

# Optical Characterisation of Materials

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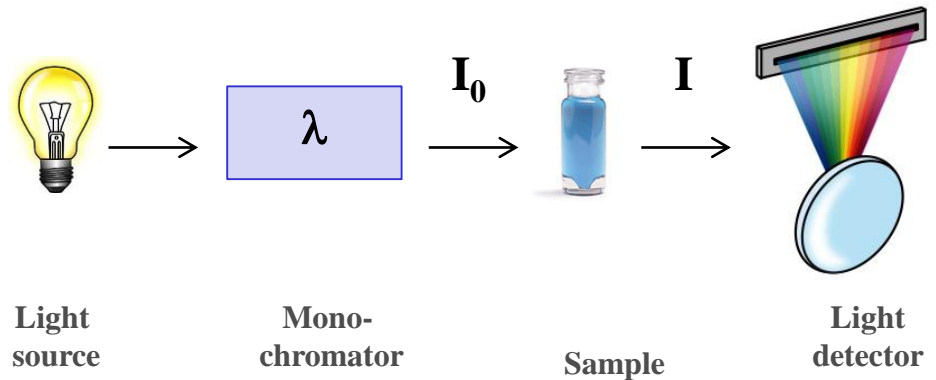
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### 4. Methods of Optical Material Characterization

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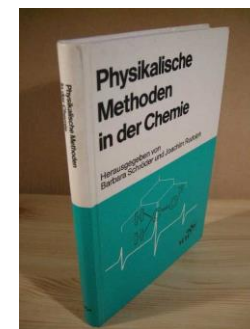
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# Literature

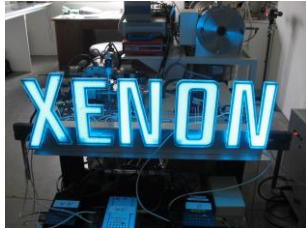
- **B. Schröder, J. Rudolph**  
**Physikalische Methoden in der Chemie, VCH, 1985**
- **H. Naumer, W. Heller**  
**Untersuchungsmethoden in der Chemie, Georg Thieme Verlag, 1990**
- **E.A.V. Ebsworth, D.R.H. Ranklin, S. Cradock,**  
**Structural Methods in Inorganic Chemistry, Blackwell Scient. Publications, 1991**
- **W. Schmidt**  
**Optische Spektroskopie, VCH, 1993**
- **M. Hesse, H. Meier, B. Zeeh**  
**Spektroskopische Methoden in der organischen Chemie, VCH, 2005**
- **J.B. Lambert, S. Gronert, H.F. Shurvell, D.A. Lightner**  
**Spektroskopie - Strukturaufklärung in der organischen Chemie, Pearson, 2012**



# Relevance of Optical Spectroscopy

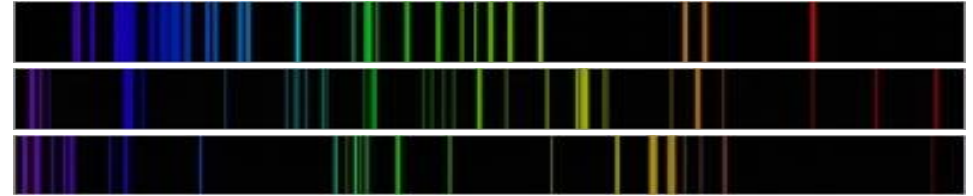
**Optical Radiation: UV, visible, and IR radiation ~ 10 nm - 1000 μm (THz - PHz)**

- Fingerprint of the elements



As  
Pb  
Hg

(Astro)physics, analytical chemistry (OES)



- Determination of elements or molecules

Analytical chemistry: Photometry, AAS, OES

- Characterisation of molecules

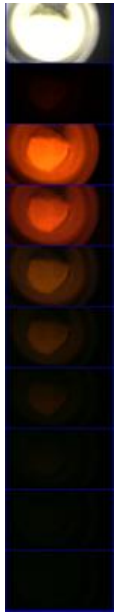
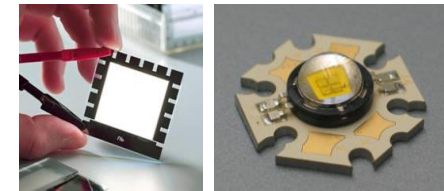
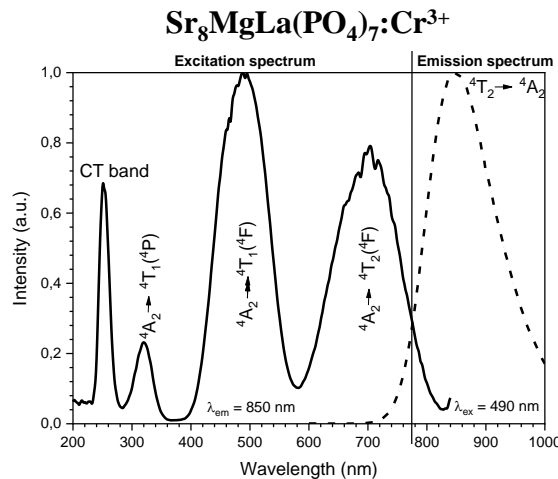
Physics, chemistry, biochemistry

- Characterisation of materials

- Pigments
- Luminescent materials
- Scintillators

- Characterisation of devices

- Light sources
- IR and UV sources
- Displays



# 1. Methods of Material Characterization

## 1. Chemical composition

<b>Elementary analysis</b>	<b>Main and secondary components</b>
<b>X-ray fluorescence analysis</b>	<b>Main and secondary components</b>
<b>Atomic absorption spectroscopy</b>	<b>Trace elements, dopants</b>
<b>Powder diffractometry</b>	<b>Phase composition</b>
<b>Infrared spectroscopy (IR)</b>	<b>Detection of functional groups</b>
<b>Raman spectroscopy</b>	<b>Detection of functional groups</b>
<b>Differential thermal analysis</b>	<b>Phase transformations, crystallization water</b>

## 2. Morphological characterization (micro and nanostructure)

<b>(Dynamic) Light scattering</b>	<b>Particle size distribution</b>
<b>Optical microscopy</b>	<b>Particle morphology</b>
<b>Scanning electron microscopy</b>	<b>Particle size distribution, surface structure</b>
<b>Transmission electron microsc.</b>	<b>Crystallinity, texture</b>
<b>BET-isotherm</b>	<b>Specific surface area</b>

# 1. Methods of Material Characterization

## 3. Structural characterization

<b>Powder diffractometry</b>	<b>Phase identification, crystal system, space group</b>
<b>X-ray structure analysis</b>	<b>Space group, atomic coordinates</b>
<b>X-ray absorption spectroscopy</b>	<b>Chemical environment of heavy atoms</b>
<b>NMR spectroscopy</b>	<b>Molecular structure</b>
<b>Infrared spectroscopy (IR)</b>	<b>Molecule identification</b>
	<b>Arrangement of functional groups</b>
<b>Raman spectroscopy</b>	<b>Arrangement of functional groups</b>
<b>Resonance-Raman spectroscopy</b>	<b>Arrangement of functional groups</b>

## 4. Surface characterization

<b>Electrosonic Amplitude (ESA)</b>	<b>Surface charge, isoelectric point</b>
<b>Mass spectroscopy (SIMS)</b>	<b>Adsorption of organic molecules at surfaces</b>
<b>X-ray photoelectron spectroscopy (ESCA/XPS)</b>	<b>Surface composition</b>

# 1. Methods of Material Characterization

## 5. Determination of physical properties

### Electronic properties

Absorption spectroscopy

EPR spectroscopy

Mössbauer spectroscopy

Ultraviolet photoelectron spectroscopy (UPS)

Electronic ground state

Oxidation states, electronic ground state

Oxidation states, coordination geometry

Band structure

### Optical properties

Absorption spectroscopy

Reflectance spectroscopy

Luminescence spectroscopy

Absorption coefficient, electronic ground state

Band gap, color point

Excitation and emission spectrum

Color point

Quantum efficiency

Luminous efficacy

Thermal quenching



### Magnetic properties

Susceptibility measurement

NMR spectroscopy

Dia-, para-, ferro-, ferri-, antiferromagnetism

Ground state

# 2. Physical Basis

**2.1 Classification of Optical Spectroscopy**

**2.2 The Electromagnetic Spectrum**

**2.3 Time Scale of Physical Processes**

**2.4 Interaction of Light and Matter**

**Types of Electromagnetic Interaction**

**Electronic States in Atoms**

**Electronic States in Solids**

**Reflection**

**Absorption**

**Refraction**

**Luminescence**

**2.5 Radiometric Quantities**

**2.6 Photometric Quantities**

**2.7 Photosynthetically Active Radiation**

# 2.1 Classification of Optical Spectroscopy

## Optical spectroscopy

### Absorption

Atom-Absorption  
(AAS)

Molecule-Absorption  
(UV/Vis/NIR)

### Reflection

Scattering  
(Raman,  
Rayleigh)

### Luminescence

Excitation

Emission

Luminescence  
spectroscopy

Energy resolved

Excitation spectrum

Temperature resolved

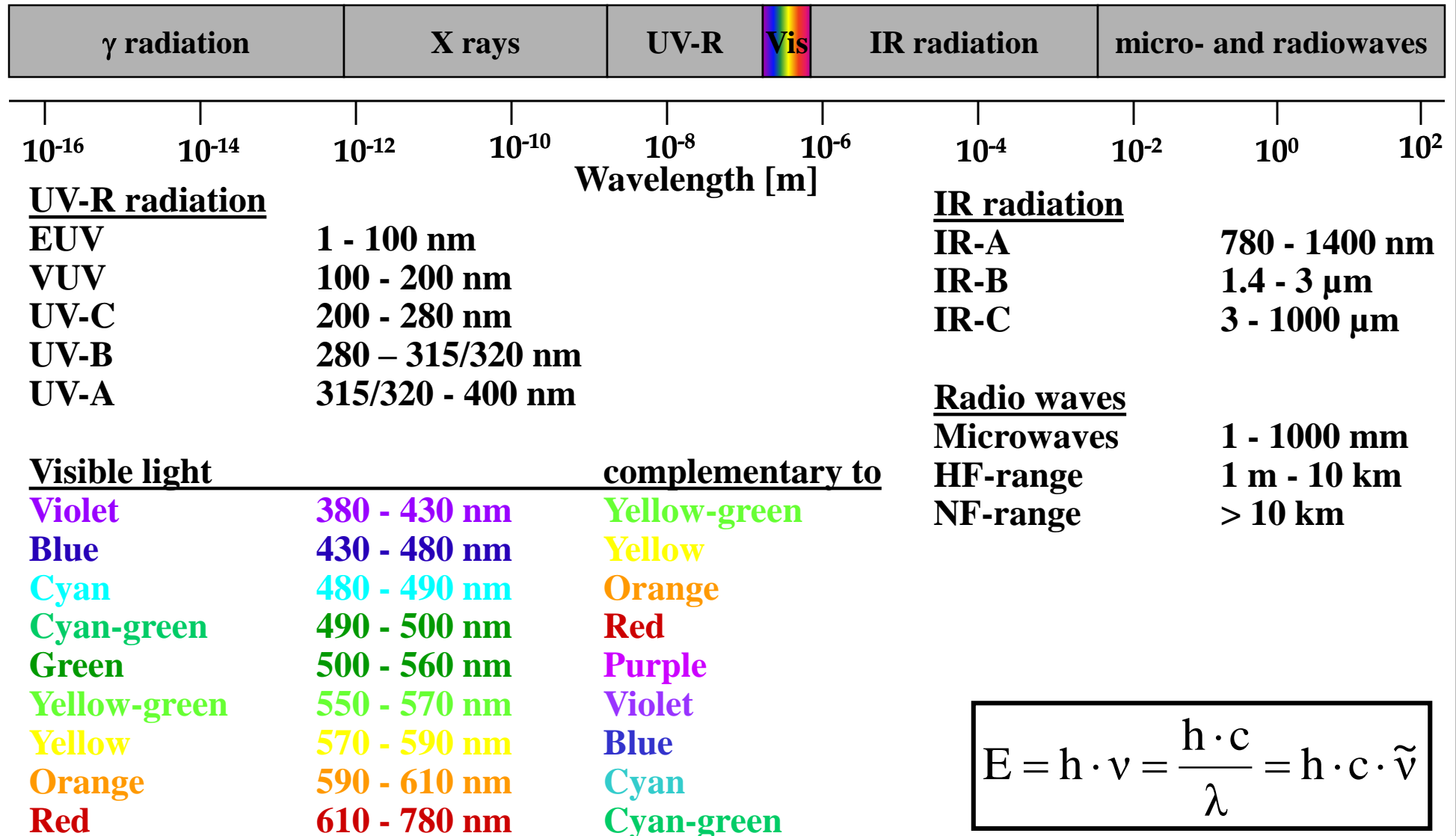
Defect or thermo luminescence  
Thermal quenching

Time resolved

Decay curves, persistent  
luminescence, flicker



# 2.2 The Electromagnetic Spectrum



$$E = h \cdot \nu = \frac{h \cdot c}{\lambda} = h \cdot c \cdot \tilde{\nu}$$

# 2.2 The Electromagnetic Spectrum

## Energy of photons

$$E = h\nu \quad h = 6.626 \cdot 10^{-34} \text{ Js}$$

$$E = hc/\lambda \quad c = 2.9979 \cdot 10^8 \text{ m/s}$$

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

The energy is thus proportional to the reciprocal length, to so-called wavenumber  $\tilde{\nu}$

with  $\tilde{\nu} = 1/\lambda$

$$E = h \cdot c \cdot \tilde{\nu}$$

$$= 1.240 \cdot 10^{-4} \cdot \tilde{\nu} [\text{eV}]$$

$$= 1240/\lambda [\text{eV}]$$

or  $1 \text{ eV} \sim 8065 \text{ cm}^{-1}$

## Parameters proportional to energy

1. Frequency  $\nu$  [Hz]
2. Wavenumber  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ]

Wavelength $\lambda$	Frequency $\nu$	Wavenumber $\tilde{\nu}$	Energy E
$10^{-16} \text{ m}$	$3 \cdot 10^{24} \text{ Hz}$	$1 \cdot 10^{14} \text{ cm}^{-1}$	12.4 GeV
$10^{-14} \text{ m}$	$3 \cdot 10^{22} \text{ Hz}$	$1 \cdot 10^{12} \text{ cm}^{-1}$	124 MeV
$10^{-12} \text{ m (1 pm)}$	$3 \cdot 10^{20} \text{ Hz}$	$1 \cdot 10^{10} \text{ cm}^{-1}$	1.24 MeV
$10^{-10} \text{ m}$	$3 \cdot 10^{18} \text{ Hz}$	$1 \cdot 10^8 \text{ cm}^{-1}$	12.4 keV
$10^{-8} \text{ m}$	$3 \cdot 10^{16} \text{ Hz}$	$1 \cdot 10^6 \text{ cm}^{-1}$	124 eV
$10^{-6} \text{ m (1 } \mu\text{m)}$	300 THz	$1 \cdot 10^4 \text{ cm}^{-1}$	1.24 eV
$10^{-4} \text{ m}$	3 THz	$100 \text{ cm}^{-1}$	12.4 meV
$10^{-2} \text{ m}$	30 GHz	$1 \text{ cm}^{-1}$	0.124 meV
$10^0 \text{ m (1 m)}$	300 MHz	$0.01 \text{ cm}^{-1}$	1.24 $\mu\text{eV}$
$10^2 \text{ m}$	3 MHz	$1 \cdot 10^{-4} \text{ cm}^{-1}$	12.4 neV

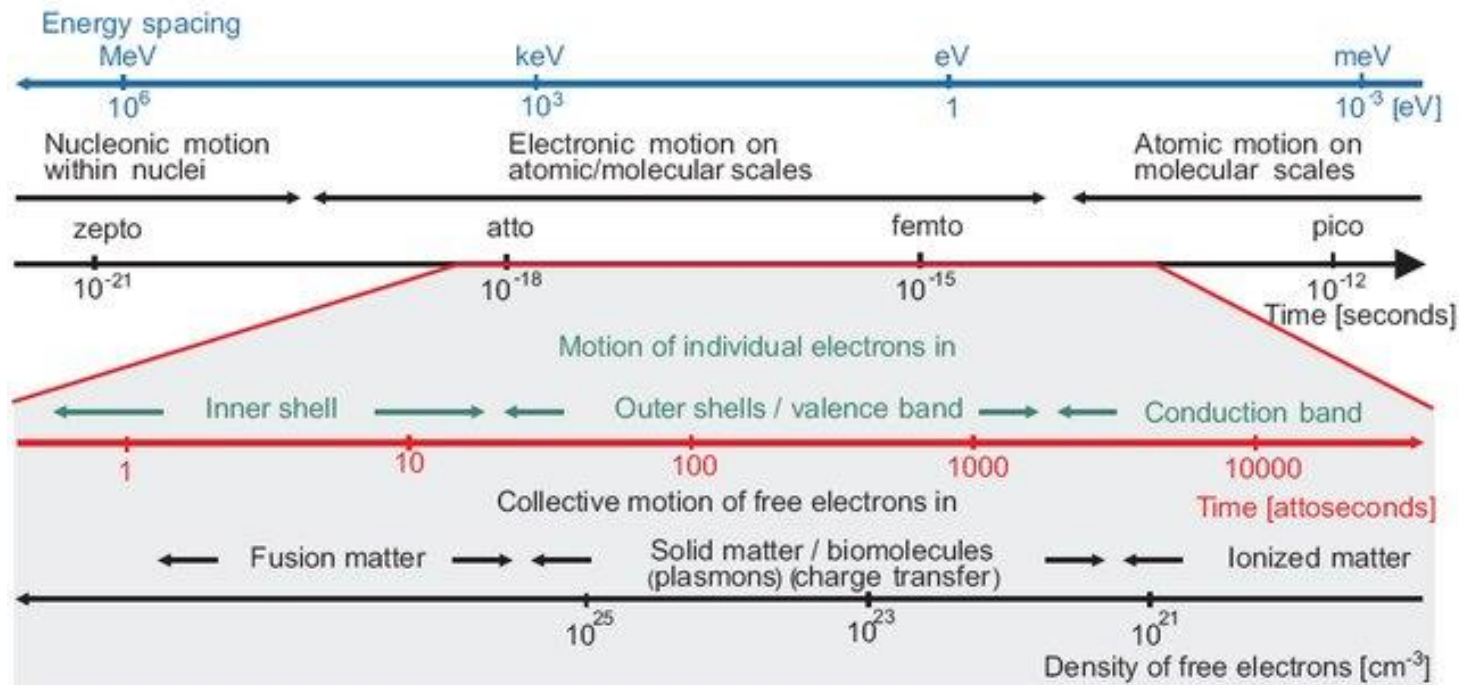
## 2.3 Time Scale of Physical Processes

**Chemical reactions < molecular rotation < molecular vibration < electron motion**

### Franck-Condon Principle

Since the nuclei are much heavier than the electrons, the electronic transition takes place so rapidly that the nuclei have no time to react → Born-Oppenheimer approximation

→ Separation of electron and nucleus motion



Lit.: Ferenc Krausz and Misha Ivanov. Attosecond physics. Reviews of Modern Physics 81 (2019) 163

# 2.4 Interaction of Light and Matter

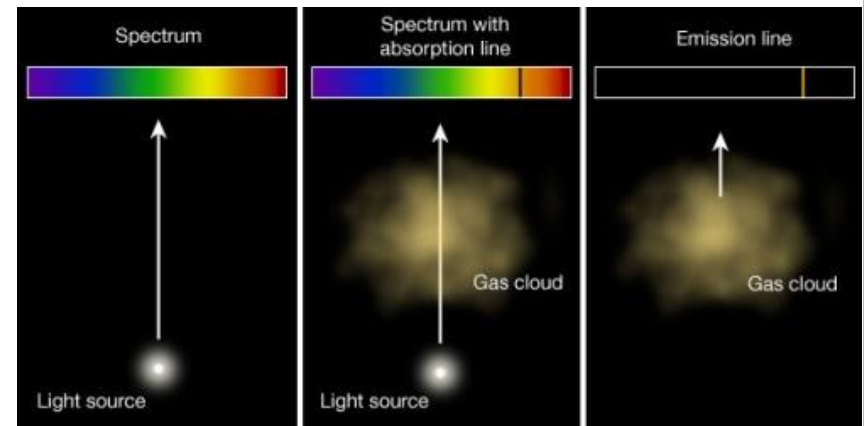
## Types of electromagnetic interaction

Radiation type	Interaction with	Physical process
$\gamma$ -radiation	Nuclei	Excitation of nuclear states
X-rays	Inner electrons	Excitation/diffraction
UV/Vis	Valence electrons	Excitation of electronic states
Infrared	Molecules	Vibrational excitation (phonons)
Microwaves	Molecules, electrons	Spin flip, rotational excitation
Radio waves	Nuclear spin	Spin flip

Macroscopic phenomena: absorption, refraction, emission, reflection (remission), transmission

Energy conservation:  $A + R + T = 1$  or  $E + R + T = 1$

Kirchhoff's law:  $A(\lambda) = E(\lambda)$  (G.R. Kirchhoff 1859)



# 2.4 Interaction of Light and Matter

## Electronic states in multi electron atoms

Atom	Electron configuration	Ground state	First excited state
Na <sup>0</sup>	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>1</sup>	<sup>2</sup> S <sub>1/2</sub>	<sup>2</sup> P <sub>3/2</sub> , <sup>2</sup> P <sub>1/2</sub>
<i>(yellow Na-double line at 589.0 and 589.6 nm ⇒ Spectrometer resolution test)</i>			
Cr <sup>3+</sup>	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 4s <sup>2</sup> 3d <sup>3</sup>	<sup>4</sup> F	<sup>4</sup> P
Ce <sup>3+</sup>	[Xe]4f <sup>1</sup>	<sup>2</sup> F <sub>5/2</sub> , <sup>2</sup> F <sub>7/2</sub>	<sup>2</sup> D
Eu <sup>3+</sup>	[Xe]4f <sup>6</sup>	<sup>7</sup> F <sub>0</sub>	<sup>5</sup> D <sub>0</sub>
Gd <sup>3+</sup>	[Xe]4f <sup>7</sup>	<sup>8</sup> S <sub>7/2</sub>	<sup>6</sup> P <sub>J</sub>

$$S = \sum s$$

$$L = |\sum l|$$

$$J = L+S, L+S-1, \dots |L-S|$$

**Russell-Saunders-Terms (energy levels)**

$$2S+1L_J$$

### Selection rules for electric dipole transitions

1. Spin selection rule  $\Delta S = 0$
  2. Orbital angular momentum  $\Delta l = +/-1, \Delta m_l = 0, +/-1$
  3. Laporte selection rule  $g \rightarrow u, u \rightarrow g, \text{ but not } g \rightarrow g, u \rightarrow u$
- With Russell-Saunders (LS) coupling:**  $\Delta L, \Delta J = 0, +/-1, \text{ but not } J = 0 \rightarrow J = 0$

## 2.4 Interaction of Light and Matter

### Electronic transitions in multi electron atoms

Type		$\epsilon$ [l mol <sup>-1</sup> cm <sup>-1</sup> ]	Example	Electron from	to
s-p transitions	$\Delta l = 1$	$10^3$ - $10^4$	Na <sup>0</sup>	3s	→ 3p
d-d transitions	$\Delta l = 0$	$< 10^2$	Cr <sup>3+</sup>	3d (t <sub>2</sub> )	→ 3d (e)
f-d transitions	$\Delta l = 1$	$10^4 - 10^5$	Ce <sup>3+</sup>	4f	→ 5d
f-f transitions	$\Delta l = 0$	$< 10^2$	Eu <sup>3+</sup>	4f	→ 4f
			Gd <sup>3+</sup>	4f	→ 4f
			Tb <sup>3+</sup>	4f	→ 4f

Forbidden due to large change in orbital angular momentum:

s-d  $\Delta l = 2$

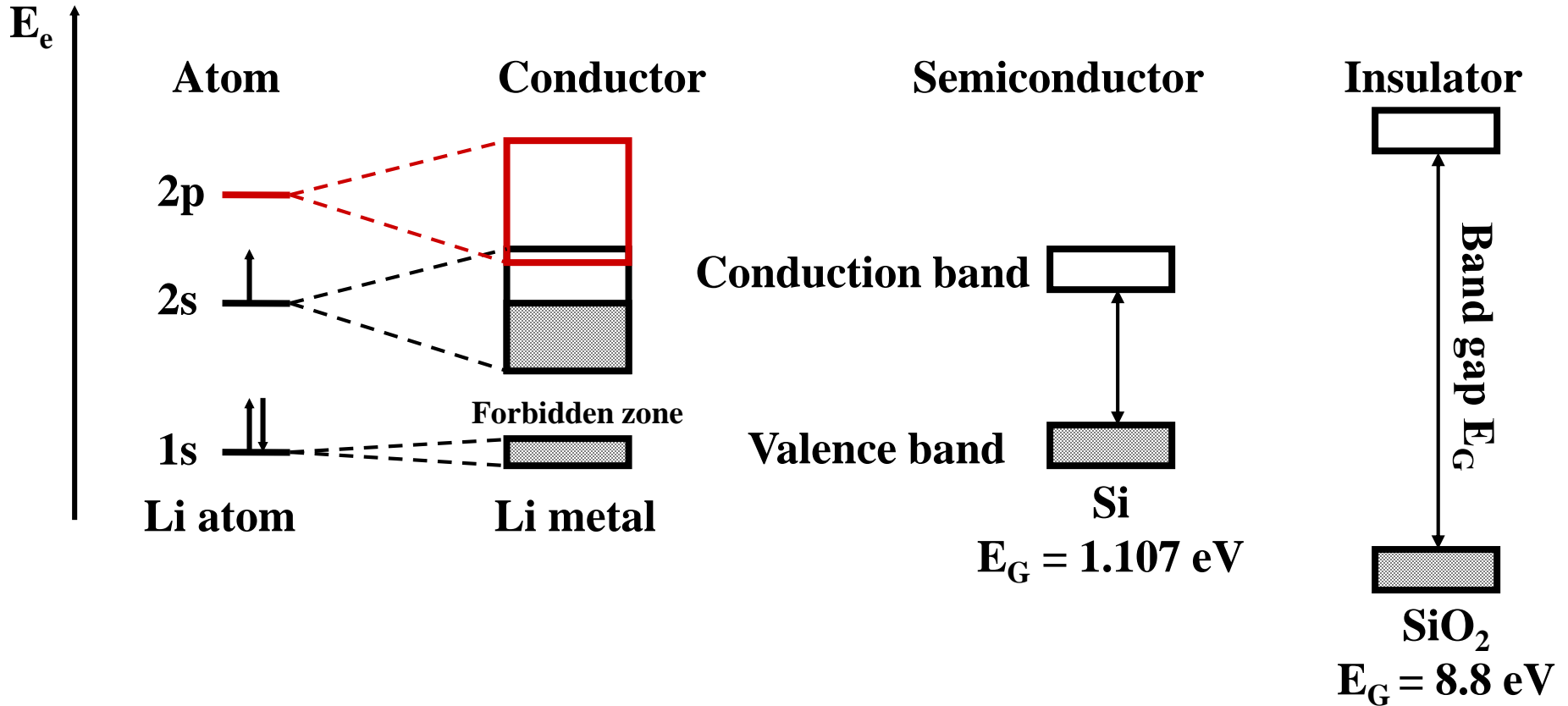
p-f  $\Delta l = 2$

s-f  $\Delta l = 3$  parity allowed

- these transitions are strongly forbidden!

# 2.4 Interaction of Light and Matter

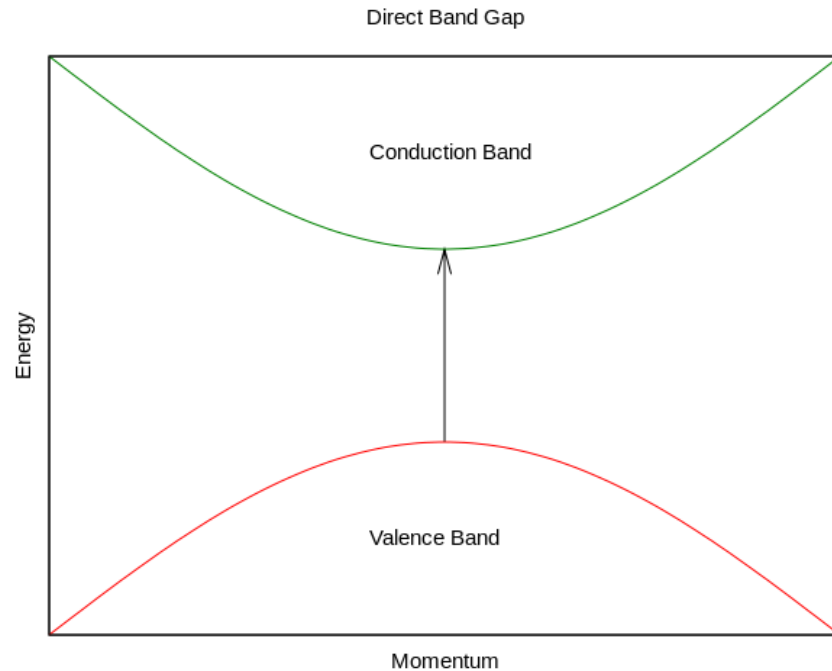
## Electronic states in solids (metals, semiconductors, ceramics)



**Semiconductors are materials with a small band gap ( $< 3.0 \text{ eV}$ ) whose conductivity are increased by structural defects, heating, or by irradiation**

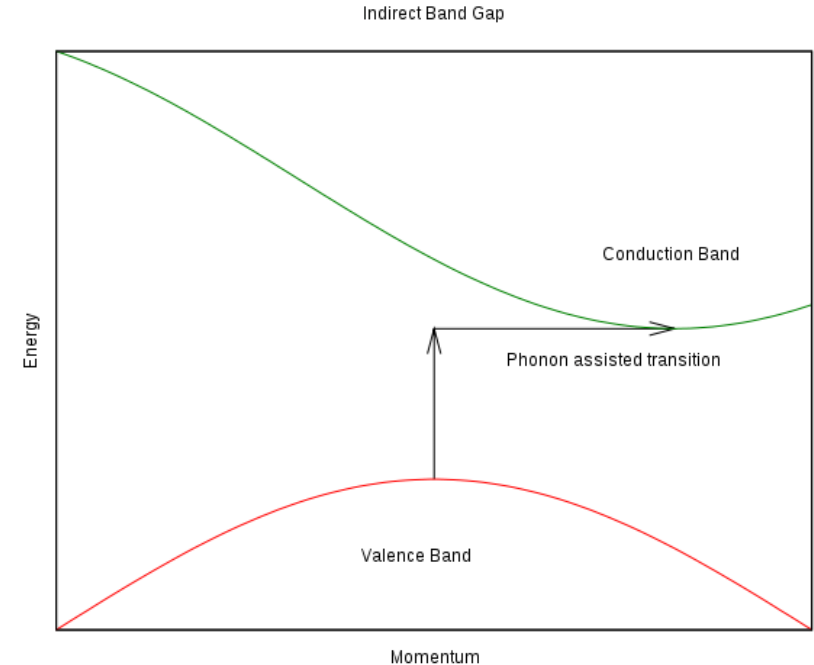
# 2.4 Interaction of Light and Matter

## Electronic states in solids (metals, semiconductors, ceramics)



**Direct semiconductors:**  
**Absorption or emission of a photon**

→ strong: GaAs, GaN



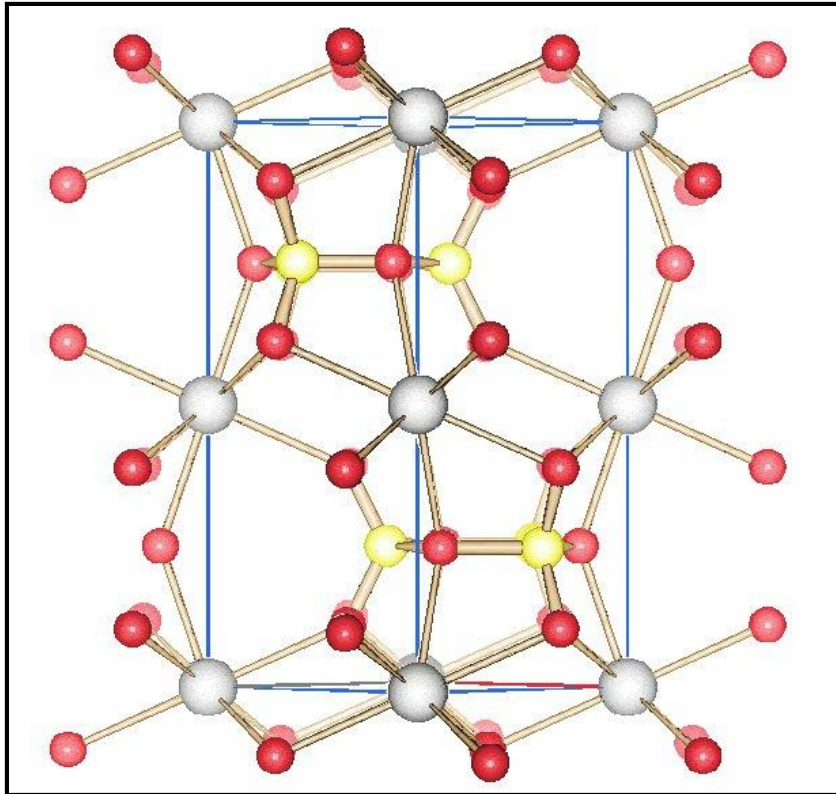
**Indirect semiconductors:**  
**Phonon assisted absorption or emission of a photon**

→ weak: Si, Ge



# 2.4 Interaction of Light and Matter

## Electronic states in solids



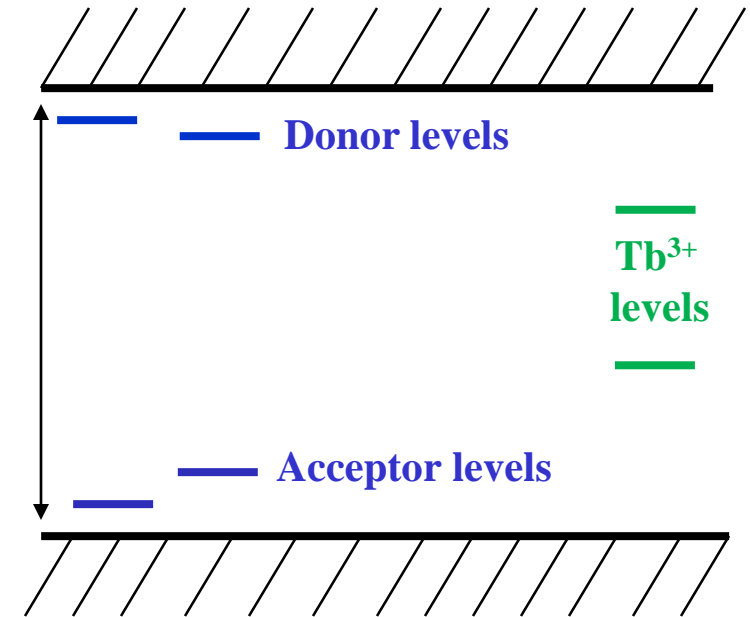
YBO<sub>3</sub> Vaterit

Band gap  $E_g = 6.5$  eV

Conduction band

Band gap  $E_g$

Valence band



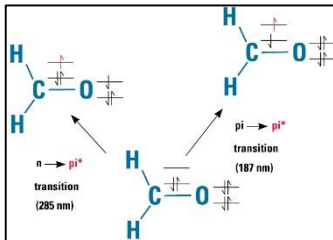
### Absorption by

- Excitation band: valence band-conduction band
- Defects (color centers) “blue ice”
- Transitions between energy levels of dopants (Tb<sup>3+</sup>) or undesired impurities

# 2.4 Interaction of Light and Matter

## Electronic transitions in solids and molecules

Type	$\epsilon$ [l $\text{mol}^{-1}\text{cm}^{-1}$ ]	Example	Transition type
Band gap transitions	$10^5 - 10^6$	TiO <sub>2</sub>	O <sup>2-</sup> $\rightarrow$ Ti <sup>4+</sup> (VB $\rightarrow$ CB)
CT transitions	$10^4 - 10^6$	WO <sub>4</sub> <sup>2-</sup>	O <sup>2-</sup> $\rightarrow$ W <sup>6+</sup> „LMCT“
		Fe(CO) <sub>5</sub>	Fe <sup>0</sup> $\rightarrow$ CO „MLCT“
		KFe[Fe(CN) <sub>6</sub> ]	Fe <sup>2+</sup> $\rightarrow$ Fe <sup>3+</sup> „MMCT“
		[(cp) <sub>2</sub> Zr(biq)] <sup>2+</sup>	cp <sup>-</sup> $\rightarrow$ biq „LLCT“
$\sigma \rightarrow \sigma^*$	$> 10^3$	CH <sub>4</sub>	HOMO $\rightarrow$ LUMO
$\pi \rightarrow \pi^*$	$10^4 - 10^6$	Butadiene	HOMO $\rightarrow$ LUMO
$n \rightarrow \pi^*$	$10^1 - 10^2$	(CH <sub>3</sub> ) <sub>2</sub> C=O	HOMO $\rightarrow$ LUMO



### In addition

- Excitation of vibrational states, i.e. phonons in the solid state or valence and deformation vibrations in molecules
- Excitation of rotational states (only molecules)

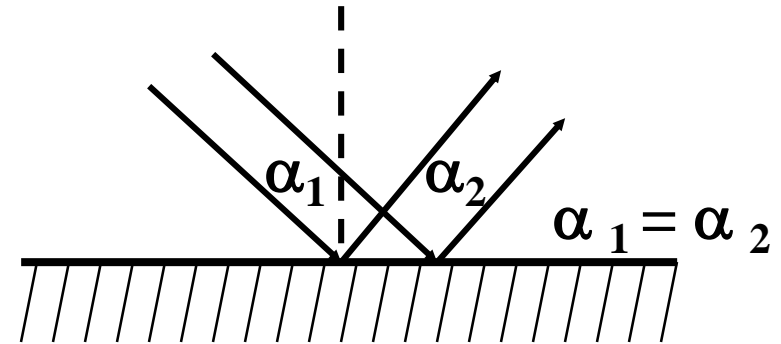
# 2.4 Interaction of Light and Matter

## Reflection

### Specular reflection (regular)

Reflection from a polished (smooth) surface in one direction (reflecting surface)

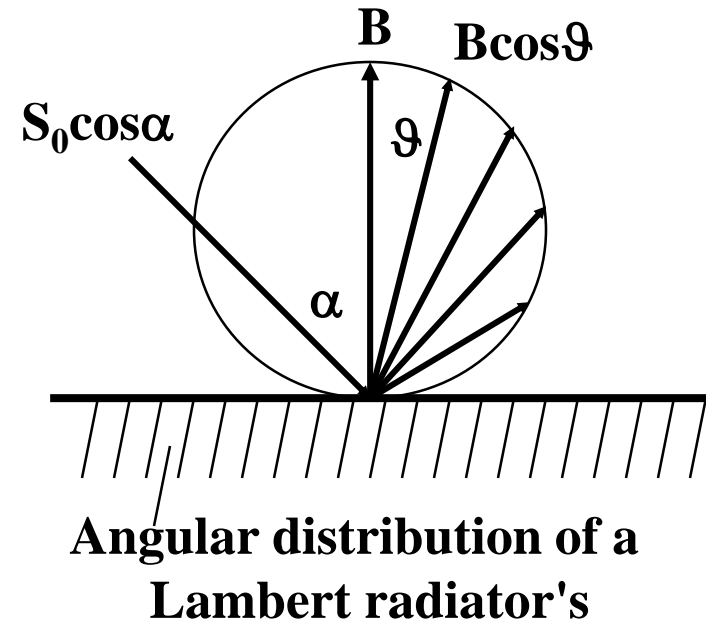
Example: metal, mirror, calm water surface



### Diffuse reflection (irregular)

Reflection from a non-polished surface in all directions of the half-space (matte surface)

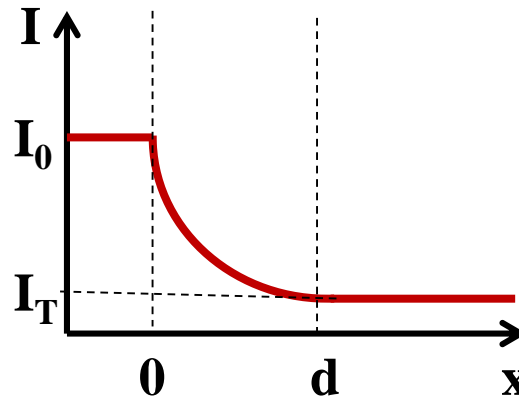
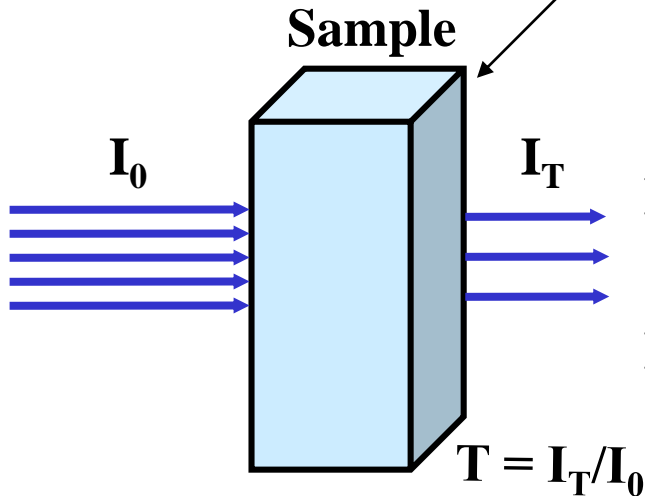
Example: paper, powder, white wall



# 2.4 Interaction of Light and Matter

## Absorption

Medium = gas, solution, crystal, transparent ceramics



### Lambert-Beer-Bouguer-law

$$I = I_0 \cdot \exp(-\alpha \cdot c \cdot d)$$

$$\Rightarrow \ln(I/I_0) = -\alpha \cdot c \cdot d$$

$$\text{Absorption: } A = \alpha \cdot c \cdot d$$

$\alpha$  = Absorption constant [ $\text{cm}^{-1}$ ]

### Fate of the absorbed energy

- Vibrations (phonons)
- Charge storage
- Luminescence
- Charge separation

### Physical effect

Heat  
Color centers  
Light emission  
Current

### Application areas

bolometer  
detectors, imaging plate  
phosphors, laser gain media  
solar cells

# 2.4 Interaction of Light and Matter

## Quantitative description of absorption

Energy conservation  
(division by  $I_0$  yield)

$$I_A + I_R + I_T = I_0$$
$$A + R + T = 1 \text{ (100\%)}$$

Transmission

$$T = I_T/I_0 \leq 1 \text{ (100\%)}$$

Absorption

$$A = 1 - T = 1 - I_T/I_0 \leq 1 \text{ (100\%)}$$

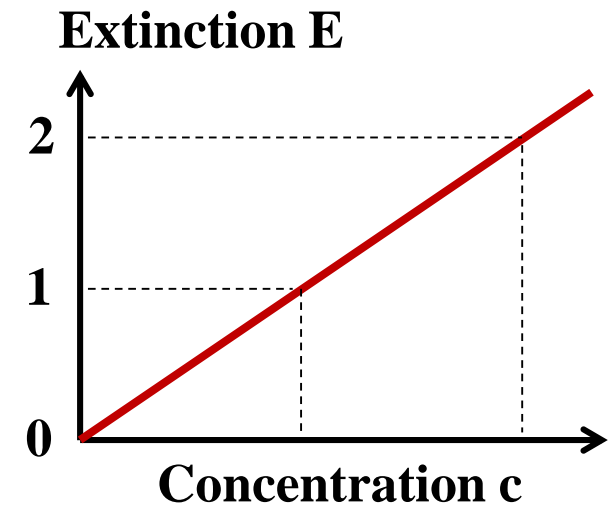
(if  $R = 0$ )

Extinction

$$E = -\lg(I_T/I_0) = \lg(I_0/I_T)$$
$$E = \varepsilon \cdot c \cdot d$$

$\varepsilon$  = molar extinction  
coefficient (material constant,  
dependent on  $\lambda$ ,  $T$ ,  $p$ )

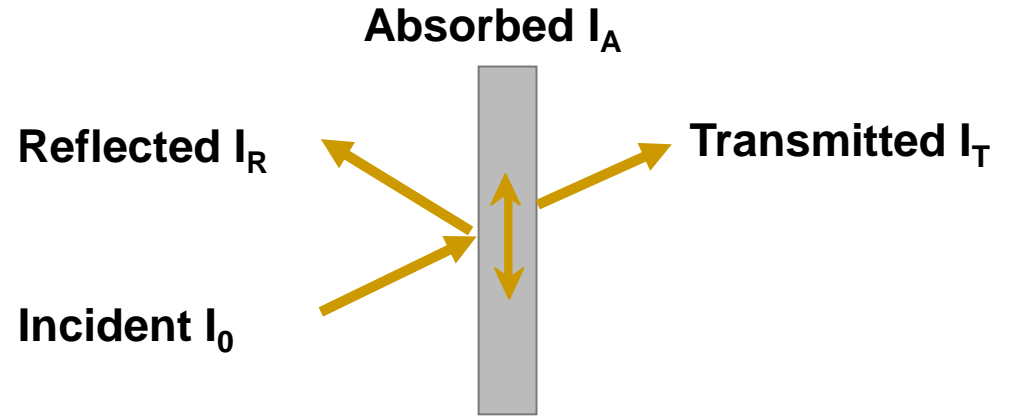
Interstellar extinction:  
2 mag / kpc = 0.83 / 3260 ly  
since 1 pc = 3.26 ly  
(due to Rayleigh scattering  
at dust particles)



# 2.4 Interaction of Light and Matter

## Transmission

$$I_T = I_0 - I_A - I_R$$



## Classification of Materials

**Transparent** = lattice parameter: unit cell  $x$

**Translucent**

**Opaque**

$\gamma =$

$\Delta =$  finite change in a p

$\epsilon =$  engineering strain (...)

