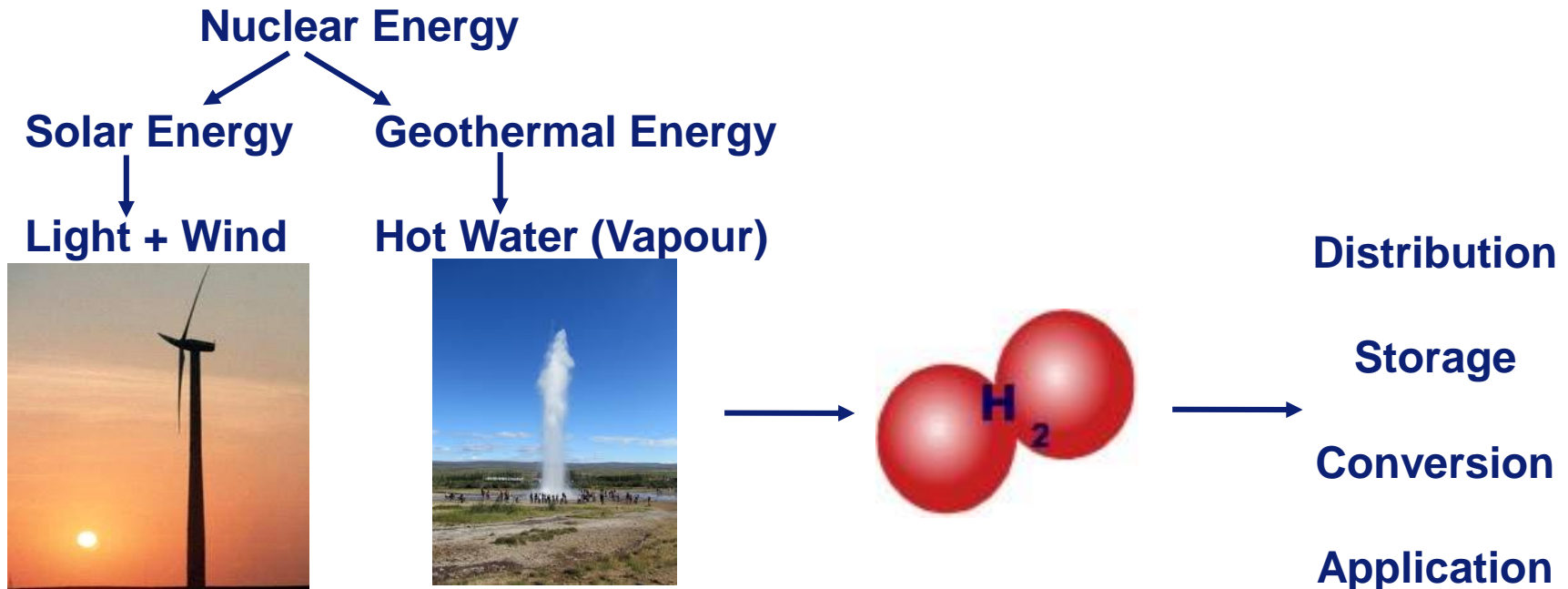


# Materials for an Energy Efficient Society



**Prof. Dr. Thomas Jüstel**

**Institute for Optical Technologies, Dpt. Chemical Engineering  
Münster University of Applied Sciences**

**Steinfurt/Münster, September 09<sup>th</sup>, 2021**

# To My Person

## CV

- **University Bochum (1987 - 1994)**      *Coordination Chemistry*
- **Max-Planck Institute Mülheim (1995)**      *Electrochemistry*
- **Philips Research Aachen (1995 - 2004)**      *Solid State Chemistry, Luminescence*
- **Münster University of Applied Sciences (since 2004)**      *Scintillators*  
*Functional Optical Materials*
- **Dean of department „Chemical Engineering“ (since 2013)**

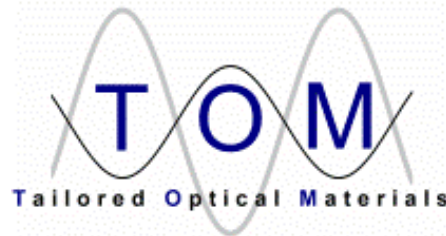
## Teaching

- **Inorganic Chemistry**
  - Solid state chemistry
  - Coordination chemistry
  - Bioinorganic chemistry
- **Material Science**
  - Optical materials
  - Luminescent materials
  - Material characterisation
- **Incoherent Light Sources, Photochemical Water Treat. & History of Science**

# Research Group Tailored Optical Materials



**Prof. Dr. Thomas Jüstel**  
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skype: thomasjuestel



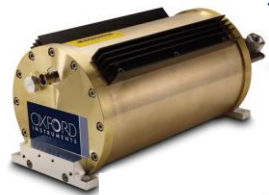
- Research Areas**
- Luminescent Pigments
  - Luminescence Physics
  - Nanoscale Pigments
  - Core-Shell particles (coatings)
  - Optical Spectroscopy
  - Solid State Chemistry

# Research Group Tailored Optical Materials

Xenon disch. lamp,  
wavelength range  
200 nm - 900 nm



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



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



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



High brightness  
LEDs from 250 -  
1100 nm



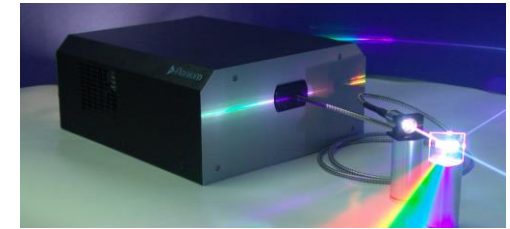
Americium source,  
 $\alpha$ - and  $\gamma$ -radiation



D<sub>2</sub> bulb, wavelength  
range 120 - 400 nm



Fianium supercontinuum  
SC450-4 white light laser,  
wavelength range 0.46 - 2.4  $\mu$ m



# Outline

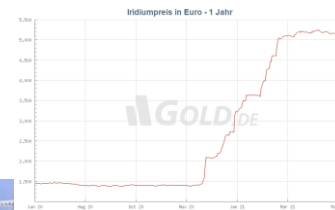
1. **Challenges of the 21<sup>st</sup> century**
2. **Metals and Materials**
3. **Matter Radiation Interaction**
4. **Photovoltaic Materials**
5. **Photochemical Water Splitting**
6. **Lighting Towards Ultimate Efficiency**
7. **Conclusions and Outlook**
8. **Literature**



# 1. Challenges of the 21<sup>st</sup> Century

## - Overview -

- **Increasing land and water consumption**
  - Endangering the safety of drinking water and food supply
  - Loss of arable land and pasture
  - Evaporation of sweetwater lakes
- **Increasing demand on raw materials endangers resource security**
  - Strategic metals: Li, Co, Cu, Ga, Ge, In, rare earth metals, W, Ir, Bi, ...
  - Plastic crises:  $\mu$ -plastics, biopolymers, recycling, critical additives and optical marker
  - Quarz crisis: Extremely growing demand on constructing materials
  - Phosphate crisis: Mines are driven at the limits
  - Iridium crisis: Water purification process via electrochlorination increases demand
- **$\mu$ -Microplastics and input of nutrients into biosphere**
  - Endangering marine and terrestrial food chains
  - Reduction of biodiversity
  - Expansion of dead zones in oceans
- **Emission of greenhouse gases and climate change**
  - Energy production without CO<sub>2</sub> emission: PV, Wind → H<sub>2</sub>, PtG, LNG, Batteries
  - CO<sub>2</sub> deposition:  $1 \cdot 10^{12}$  t CO<sub>2</sub> until 2100 for 2° Goal (SdW 08/19) → geochemistry?
  - New types of mobility: Electrical engines, fuel cells, artificial fuels



# 1. Challenges of the 21<sup>st</sup> Century

## - Air, Soil, and Water Pollution -

Reduce or prevent application of hazardous substances

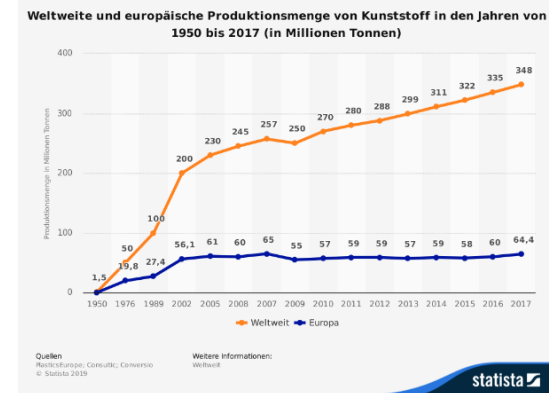
- Radioactive materials, U, Th, T, Pm, .....
- Heavy metals, e.g. Hg, Tl, Pb, Cd, .....
- Toxic, bioactive, or non-biodegradable organic compounds → plastics: “Great Pacific Garbage Patch”
- 2050: More plastic than fish in ocean water!

⇒ Apply green chemistry: Technologies that

- minimize or preferably eliminate the formation of waste
- avoid use of toxic & hazardous solvents and reagents
- utilize renewable raw materials
- are energy efficient

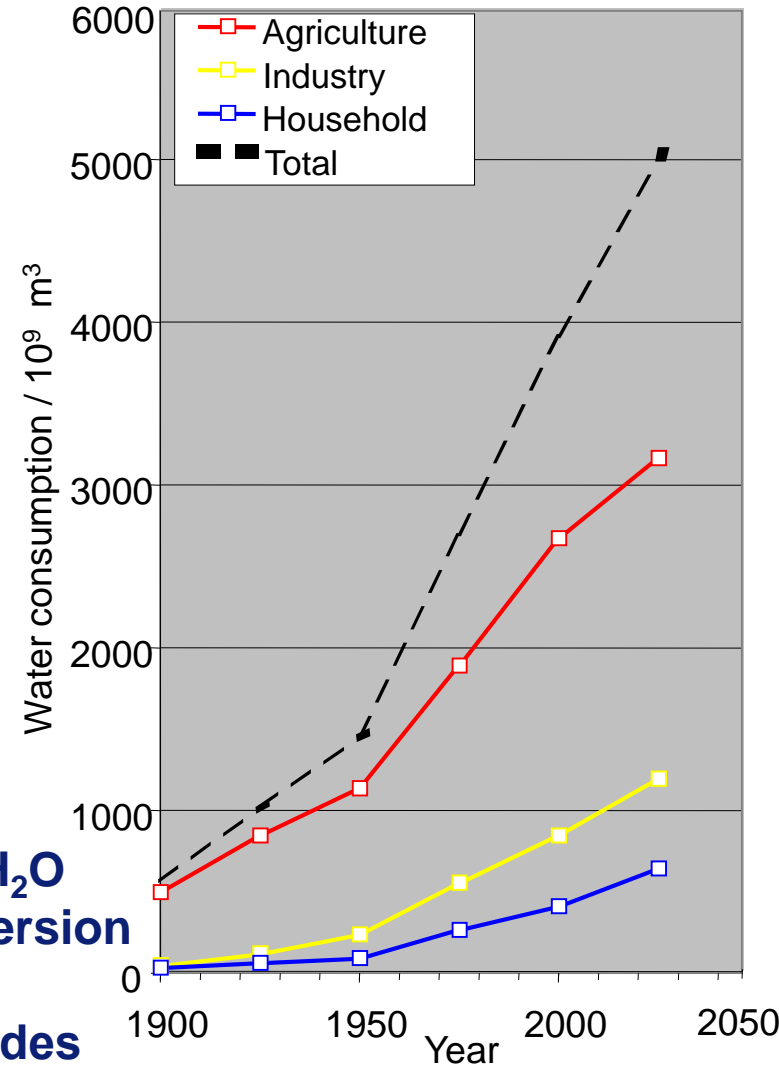
- Bioreactors
- Catalysis
- Photochemistry
- Solar chemistry
- Fast analytics @ point of use

- Biochemistry, microorganism design
- Catalytic pigments/coatings, reactor design
- Frequency selective radiation sources
- Solar radiation + converter or concentrator
- Advanced optical spectroscopy



# 1. Challenges of the 21<sup>st</sup> Century

## - Air, Soil, and Water Pollution -



- UV-C Radiation (265 nm) inactivates micro organisms due to photochemistry of DNA
  - VUV Radiation (180 - 200 nm) oxidizes due to H<sub>2</sub>O cleavage into radical species and O<sub>2</sub> to O<sub>3</sub> conversion
- Industrial installations → discharge lamps  
 Mobile devices → discharge lamps / (laser) diodes



# 1. Challenges of the 21<sup>st</sup> Century

## - Demand for Strategic Metals -

- Electric & hybrid vehicles (~30 kg Rare Earth / hybrid car): Growing mobility!  
Co, **Li** (ion batteries), Rare Earth Elements (REE), Cu
- Fuel cells  
Pt, (Ru, Pd, Au)
- Thermoelectrics, Optoelectronics, ILEDs, OLEDs, ( $\mu$ -LED) displays  
Bi, Te, Si, **In, Ga**, As, Se, Ge, Sb, Ir, Pt
- Photo voltaics  
Si, Ag, **In, Ga**, Se, Te, Ge, (Ru)
- Wind turbines, generators, electrical engines, magnets  
Nd, Sm, Pr, Dy, Cu



# 1. Challenges of the 21<sup>st</sup> Century

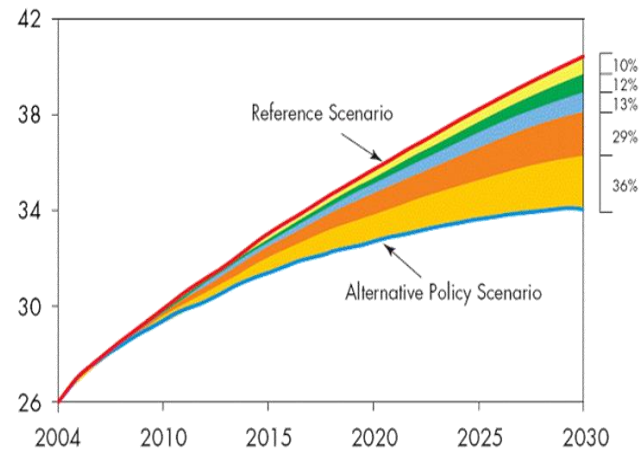
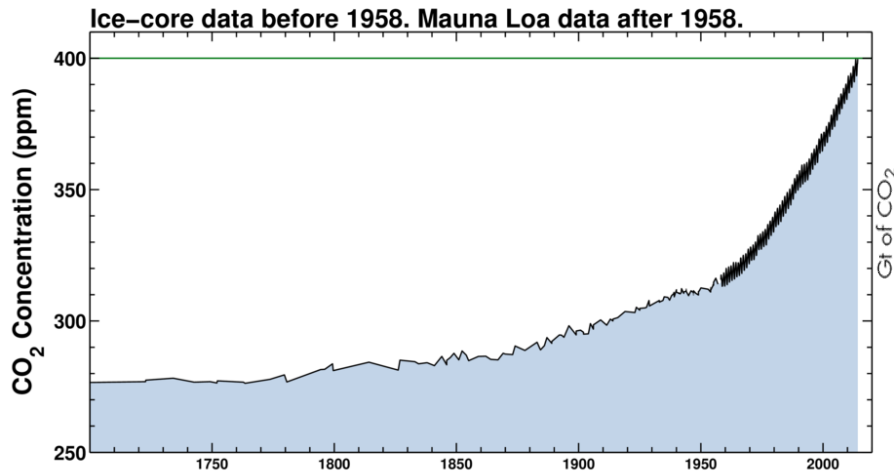
## - Dissipation of Heavy Metals -

- Hg from discharge lamps, batteries, thermometers, combustion of coal ends up at earth's cold spots, mainly at polar regions
- Pb and Ba from accumulators, displays, and high refractive glass ends up in Ca metabolism
- Sn from paints goes into aquatic system + reacts to toxic metalorganic compounds
- Cr, As, Sb, and Bi from paints, pigments modify DNA
- **Ga and In** from LEDs, LCDs, OLEDs are harmful to the kidney and liver metabolism
- Cu, Ag, Pt, and Au from electronic devices are bioactive
- Actinides from nuclear industry, U also from artificial fertilisers (phosphates)



# 1. Challenges of the 21<sup>st</sup> Century

## - Climate Change Due to CO<sub>2</sub> Emission -



- Increased nuclear
- Increased renewables in power generation and biofuels
- Improved efficiency and fuel switching in the power sector
- Demand-side electricity-efficiency measures
- Demand-side fossil-fuel-efficiency measures

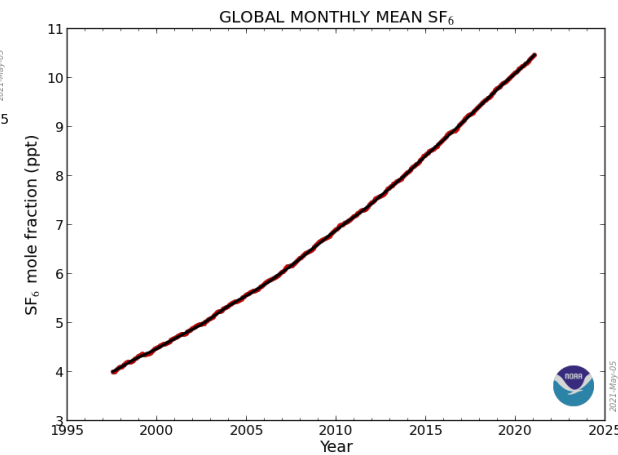
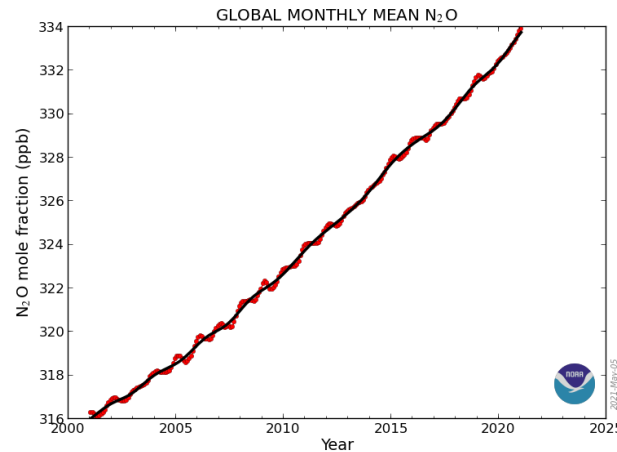
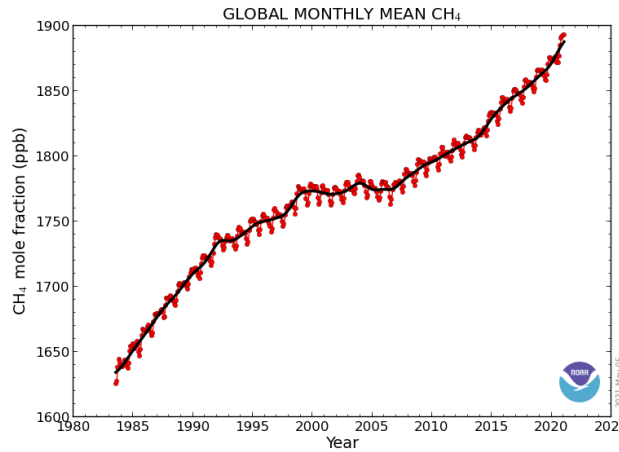
Source: International Energy Agency  
*World Energy Outlook 2006*

### Further consequences of CO<sub>2</sub> emission

- Acidification of oceans: endanger marine ecosystems
- Reduction of glacier and polar ice: sea water level rise
- Modification of plant physiology: increasing sugar content
- Increasing water and soil temperature: Emission of CH<sub>4</sub> from permafrost areas
- Reduction of air quality

# 1. Challenges of the 21<sup>st</sup> Century

## - Climate Change Due to other Greenhouse Gas Emission -

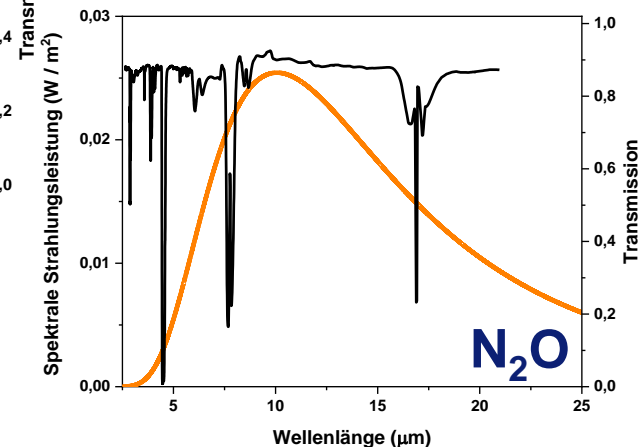
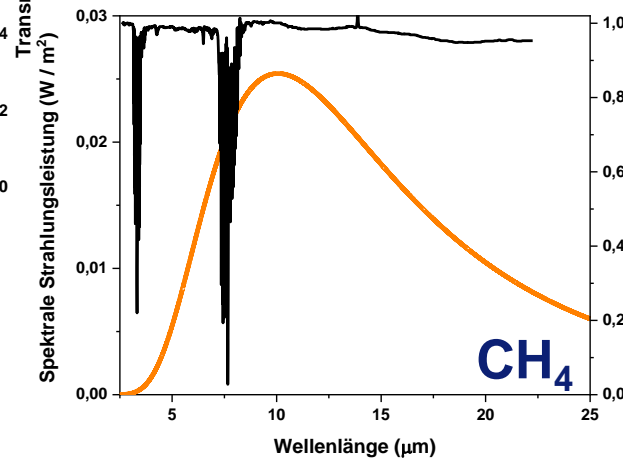
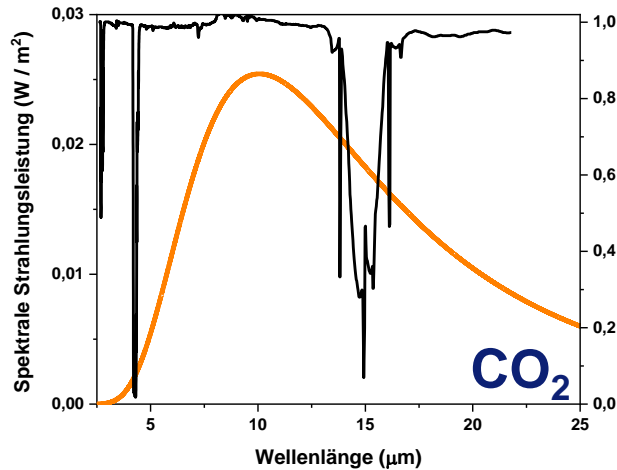


<u>Greenhouse gas</u>	<u>concentration 2021</u>	<u>GTP100</u>
CO <sub>2</sub>	417 ppm	1
CH <sub>4</sub>	1891 ppb	11
N <sub>2</sub> O	334 ppb	297
CF <sub>4</sub>	~ 90 ppt	9560
SF <sub>6</sub>	10.56 ppt	28200

# 1. Challenges of the 21<sup>st</sup> Century

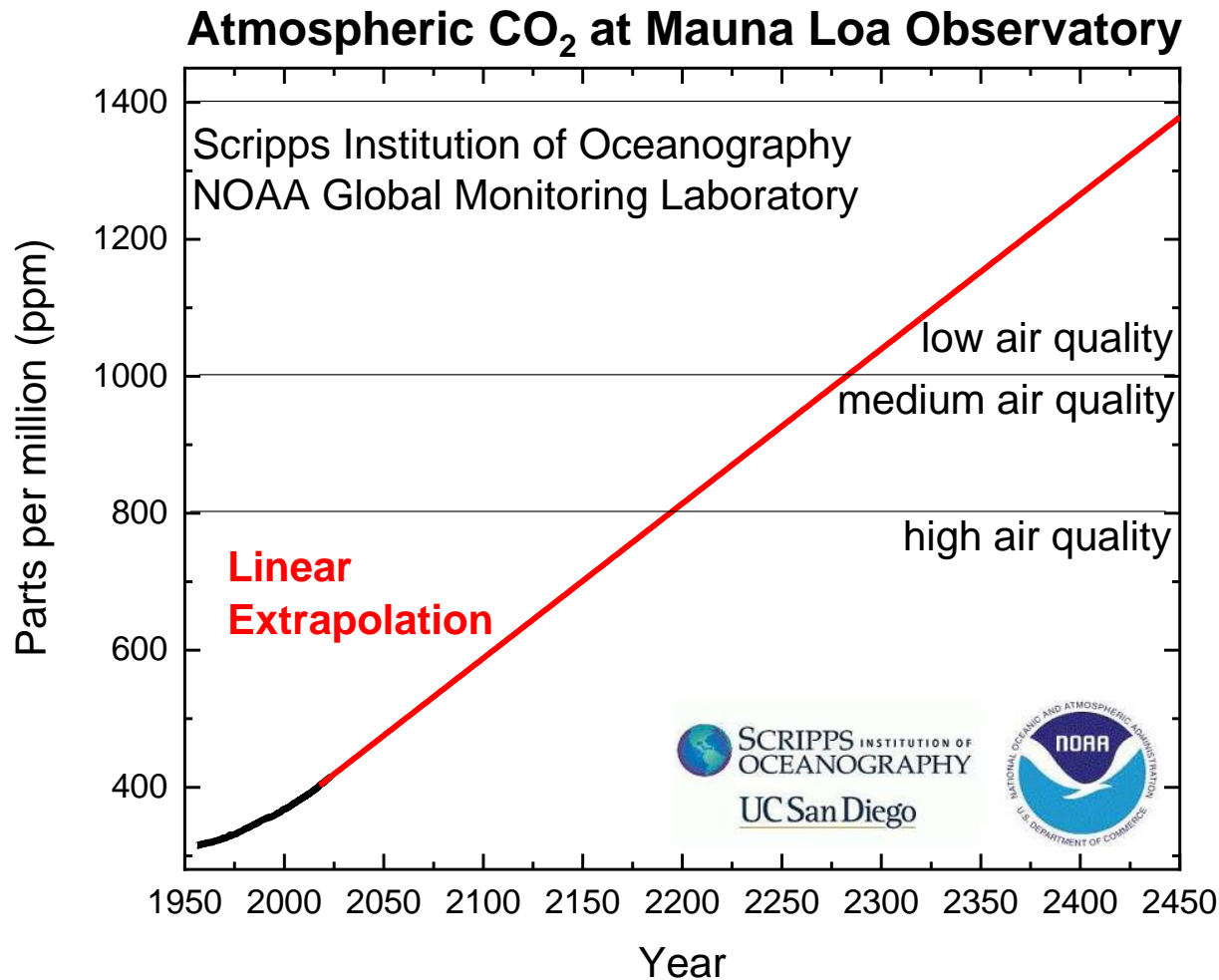
## - Climate Change Due to Greenhouse Gases -

Greenhouse gas potential depends on the absorption spectra of trace gases and average global temperature of the Earth's surface ( $T_e \sim 288 \text{ K} \sim \text{Planck spectrum}$ )



# 1. Challenges of the 21<sup>st</sup> Century

## - Loss in Brain Power Due to CO<sub>2</sub> Emission -



# 1. Challenges of the 21<sup>st</sup> Century

## - Causes of Greenhouse Gas Emission -

### CO<sub>2</sub>

- Illumination (5%)
- Transport (~ 25%)
- Buildings (6%)
- IT (2%)
- Steel production (5%)
- Cement production (6-7%)
- Ammonia synthesis (1-2%)
- Chloralkali electrolysis (~1%)

LED technology

Novel engines and fuels

Thermal insulation

Server architecture, PV use

H<sub>2</sub> as reductive agent

Reduction of cement fraction in concret

N<sub>2</sub> hydration by water vapor, N<sub>2</sub> photolysis

Change to membrane process, heat recovery



### CH<sub>4</sub>/N<sub>2</sub>O

- Agriculture and feedstock
- HNO<sub>3</sub> and Nylon production

Reduction of meat consumption

Optimisation of Ostwald process,



### SF<sub>6</sub>/NF<sub>3</sub>

- (Consumer) Electronics

Other insulator gases, optimisation of processes for the production of displays & solar cells



# 1. Challenges of the 21<sup>st</sup> Century

## Energy Efficient Date Storage and Transfer: Rebound Effect

### Discoveries & inventions for knowledge management

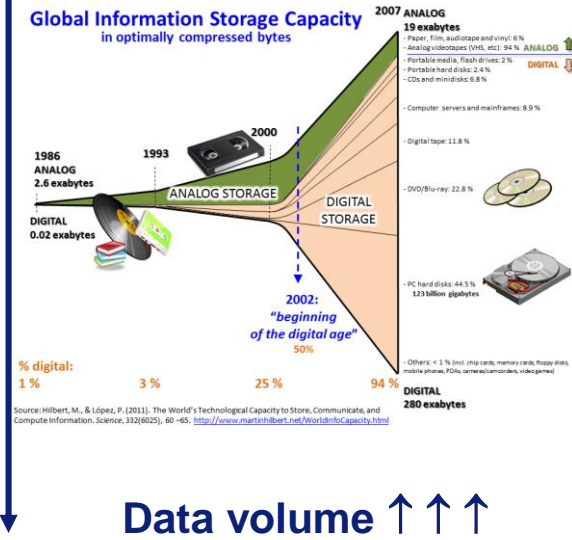
- 1015 Ibn Al Haythem (Basra, 965 – 1040) “Book of Optics“
- 1455 Gutenberg Bible: 1<sup>st</sup> book printed with movable metal types
- 1815 Fresnel and the wave nature of light
- 1865 Maxwell and electromagnetic waves
- 1915 General relativity – light in space and time
- 1945 Z4 of Konrad Zuse (2200 Relais)
- 1965 Cosmic microwave background  
& Optical fibre technology
- 1989 Birth year of the WWW
- 2002 Beginning of the digital age
- 2007 ~ 300 exabyte stored
- 2010 50 Gbps transmitter (by four laser)
- 2014 Data transfer rate > 100 Gbps
- 2015 International Year of Light (IYL), > 1 ZB stored....
- 2018 ~ 4-5 ZB stored, 1+ bill. google searches,  
294 bill. mails, and 230 mill. tweets/day
- 2020 ~ 44 ZB stored
- 2030 Internet ~ 21% of projected electricity demand (Ref.: Nature 561 (2018) 163)



Energy demand / bit ↓

Efficiency ↑

$$\text{Limit: } E_{\text{bit,min}} = \ln(2) \cdot k_B \cdot T$$





# 2. Metals and Materials - Electronics

1		Groups										13						18		
1	2											13	14	15	16	17	18	1		
1 H																		2 He	1	
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	2		
11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	3		
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	4		
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	5		
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	6		
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og	7		
			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	6			
			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			

Energy storage materials

Active or passive components

Electrical engines/magnets

Detectors/catalysts

Solid oxid fuel cells (components)

Electrode/conductor materials

# 2. Metals and Materials - Lighting

1		Groups										13						14	15	16	17	18	
1 H	2											5 B	6 C	7 N	8 O	9 F	10 Ne	1					
3 Li	4 Be											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	2					
11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	3					
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	4					
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	5					
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	6					
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og	7					
			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	6						
			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						

**Filling of metal halide lamps**  
**Electrode component**

**Activator in phosphors/laser gain media**  
**Host component of phosphors/laser gain media**

## 2. Metals and Materials

### Transition Metals

#### Electron configuration of the 3d transition metals

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

#### Electron configuration of the 4d transition metals

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

#### Electron configuration of the 5d transition metals

	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

Transition metals are very common catalysts due to

- many redox states
- coordinative bonds
- crystal-field effects
- high-spin ↔ low-spin transitions
- cluster formation
- magnetic interaction
- rather high abundance of 3d transition metals and thus reasonable costs
- long-term catalytic activity (Ru, Rh, Pd, Re, Ir, and Pt)

⇒ Stable configurations due to lower energetic states of the nd-orbitals

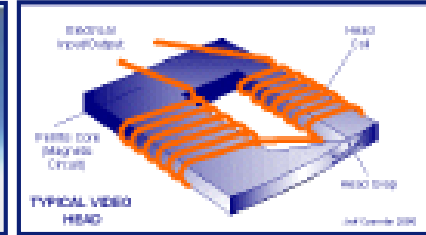
## 2. Metals and Materials

### The Transition Metal Iron

#### Use in Ferrites

Magneto ceramic materials

⇒ Binary/ternary iron oxides



#### Soft ferrites

- are easily and efficiently magnetised by an external magnetic field
- Magnets in writing and reading heads in audio and video recorders, hard drives etc.
- Electrical isolators, ferrimagnetic compounds with low saturation magnetisation in combination with low anisotropy in terms of the crystal structure
- $MFe_2O_4$  (spinel) with  $M = Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Mg^{2+}$
- Typical composition: Fe-Mn-Zn-oxide with 70% Fe, 25% Mn, and 5% Zn

#### Hard ferrites

- maintain their magnetic properties after the initial magnetisation
- Permanent magnets in electric motors, speaker, generators, and son on
- $MFe_{12}O_{19}$  with  $M = Sr^{2+}, Ba^{2+}$

## 2. Metals and Materials

### The Transition Metal Manganese

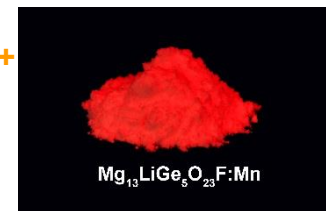
#### Mn Ions in (photo)catalysis

- Mn dependent catalase
- Percarbonate decomposition
- Superoxide dismutase
- Photosystem II
- Photocatalytic water splitting



#### Mn Ions in photoluminescence

- Green CRT and PDP phosphor
- Green FL phosphor
- Orange electroluminesc. pigment
- Dichromatic FL phosphor
- Red LED phosphor
- Deep red FL phosphor



# 2. Metals and Materials

## Rare Earth Metals

### Metals

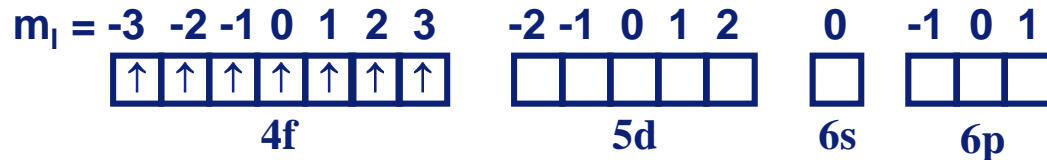
[Xe]	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
6s	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
5d	1	1	0	0	0	0	0	1	0	0	0	0	0	0	1
4f	0	1	3	4	5	6	7	7	9	10	11	12	13	14	14

### Cations

[Xe]	La <sup>3+</sup>	Ce <sup>3+</sup>	Pr <sup>3+</sup>	Nd <sup>3+</sup>	Pm <sup>3+</sup>	Sm <sup>3+</sup>	Eu <sup>3+</sup>	Gd <sup>3+</sup>	Tb <sup>3+</sup>	Dy <sup>3+</sup>	Ho <sup>3+</sup>	Er <sup>3+</sup>	Tm <sup>3+</sup>	Yb <sup>3+</sup>	Lu <sup>3+</sup>
	Ce <sup>4+</sup>	Pr <sup>4+</sup>	Nd <sup>4+</sup>				Sm <sup>2+</sup>	Eu <sup>2+</sup>	Dy <sup>4+</sup>					Tm <sup>2+</sup>	Yb <sup>2+</sup>
								Tb <sup>4+</sup>							
4f	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

### Electron configuration

e.g. of Gd<sup>3+</sup>/Eu<sup>2+</sup>/Tb<sup>4+</sup> [Xe]4f<sup>7</sup>



Ce<sup>3+</sup> - Yb<sup>3+</sup>, Pr<sup>4+</sup>, Nd<sup>4+</sup>, Tb<sup>4+</sup>, Dy<sup>4+</sup>, Sm<sup>2+</sup>, Eu<sup>2+</sup>, Tm<sup>2+</sup>  
Gd<sup>0</sup>, Tb<sup>0</sup>, Dy<sup>0</sup>

→ paramagnetic ions  
→ ferromagnetic ordering (T<sub>C</sub> < RT)

