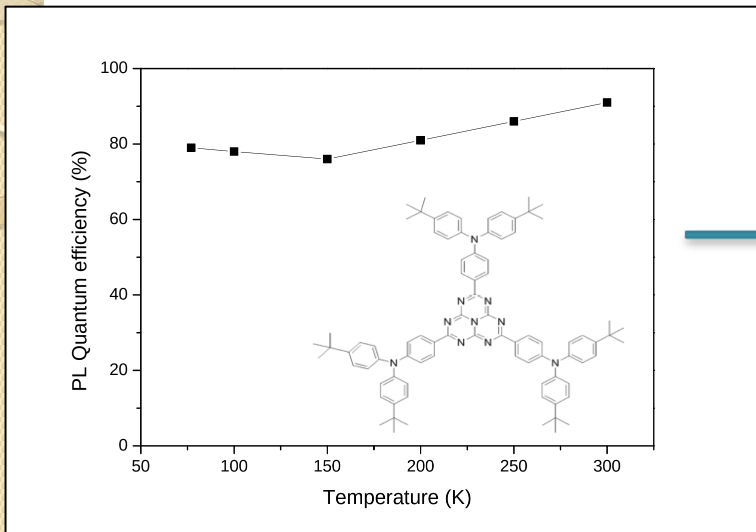
Stability

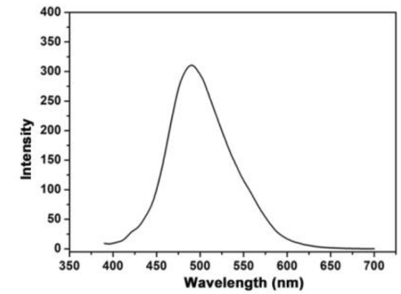




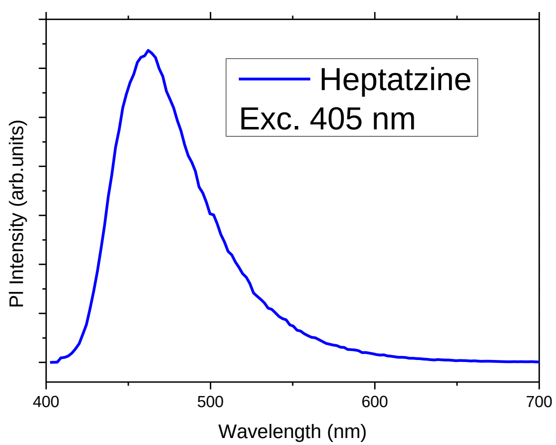
The temperature close to the junction reaches 300 °C !!!

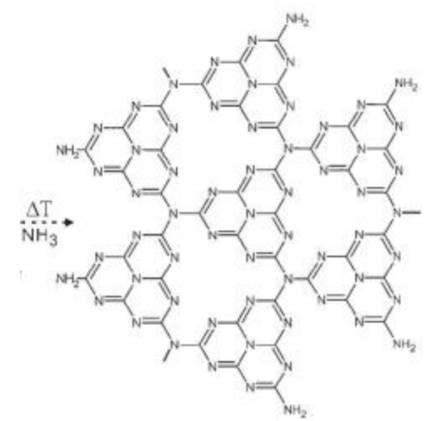
New class of organic phosphors





Exc. 365 nm!!