$\epsilon =$  dielectric permittivity (18.16)

$\epsilon_r =$  dielectric constant (relative

$\epsilon_T =$

$\eta =$

single crystal

polycrystalline dense

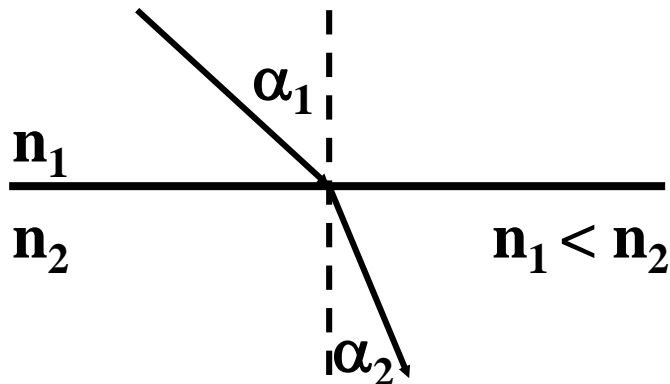
polycrystalline porous

Adapted from Fig. 21.10, Callister 6e. (Fig. 21.10 is by J. Telford, with specimen preparation by P.A. Lessing)

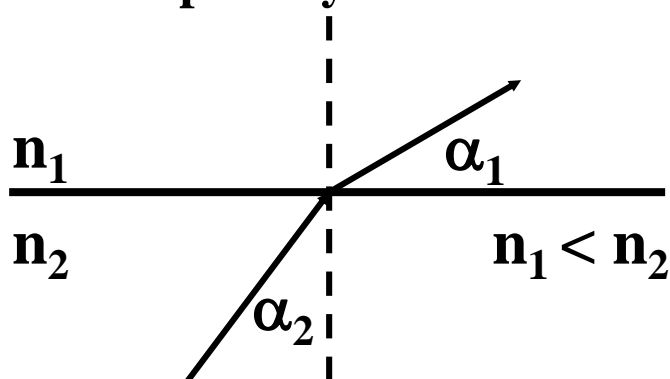
# 2.4 Interaction of Light and Matter

## Refraction

Transition from an optically thin into an optically denser medium



Transition from an optically dense into an optically thinner medium



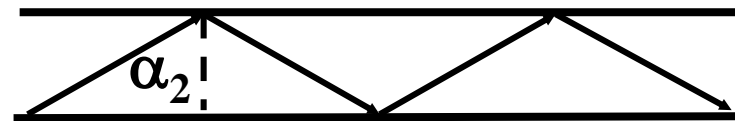
$$n_1 \cdot \sin \alpha_1 = n_2 \cdot \sin \alpha_2 \text{ (Snellius equation)}$$

**Total reflection occurs at the transition from an optically dense to an optically thinner medium, if the critical angle  $\alpha_T$  is exceeded**

Critical angle  $\alpha_2 = \arcsin(n_1/n_2)$

Vacuum/air  $\alpha_T = \arcsin(1/n)$

Principle of light guiding in glass fibers (light guides)



# 2.4 Interaction of Light and Matter

## Refractive indices of some substances at 589.3 nm (center of Na double line)

<u>Substance</u>	<u>Refractive index n</u>
Vacuum	1.000
Air	1.0003
Water	1.333
Ethanol	1.360
CCl <sub>4</sub>	1.460
Benzene	1.501
CS <sub>2</sub>	1.628
Ice	1.309
Teflon	1.35
CaF <sub>2</sub>	1.434
Quartz glass	1.459
PMMA	1.49
NaCl, α-quartz	1.54
ZrSiO <sub>4</sub> (Zircon)	1.923
Diamond	2.417
TiO <sub>2</sub> (Rutil)	2.68

### Critical angle for total reflection

Vacuum/air

$$\alpha_T = \arcsin(1/n_{\text{air}})$$

$$= 88.6^\circ$$

(air glimmering)

Quartz glass/air

$$\alpha_T = \arcsin(n_{\text{air}}/n_{\text{glass}})$$

$$= 43.3^\circ$$

(silica fibre)

Diamond/air

$$\alpha_T = \arcsin(n_{\text{air}}/n_{\text{diamond}})$$

$$= 24.5^\circ$$

("Fire" of diamonds, since n strongly depends on wavelength)



# 2.4 Interaction of Light and Matter

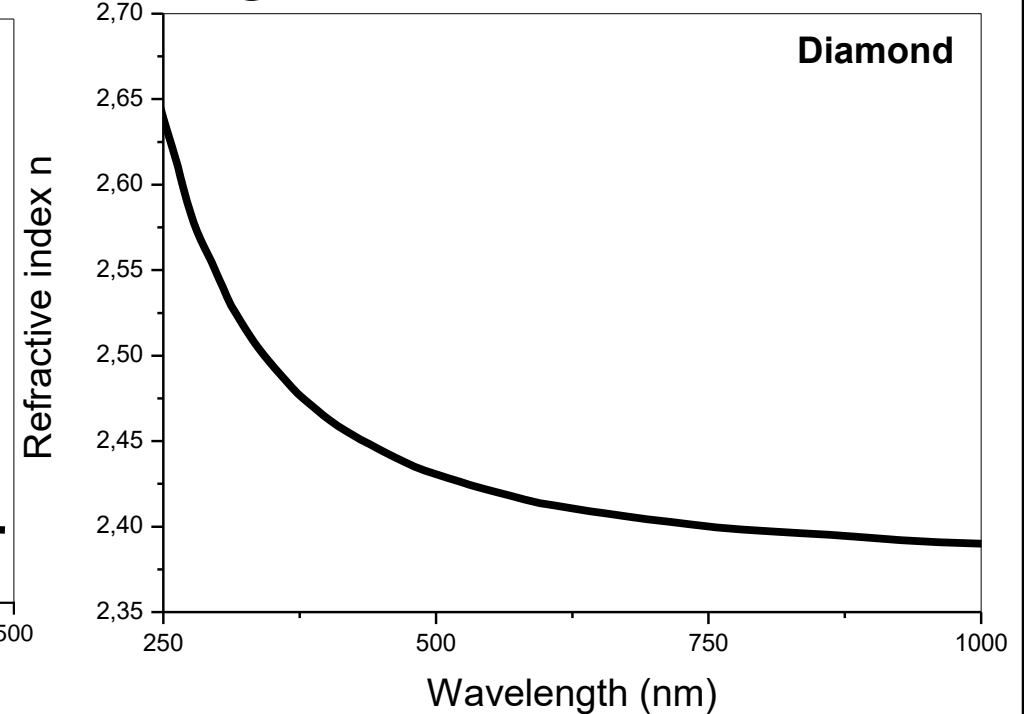
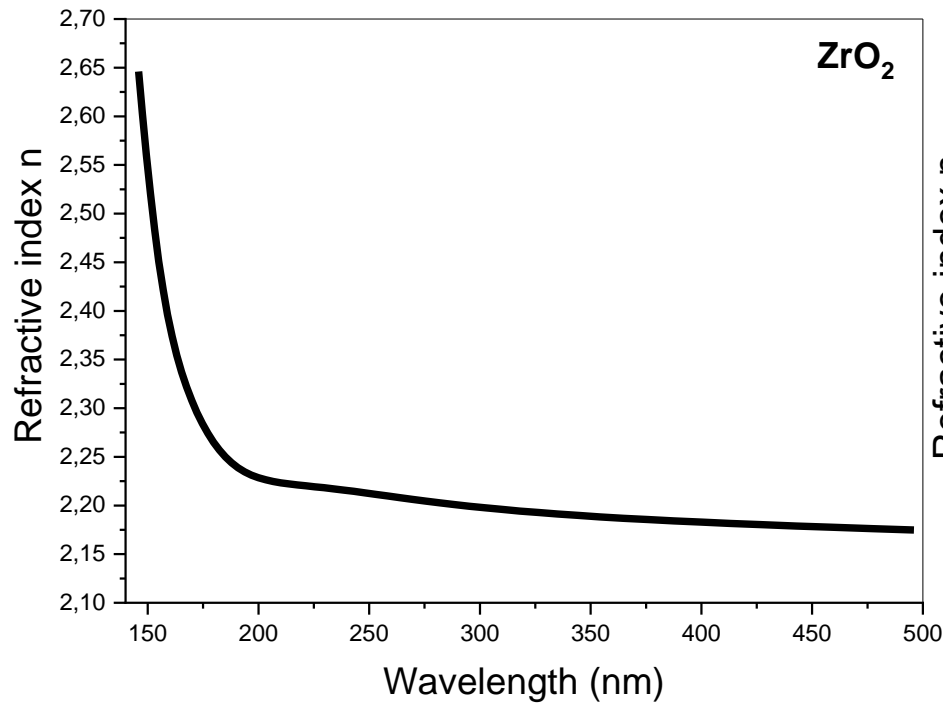
## Refractive indices as a function of wavelength (dispersion)

→ Causes chromatic aberration

weak dispersion

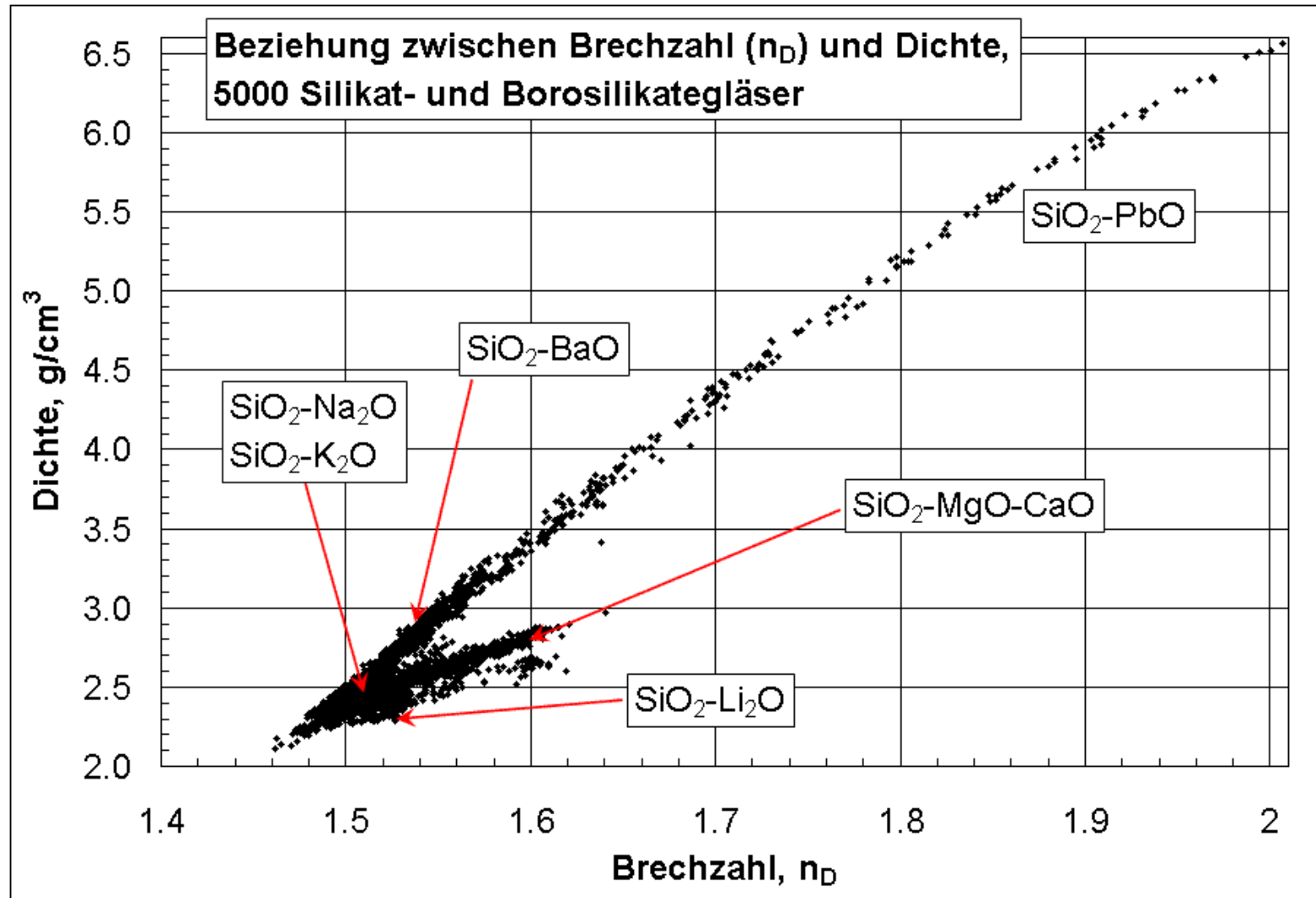
strong dispersion

in the visible range



# 2.4 Interaction of Light and Matter

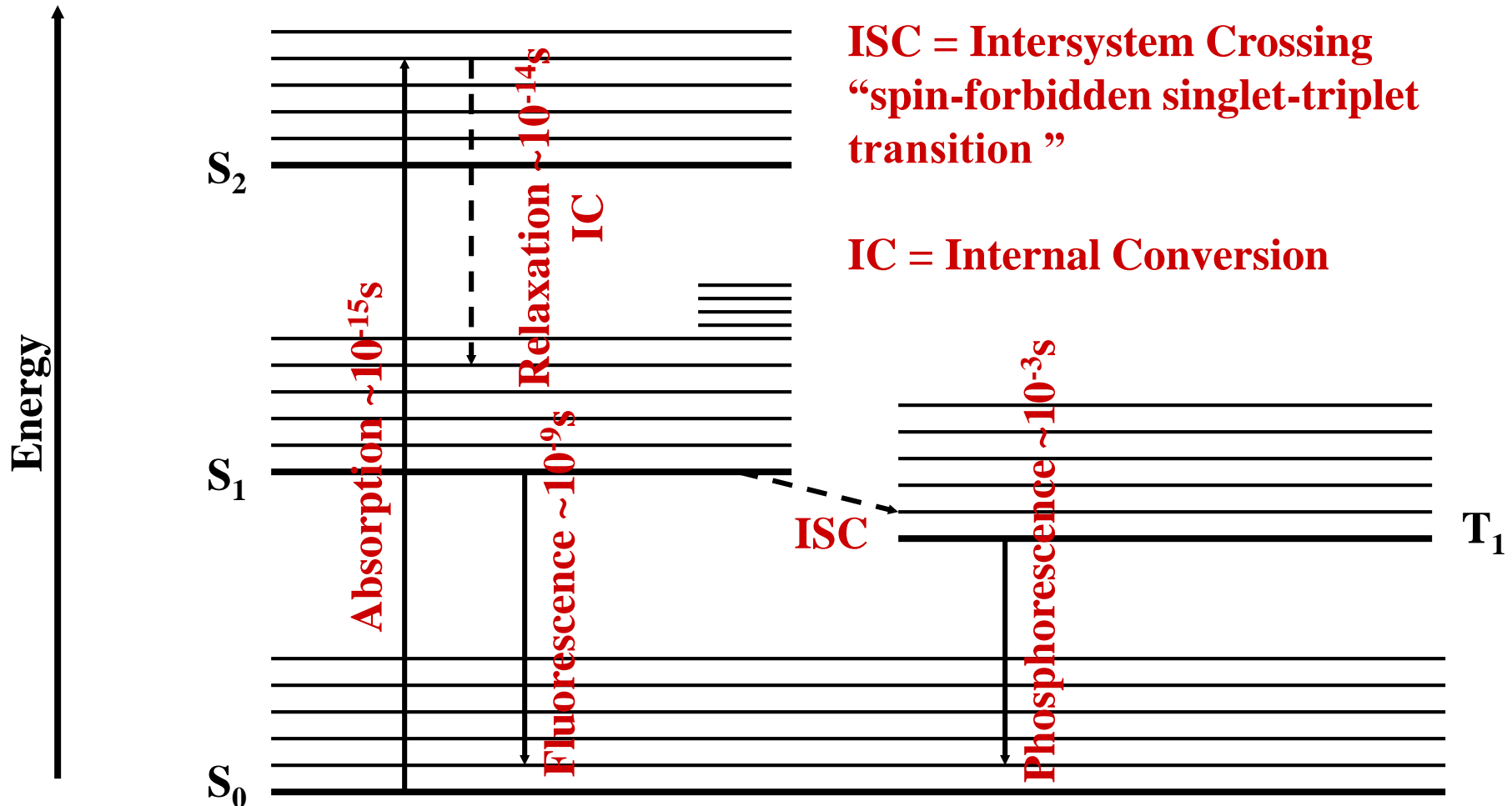
## Refractive indices as a function of the density of glasses



# 2.4 Interaction of Light and Matter

## Luminescence

*Jablonski diagram of an arbitrary organic molecule*



## 2.5 Radiometric Quantities

**Measured variables for describing the performance (proportional to the number of photons per unit of time) = energetic parameters**

**Measured variables at the detector (photomultiplier tube, photodiode, eye)**

**(Radiant) intensity       $I$       = number of photons /area\*time    [ $N_{h\nu}/m^2s$ ]**

**Irradiance                       $E_e$       = number of photons /area\*time    [ $J/m^2s = W/m^2$ ]**

**⇒ These parameter are proportional to the detector count rate      [Counts/s]**

**⇒ Technically, intensity is measured with a PMT or a photodiode**

**(Integration over a given area, i.e. area of the window of the detector)**

**Radiant exposure                                      = number of photons /area      [ $J/m^2$ ]**

## 2.5 Radiometric Quantities

<u>Physical variable</u>	<u>Symbol</u>	<u>Definition</u>	<u>Unit</u>
Radiant power/flux	$\Phi_e$	= dW/dt	[W] bzw. [J/s]
Spectral radiant power/flux	$\Phi_e(\lambda)$	= d $\Phi_e$ /d $\lambda$	[W/nm]
Radiant emittance, irradiance	$E_e$	= d $\Phi_e$ /dA	[W/m <sup>2</sup> ]
Spectral irradiance	$L_e$	= d $D_e$ /d $\lambda$	[W/m <sup>2</sup> nm]

**Irradiance of the Earth:**  $E_e = 1.376 \cdot 10^3 \text{ J/m}^2\text{s} = 1.376 \text{ kW/m}^2$  (= solar constant)

**Number of photons:**  $E = h\nu = hc/\lambda$  and  $h\nu_{550} = 4 \cdot 10^{-19} \text{ J}$   
 $\Rightarrow 1 \text{ W} = 1 \text{ J/s} = 2.5 \cdot 10^{18} \text{ photons per second}$   
 with wavelength 550 nm  
 $\Rightarrow 3.375 \cdot 10^{21} \text{ Photons/m}^2 \text{ for } 1.376 \text{ kW/m}^2$

## 2.6 Photometric Quantities

**Measured variables involving the spectral sensitivity of the observer (human eye)**

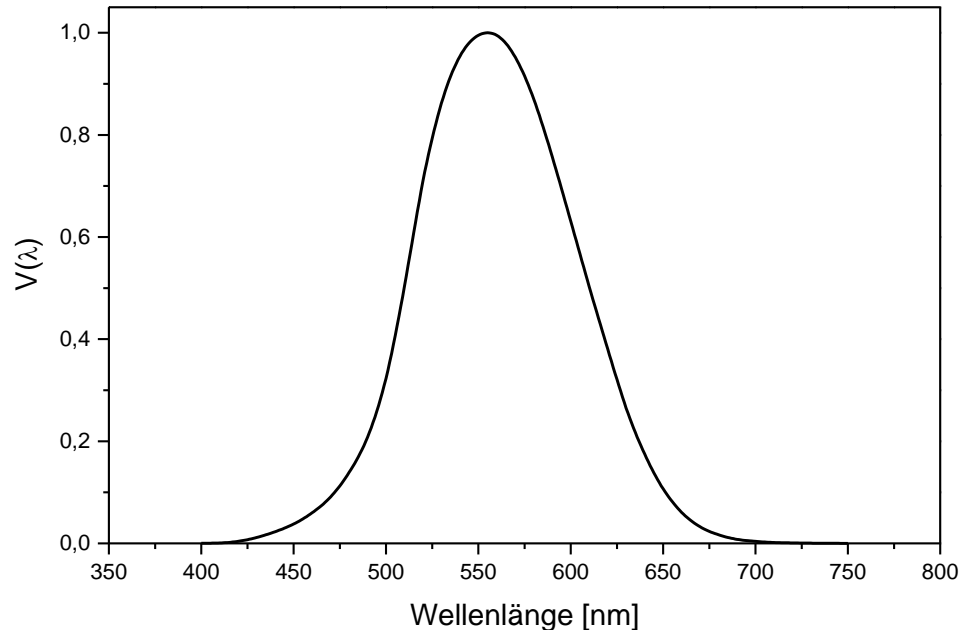
**Luminous flux  $\Phi_v = \Phi_e/M_0$  [lm]**

**$M_0 =$  Energetic light equivalent**

**$= 0.00146$  W/lm (1/683 W/sr)**

**$K_{\max} = 683$  lm/W (bei 555 nm)**

**$K(\lambda) = K_{\max} V(\lambda)$**



$$\Phi_v = K_{\max} \int_{380}^{780} V(\lambda) \Phi_e(\lambda) d\lambda$$

**Luminous intensity  $I = d\Phi_v/d\Omega$  [lm/sr = cd]**

**$\Omega =$  Solid angle [sr]**

**(surface of a sphere =  $4\pi r^2 = 4\pi$ sr)**

**A 1 cd (1 lm / sr) light source emits  $4\pi$  lm, i.e. 12.57 lm, isotropically in all spatial directions  $\Rightarrow$  Luminance spectrometer**

# 2.6 Photometric Quantities

**Origin of the quantity of the energetic light equivalent  $M_0 = 0.00146 \text{ W/lm}$**

**Reference light source is the candle**

**Emission spectrum of a diner light (~ 16 g)**

**$P \sim 40 \text{ W} = 40 \text{ J/s}$  (fuel: paraffine ~ 42 MJ/kg)**

**$P_{\text{optical}} = 0.0184 \text{ W}$  (integrating sphere)**

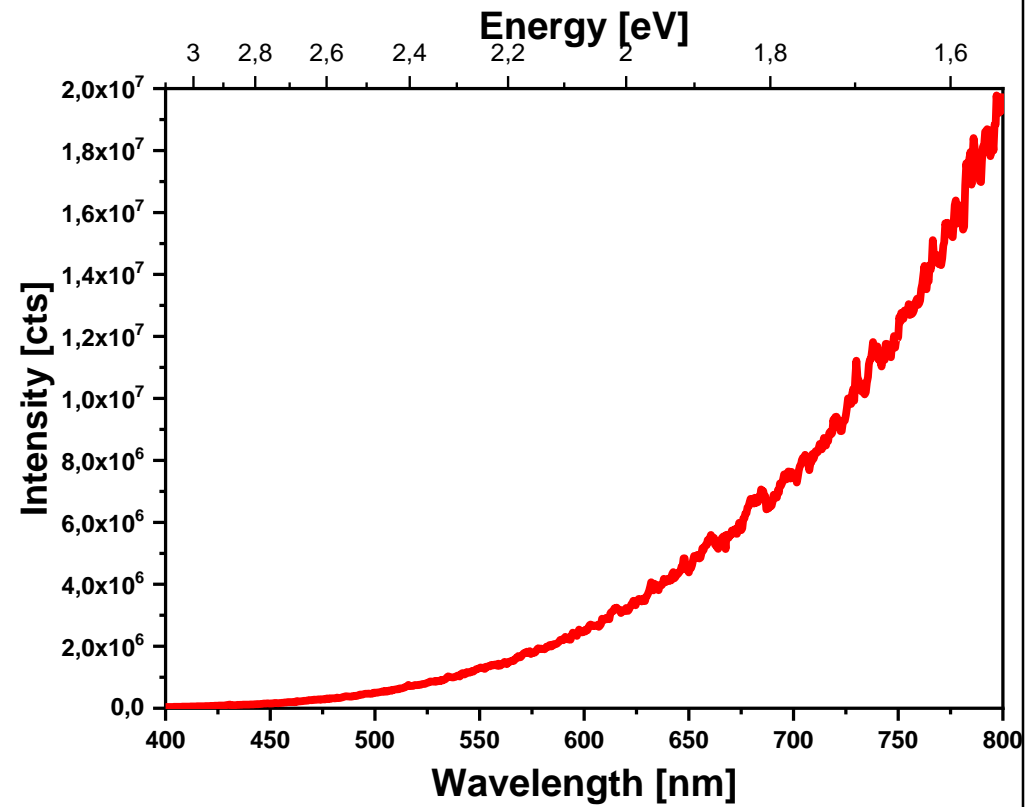
**$\eta = 0.00046$  or **0.046%****

**$I_v = 1 \text{ cd} = 4\pi \text{ lm} \sim 12.566 \text{ lm}$**

**$\Rightarrow \eta_v = 0.31415 \text{ lm/W} \Rightarrow 3.1832 \text{ W/lm}$**

**Efficiency  $\eta = 0.00046$**

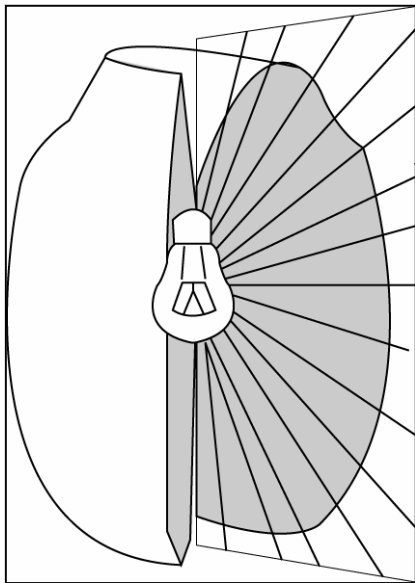
**$\Rightarrow 0.001464 \text{ W/lm}$  or **683 lm/W** (q.e.d.)**



## 2.6 Photometric Quantities

**Luminous flux** Total radiation power emitted from a light source in all spatial directions, which is measured via the sensitivity of the human eye [lm]. It is determined by measurement with an integrating sphere.

**Luminous int.** Luminous flux emitted per unit solid angle with the value of one steradian [cd]. For this purpose, the luminous flux detected only in a certain solid angle, typically in the range of the maximum beam intensity.



*Luminous flux:* 
$$\Phi_v = 683 \int_{380}^{780} V_{rel}(\lambda) \Phi_e(\lambda) d\lambda$$



## 2.6 Photometric Quantities

### Illuminance

Ratio of luminous flux to the illuminated surface

[lux = lm/m<sup>2</sup>].

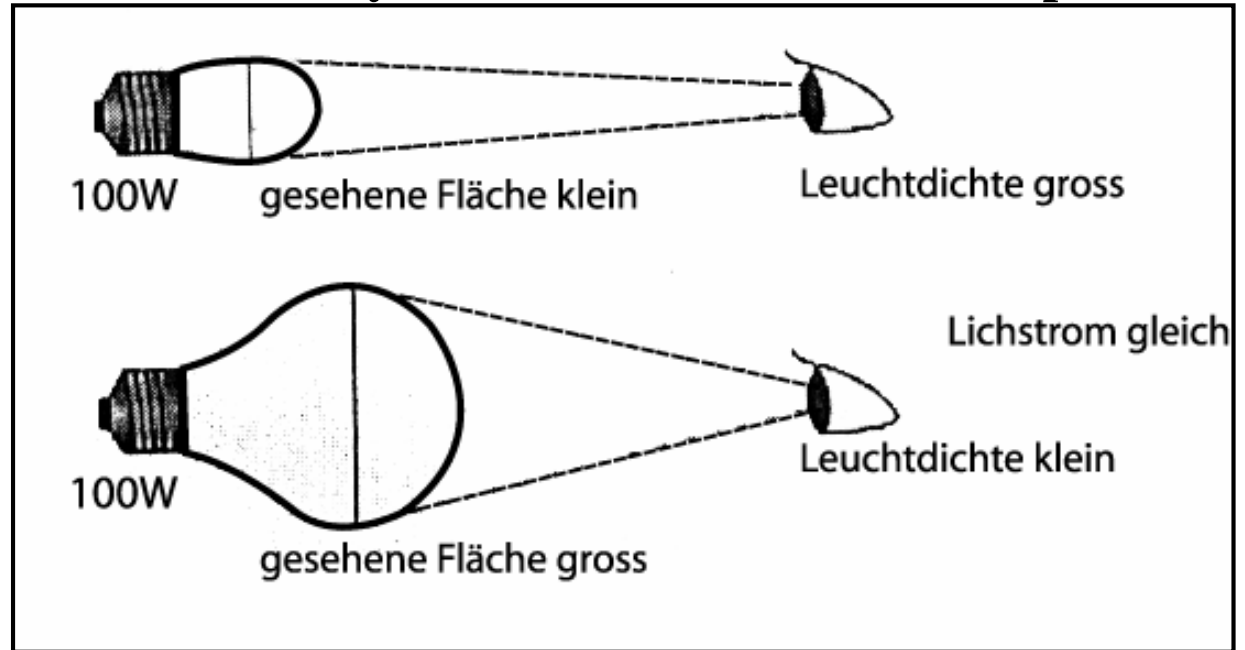
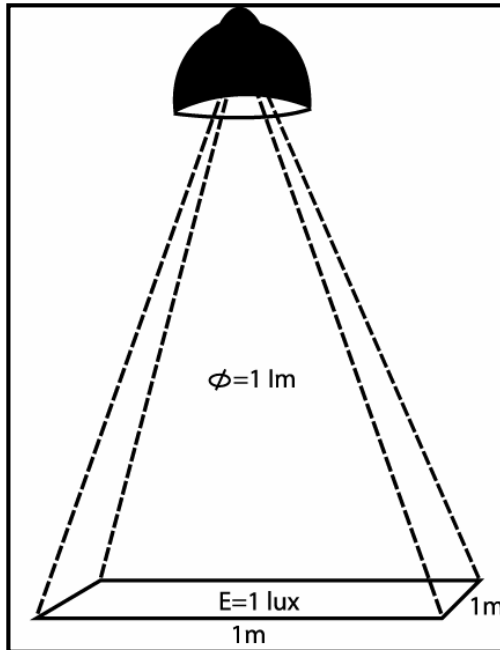
It is determined by measurement with a lux meter.

### Luminance

Perceived brightness of a light source [cd/m<sup>2</sup>].

It is measured with a CCD camera.

Vision limit human eye ~ 0.000003 cd/m<sup>2</sup> ~ 250000 photons



## 2.6 Photometric Quantities

### Integral Quantities

Luminous flux  $\Phi_v = \Phi_e/M_0$  [lm]

Intensity of illumination  $E = d\Phi_v/dA$  [lux = lm/m<sup>2</sup>]

### Solid angle related parameters

(for 1 sr)

Luminous intensity  $I = d\Phi_v/d\Omega$  [cd]

Light density  $L = dI/dA \cos\gamma$   
[cd/m<sup>2</sup>] = [nit] (luminance)

Light source	Light density / Luminance [cd/cm <sup>2</sup> ]
Sun	150000
Arc discharge	20000 - 100000
Bulb (clear)	200 – 2000
Bulb (matte)	5 – 50
Fluorescent lamp	0.4 – 1.4
Candle	0.75
Blue sky	0.3 – 0.5
Full moon	0.25
TV	0.05

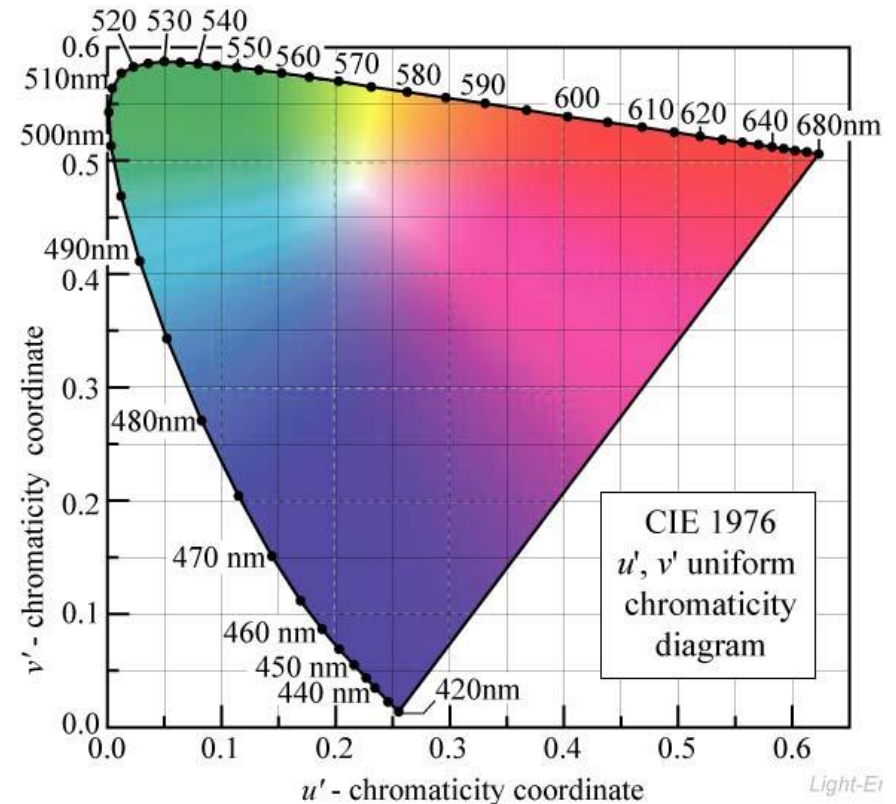
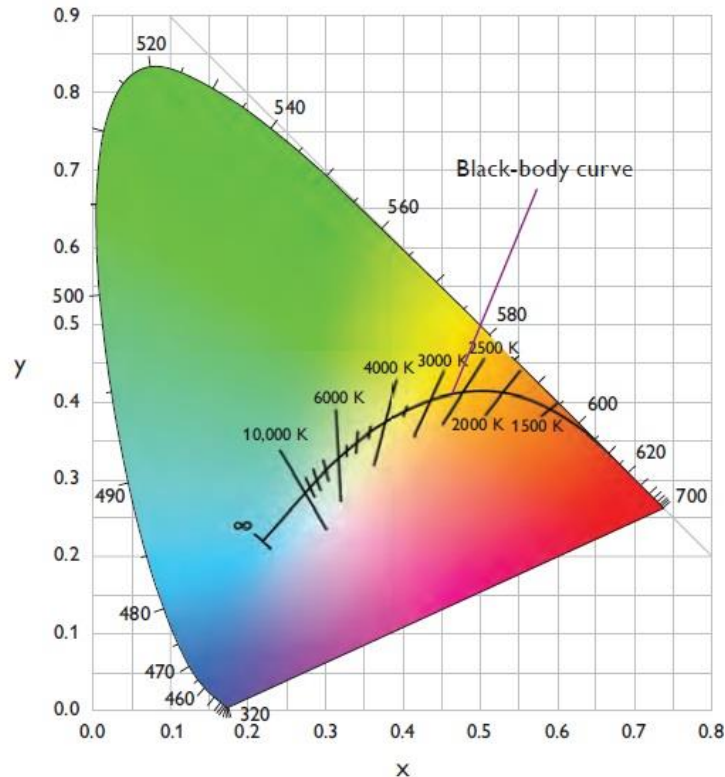
# 2.6 Photometric Quantities

## Color Coordinates

Quantifies the perceived color of an emission spectrum (additive color mixing)

Various systems exist to represent the color:

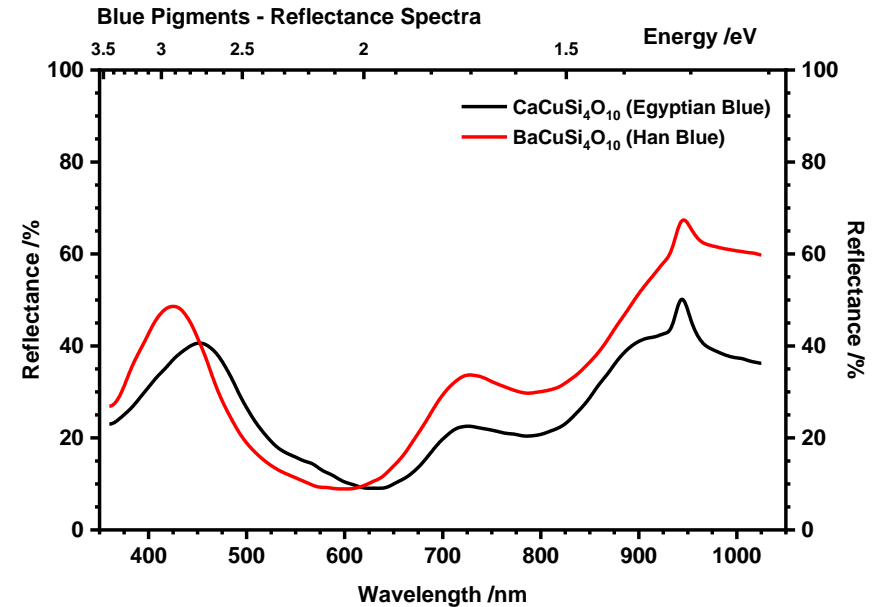
CIE1931, CIE1976, CIElab (includes luminance), ...



# 2.6 Photometric Quantities

## Body Colour

- The perceived color of a subject. A result of subtractive color mixing
- Depends both on the absorption spectrum of the substance, as well as the emission spectrum of the light source
- A standard measurement is D65, where the light source mimicks solar light
- With very efficient phosphors the body color can be influenced by their luminescence. Absorbed UV radiation is converted into visible light



# 2.7 Photosynthetically Active Radiation

## Photosynthetically Active Radiation (PAR)

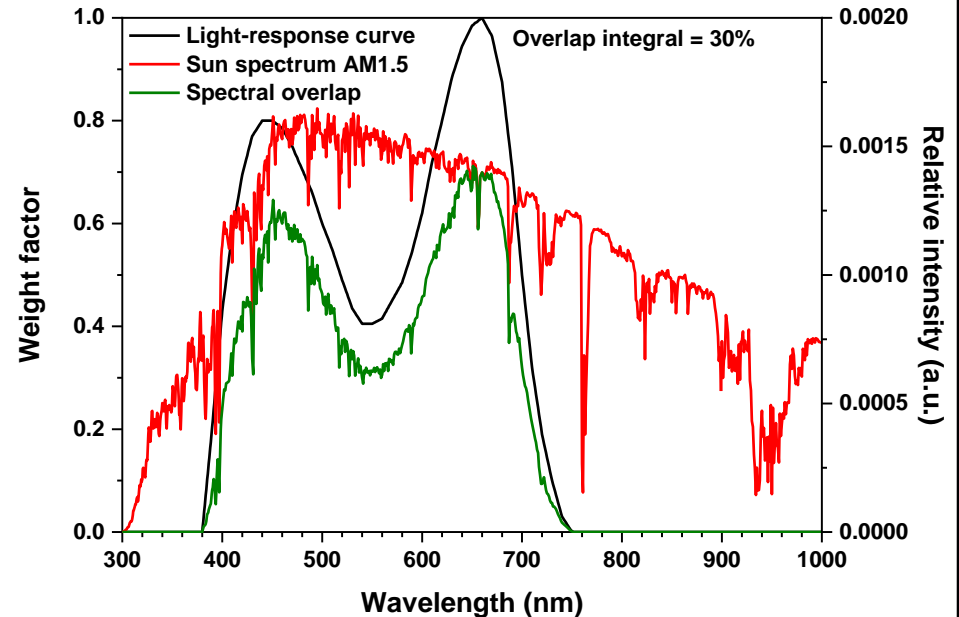
Most autotrophic organism use phototosynthesis for energy production and thus utilize photons of a specific wavelength range, mainly visible light

### Photosynthetic photon flux (PPF)

- Number of 400-700 nm photons per time unit (treats all photons equally)
- Unit: [ $\mu\text{mol} \cdot \text{s}^{-1}$ ]

### Photosynthetic photon flux density (PPFD)

- Number of 400-700 nm photons per irradiated area and time
  - Unit: [ $\mu\text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2} = \text{W} \cdot \text{m}^{-2}$ ]
- Does not take the efficacy into account!