## 2. Metals and Materials

### Rare Earth Alloys and Compounds: Application Areas in Electrics

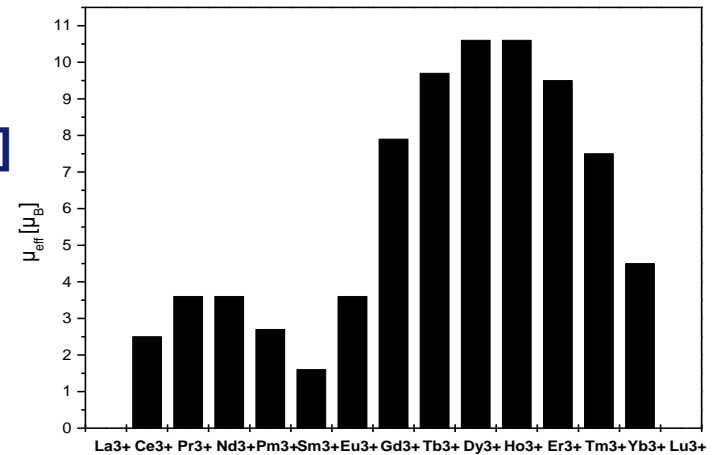
<i>Magnets</i>	<i>Superconductors</i>	<i>Ion Conductors</i>	<i>Thermistors</i>
Engines, generators, speakers, microphones, telephones, headphones, hearing aids, magnetic couplers, sensors, cranes, overhead platforms, ....	NMR devices Particle accelerators Fusion reactors SQUIDs	Fuel cells Lambda probes Sensors	Temperature sensors Inrush current limiter Voltage stabilisers
$\text{Nd}_2\text{Fe}_{14}\text{B}$ $\text{SmCo}_5$ $\text{Sm}_2\text{Co}_{17}$	$(\text{La.Ba})_2\text{CuO}_4$ $\text{YBa}_2\text{Cu}_3\text{O}_7$	$\text{LaCoO}_3\text{:Sr}$ $\text{CeO}_2\text{:Sm}$ $\text{ZrO}_2\text{:Y}$ $\text{LaCeO}_3\text{:Ba}$	$\text{Sm}_2\text{O}_3\text{-Tb}_2\text{O}_3$

## 2. Metals and Materials

### Rare Earth Alloys and Compounds: Advantages in Magnets

#### Highly paramagnetic as cations

- $\text{Gd}^{3+} \Rightarrow$  magnetic contrast agent [ $\text{Gd}^{3+}(\text{dota})$ ]
- $\text{Dy}^{3+}/\text{Ho}^{3+} \Rightarrow$  maximal magnetic moment of all elemental cations  $\sim 10.6 \mu_B$
- For comparison:  $\text{Fe}^{3+}/\text{Mn}^{2+} \mu_{\text{eff}} = 5.9 \mu_B$

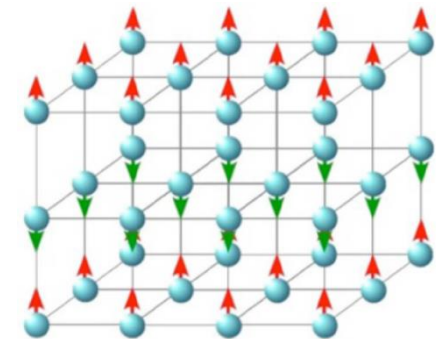


#### Ferromagnetic as metal or alloy

- Gd/Tb/Dy
- $\text{Nd}_2\text{Fe}_{14}\text{B}$
- $\text{SmCo}_5$  and  $\text{Sm}_2\text{Co}_{17}$

#### As building block in ferromagnetic materials

- $\text{Y}_3\text{Fe}_5\text{O}_{12}$  „YIG“
- $\text{Gd}_3\text{Fe}_5\text{O}_{12}$  „GdIG“



Ferromagnetic ordering  
in 4f ferromagnets



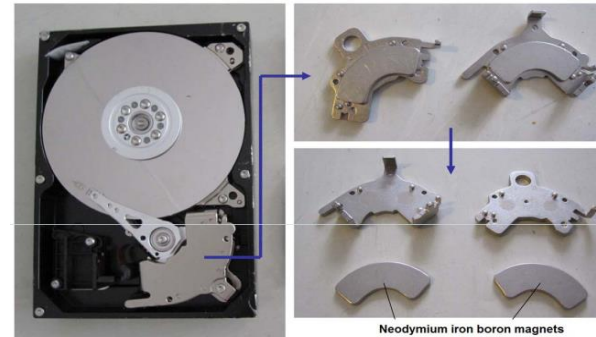
## 2. Metals and Materials

### Application Areas of $\text{Nd}_2\text{Fe}_{14}\text{B}$ , $\text{SmCo}_5$ , and $\text{Sm}_2\text{Co}_{17}$

- Application in electric engines in automotive industry  
> 25 actuating motors per car  
electric drive & brake



- Hard Disc Drives (HDDs)  
Magnets: 2 wt-% of HDD  
Rare earths: 0.6 wt-% of HDD



- Wind power stations  
Off-shore: 650 kg Nd/station  
~ 100 kg/MW power output



## 2. Metals and Materials

### Magnetic Properties of TM and RE Based Alloys

Important figures of magnetic materials:

- Coercitive field strength  $\Rightarrow$  **Soft-** or **hard** magnetic materials
- Energy density  $\Rightarrow$  Conversion efficiency

Alloy	Coercitive field strength $H_c$ [kA/m]	Typical energy density $(BH)_{max}$ [kJ/m <sup>3</sup> ]
<b>Steel (0.9% C, 1.0% Mn)</b>	<b>4</b>	<b>1.6</b>
<b>Martensitic Steel (9% Co)</b>	<b>11</b>	<b>3.3</b>
<b>AlNiCo (21% Ni, 12% Al, 5% Co, Fe)</b>	<b>35</b>	<b>11</b>
<b>CuNiFe (60% Cu, 20% Fe, 20% Ni)</b>	<b>44</b>	<b>12</b>
<b>SrFe<sub>12</sub>O<sub>19</sub></b>	<b>260</b>	<b>29</b>
<b>SmCo<sub>5</sub></b>	<b>760</b>	<b>200</b>
<b>Sm<sub>2</sub>Co<sub>17</sub></b>	<b>720</b>	<b>250</b>
<b>Nd<sub>2</sub>Fe<sub>14</sub>B:Dy,Pr</b>	<b>880</b>	<b>360</b>

## 2. Metals and Materials

### Replacement of $\text{Nd}_2\text{Fe}_{14}\text{B}$ , $\text{SmCo}_5$ , and $\text{Sm}_2\text{Co}_{17}$ ?

- Permanent magnets on the basis of iron oxides by addition of other oxides?  
Problem: Energy product  $(\text{BH})_{\text{max}} \sim 10$ times smaller than that of RE magnets  
⇒ Not applicable in high performance engines and turbines!
- Nanoscale Fe/Co compounds?  
Nano rods with magnetic ordering resulting in a matrix of particles which are equal to ferromagnetic domains  
⇒ Rather demanding technology
- Molecular magnets?  
 $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{CH}_3\text{COOH} \cdot 4\text{H}_2\text{O}$  „ $\text{Mn}_{12}\text{ac}$ “  
Prussian Blu analagous: „ $\text{Fe}_4$ “ or „ $\text{Fe}_8$ “  
⇒ long-term R&D projects



# 2. Metals and Materials

## Optical Properties of RE: Absorption

**La**       $\text{La}_2\text{O}_3$       Highly refractive glasses for lenses  
in cameras or telescopes (Galilei type)

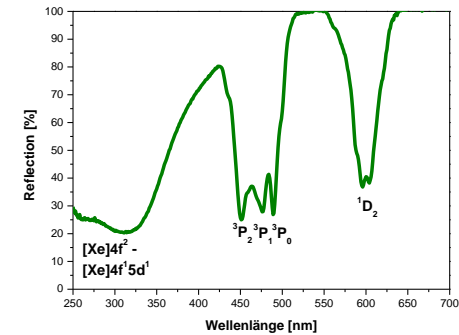


**Ce**       $\text{Ce}_2\text{O}_3/\text{CeO}_2$       UV filters in light sources

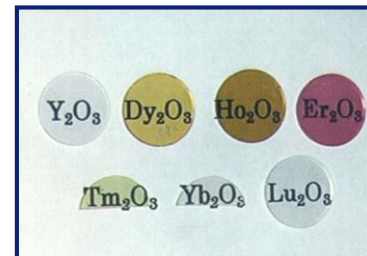
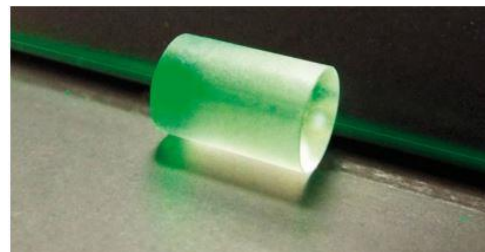
**Pr**       $\text{Pr}_2\text{O}_3/\text{PrO}_2$       Colour filters



**Nd**       $\text{Nd}_2\text{O}_3$       Colour filters

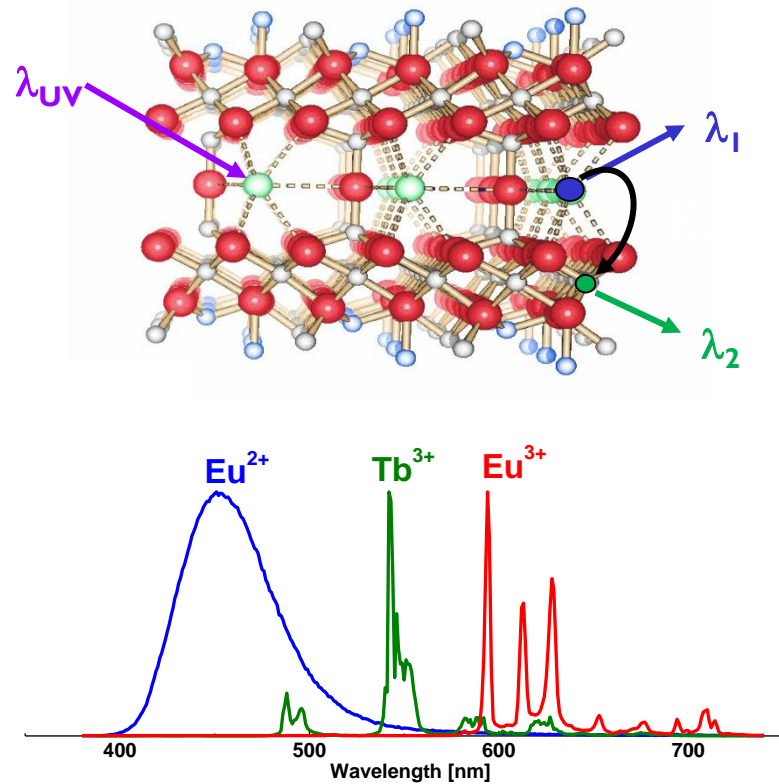


**Tb**       $\text{KTb}_3\text{F}_{10}$   
 $\text{Tb}_3\text{Ga}_5\text{O}_{12}$       High power laser Faraday isolator

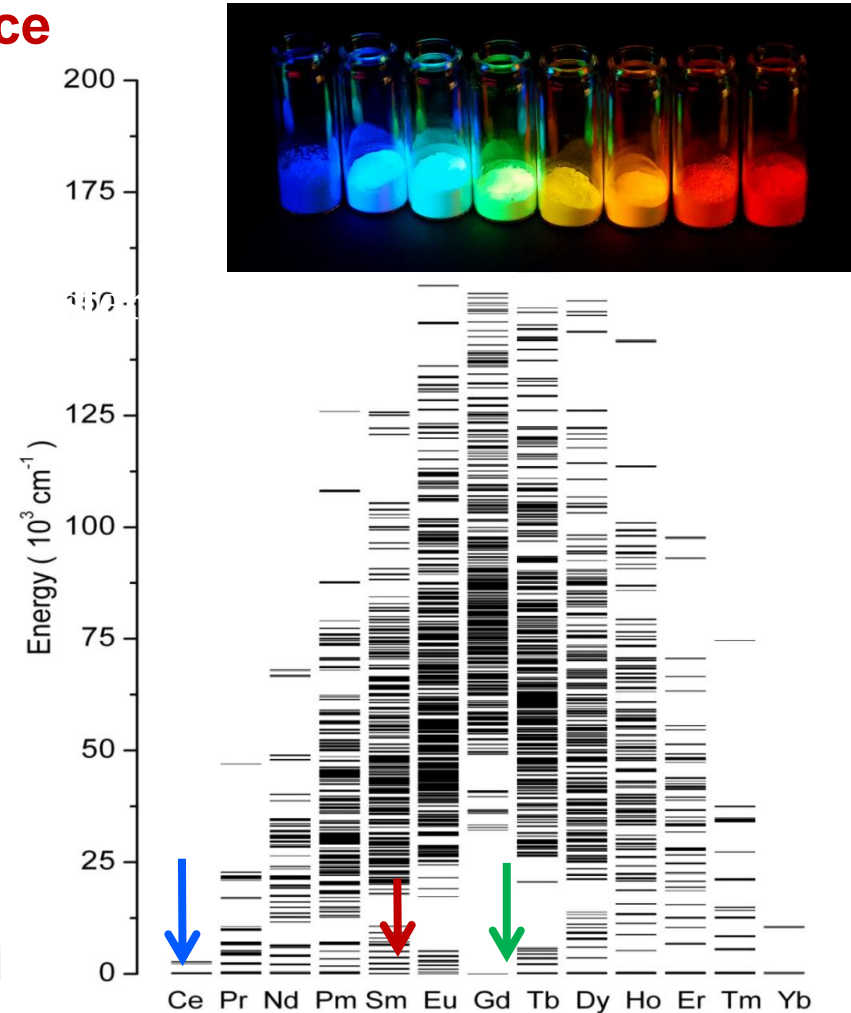


# 2. Metals and Materials

## Optical Properties of RE: Luminescence

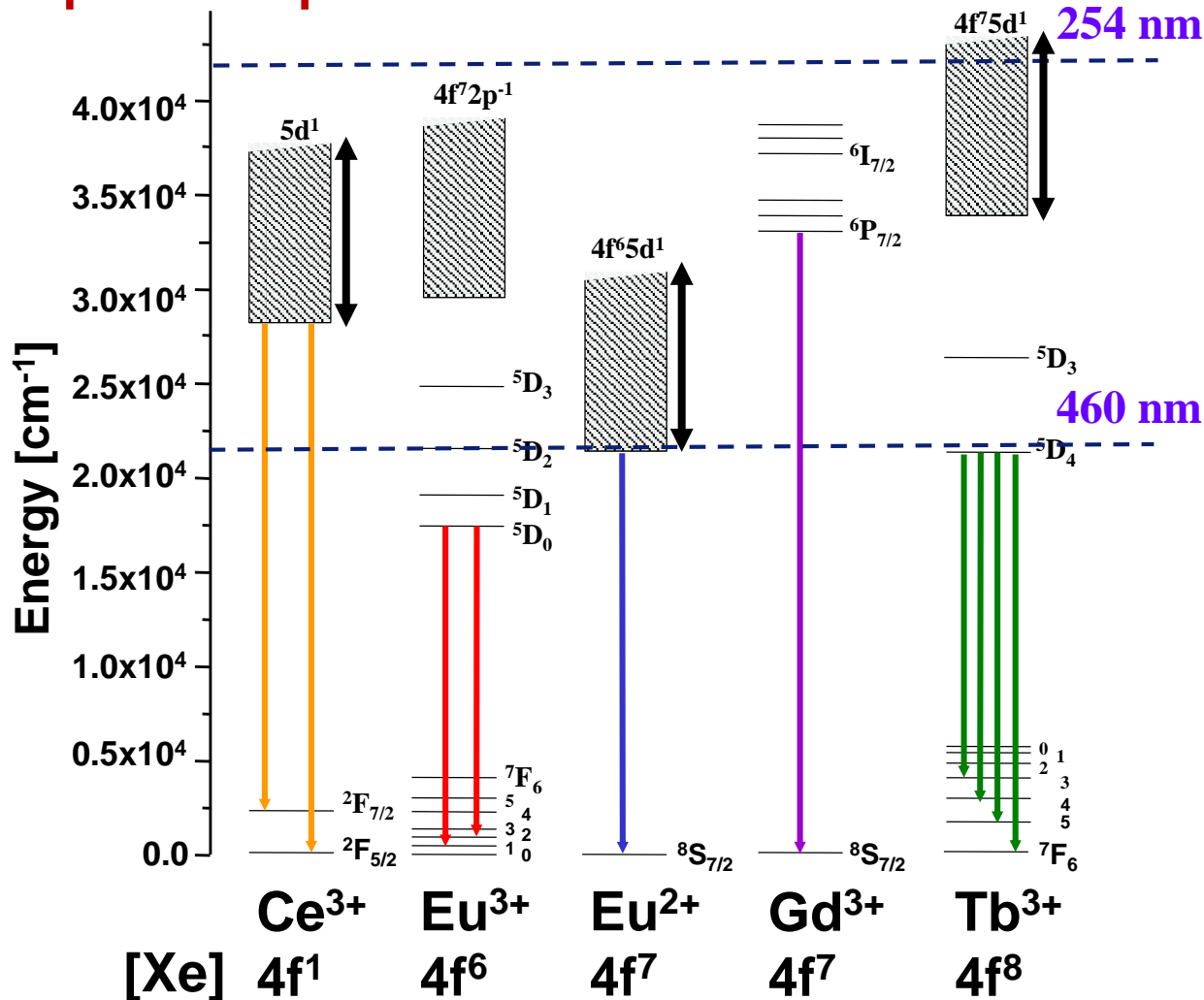


$Ln^{3+} \Rightarrow$  Multiple energy levels and thus many optical transitions in the UV, VIS and NIR range



# 2. Metals and Materials

## Optical Properties of selected RE ions



### Typical Line emitter

- $\text{Pr}^{3+}$  Scintillators
- $\text{Nd}^{3+}$  Laser gain media
- $\text{Sm}^{2+/3+}$  Detectors
- $\text{Eu}^{3+}$  Fluorescent lamps
- $\text{Gd}^{3+}$  UV-B lamps
- $\text{Tb}^{3+}$  Fluorescent lamps
- $\text{Dy}^{3+}$  Afterglow pigments
- $\text{Ho}^{3+}$  Laser gain media
- $\text{Er}^{3+}$  Laser
- $\text{Tm}^{3+}$  Plasma displays
- $\text{Yb}^{3+}$  Laser gain media

### Typische Bandenemitter

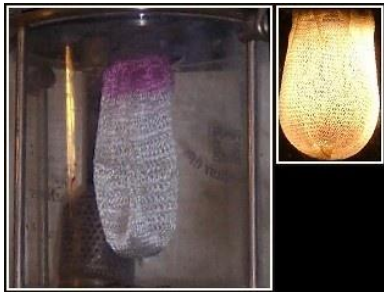
- $\text{Ce}^{3+}$  LEDs, UV lamps
- $\text{Pr}^{3+}$  Detectors
- $\text{Nd}^{3+}$  UV lamps
- $\text{Eu}^{2+}$  LEDs
- $\text{Yb}^{2+}$  Laser

## 2. Metals and Materials

### Rare Earth Alloys and Compounds: Application Areas in Optics

#### *Thermo luminescence*

Gas mantle:  
99% ThO<sub>2</sub> +  
1% CeO<sub>2</sub>



Flint stones:  
„Misch metal“ =  
30% Fe + 70% La-Sm

#### *Thermal Radiators*

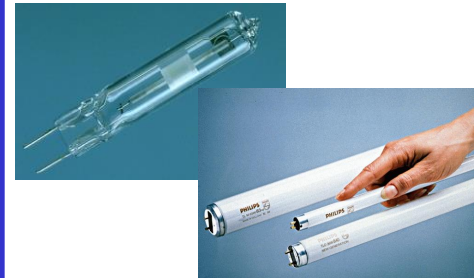
Incandescent and  
halogen lamps



Glass additives  
La<sub>2</sub>O<sub>3</sub> / Ce<sub>2</sub>O<sub>3</sub>

#### *Low and High Pressure Discharges*

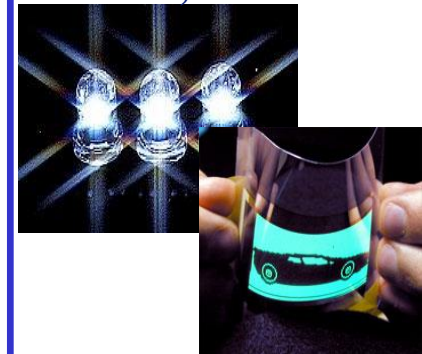
Na and Hg Vapour lamps  
Metal halide lamps



Electrodes: Sc<sup>3+</sup>, Y<sup>3+</sup>  
Gas fillings:  
DyI<sub>3</sub>, HoI<sub>3</sub>, TmI<sub>3</sub>  
+ **Phosphors**

#### *Electro luminescence*

Inorganic LEDs,  
OLEDs, and PLEDs



Ceramic lenses  
Y, La, Ce, Eu, Gd, Tb,  
Lu comprising  
**Phosphors**

# 3. Matter Radiation Interaction

**Physics and chemistry of the photon are key for advances in 21<sup>st</sup> century**

## 1. Life Science

- Photoreactor: Earth's atmosphere and „surface layer“
- Photoreactor: Plants and algae → Photosynthesis
- Photoreactor: Eye
- Photoreactor: Skin
- Medical diagnostics
- Medical therapy

## 2. Material Science

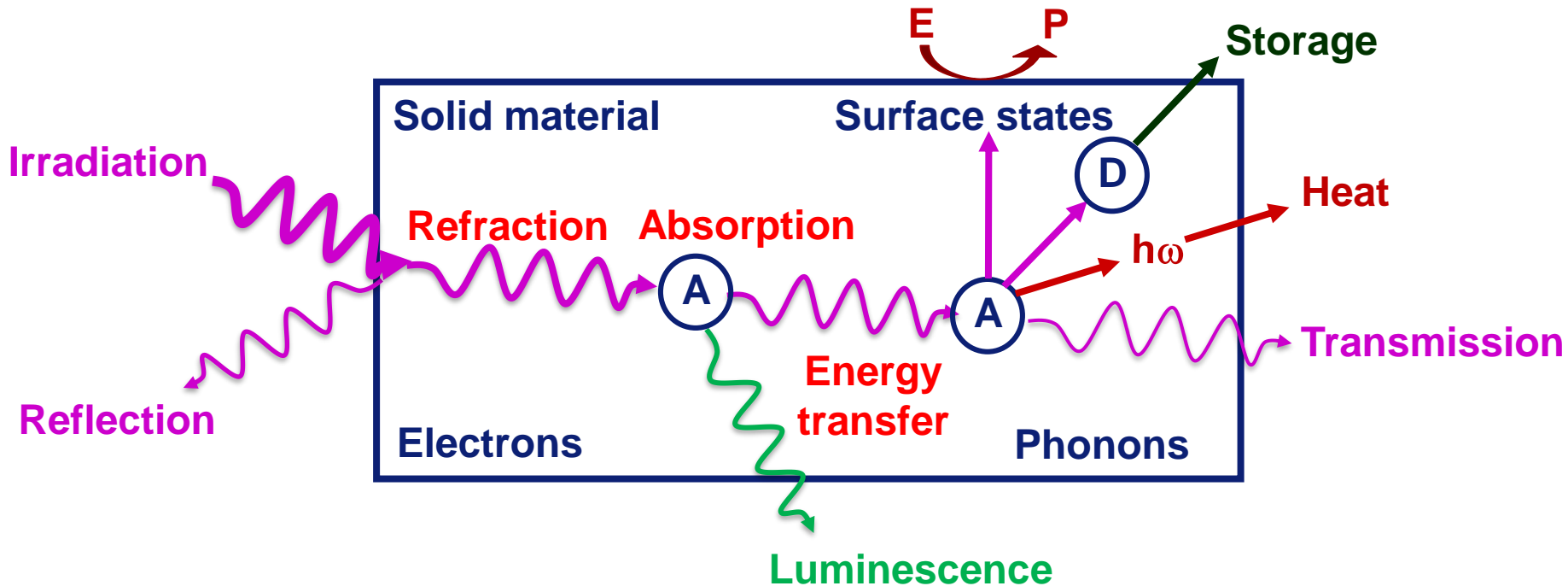
- Converter for LEDs, Laser diodes, and OLEDs
- Novel materials for photovoltaic cells
- Photocatalysts for photoreactors (solar chemistry)
- Photonic sensors
- Photonic switches
- Photonic computing
- Solar driven disinfection



# 3. Matter Radiation Interaction

## Inorganic Solid State Materials

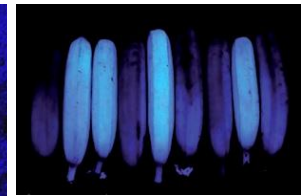
- Absorption
- Photothermalisation
- Pigments
- Activation
- Photochemistry
- Photocatalysts
- Emission
- Photoluminescence
- Phosphors
- Charge separation
- Photoconductivity
- Photovoltaics
- Charge trapping
- Photostorage
- Photoimaging, afterglow



# 3. Matter Radiation Interaction

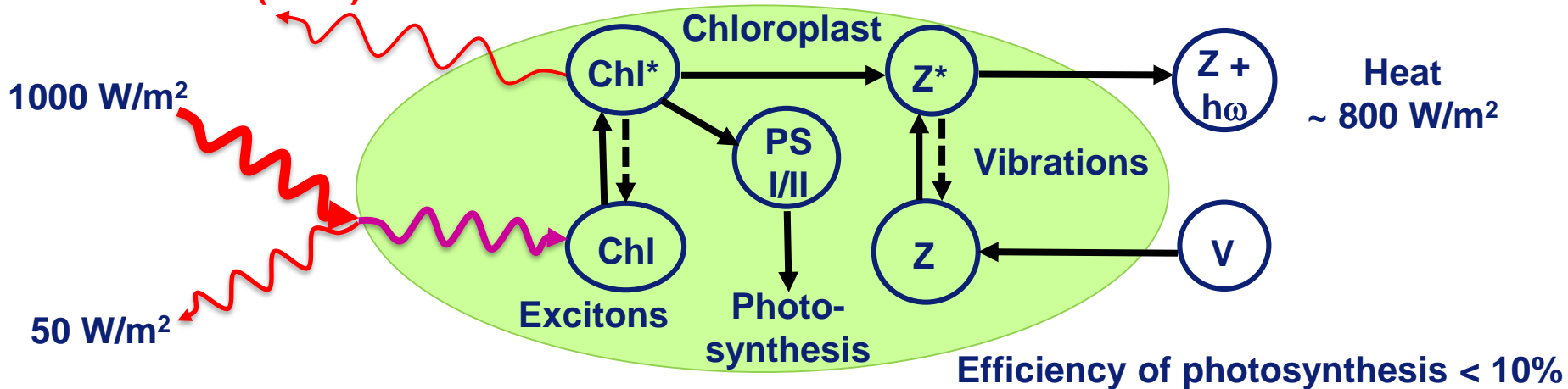
## Organic Biomatter

- Absorption
  - Activation
  - Emission
  - Charge separation
  - Charge trapping
- Multiphononrelaxation
  - Photochemistry
  - Photoluminescence
  - Water cleavage
  - Photostorage
- Plant pigments
  - Photocatalytic pigments
  - Plants, scorpions
  - Photosynthesis
  - ???



Z = Zeaxanthine  
V = Violaxanthine

Luminescence (~ 5%)



# 3. Matter Radiation Interaction

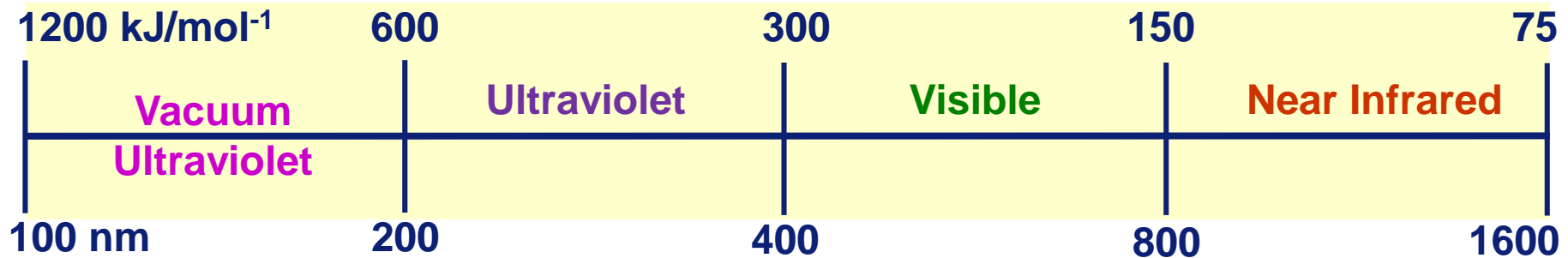
## Photochemistry

Energy of chemical bonds  
10 – 1100 kJ/mol

Energy of optical radiation

$$E = N_A hc / \lambda = 119226 / \lambda \text{ kJmol}^{-1}$$

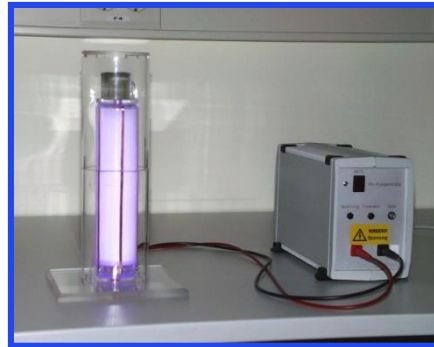
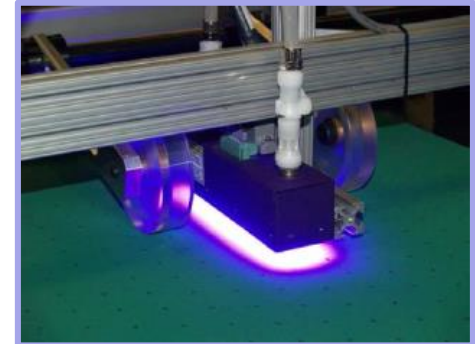
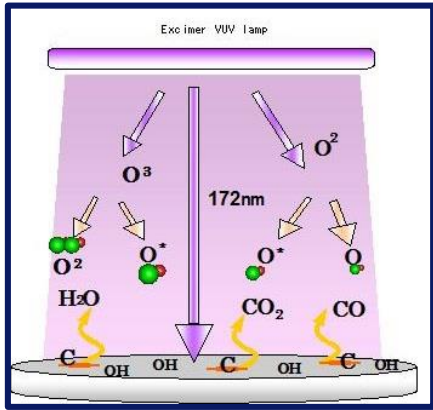
E-E	100 – 500 kJ/mol	F-F	159 kJ/mol
		C-C	348 kJ/mol
E=E	400 – 700 kJ/mol	O=O	498 kJ/mol
		C=C	648 kJ/mol
E≡E	800 – 1100 kJ/mol	N≡N	946 kJ/mol
		C≡C	839 kJ/mol
H-bridges	10 - 160 kJ/mol	H...F > H...O > H...N	
Van-der-Waals	0.5 - 5 kJ/mol		



Thus (V)UV to VIS radiation is able to cleave covalent chemical bonds

# 3. Matter Radiation Interaction

## Penetration Depth of UV Radiation



**Vacuum UV**

**UV-C**

**UV-B**

**UV-A**

Penetration depth increases ... but solely within  $\mu m$  range



# 3. Matter Radiation Interaction

## Into Earth's Atmosphere

### Vacuum UV (100 - 200 nm)

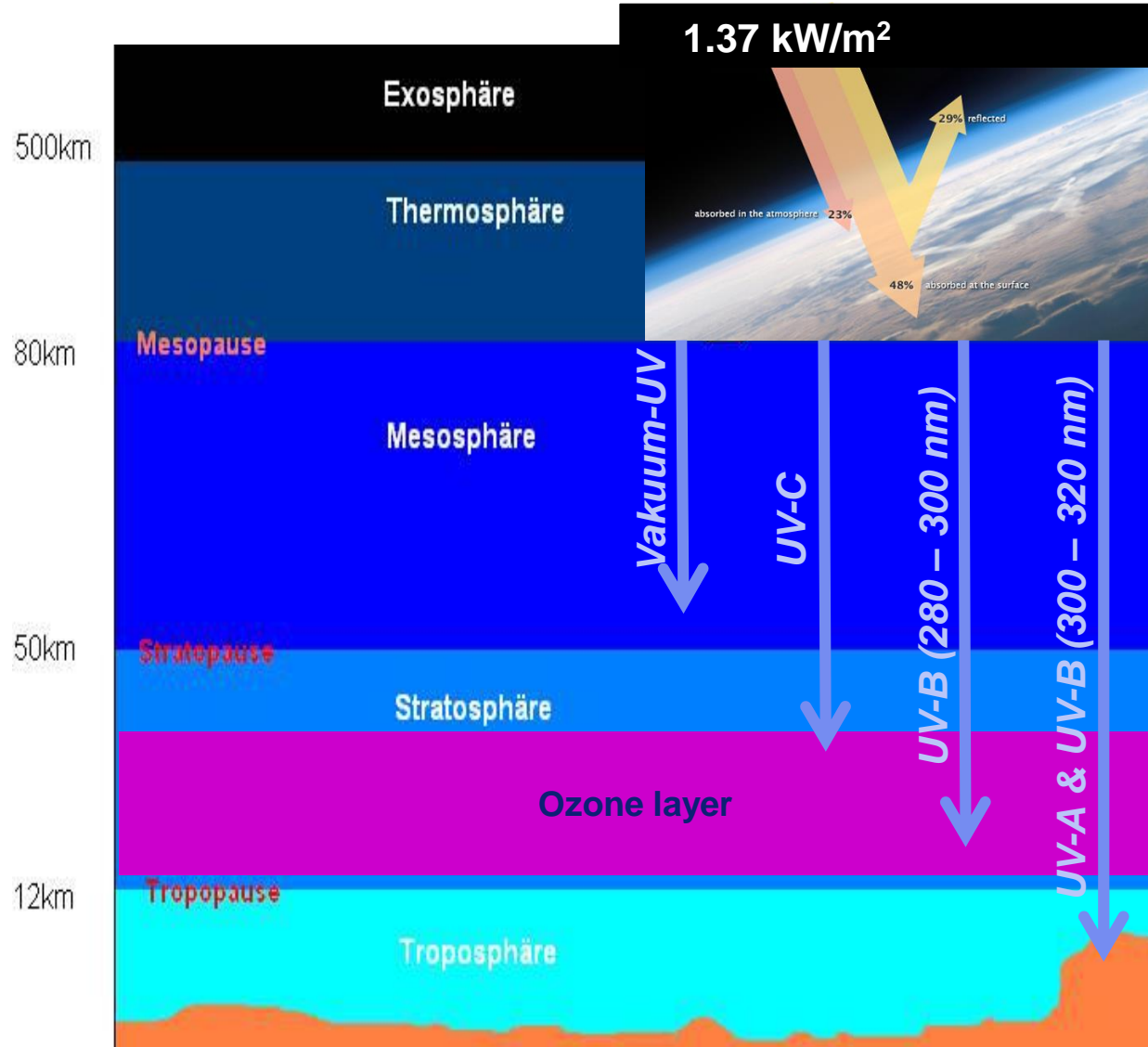
- Photolysis of water
- Cleavage of N<sub>2</sub> and O<sub>2</sub>
- Ozone formation

### UV-C (200 - 280 nm) & UV-B (280 - 300 nm)

- Ozone cleavage

### UV-B (300 - 320 nm) & UV-A (320 - 380 nm)

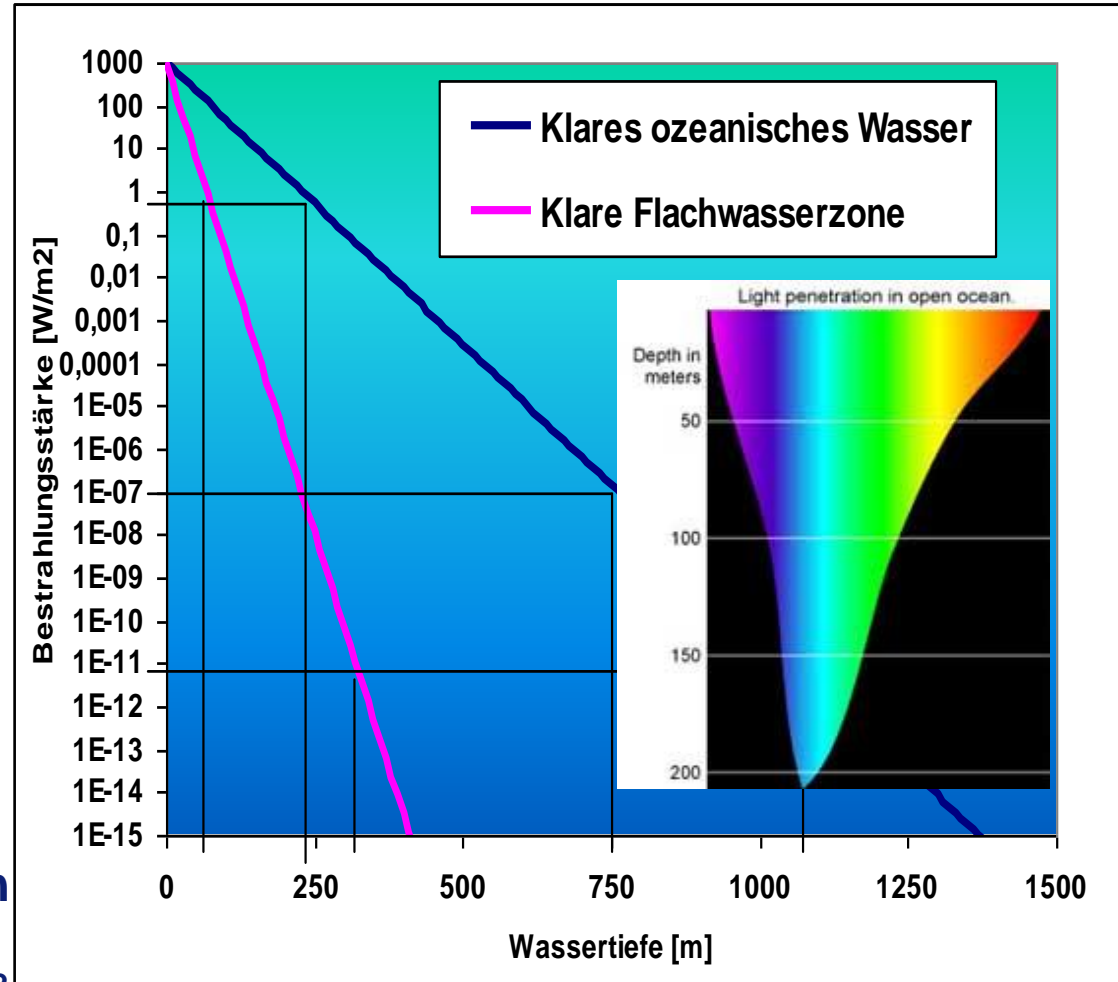
- Photochemical decline of air pollutants
- Ozon formation in presence of NO<sub>x</sub>
- Disinfection at photocatalytically active sites



# 3. Matter Radiation Interaction

## Into Water

- Power density @ surface:  
 $1000 \text{ W/m}^2$
- Photosynthesis feasible:  
 $1 - 10 \text{ W/m}^2$
- Phototaxis of crustacea:  
 $10^{-7} - 10^{-8} \text{ W/m}^2$   
(Full moon  $\sim 5 \times 10^{-3} \text{ W/m}^2$ )
- Light perception:  
Deep sea fish  $10^{-11} \text{ W/m}^2$   
Comparison: Scotopic vision  
Homo sapiens:  $10^{-7} \text{ W/m}^2$   
Perception limit at  $10^{-12} \text{ W/m}^2$   
( $\sim$  star of 6<sup>th</sup> magnitude)



UV radiation solely penetrates surface layer!