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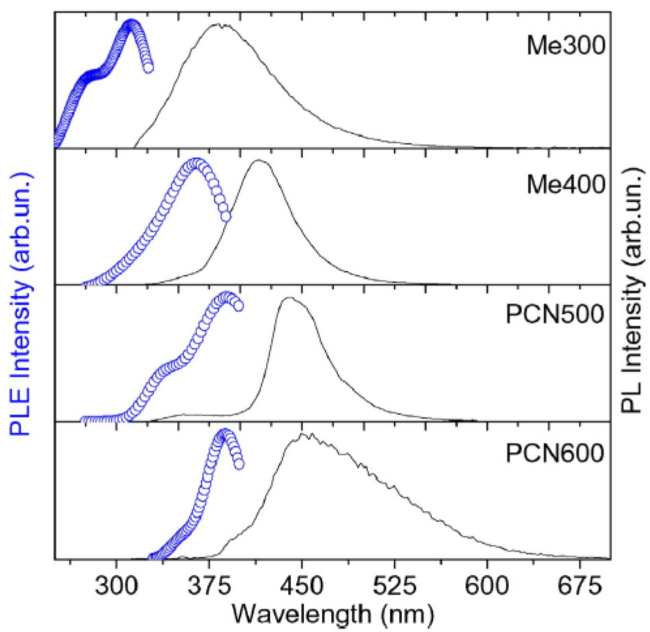
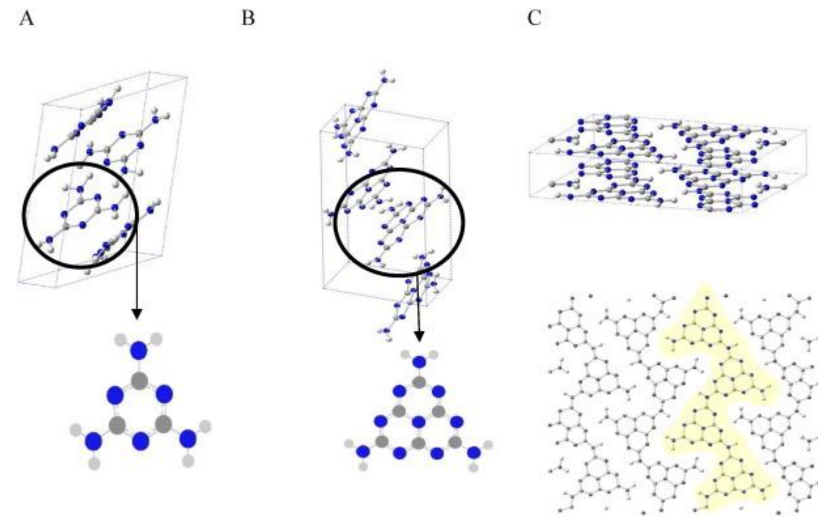
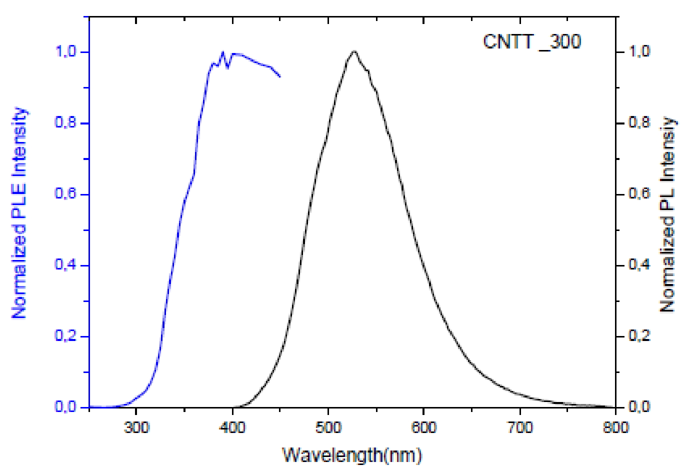
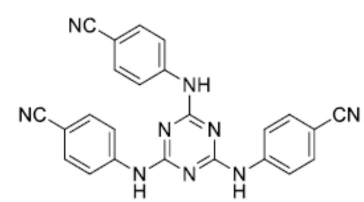

Me300
Me400
PCN500
PCN600
PLE Intensity (arb.un.)
PL Intensity (arb.un.)
300
375
450
525
600
675
Wavelength (nm)

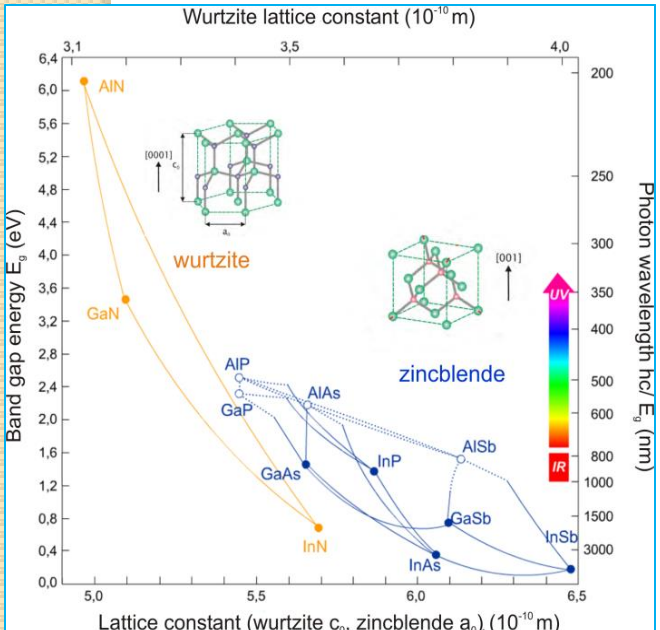

A
B
C

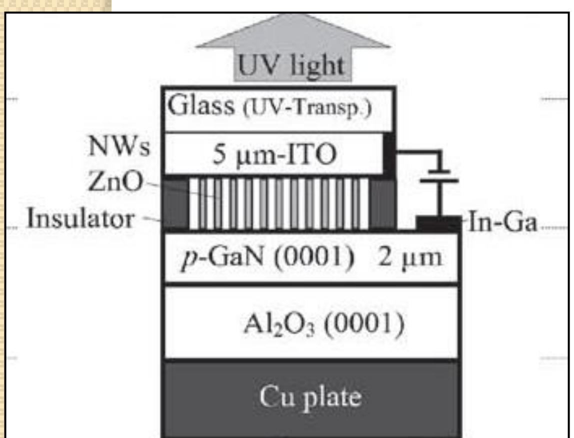

CNTT _300
Normalized PLE Intensity
Normalized PL Intensiy
Wavelength(nm)