# 2.7 Photosynthetically Active Radiation

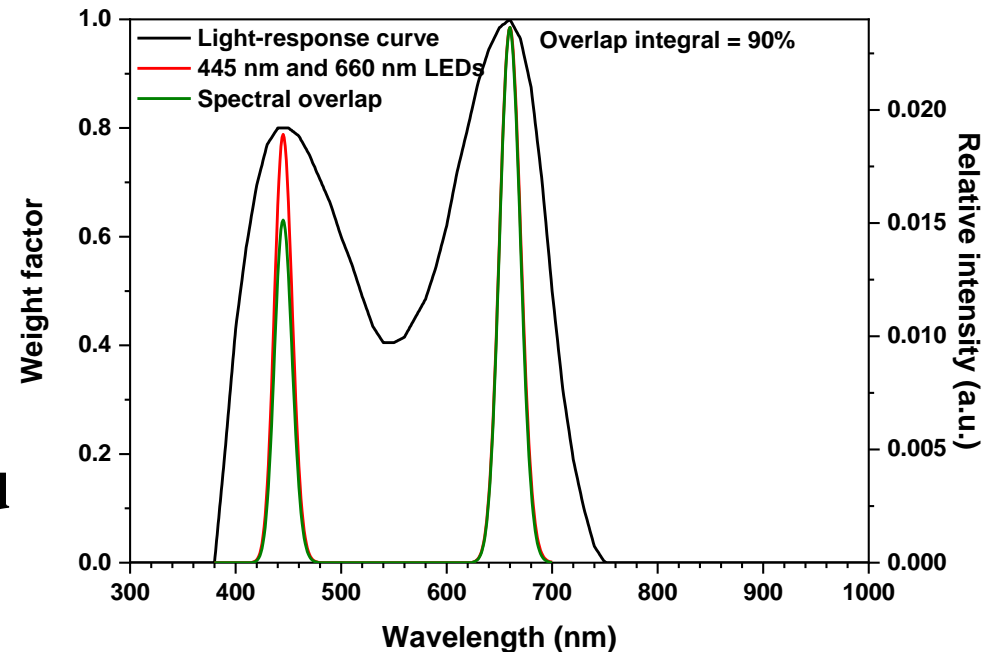
## Photosynthetically Active Radiation (PAR)

### Yield Photon Flux (YPF)

- Since the photosynthesis efficiency depends on the respective wavelength of the photon, a weight function is used
- Number of photons from 360-760 nm per time unit weighted by photosynthetic response
- Unit:  $[\mu\text{mol} \cdot \text{s}^{-1}]$
- The spectral overlap integral (OI) quantifies the overall efficiency, thus  $\text{YPF} = \text{OI} \cdot \text{PPF}$

### Yield Photon Flux Density (YFPD)

- Number of photons from 360-760 nm per time unit and area weighted based on the photosynthetic response
- Unit:  $[\mu\text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2} = \text{W} \cdot \text{m}^{-2}]$



# 3. Experimental Setup

## 3. Experimental Setup

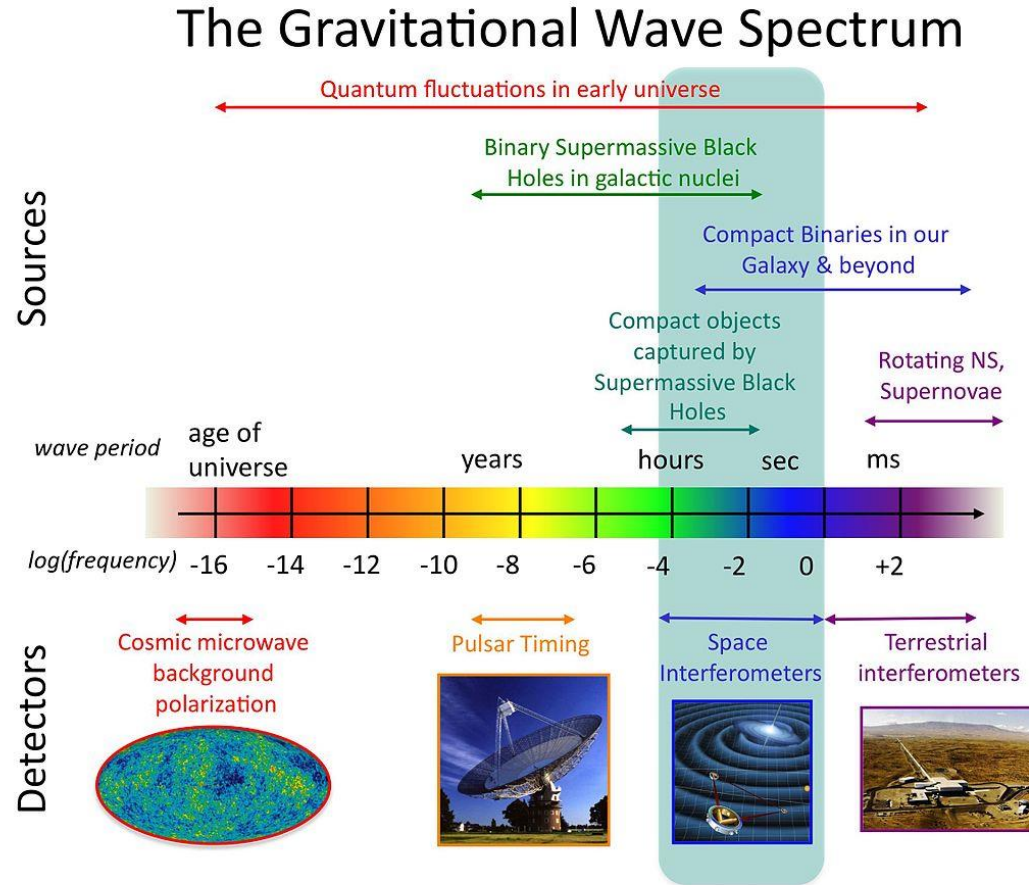
### 3.1 Construction of a Spectrometer

### 3.2 Excitation Sources

### 3.3 Dispersive Elements

### 3.4 Detectors

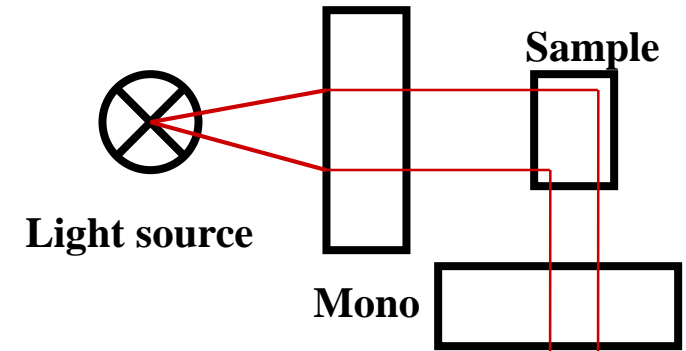
### 3.5 Sample Chamber



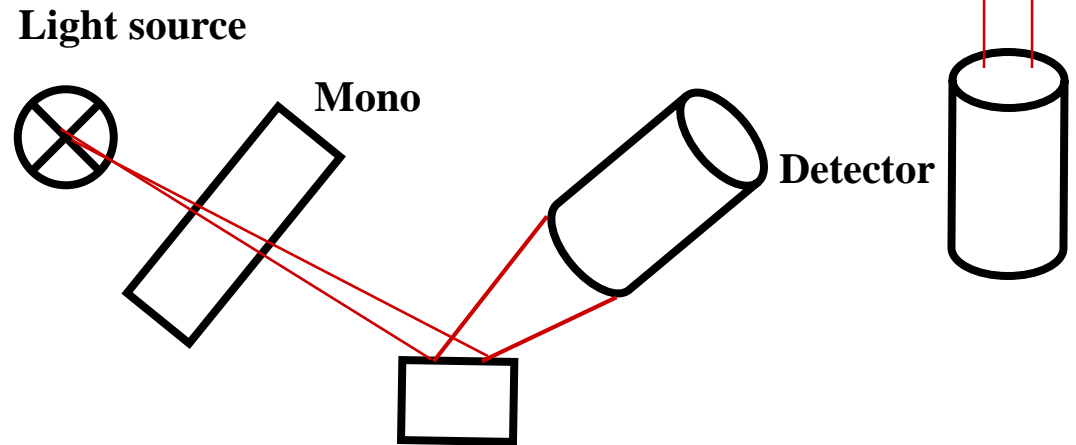
# 3.1 Construction of a Spectrometer

## Geometries

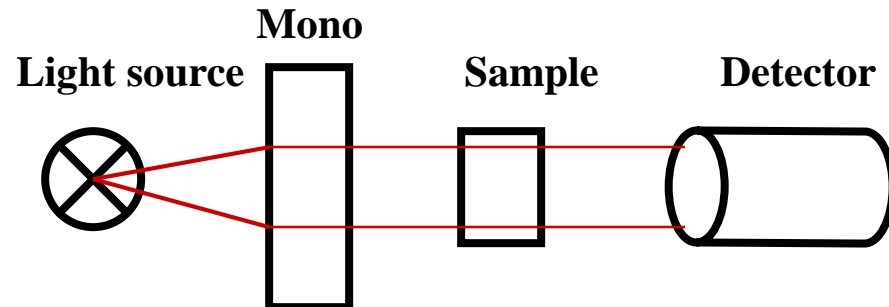
Fluorescence, phosphorescence  
of solutions  
(rectangular geometry)



Reflection, scattering,  
fluorescence, phosphorescence of  
solids (rectangular geometry)



Absorption, transmission  
of solutions, gases  
(linear geometry)





## 3.2 Excitation Sources

### Typical radiation sources

- |   |                           |
|---|---------------------------|
| • <b>Celestial objects (only of interest for astrophysics)</b>                    | <b>Continuous + Lines</b> |
| • <b>Halogen lamps</b>  | <b>Continuous</b>         |
| • <b>Gas discharge lamps</b>  |                           |
| – <b>Xe-medium pressure lamps</b>   | <b>Quasi-continuous</b>   |
| – <b>Low-pressure mercury lamps</b>   | <b>Lines</b>              |
| – <b>Medium pressure mercury lamps</b>  | <b>Quasi-continuous</b>   |
| – <b>High pressure mercury lamps</b>  | <b>Quasi-continuous</b>   |
| – <b>H<sub>2</sub>/D<sub>2</sub>-lamps</b>  | <b>Quasi-continuous</b>   |
| • <b>LEDs</b>   | <b>narrow band</b>        |
| • <b>Laser (less suitable for excitation spectra!)</b>                            | <b>narrow line</b>        |
| – <b>Gas laser (CO<sub>2</sub>, N<sub>2</sub>, Kr, excimers: ArF*, XeF* etc.)</b> |                           |
| – <b>Solid-state laser</b>  |                           |
| – <b>Dye laser</b>  |                           |
| – <b>Laser diodes</b>   |                           |
| • <b>Synchrotrons (BESSY, DELTA, DESY, CERN, ...)</b>                             | <b>White!</b>             |

# 3.2 Excitation Sources

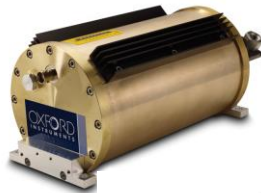
## Radiation sources for fluorescence spectroscopy

Xenon disch. lamp,  
wavelength range  
200 - 900 nm



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

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

# 3.2 Excitation Sources

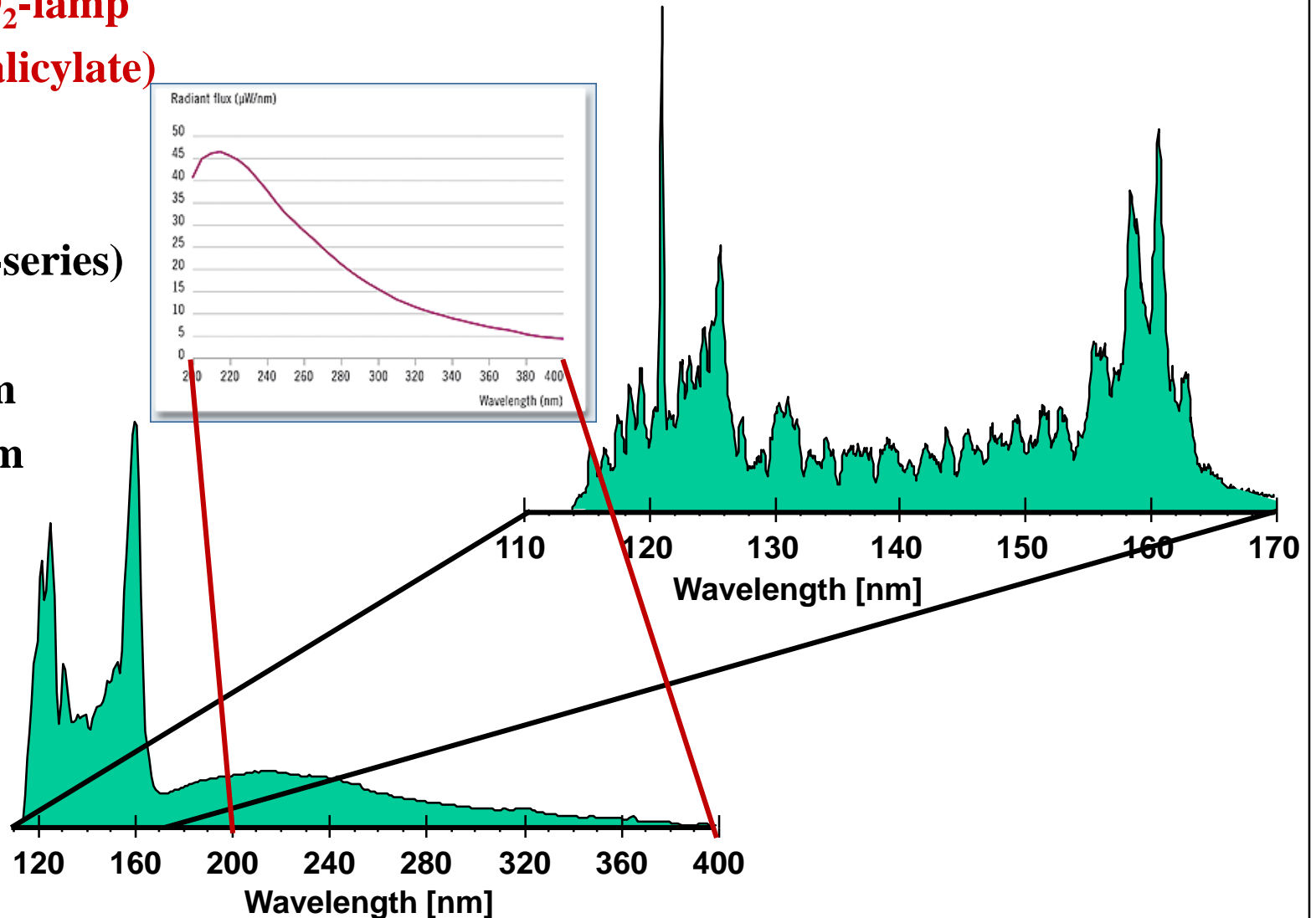
## Spectrum of a D<sub>2</sub>-lamp (Standard Na-salicylate)

110 – 170 nm

D-lines (Lyman-series)

170 nm – 400 nm

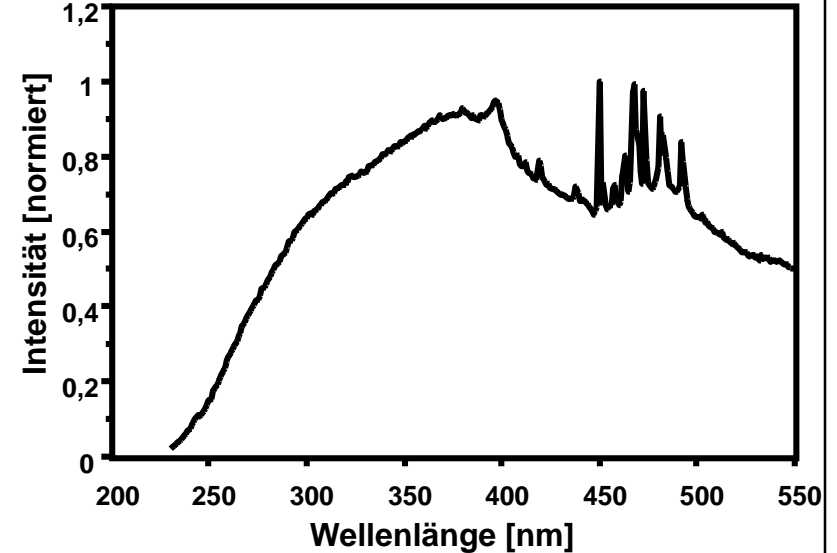
Quasi-continuum



## 3.2 Excitation Sources

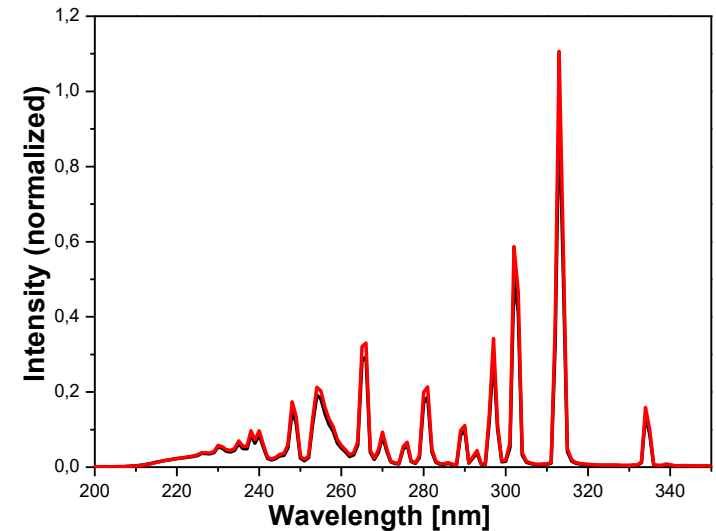
### Spectrum of a Xe-medium pressure lamps

- 220 – 450 nm  
Quasi-continuum
- > 450 nm  
Quasi-continuum + Xe-lines



### Spectrum of a high pressure mercury lamps

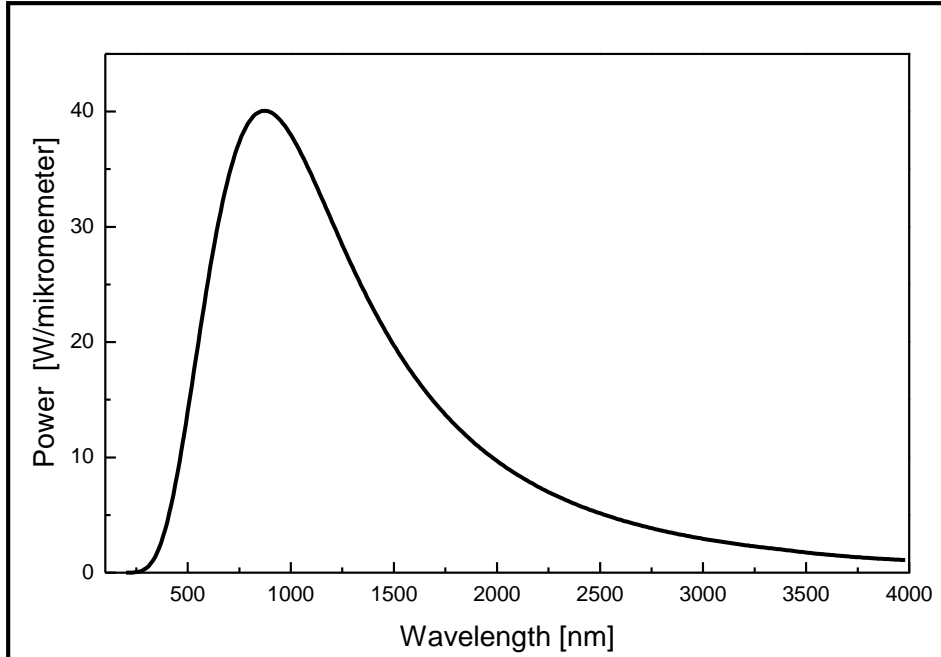
- 210 – approx. 300 nm  
Quasi-continuum
- Hg-lines at 248, 254, 265, 303, 313, 365, 405, 435, 546 and 579 nm



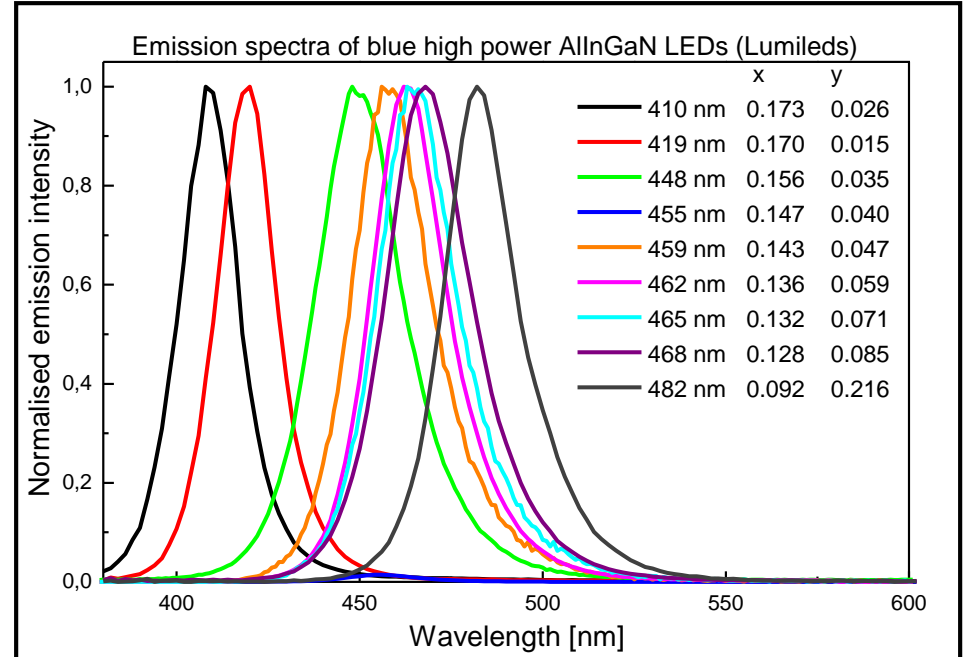
# 3.2 Excitation Sources

## Spectra of halogen lamps and LEDs

**Halogen lamp (broad band emitter)**



**LEDs (narrow band emitter)**



**LEDs are very flexible light sources (geometric and spectral)**

**(In,Ga)N            365 – 500 nm**

**(Al,In,Ga)P        580 – 700 nm**

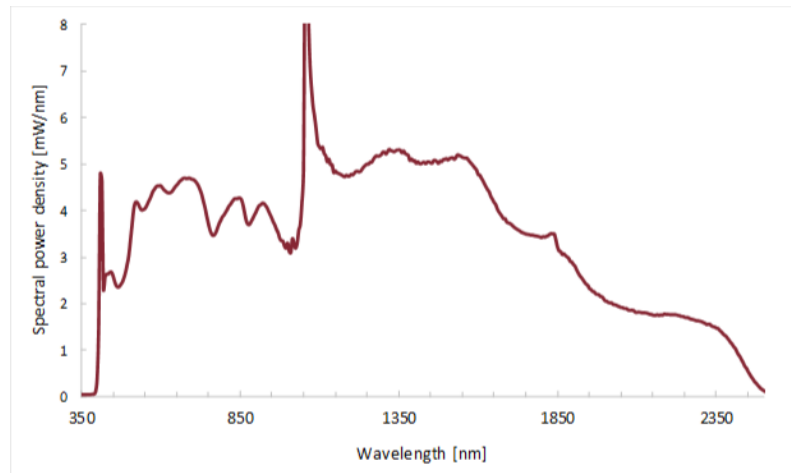
**(Al,Ga)N            210 – 365 nm**

**Ga(As,P)            > 650 nm**

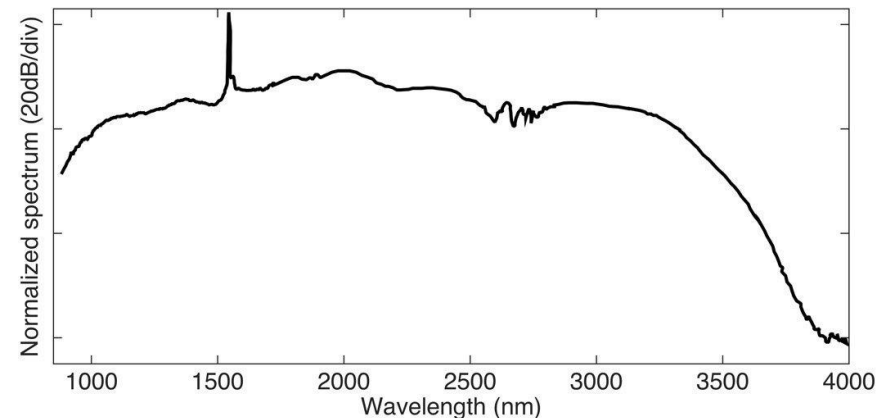
## 3.2 Excitation Source

### Super continuum laser (white laser)

- Spectral broadening of a laser line via non-linear effects in a glass fiber
- In the spectrum the primary laser line can still be observed (e. g. 1064 nm of YAG:Nd)
- The optical power in  $\text{W nm}^{-1}$  is comparatively low, as the laser output power is spread over the whole spectrum



**NKT Photonics „SuperK FIANIUM“**  
**Optical power: 1.5 W**

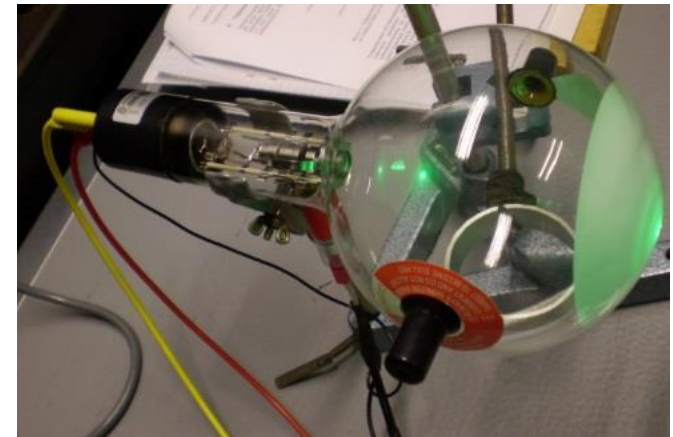
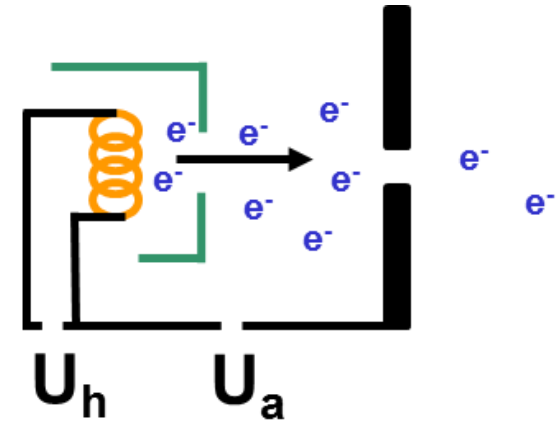


**Experimental NIR SC-laser**  
**Lit.: DOI 10.1117/2.1201510.006199**

## 3.2 Excitation Sources

### Electron gun

- By applying a high voltage between the **coil** and the anode plate, electrons are accelerated from the coil to the anode
- To allow electrons to be removed from the coil, it is electrically heated to 800 - 1000 °C
- The higher the temperature (heating current), the more electrons are emitted from the coil. The higher the voltage  $U_a$ , the higher is the energy of the electrons.
- The electron beam is focused by a positively charged **Wehnelt cylinder**

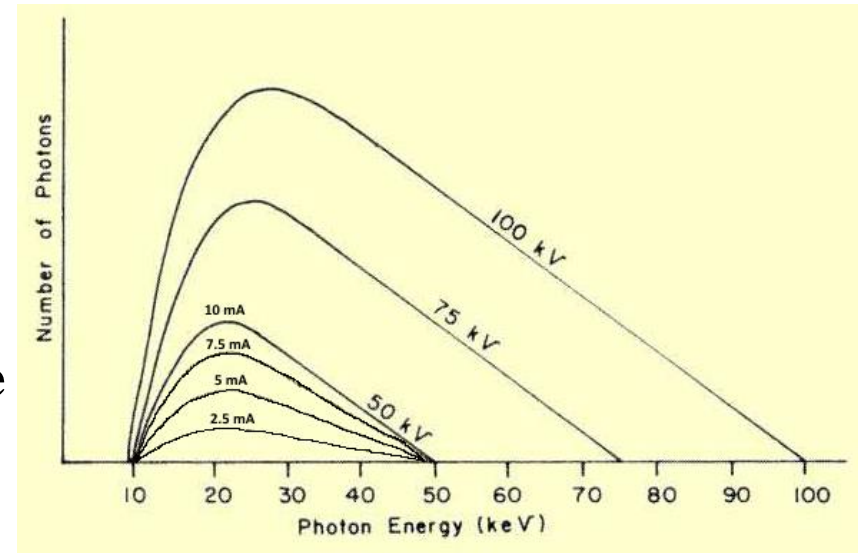
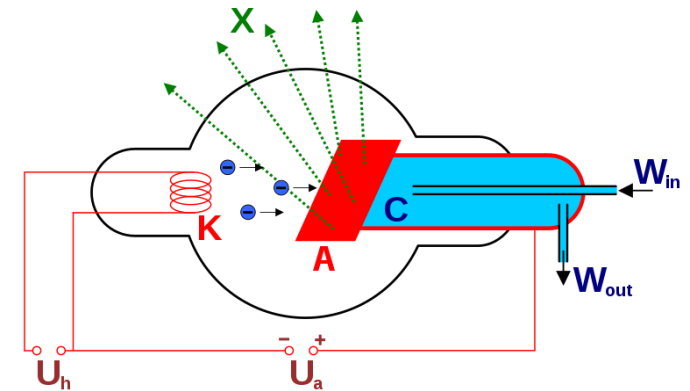


Source: Wikipedia

# 3.2 Excitation Sources

## X-ray tubes

- Electrons emitted by a cathode (**K**) are accelerated and hit a target (**A**) (e. g. tungsten)
- The electrons are slowed down and emit the kinetic energy in the form of radiation (Bremsstrahlung) and heat
- The accelerating voltage  $U_a$  determines the intensity and spectral width of the x-rays
- The amount of electrons is controlled by the heating current and solely influences the intensity, not the shape, of the spectrum



Lit.: Perry Sprawls, "Physical Principles of Medical Imaging"

$$\text{Efficiency (\%)} \approx U_a \cdot Z \cdot 10^{-4}$$

$$60 \text{ kV, tungsten: } 60 \cdot 74 \cdot 10^{-4} = 0.4\% (!)$$



## 3.2 Excitation Sources

### $\alpha$ -, $\beta$ -, $\gamma$ -emitter

#### $\alpha$ : $\text{He}^{2+}$ cations

- typical  $\alpha$ -emitters:  $^{241}\text{Am}$ ,  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$
- penetration depth: 10-15  $\mu\text{m}$  (YAG, 5 MeV)

#### $\beta$ : electrons, $e^-$

- typical  $\beta$ -emitters:  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ,  $^3\text{H}$
- penetration depth: < 1  $\mu\text{m}$  (10 keV), 8-10  $\mu\text{m}$  (70 keV)

#### $\gamma$ : high-energy photons

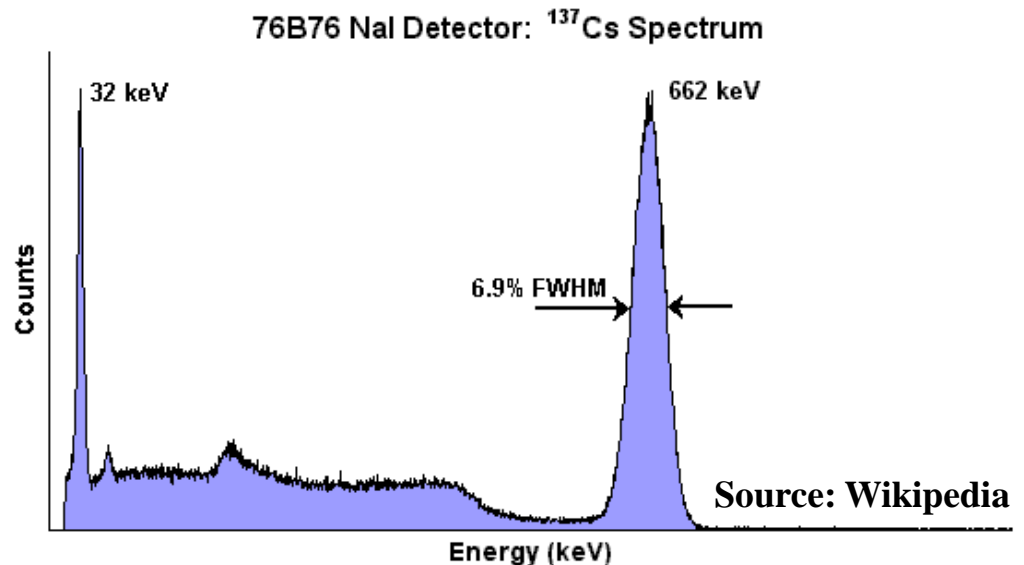
- typical  $\gamma$ -emitters:  $^{137}\text{Cs}$ ,  $^{60}\text{Co}$
- simultaneously emitted  $\alpha$  or  $\beta$  particles are stopped by an thin metal absorber
- interacts with the whole particle



Tritium filled tube coated with  $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$



Commercial  $\beta$ -source

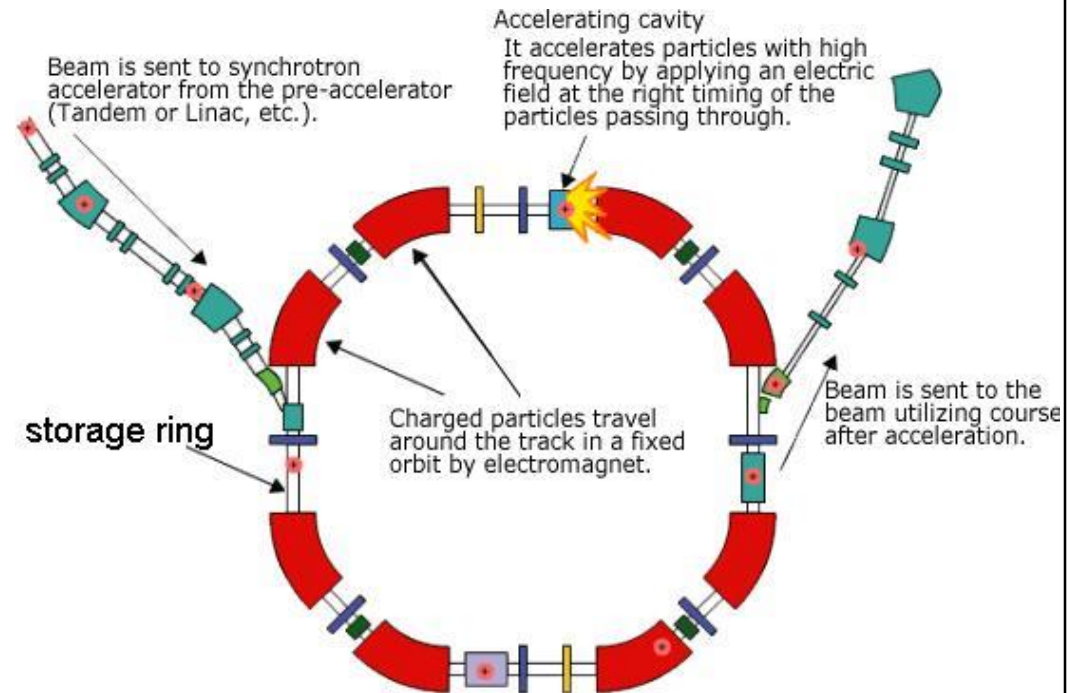


## 3.2 Excitation Sources

### Synchrotron

**Generates a continuous spectrum by accelerating electrons**

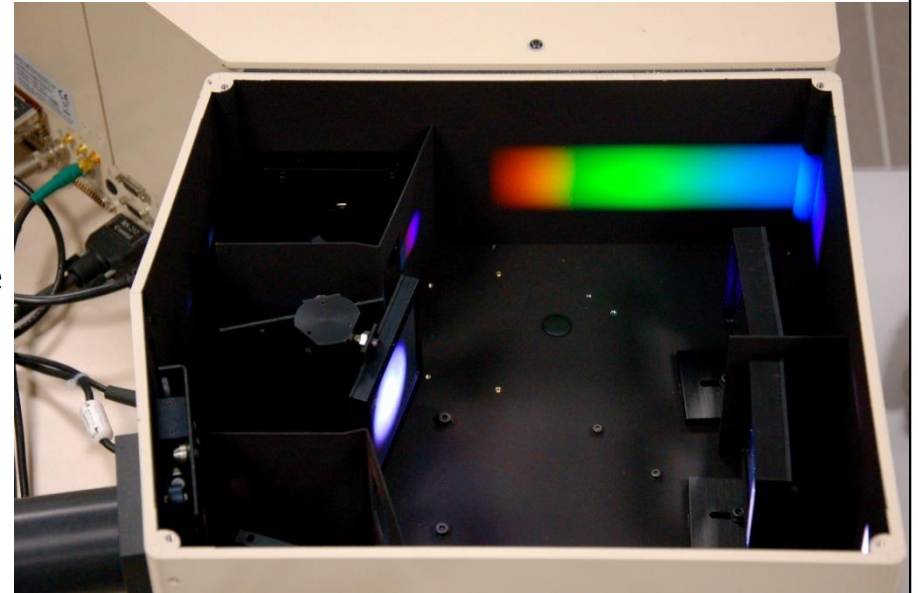
- **Energy (wavelength) depends on the acceleration and can range from  $< 1 \text{ eV}$  ( $> 1 \text{ }\mu\text{m}$ , NIR) to  $> 1 \text{ GeV}$  ( $< 1 \text{ fm}$ )**
- **Special magnet setups cause the spectrum to get narrower**
- **Very expensive and only used for specific experiments where high-intensity or short-pulsed radiation is required**



Source: Wikipedia

## 3.3 Dispersive Elements

- **Many excitation sources generate light over a broad spectral range. The dispersive element allows to select a specific wavelength**
- **The common PMT type detectors cannot distinguish between photons of different wavelength. Thus, the light emitted by the sample also has to be fed through a dispersive element**
- **Notch, short or long pass filters are be a simple method for wavelength selection, but they do not allow dynamic selection. For that reason prisms or gratings are used.**



# 3.3 Dispersive Elements

- Dispersion prisms**

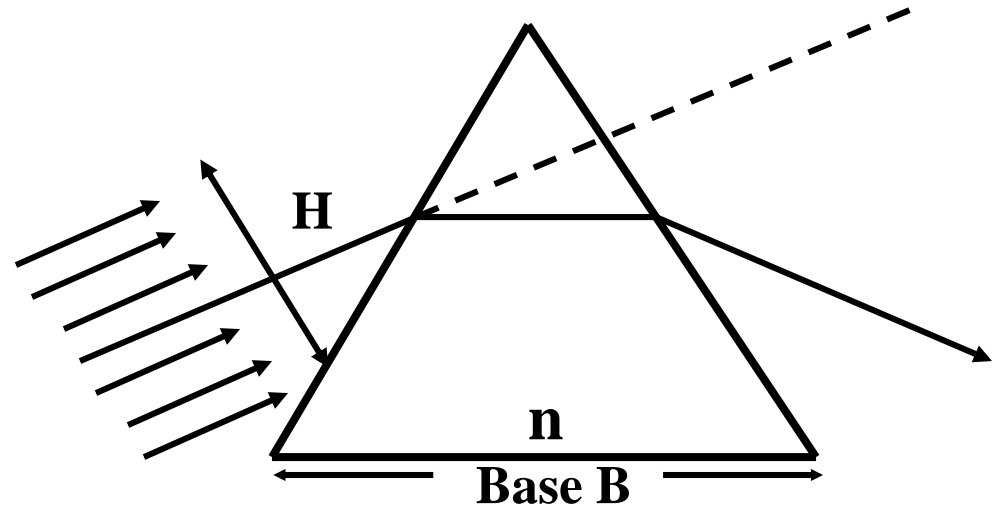
Angular dispersion:

$$d\delta/d\lambda = - B/H * dn/d\lambda$$

B = Prism base

H = Height of beam (slit width)

n = Refractive index



- Dispersion gratings**

Grating constant (lines / mm) determines the usable area  $\Rightarrow$  "Gratings"

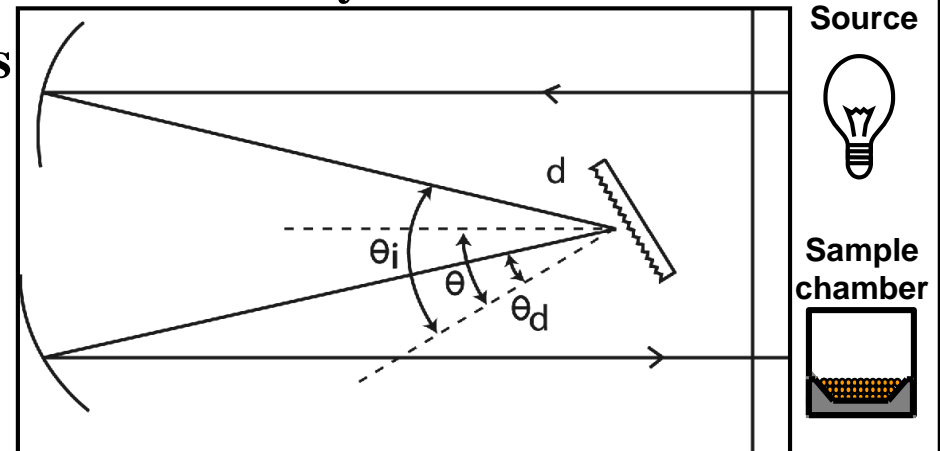
e.g. 1200 or 2400 lines / mm

Resolution :  $R = \lambda / d\lambda = m * N$

m = Order

N = Slit number

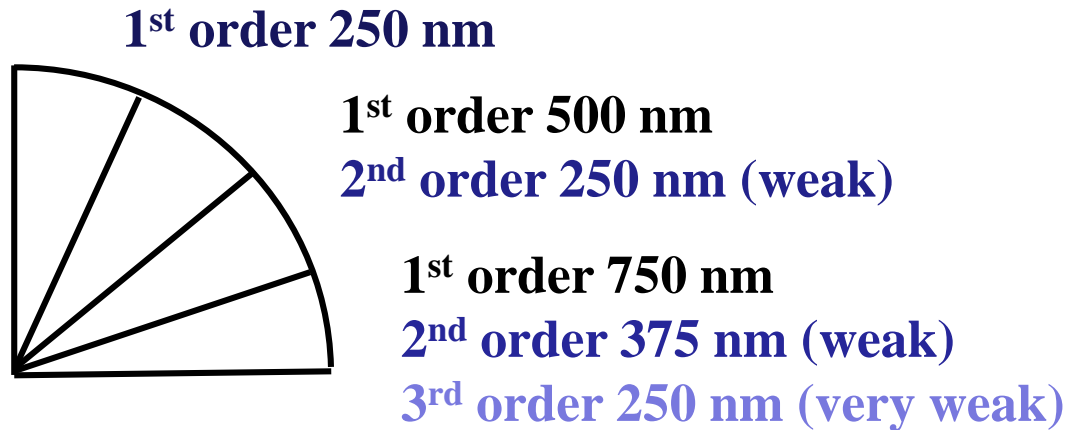
Czerny-Turner



Attention! Reflections of higher order  $\Rightarrow$  Filter

## 3.3 Dispersive Elements

### Higher orders upon use of a grating



**The second order has to be removed with a filter!**

**Example: 350 nm excitation, emission recorded from 450 to 800 nm**

**The grating will group 2<sup>nd</sup> order 350 nm photons from the lamp together with the 1<sup>st</sup> order 700 nm photons from the sample.....**

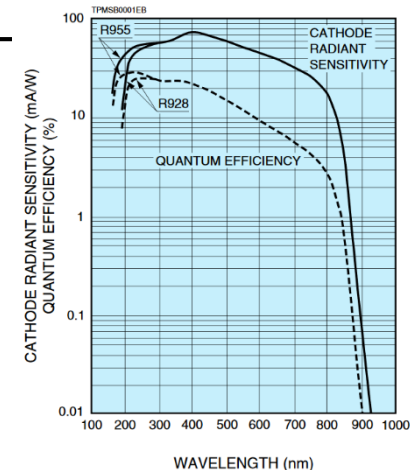
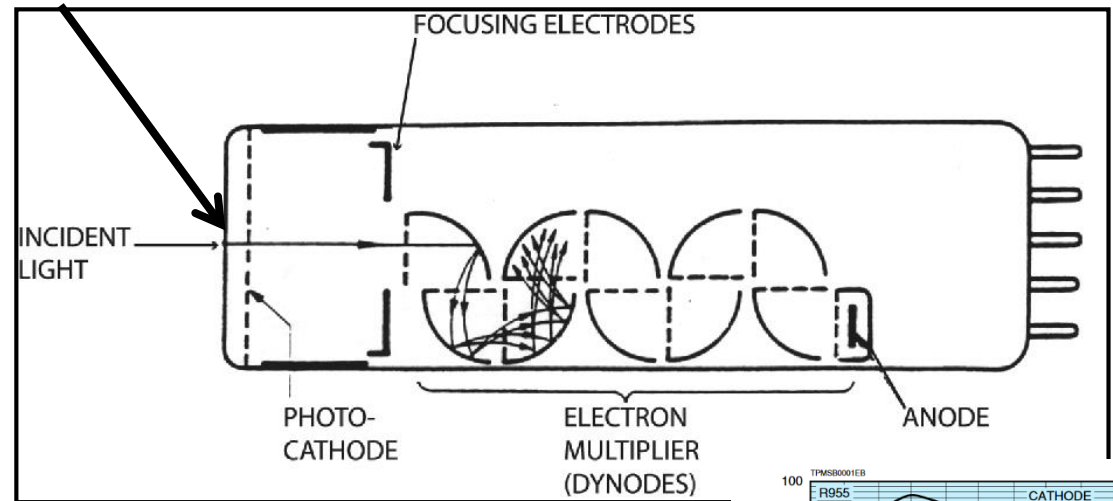
**Solution: A 400 nm long pass filter behind the sample blocks the 350 nm photons**