# 3. Matter Radiation Interaction

## Into Biomatter

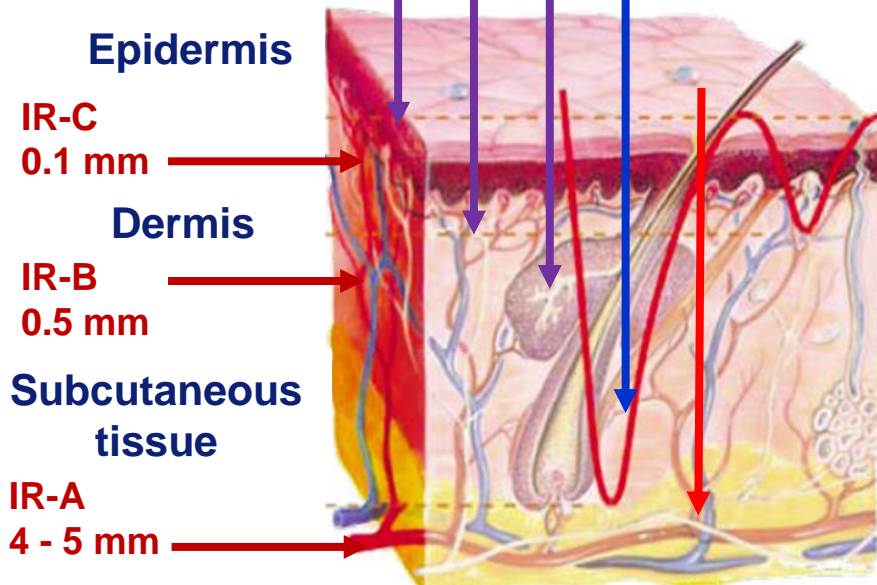
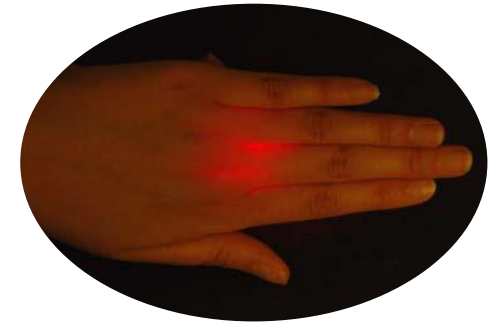
UV-C → Genetic damages

UV-B → Vitamin D formation

UV-A → Melanin oxidation

Blue → Degradation of bilirubin, NO formation

Red & NIR → Vasodilatory effect



- Red and NIR radiation is able to penetrate epidermis, dermis, and subcutaneous tissue (up to ~ 5 mm)
- UV radiation impact is limited to surfaces (up to ~ 50  $\mu\text{m}$ )
- VUV radiation is even heavily absorbed by water and air

# 3. Matter Radiation Interaction - Sources

## Overview

### Solar radiation

### Hg discharge lamps

- low pressure
- amalgam
- medium pressure

### Xe/(Hg) discharge lamps

### D<sub>2</sub> discharge lamps

### Excimer lasers

- ArF\*

### Excimer discharge lamps (Dielectric Barrier Discharges: DBD)

- Xe<sub>2</sub>\*
- KrCl\*
- XeBr\*
- XeCl\*

### Solid state lasers

- Al<sub>2</sub>O<sub>3</sub>:Cr
- Al<sub>2</sub>O<sub>3</sub>:Ti
- YAG:Nd

### (Al,Ga)N LEDs

### (In,Ga)N LEDs

> 300 nm

185, 254 nm

185, 254 nm

200 – 400 nm

230 – 800 nm

110 – 400 nm

193 nm

172 nm

222 nm

282 nm

308 nm

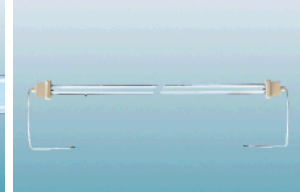
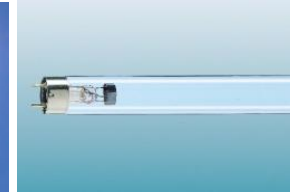
694 nm

800 nm

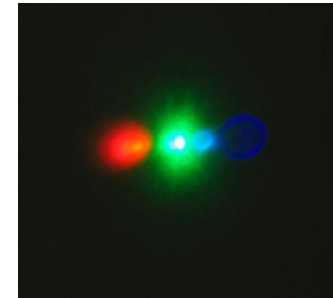
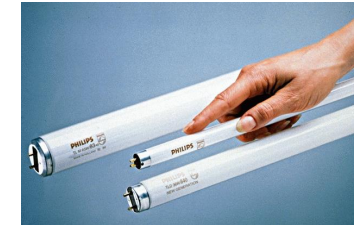
1064 nm

210 – 370 nm

370 – 550 nm



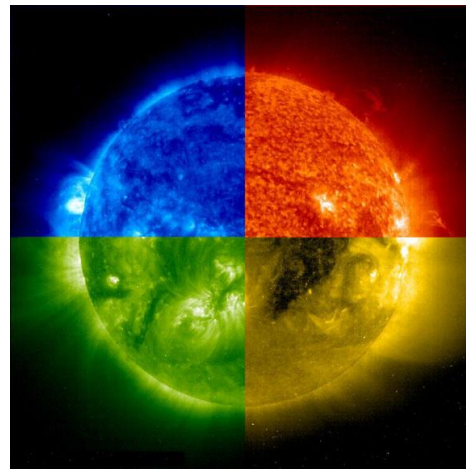
+ phosphor → 300 - 800 nm





# 3. Matter Radiation Interaction - Sources

## The Sun – Gravity Center and Heat & Light Source of the Solar System



# 3. Matter Radiation Interaction - Sources

**Photosynthesis: Almost All Energy Consumed by Living Organisms Stems from Solar Energy (Exception: Thermophiles in Deep Sea)**

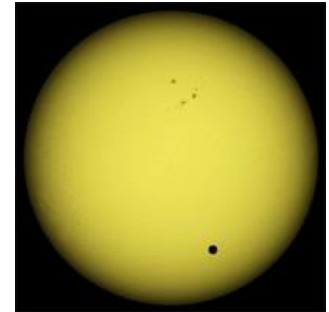
Energy source in solar system: The sun

Luminosity (radiation flux):  $3.83 \cdot 10^{26}$  W

Annual radiation power:  $1.24 \cdot 10^{34}$  J (at present)

Habitable zone:

Venus (early stage of solar system), earth (today), mars (late phase...)

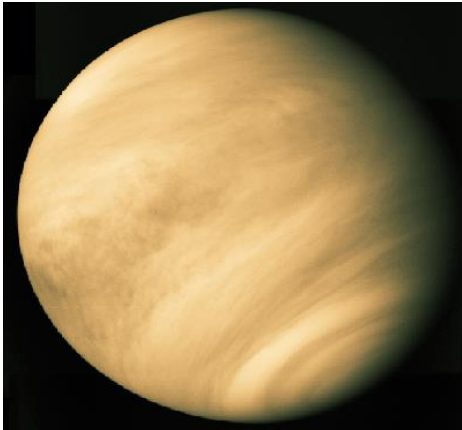


Planet	Perihelion- and aphelion-distance in astronomic units (149.6 Mio km)	Solar radiation maximum und minimum (W/m <sup>2</sup> )
<b>Mercury</b>	<b>0.3075 – 0.4667</b>	<b>14446 – 6272</b>
<b>Venus</b>	<b>0.7184 – 0.7282</b>	<b>2647 – 2576</b>
<b>Earth</b>	<b>0.9833 – 1.017</b>	<b>1413 – 1321</b>
<b>Mars</b>	<b>1.382 – 1.666</b>	<b>715 – 492</b>
<b>Jupiter</b>	<b>4.950 – 5.458</b>	<b>55.8 – 45.9</b>
<b>Saturn</b>	<b>9.048 – 10.12</b>	<b>16.7 – 13.4</b>
<b>Uranus</b>	<b>18.38 – 20.08</b>	<b>4.04 – 3.39</b>
<b>Neptune</b>	<b>29.77 – 30.44</b>	<b>1.54 – 1.47</b>

# 3. Matter Radiation Interaction - Sources

**Photosynthesis: The energetic base of the biosphere, i.e.  $Mn^{n+}$  catalysed water splitting,  $2 H_2O \rightarrow 4 H^+ + 4 e^- + O_2 \uparrow$**

Venus



2.61 kW/m<sup>2</sup>

Albedo = 0.76

→ T<sub>E</sub> = 232 K

96% CO<sub>2</sub> + 3% N<sub>2</sub> +  
SO<sub>2</sub> + H<sub>2</sub>O + Ar (ppm)

93 bar → T<sub>eff</sub> = 740 K

Earth



1.37 kW/m<sup>2</sup> = 1.56 · 10<sup>18</sup> kWh/a

Albedo = 0.30

→ T<sub>E</sub> = 255 K

78% N<sub>2</sub> + 21% O<sub>2</sub> + 0.9% Ar  
+ CO<sub>2</sub> + H<sub>2</sub>O + CH<sub>4</sub> (ppm)

1 bar → T<sub>eff</sub> = 288 K

Life = aquatic chemistry

Water → 2 H<sub>2</sub> and O<sub>2</sub> → energy!

Mars



0.59 kW/m<sup>2</sup>

Albedo = 0.15

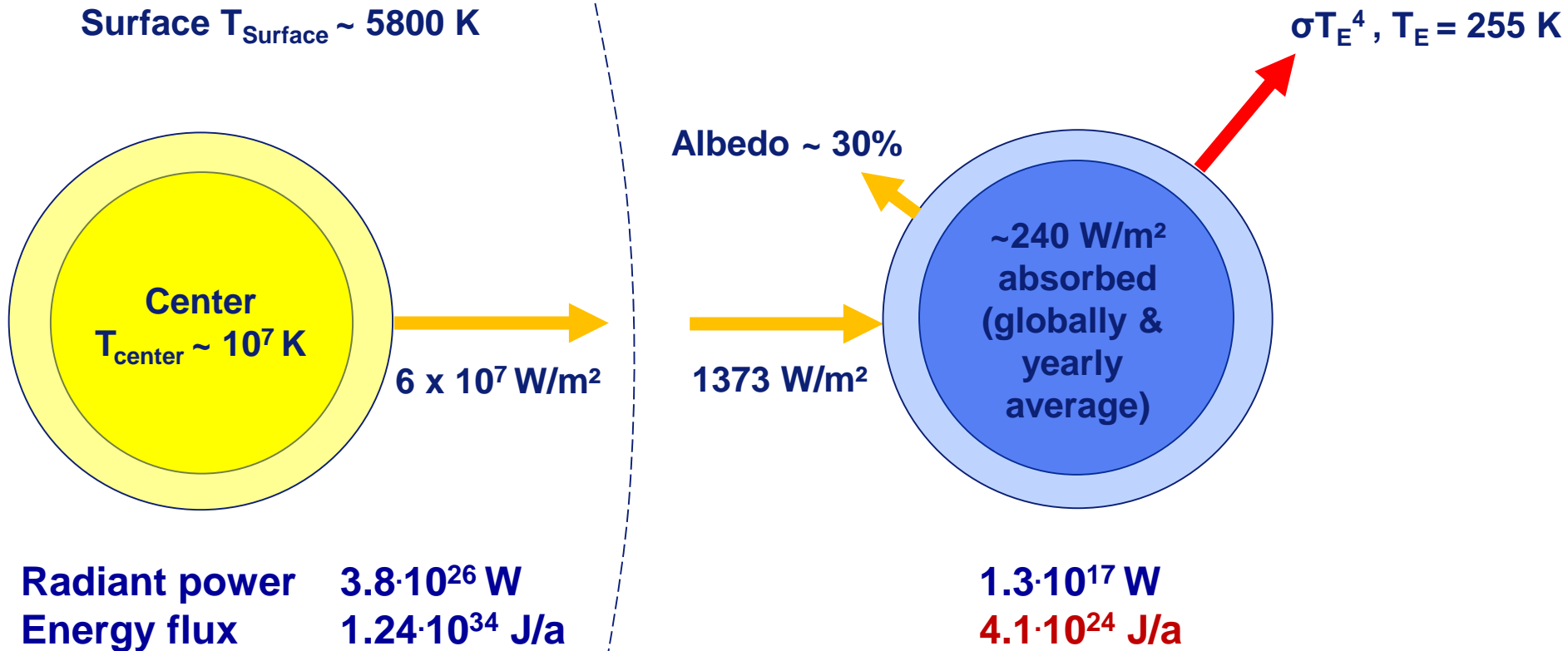
→ T<sub>E</sub> = 213 K

95% CO<sub>2</sub> + 3% N<sub>2</sub> + 1.5%  
Ar + H<sub>2</sub>O (ppm)

5.6 mbar → T<sub>eff</sub> = 225 K

# 3. Matter Radiation Interaction - Sources

## The Sun – Our Central Energy Source

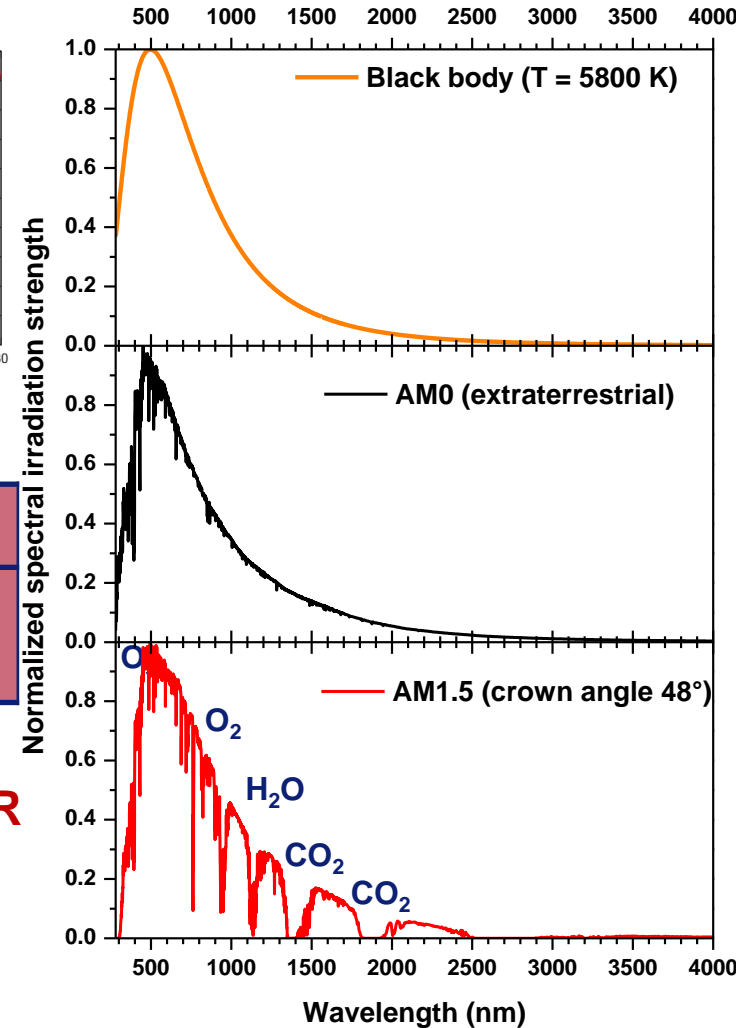
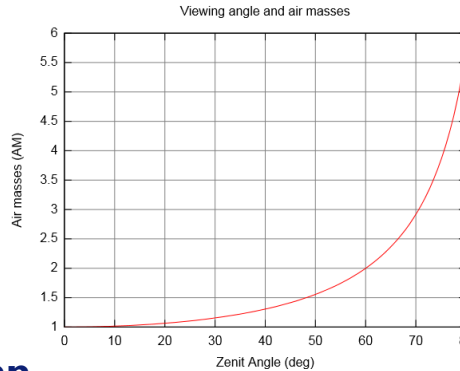
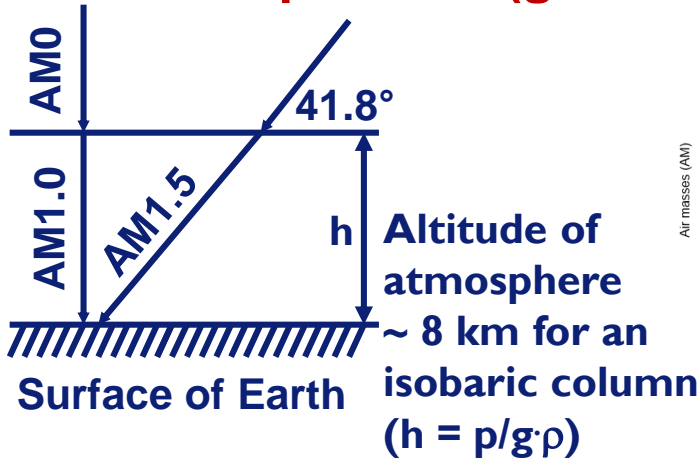


For comparison:

Global energy consumption 2015  $\sim 5.2 \cdot 10^{20} \text{ J/a}$

# 3. Matter Radiation Interaction - Sources

## The solar spectrum (global radiation)



<400	400-500	500-600	600-700	>700
37.8 W/m <sup>2</sup>	130.4 W/m <sup>2</sup>	144.6 W/m <sup>2</sup>	134.0 W/m <sup>2</sup>	269.2 W/m <sup>2</sup>
5.3%	18.2%	20.2%	18.7%	37.6%

~ 5% UV

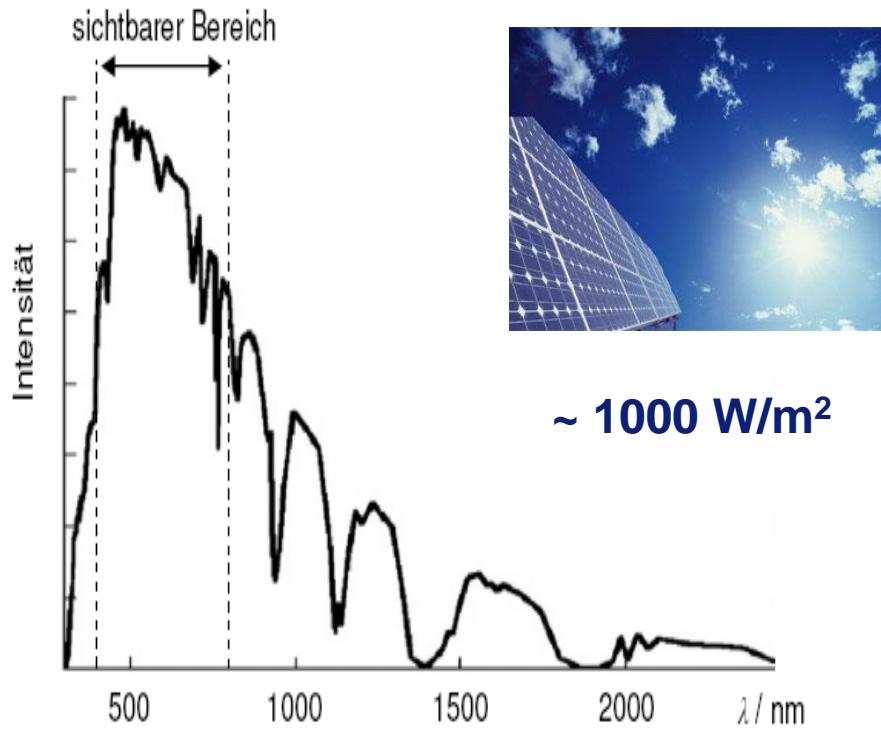
~ 55% VIS

~ 40% IR

Solar spectrum depends on daytime & season, air pressure, humidity, clouds, dust, and so on

# 3. Matter Radiation Interaction - Sources

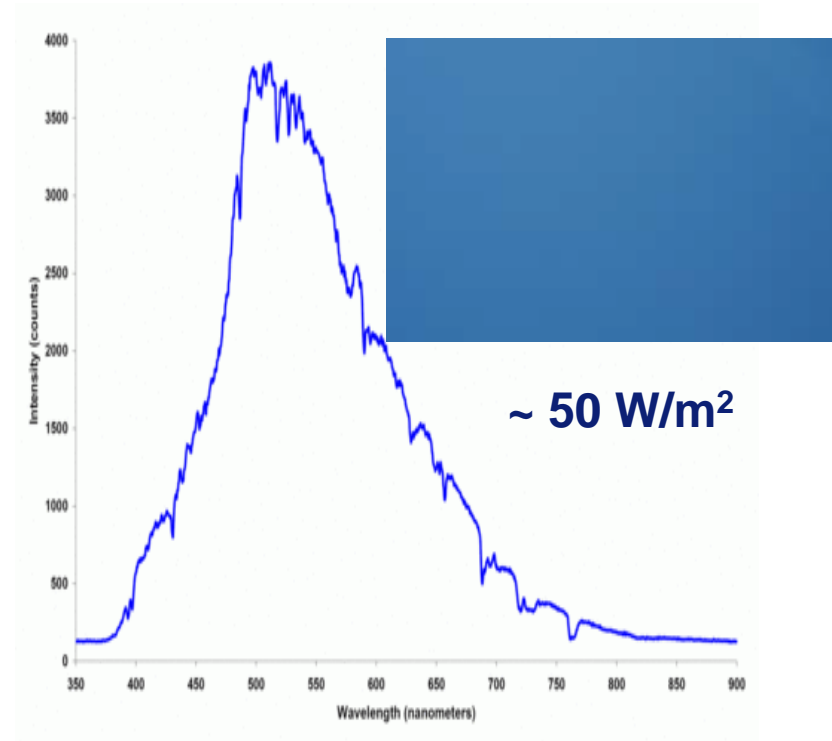
## Direct radiation



Colour temperatur  $\sim 5500 - 6500 \text{ K}$

$50 \text{ W/m}^2 \text{ UV}$  and  $0.1 \text{ W/m}^2 \text{ UV-B}$

## Diffuse radiation „Blue sky“



$\sim 10600 \text{ K}$

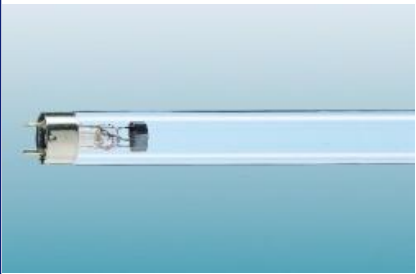

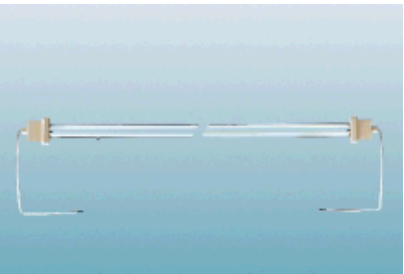
Almost no UV!

# 3. Matter Radiation Interaction - Sources

## Hg vapour discharge lamps - Overview

Hg lamp  
invented  
1904 for  
Rachitis  
therapy

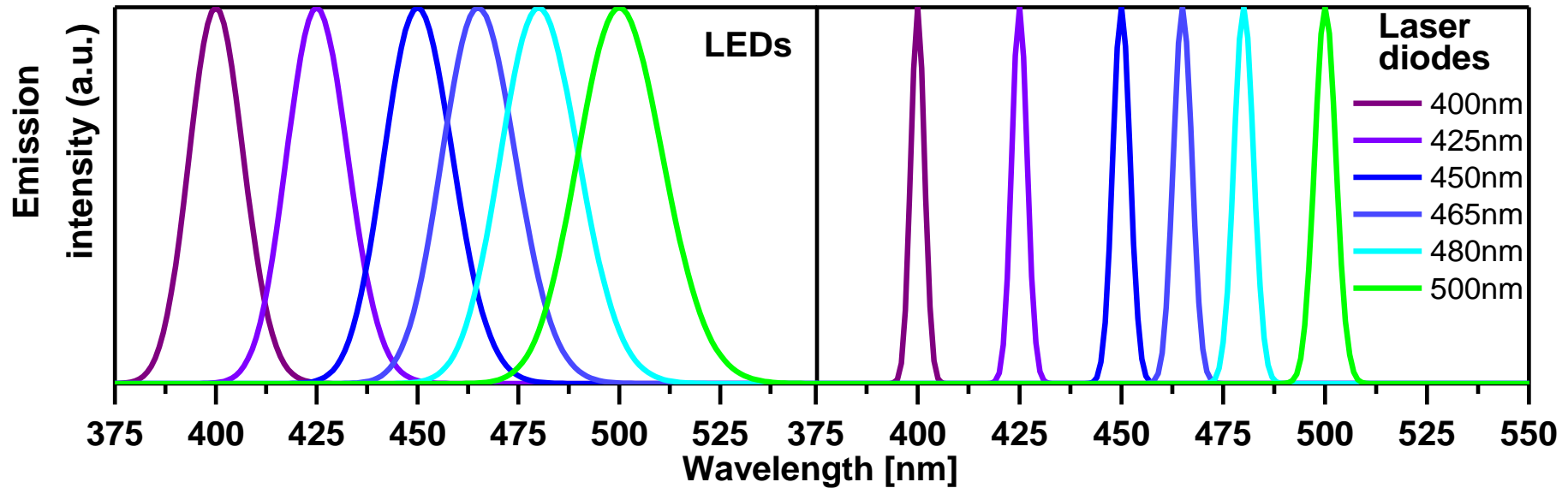


	Low Pressure Hg	Amalgam	Medium Pressure Hg
			
UV-C wavelength	254 nm	254 nm	200 - 280 nm
Typical lamp power	4 ... 100 W	100 ... 300 W	1 ... 17 kW
Lamp efficiency	< 40%	30 ... 35%	10 ... 15%
GAC factor	85%	85%	80%
UV-C power per length	0.2 W / cm	0.7 W / cm	15 W / cm
Wall temperature	40 °C	100 °C	600 - 800 °C

Spectra can be modified by additional filling gases and phosphors

# 3. Matter Radiation Interaction - Sources

## LEDs and laser diodes



### „LED platform“

- 465 nm LEDs Illumination
- 410 nm LEDs Full conversion
- 365 nm LEDs Black light
- 265 nm LEDs Disinfection

### „Laser diode platform“

- 940 nm Remote control
- 785 nm CD
- 655 nm DVD
- 405 nm Blue ray DVD



# 3. Matter Radiation Interaction - Sources

## Devices using a Dielectric Barrier Excimer Discharge (either O<sub>2</sub> or Xe)

Ozone generator  
(Wedeco AG)



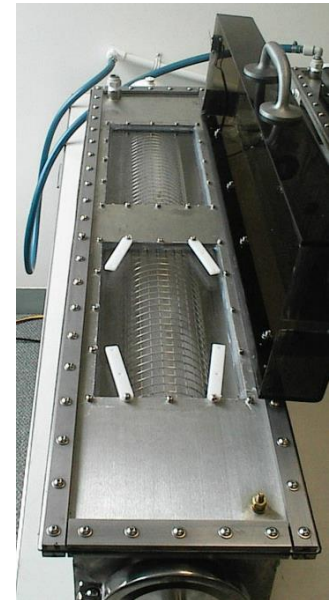
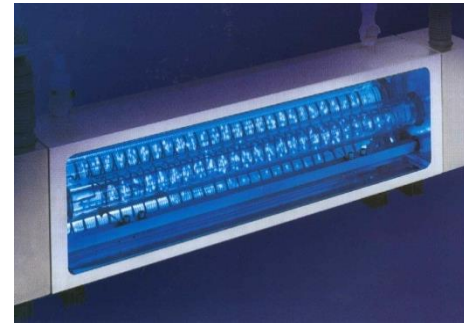
Exhaust treatment  
(Siemens AG)



UV Radiation sources (Xenon)

Triton

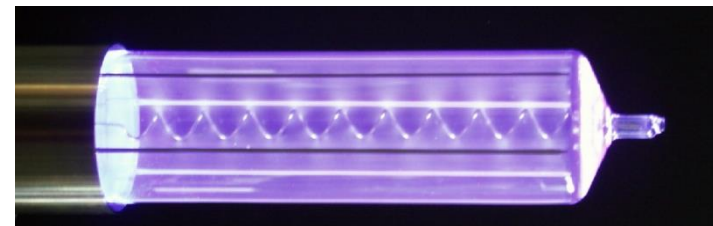
Heraeus Noblelight



Flat lamp  
for LCD  
Backlighting  
(Osram AG)



Osram Xeradex



# 4. Photovoltaic Materials

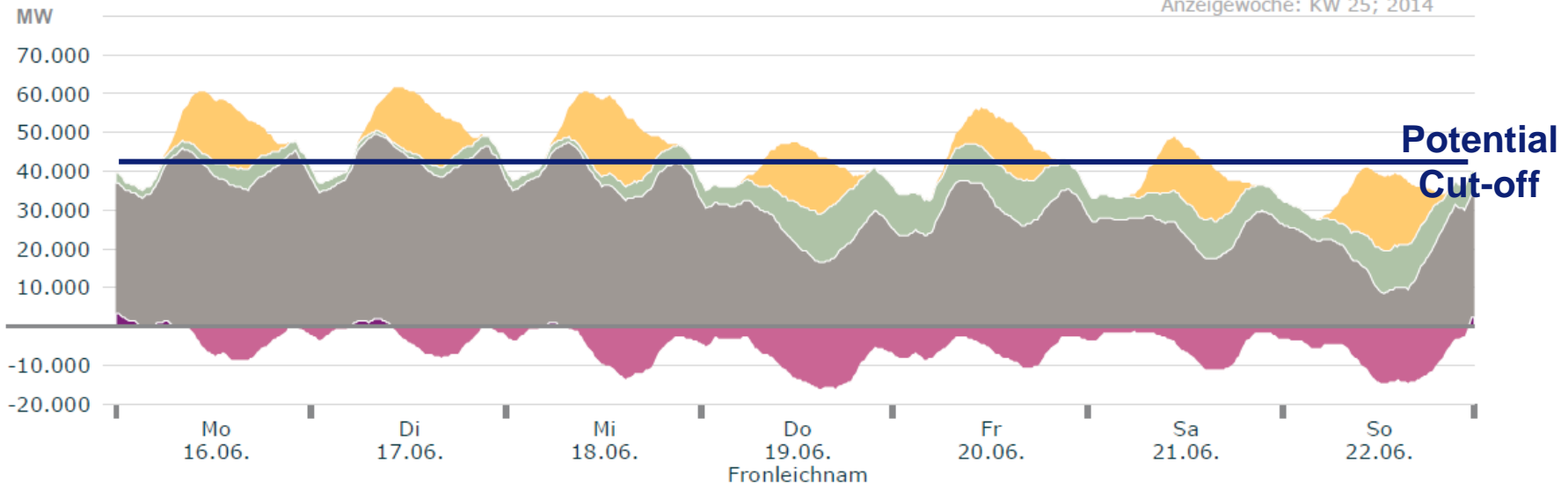
## Solar and wind energy market is strongly growing

Situation in Germany

Year	Installed peak power
2011	18 GW solar 28 GW wind
2014	36 GW solar 34 GW wind
2020	~50 GW solar ~40 GW wind

Some days at noon conventional power was not necessary anymore  
power production spikes will be increased due to growth in PV!

Anzeigewoche: KW 25; 2014

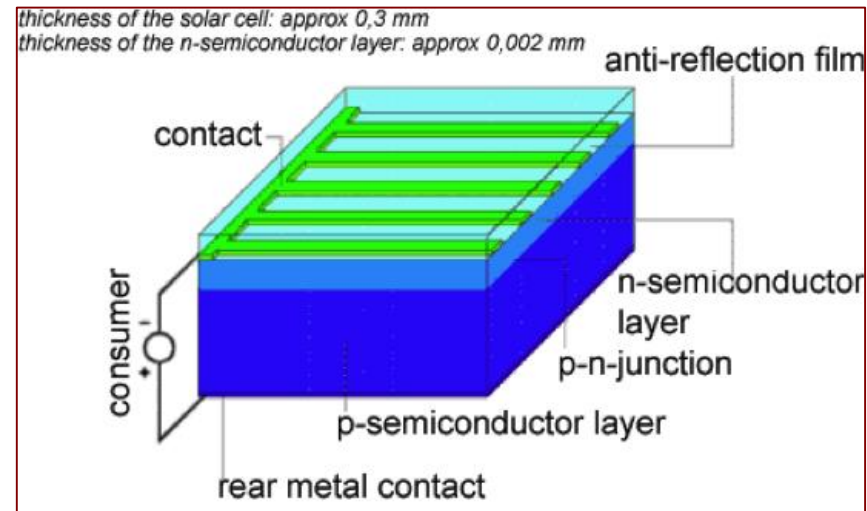
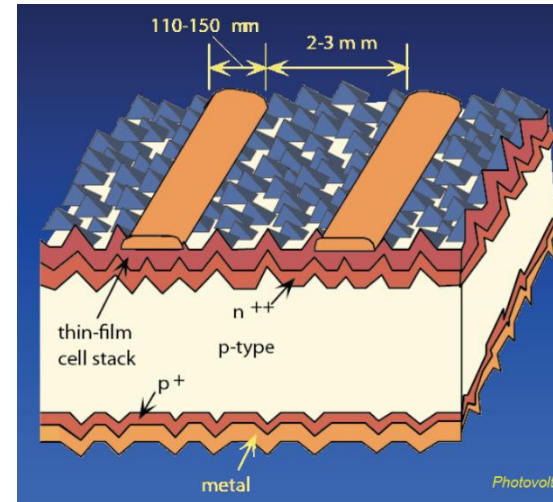


Cut-off PV solar energy production by photocatalysis to store energy is of large interest!