NC
NH
NC
N
N
N
CN
N
H
N
H

Alternatives to InGaN based LED

Electroluminescent alternatives





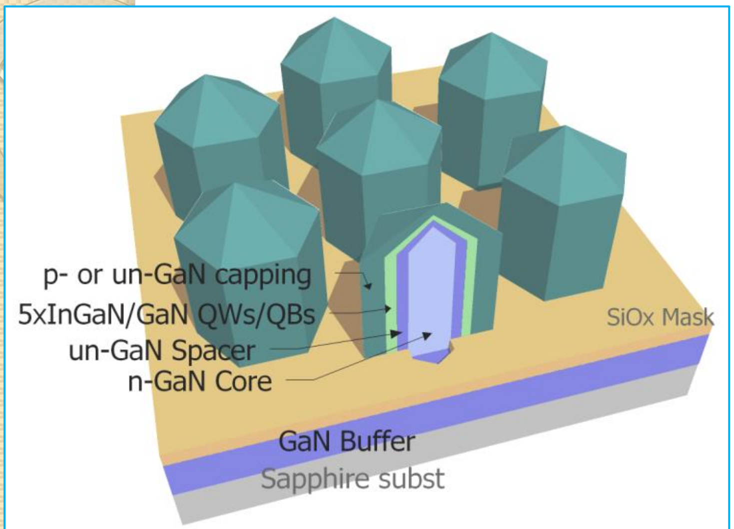
Direct wide band gap:

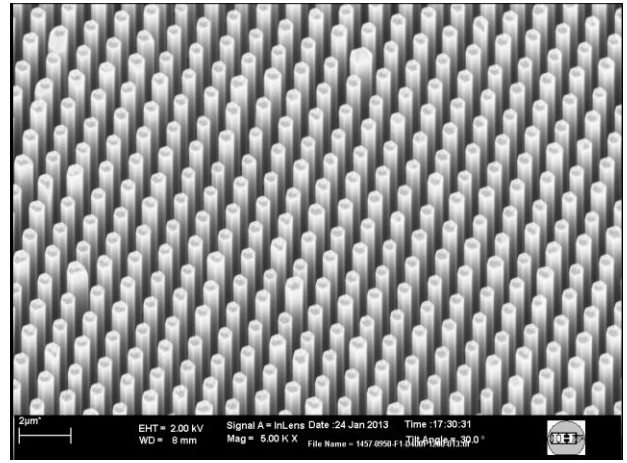
ZnS (3.5 eV)

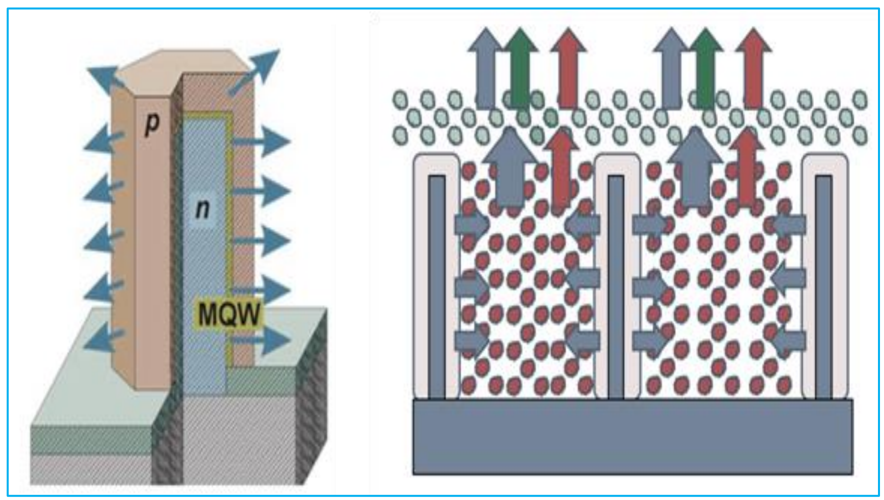
ZnO (3.37 eV)

Growth technique	Structure	Light emission (nm)
	n-ZnO/p-GaN	570
	n-ZnO/p-GaN	450, 520
MBE	n-ZnO:Ga/p-GaN:Mg	430
	n-MgZnO/CdZnO/p-GaN	390, 410
	n-MgZnO/n-ZnO/p-AlGaN/p-GaN	390

3 Dimensional hybrid concept







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Conclusions

- The research of new solution for lighting system is open
- New phosphors as well new design for LED are needed
- The research should take care the whole process for effective solutions

Thank You for your attention

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