# 3.4 Detectors

## Types of detectors

- With external photoeffect
  - Photocells
  - Photomultiplier (PMT) →
- With internal photoeffect
  - Photoresistors
  - Photodiodes
- Photochemical detectors
  - for absolute measurements (actinometry)
  - Photochemical reaction with a known quantum yield QY
  - $2 [\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]^{3-} \rightarrow 2 \text{Fe}^{\text{II}} + 5 \text{C}_2\text{O}_4^{2-} + 2 \text{CO}_2 \uparrow$
  - Reaction of  $\text{Fe}^{2+}$  with phenanthroline + measuring the absorbance at 510 nm
  - Photons/s = number of formed product's molecules / (QY \* irradiation time)

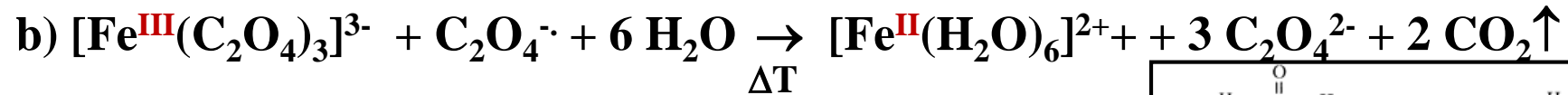
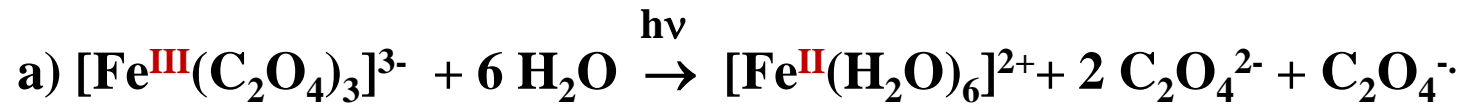
Window



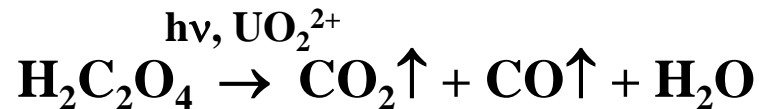
# 3.4 Detectors

## Actinometer (Photochemical detectors)

- Ferrioxalate actinometer (UV – 500 nm)



- Uranyloxalat actinometer (208 – 426 nm)

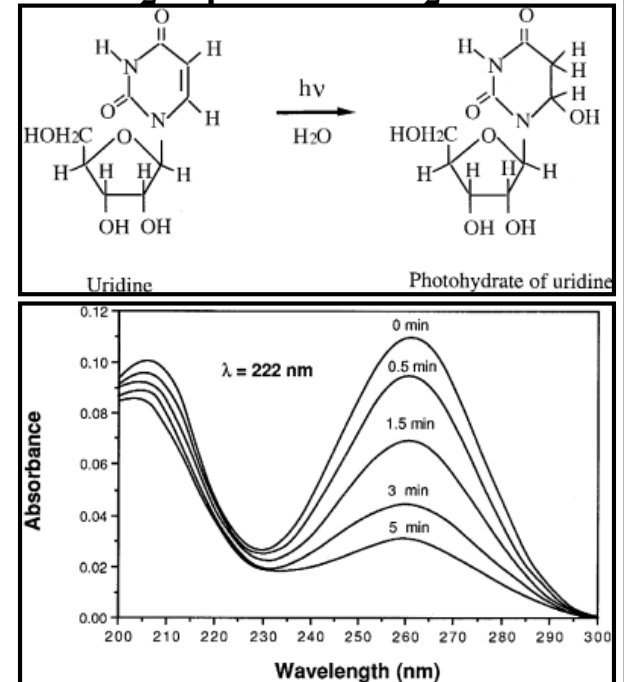


- KI/KIO<sub>3</sub> actinometer (UV/Vis ⇔ Grätzel cell)

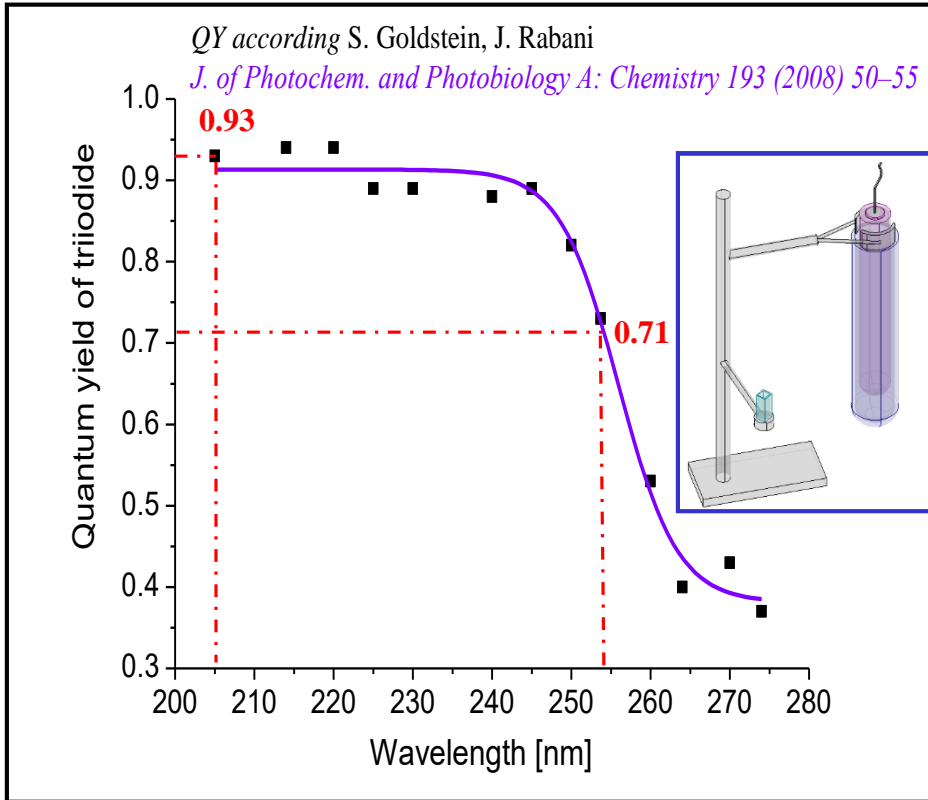


- Uridine actinometer (200 – 290 nm)

Lit.: J.-Y. Zhang et al., Applied Surface Science 109/110, 1997, 482



# 3.4 Detectors



**A = Absorbance at 352 nm (UV/Vis spectroscopy)**

**d = 1 cm cuvette**

**V = 3 cm<sup>3</sup>**

**S: Irradiated surface 3 cm<sup>2</sup>**

**F: Represent photon energy [mJ·mol<sup>-1</sup>] at emission wavelength of radiation source**

**Φ = Quantum yield of actinometer at emission wavelength of radiation source**

**ε = 27600 M·cm: molar absorption coefficient of I<sub>3</sub><sup>-</sup> at 352 nm**

**h = Planck constant = 6.626·10<sup>-34</sup> Js**

**c = Speed of light in vacuum = 3·10<sup>8</sup> ms<sup>-1</sup>**

**N<sub>A</sub> = Avogadro constant = 6.022·10<sup>23</sup> mol<sup>-1</sup>**

**λ = Wavelength of emitted radiation, e.g. 254 nm**

$$\text{Energy of photons/mol } F = \frac{h \cdot c \cdot N_A}{\lambda}$$

$$\text{Irradiance } H = \frac{A \cdot V \cdot F}{\emptyset \cdot \epsilon \cdot d \cdot S} \text{ [mW/cm}^2\text{]}$$



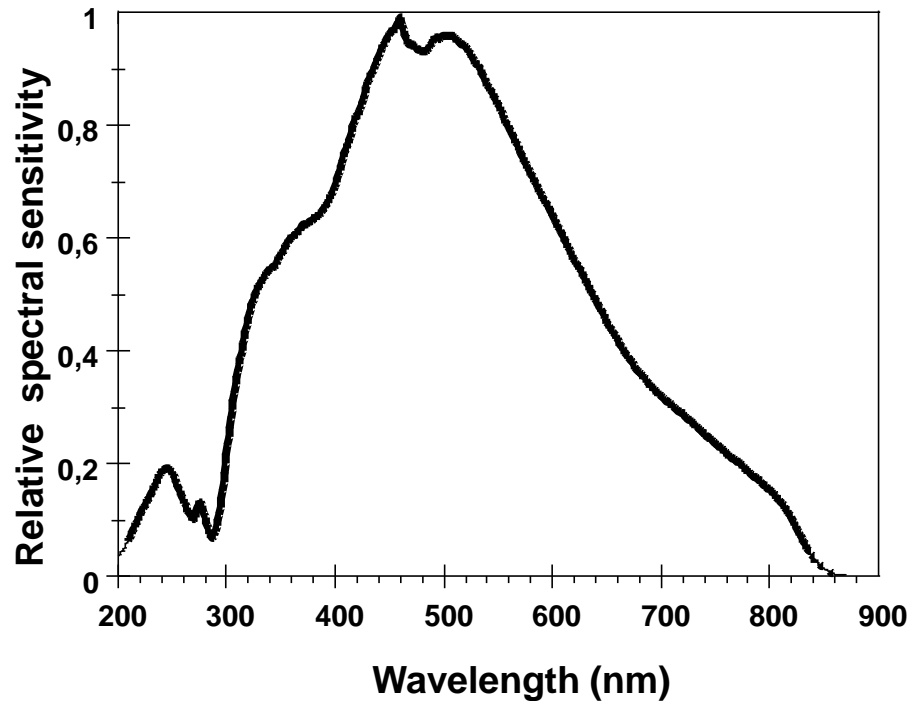
# 3.4 Detectors

## Spectral sensitivity

**Photomultiplier tube (PMT)**

**200 – 850 nm**

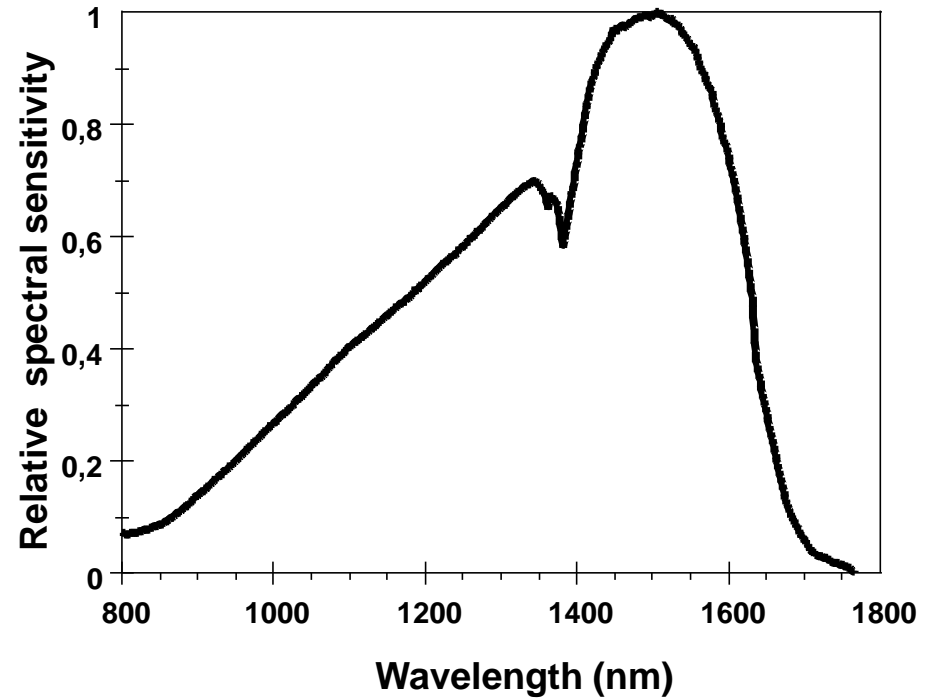
**(Peltier element cooling ~ 253 K)**



**Ge semiconductor detector**

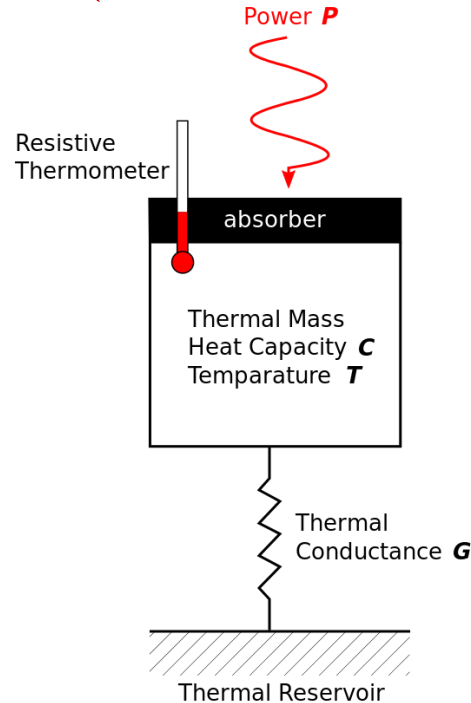
**800 – 1750 nm**

**(Liquid N<sub>2</sub> cooling 77 K)**



# 3.4 Detectors

## Bolometer (micro and radio waves)



- **Measurement of the spectral intensity via an increase in temperature caused by absorption of photons**
- **Slow, but very high sensitivity**

## Scintillation detector (ionizing radiation)

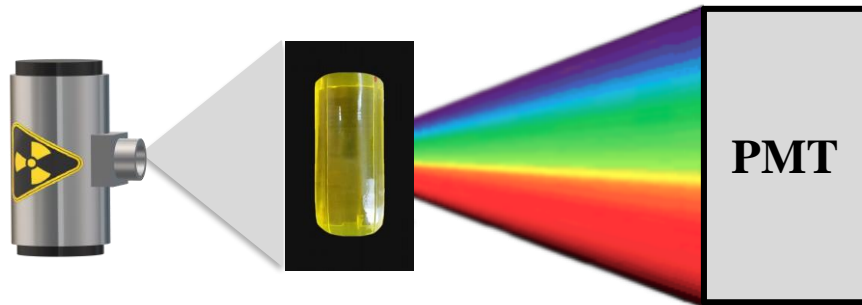


- **Ionizing radiation is converted into visible radiation and detected by a common PMT or CCD**
- **Fast and very high sensitivity**

# 3.4 Detectors

## Scintillators

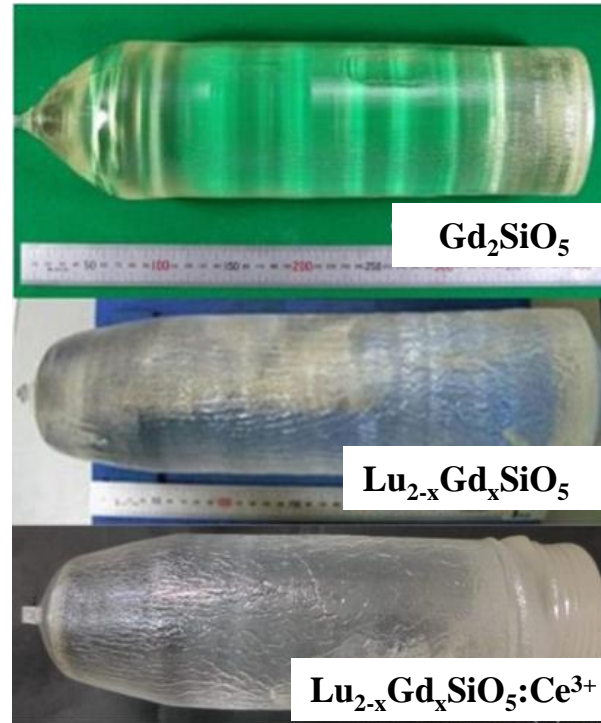
Scintillators absorb ionizing radiation and convert it to optical radiation, especially UV or visible radiation → X-ray and gamma detectors or cameras, space telescopes



**PMT = PhotoMultiplier Tube**

### Scintillator materials (selection)

- $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$  525 nm
- $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  500 nm
- $\text{PbWO}_4$  420 nm
- $\text{Lu}_{2-x}\text{Gd}_x\text{SiO}_5:\text{Ce}$  420 nm
- $\text{NaI}:\text{Tl}$  415 nm
- $\text{Lu}_2\text{Si}_2\text{O}_7:\text{Ce}$  380 nm
- $\text{LuPO}_4:\text{Ce}$  350 nm
- $\text{LuPO}_4:\text{Pr}$  235 nm



Inorganic scintillators are the technological backbone of modern medical diagnostic techniques, viz. CT, SPECT, PET

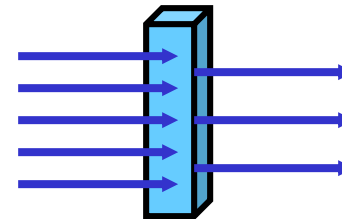
Source: <https://www.opt-oxide.com/en/singlecrystals> (03.12.2018)

# 3.5 Sample Chamber

## Geometry

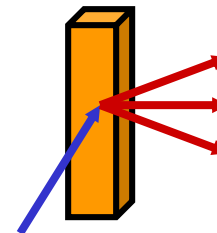
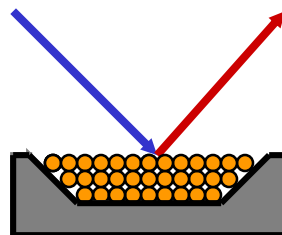
### Absorption spectroscopy

- **Linear arrangement: laser source - mono - sample - detector**
- **One-or two-beam arrangement**



### Fluorescence spectroscopy

- **Rectangular arrangement: laser source - mono1 - sample - mono2 - detector**
- **Sample is lying (powder sample holder) or standing (quartz cells for solutions)**



# 3.5 Sample Chamber

## Atmosphere

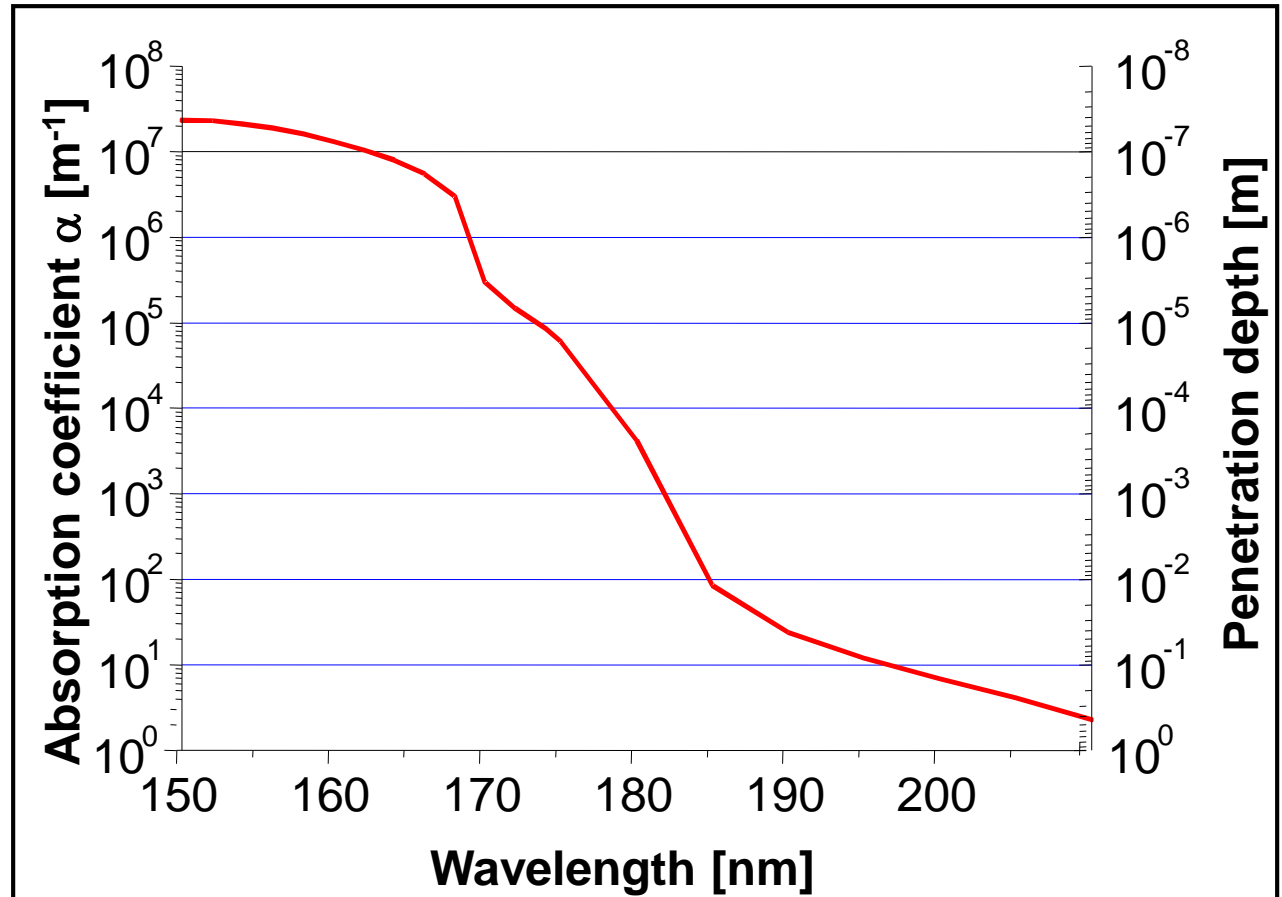
**H<sub>2</sub>O and O<sub>2</sub> absorb radiation below approximately 200 nm**

**UV/Vis-measurements  
(200 – 800 nm excitation)**

⇒ air /water

**VUV- measurements  
(100 – 200 nm excitation)**

⇒ Vacuum, Ar, or N<sub>2</sub>

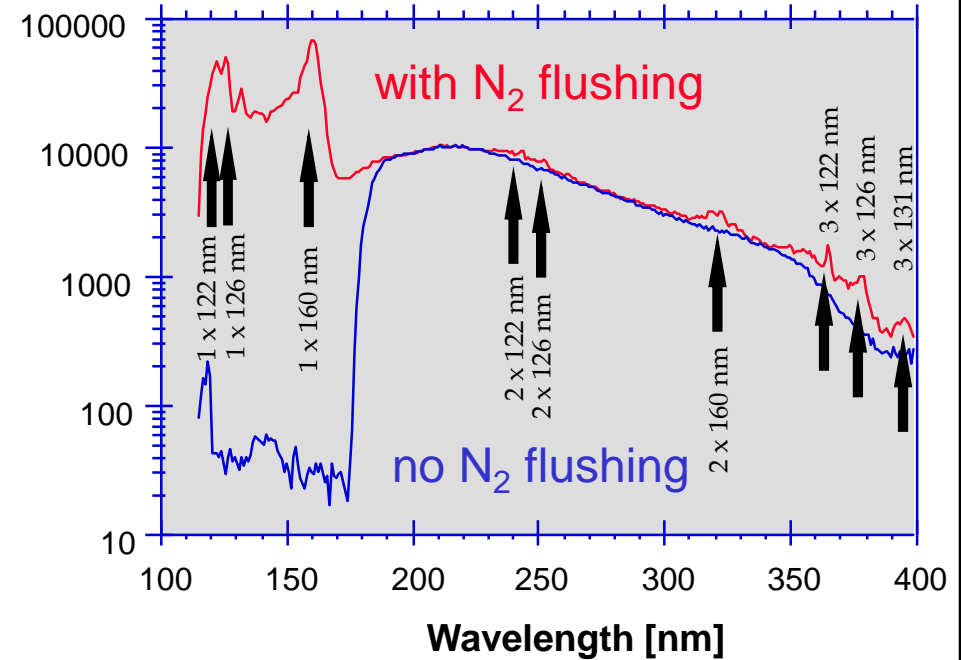
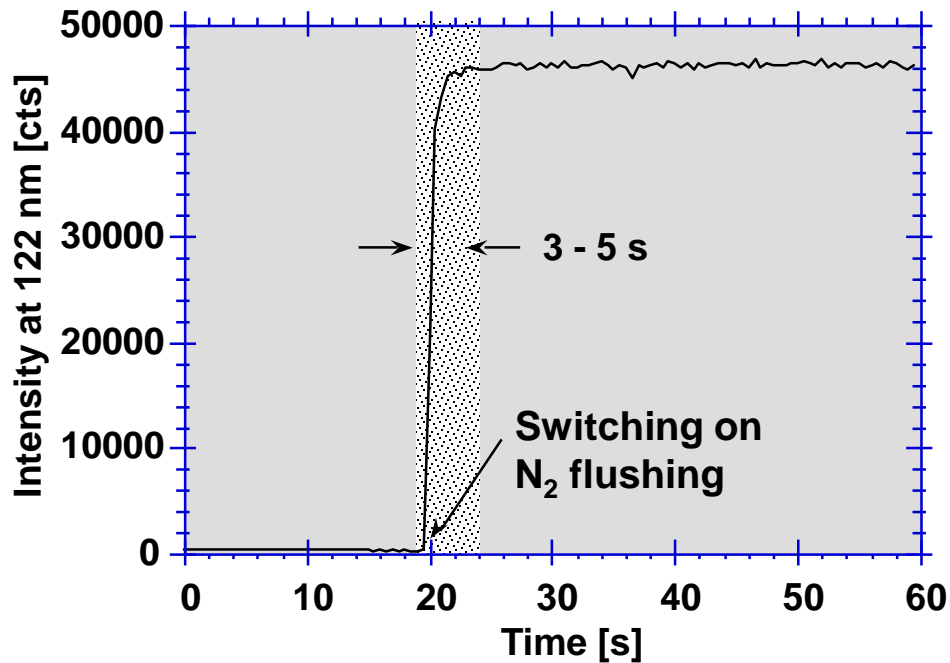


# 3.5 Sample Chamber

## Atmosphere

Effect of flushing with an inert gas, e.g. N<sub>2</sub>

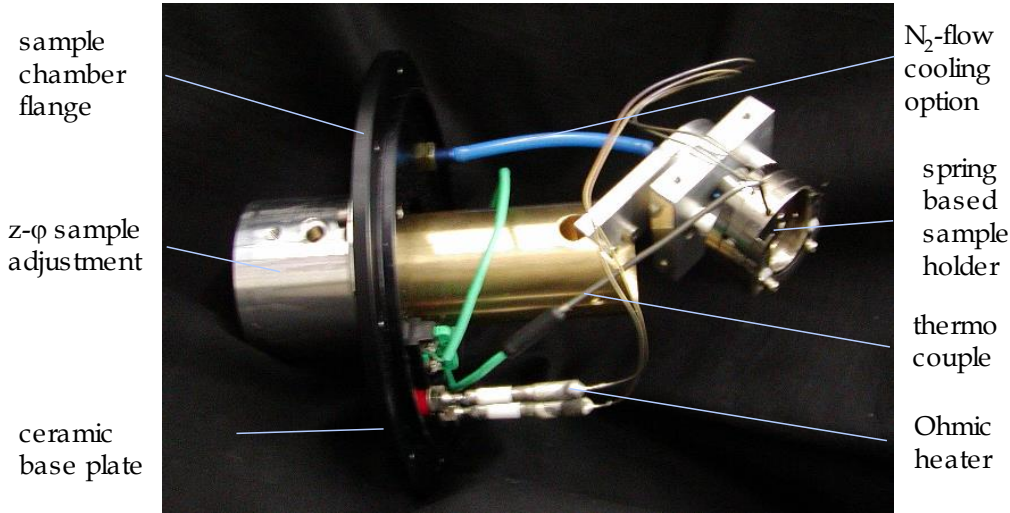
1. Transmission up to about 120 nm
2. Loss of the filtering effect for higher-order maxima (2<sup>nd</sup> & 3<sup>rd</sup> order)



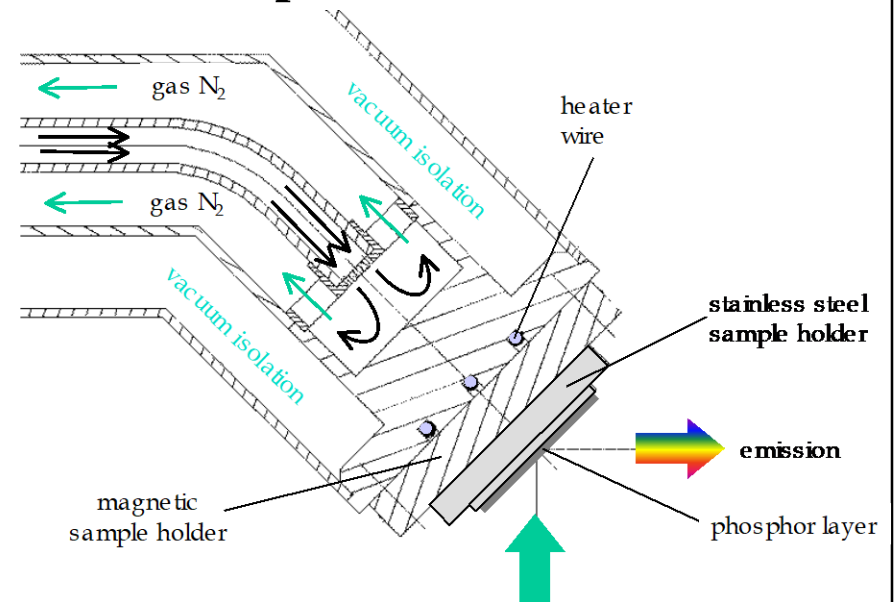
# 3.5 Sample Chamber

Depending on required conditions, the sample can be heated or cooled

## Sample holder with heater



## Schematics of a coolable sample holder



# 3.5 Sample Chamber

## He cryostat

- **Temperatures around 0.8 – 4.2 K**
- **Continuous flow cryostats have a high He consumption (cost ~ 7 €/l)**
- **Closed-cycle cryostats cool the He vapour have a high energy consumption**
- **Pulse tube cryostats do not consume He. They work similar to a Refrigerator. Aquisition is rather expensive ~ 50,000 €**



**Pulse tube cryocooler  
(Image: Oxford Instruments)**



# 4. Methods of Optical Spectroscopy

## 4.1 Absorption Spectroscopy

4.1.1 Bouguer-Lambert-Beer-Law

4.1.2 Validity of the Lambert-Beer-Law

4.1.3 Deviation from the Lambert-Beer-Law

4.1.4 Extinction of Biologically Relevant Molecules

4.1.5 Atomic Absorption Spectroscopy

# 4.1.1 Bouguer-Lambert-Beer-Law

## Derivation

The weakening of the intensity is proportional to the intensity and the layer thickness (**Bouguer-Lambert**):

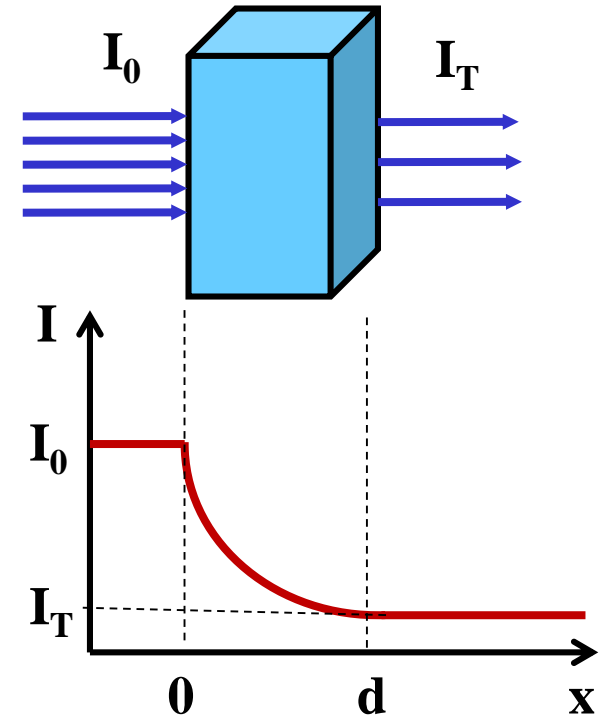
$$dI \sim I \cdot dx \quad \text{or} \quad dI = -\alpha(\lambda) \cdot I \cdot dx$$

The proportionality factor  $\alpha(\lambda)$  is proportional to concentration  $c$  (**Beer 1852**):

$$dI = -\alpha(\lambda) \cdot c \cdot I \cdot dx \Rightarrow dI/I = -\alpha(\lambda) \cdot c \cdot dx$$

Integration yields  $\ln(I_0/I_T) = \alpha(\lambda) \cdot c \cdot x$  or  $\log(I_0/I_T) = \alpha(\lambda) \cdot c \cdot x / \ln 10$

Combining gives  $\log(I_0/I_T) = \varepsilon(\lambda) \cdot c \cdot x = A$  with  $\varepsilon(\lambda) = \alpha(\lambda) / \ln 10$   
= molar extinction coefficient [ $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ]

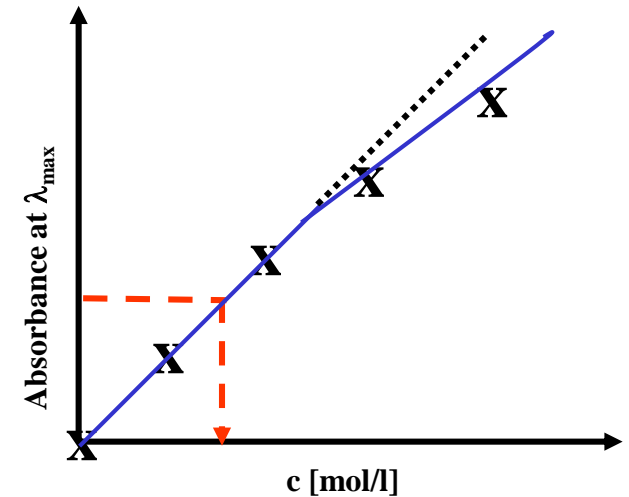


# 4.1.2 Validity of the Lambert-Beer-Law

**The formulation and the validity depends on several boundary conditions**

## Conditions

1. The incident light must be collimated and monochromatic
2. The absorbing molecules must be highly diluted that a mutual interaction of the chromophoric groups of different molecules does not occur
3. The pure solvent does not absorb radiation of measuring wavelength
4. Radiation losses due to reflection from the plane-parallel walls of the cuvette and by scattering by particles does not occur

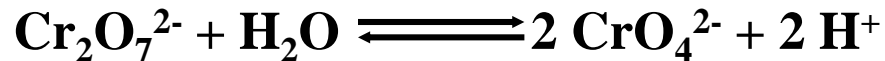


# 4.1.3 Deviation from the Lambert-Beer-Law

## Apparent and real deviations

### Apparent: Technical measurement inadequateness

- Sieve effects: scattering centers in the solution
- Dissociation or association equilibria, e.g.



$$A = \log \frac{I_0 + I_s}{I + I_s}$$

- Lack of monochromaticity of the applied radiation (false light  $I_s$ ) leads to a background signal that reduces the dynamic  
Maximum absorption dynamics  $A = 1.04$  for 10% false light  
Maximum absorption dynamics  $A = 4.00$  for 0.01% false light  
(typical of single monochromators)

### Real: Intermolecular interaction

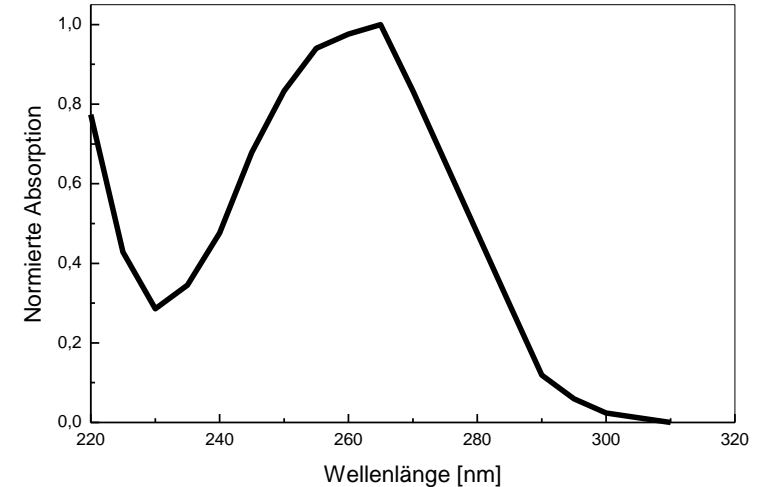
- Too high concentration  $> 10^{-3}$  mol/l  
⇒ Mutual interaction of the chromophores in the solution

# 4.1.4 Extinction of Biologically Relevant Molecules

## Analysis of biomolecules

Species	$\lambda_{\max}$ [nm]	$\epsilon$ [l $\cdot$ mol $^{-1}$ cm $^{-1}$ ]	Transition
Cytochrome c Fe $^{2+}$	420	120000	$\pi$ - $\pi^*$
Cytochrome c Fe $^{3+}$	410	110000	$\pi$ - $\pi^*$
Hemoglobin	560	12000	$\pi$ - $\pi^*$
Oxyhemoglobin	550, 574	13000, 14000	$\pi$ - $\pi^*$
Adenine	260	13400	$n$ - $\pi^*$ , $\pi$ - $\pi^*$
Guanine	275	8100	$n$ - $\pi^*$ , $\pi$ - $\pi^*$
Cytosine	267	6100	$n$ - $\pi^*$ , $\pi$ - $\pi^*$
Thymine	264	7900	$n$ - $\pi^*$ , $\pi$ - $\pi^*$
AMP	260	15500	$n$ - $\pi^*$ , $\pi$ - $\pi^*$
ss-poly-AMP	260	10600	$n$ - $\pi^*$ , $\pi$ - $\pi^*$
ds-poly-ATMP	258	9600	$n$ - $\pi^*$ , $\pi$ - $\pi^*$

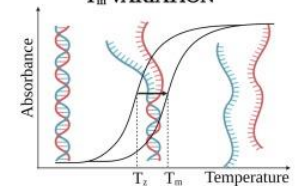
Absorption spectrum of dTMP



## Applications areas

- Fusing of DNA
- Oxidation state of hemoglobin and Cytochromes

SPECIFIC BUFFER EFFECT ON DNA  $T_m$  VARIATION



DNA stabilization buffer series:

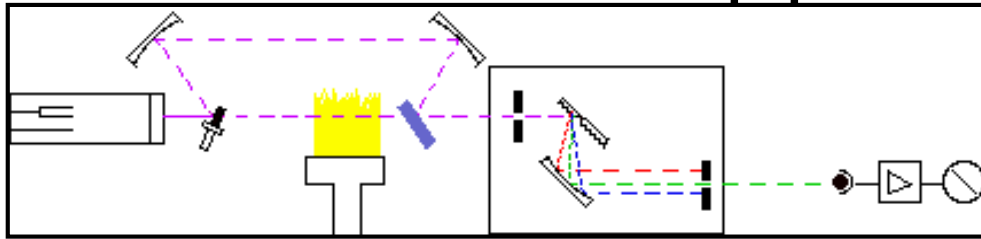
Tris > Cacodylate > Phosphate > Citrate

# 4.1.5 Atomic Absorption Spectroscopy

## Principle and application of Atomic Absorption Spectroscopy (AAS)

**Kirchoff's law:** Any material can also absorb the radiation, which was emitted by itself (each element has a characteristic line spectrum).