# 4. Photovoltaic Materials

## Solar Cells from 1954 till today

First practical photovoltaic cell:  
Chapin, Fuller, Pearson at  
Bell Labs, 1954: 6% efficiency



# 4. Photovoltaic Materials

## Solar cell generations by materials

c-Si (crystalline) cells

1<sup>st</sup> generation cells

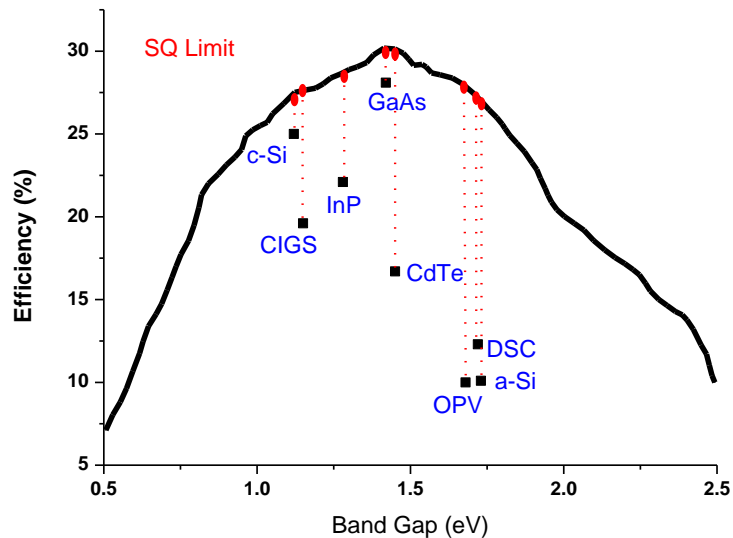
(thin film) CdTe, GaAs, Cu(In,Ga)S<sub>2</sub>, a-Si

2<sup>nd</sup> generation cells

Dye cells, organic cells, perovskite cells

3<sup>rd</sup> generation cells

**Main problem:** Shockley-Queisser\* (SQ) Limit → PV efficiency < 30%



Optimal band gap: 1.34 eV!

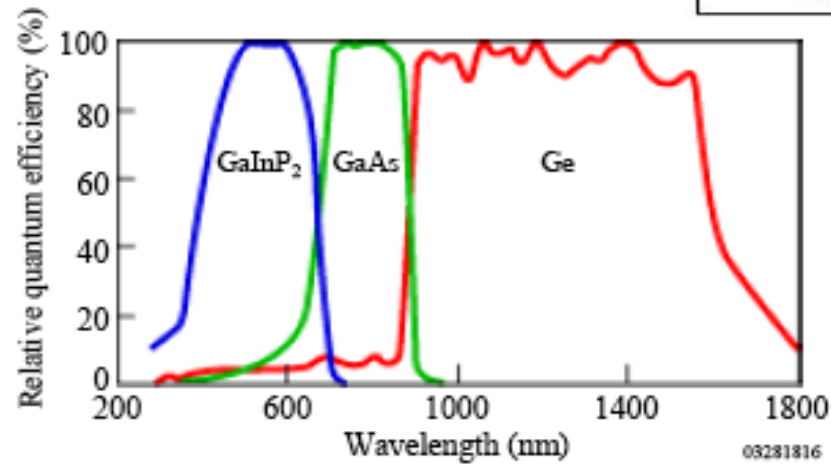
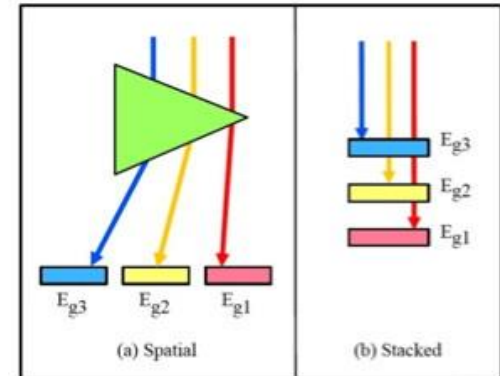
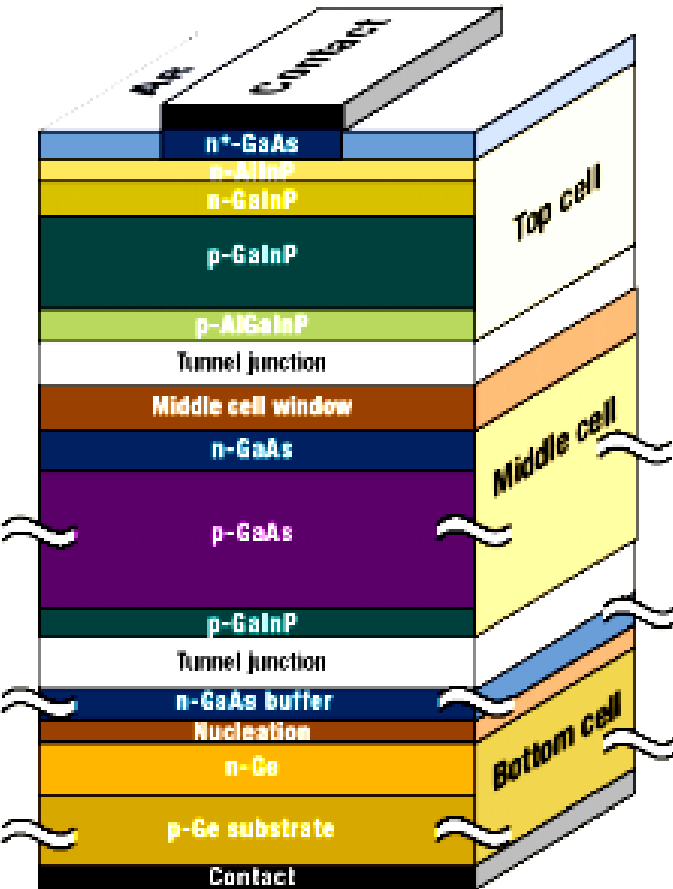
Reference:

- Prince, *JAP* 26 (1955) 534
- Loferski, *JAP* 27 (1956) 777
- \*W. Shockley, H.J. Queisser, *JAP* 32 (1961) 510

# 4. Photovoltaic Materials

How to circumvent SQ limit and other losses?

Photon management: Multi band gap, multi-junction photovoltaics



**GaInP<sub>2</sub>**  $E_g = 1.8 - 1.9 \text{ eV}$

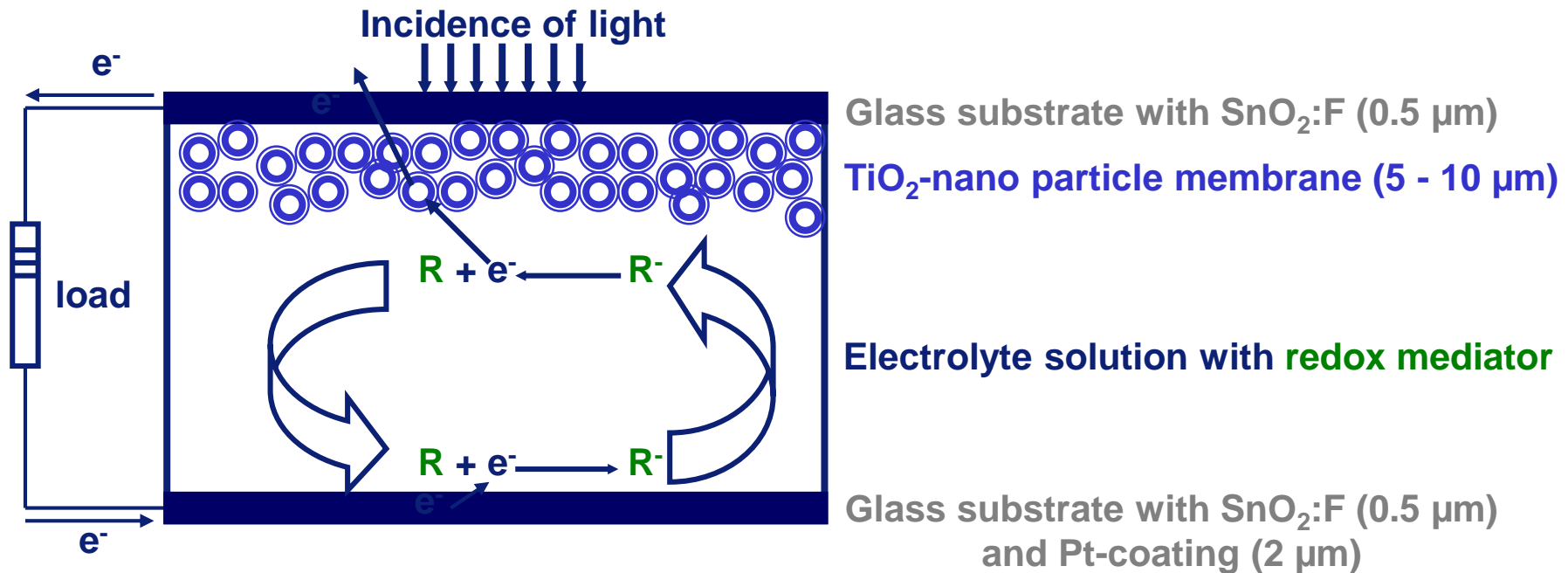
# 4. Photovoltaic Materials

## Material challenges and development routes

<u>Semiconductor</u>	<u>SQ limit</u>	<u>Challenges</u>	<u>Possible solutions</u>
c-Si	25%	Absorption strength	Light in-coupling foils
a-Si	10%	SQ limit	Down/Up-converter
GaAs	28%	Toxicity	?
Cu(In,Ga)S <sub>2</sub>	20%	stability, price	Coatings, solid solut.
CdTe	17%	Toxicity	?
APbX <sub>3</sub> (perovskites) A = CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup> , ... X = Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup>	30%	Stability, hydrolysis	Encapsulation

# 4. Photovoltaic Materials

## Dye Sensitised Cells (Grätzel Cells): Inventor Prof. Michael Grätzel



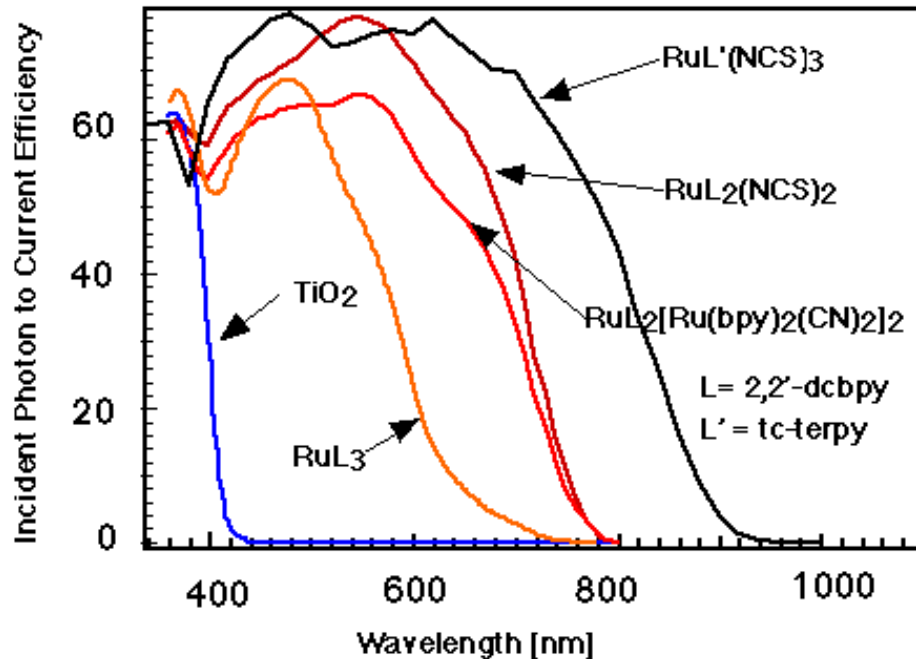
$\text{TiO}_2$  is the catalyst for the charge separation, but does not absorb visible light

# 4. Photovoltaic Materials

## Dye Sensitised Cells (Grätzel Cells)

### Photosensitisers

Absorption spectra of  $\text{TiO}_2$  and octahedral  $\text{Ru}^{2+}$ -complexes



### Advantages of $\text{Ru}^{2+}$ -chelating complexes

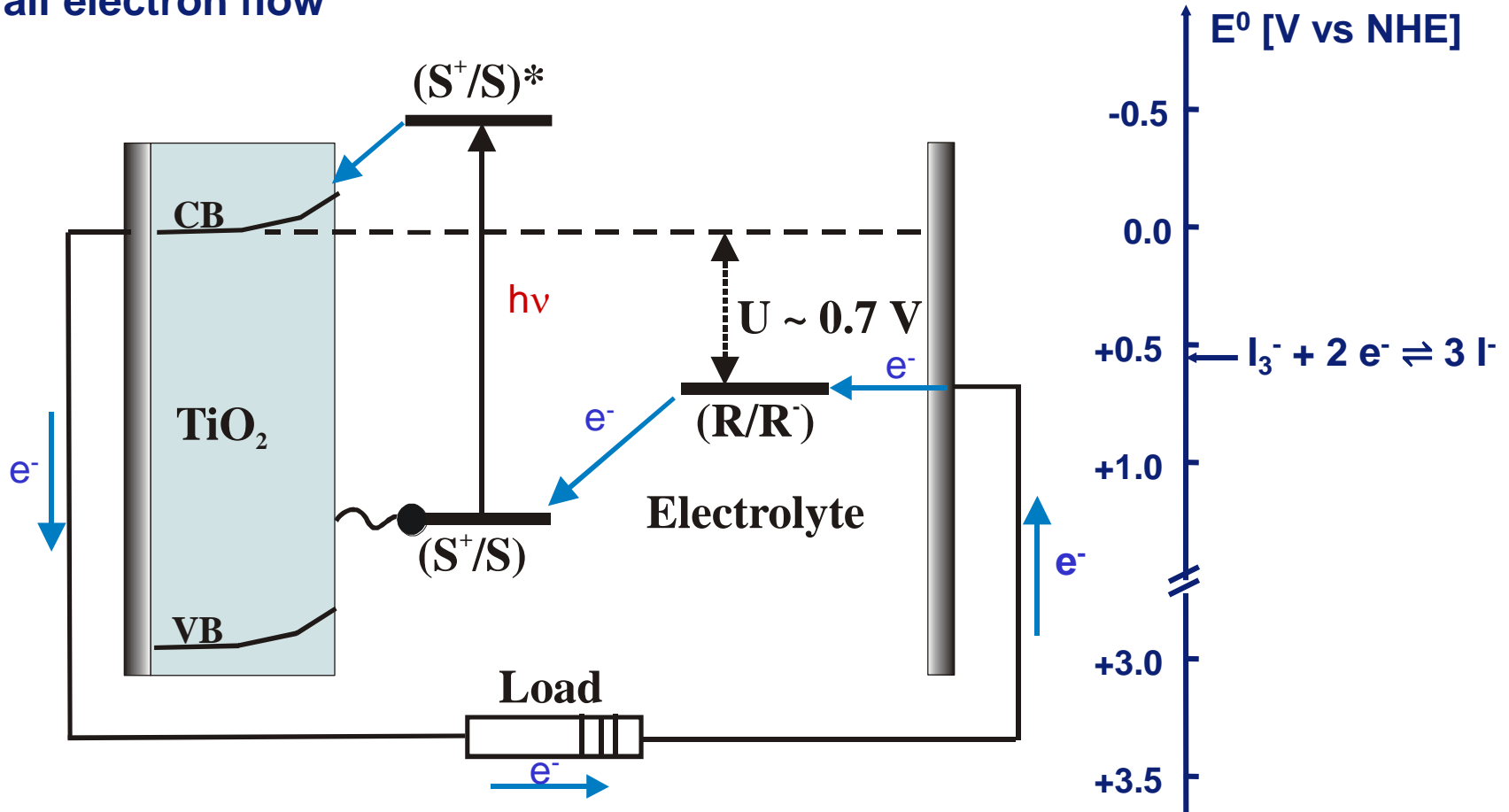
- Reversible  $\text{Ru}^{2+}/\text{Ru}^{3+}$  redox pair
- Electronic low-spin configuration (anti-bonding orbitals are unoccupied)
- Chelating effect (entropic effect)  
⇒ kinetically very stable (slow ligand exchange reaction)
- Allowed MLCT transitions at relative low energies  
⇒ intense absorption bands in the visible range of the spectrum



# 4. Photovoltaic Materials

## Dye Sensitised Cells (Grätzel Cells)

Overall electron flow



## 4. Photovoltaic Materials

### Photovoltaic Energy Conversion Requires Strong Absorption of Light and Efficient Charge Carrier Separation

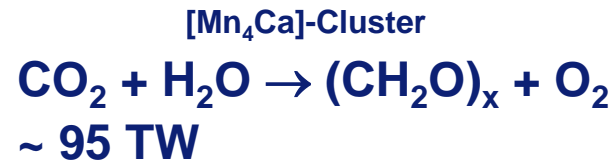
Solar cell type	absorption process	charge carrier separation
pn-semiconductor	band to band	by an electrostatic field at the pn-junction
Graetzel	MLCT on $[\text{RuL}_2\text{X}_2]$	electron transfer to n-TiO <sub>2</sub> + oxidation of I <sup>-</sup> to $\frac{1}{2}$ I <sub>2</sub>
„Chloroplast“	$\pi$ - $\pi^*$ on chlorophyll	electron transfer to NADP <sup>+</sup> + oxidation of O <sup>2-</sup> to $\frac{1}{2}$ O <sub>2</sub>

- Energy conversion efficiency of best practice Graetzel Cells is about 10%
- Lifetime is a problem due to cell sealing and electrolyte leakage

# 5. Photochemical Water Splitting

## World wide energy demand and production

Global annual photosynthetic  
produced biomass  $\sim 3.0 \cdot 10^{21} \text{ J}$   
= 700 Gt (efficiency  $\eta \sim 0.15\%$ )

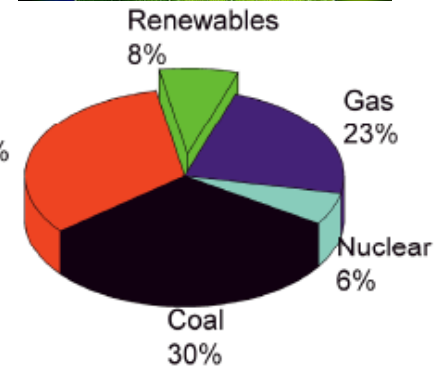


World energy  
consumption

Y2010	$\sim 14 \text{ TW}$
Y2050	$\sim 25 \text{ TW}$
Y2100	40-50 TW

### Potential

Biomass	5-7 TW
Wind	14 TW
Solar	100000 TW



**Conclusion:** Energy consumption of human society must be supported by distributed harvesting of solar energy on the long term!

- Solar thermal processes
- Photovoltaics
- Photochemistry (artificial photosynthesis)

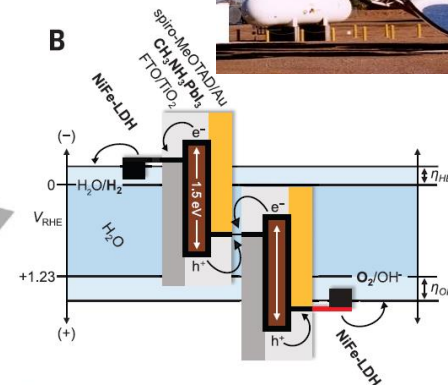
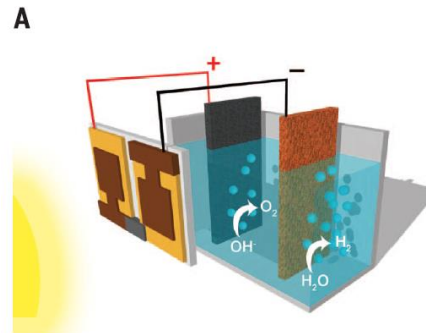
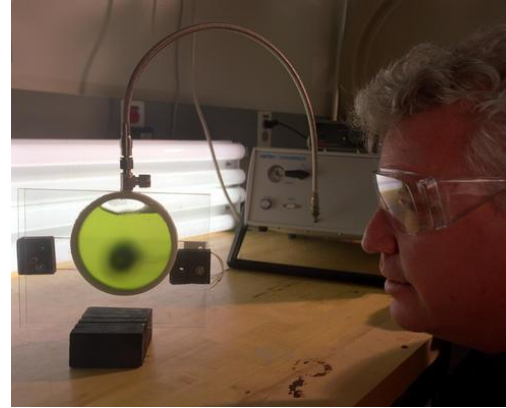
**Challenges:** Efficiency + Scalability + Lifetime

# 5. Photochemical Water Splitting

## Pathways towards water cleavage



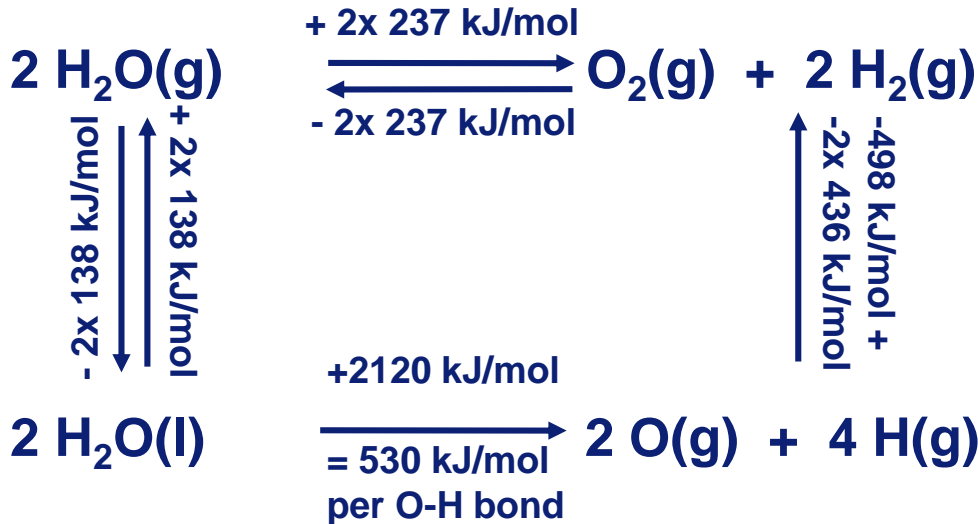
- Photosynthesis
  - Plants
  - Algae
- Thermolysis
- Electrolysis
- Photolysis
- Photocatalysis



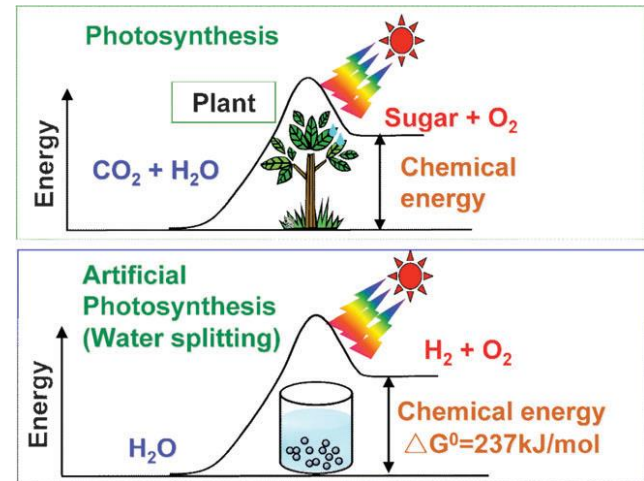
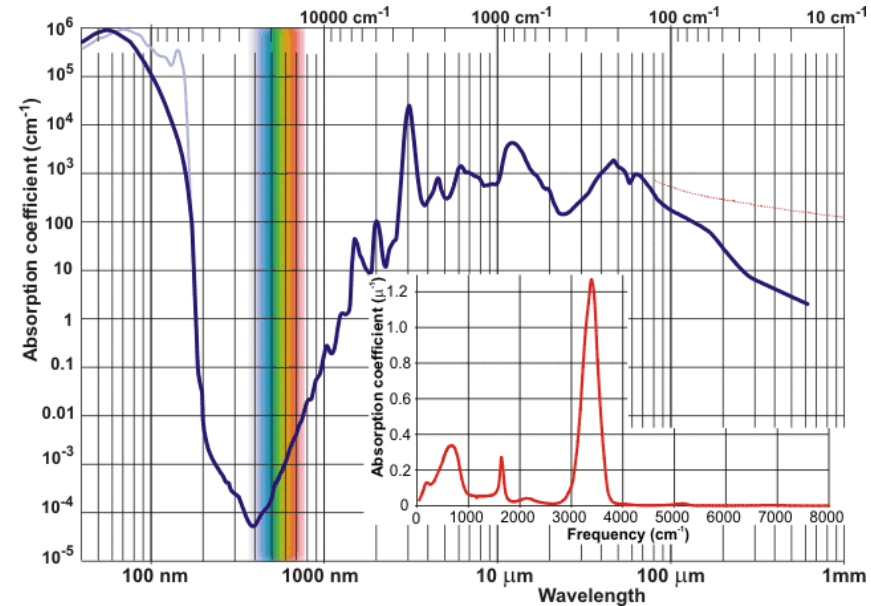
A B

# 5. Photochemical Water Splitting

## Energy Balance



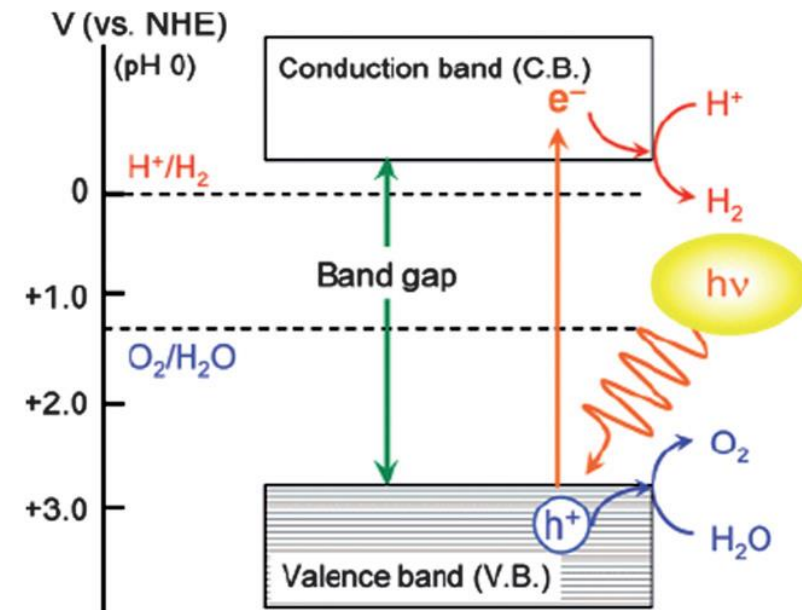
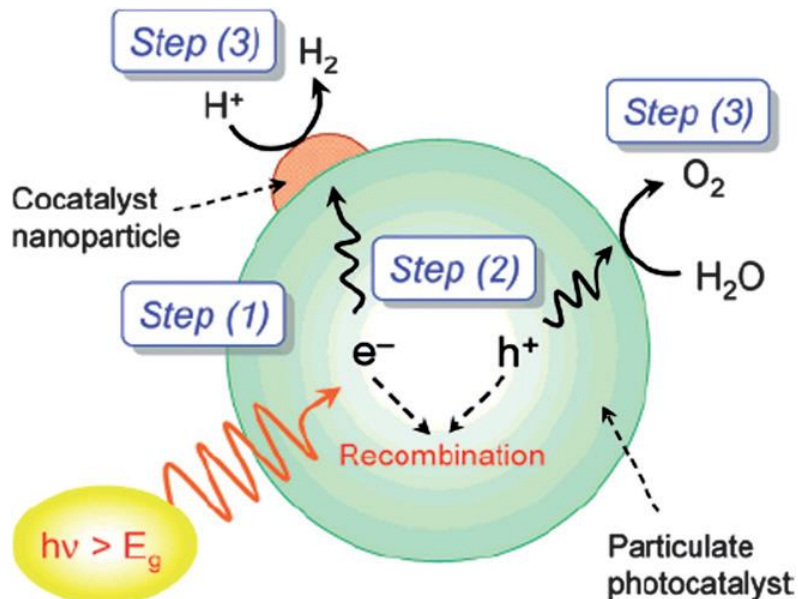
**Photolysis** of water without any photocatalyst requires VUV or EUV Radiation (10 – ~200 nm)  
 → Stratosphere and Mesosphere



# 5. Photochemical Water Splitting

## Photocatalytic Process by Using Semiconductors

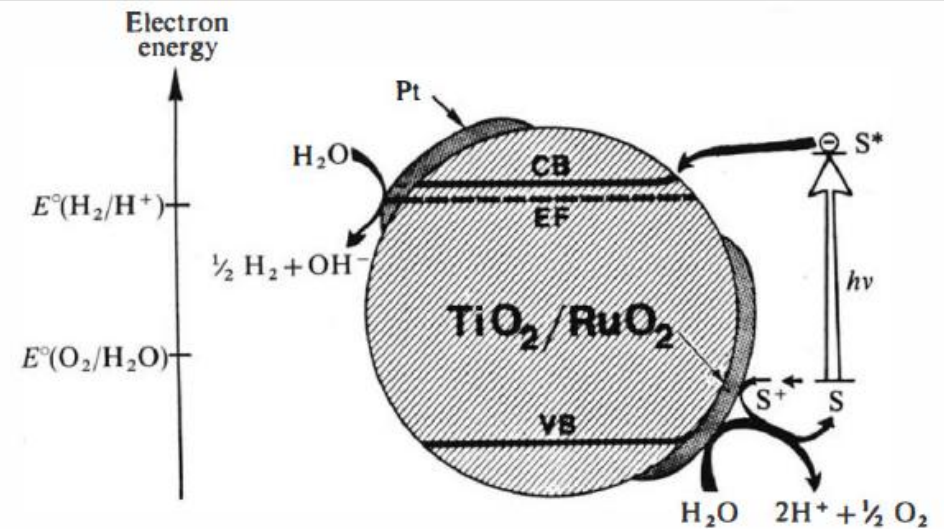
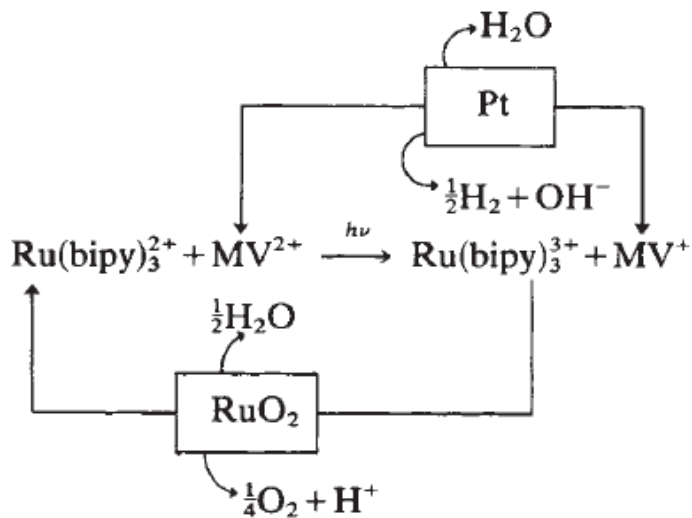
- First system explored in 1971 by A. Fujishima and K. Honda (Nature 238 (1972) 38) →  $\text{TiO}_2$  with Pt as a co-catalyst
- In general water splitting is possible at around 1000 nm (1.23 eV), in real systems voltage is higher  $> \sim 1.8$  V



# 5. Photochemical Water Splitting

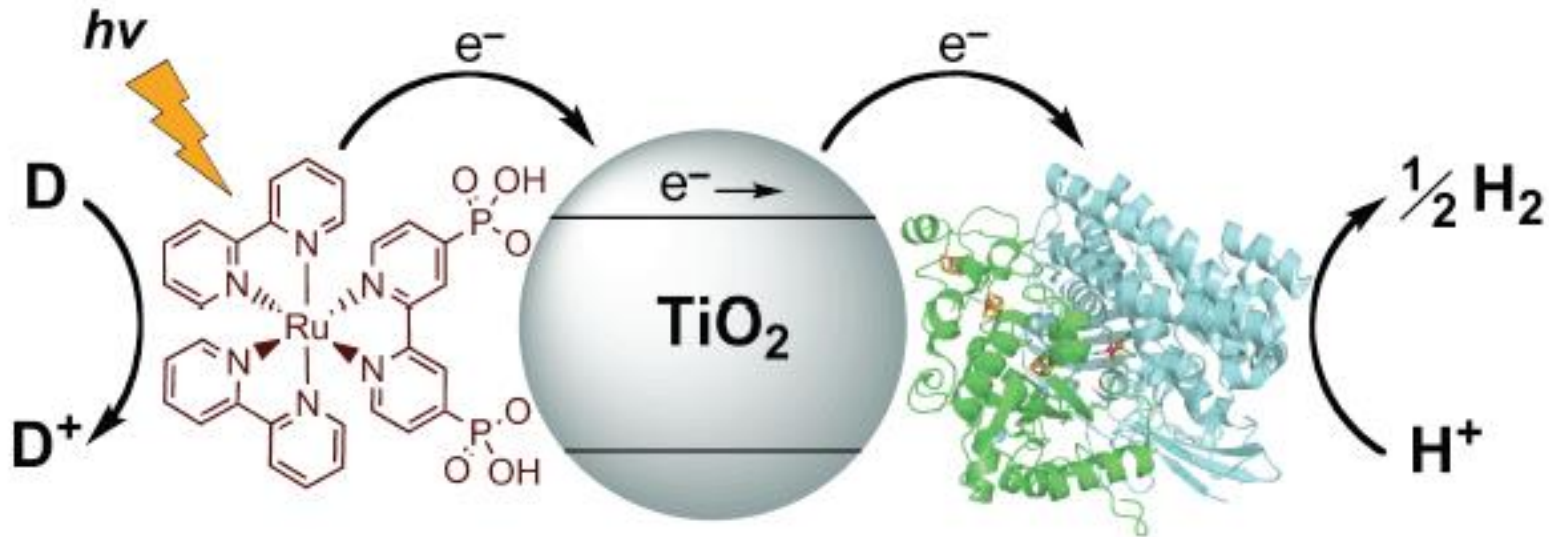
## Photocatalytic Process by Using Semiconductors and a Sensitizer

- First system using a sensitizer presented in 1981 by M. Graetzel (Nature 289 (1981) 158)
- →  $\text{TiO}_2$  with Pt and  $\text{RuO}_2$  as co-catalysts and  $[\text{Ru}(\text{bpy})_3]^{2+}$  and methylviologen as sensitizers (antennae)
- Synthesis of Pt nanoparticles from  $\text{H}_2\text{PtCl}_6$  and citrate



# 5. Photochemical Water Splitting

## Solar Hydrogen Generation



Schematic representation of visible light-driven H<sub>2</sub> production with D [NiFeSe]-H attached on ruthenium-dye sensitized TiO<sub>2</sub> nanoparticles, in the presence of a sacrificial electron donor D.

Visible light irradiation ( $\lambda > 420$  nm) excites the Ru(bipy)<sub>3</sub> photo-sensitizer, which injects electrons into the conduction band of TiO<sub>2</sub> and on to the hydrogenase, resulting in H<sup>+</sup> reduction.