### Basic construction of an AAS equipment



**Hollow cathode lamps**

**Burners (air / acetylene: 2300 °C)**

**Monochromator or filter**

**Detector**

The weakening of the emission (absorption) is determined by a calibration process

### Some application areas of AAS

- Metal analysis in alloys
- Lead in fuel
- Pollutants in environment
- Mg in plants

# 4. Methods of Optical Spectroscopy

## 4.2 Luminescence Spectroscopy

### 4.2.1 Definition and Applications

### 4.2.2 Construction of a Fluorescence Spectrometer

### 4.2.3 Emission Spectroscopy

### 4.2.4 Excitation Spectroscopy

### 4.2.5 Quantum Yield

### 4.2.6 Light output

### 4.2.7 Temperature Resolved Spectroscopy

### 4.2.8 Time Resolved Spectroscopy

# 4.2.1 Definition and Applications

## Definition

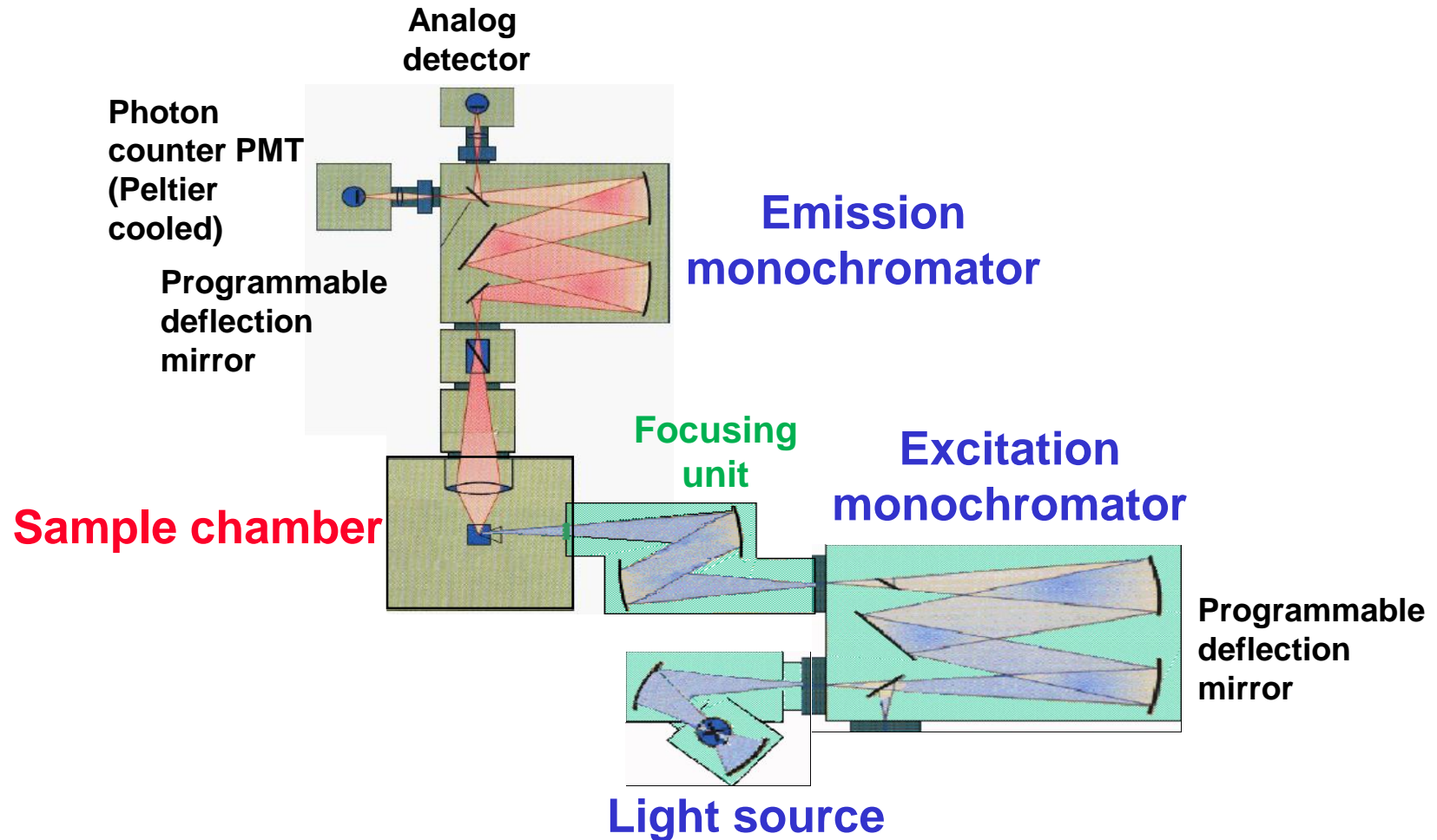
**Luminescence is the emission of radiation by a system (solid, liquid or molecule) in a non-equilibrium state after energy has been supplied to the system**

## Applications

- **Characterization of the spectral energy distribution of the emission of liquid or solid samples (glass, ceramics, solutions, or powders)**
  - ⇒ **Emission spectra**
- **As a function of excitation energy/wavelength**
  - ⇒ **Excitation spectra**
- **As a function of temperature**
  - ⇒ **Thermal quenching**
  - ⇒ **Glow curves and thermo luminescence**
- **As a function of time after the excitation pulse**
  - ⇒ **Decay curves and constants**



# 4.2.2 Construction of a Fluorescence Spectrometer



Typical excitation wavelength from 100 to 1000 nm

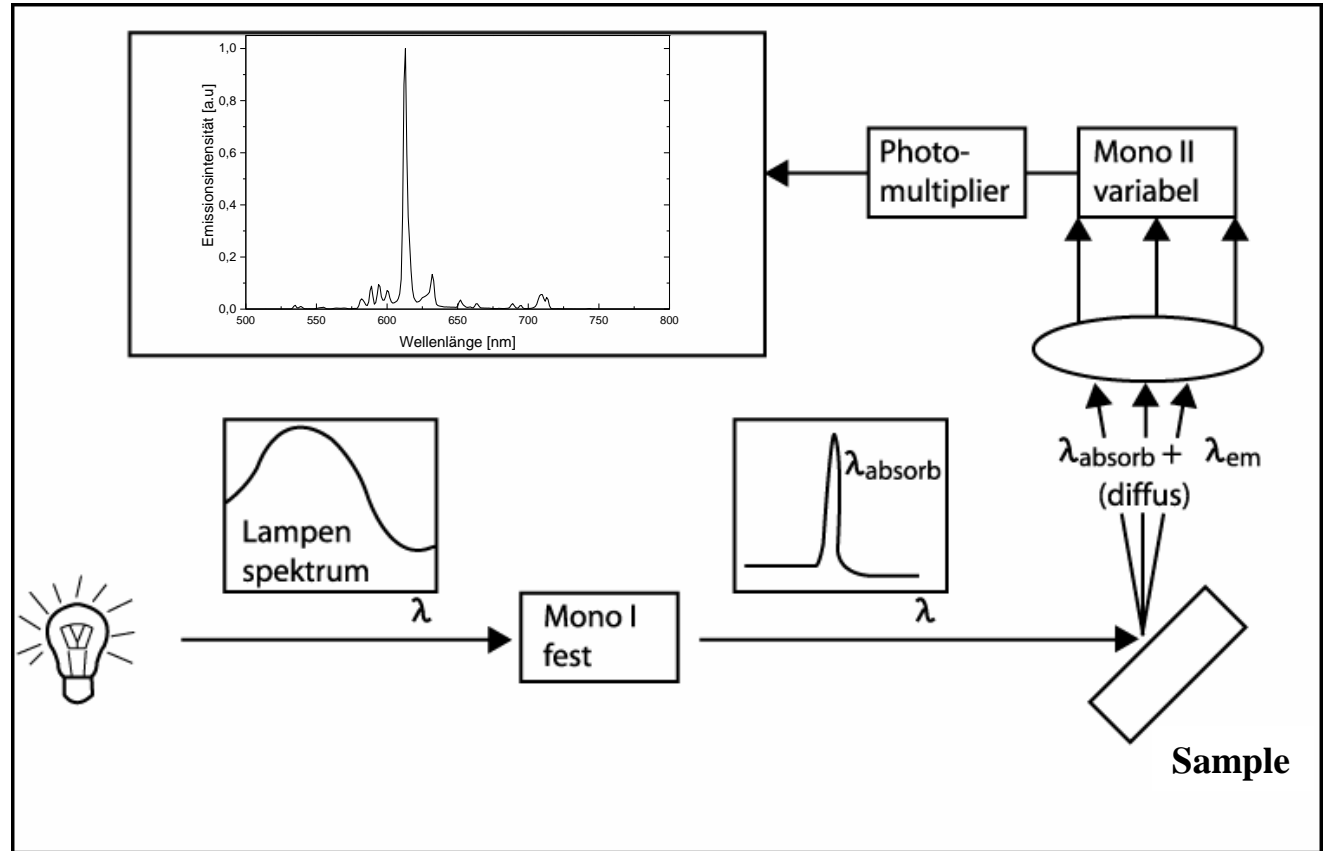
## 4.2.3 Emission Spectroscopy

### Measurement of the intensity as a function of emission wavelength

**Mono 1:**  
Constant, e.g. @ 254 nm

**Mono 2:**  
variable, e.g. from 500  
to 800 nm

**Slit width determines  
the maximum attainable  
optical resolution**

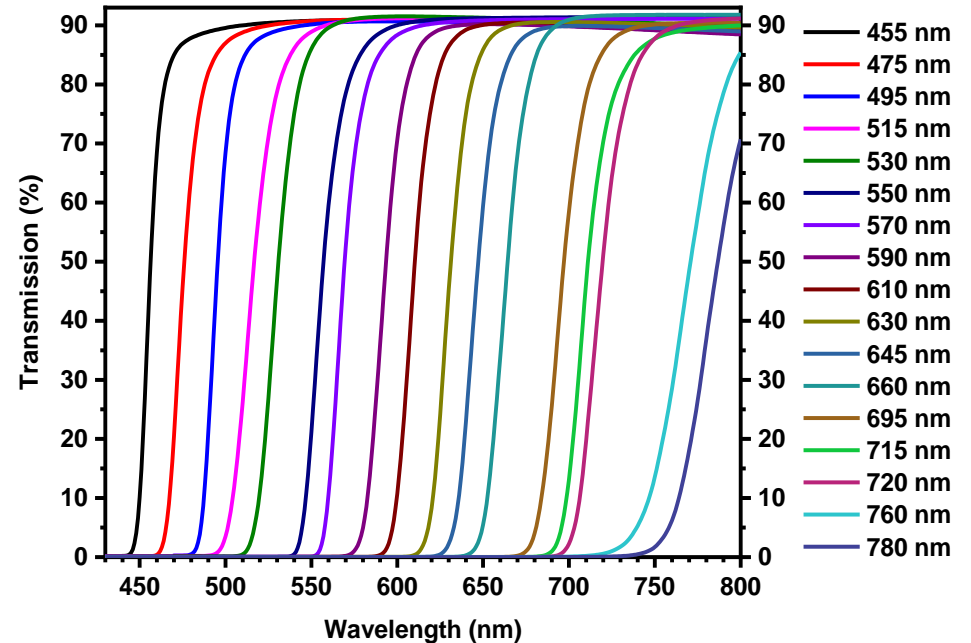
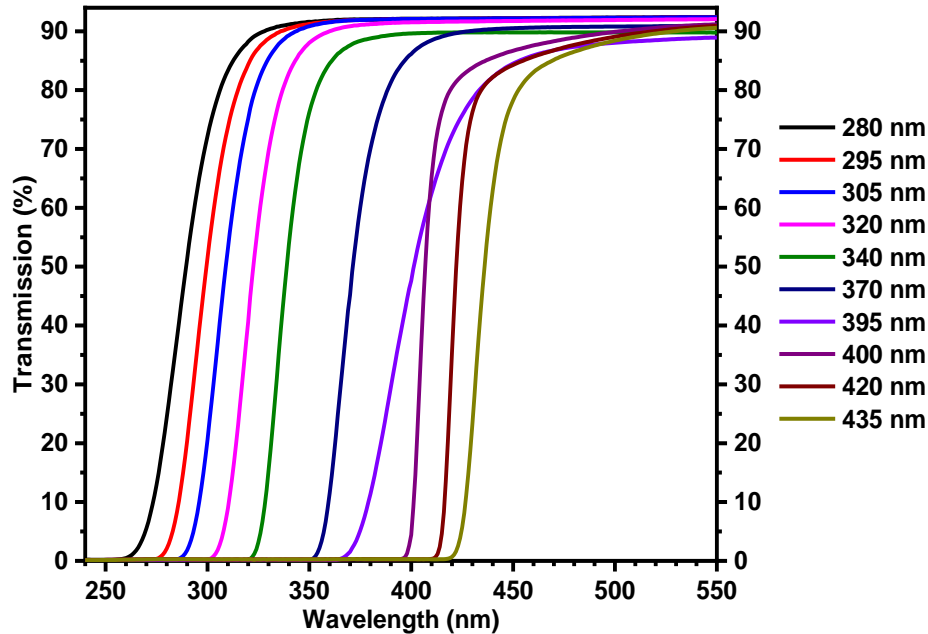


**$I(\lambda)$  must be compensated for the fluctuations of the light source, for example, by a quantum counter, reflected monochromatic light of excitation beam must be filtered**

# 4.2.3 Emission Spectroscopy

## Measurement of the intensity as a function of emission wavelength

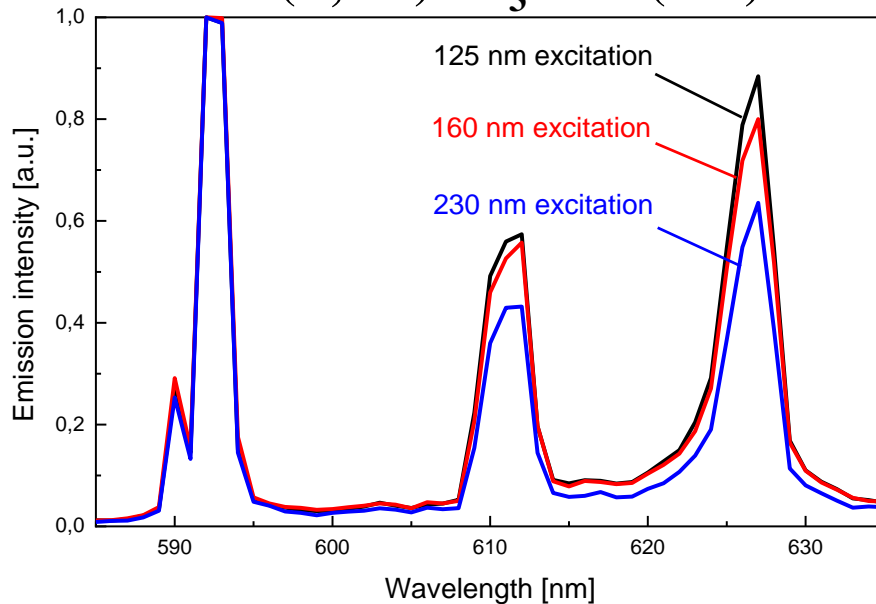
### Removal of reflected monochromatic light of excitation beam by a long-pass filter



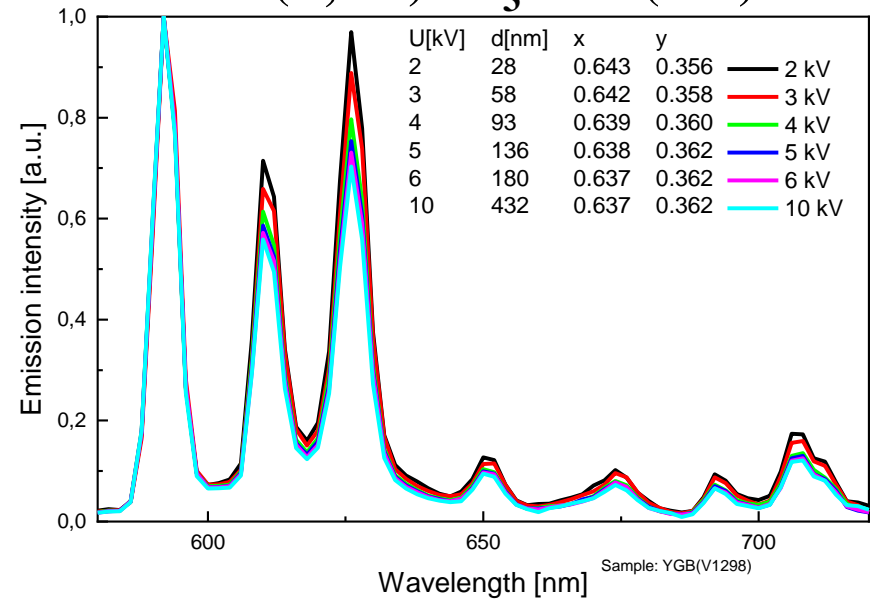
# 4.2.3 Emission Spectroscopy

The emission spectrum of a sample depends on the excitation energy

**Photoluminescence  
of (Y,Gd)BO<sub>3</sub>:Eu<sup>3+</sup>(5%)**



**Cathodoluminescence  
of (Y,Gd)BO<sub>3</sub>:Eu<sup>3+</sup>(5%)**



The excitation energy or wavelength determines the penetration depth of the radiation or of the electrons in the sample, whereby the emission spectrum might be modulated → change of CIE colour coordinates x, y

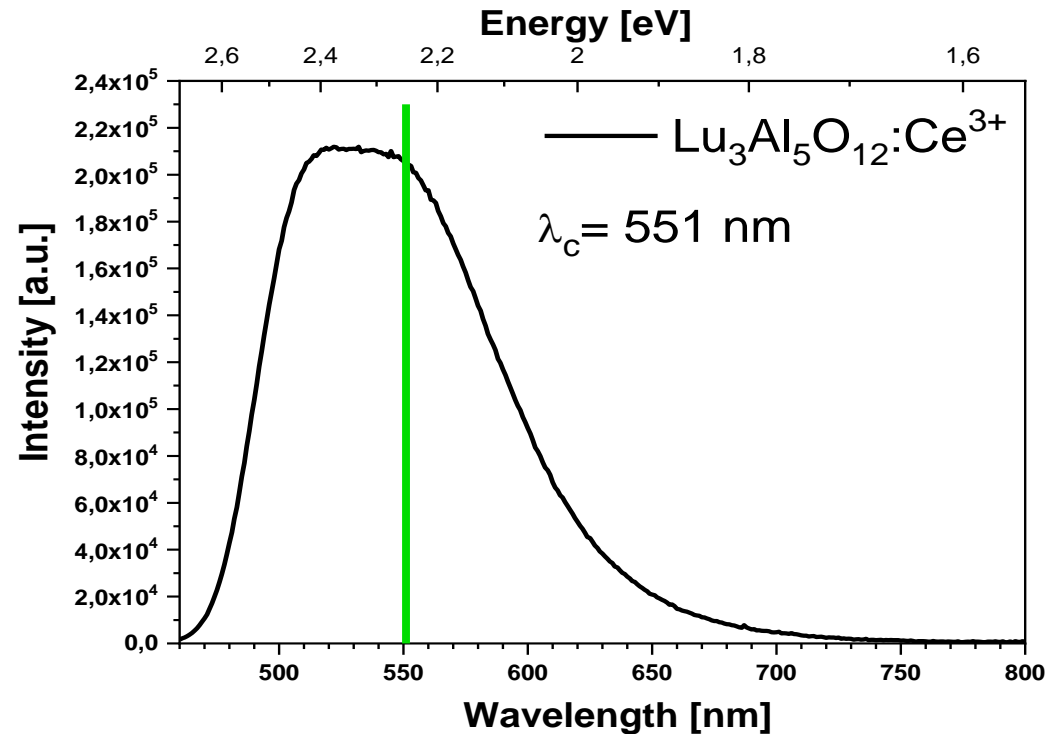
Penetration depth of electrons:  $r \sim 0.046 \cdot U^{5/3} / \rho$  [ $\mu\text{m}$ ] → 2 kV: 30 nm, 10 kV: 400 nm

## 4.2.3 Emission Spectroscopy

**From the emission spectrum the emission maxima is obtained and the centroid wavelength can be calculated**

The centroid wavelength  $\lambda_c$  is the wavelength, at which the integral of an emission spectrum is subdivided into two equal fractions. It thus corresponds to the median photon energy of the emission spectrum.

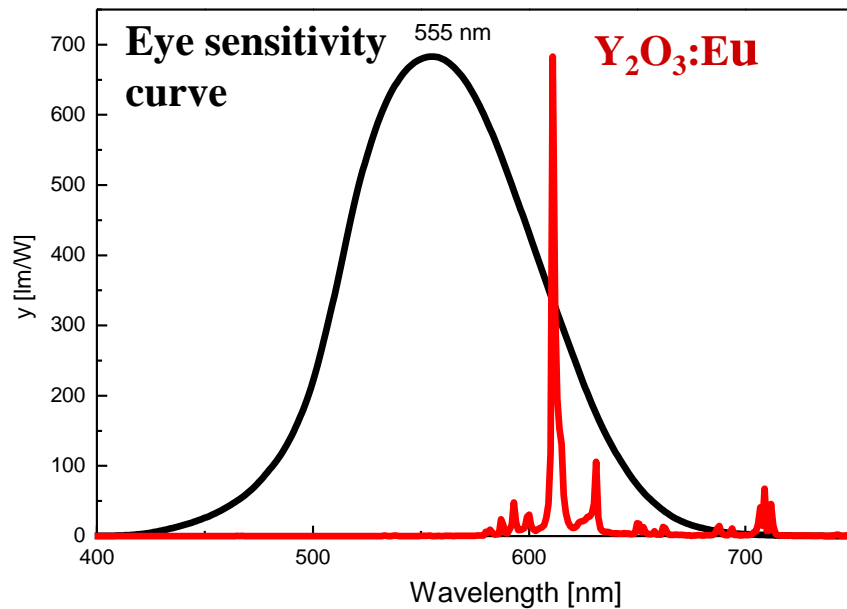
$$\lambda_c = \frac{\int_{\lambda_1}^{\lambda_2} \lambda \cdot S(\lambda) \cdot d\lambda}{\int_{\lambda_1}^{\lambda_2} S(\lambda) \cdot d\lambda}$$



# 4.2.3 Emission Spectroscopy

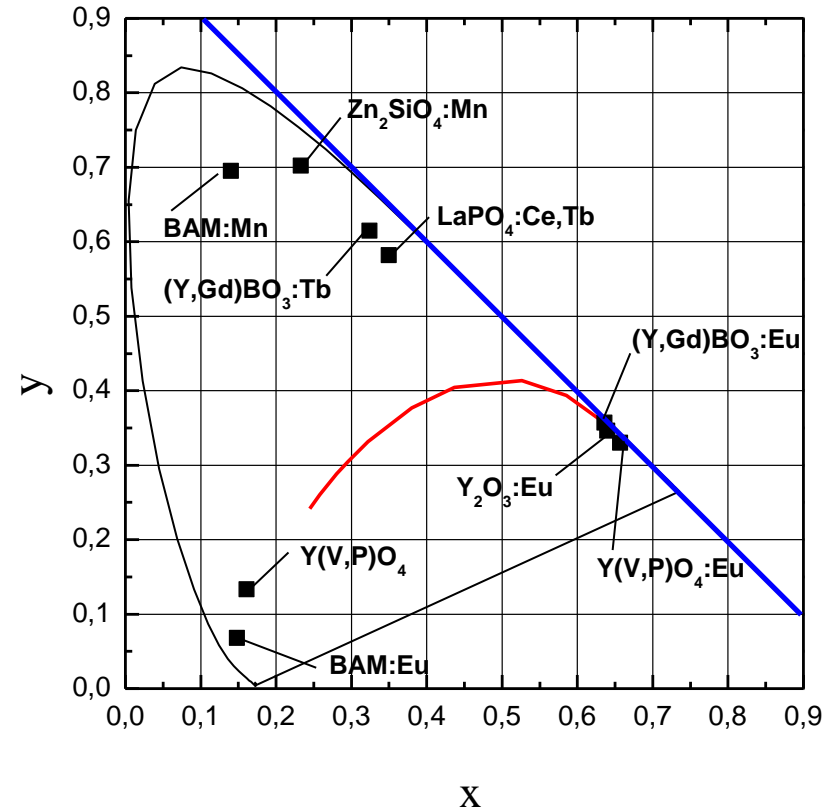
From the emission spectrum of light physiological figures can be calculated

Lumen equivalent LE [lm/W]



These quantities characterize inter alia the emission spectrum of light sources and phosphors

Chromaticity coordinate x, y (CIE 1931) or coordinate  $u'$ ,  $v'$  (CIE 1976)



# 4.2.3 Emission Spectroscopy

## VUV Spectroscopy

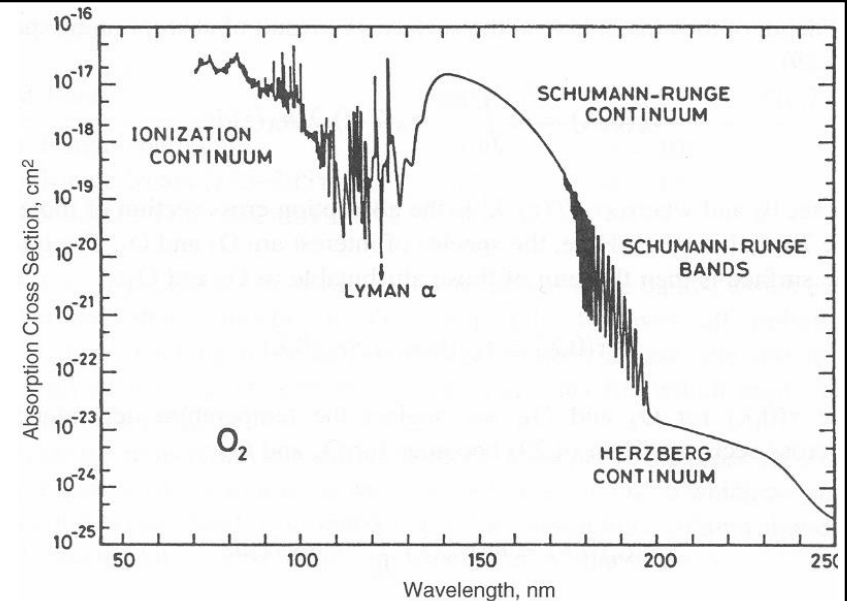
VUV spectroscopy requires a special instrumental setup, as VUV radiation is absorbed by  $O_2$  and  $H_2O$ .  $CO_2$  will be split photochemically into C and  $O_2$  (dark layer on mirrors)

- Lamp (deuterium), monochromator and detector in high vacuum ( $10^{-6}$  mbar)
- The sample chamber can be flooded with  $N_2$ . This facilitates changing of the sample. The sample chamber is connected to the rest of the system via LiF or  $MgF_2$  windows

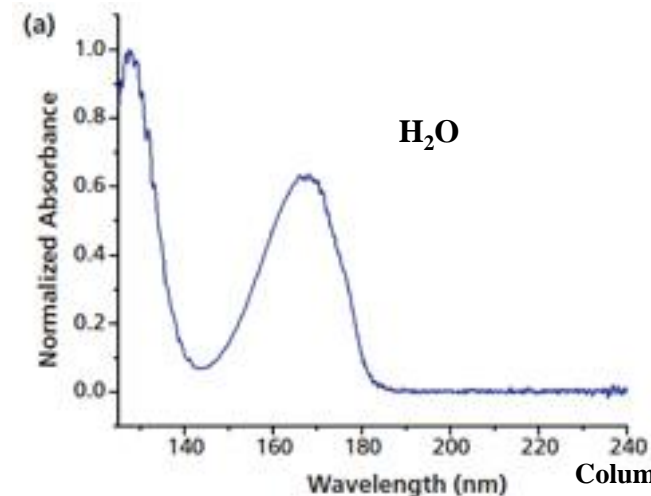
$MgF_2$ :  $E_g = 10.8$  eV (115 nm)

$LiF$ :  $E_g = 13 - 14$  eV (89 - 95 nm)

**Problem: Fluorides degrade due to OH take-up**



J. Seinfeld, S. Pandis, *Atmospheric Chemistry and Physics*



Column 13 (2017) 9

# 4.2.3 Emission Spectroscopy

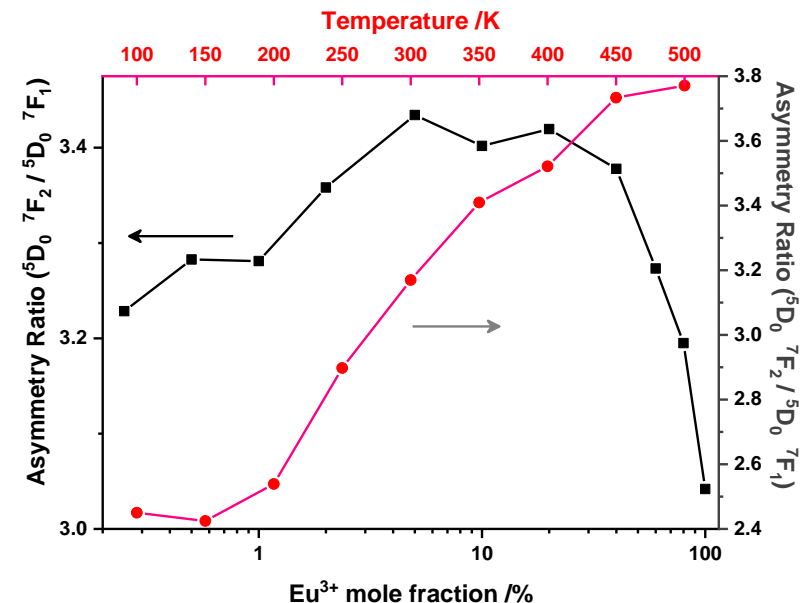
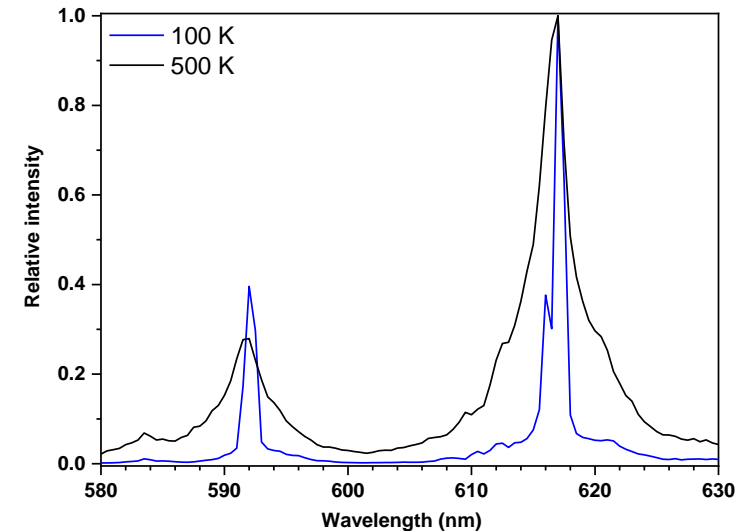
## Impact of temperature and site symmetry

Temperature increase results in line broadening due to coupling to vibronic levels

Some  $\text{Eu}^{3+}$  related optical transitions, e. g. at about 615 nm, are the less probable, the closer the local site symmetry is to an inversion symmetry.

The intensity ratio of  $I_{615}/I_{590}$  is called **asymmetry ratio** – the larger the value, the less symmetrical the dopant site.

The asymmetry ratio can change depending on temperature, pressure or other parameters



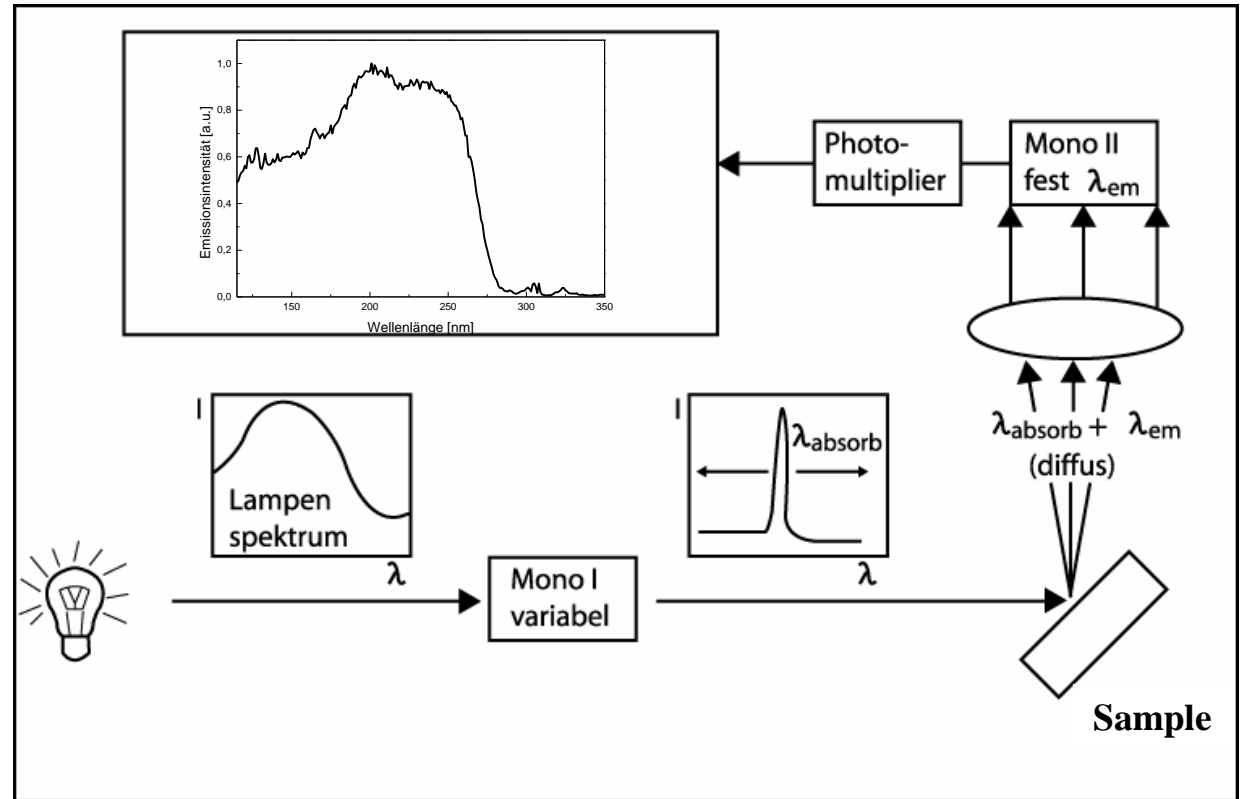


# 4.2.4 Excitation Spectroscopy

## Measurement of the intensity as a function of excitation wavelength

**Mono 1:**  
variable, e.g. from 120  
to 400 nm

**Mono 2:**  
constant, e.g. 611 nm  
( $\text{Y}_2\text{O}_3:\text{Eu}$ )



**Correction of the excitation spectrum for the spectrometer transfer function (set)  
by use of rhodamine B (constant quantum yield below approximately 500 nm)**

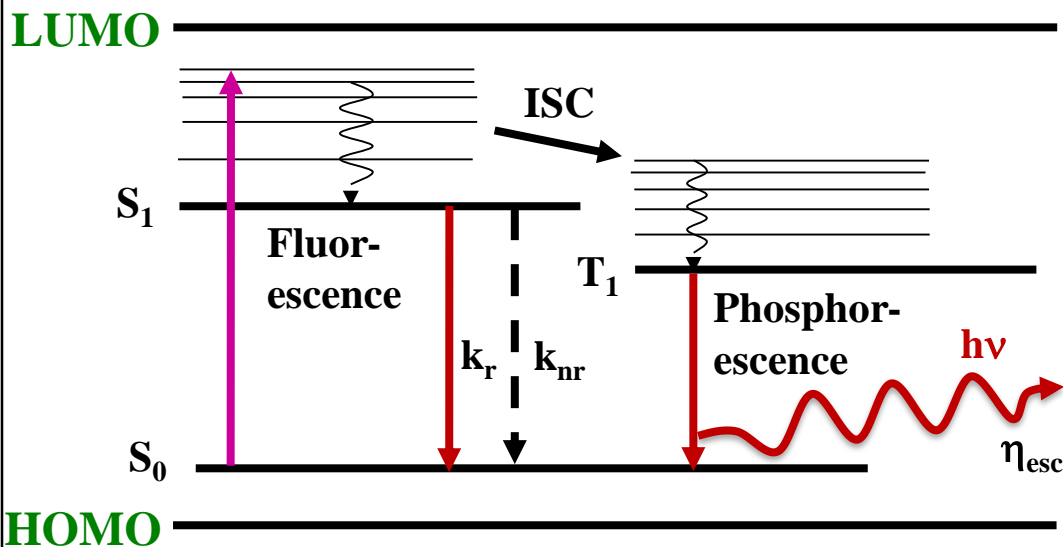
$$I(\lambda_{\text{exc}}) = I^{\text{sample}}(\lambda_{\text{exc}}) / I^{\text{set}}(\lambda_{\text{exc}})$$

# 4.2.5 Quantum Yield

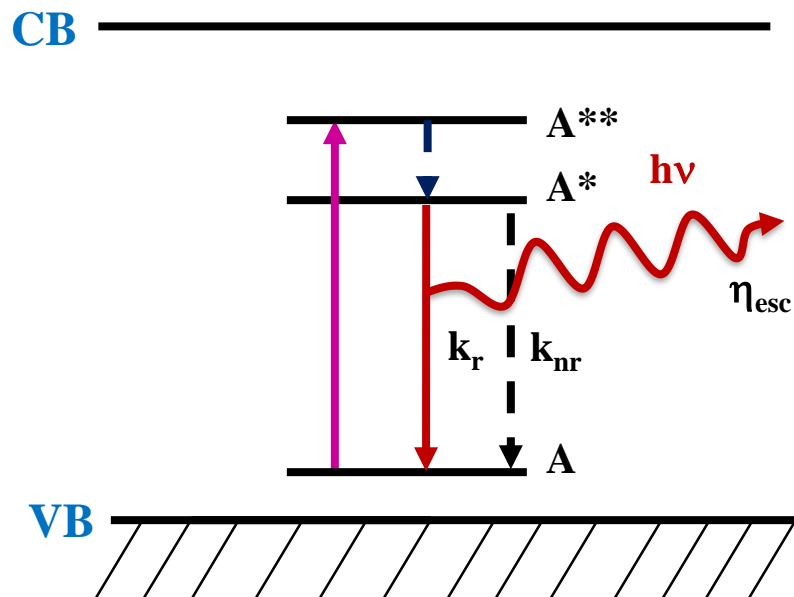
Absorption of radiation yields excited states, which then return to the ground state

Excitation energy <  $E_G$  of solvent or host crystal  $\sim \Delta E$  of optical centres

Organic materials (luminophores, dyes)



Inorganic materials (phosphors)



$$QY = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}}$$

Such QY has to be corrected by

- absorption strength
- refractive indices

## 4.2.5 Quantum Yield

### Definitions

- The PL quantum efficiency QY is defined as the ratio of the number of emitted photons by the number of absorbed photons, while this figure can be regarded as the external quantum yield (EQY), which is the macroscopic view on a material
- In practice, QY is often determined by comparative measurements with a reference compound for which it has been determined with a high degree of accuracy, e.g. from US NIST or German PTB
- Ideally, a reference compound should have
  - the same absorbance (A) as the compound of interest at given excitation wavelength
  - similar excitation-emission characteristics to compound of interest, otherwise instrument's transfer function should be taken into account
  - Same solvent/matrix, because intensity of emitted light is dependent on refractive index (n), otherwise a correction has to be applied
  - Yields similar fluorescence intensity to ensure measurements are taken within the range of linear instrument response

$$\frac{QY^u}{QY^s} = \frac{I^u}{I^s} \times \frac{n^2(u)}{n^2(s)}$$

# 4.2.5 Quantum Yield

## Relative measurements in comparison to references

### Typical reference materials (determined by PTB, Germany)

Spectral region	Material	QY at 253.7 nm (Hg line)
UV-B	LaPO <sub>4</sub> :Ce	90%
UV-A	BaSi <sub>2</sub> O <sub>5</sub> :Pb	88%
Blue	BaMgAl <sub>10</sub> O <sub>17</sub> :Eu	89%
Green	Zn <sub>2</sub> SiO <sub>4</sub> :Mn	80%
Red	Y <sub>2</sub> O <sub>3</sub> :Eu	84%

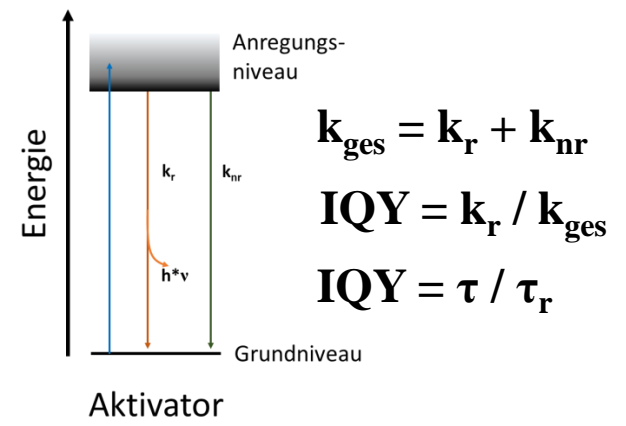
For the determination of the quantum yield one determines the integral  $I$  of the emission spectrum (proportional to the number of emitted photons) and the reflectance  $R$  of the substance or the reference at the excitation wavelength  $\lambda_{\text{exc}}$

$$\Phi_{\text{sample},\lambda_{\text{exc}}} = \Phi_{\text{reference},\lambda_{\text{exc}}} \cdot \frac{\int I_{\text{sample}} d\lambda - \int I_{\text{black}} d\lambda}{\int I_{\text{reference}} d\lambda - \int I_{\text{black}} d\lambda} \cdot \frac{1 - R_{\text{reference},\lambda_{\text{exc}}}}{1 - R_{\text{sample},\lambda_{\text{exc}}}}$$

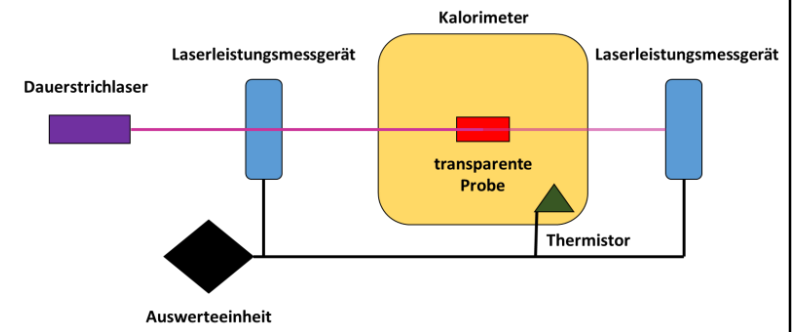
# 4.2.5 Quantum Yield

## Absolute methods for the determination of QY

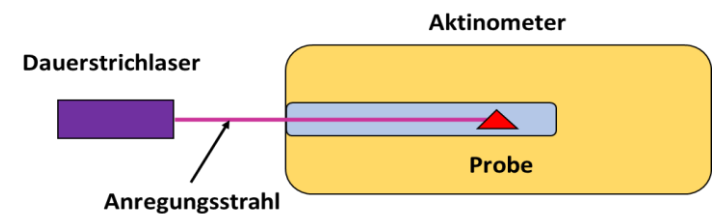
• Internal quantum yield: decay time



• External quantum yield: calorimetric

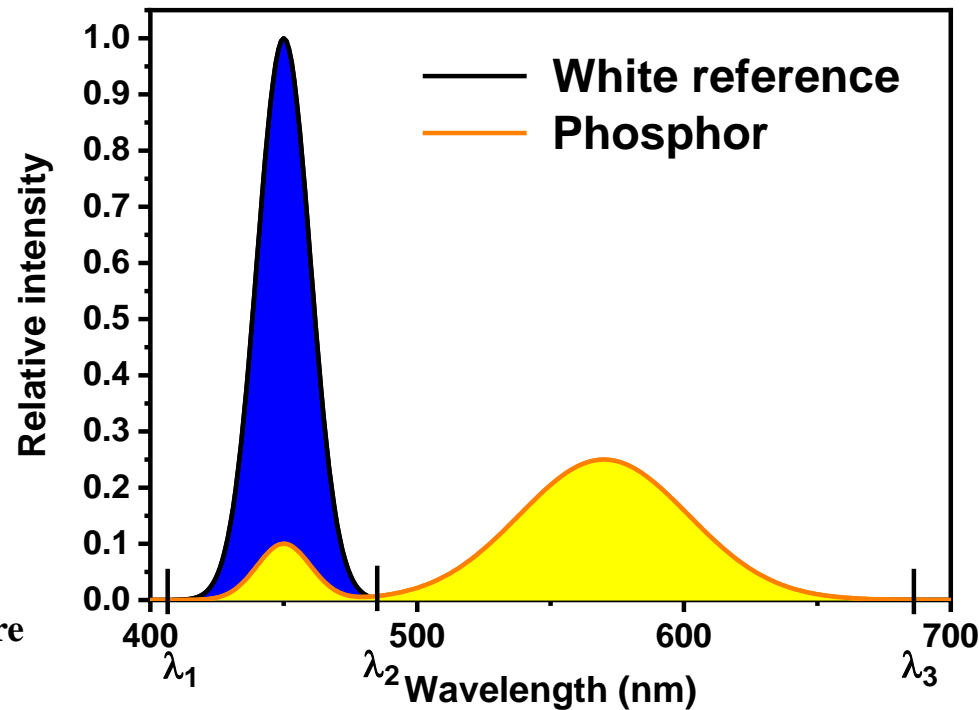
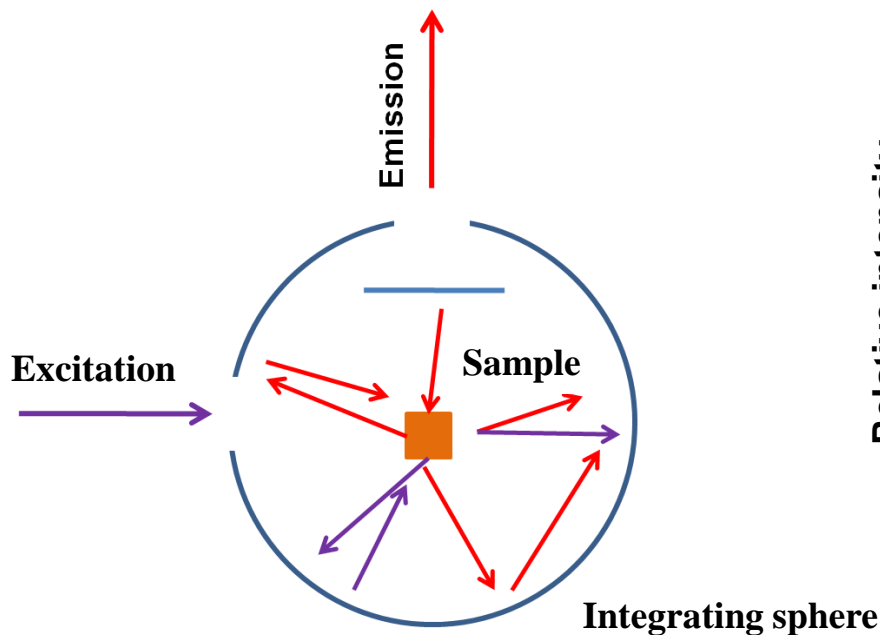


• External quantum yield: actinometric



# 4.2.5 Quantum Yield

**External quantum yield: absolute methods by using an integration sphere**  
 (Lit.: Jap. J. Applied Physics 43 (2004) 7729)



Material	$\lambda_{PL}$ (nm)	$\eta_{PL}$	$\tau_{PL}$ ( $\times 10^{-9}$ s)	$k_r$ ( $s^{-1}$ )
Alq <sub>3</sub>	520	0.20 ± 0.01	15	1.3 × 10 <sup>6</sup>
BAIq <sub>2</sub>	492	0.42 ± 0.02	29	1.4 × 10 <sup>6</sup>
TPD <sup>(9)</sup>	424	0.41 ± 0.02	0.6	6.8 × 10 <sup>8</sup>
$\alpha$ -NPD <sup>(9)</sup>	445	0.29 ± 0.02	3.5	8.0 × 10 <sup>7</sup>
CBP <sup>(9)</sup>	393	0.61 ± 0.04	0.7	8.7 × 10 <sup>8</sup>
Ir(ppy) <sub>3</sub> <sup>(3)</sup>	512	0.97 ± 0.02	1.3 × 10 <sup>3</sup>	7.5 × 10 <sup>5</sup>

$$EQY_{\text{sample}} = \frac{n_{\text{emission}}}{n_{\text{absorption}}} = \frac{\int_{\lambda_2}^{\lambda_3} \frac{\lambda}{hc} [I_{\text{emission}}^{\text{sample}}(\lambda) - I_{\text{emission}}^{\text{reference}}(\lambda)] d\lambda}{\int_{\lambda_1}^{\lambda_2} \frac{\lambda}{hc} [I_{\text{excitation}}^{\text{reference}}(\lambda) - I_{\text{excitation}}^{\text{sample}}(\lambda)] d\lambda}$$

## 4.2.5 Quantum Yield

### Definition by the lifetime of the excited state of the luminescent center

- Another definition for QY is given by ....  
wherein  $k_r$  is the radiative rate constant  
and  $\Sigma k$  is the sum of the rate constants for  
all processes that depopulate the excited state
- Radiative lifetime  $\tau_r$  is related to  $k_r$
- Measured lifetime  $\tau$  depends on the sum of the rate constants
- The observed fluorescence lifetime  $\tau$ , is the average  
time the molecule spends in the excited state  
 $\Rightarrow$  Measured lifetime is proportional to quantum yield

$$QY = \frac{k_r}{\sum_i k_i}$$

$$\tau_r = \frac{1}{k_r}$$

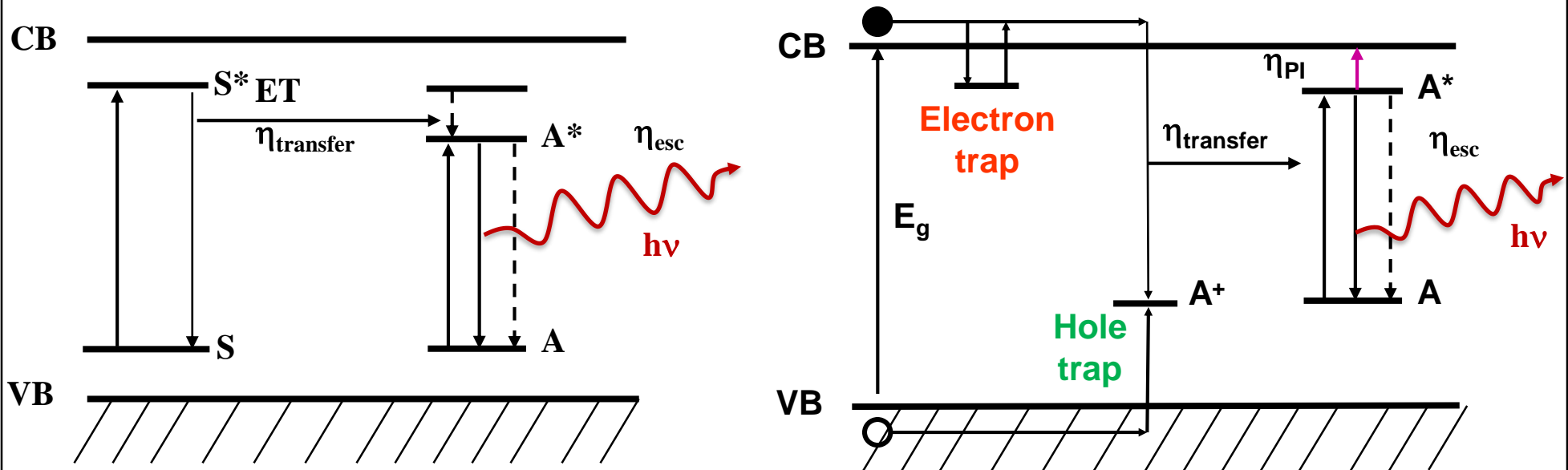
$$\tau = \frac{1}{\sum_i k_i}$$

$$QY = \frac{\tau}{\tau_r}$$

# 4.2.5 Quantum Yield

## Excitation by VUV or EUV radiation

Excitation energy  $\sim \Delta E$  of sensitisers or  $E_G$  of the host matrix/solvent



$$\eta_{total} = \eta_{act} * \eta_{transfer} * \eta_{esc} * (1 - \eta_{PI}) \text{ with PI = Photoionisation}$$

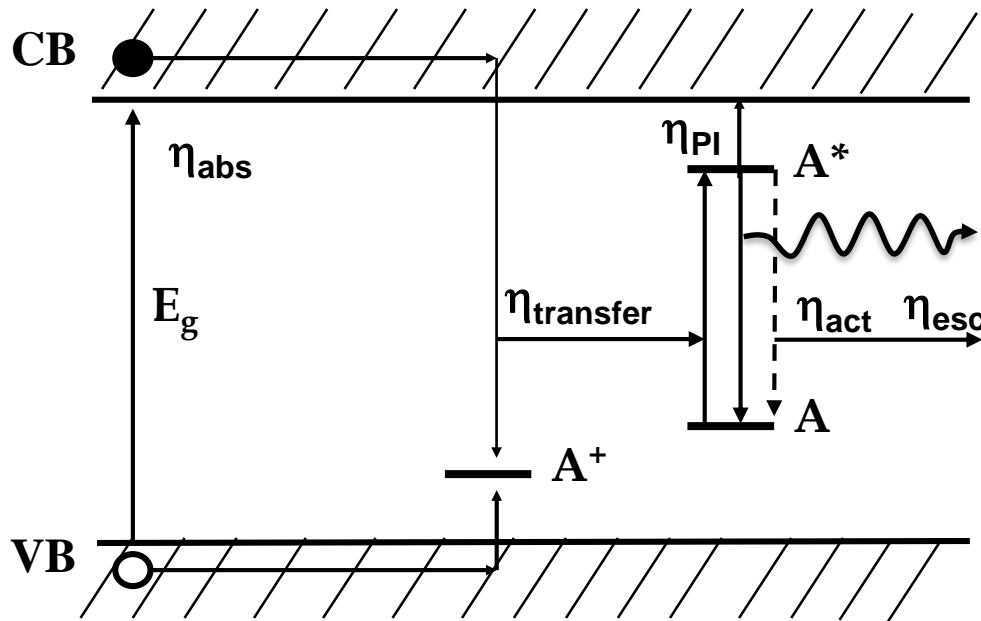
$\eta_{total}$  = External Quantum Yield (EQY) or External Quantum Efficiency (EQE)

$\eta_{act}$  = Internal Quantum Yield (IQY) or Internal Quantum Efficiency (IQE)



# 4.2.5 Quantum Yield

Quenching is caused by the luminescent center, e.g. the activator ion, (IQY↓)  
and/or the host matrix (EQY↓)



## Internal Quantum Yield (Efficiency)

$$\begin{aligned} \text{IQY} &= \eta_{act} \\ &= k_r / (k_r + k_{nr}) \\ &= \tau / \tau_r \end{aligned}$$

with  $1/(k_r + k_{nr}) = \tau$  and  $k_r = 1/\tau_r$   
(anti proportional to decay time)

**Decay time (Fluorescence spectrometer)**

## External Quantum Yield (Efficiency)

$$\begin{aligned} \text{EQY} &= N_{hv(\text{emitted})} / N_{hv(\text{absorbed})} \\ &= \eta_{transfer} * \eta_{act} * \eta_{esc} * (1 - \eta_{PI}) \end{aligned}$$

(No correlation to decay time!)

**Emission spectrum (Ulbricht sphere)**

## Light Yield (Fluorescence Intensity)

$$\text{LY} = \text{EQY} * \eta_{abs}$$

(No correlation to decay time!)

**Absorption via reflection spectrum and Kubelka-Munk-Function (Ulbricht sphere)**

# 4.2.5 Quantum Yield

## Comparison: Internal Quantum Yield (IQY) vs. External Quantum Yield (EQY)

### Internal Quantum Yield (Efficiency)

Efficiency of a luminescent center

Microscopic view

Decay time measurement

Fluorescence spectrometer

### External Quantum Yield (Efficiency)

Efficiency of a luminescent powder or solution

Macroscopic view

Emission spectrum measurement

Ulbricht (integrating) sphere

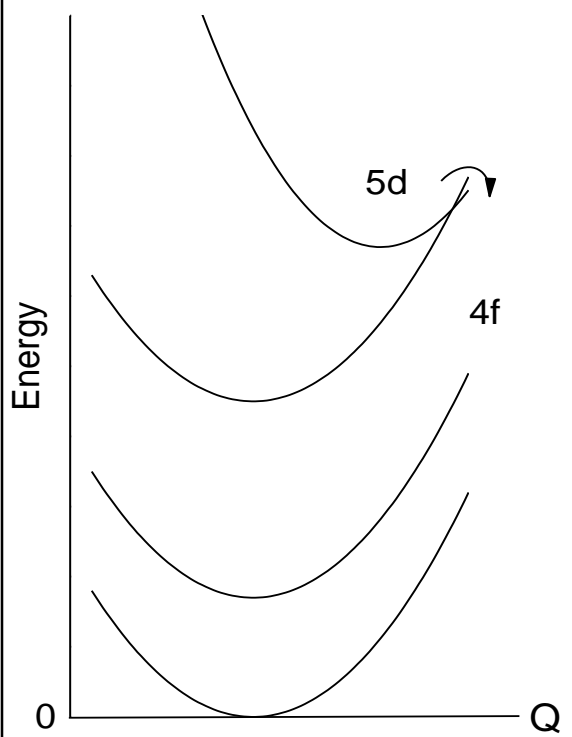
$$\text{IQY} = \frac{\tau}{\tau_r}$$

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

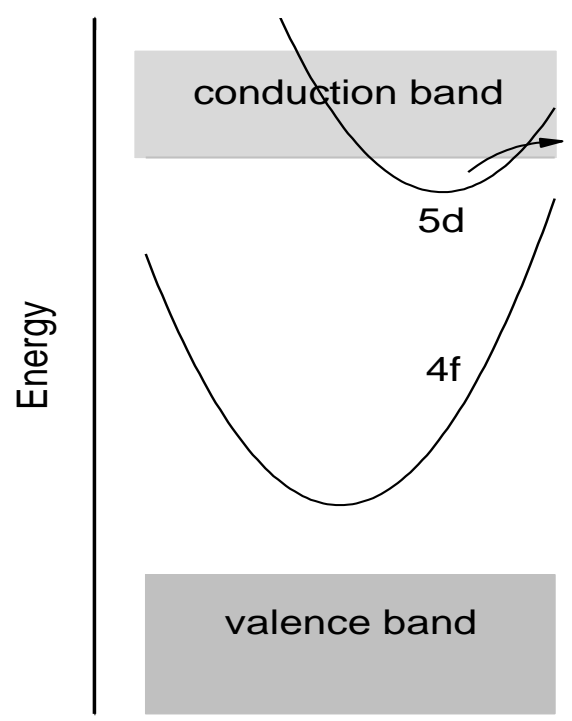
with  $\tau$  = experimental lifetime and  $\tau_r$  = radiative lifetime

# 4.2.5 Quantum Yield

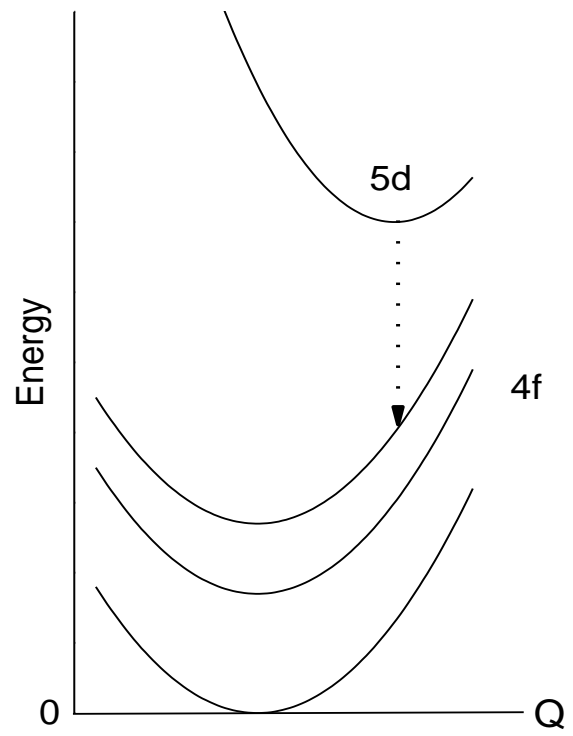
Several mechanisms for the quenching of luminescent materials results in the reduction of the photoluminescence quantum yield, e.g.



**Thermally activated InterSystem Crossing (ISC)**



**Thermally activated PhotoIonization (PI)**

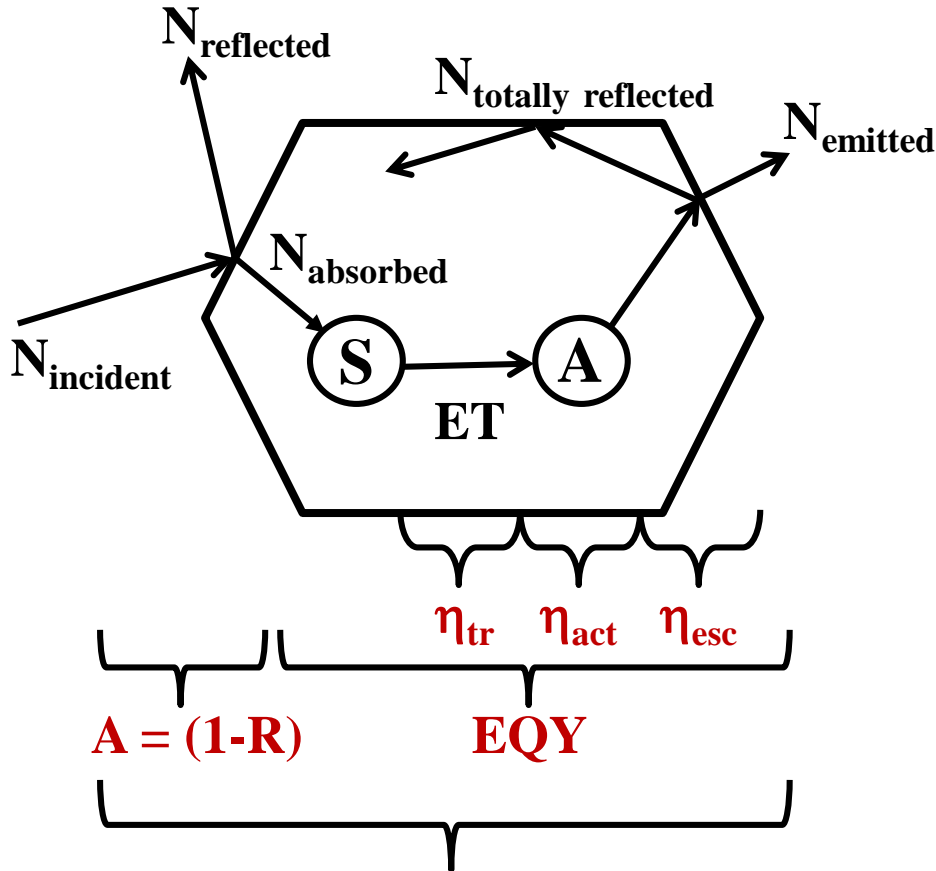


**Multi Phonon Relaxation (MPR)**

# 4.2.6 Light Yield

**Light Yield LY = Fluorescence Intensity  $\sim I(\lambda_{exc})$  (or integral lamp output)**

**Light conversion at a phosphor particle**



**External Quantum Yield (EQY)**

$$EQY = N_{emitted} / N_{absorbed}$$

**Absorption A**

$$A = N_{absorbed} / N_{incident}$$

**Reflectance R**

$$R = 1 - A \quad (\text{for transmission } T = 0)$$

**Light Yield LY**

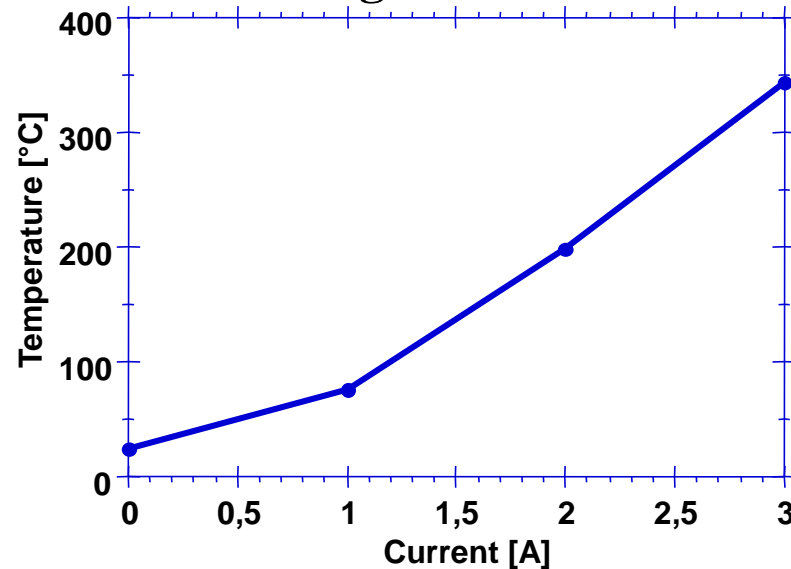
$$LY = \frac{N_{emitted}}{N_{incident}} = \frac{N_{emitted}}{N_{absorbed}} * \frac{N_{absorbed}}{N_{incident}}$$

$$LY = EQY * A = EQY * (1 - R) \quad [0 \dots 1]$$

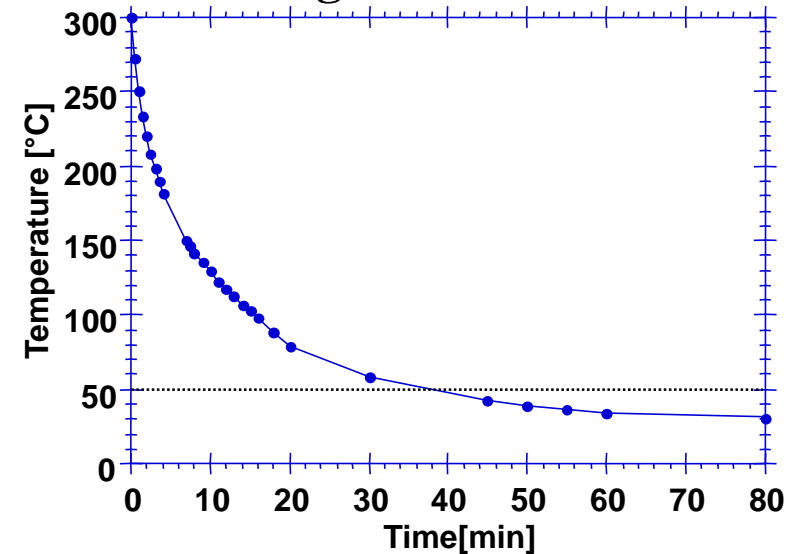
# 4.2.7 Temperature Resolved Spectroscopy

## Heating and cooling behavior of a sample holder for temp. resolved spectroscopy

### Heating characteristics



### Cooling characteristics



### Heating the sample

**N<sub>2</sub>-flushing cools the sample**

**⇒ Actual temperature of the sample is  
5-10 °C below the measured value**

### Cooling the sample

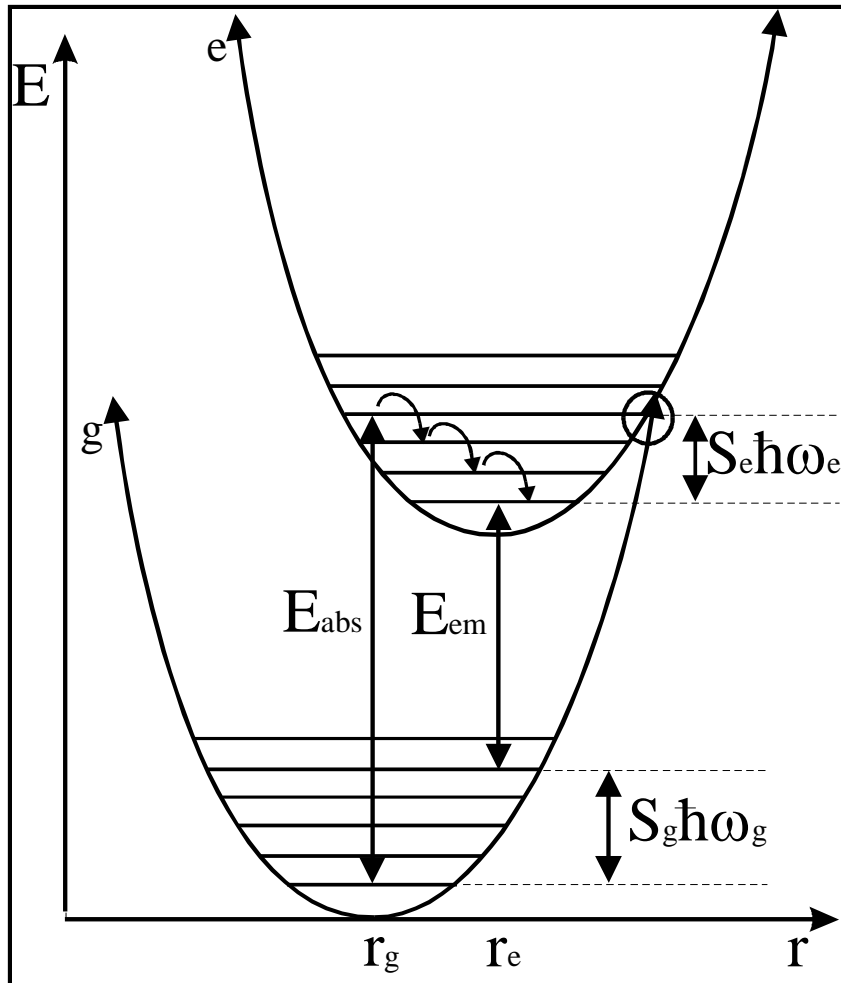
**< 0 °C: H<sub>2</sub>O Resublimation**

**< -78 °C: CO<sub>2</sub> Resublimation**

**⇒ Additional absorption in  
the VUV range**

# 4.2.7 Temperature Resolved Spectroscopy

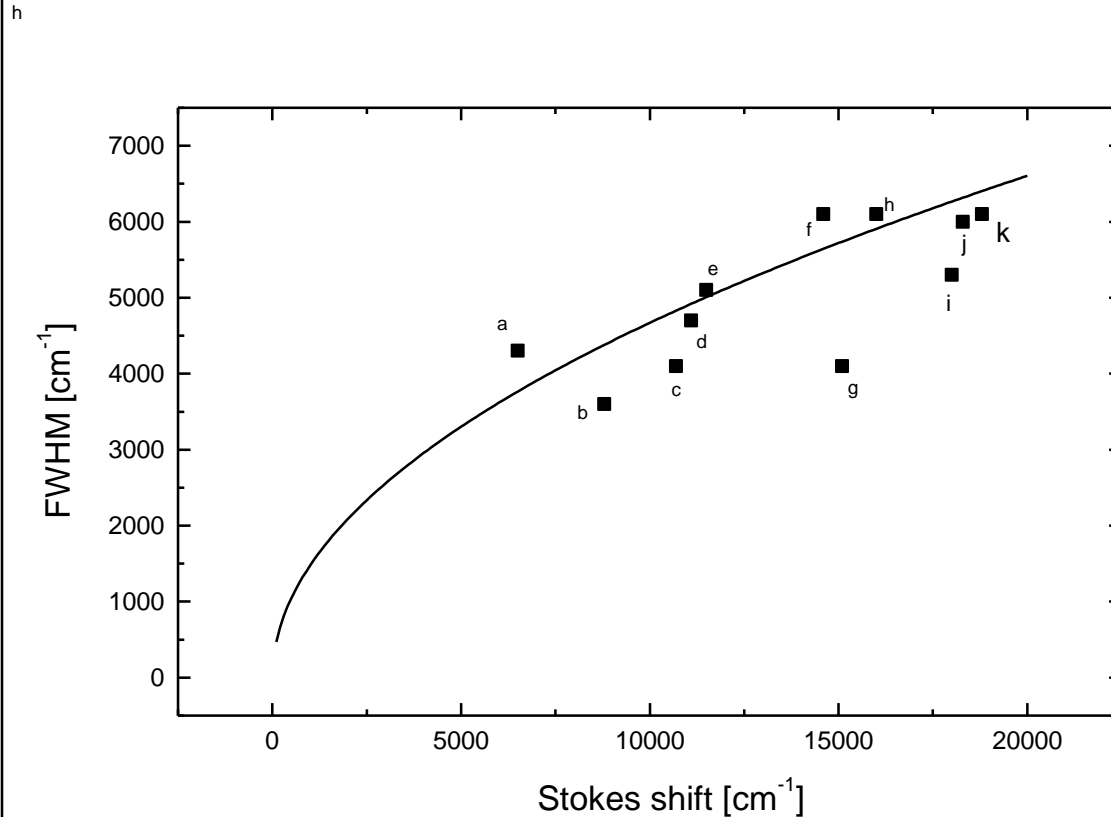
## Thermal quenching of luminescence processes



- **Stokes shift**  
Energy gap between absorption and emission band  
$$S = S_e \hbar \omega_e + S_g \hbar \omega_g$$
- **Full width at half maximum of the emission band**  
$$FWHM \sim \sqrt{S}$$
- **Thermal quenching decreases with increasing  $\Delta R = r_e - r_g$**
- **$\Delta R$  depends on the activator-host lattice interaction**

# 4.2.7 Temperature Resolved Spectroscopy

Thermal quenching of luminescence processes:  $\text{FWHM} = f(\text{Stokes Shift})$



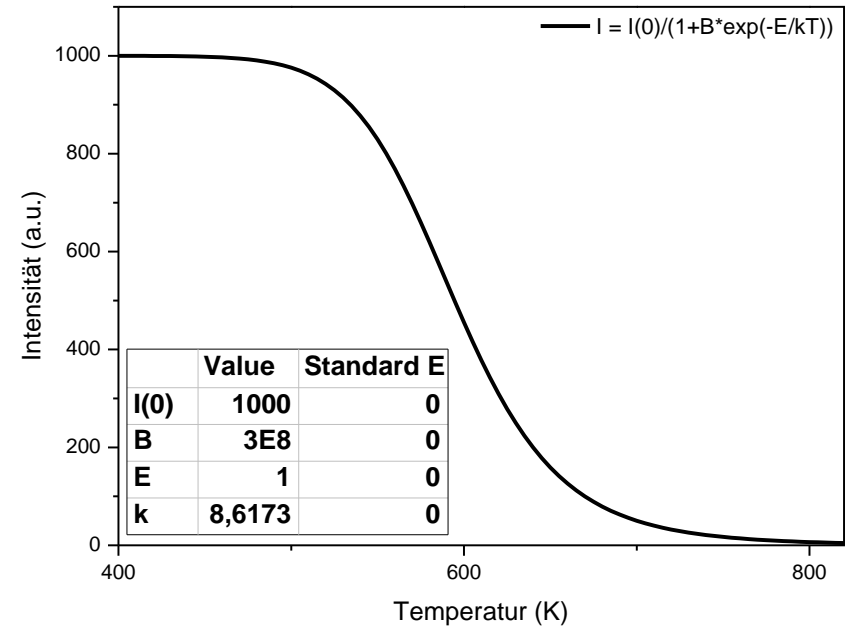
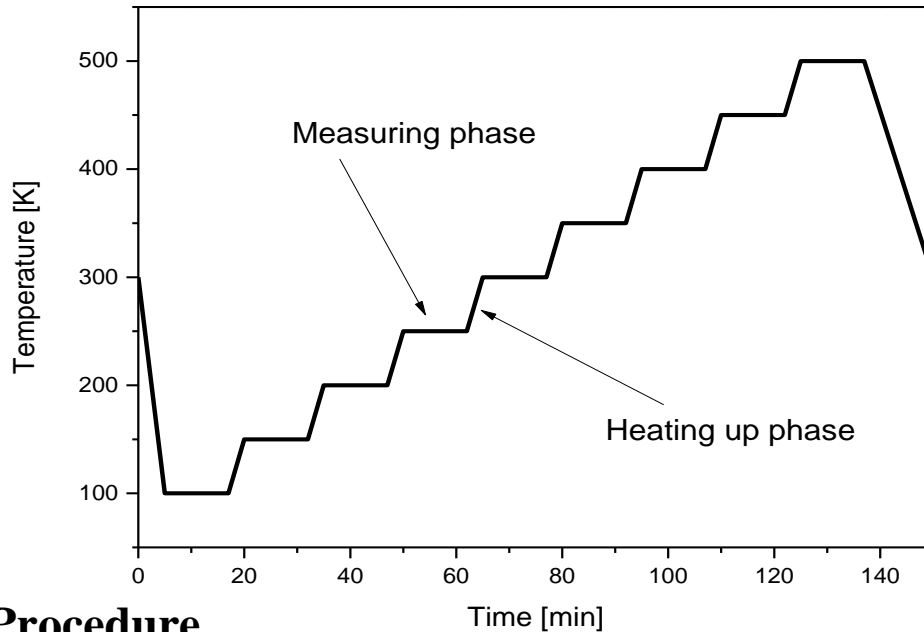
- a  $\text{Ba}_2\text{MgGe}_2\text{O}_7:\text{Bi}$
- b  $\text{Ca}_3\text{Si}_2\text{O}_7:\text{Pb}$
- c  $\text{LaOCl}:\text{Bi}$
- d  $\text{BaLaYB}_9\text{O}_{16}:\text{Sb}$
- e  $\text{Y}_2\text{Si}_2\text{O}_7:\text{Bi}$
- f  $\text{CaZrB}_2\text{O}_6:\text{Pb}$
- g  $\text{LaOCl}:\text{Sb}$
- h  $\text{CaWO}_4$
- i  $\text{SrLaBO}_4:\text{Pb}$
- j  $\text{YTao}_4:\text{Nb}$
- k  $\text{CaMgSi}_2\text{O}_6:\text{Ti}$

Extent of Thermal Quenching  
↓

$$\text{FWHM} \sim \sqrt{S}$$

# 4.2.7 Temperature Resolved Spectroscopy

Thermal quenching experiments  $\Rightarrow$  Intensity/integral as  $f(T)$



## Procedure

- Heating up to temperature  $T$  (step wisely)
- Measurement of the emission spectrum at  $\lambda_{\max}$  upon excitation of the sample at  $\lambda_{\text{exc}}$ .
- Plotting of the integral and/or of the peak intensity as function of  $T$
- Fitting of the obtained quenching curve by the following function

$$I(T) = A_0 + I_0/(1 + B \exp(-\Delta E/k_B T)) \quad \text{Fitting by the „Struck-Fonger-Model“}$$



# 4.2.7 Temperature Resolved Spectroscopy

## Curve fitting

$N_{NR}(T)$  is the non-radiative transition rate at temperature  $T$  ( $s^{-1}$ )

$N_{NR,max}$  is the maximal non-radiative transition rate ( $s^{-1}$ )

$E$  is the activation energy for thermal quenching (eV,  $cm^{-1}$ , ...)

$k$  is the Boltzmann constant (eV,  $cm^{-1}$ , ...)

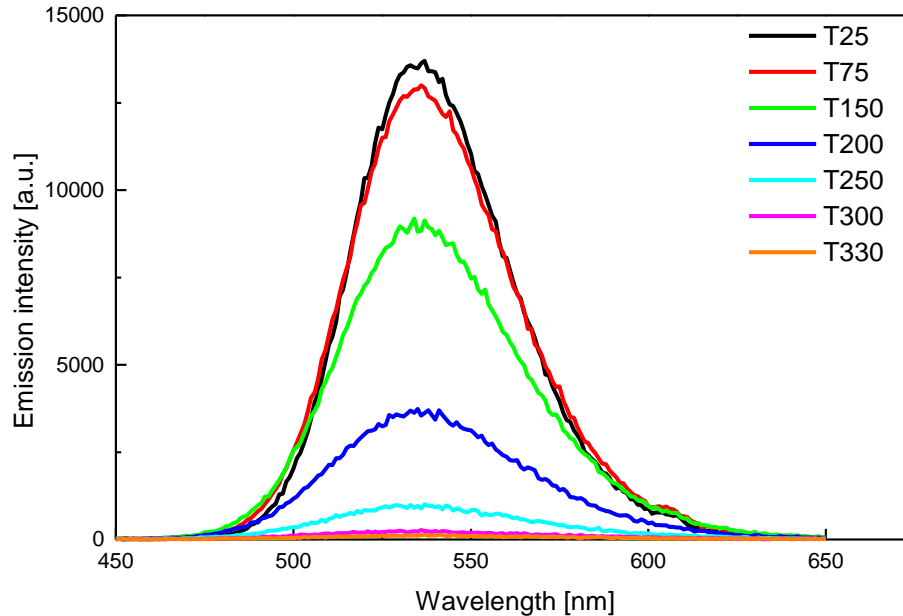
$$N_{NR} = N_{NR,max} * e^{-\frac{E}{kT}}$$

$$IQE = \frac{N_R}{N_R + N_{NR}} = \frac{1}{1 + \frac{N_{NR}}{N_R}}$$

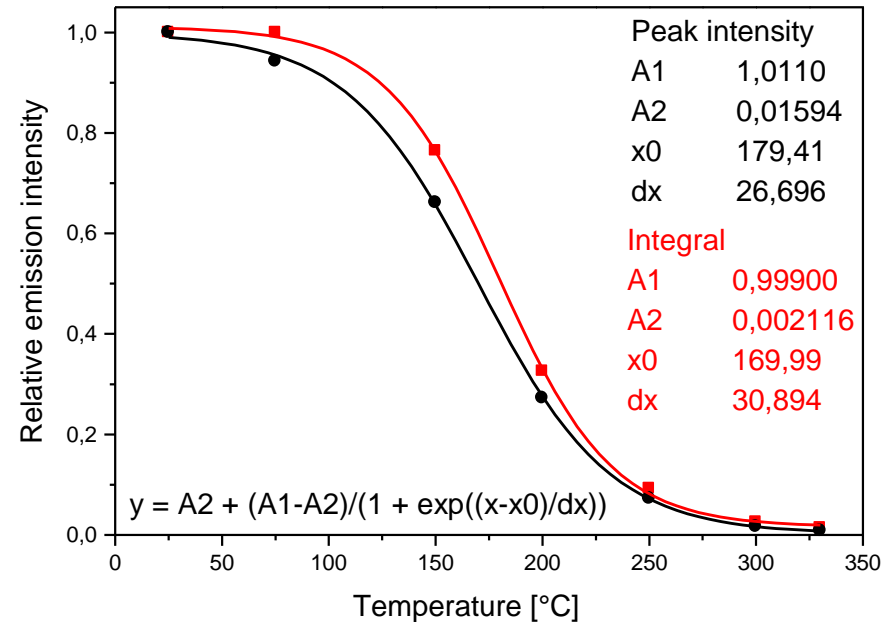
# 4.2.7 Temperature Resolved Spectroscopy

## Example of SrGa<sub>2</sub>S<sub>4</sub>:Eu

### Emission spectrum (460 nm excitation)



### Emission intensity

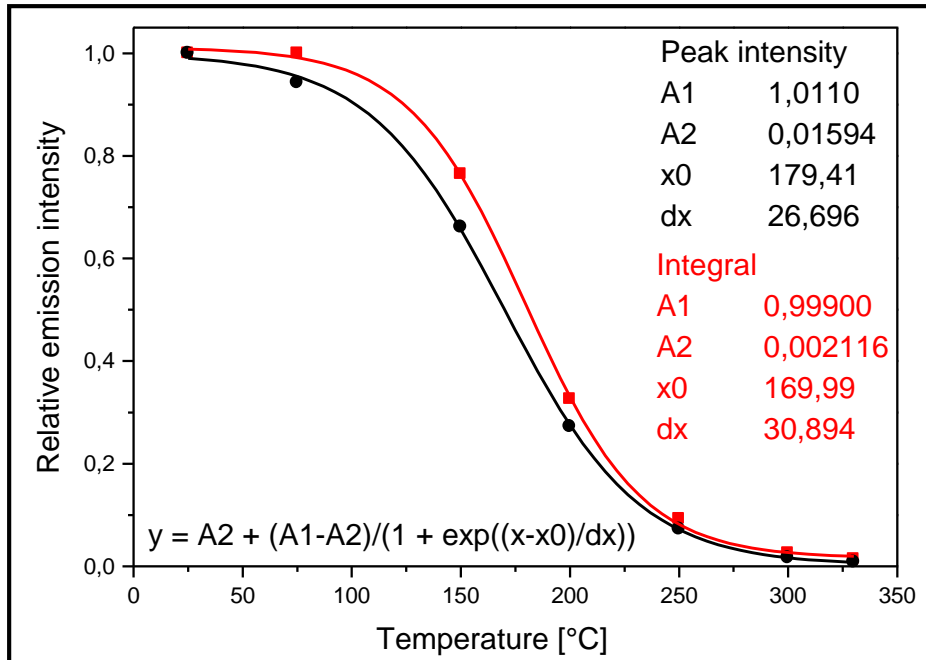


- **$T_{1/2}$  = Temperature at which the luminescence process declines by 50% of its low temperature emission intensity (SrGa<sub>2</sub>S<sub>4</sub>:Eu ~ 170 °C)**
- **In many applied inorganic phosphors the quantum yield starts increasing distinctly from 100 – 150 °C upwards**

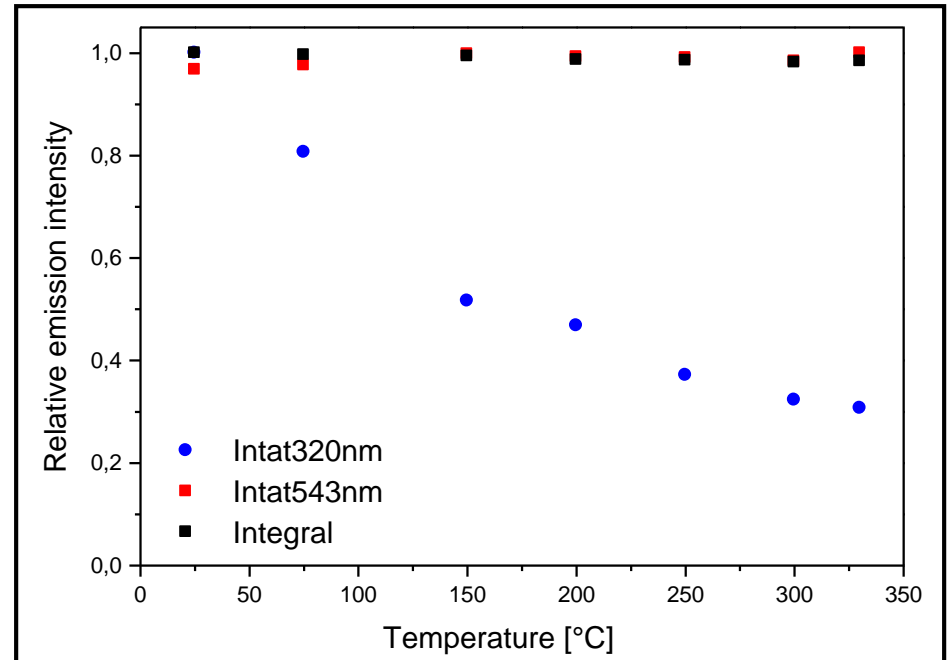
# 4.2.7 Temperature Resolved Spectroscopy

## Comparison between a line and a band emitter

**SrGa<sub>2</sub>S<sub>4</sub>:Eu (460 nm excitation)**

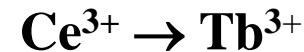


**LaPO<sub>4</sub>:Ce,Tb (254 nm excitation)**



## Temperature resolved spectra for the investigation of

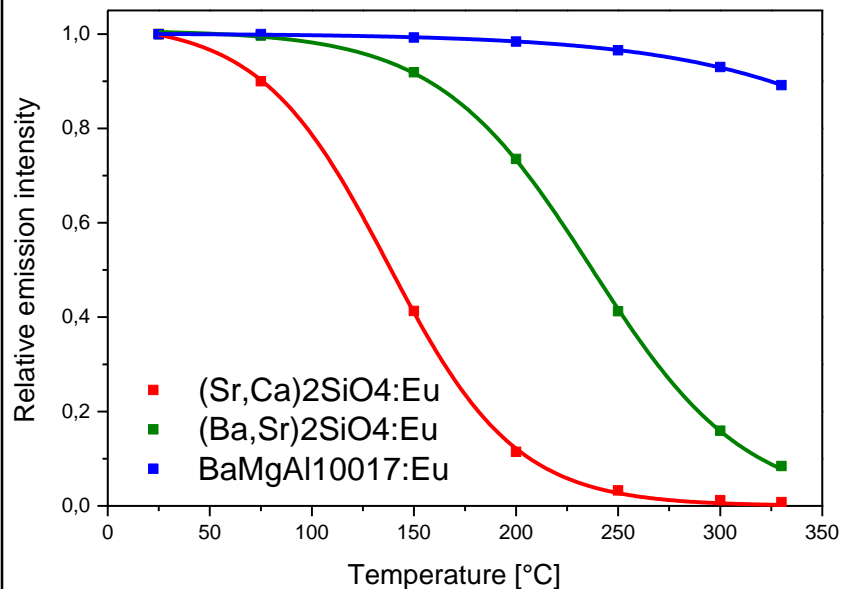
- Thermal quenching of the luminescence
- Energy transfer, e.g. in LaPO<sub>4</sub>:Ce,Tb



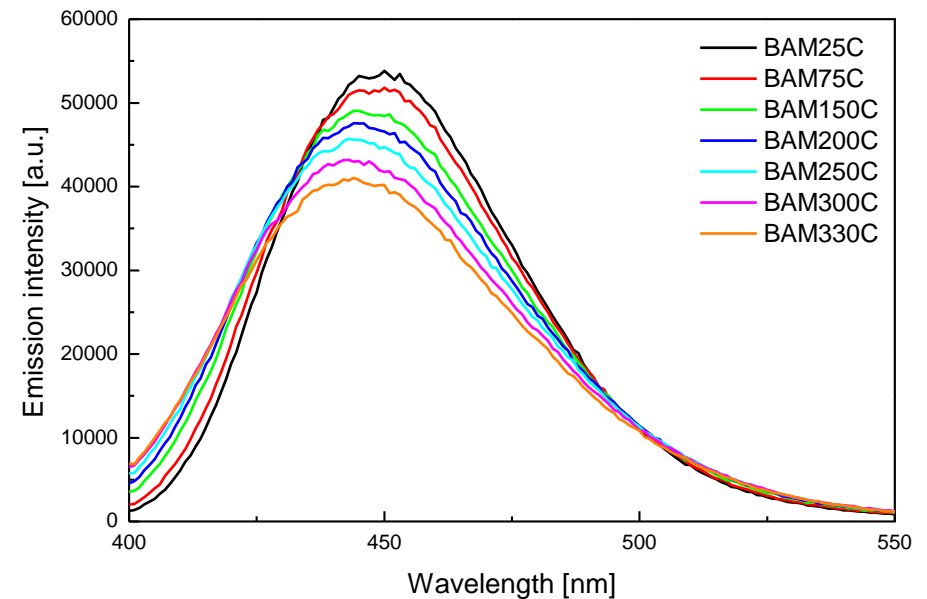
# 4.2.7 Temperature Resolved Spectroscopy

## Thermal quenching of $\text{Eu}^{2+}$ phosphors

Quantum yield as a function of temperature



Spectral width of the emission band of  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$  as a function of T



Stokes shift

$\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu} < (\text{Ba,Sr})_2\text{SiO}_4:\text{Eu} < (\text{Sr,Ca})_2\text{SiO}_4:\text{Eu}$

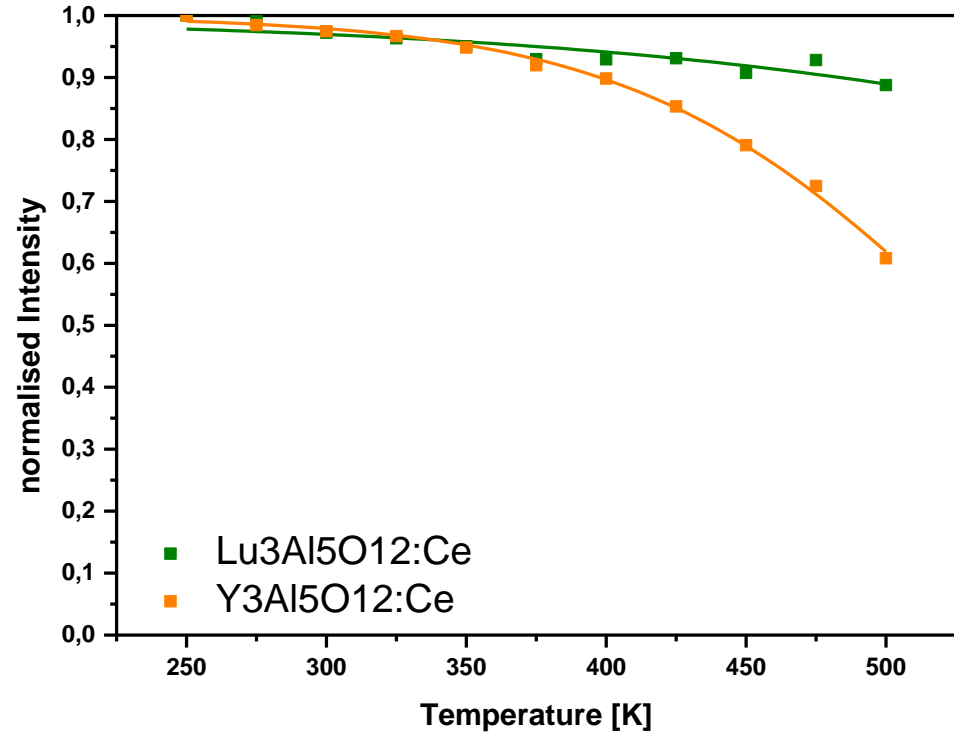
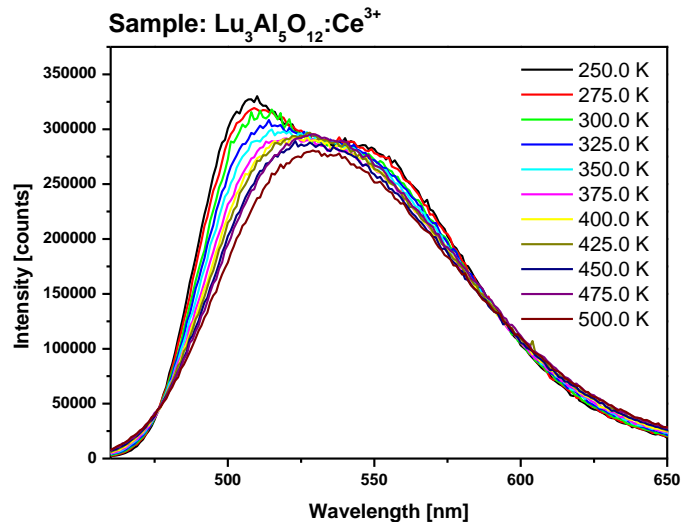
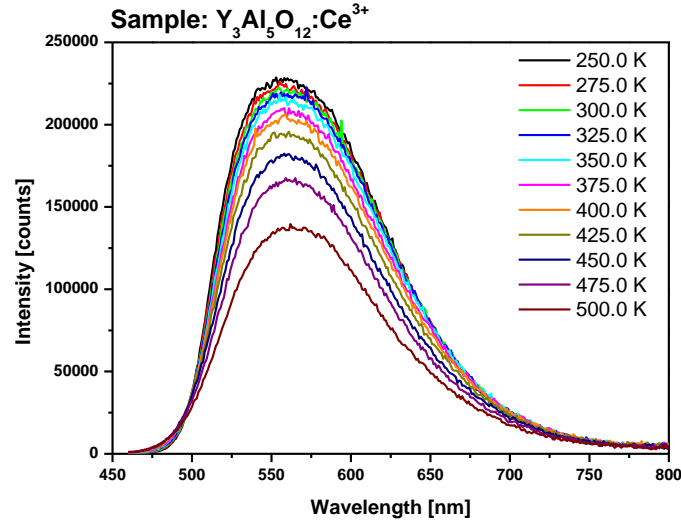
Thermal quenching

$\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu} < (\text{Ba,Sr})_2\text{SiO}_4:\text{Eu} < (\text{Sr,Ca})_2\text{SiO}_4:\text{Eu}$

Blue shift due to thermal expansion of the host and thus reduction in crystal field splitting!