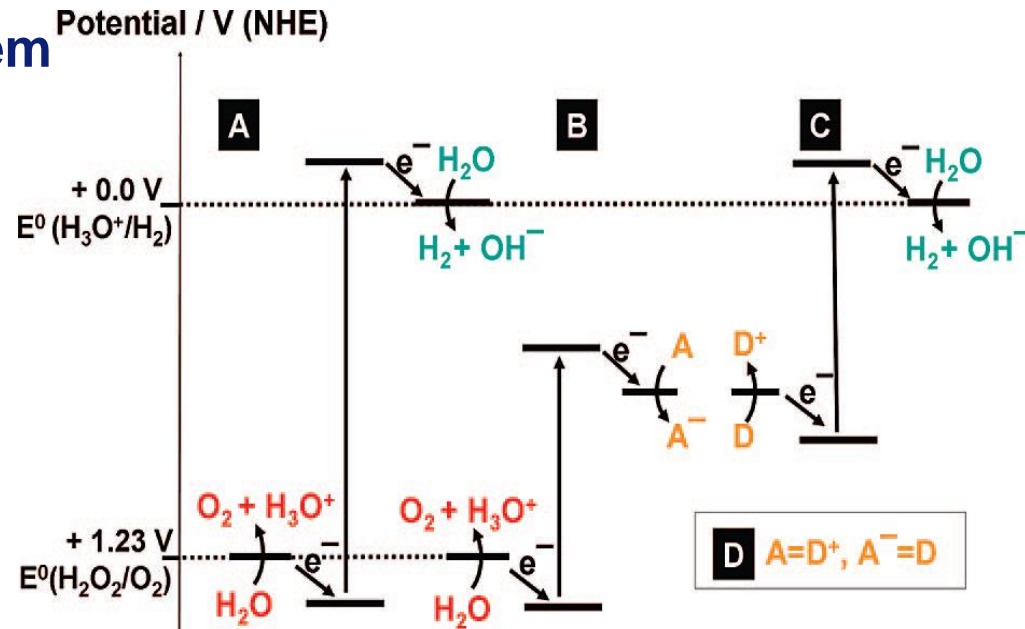
Ref.: F.A. Armstrong, E. Reisner et al., Chemical Society Reviews 108 (2008) 2439



# 5. Photochemical Water Splitting

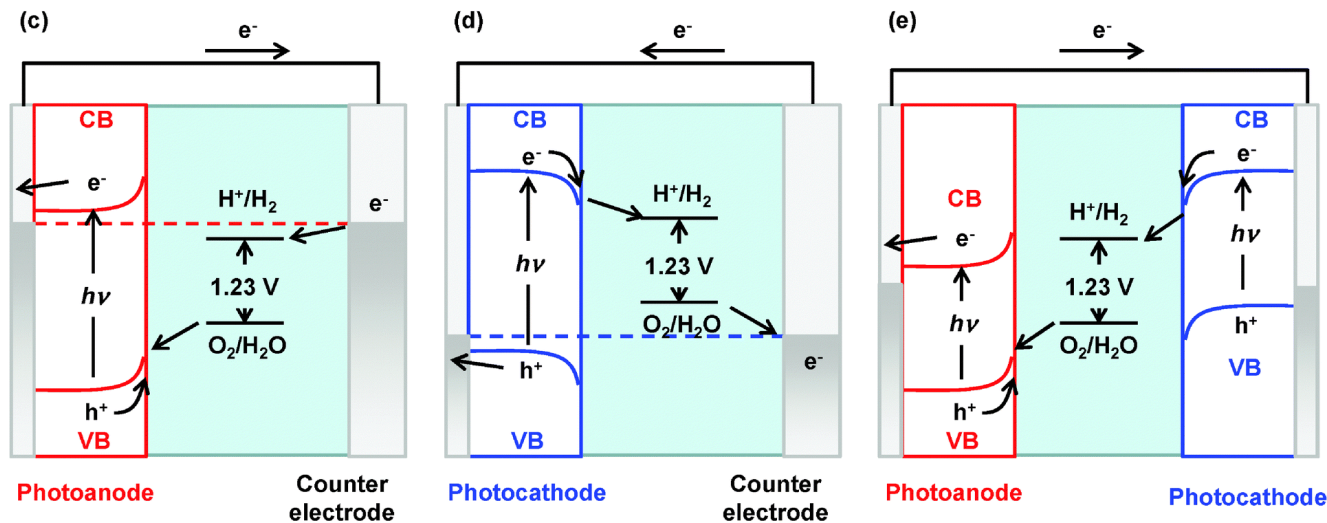
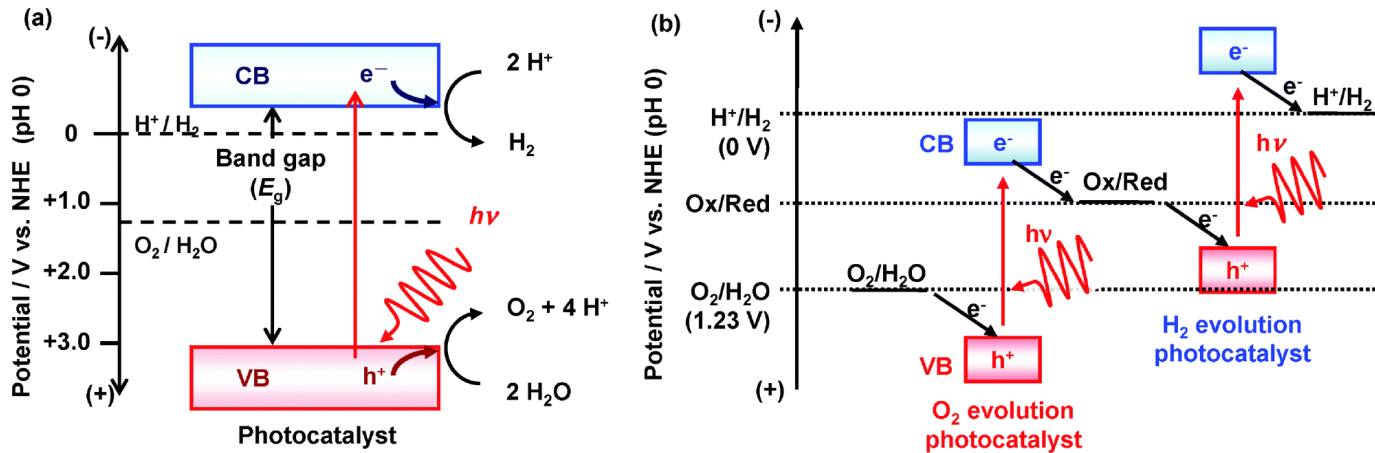
## Photocatalytic Process by Using Semiconductors - Approaches

- **A: single semiconductor system**
- **B: single semiconductor system with electron acceptor  $\rightarrow$   $O_2$**
- **C: single semiconductor system with electron donor  $\rightarrow$   $H_2$**
- **D: combination of B and C (tandem system)**
- **Additionally: Powders in solution ( $\rightarrow$  detonating gas formation)**



# 5. Photochemical Water Splitting

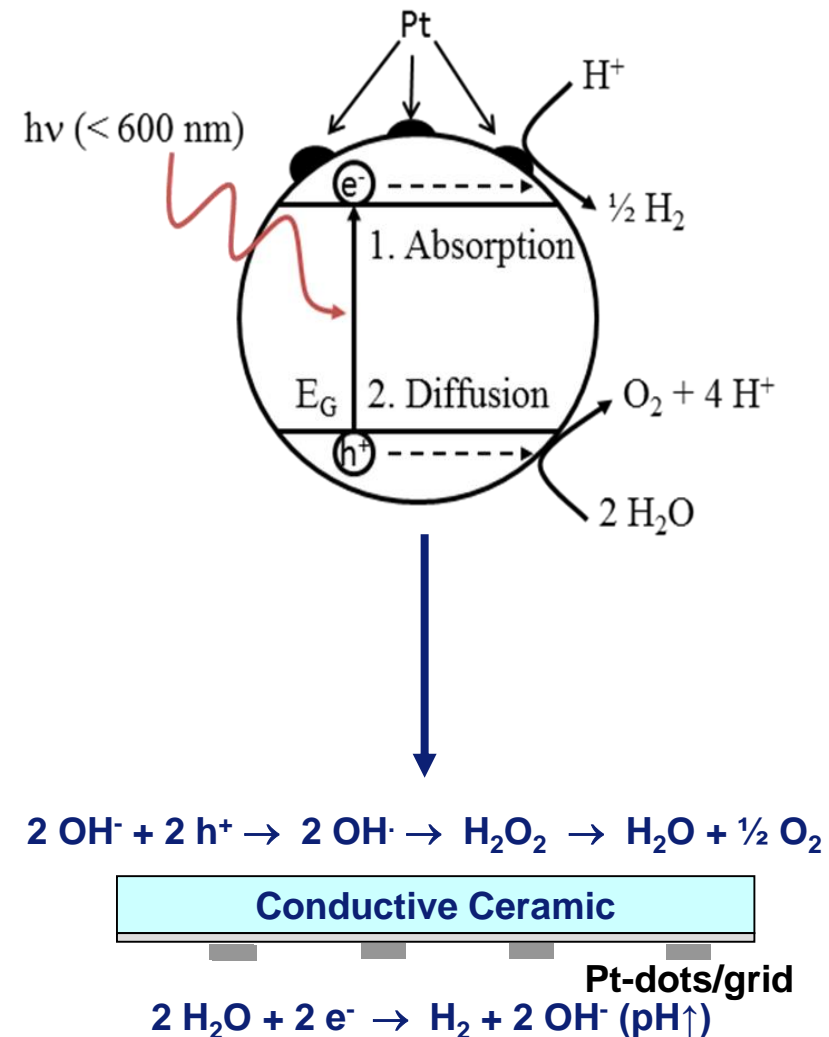
## Photocatalytic Process by Using Semiconductors - Approaches



# 5. Photochemical Water Splitting

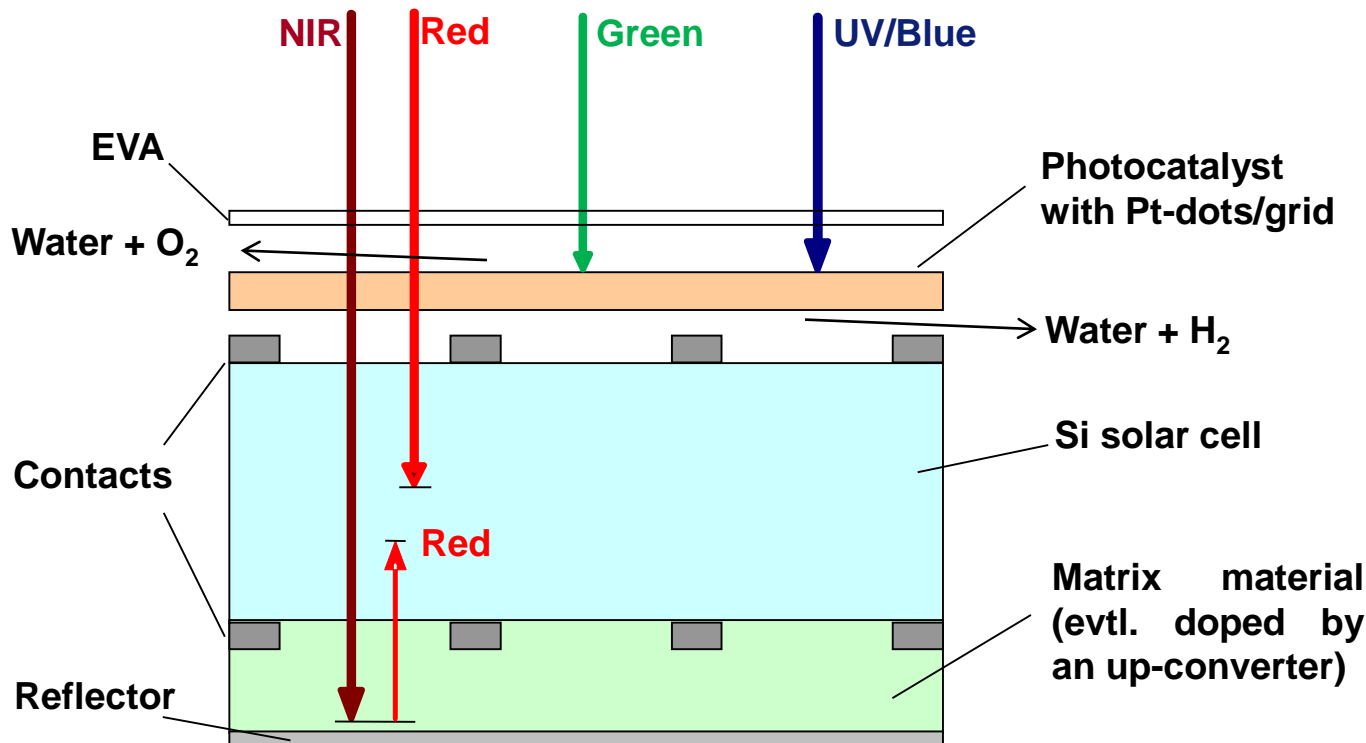
## From Powder to Ceramics for a Light Splitting Tandem Cell

- **Top structure (UV - Blue)**
  - Water splitting by an inorganic & stable photocatalyst
  - Conductive ceramic is required
  - Structured Platin deposition
- **Bottom structure (Green – NIR)**
  - Photovoltaic unit
  - Options: Modification by up-converter and/or down-converter



# 5. Photochemical Water Splitting

## Light Splitting Tandem Cell: PV Unit & Photocatalytical Unit



### Advantages

Cooling of the PV unit

Less thermalisation

Less damage of the PV unit by UV to blue radiation

Ref.: T. Jüstel et al., German Patent Application, Energy Conversion System, DE102014107268

# 5. Photochemical Water Splitting

## Requirements on the Photocatalyst

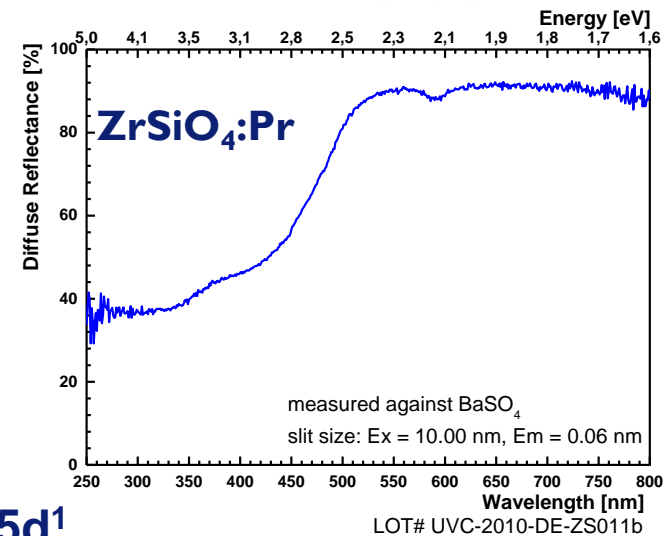
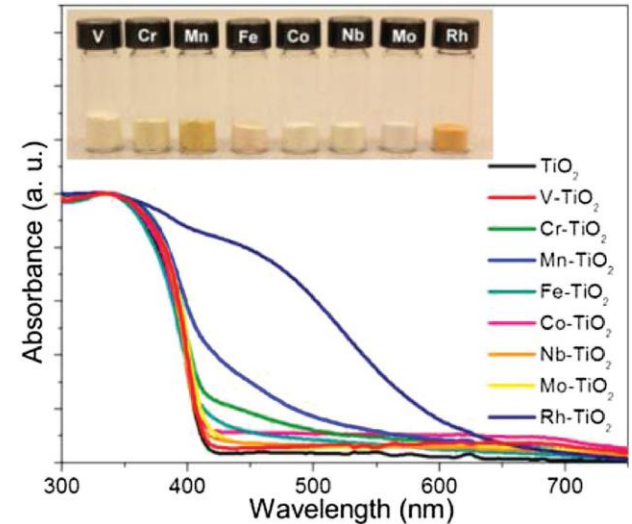
- **Stability**  
The most photochemically stable semiconductors in aqueous solution are oxides, but their band gaps are either too large for efficient light absorption ( $\sim 3$  eV), or their semiconductor characteristics are poor.
- **Efficiency (band gap)**  
For reasonable solar efficiencies, the band gap must be less than 2.2 eV, unfortunately, most useful semiconductors with band gaps in this range are photochemically unstable in water.
- **Energetics**  
In contrast to metal electrodes, semiconductor electrodes in contact with liquid electrolytes have fixed energy levels where the charge carriers enter the solution. So even though a semiconductor electrode may generate sufficient energy to effect an electrochemical reaction, the energetic position of the band edges may prevent it from doing so. For spontaneous water splitting, the oxygen and hydrogen reactions must lie between the valence and conduction band edges, and this is almost never the case.

# 5. Photochemical Water Splitting

## Photocatalyst Stability

Oxide	Band gap [eV]	Colour
ZrSiO <sub>4</sub>	6.5	white
ZrO <sub>2</sub>	5.0	white
CaWO <sub>4</sub>	4.1	white
ZnS	3.8	white
KTaO <sub>3</sub>	3.4	white
ZnO	3.3	white
SrTiO <sub>3</sub>	3.2	white
TiO <sub>2</sub>	3.0	white
CeO <sub>2</sub>	2.8	yellow
WO <sub>3</sub>	2.7	yellow
BiVO <sub>4</sub>	2.4-2.5	yellow
CdS	2.3	orange
Fe <sub>2</sub> O <sub>3</sub>	2.0	red
InN	1.9	red

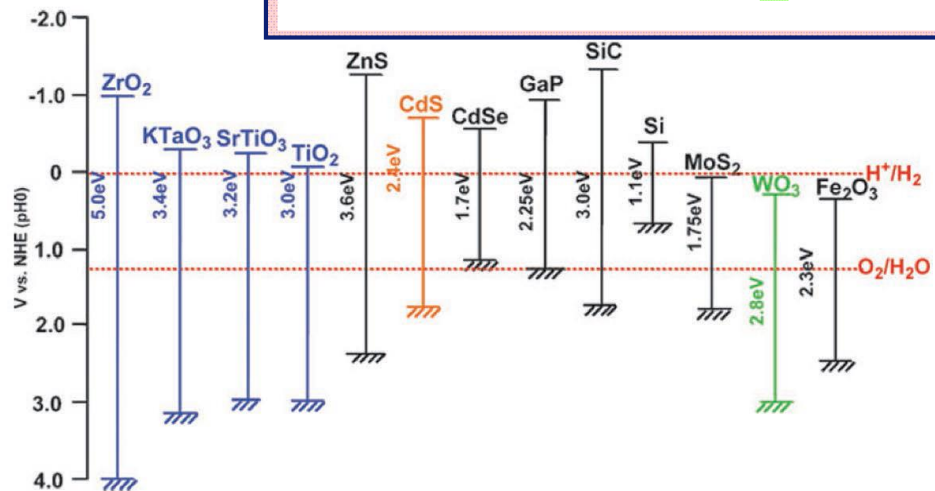
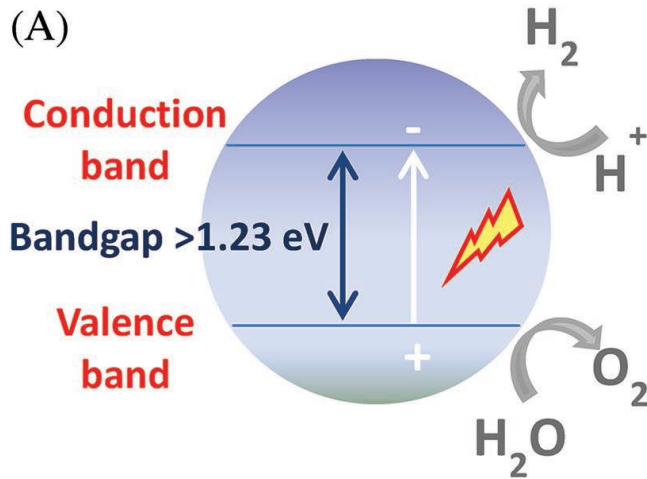
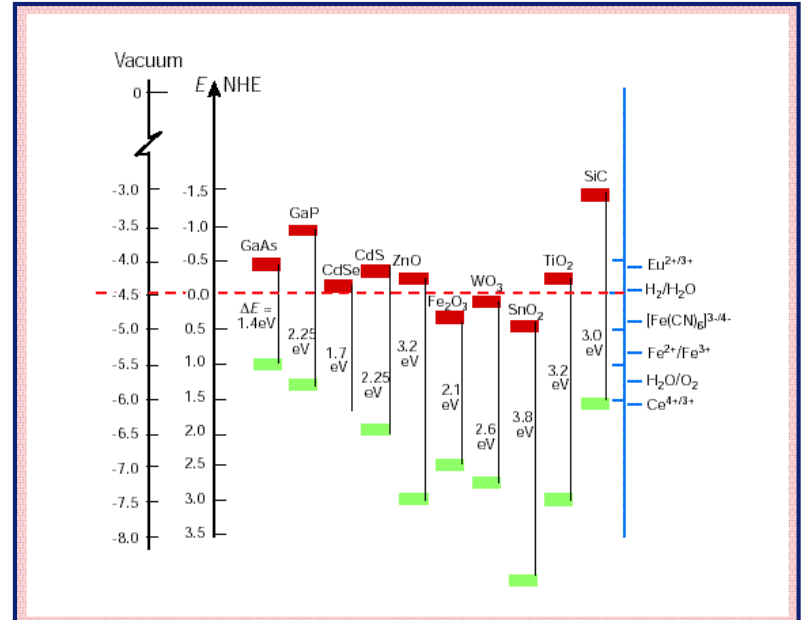
Doping by  $Ce^{3+}, Pr^{3+}, Tb^{3+}$  MMCT  
 $Eu^{2+}$   $[Xe]4f^7 - [Xe]4f^65d^1$



# 5. Photochemical Water Splitting

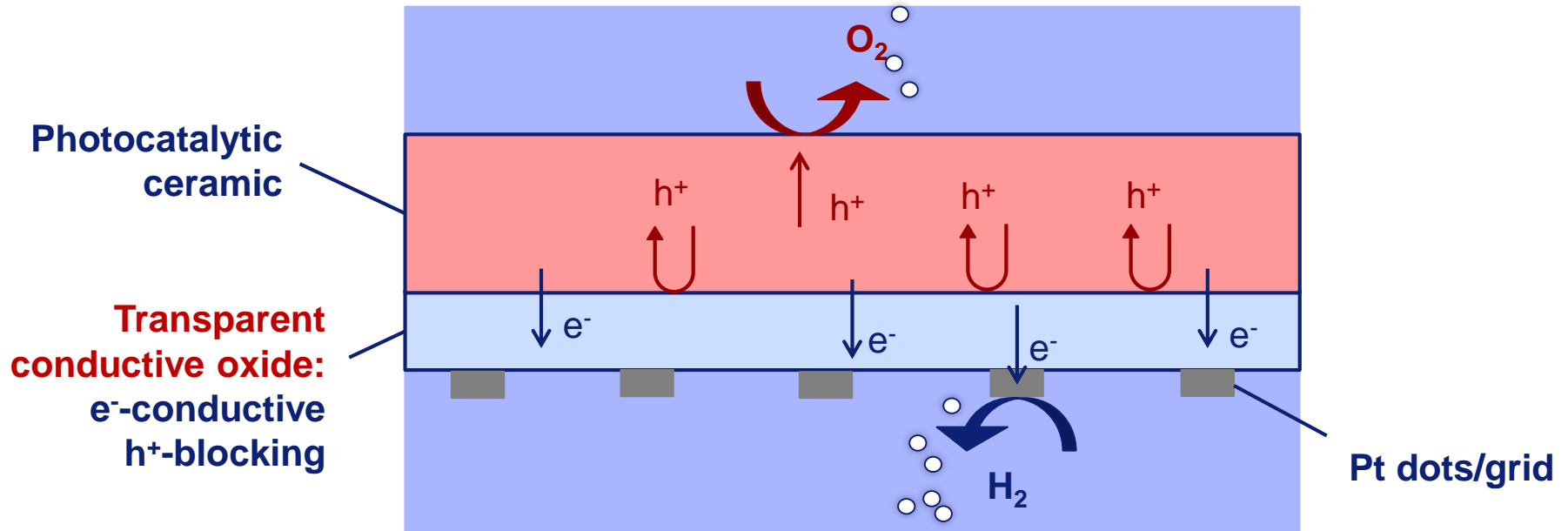
## Photocatalyst Efficiency and Energetics

- Band gap** 2.0 – 3.0 eV
- VB** ~ -6.0 V below vacuum level
- CB** ~ -4.0 V below vacuum level



# 5. Photochemical Water Splitting

**Final Goal: Develop photocatalytic unit, comprising a hole blocking layer**



## Technology already applied in

- OLEDs and PLEDs
- Inverted Polymer Solar Cells
- Other photocatalysts
- .....

## Deposition methods

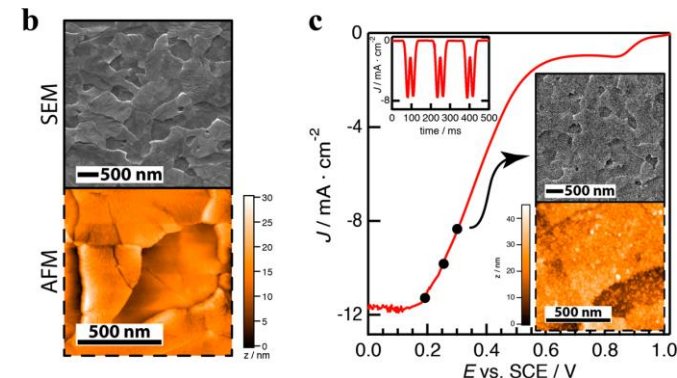
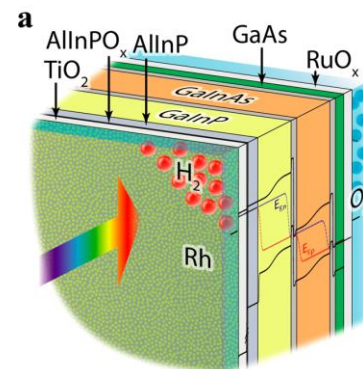
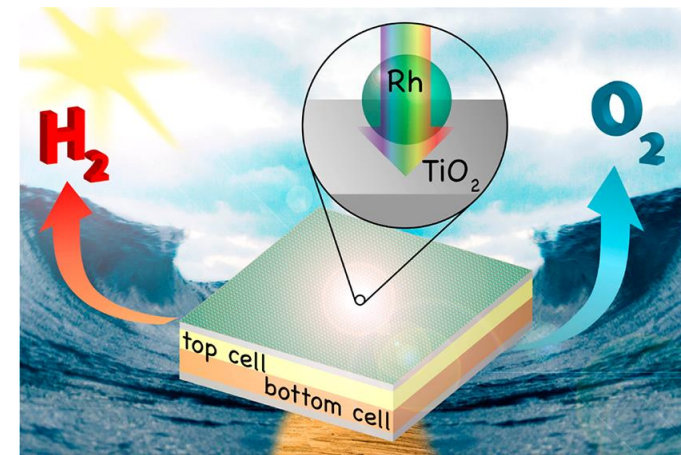
- Sol-gel method
- Spin-coating
- Sputtering (RF-MS)
- .....



# 5. Photochemical Water Splitting

## Recent Embodiment

- Charge carrier separation and  $e^- / h^+$  conduction by epitactically grown AlInP, AlInPO layers
- Rh onto  $TiO_2$  as photocathode
- $RuO_x$  onto GaAs as photoanode
- Problem: Relief of evolving pH gradient



Ref.: ACS Energy Lett. 3 (2018) 1795-1800

# 6. Lighting Towards Ultimate Efficiency

About 20% of the produced electrical energy is used for lighting (source: NASA)



Even more than 25 years after Germany's reunification  
East and West Berlin can be diminished by lighting

- 1961 Construction of the Berlin Wall
- 1989 End of the Berlin Wall "The wind of change"
- 1990 Germany's reunification
- 1993 Blue LED: (In,Ga)N
- 1996 White LED: YAG "The light of change"
- 2014 White LED > 300 lm/W & Nobel price
- 2021 LED dominate lighting business



# 6. Lighting Towards Ultimate Efficiency

## Historical Development

10000 B.C.

19<sup>th</sup> century

20<sup>th</sup> century

21<sup>st</sup> century



First there  
was open  
fire...



...then the  
fire was  
tamed...



...put into a  
glass  
bulb...



...and made  
more  
efficient...



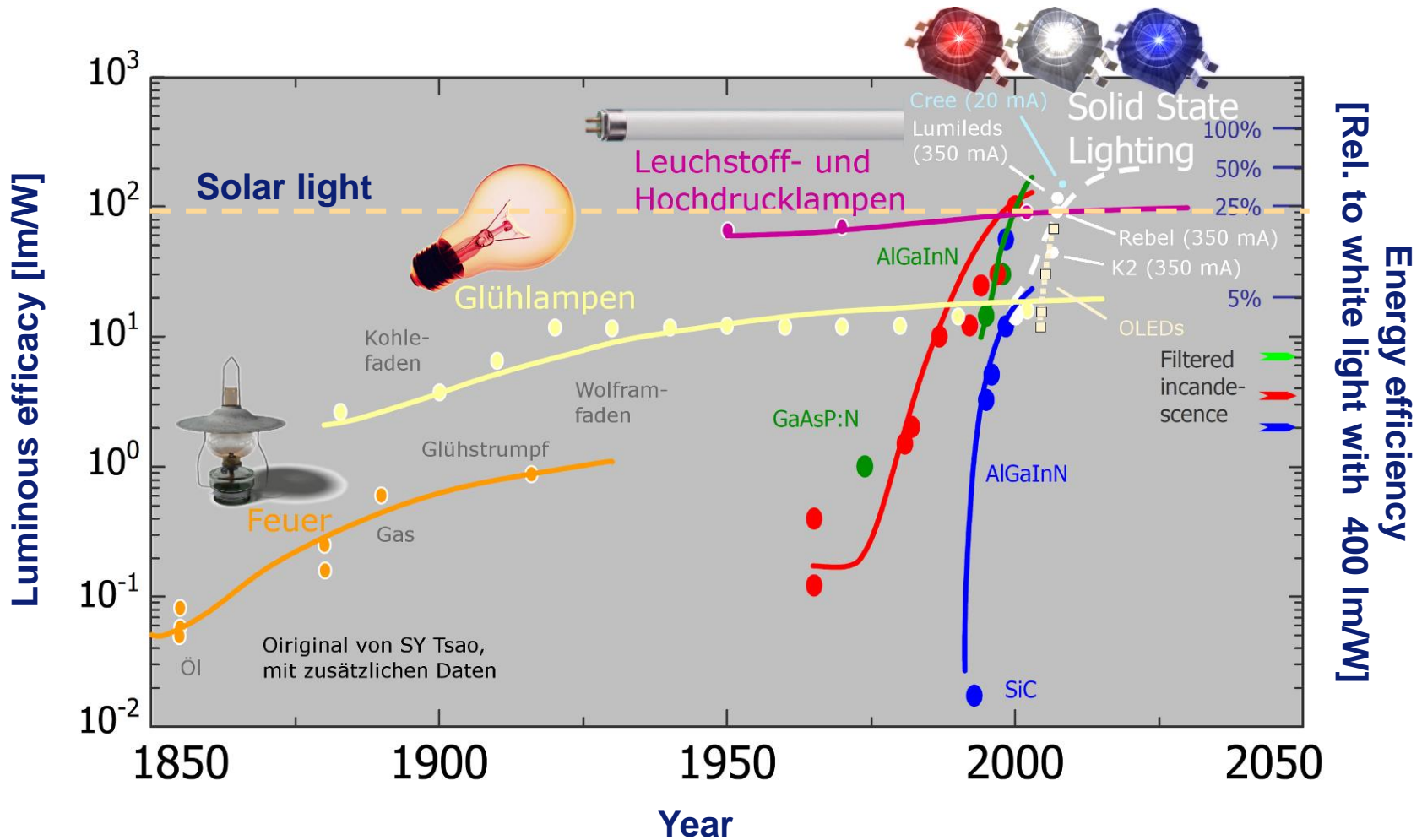
...then the fire  
vanished and light  
only prevailed !

*From chemical light sources*

*to electrical light sources*

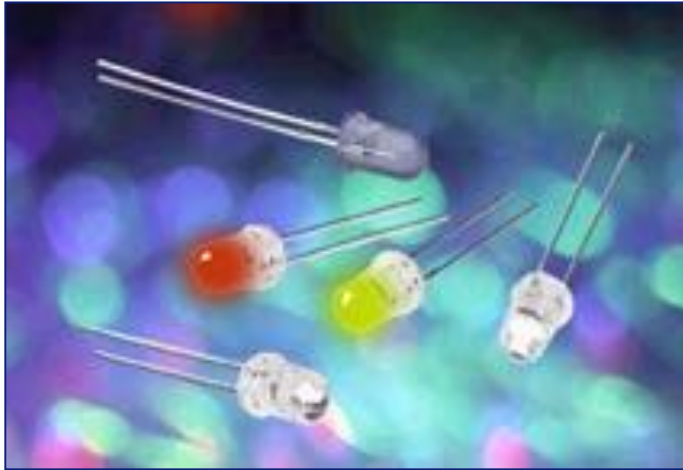
# 6. Lighting Towards Ultimate Efficiency

## Historical Development: Luminous Efficacy and Energy Efficiency

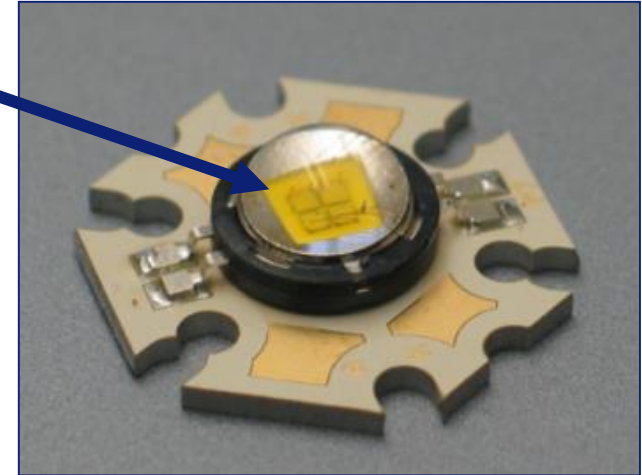


# 6. Lighting Towards Ultimate Efficiency

## Historical Development: Colours and Power Density



Luminescent  
screen



**1970**

**(Ga,As)P**

< 0.1 W

< 1.0 lm

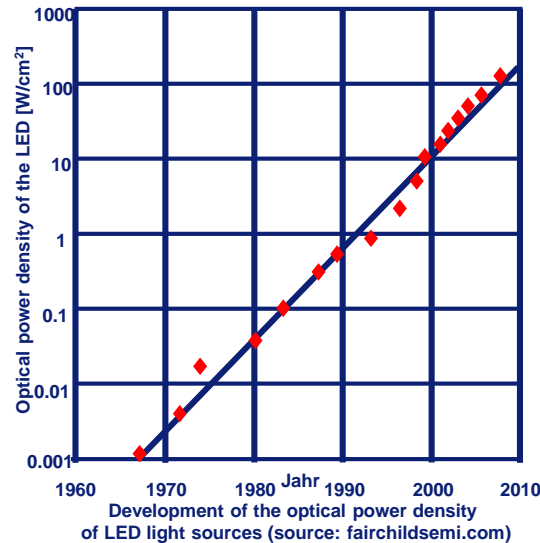
< 10 lm/W

< 120 °C

< 100 W/cm<sup>2</sup>

> 120 K/W

yellow, red, NIR



**2019**

**(Al,In,Ga)P, (In,Ga)N, (Al,Ga)N**

1 - 10 W

> 100 lm

up to 303 lm/W

120 - 200 °C

100 - 200 W/cm<sup>2</sup>

2 - 12 K/W

UV-A/B/C, all colors, NIR

# 6. Lighting Towards Ultimate Efficiency

## Power Saving Potential by LEDs



Electric lighting consumes worldwide  
2,600,000,000,000,000 Wh (2600 TWh) p.a.  
(~20% of total global electricity production)

LED energy saving potential: 1500 TWh

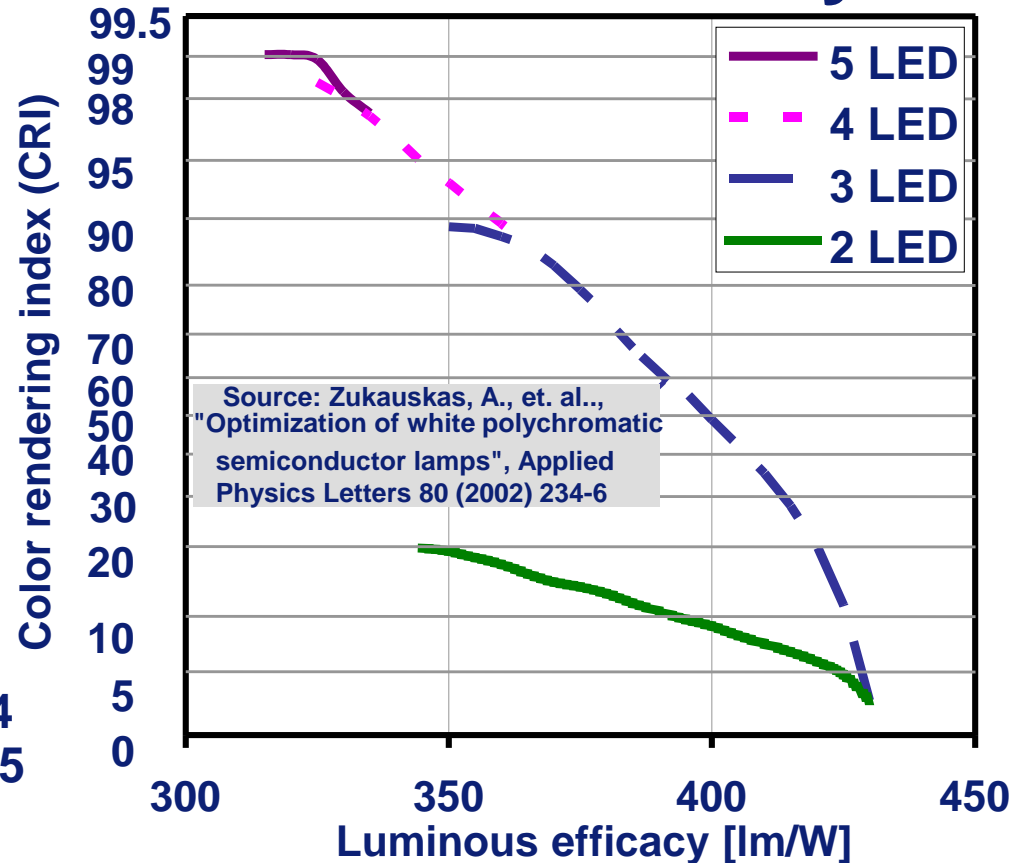
- Reductions in power plants:
- 200 nuclear power plants or
  - 200 fossil power plants

Ref.: IEA, International Energy Agency

# 6. Lighting Towards Ultimate Efficiency

## Multichip LED Lamps

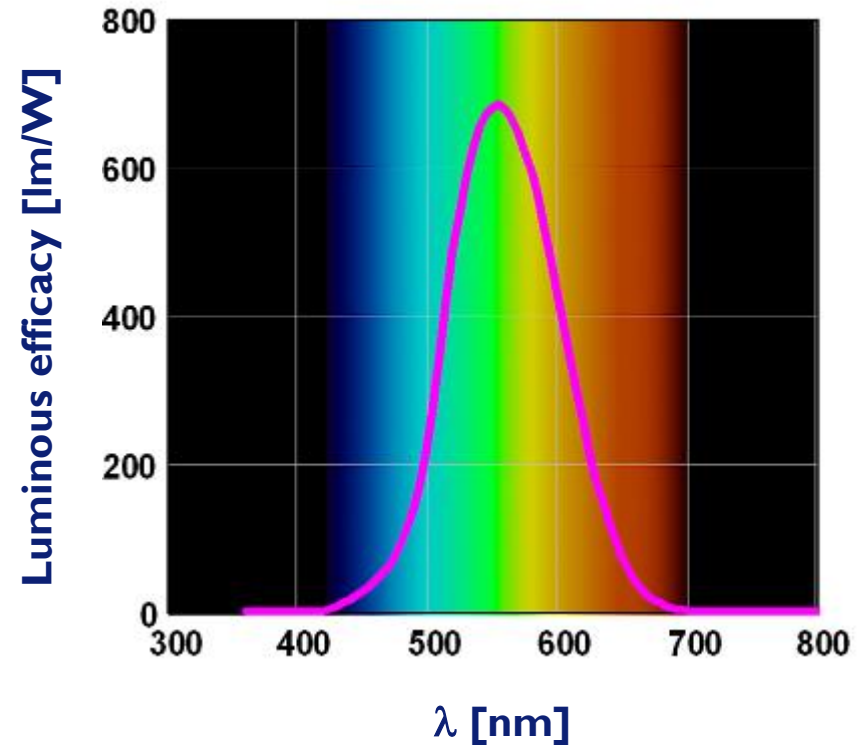
- Narrow band emitter e.g. LEDs
  - $\lambda_{1/2} = 30 \text{ nm}$
  - Several colored LEDs
- Theoretical maximum
  - 430 lm/W for
  - CCT = 4870 K
  - CRI = 3 (!)
- Feasible values
  - ~ 350 lm/W for CRI 90, n = 3 - 4
  - max. 320 lm/W for CRI 99, n = 5
- Problems
  - Thermal stability of the LEDs
  - LED efficiency
    - Red and blue high
    - Green and yellow moderate → Phosphors!