# 4.2.7 Temperature Resolved Spectroscopy

## Thermal quenching of Ce<sup>3+</sup> phosphors



Stokes shift:

Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce < Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce

Thermal quenching:

Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce < Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce

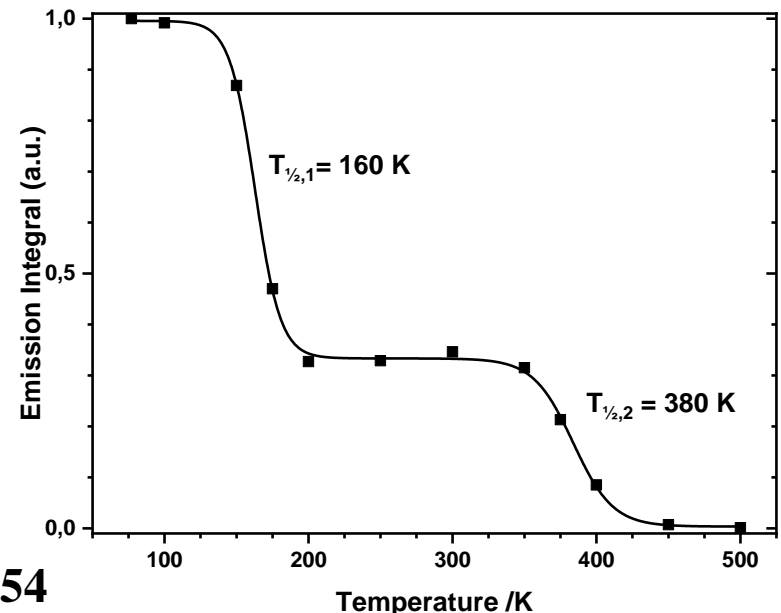
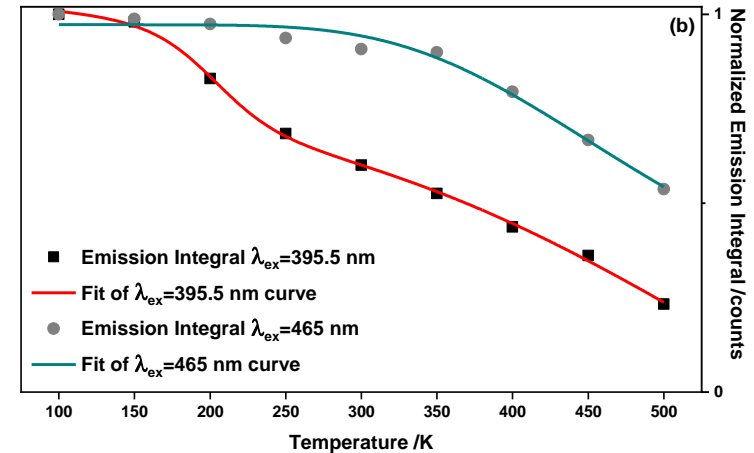
Re-absorption leads to the observed color point shift!

# 4.2.7 Temperature Resolved Spectroscopy

## Special cases

- Simultaneous excitation via band gap and direct excitation of the activator can result in a bi-sigmoidal curve (example:  $\text{LiEuMo}_2\text{O}_8$ )
- Simultaneous emission of two luminescent centers in the same spectral region can also result in a bi-sigmoidal curve (example:  $\text{Rb}_2\text{Ge}_4\text{O}_9:\text{Mn}^{4+}$ )
- The curve can be fitted via weighted addition of two fitting functions. This yield two  $T_{1/2}$  values:

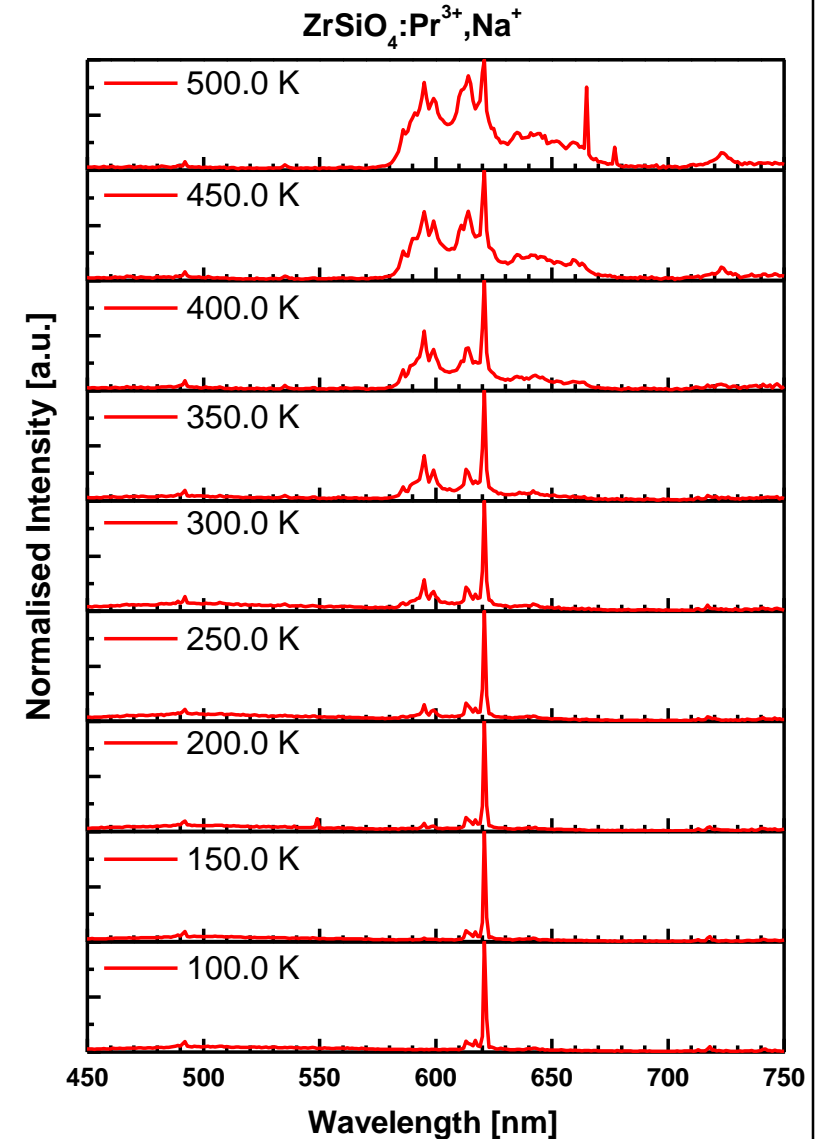
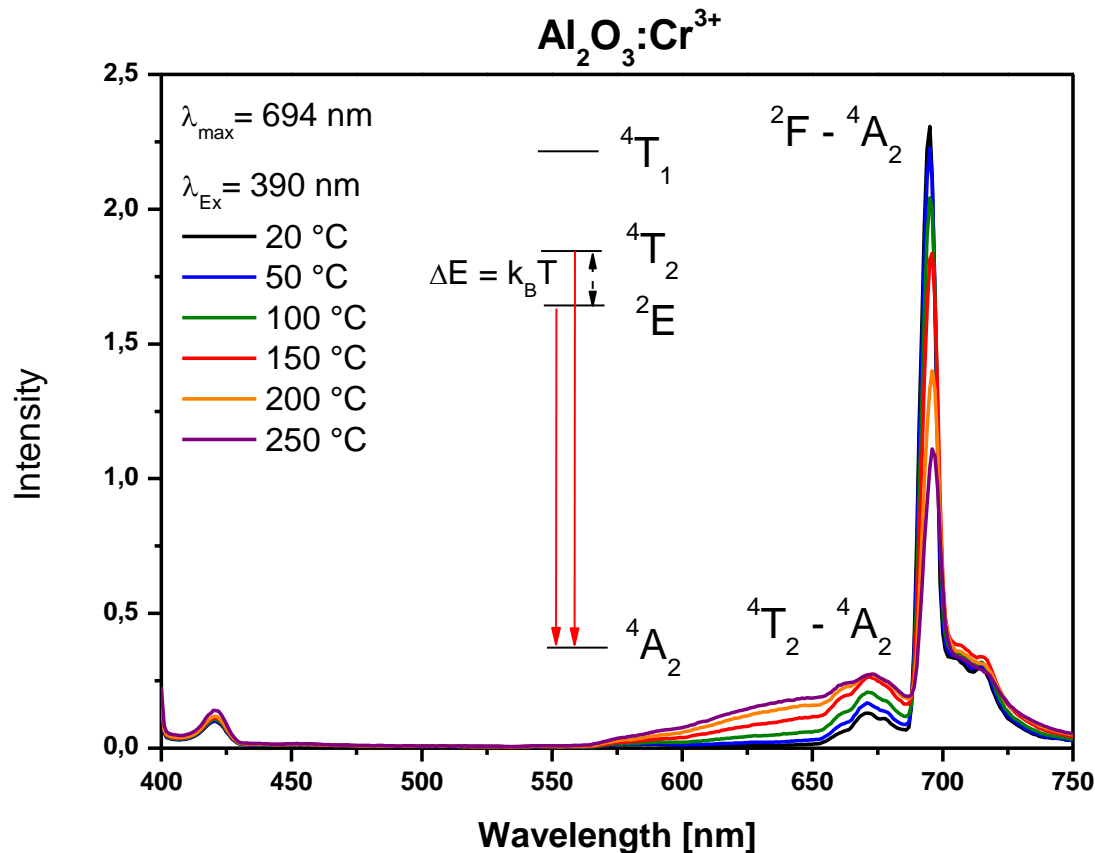
$$I_{\text{total}}(T) = A \cdot I_1(T) + (1-A) \cdot I_2(T)$$



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

# 4.2.7 Temperature Resolved Spectroscopy

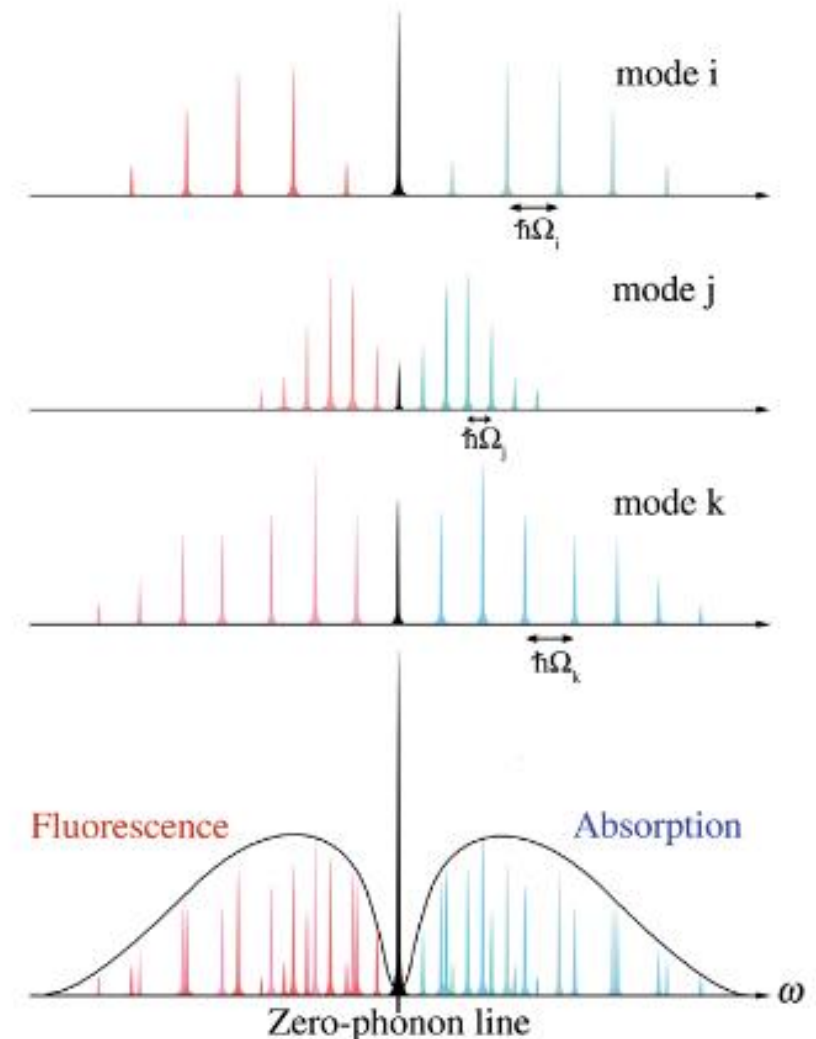
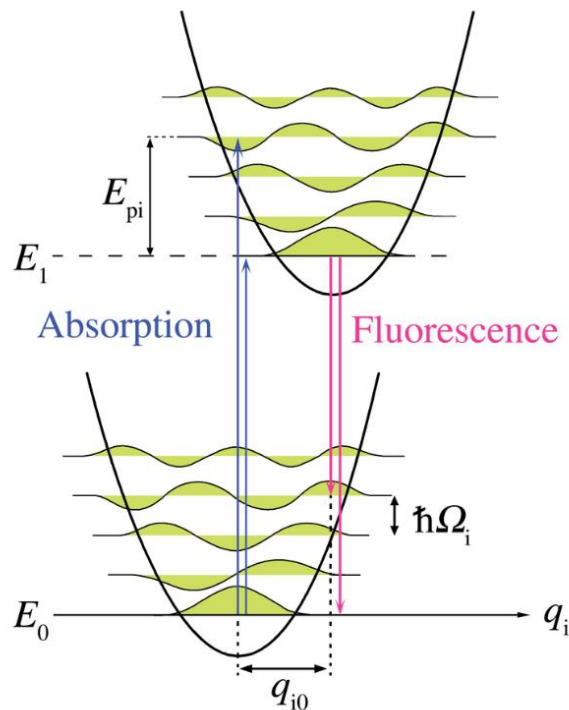
## Thermal excitation of higher radiative states



# 4.2.7 Temperature Resolved Spectroscopy

## Zero Phonon Line

The higher the temperature, the more is the luminescence influenced by lattice vibrations (phonons) – instead of a line, a band will be observed



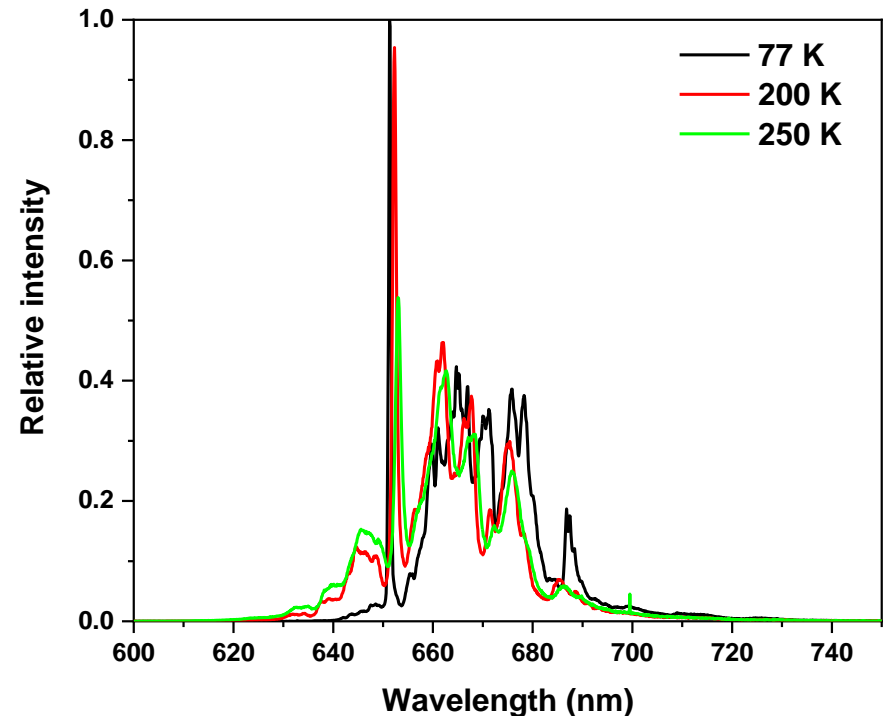


# 4.2.7 Temperature Resolved Spectroscopy

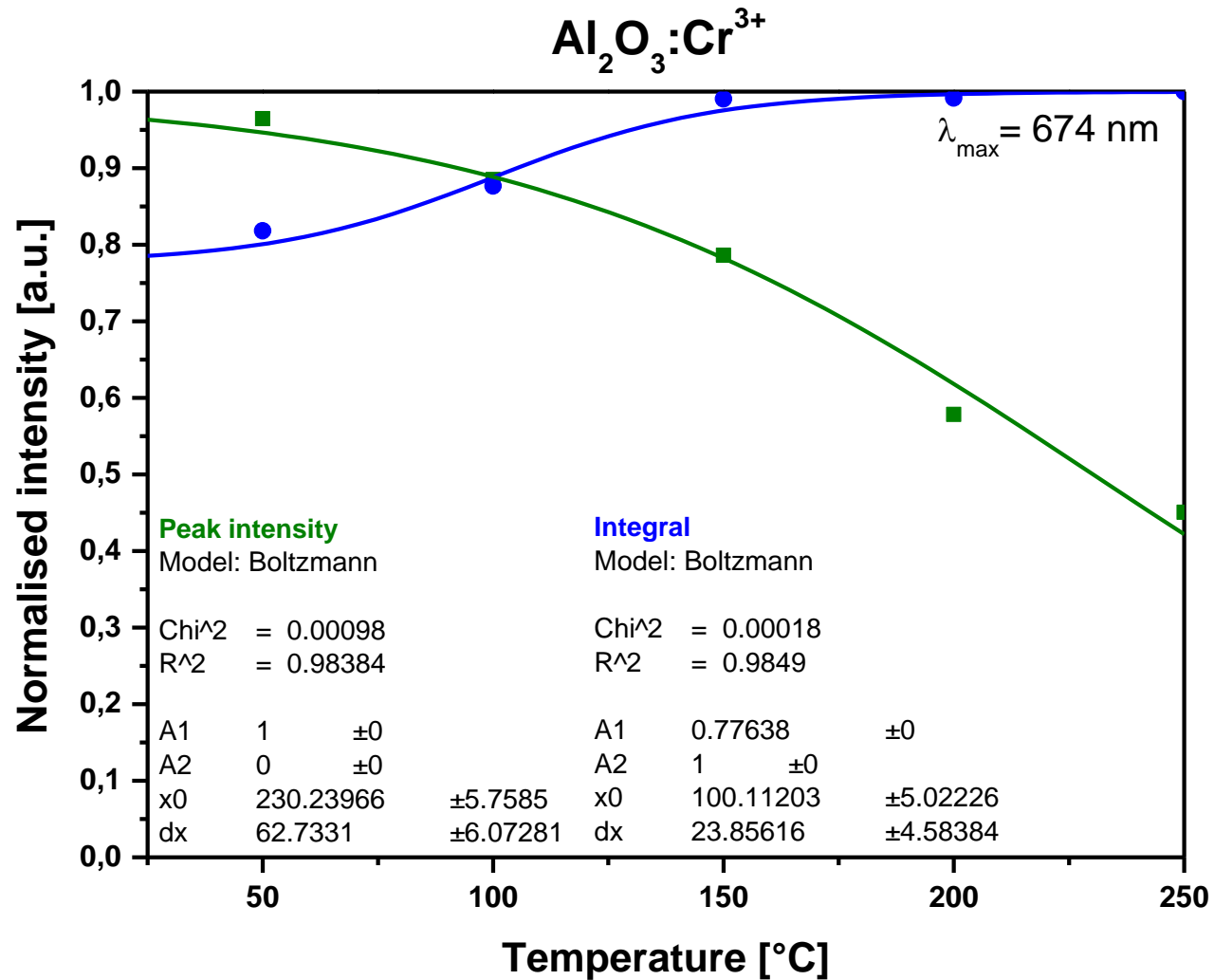
## Zero Phonon Line

In emission spectra, the Stokes transitions are at a lower energy (generation of phonons / heat), the anti-Stokes transitions are at higher energy (extinction of phonons / cooling)

- The intensity and number of ZPLs depend on the site symmetry and number of dopant sites
- The spectral position of vibrational lines depends on the phonon energy

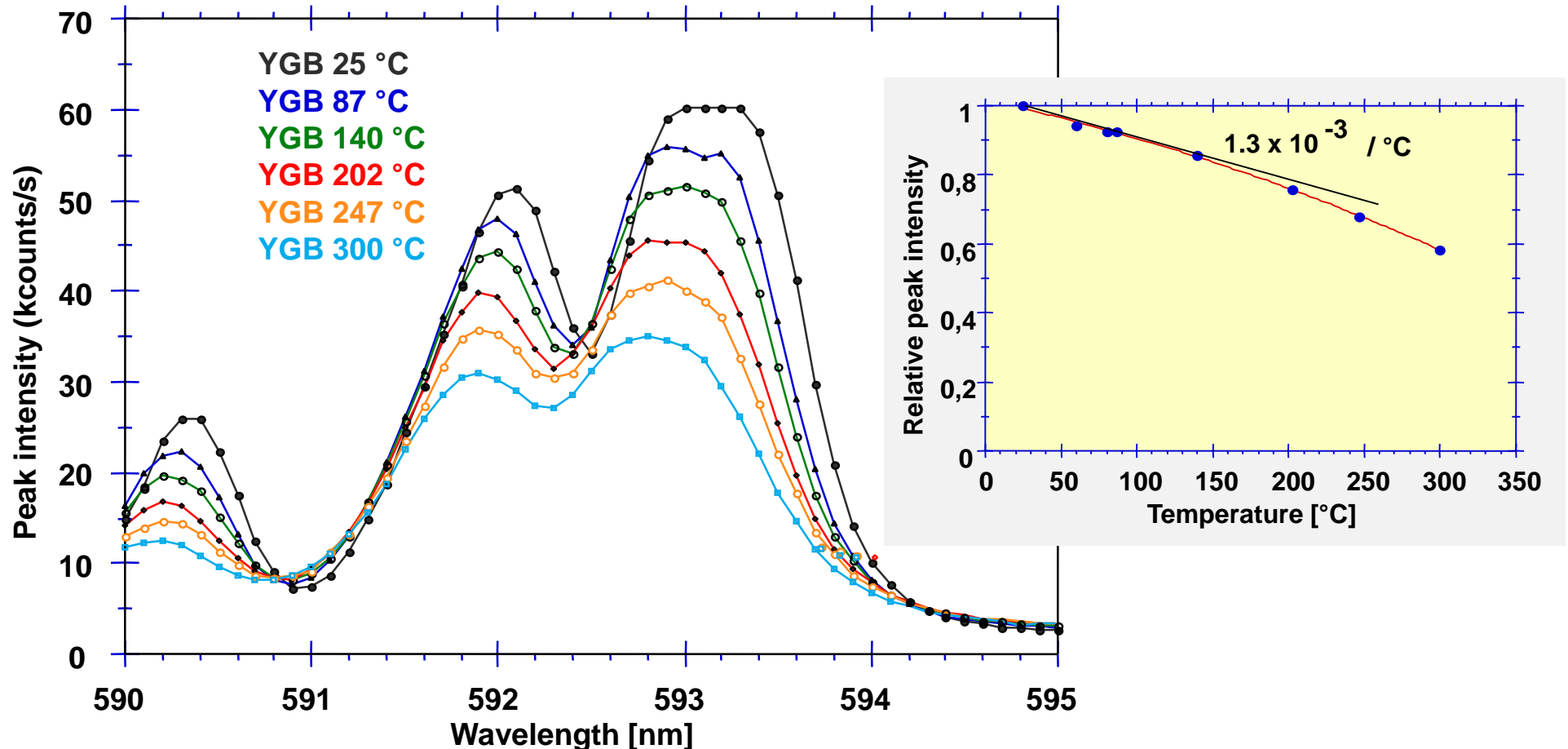


# 4.2.7 Temperature Resolved Spectroscopy



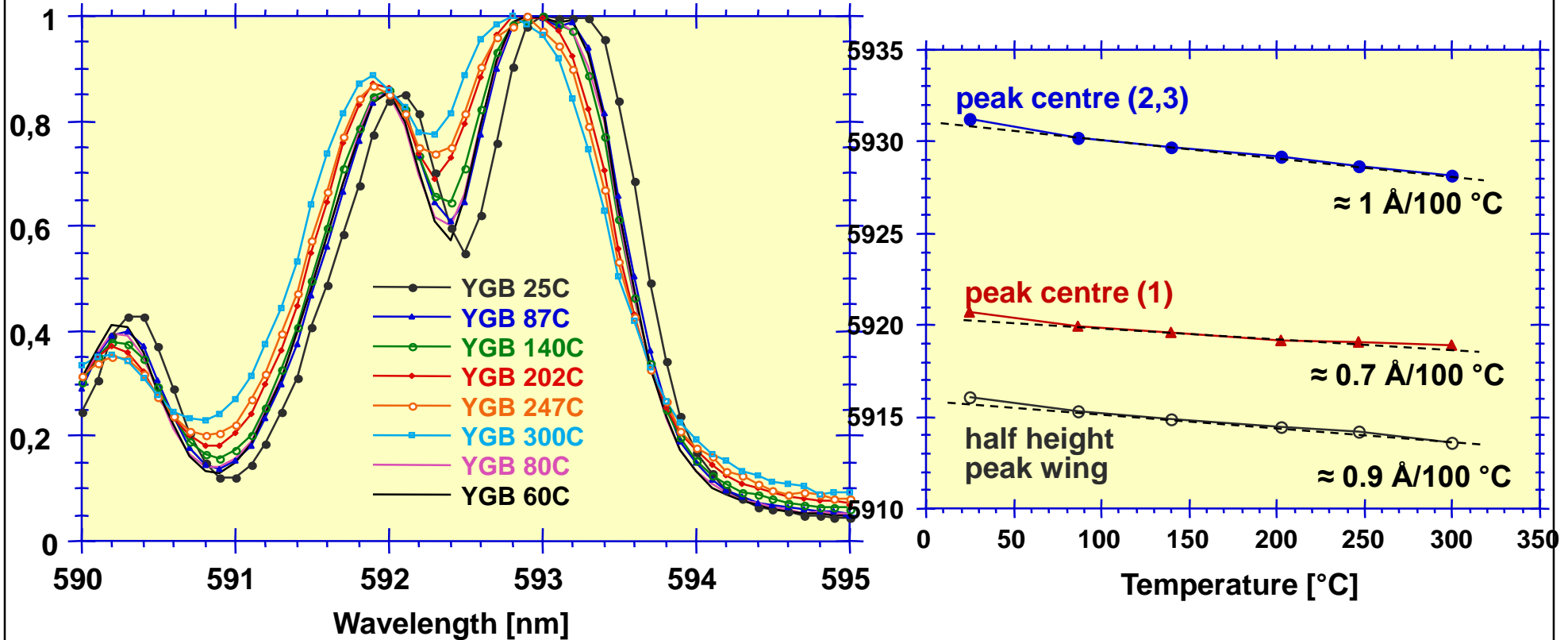
# 4.2.7 Temperature Resolved Spectroscopy

Red PDP phosphor (Y,Gd)BO<sub>3</sub>:Eu<sup>3+</sup>(YGB:Eu) → <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub> transition as a temperature sensor since it shows reversible change of the emission spectrum



# 4.2.7 Temperature Resolved Spectroscopy

Red PDP phosphor (Y,Gd)BO<sub>3</sub>:Eu<sup>3+</sup>(YGB:Eu) → <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub> transition as a temperature sensor since it shows reversible change of the emission spectrum



Optical temperature sensing:

- Line/band shift
- Line/band broadening
- Line/band intensity (ratio)

# 4.2.7 Temperature Resolved Spectroscopy

## Thermoluminescence

### Technology

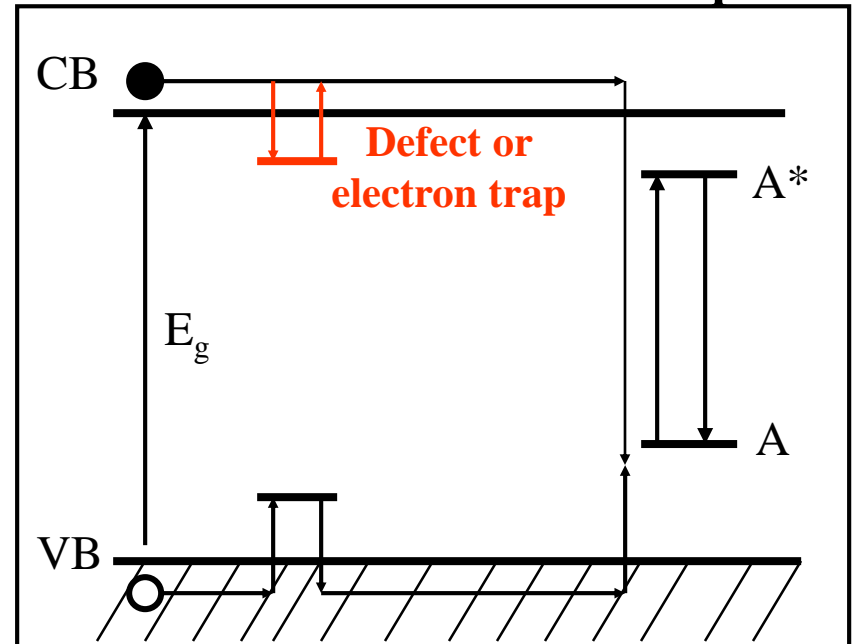
- Sample is cooled e.g. down to  $-196\text{ }^{\circ}\text{C}$  (77 K) or  $-269\text{ }^{\circ}\text{C}$  (4.2 K)
- Irradiation with UV-, VUV-, X-ray radiation or electrons
- The intensity of the emitted radiation is, during up-heating, measured with a constant time-dependent heating rate

### Thermoluminescence (TL) (glow curves)

- Integral of the bands: Defect density
- Position of the bands: Energetic position of the defects
- Number of bands: Number of defect types

⇒ Insights in charge carrier trapping and luminescence quenching mechanisms

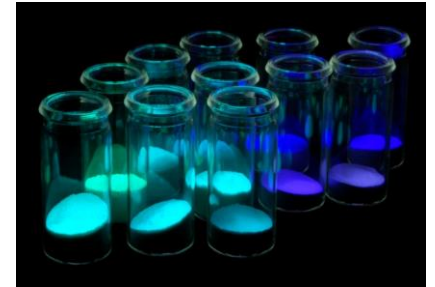
### Band model of a solid state compound



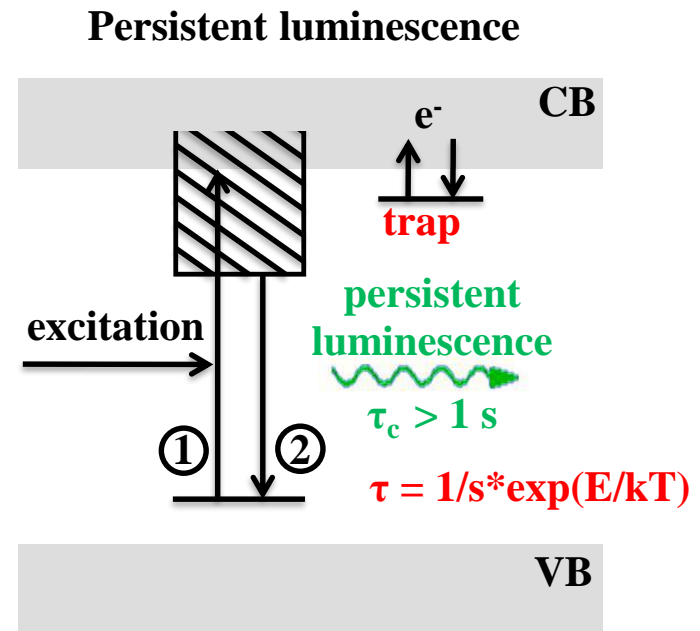
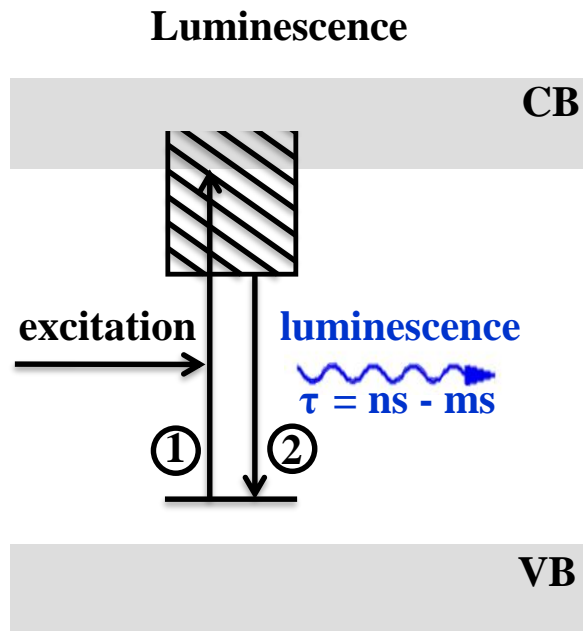
# 4.2.7 Temperature Resolved Spectroscopy

## Thermoluminescence: Application Areas

- Age determination
- Dosimetry and x-ray diffraction
- Characterization of (persistent) luminescent materials
  - Afterglow and display phosphors, scintillators



$\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$  samples



# 4.2.7 Temperature Resolved Spectroscopy

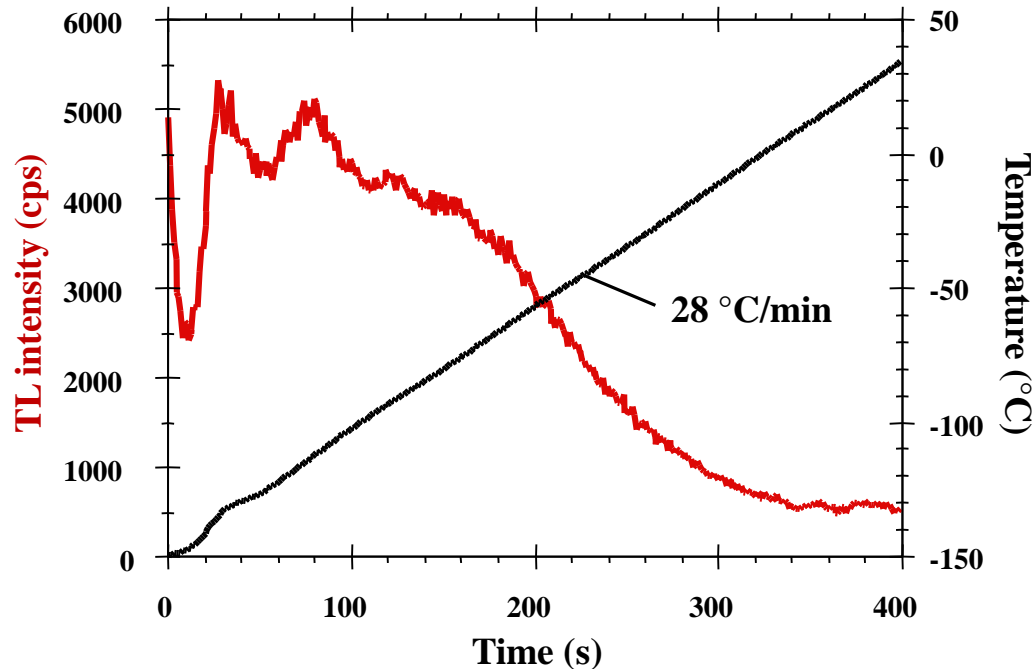
## Thermoluminescence: Persistent luminescent materials

Host matrix	Luminescence center	Co-dopant	Emission maximum [nm]	Afterglow duration
MgAl <sub>2</sub> O <sub>4</sub>	Eu <sup>2+</sup>	Dy <sup>3+</sup>	480	> 1 min
CaAl <sub>2</sub> O <sub>4</sub>	Eu <sup>2+</sup>	Nd <sup>3+</sup>	440	> 5 h
Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub>	Eu <sup>2+</sup>	Nd <sup>3+</sup>	440	> 5 min
SrAl <sub>12</sub> O <sub>19</sub>	Eu <sup>2+</sup>	Dy <sup>3+</sup>	400	> 2 h
SrAl <sub>4</sub> O <sub>7</sub>	Eu <sup>2+</sup>	Dy <sup>3+</sup>	480	> 1 h
Sr <sub>4</sub> Al <sub>14</sub> O <sub>25</sub>	Eu <sup>2+</sup>	Dy <sup>3+</sup>	405, 490	> 10 h
SrAl <sub>2</sub> O <sub>4</sub>	Eu <sup>2+</sup>	Dy <sup>3+</sup>	445, 520	> 10 h
Sr <sub>3</sub> Al <sub>2</sub> O <sub>6</sub>	Eu <sup>2+</sup>	Dy <sup>3+</sup>	535, 620	> 10 min
BaAl <sub>2</sub> O <sub>4</sub>	Eu <sup>2+</sup>	Dy <sup>3+</sup>	505	> 2 h
SrMgAl <sub>10</sub> O <sub>17</sub>	Eu <sup>2+</sup>	Dy <sup>3+</sup>	460, 515	> 3 min
BaMgAl <sub>10</sub> O <sub>17</sub>	Eu <sup>2+</sup>	Co <sup>3+</sup>	450	> 5 min
BaCa <sub>2</sub> Al <sub>8</sub> O <sub>15</sub>	Eu <sup>2+</sup>	Dy <sup>3+</sup>	435	> 5 min
Ca <sub>2</sub> Si <sub>5</sub> N <sub>8</sub>	Eu <sup>2+</sup>	Tm <sup>3+</sup>	610	> 1 h
CaAl <sub>2</sub> B <sub>2</sub> O <sub>7</sub>	Eu <sup>2+</sup>	Nd <sup>3+</sup>	464	> 1 h
SrAl <sub>1.7</sub> B <sub>0.3</sub> O <sub>4</sub>	Eu <sup>2+</sup>	-	520	> 2 h
Ca <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	Eu <sup>2+</sup>	Y <sup>3+</sup>	415	> 6 h
Sr <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	Eu <sup>2+</sup>	Y <sup>3+</sup>	420	> 8 h
SrMg <sub>2</sub> P <sub>2</sub> O <sub>8</sub>	Eu <sup>2+</sup>	Ce <sup>3+</sup> /Gd <sup>3+</sup>	400	> 2 h
CaS	Eu <sup>2+</sup>	Tm <sup>3+</sup> /Pr <sup>3+</sup>	650	> 1 h
CaGa <sub>2</sub> S <sub>4</sub>	Eu <sup>2+</sup>	Ho <sup>3+</sup>	555	> 30 min
Ca <sub>2</sub> SiS <sub>4</sub>	Eu <sup>2+</sup>	Nd <sup>3+</sup>	660	> 30 min
Sr <sub>3</sub> Al <sub>2</sub> O <sub>5</sub> Cl <sub>2</sub>	Eu <sup>2+</sup>	Tm <sup>3+</sup> /Dy <sup>3+</sup>	620	> 5 min

# 4.2.7 Temperature Resolved Spectroscopy

## Thermoluminescence

Example:  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$



### Arrhenius equation

$$A = s \cdot \exp(-E/kT)$$

$s$  = frequency factor [ $\text{s}^{-1}$ ]