# 6. Lighting Towards Ultimate Efficiency

## Luminous Efficacy of Light Sources

- Strong dependence on emission spectrum
- Optimum is at 555 nm
  - $V(\lambda) = 683 \text{ lm/W}$  (100%)
- Lumen output
  - 1000 lm at 555 nm requires 1.5 W
  - Incandescent bulb ~ 80 W, i.e. 12.5 lm/W
- Blue and red radiation
  - $V(\lambda) < 70 \text{ lm/W}$  (10%)

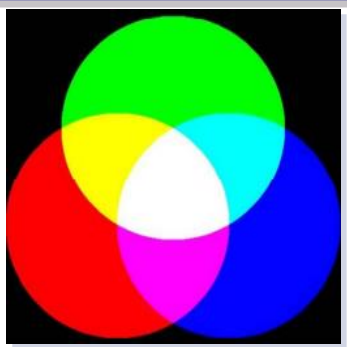
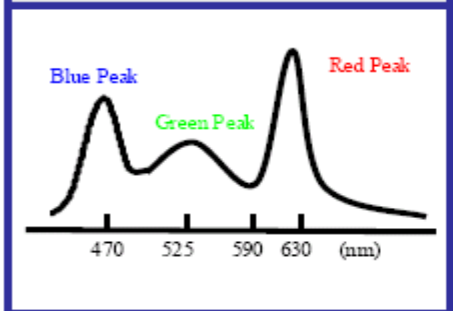
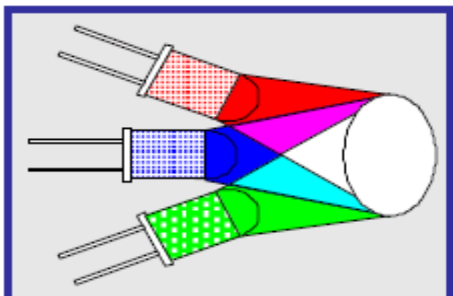




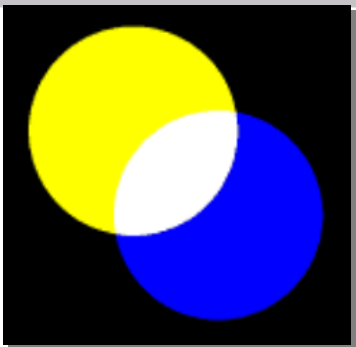
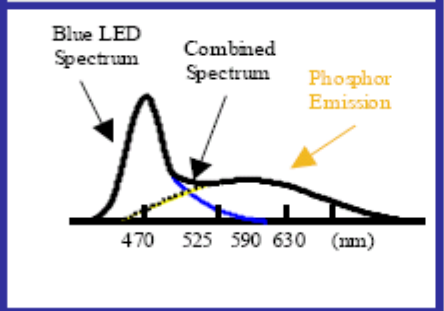
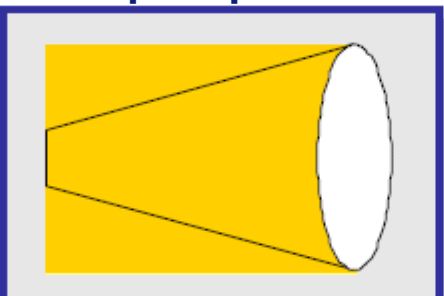
# 6. Lighting Towards Ultimate Efficiency

## General Approaches

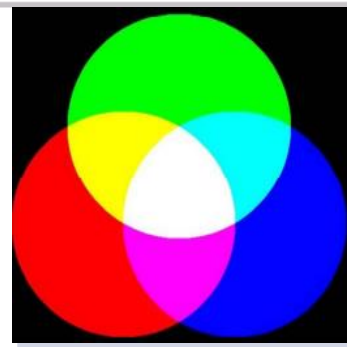
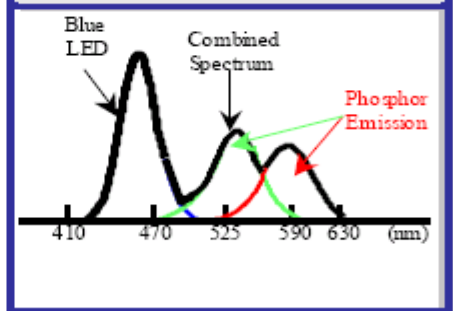
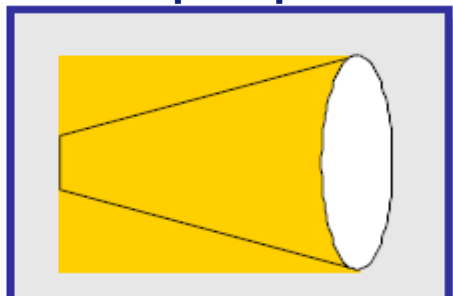
Red + Green + Blue LEDs



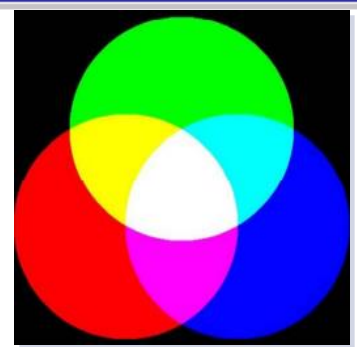
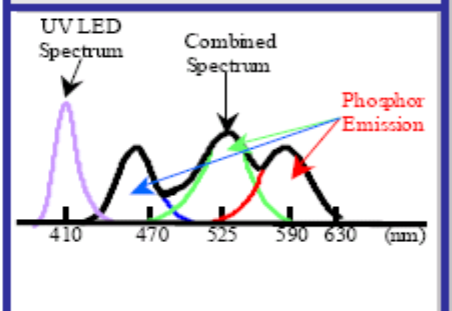
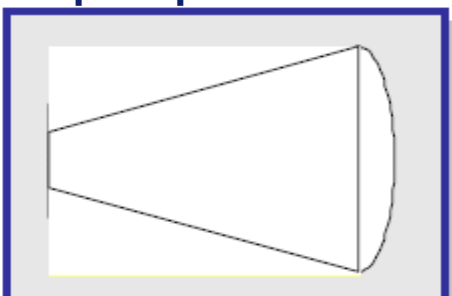
Blue LED + yellow phosphor



Blue LED + yellow + red phosphor

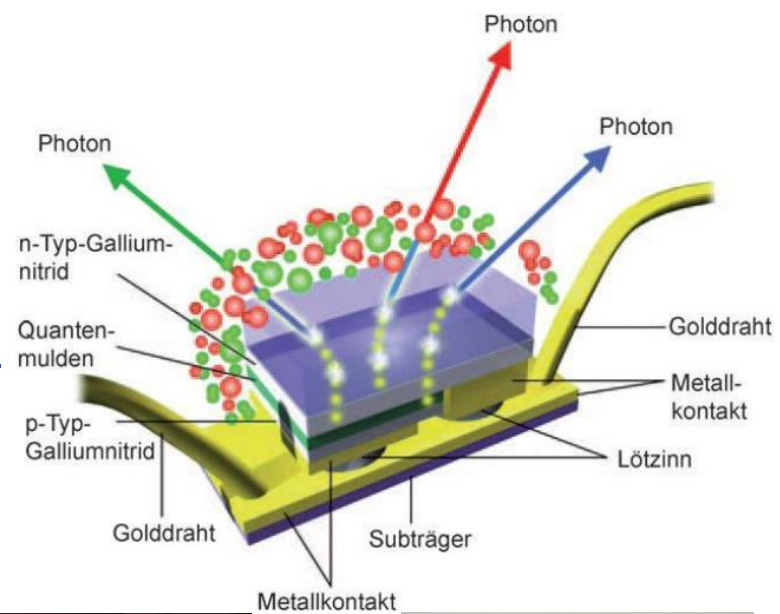
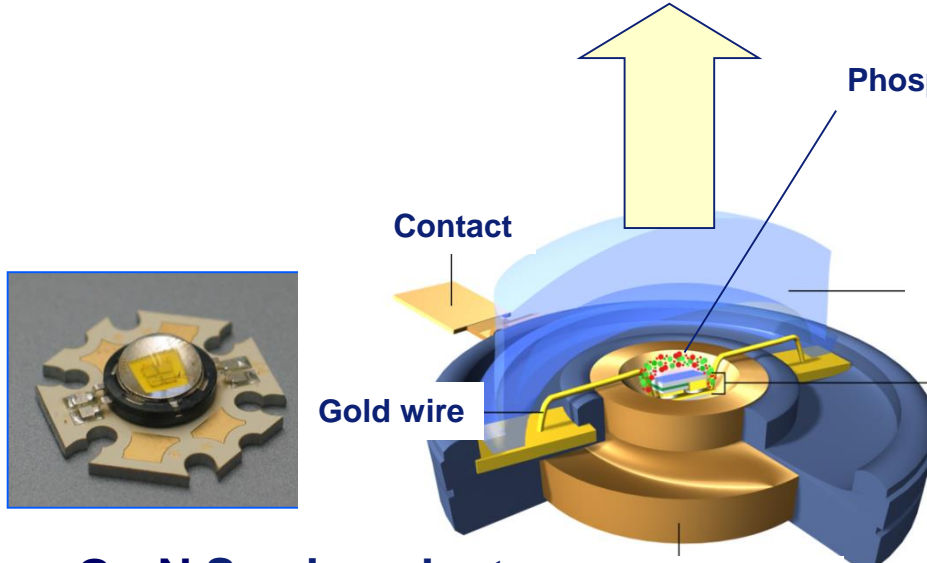


UV LED + RGB phosphor blend

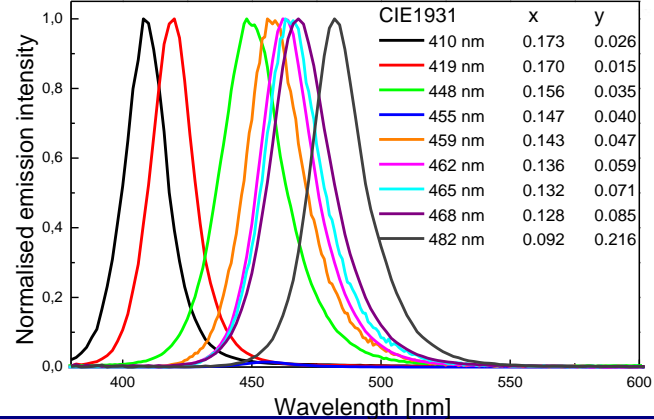


# 6. Lighting Towards Ultimate Efficiency

## “Phosphor Converted” (pc) LED



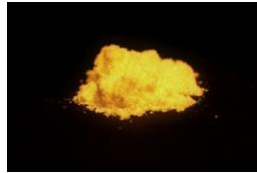
### In<sub>1-x</sub>Ga<sub>x</sub>N Semiconductor



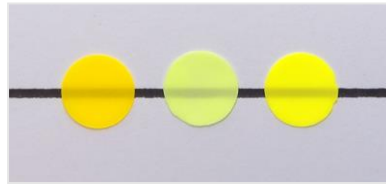
# 6. Lighting Towards Ultimate Efficiency

## Micropowders or Ceramics

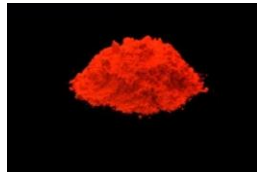
**Aluminates** →  $Ce^{3+}$   
 $(Y,Gd,Tb)_3Al_5O_{12}:Ce$   
 $Lu_3(Ga,Al)_5O_{12}:Ce$



**Sulphides** →  $Eu^{2+}$   
 $(Ca,Sr)S:Eu$

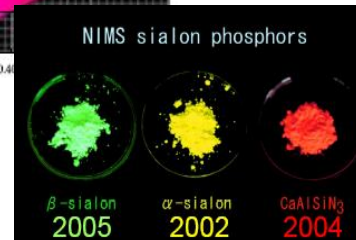
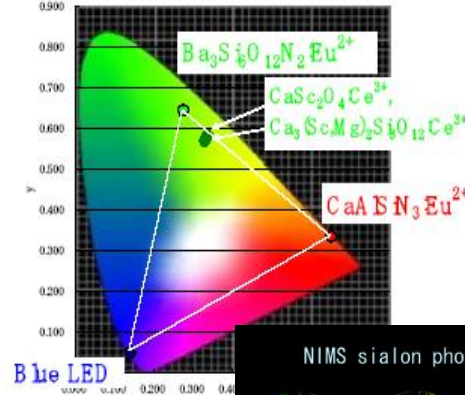
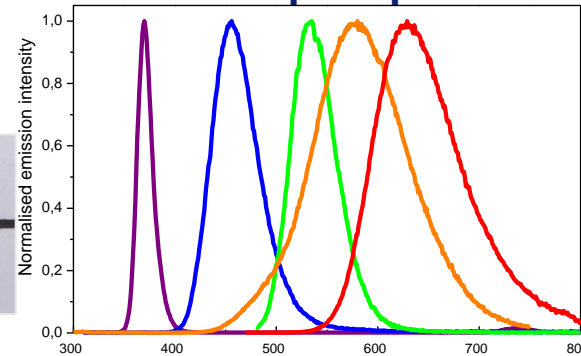


**Oxides** →  $Eu^{2+}$  or  $Ce^{3+}$   
 $CaSc_2O_4:Ce,Mg$   
 $(Ca,Sr,Ba)_2SiO_4:Eu$   
 $(Ca,Sr,Ba)_3SiO_5:Eu$

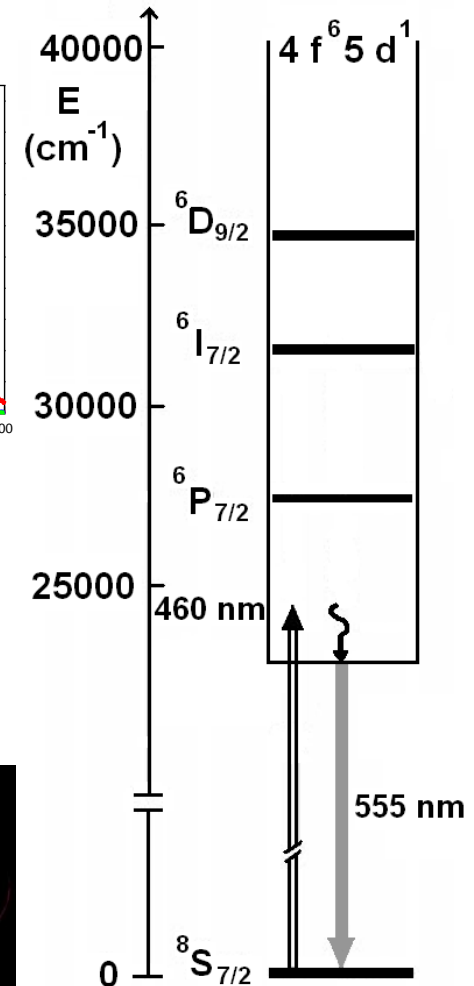


**(Oxy)Nitrides** →  $Eu^{2+}$  or  $Ce^{3+}$   
 $(Sr,Ca,Ba)_2Si_5N_8:Eu$  „2-5-8“  
 $(Sr,Ca,Ba)Si_2N_2O_2:Eu$  „1-2-2-2“  
 $(Ca,Sr)AlSiN_3:Eu$  „1-1-1-3“  
 $La_3Si_6N_{11}:Ce$  „3-6-11“  
 $Ba_3Si_6O_{12}N_2:Eu$   
 $\alpha,\beta-Si_{3-x}Al_xN_{4-x}O_x:Eu$  SiAlON

Typical spectra of  $Eu^{2+}$  phosphors



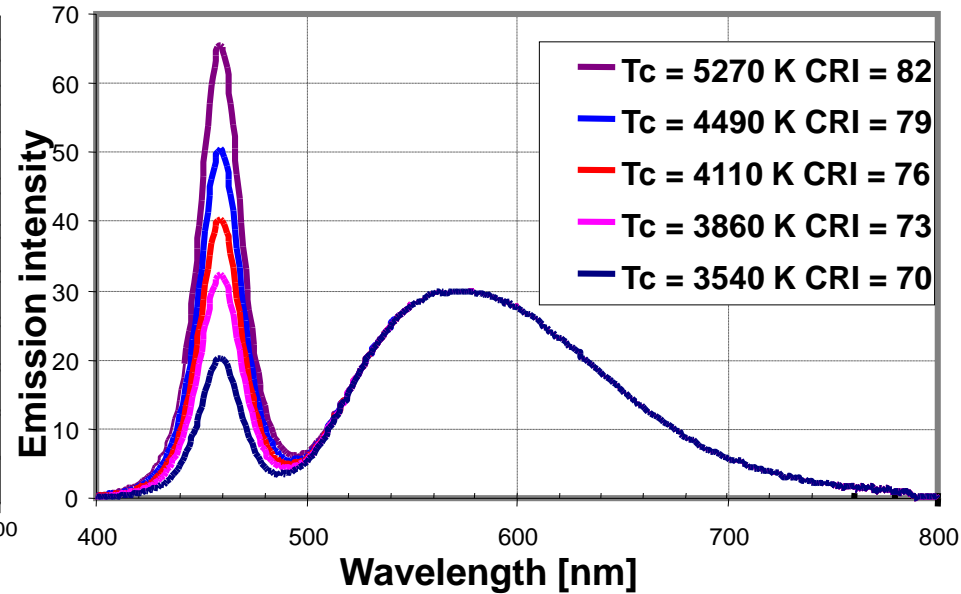
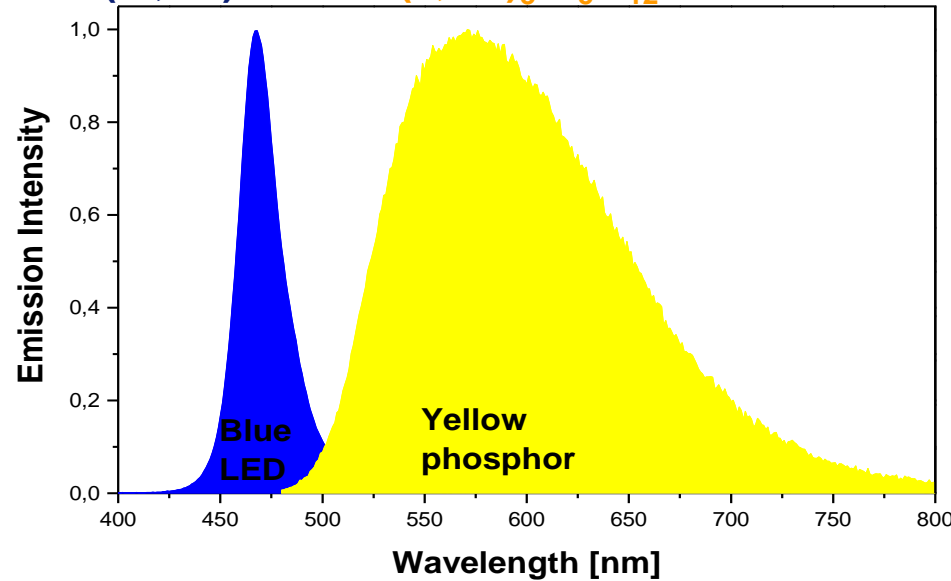
Simplified energy level scheme of  $Eu^{2+}$



# 6. Lighting Towards Ultimate Efficiency

1<sup>st</sup> Generation pcLEDs: Wall Plug efficiency (WPE) >> Discharge lamps

(In,Ga)N LED (Y,Gd)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce



## Status quo cool white phosphor converted LEDs @ 2021

Yellow phosphors

garnets: (Y,Gd,Tb)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce<sup>3+</sup>

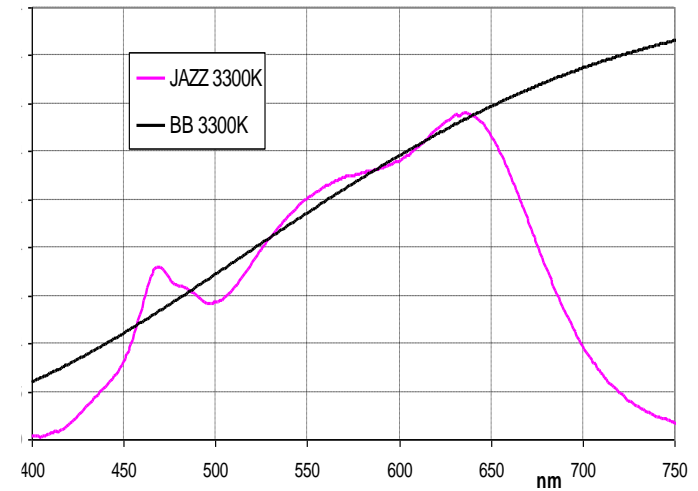
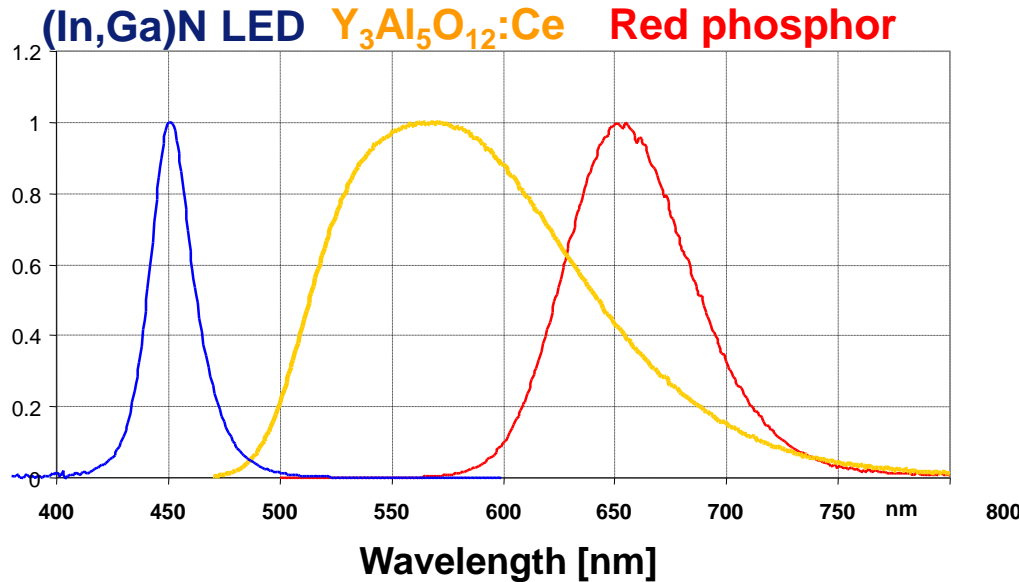
ortho-silicates: (Ca,Sr,Ba)<sub>2</sub>SiO<sub>4</sub>:Eu<sup>2+</sup>

- LE 300 lm/W (WPE > 80%)
- CRI 70 - 80
- CCT > 5000 K

Element	Y	Gd	Ce	Al	O	(Y <sub>0,77</sub> Gd <sub>0,2</sub> Ce <sub>0,03</sub> ) <sub>3</sub> Al <sub>5</sub> O <sub>12</sub>
Molar Mass (g/mol)	88,91	157,25	140,12	26,98	16,0	639,243
Coefficient	2,31	0,6	0,09	5	12	
Mass fraction	32%	15%	2%	21%	30%	100%

# 6. Lighting Towards Ultimate Efficiency

## 2<sup>nd</sup> Generation pcLEDs: Enhancement of CRI and reduction of CCT



### Status quo warm white phosphor converted LEDs @ 2019

- **Red phosphor** **Eu<sup>2+</sup> activated**
- LE 80 - 150 lm/W
- CRI 85 – 95
- CCT 2500 - 4000 K

Ref.: R. Mueller-Mach, G.O. Mueller, P.J. Schmidt,

T. Jüstel, Red Deficiency Compensating Phosphor LED, Light Emitting Device, US Patent 2003/0006702

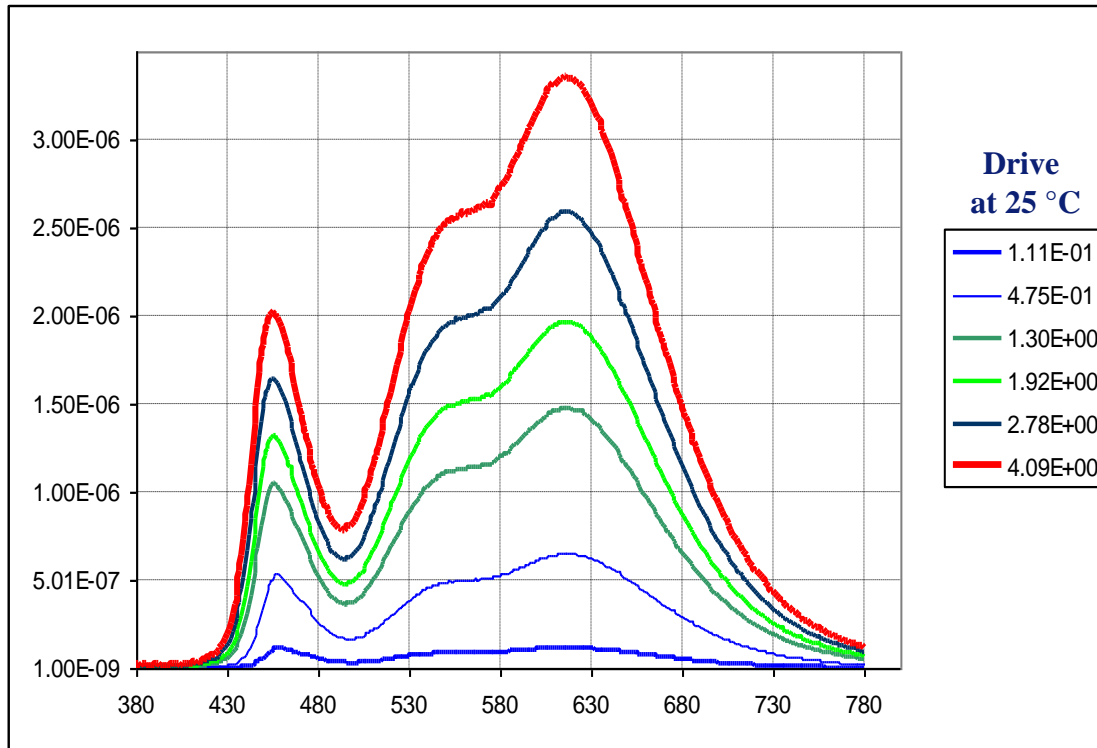
Phosphor	Molar Mass (g/mol)	Coefficient for Eu <sup>2+</sup>	Mass fraction Eu <sup>2+</sup>
$Ca_{0,5}Sr_{0,45}Eu_{0,05}S$	99,14	0,05	8%
$(Sr_{0,95}Eu_{0,05})_2Si_5N_8$	434,12	0,1	4%
$Ca_{0,5}Sr_{0,45}Eu_{0,05}AlSiN_3$	168,14	0,05	5%

# 6. Lighting Towards Ultimate Efficiency

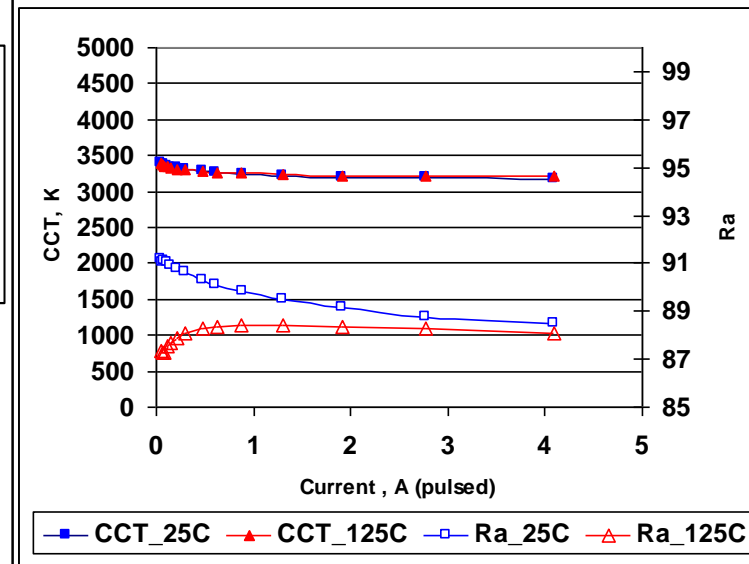
First all nitride LED demonstrated in 2005 ( $QY > 0.9$ ,  $QY_{rel}(200\text{ °C}) > 0.95$ )

(In,Ga)N LED +  $SrSi_2N_2O_2:Eu$  +  $Sr_2Si_5N_8:Eu$

or  $(Sr,Ca)AlSiN_3:Eu$  or  $\alpha$ -SiAlONes



Colour rendering index CRI > 88  
Excellent colour point consistency  
with drive is achieved

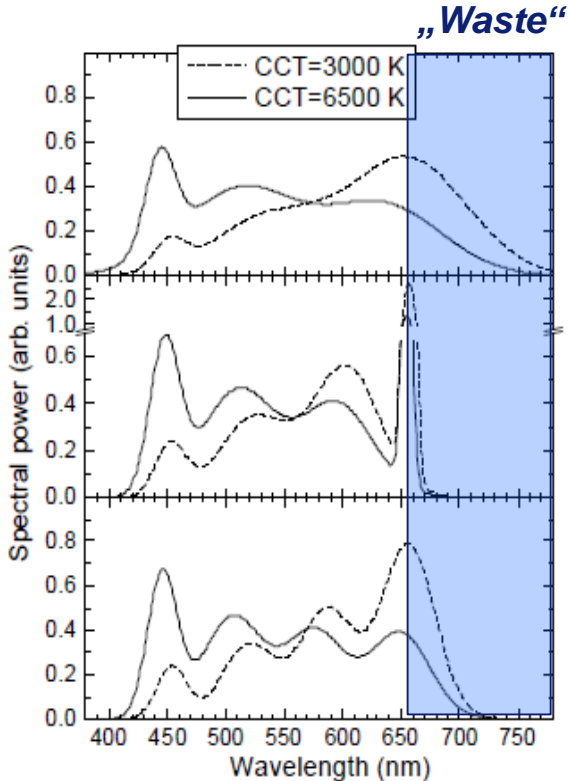
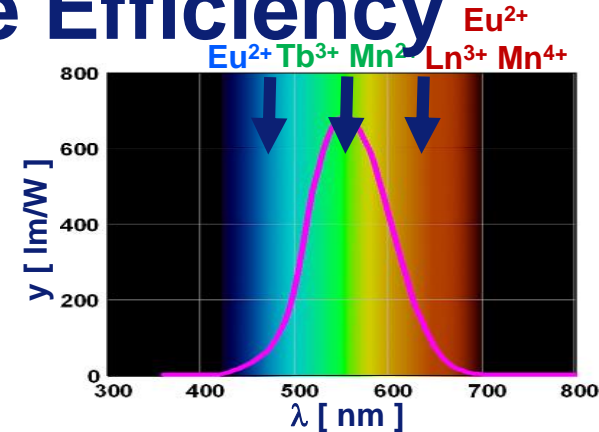


Ref.: R. Mueller-Mach, G.O. Mueller, M.R. Krames, H. Höpfe, F. Stadler, W. Schnick, T. Jüstel, P.J. Schmidt, Highly efficient all nitride phosphor converted white light emitting diode, Phys. Stat. Sol. A 202 (2005) 1727

# 6. Lighting Towards Ultimate Efficiency Eu<sup>2+</sup>

**Red band emitter cause reduction in lum. efficacy**

1. Spectral interaction due to re-absorption
2. Reduction in lumen equivalent



Band width [nm]	Position (nm)	LE (lm/W)	Red LED Phosphor
90 - 120	635	257	(Ca,Sr)S:Eu (Ca,Sr,Ba) <sub>2</sub> Si <sub>5</sub> N <sub>8</sub> :Eu (Ca,Sr)AlSiN <sub>3</sub> :Eu
20 - 30	655	278	Mg <sub>2</sub> TiO <sub>4</sub> :Mn <sup>4+</sup>
20 - 30	620	320	Ln <sup>3+</sup> activated (Ln = Eu, Sm, Pr) Mn <sup>4+</sup> activated
50 - 60	655	269	Eu <sup>2+</sup> - activated
50 - 60	620	300	Eu <sup>2+</sup> - activated

Ref.: A. Zukauskas et al., Appl. Phys. Lett. 93 (2008) 051115

# 6. Lighting Towards Ultimate Efficiency

## Requirements to an „ideal“ red LED phosphor

- **Narrow FWHM ~ 20 - 60 nm**
- Emission peak at ~ 630 nm
- QY (excitation at 450 nm) > 90%
- Absorption at 450 nm > 50%
- $T_{1/2} > 200 \text{ }^\circ\text{C}$
- Decay time < 10 ms
- **No saturation up to 100 W/mm<sup>2</sup> (good linearity)**
- High (photo)chemical and thermal stability



Activator	Spectral range [nm]	Lumen equivalent [lm/W <sub>opt</sub> ]	Decay time $\tau$	QY [%]	Absorption at 450 nm
<i>RE-Ions</i>					
<b>Eu<sup>2+</sup></b>	<b>360 - 700</b>	<b>50 – 550</b>	<b>~ 1 <math>\mu</math>s</b>	<b>high</b>	<b>strong</b>
Eu <sup>3+</sup>	590 - 710	200 – 360	~ 1 ms	high	weak
Sm <sup>2+</sup>	670 - 770	< 100	~ 1 $\mu$ s	high	moderate
Sm <sup>3+</sup>	560 - 710	240 – 260	0.5 ms	moderate	weak
Pr <sup>3+</sup>	590 - 680	100 – 220	0.1 ms	moderate	weak
<i>TM-Ions</i>					
Mn <sup>2+</sup>	500 - 650	100 - 550	5-15 ms	high	weak
Mn <sup>4+</sup>	620 - 680	80 – 230	1-10 ms	high	moderate
Cr <sup>3+</sup>	680 - 750	< 100	1-10 ms	high	moderate

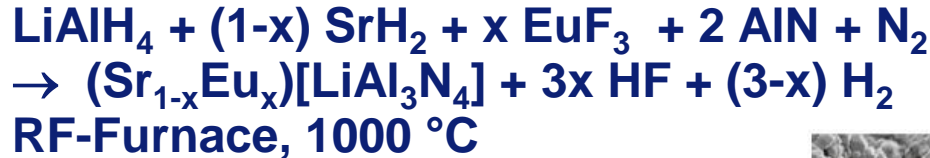


# 6. Lighting Towards Ultimate Efficiency

## Narrow band red emitter $\text{Sr}[\text{LiAl}_3\text{N}_4]:\text{Eu}^{2+}$

Claimed as next generation LED-phosphor material''

### Synthesis



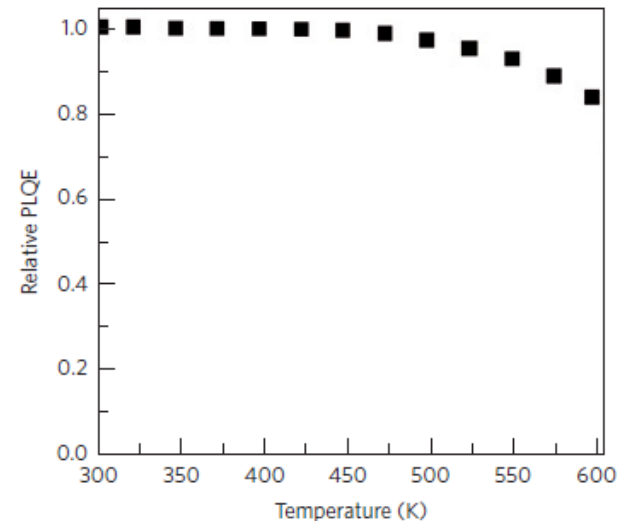
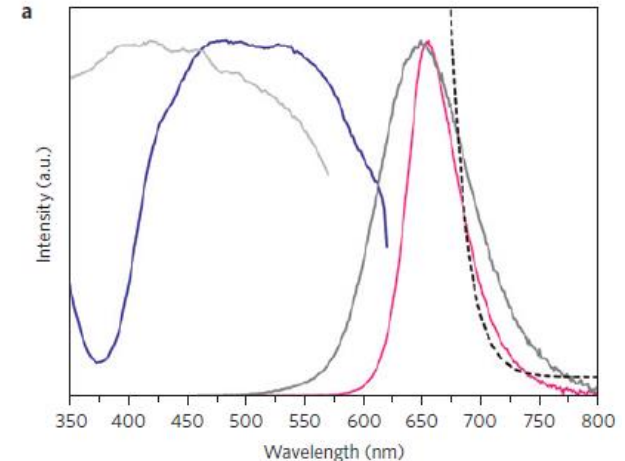
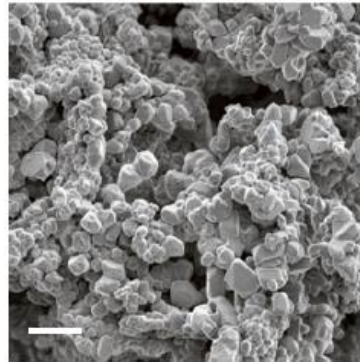
### Optical Properties

$\lambda_{\text{max}} = 651 \text{ nm}$  for 5%  $\text{Eu}^{2+}$

**FWHM = 1180  $\text{cm}^{-1}$  (~ 60 nm)**

QY(200 °C) > 95% rel. to QY(RT)

Decay time of  $\text{Eu}^{2+} \sim 1.1 \mu\text{s}$



Problems: Excitation @ 410 nm → photoionisation  
and strong re-absorption of YAG:Ce/LuAG:Ce PL

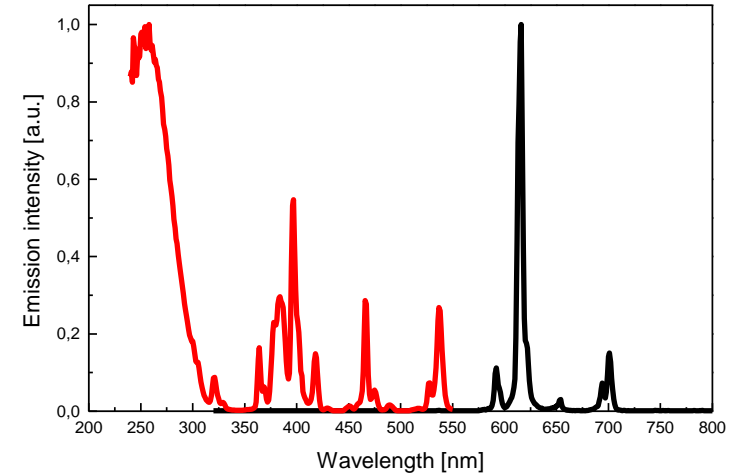
Ref.: W.S. Schnick et al., Nature Materials (2014) 1-6

# 6. Lighting Towards Ultimate Efficiency

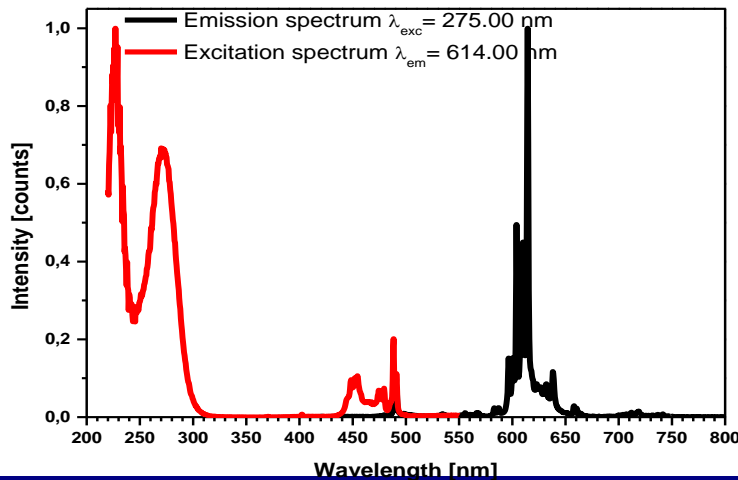
## Remaining Options

Red emitter	LE [ $\text{lm/W}_{\text{opt.}}$ ]	QY at RT
$\text{Eu}^{3+}$	220 – 360	high
$\text{Pr}^{3+}$	200 – 220	moderate
$\text{Mn}^{4+}$	5 – 200	high

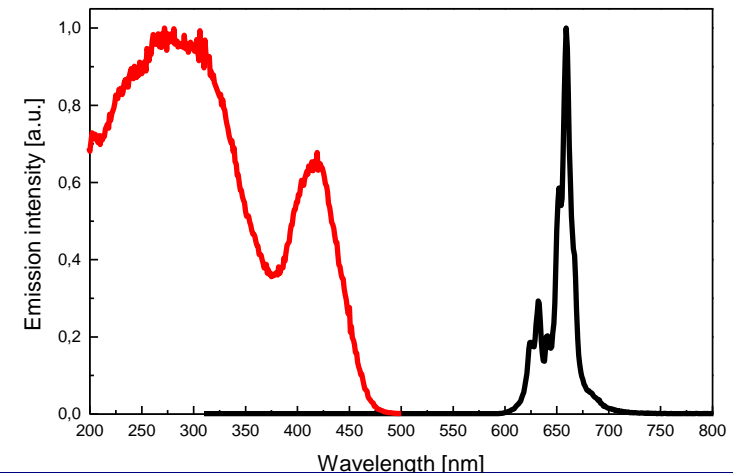
$\text{La}_2\text{W}_3\text{O}_{12}:\text{Eu}$



$\text{LuTaO}_4:\text{Pr}$

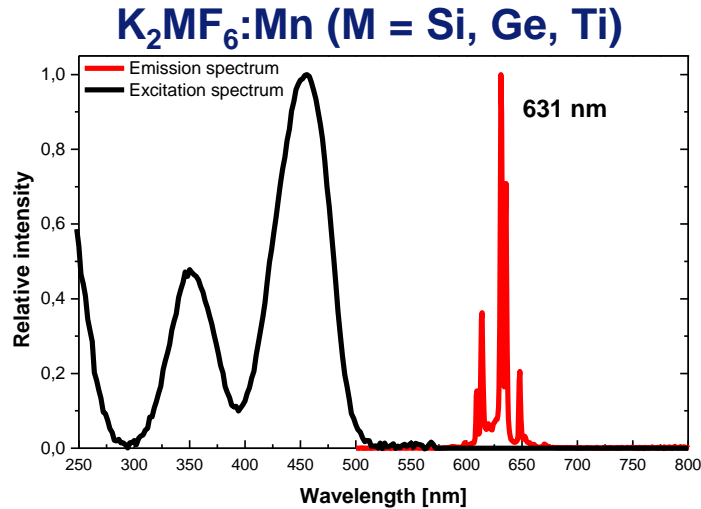


$\text{Mg}_4\text{GeO}_{5.5}\text{F}:\text{Mn}$

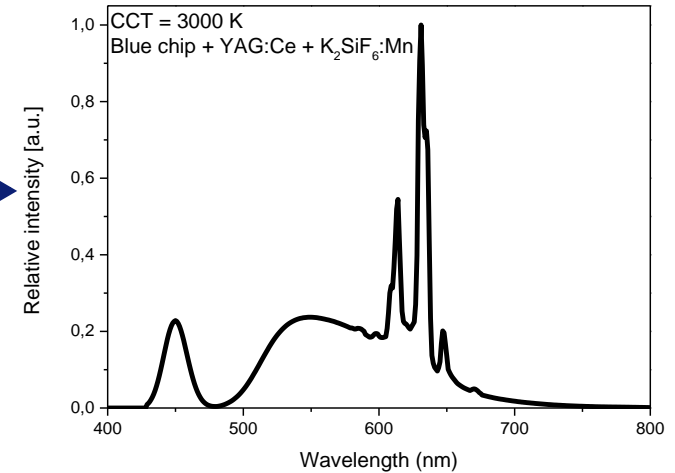


# 6. Lighting Towards Ultimate Efficiency

Red line emitter → Mn<sup>4+</sup>



**Warm white pcLED**



LED Chip  
Converter

Blue

420 – 480 nm

Yellow

(Y,Gd,Tb,Lu)Al<sub>5</sub>O<sub>12</sub>:Ce

Red

Mn<sup>4+</sup>- phosphor

Typical yellow/red blend  
Problems

Tb<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:3%Ce + K<sub>2</sub>[MF<sub>6</sub>]:Mn<sup>4+</sup> (M = Si, Ge, Sn, Ti, Zr)

Absorption strength, linearity, and stability of Mn<sup>4+</sup>



Ref.: A. Srivastava et al., GE, US Patent US2006/0169998

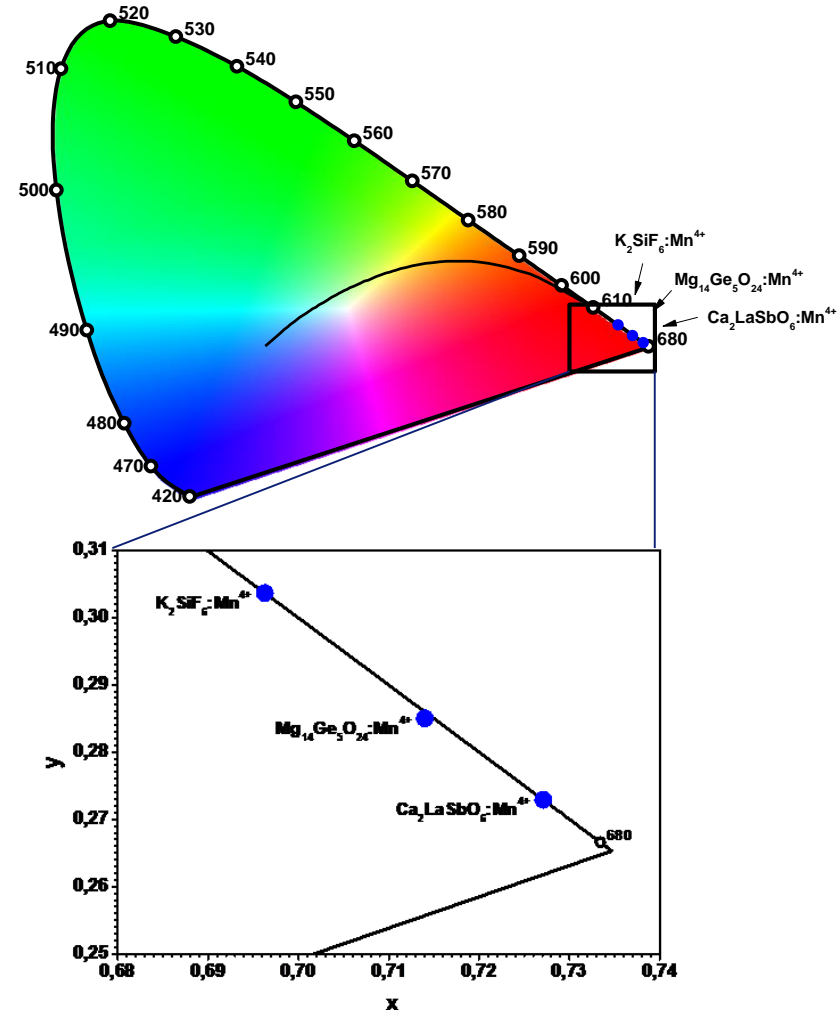
# 6. Lighting Towards Ultimate Efficiency

**Red line emitter → Mn<sup>4+</sup>**

Phosphor	LE [lm/W]	Peak λ <sub>em</sub> [nm]
K <sub>2</sub> SiF <sub>6</sub> :Mn <sup>4+</sup>	196	631.0
K <sub>2</sub> TiF <sub>6</sub> :Mn <sup>4+</sup>	192	631.8
K <sub>2</sub> GeF <sub>6</sub> :Mn <sup>4+</sup>	191	632.0
Mg <sub>14</sub> Ge <sub>5</sub> O <sub>24</sub> :Mn <sup>4+</sup>	80	658
K <sub>2</sub> Ge <sub>4</sub> O <sub>9</sub> :Mn <sup>4+</sup>	46	663*
Rb <sub>2</sub> Ge <sub>4</sub> O <sub>9</sub> :Mn <sup>4+</sup>	38	667*
Ca <sub>2</sub> YNbO <sub>6</sub> :Mn <sup>4+</sup>	15	680
Ca <sub>2</sub> LaSbO <sub>6</sub> :Mn <sup>4+</sup>	7	699
LaScO <sub>3</sub> :Mn <sup>4+</sup>	7	703

Ref.: F. Baur, T. Jüstel, J. Luminescence 177 (2016) 354

- Fluorides → Rather high luminous efficacy, but stability is a challenge
- Oxides → Very stable, but low luminous efficacy



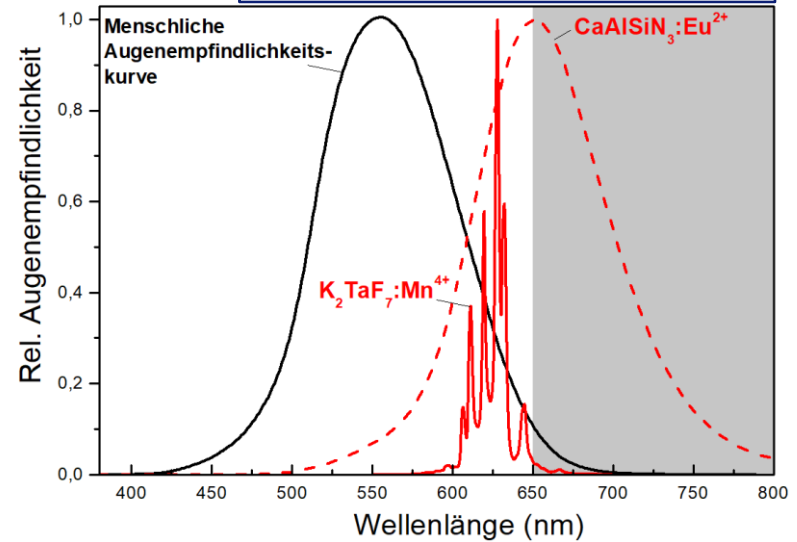
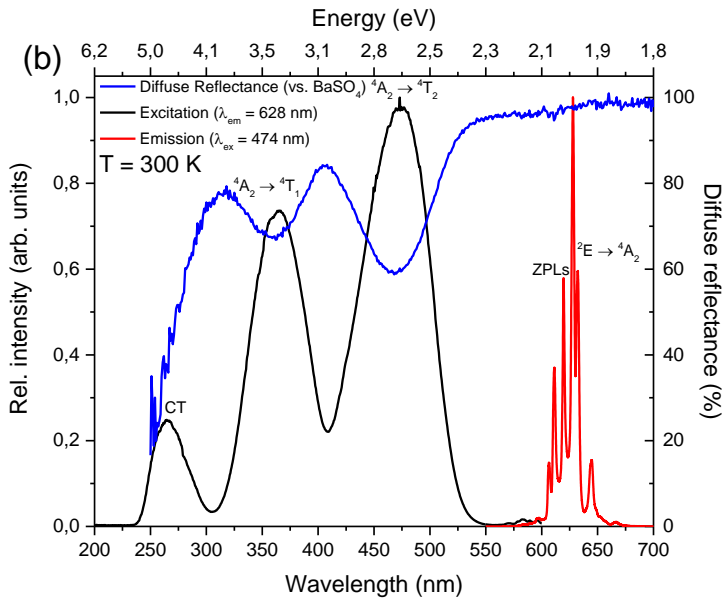
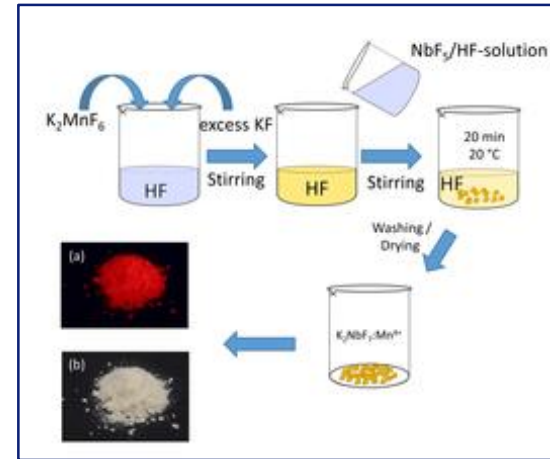
# 6. Lighting Towards Ultimate Efficiency

Red line emitter →  $K_2(Nb,Ta)F_7:Mn^{4+}$

$\lambda_{max} = 628 \text{ nm}$

LE = 228 lm/W

CIE1931: x = 0.690; y = 0.310

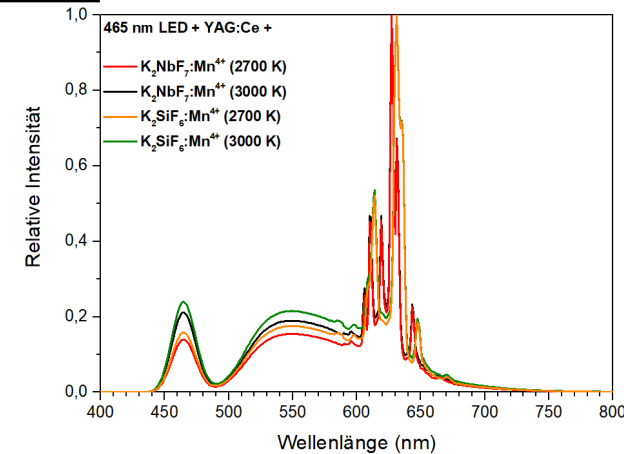


Ref.: T. Jansen, F. Baur, T. Jüstel, Red Emitting  $K_2NbF_7:Mn^{4+}$  and  $K_2TaF_7:Mn^{4+}$  for Warm-White LED Applications, J. Luminescence 192 (2017) 644

# 6. Lighting Towards Ultimate Efficiency

Red line emitter →  $K_2(Nb,Ta)F_7:Mn^{4+}$  with superior luminous efficacy (LE)

Blue LED + YAG:Ce +	CCT [K]	LE [ $lm/W_{opt}$ ]	CRI
$K_2NbF_7:Mn^{4+}$	3000	346	95
	2700	345	95
$K_2TaF_7:Mn^{4+}$	3000	345	95
	2700	345	94
$Na_3AlF_6:Mn^{4+}$	3000	345	95
	2700	344	95
$K_2SiF_6:Mn^{4+}$	3000	339	95
	2700	297	95
$Mg_{14}Ge_5O_{24}:Mn^{4+}$	3000	254	83
	2700	241	78
$Y_2Mg_3Ge_3O_{12}:Mn^{4+}$	3000	255	84
	2700	242	79
$CaAlSiN_3:Eu^{2+}$	3000	272	93
	2700	260	95



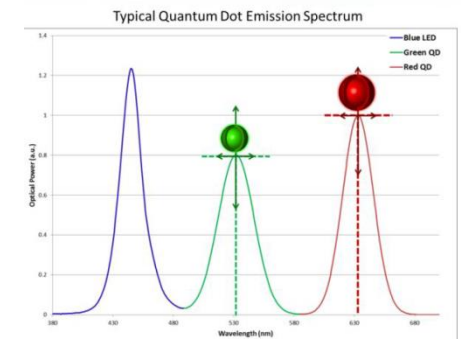
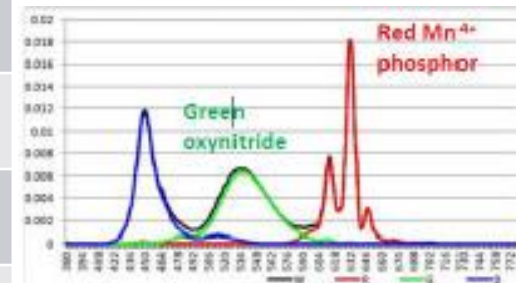
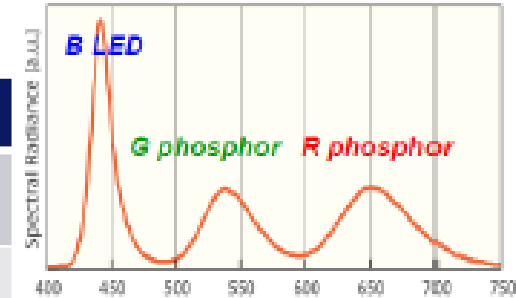
A 2700 K LED comprising YAG:Ce and  $K_2TaF_7:Mn^{4+}$  shows a 15% higher LE than an LED comprising YAG:Ce and  $K_2SiF_6:Mn^{4+}$

# 6. Lighting Towards Ultimate Efficiency

## The Quest for a Narrow Band Red Emitter

$\text{Eu}^{2+} \rightarrow \text{Mn}^{4+}$  or CdSe / InP QDots

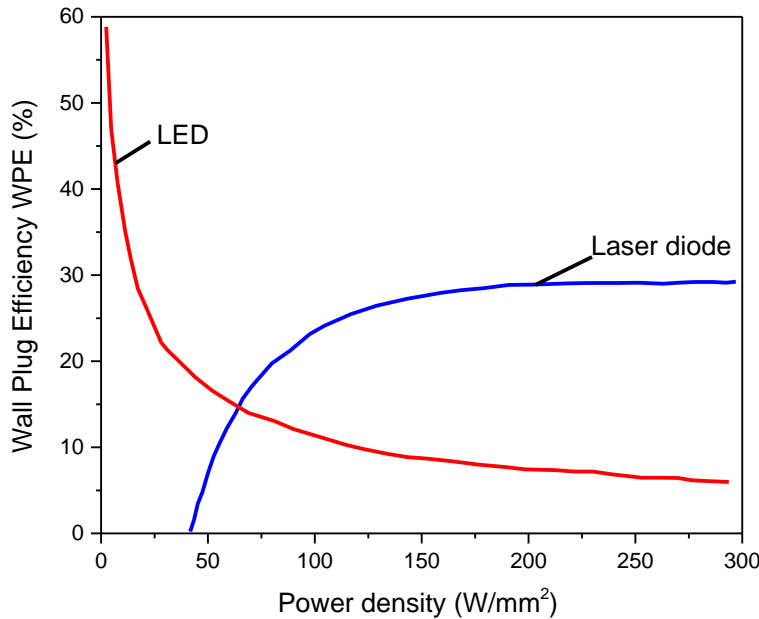
Material	Peak at [nm]	FWHM [nm]	Pros	Cons
(Sr,Ca)S:Eu	615 - 650	60 - 70	Rather narrow band	Low chemical stability
(Sr,Ba) <sub>2</sub> Si <sub>5</sub> N <sub>8</sub> :Eu	585 - 625	80 - 100	Reliability	IR spillover
(Ca,Sr)AlSiN <sub>3</sub> :Eu	610 - 655	80 - 90	Reliability	IR spillover
SrLiAl <sub>3</sub> N <sub>4</sub> :Eu	650	50 nm	Narrow band	Self absorption, some IR spillover
K <sub>2</sub> SiF <sub>6</sub> :Mn	631	Lines < 2 nm	Very narrow band, low stab.	Moderate absorption
CdSe QDots	Tunable green to red	30 - 50	Narrow band	Reliability, Reabsorption
InP QDots	Tunable green to red	45 - 65	Narrow band	Reliability, Reabsorption
Direct red LEDs	Tunable red	25 - 35	No Stokes loss Narrow band	Strong TQ, more complex
K <sub>2</sub> (Ta,Nb)F <sub>7</sub> :Mn	628	Lines < 2 nm	Very narrow band, stability?	Moderate absorption



Modified from GE, PGS2016, Newport Beach, CA, USA

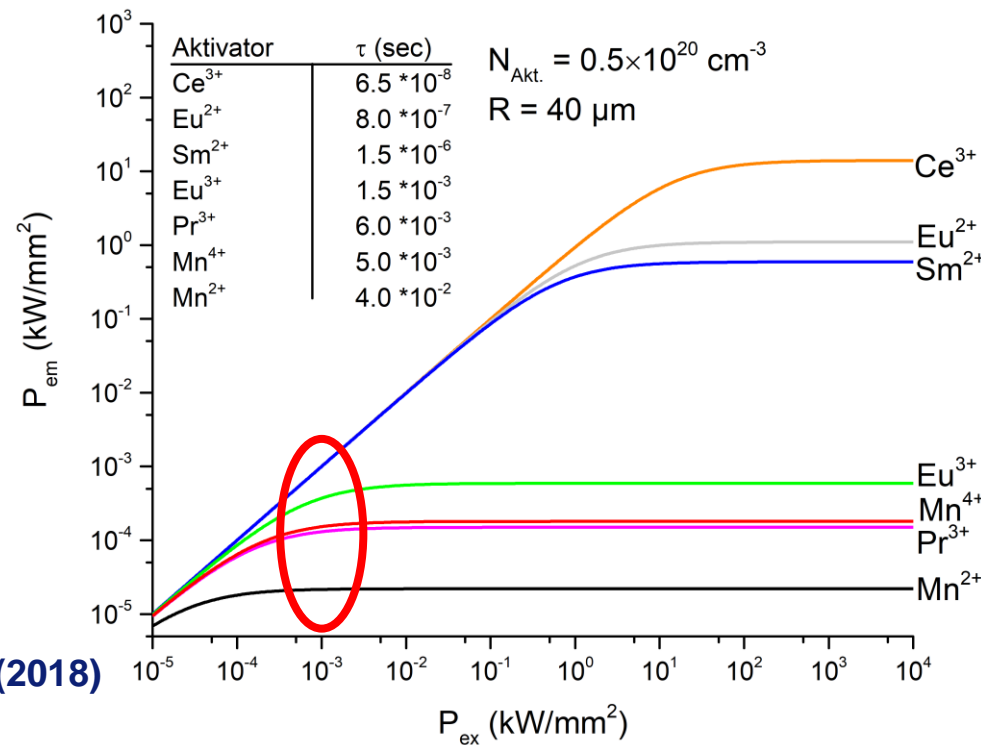
# 6. Lighting Towards Ultimate Efficiency

Red line emitter → Remaining problem: Saturation at ~ 1 W/mm<sup>2</sup>



Brils Modell\*:  $P_{em,max} = N_{act} E_{hv} C_{extraction} R / \tau_r$

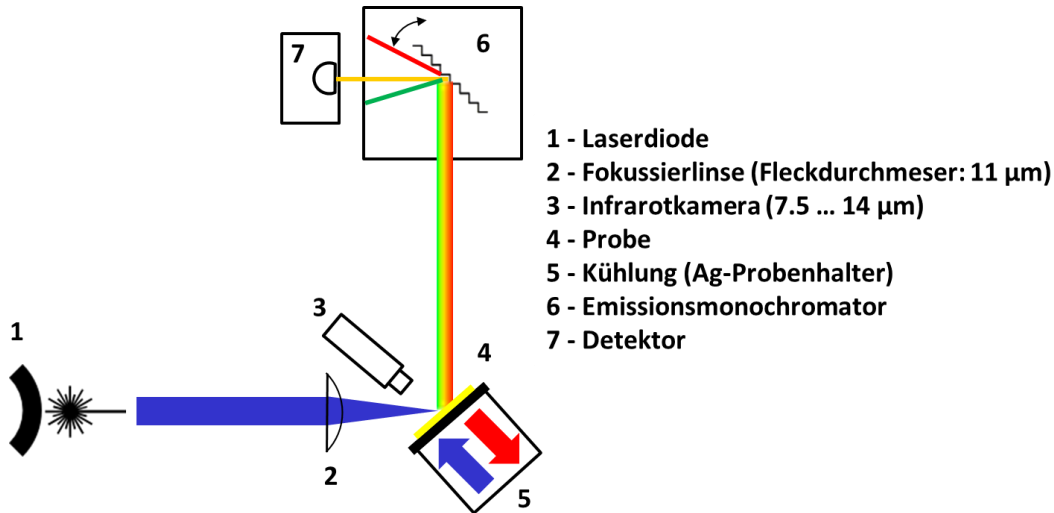
$$\eta = \frac{P_{em}}{P_{abs}} = \frac{\eta_0}{1 + (P_{abs} \eta_0 / P_{em,max})}$$



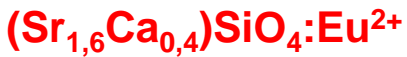
Ref.: Dissertation WWU Münster, Thomas Jansen (2018)  
\*A. Bril, Physica 15 (1949) 361-379



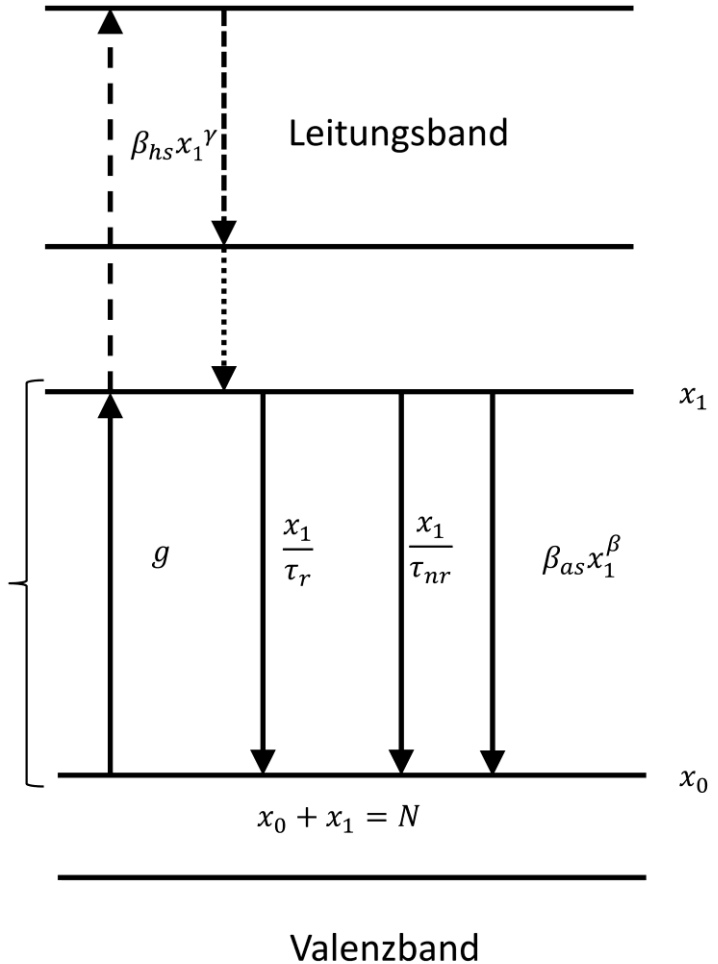
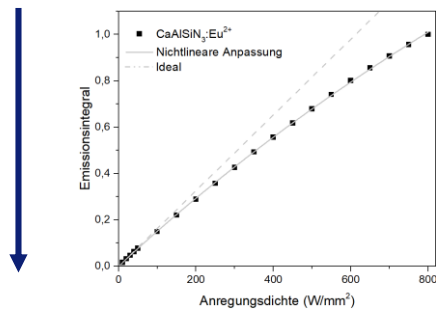
# 6. Lighting Towards Ultimate Efficiency



**Saturation by photoinsation**



$E_g$



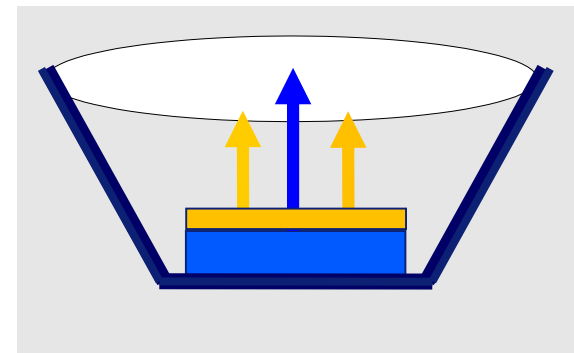
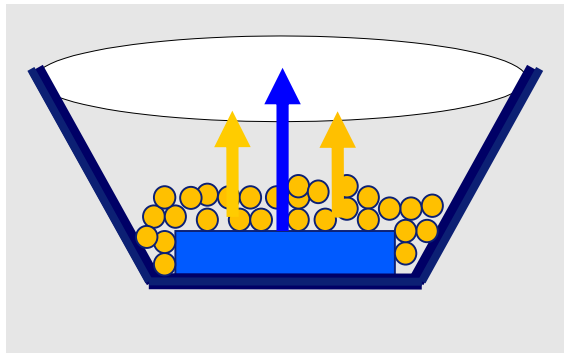
*T. Jansen, D. Böhnisch, T. Jüstel, On the Photoluminescence Linearity of  $\text{Eu}^{2+}$  based LED Phosphors upon High Excitation Density, ECS J. Solid State Sci. Technol. 5 (2016) R91*

# 6. Lighting Towards Ultimate Efficiency

**Morphology of converter:  $\mu$ -powders  $\rightarrow$  Nanopowders or ceramics**

Blue (In,Ga)N LED + YAG:Ce  $\mu$ -powder  
(many products, industrial standard)

Blue (In,Ga)N LED + (Y,Lu)AG:Ce  
ceramic body (Philips: Lumiramic,  
Osram: c<sup>2</sup>, Schott)



$\rightarrow$  (Y,Gd)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce (Y,Gd)AG

$\rightarrow$  SrSi<sub>2</sub>N<sub>2</sub>O<sub>2</sub>:Eu SSONE

$\rightarrow$  Ba<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu BSSNE

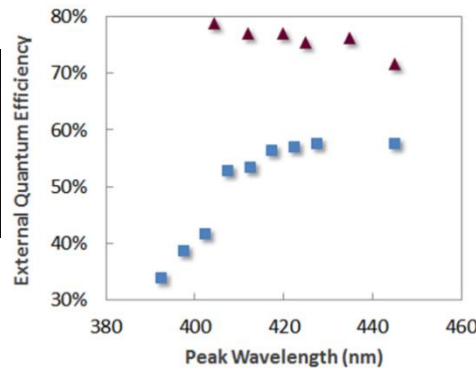
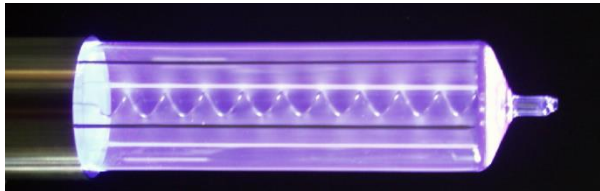
$\rightarrow$  CaAlSiN<sub>3</sub>:Eu eCAS



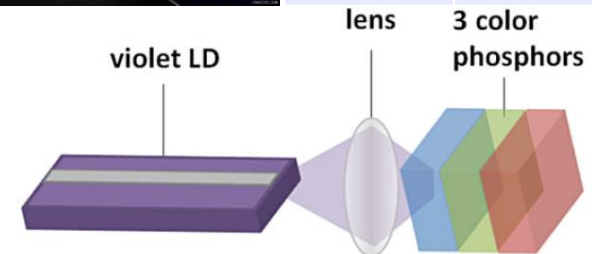
# 7. Summary and Outlook

## 21<sup>st</sup> Century Light/Radiation Sources

Parameter	Xe Excimer Discharge	LED	Laser Diode (LD)
Power density	1-10 W/cm <sup>2</sup>	100-1000 W/cm <sup>2</sup>	> 1000 W/cm <sup>2</sup>
Spectral range	170 - 700 nm	210 - MIR	210 - MIR
Life time	> 10000 h	> 30000 h	> 10000 h
Application areas	<i>Plasma displays Disinfection Purification Photochemistry Lithography</i>	<i>Illumination Photopolym. Photomedicine Agriculture Automotive Aviation</i>	<i>Projection Data transfer Photomedicine Signalling Automotive Photophysics</i>



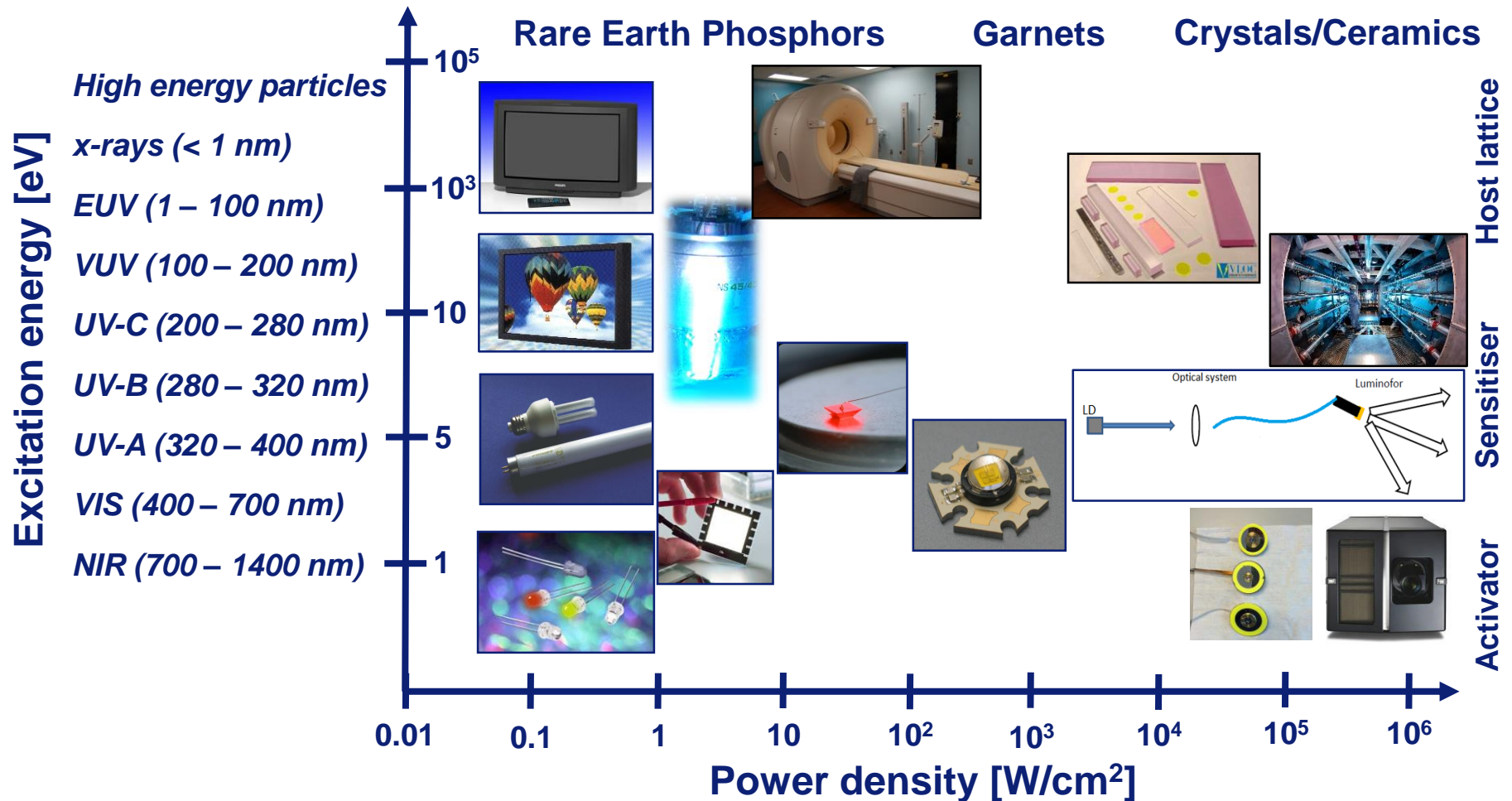
Wi-Fi	Li-Fi
10 <sup>9</sup> Hz	10 <sup>14</sup> Hz
7 Gb/s	3 Tb/s



Ref.: C. Hurni et al., Applied Physics Letters 106, 031101 (2015)

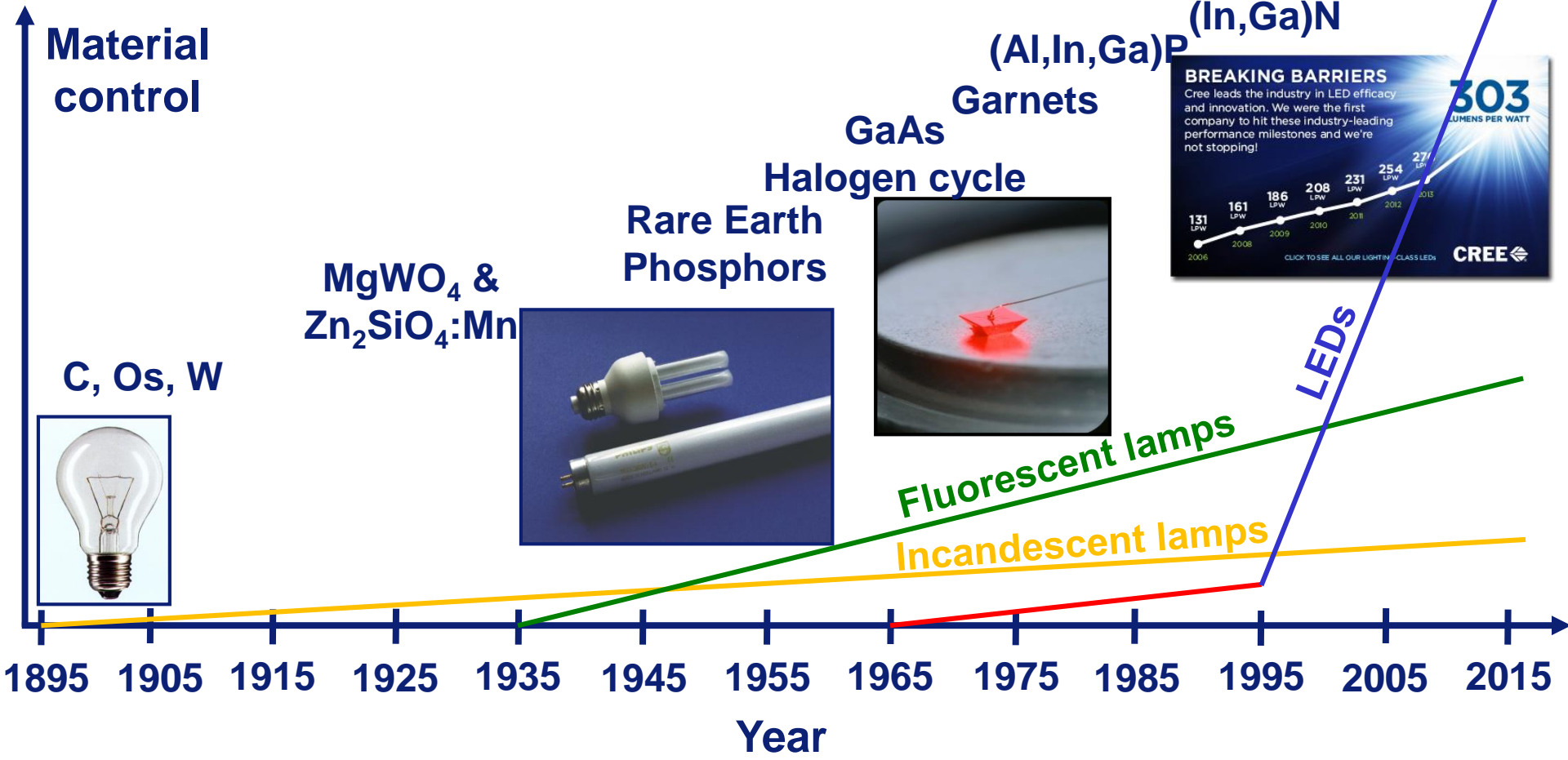
# 7. Summary and Outlook

Increase of energy density drives search for novel materials



# 7. Summary and Outlook

## Development of light sources driven by material science



# 7. Summary and Outlook

## Demands on converter materials & photo catalysts

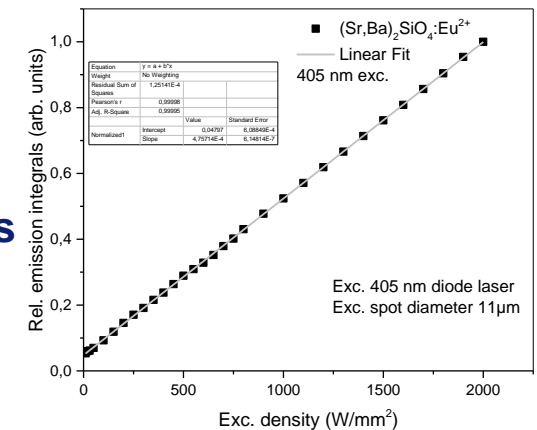
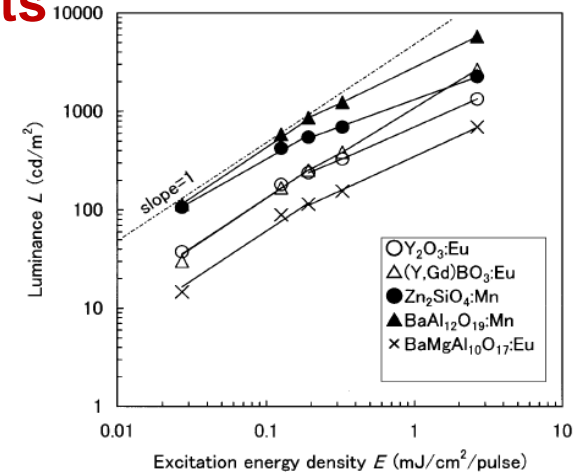
⇒ Materials with

- High thermal quenching temperature
- Reduced (photo)chemical aging
- Increased linearity and thus absorption strength
- Reduced tendency for photoionisation

⇒ Rigid host materials with high thermal conductivity, little thermal expansion, low defect density and optimised  $e^-/h^+$  mobility

⇒ Future activities

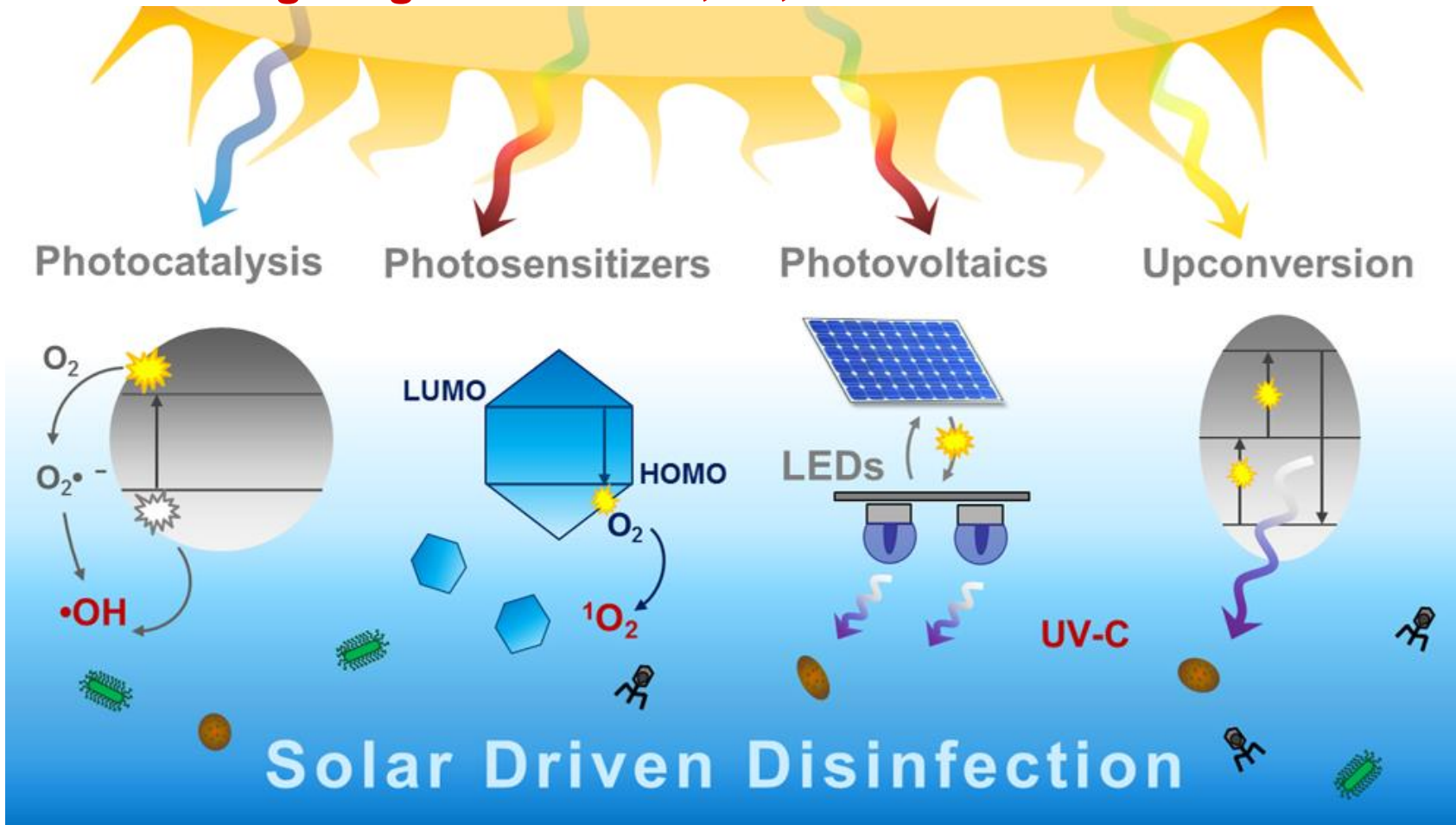
- Development of suitable analytical tools and spectroscopy
- Link CF- and JO-theory to predict intens. of 4f-4f transitions
- Find rigid hosts for VUV, UV-C or, x-ray excitation
- Develop core-shell particles & translucent ceramics
- Photochemistry with excimer lamps, LEDs, and Laser
- Photochemical processes for nanoscale coatings



Ref.: T. Jansen, D. Böhnisch, T. Jüstel,  
ECS J. of Solid State Science and  
Technology 5 (2016) R91

# 7. Summary and Outlook

**Trend: Use solar light & combine with traditional light sources, e.g. for indoor lighting and/or water, air, and surface disinfection**

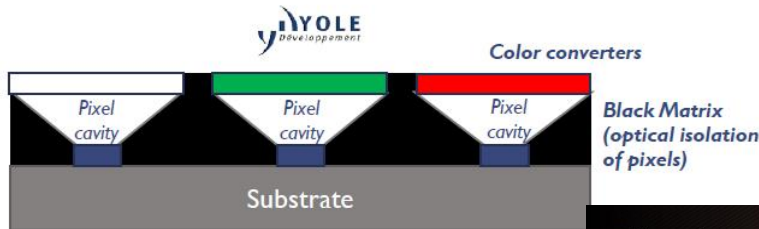
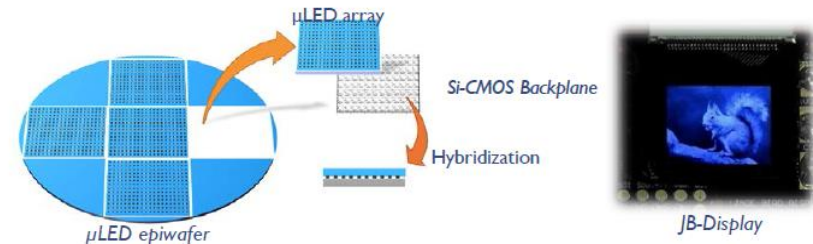
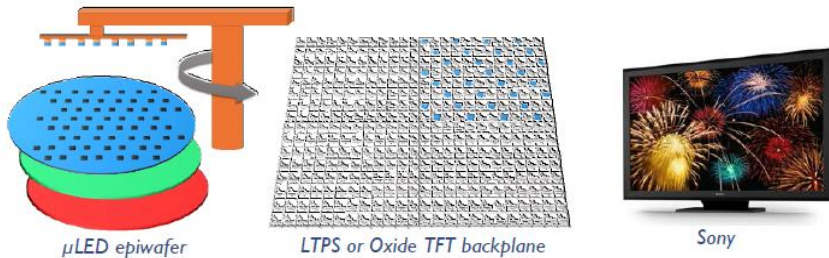


# 7. Summary and Outlook

## Trend: Micro LEDs for next generation displays (beyond LCD and OLED)

Large displays with low pixel densities  
(TV, smartphones...):  
R,G,B LED or Blue + color converter

High resolution/pixel density integrated arrays  
for microdisplays (AR/MR/VR):

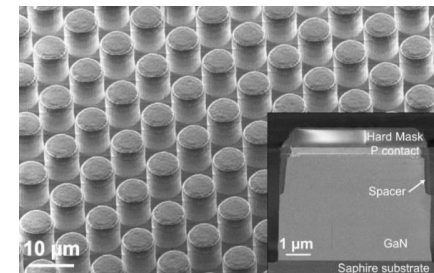


Ref.: Eric Virey, YOLE,  
Phosphor Global Summit,  
March 2018, San Diego, CA  
Energy efficient μ-LEDs  
cinemas are under construction  
worldwide

Companies scrambling for Micro LED patents

Micro LED supply chain			
LED	Mass Transfer	Driver IC	Panel
EPSTAR	LuxVue	Macroblock	Samsung Display LG Display
OSRAM	X-Celeprint	Himax	AUO INNOLUX
Nichia	Leti	Raydium	Sharp Sony
Lextar	ITRI	Novatek	BOE CSOT
PlayNitride	Mikro Mesa		

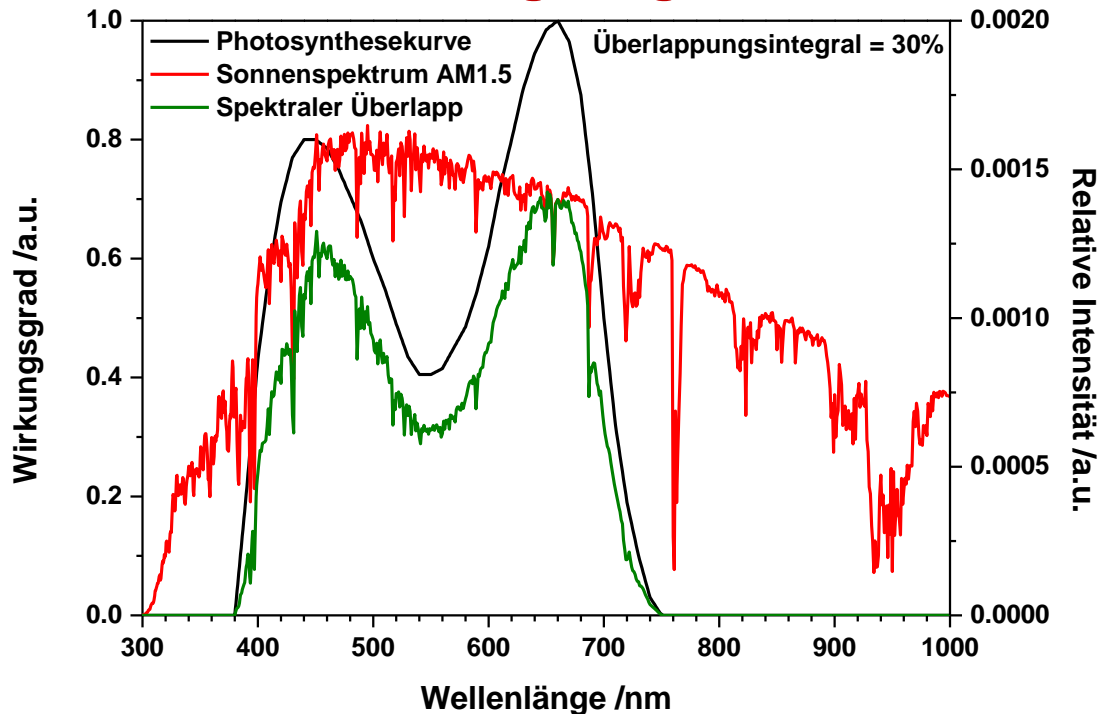
Currently, the Micro LED supply chain is slowly shaping up. Apart from major LED giants, driver IC makers, and display behemoths, a number of startups, including Apple's newly procured display company LuxVue, and research institutions are also starting their development of Micro LED mass transfer. Here in Taiwan, ITRI and Mikro Mesa, founded by Li-yi Chen, former Vice President of Huaxing Photoelectric Technology, also joins the development of Micro LED.





# 7. Summary and Outlook

## Trend: Horticulture Lighting



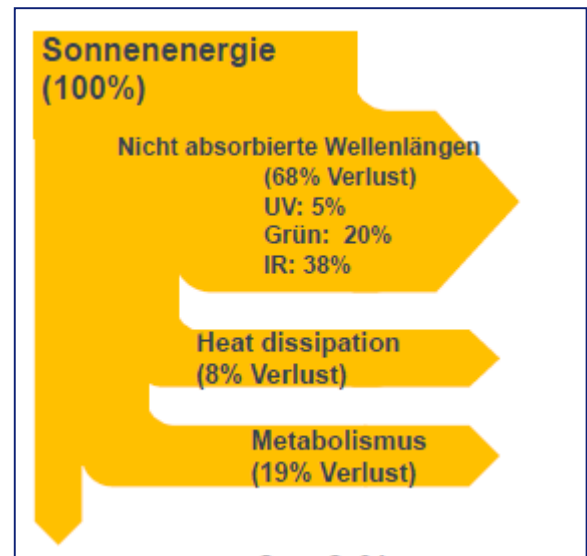
Solar spectrum AM1.5

Overlap integral: 30% → ~ 70% loss

Heat dissipation loss: ~ 8%

Metabolism losses: ~19% →

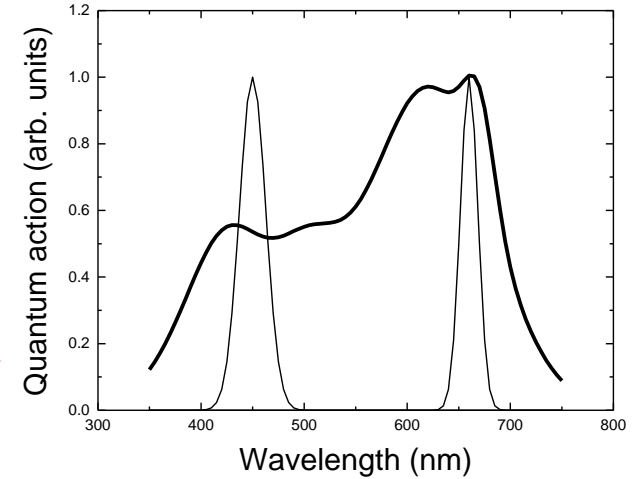
Efficiency ~ 5%



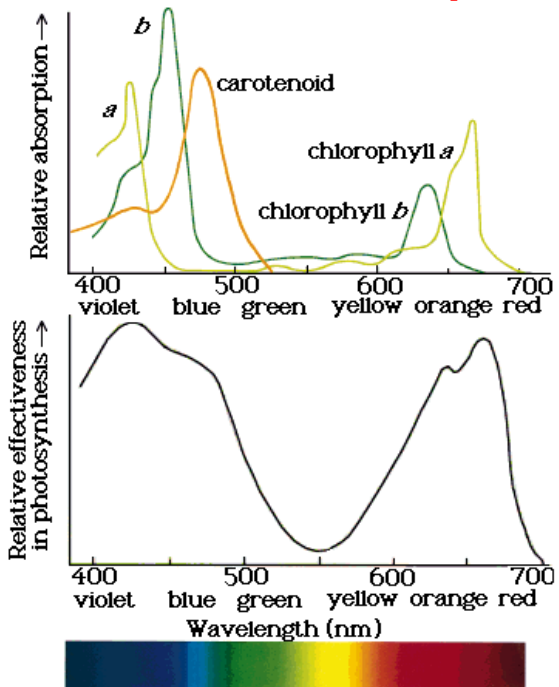
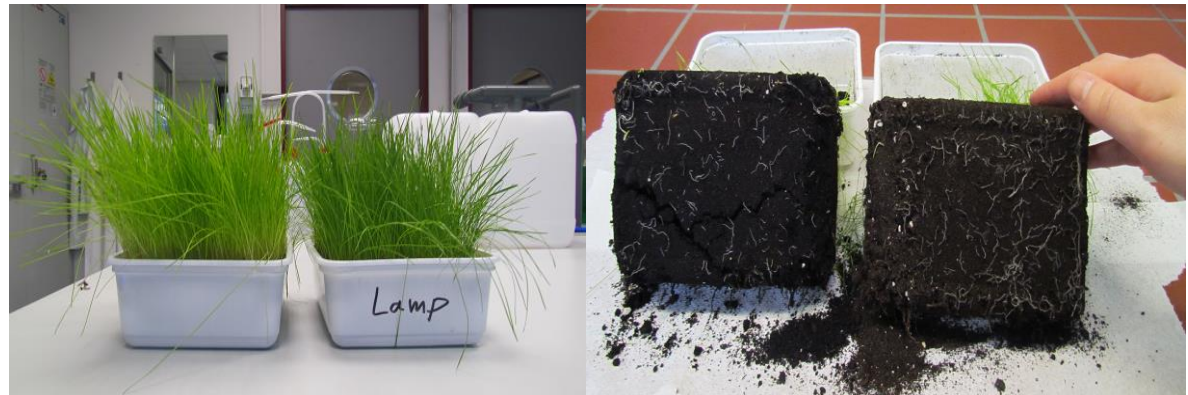
# 7. Summary and Outlook

## Trend: Horticulture Lighting by using LEDs

- Na low-pressure discharge lamps
- Fluorescent lamps with RB phosphor blend
- Blue and red LEDs
- **Blue LEDs + red phosphor (~ 680 nm) → Efficacy↑**

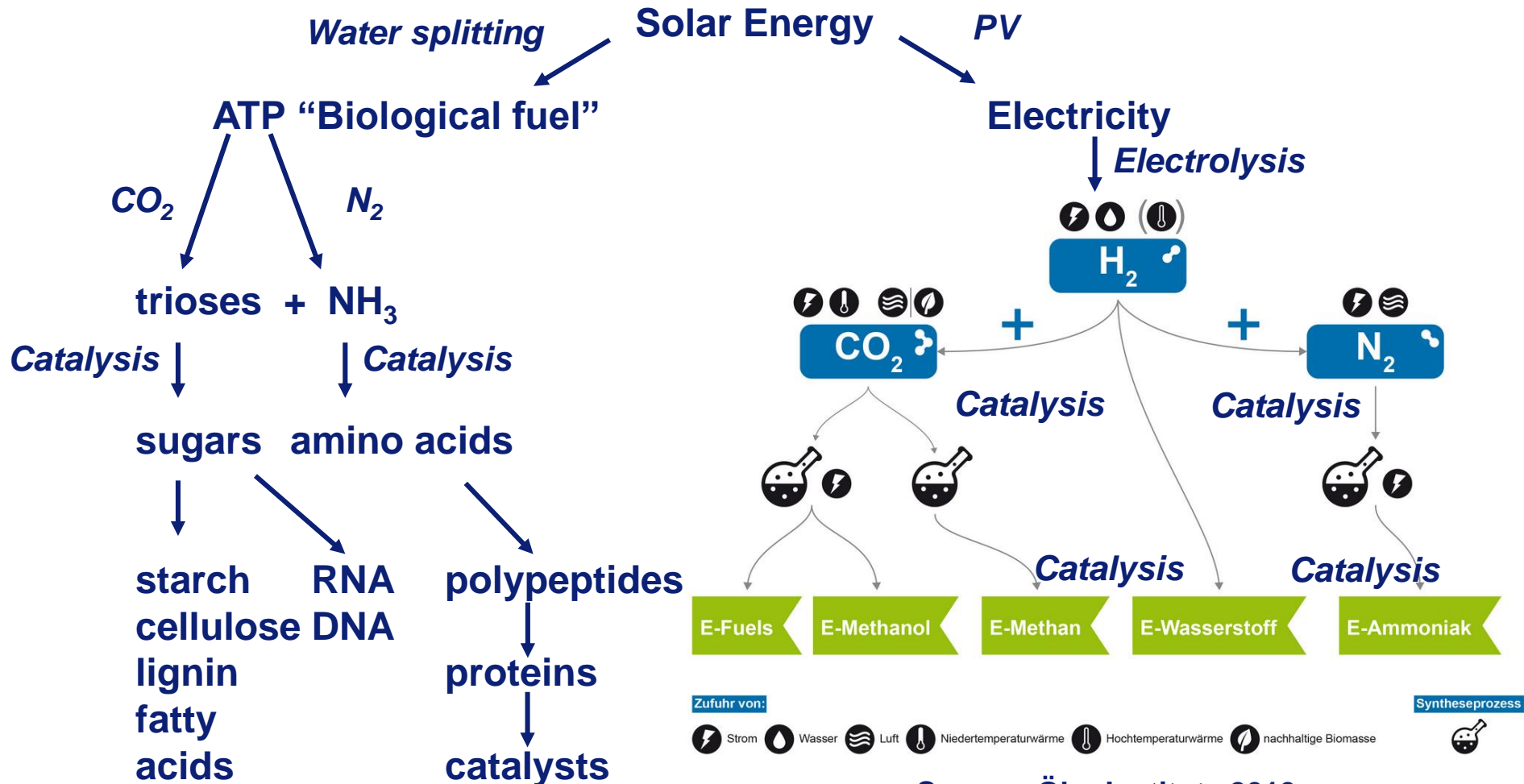


Grass cultivated upon daylight or upon LED illumination  
 Daylight (left vessel) and LED illumination (right vessel)  
 Plants Roots



# 7. Summary and Outlook

**Trend: „Biomimetic economy“**



Source: Öko-Institute 2019

# Literature

## Internet-Links

- Homepage T. Jüstel (Download-Portal, PISA & LISA) [www.fh-muenster.de/juestel](http://www.fh-muenster.de/juestel)

## Further Reading

- T. Jüstel, H. Nikol, C.R. Ronda, New Developments in the Field of Luminescent Materials for Lighting and Displays, *Angew. Chem.* 110 (1998) 3250
- T. Jüstel, H. Nikol, Optimization of Luminescent Materials for Plasma Display Panels, *Adv. Materials* 12 (2000) 527
- M. Born, T. Jüstel, Elektrische Lichtquellen, *Chemie in unserer Zeit* 40 (2006) 294
- H. Hummel, P.K. Bachmann, T. Jüstel, J. Merikhi, C.R. Ronda, V. Weiler, Near-Infrared Luminescent Nano Materials for In-Vivo Optical Imaging, *J. Nanophotonics* 2 (2008) 021920
- T. Jüstel, S. Möller, H. Winkler, W. Adam, Luminescent Materials in Ullmann's Encyclopedia of Industrial Chemistry, Vol. A1-28, Wiley-VCH (2012)
- M. Kubus, D. Enseling, T. Jüstel, H.-Jürgen Meyer, Synthesis and Luminescent Properties of Red-Emitting Phosphors:  $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$  and  $\text{ZnGeF}_6 \cdot 6\text{H}_2\text{O}$  Doped with  $\text{Mn}^{4+}$ , *J. Luminescence* 137 (2013) 88
- T. Jüstel, Anorganische Leuchtstoffe und LEDs, *CHEManager* 5 (2017)
- J. Chen, S. Loeb, J-H. Kim, LED Revolution: Fundamentals and Prospects for UV Disinfection Applications, *Envir. Sci.: Water Res. Technol.* 3 (2017) 188
- T. Jansen, M. Kirm, M.G. Brik, S. Vielhauer, M. Oja, N.M. Khaidukov, V.N. Makhov, T. Jüstel, *ECS JSSST* 7 (2018) R3086
- R. Pöttgen, T. Jüstel, C. Strassert, Rare Earth Element Chemistry, Wiley-VCH (2020)

# Literature

## Further Reading

- Influence of Carbonic Acid upon Temperature of the Ground (Phil. Mag. J. Science 41 (1896) 237) !!!
- H<sub>2</sub> aus H<sub>2</sub>O und Sonnenenergie (Bulletin SEVVSE 24-25 (2005) 11)
- CO<sub>2</sub>-storage by silicate chemistry (Energy Procedia 1 (2009) 3149)
- Global Hg Emissions to the atmosphere (Atmos. Chem. Phys. 10 (2010) 5951)
- Extreme melt on Canadas Arctic ice caps in the 21st century (Geophys. Res. Lett. 38 (2011) L11501)
- September Arctic sea ice predicted to disappear near 2°C global warming above present (J Geophys Res 117 (2012) D06104)
- Global warming releases microplastic legacy frozen in Arctic Sea ice (Earths Future 2 (2014) 315)
- Global oxygen budget and its future projection (Science Bull. 63 (2018) 1180)
- The Information Factories (Nature 561 (2018) 163)
- Kunststoffe in der Umwelt (Fraunhofer Umsicht Juni 2018)
- Arctic sea ice is an important temporal sink for microplastic (Nature Comm. (2018) 1)
- Plastic degradation in cold marine habitats (Appl. Microbiol. Biotech. 102 (2018) 7669)

# Literature

## Further Reading

- **Ecotoxicity of the two veterinarian antibiotics ceftiofur and cefapirin before and after phototransformation (Science Total Environment 619-620 (2018) 866)**
- **Existential climate-related security risk (Policy Paper May 2019)**
- **CO<sub>2</sub>-Das Klimagas vergraben (Spektrum der Wissenschaft 7 (2019) 62)**
- **Rapid increase in Asian bottles in the South Atlantic Ocean (PNAS (2019) 1)**
- **Assessing Plastic Ingestion from Nature to People (Dalberg WWF analysis (2019) 1)**
- **UN Report: Nature's Dangerous Decline Unprecedented; Species Extinction Rates Accelerating (2019)**
- **New elevation data triple estimates of global vulnerability to sea-level rise and coastal flooding (Nature Commun. 10 (2019) 4844)**
- **Four Decades of Antarctic Ice Sheet Mass Balance from 1979-2017 (PNAS 116 (2019) 1097)**
- **How hot will earth get until 2100? (Nature 580 (2020) 444)**
- **Permian–Triassic mass extinction pulses (Nature Geosciences (2020))**
- **Global food system emissions could preclude achieving the 1.5 and 2 °C climate change targets (Science (2020))**
- **Global human-made mass exceeds all living biomass (Nature (2020))**