$E$  = trap depth [eV]

Activation i.e., emptying the electrons in the traps leads to emission of radiation

First order kinetics i.e., no retrapping:

$$I(t) = -dn_t/dt = -n_t s \cdot \exp(-E/kT)$$

“Glow curve” = Luminescence intensity as a function of time or temperature



# 4.2.7 Temperature Resolved Spectroscopy

## Randall-Wilkins first-order glow peak

### Intensity at a given temperature

$$I(t) = -dn_t/dt = -n_t s \exp(-E/kT)$$

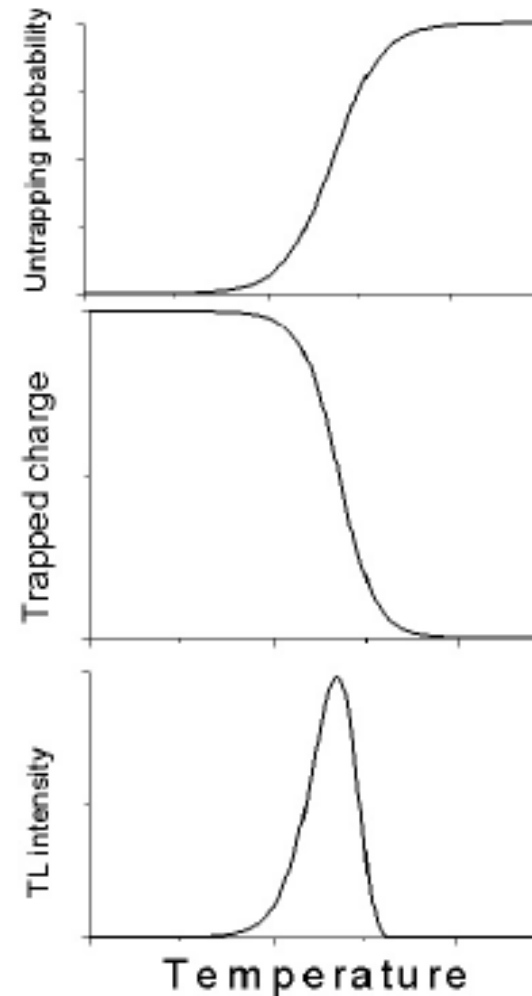
### Temperature profile in TL experiments

$$T(t) = T_0 + \beta \cdot t$$

$T_0$  = start temperature

$\beta$  = heating rate

$k$  or  $k_B = 1.38 \cdot 10^{-23} \text{ JK}^{-1}$  (Boltzmann constant)



## 4.2.7 Temperature Resolved Spectroscopy

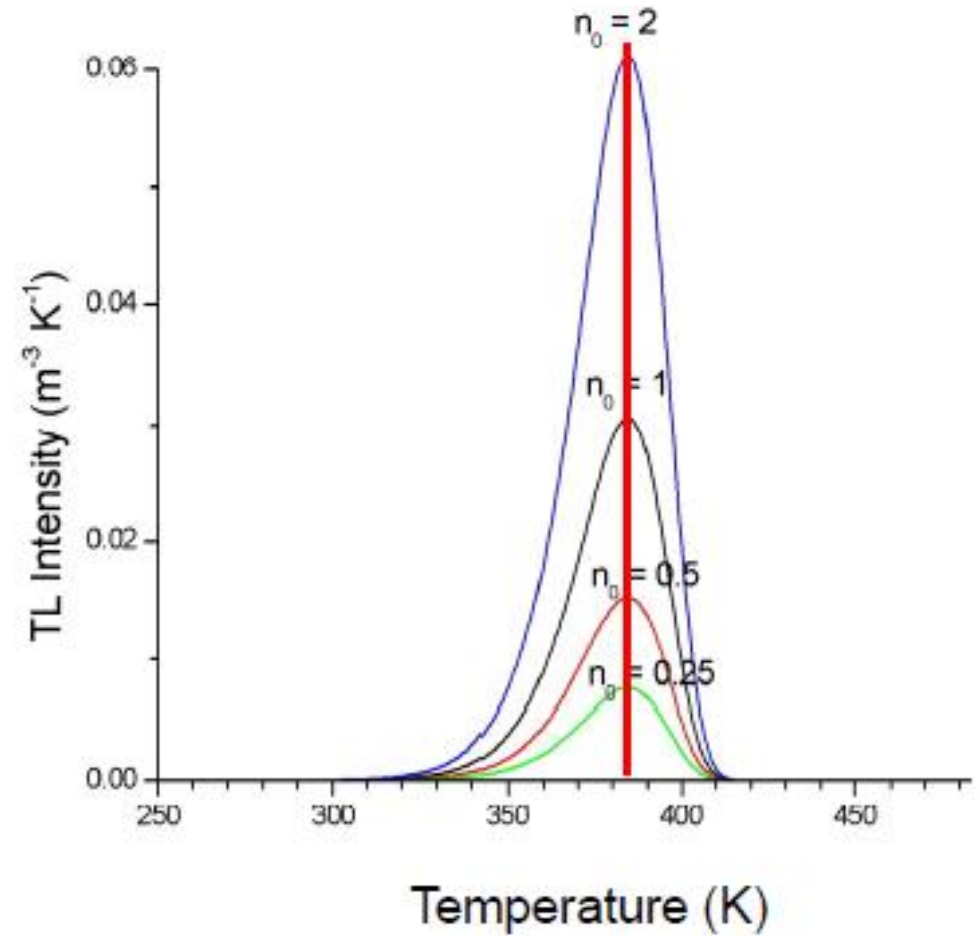
### First-order glow peak - Variation in $n_0$ (Number of traps)

$$\int_0^{\infty} I(t) dt = - \int_0^{\infty} \frac{dn}{dt} dt = - \int_{n_0}^{n_{\infty}} dn = n_0$$

#### Findings for $n_0$

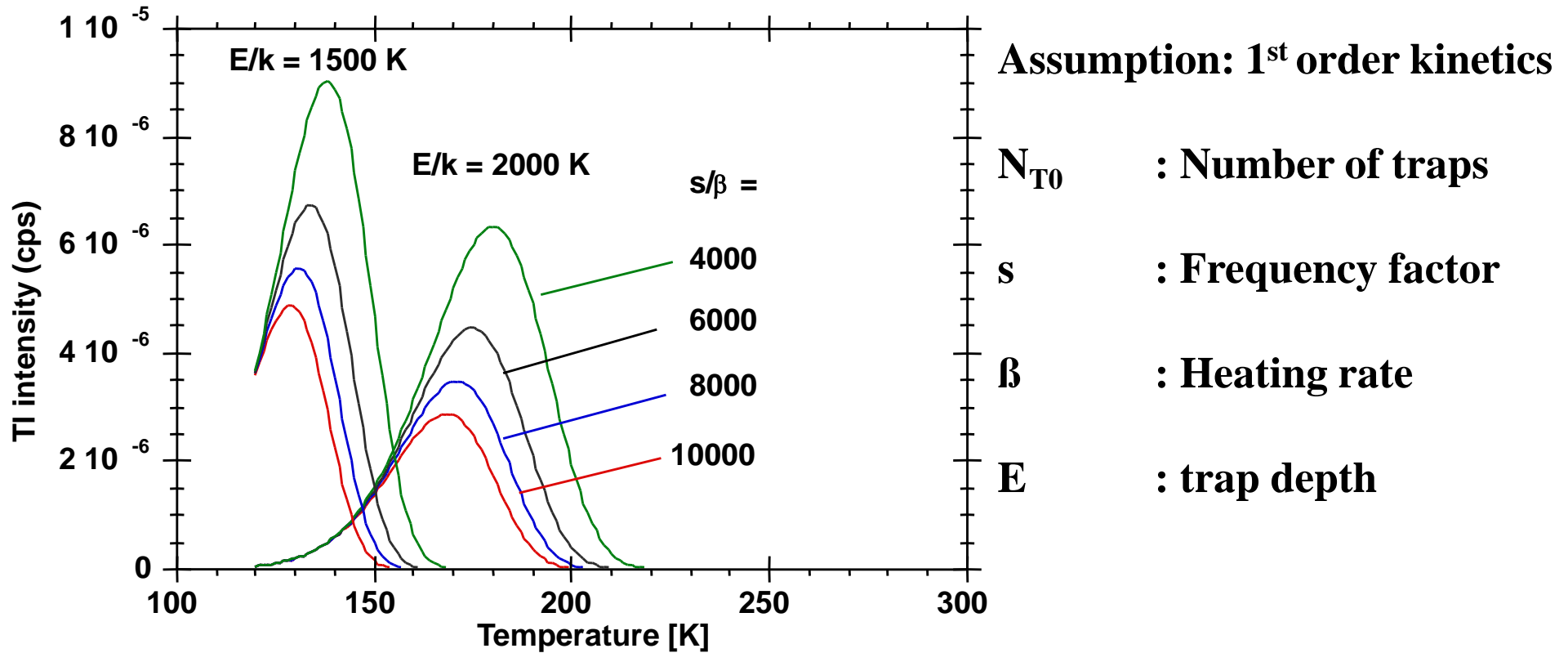
- ~ Peak area
- ~ Peak height
- Independent of peak maximum

→ relates to defect density of material



# 4.2.7 Temperature Resolved Spectroscopy

## First-order glow peak - Variation in E and s or $\beta$



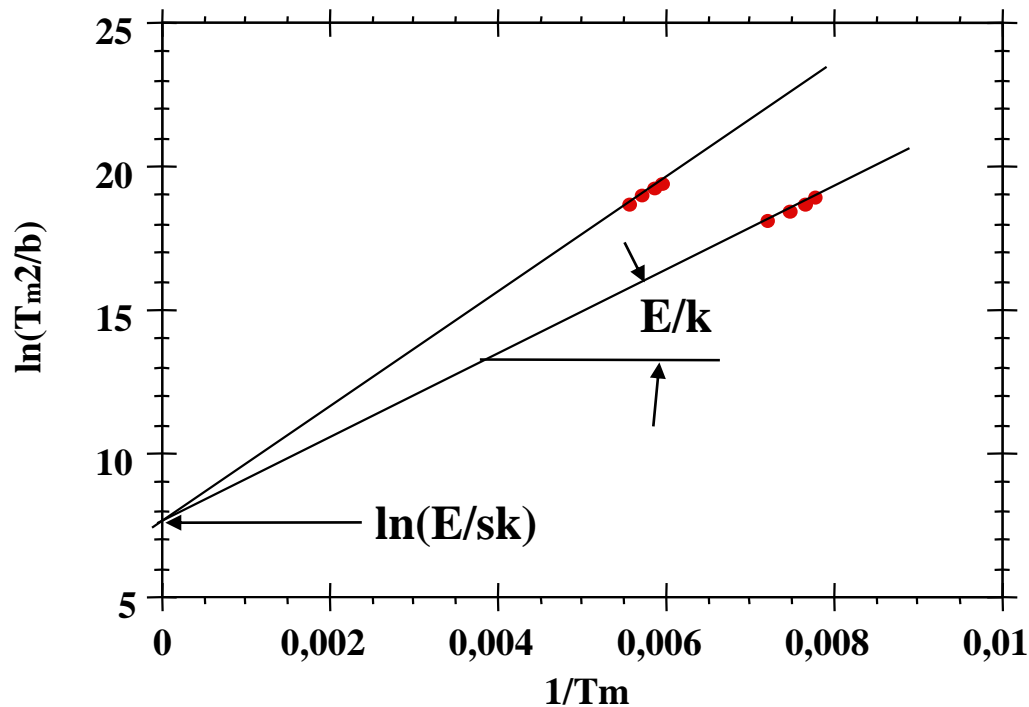
$$I_{TL} = N_{T0} s \exp(-E/kT) \cdot \exp \left[ -s/\beta \int_{T_0}^T \exp(-E/kT) dT \right]$$

Randall, Wilkins 1945

# 4.2.7 Temperature Resolved Spectroscopy

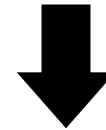
## Analysis of thermoluminescence measurements

$$I_{TL} = N_{T_0} s \exp(-E/kT) \cdot \exp \left[ -s/\beta \int_{T_0}^T \exp(-E/kT) dT \right]$$



**First order kinetics**

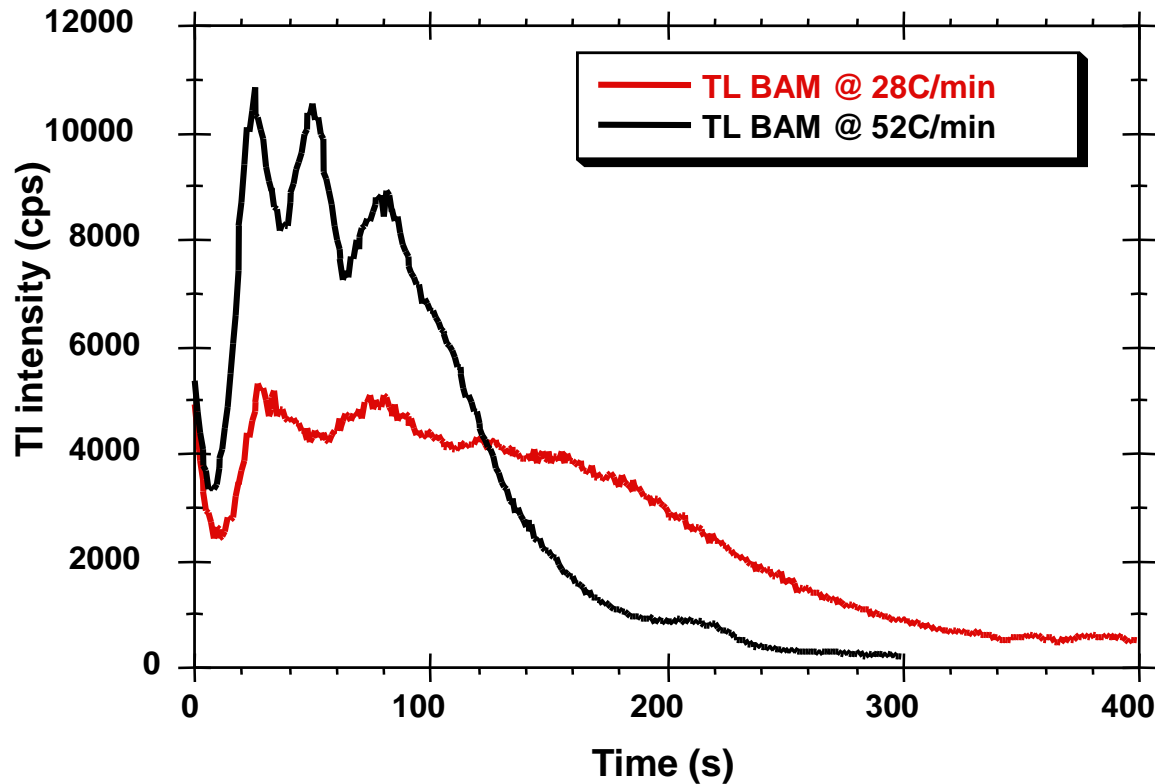
$$\frac{dI_{TL}}{dT} = 0 \quad \text{at } T = T_m$$



$$\frac{\beta \cdot E}{k T_m^2} = s \cdot \exp(-E/kT_m)$$

# 4.2.7 Temperature Resolved Spectroscopy

## a) Thermoluminescence analysis of BaMgAl<sub>10</sub>O<sub>17</sub>:Eu (BAM:Eu)



As a function of heating rate

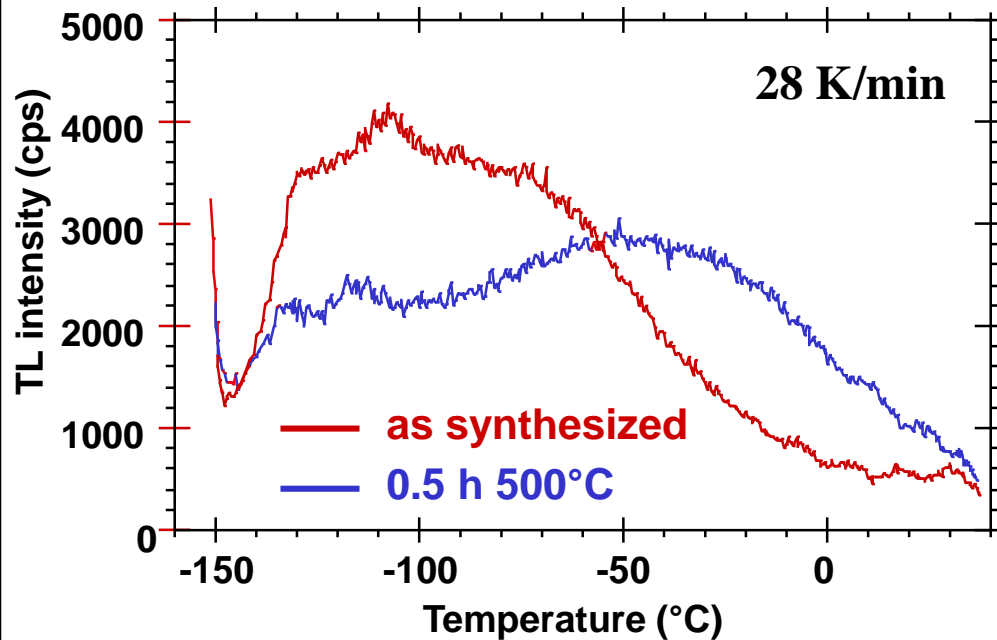
$\beta$ [°C/min]	$\int I_{TL} dt$ [Mcps*s]
11	0.898
15	1.117
22	1.104
28	1.050
45	1.027
52	1.078

# 4.2.7 Temperature Resolved Spectroscopy

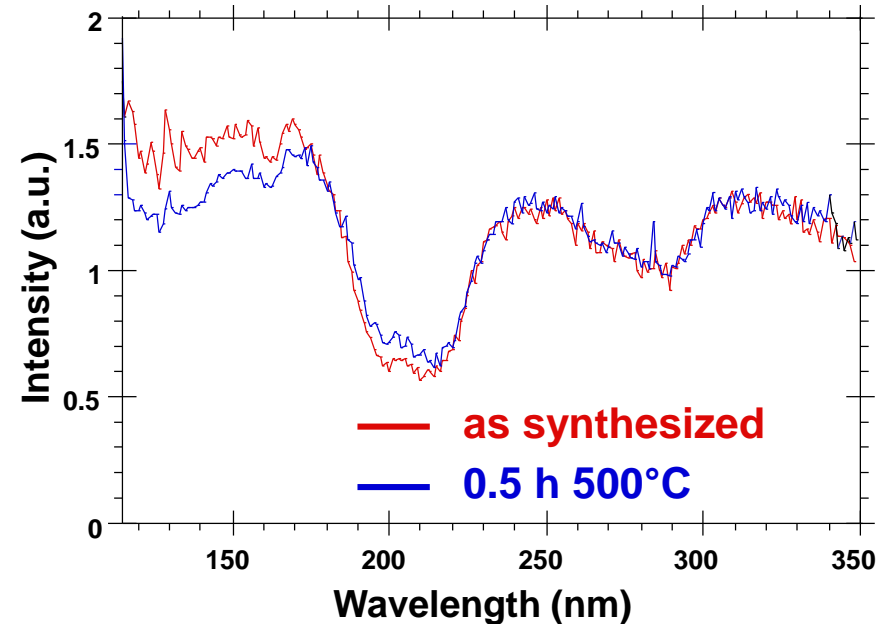
## a) Thermoluminescence analysis of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ (BAM:Eu)

BAM:Eu is at  $T > 300\text{ }^\circ\text{C}$  sensitive to oxidation:  $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$

Glow curves



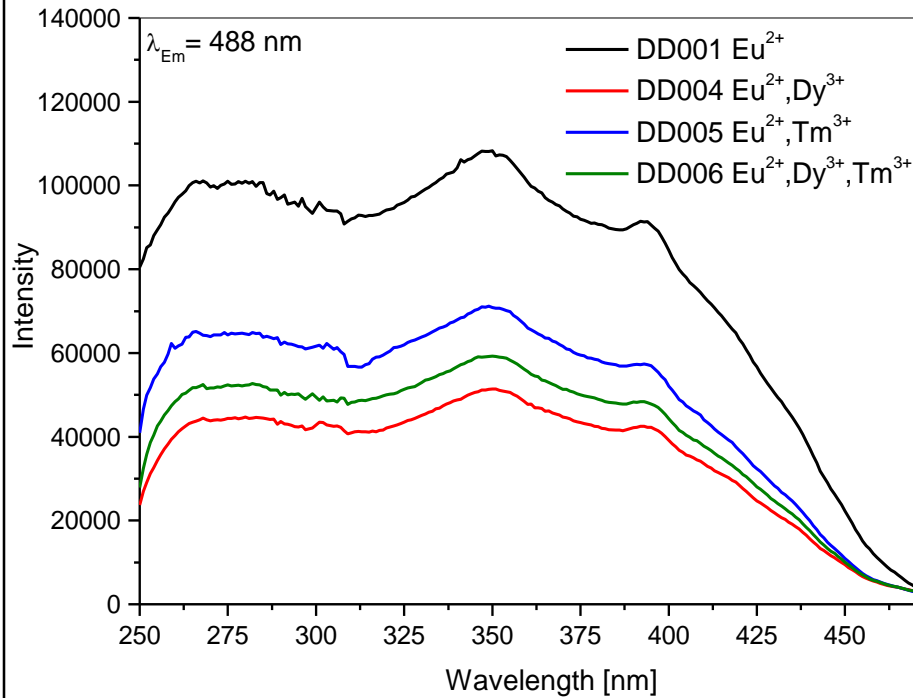
Excitation spectra



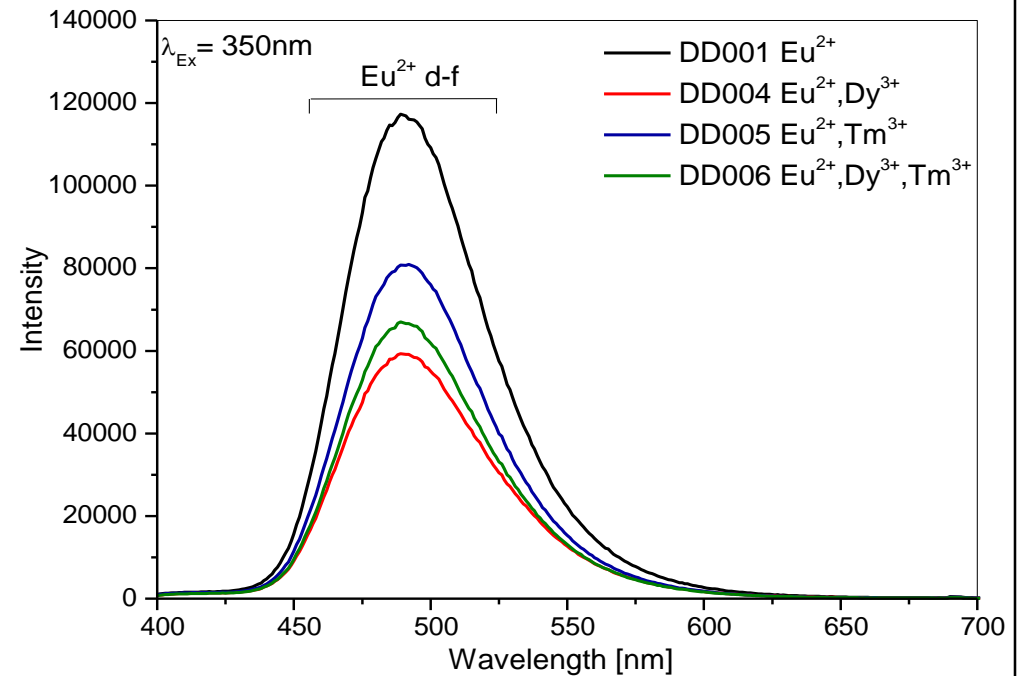
"High temperature" TL traps are generated by the oxidation (direct evidence for the formation of  $\text{Eu}^{3+}$ )

# 4.2.7 Temperature Resolved Spectroscopy

## b) Luminescence spectra of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}(\text{X})$ with $\text{X} = \text{Dy}, \text{Nd}, \text{Tm}$



**Excitation spectrum  
of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{X}$**



**Emission spectrum  
of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{X}$**

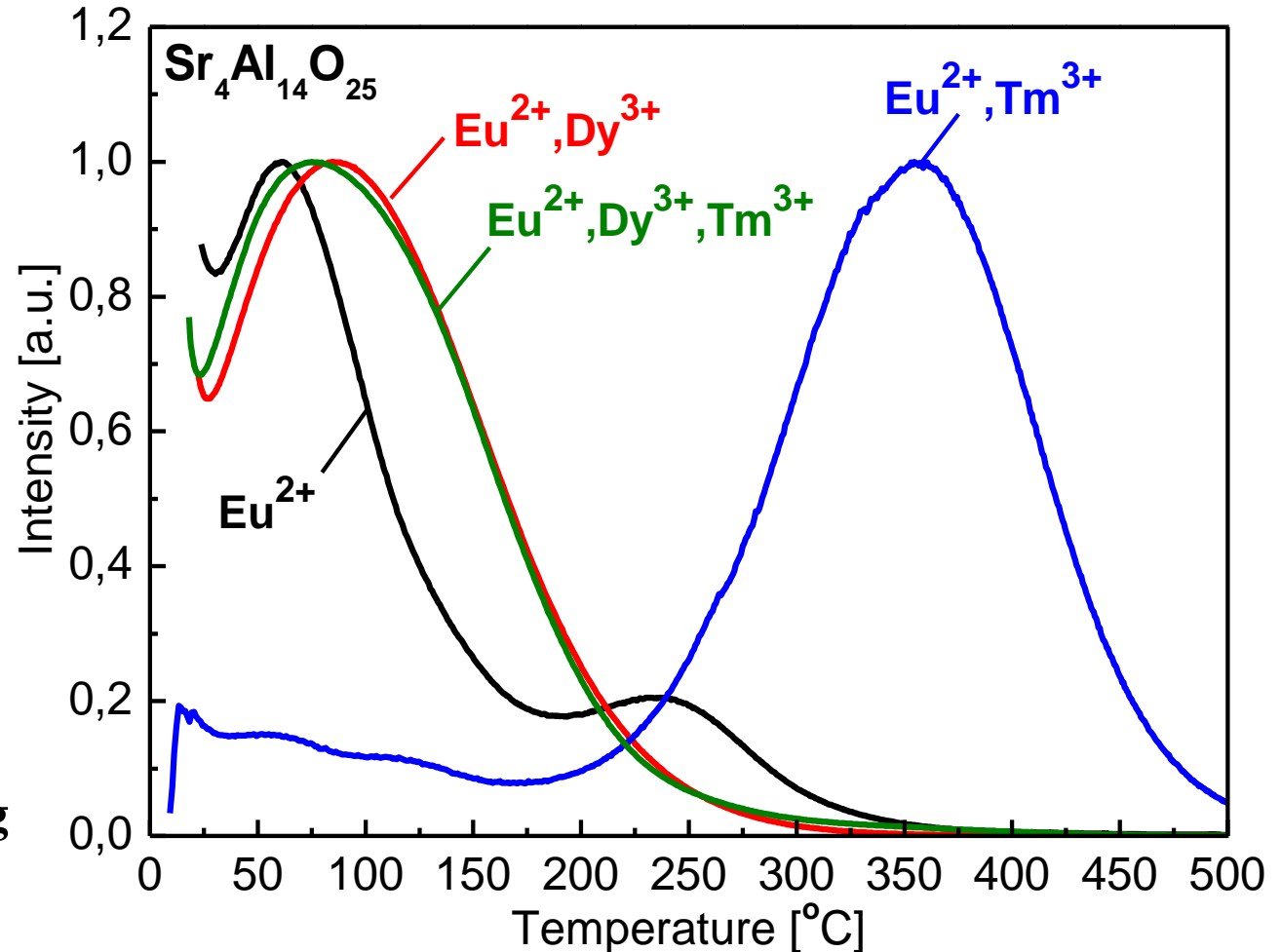
## 4.2.7 Temperature Resolved Spectroscopy

### b) Thermoluminescence analysis of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$

Co-doping with  $\text{Dy}^{3+}$  results in „afterglow” at room temperature

Further doping with  $\text{Tm}^{3+}$  results in „afterglow” also at high temperature (→ Storage phosphors)

As soon as  $\text{Dy}^{3+}$  is incorporated,  $\text{Tm}^{3+}$  hardly plays a role in the trapping of charge carriers



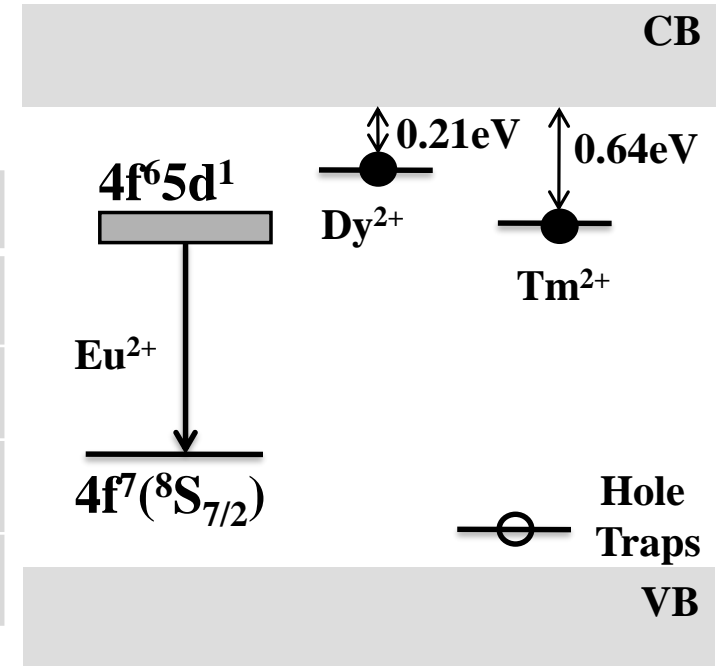


# 4.2.7 Temperature Resolved Spectroscopy

## b) Thermoluminescence analysis of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$

Data from the "peak shape" method

Compound	„Trap“ depth [eV]
$\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$	0.26, 0.55
$\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$	0.21
$\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Tm}^{3+}$	0.64
$\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+},\text{Tm}^{3+}$	0.23



- $\text{Dy}^{2+/3+}$  is energetically closer to the conduction band than  $\text{Tm}^{2+/3+}$
  - Energy gap between Dy and Tm is about  $0.4\text{ eV}$
- (see also publications by Pieter Dorenbos, TU Delft)

## 4.2.8 Time Resolved Spectroscopy

### Requirement: Pulsed, highly intense light source

- $\mu\text{s}$ -flash lamps
- ns-flash lamps
- Laser:  $\text{N}_2$ , excimer,  $\text{Al}_2\text{O}_3:\text{Cr}$ , YAG:Nd, .....
- LEDs: (Al,In,Ga)N, (Al,In,Ga)P, Ga(As,P), .....

### Measurement Procedure

- Pulsed or continuous wave excitation of the sample
- Measurement of the luminescence intensity as the function of time after the excitation source has been switched off (or single photon counting)
- Fitting of the obtained decay curve with one or several e-functions:

$$I(t) = A_0 + B_1 \cdot \exp(-t/\tau_1) + B_2 \cdot \exp(-t/\tau_2) + \dots \quad \text{with } B_1 + B_2 + \dots + B_n = 1.0$$

# 4.2.8 Time Resolved Spectroscopy

## Lifetime of the excited state

### First order kinetics (two level system, no quenching)

$$dN_e/dt = - N_e * k_{eg}$$

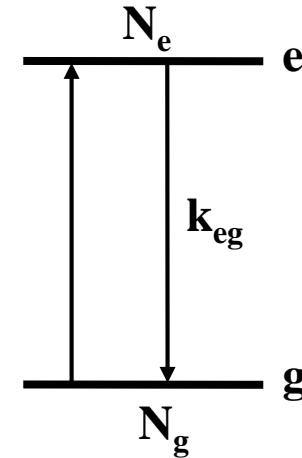
$$\Rightarrow dN_e/N_e = -k_{eg} * dt$$

$$\Rightarrow \ln(N_e(t)/N_e(0)) = -k_{eg} * t$$

$$\Rightarrow N_e(t) = N_e(0) * \exp(-t/\tau)$$

Integration

$$\tau = 1/k_{eg} = 1/k_r$$



Allowed transitions

10<sup>-6</sup> to 10<sup>-9</sup> s (4f - 5d, 6s - 6p)

Eu<sup>2+</sup>

Forbidden transitions

~ 10<sup>-3</sup> s (4f - 4f, 5d - 5d)

Eu<sup>3+</sup>

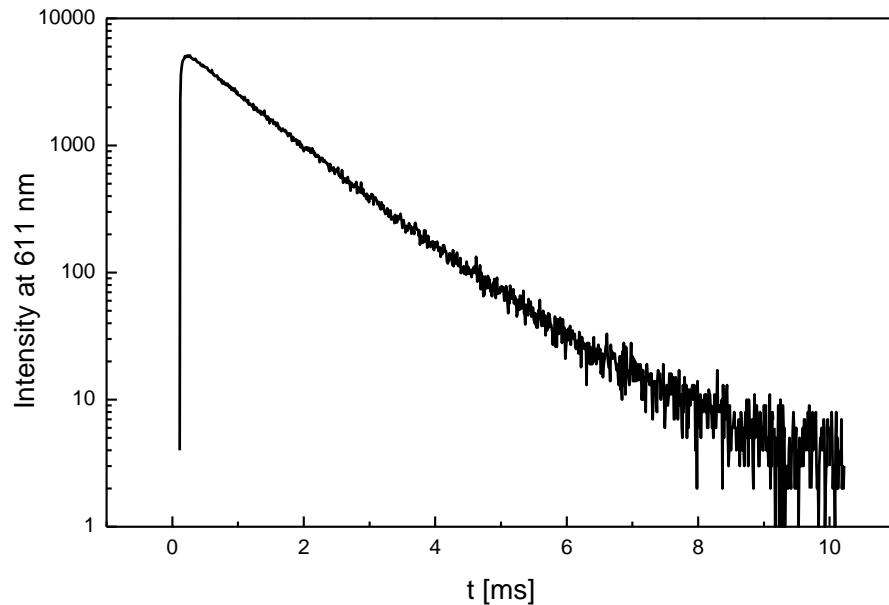
# 4.2.8 Time Resolved Spectroscopy

## Mono- and bi-exponential decay

mono-exponential behavior, e.g.  $\text{Eu}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Tb}^{3+}$

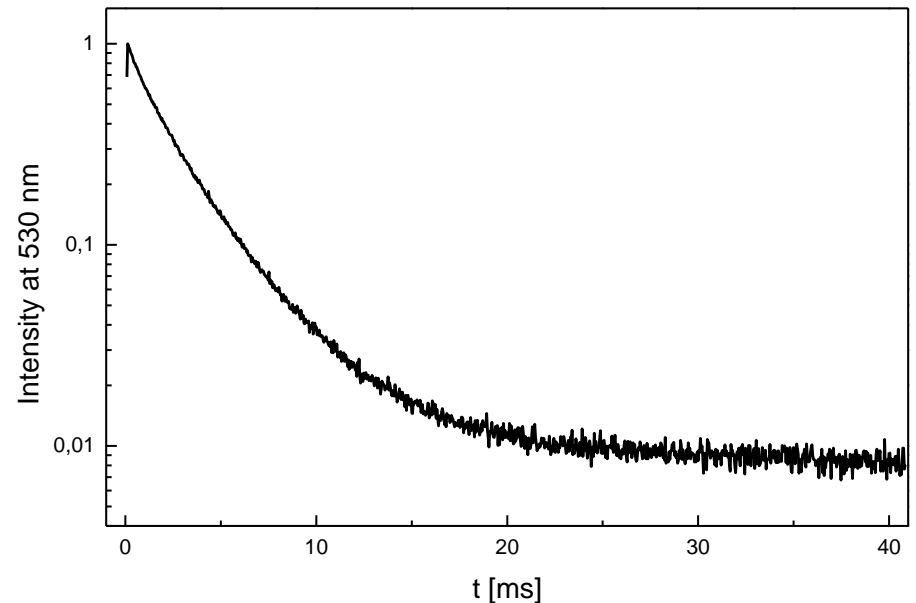
bi-exponential behavior, e.g.  $\text{Mn}^{2+}$  due to  $\text{Mn}^{2+}$ -O- $\text{Mn}^{2+}$  antiferromagnetic coupling

$(\text{Y,Gd})_2\text{O}_3:\text{Eu}^{3+}$



$$B_1 = 1.0 \quad \tau_1 = 1.1 \text{ ms}$$

$\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$



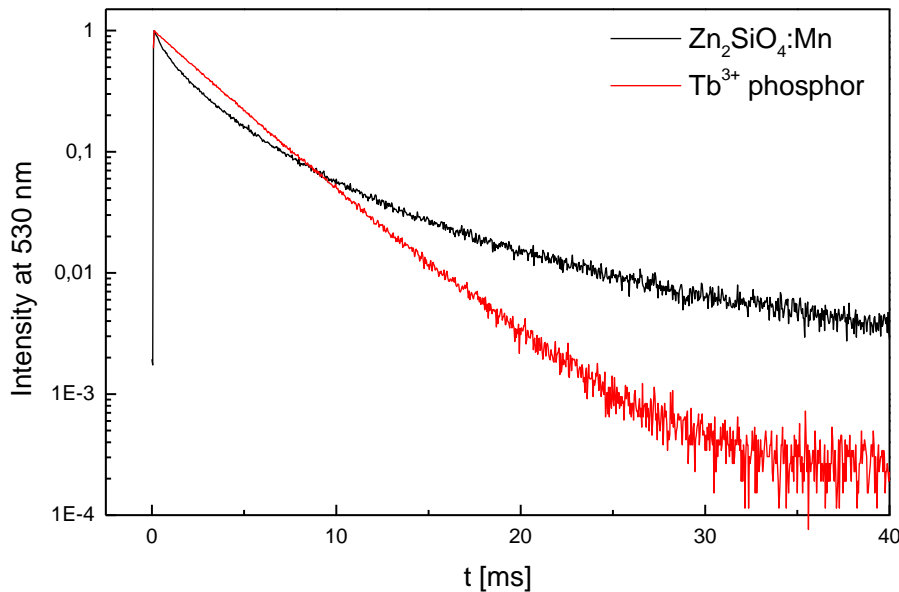
$$B_1 = 0.44 \quad \tau_1 = 5.6 \text{ ms}$$

$$B_2 = 0.56 \quad \tau_2 = 2.3 \text{ ms}$$

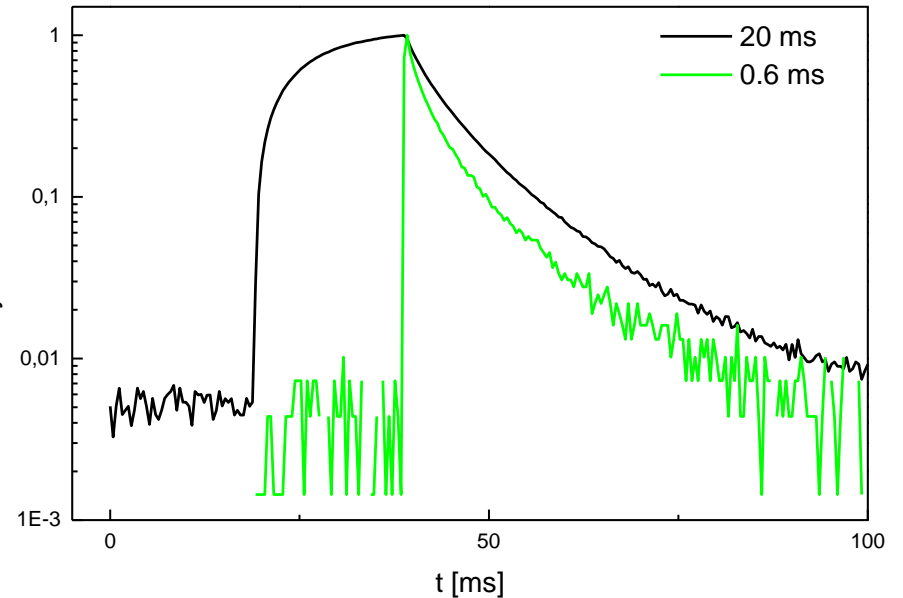
# 4.2.8 Time Resolved Spectroscopy

## Mono- and bi-exponential decay

Single-pulse excitation of  $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$  and  $(\text{Y,Gd})\text{BO}_3:\text{Tb}^{3+}$



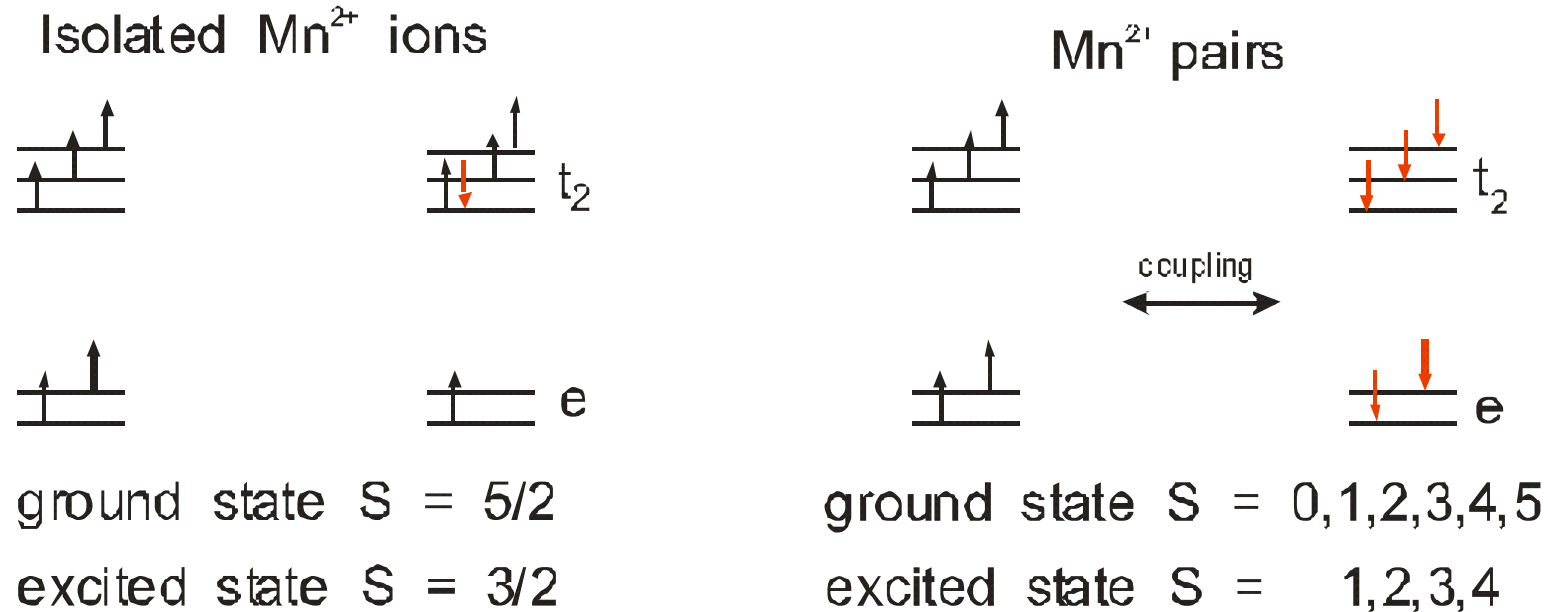
Decay curve of  $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$  (Single pulse and continuous wave excitation)



Phosphor	Decay curve	Single pulse	Continuous wave
• $(\text{Y,Gd})\text{BO}_3:\text{Tb}^{3+}$	mono-exponential	9 ms	10 ms
• $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$	bi-exponential	11 ms	17 ms

# 4.2.8 Time Resolved Spectroscopy

## Exchange interaction in Mn<sup>2+</sup> phosphors



**High Mn<sup>2+</sup> concentration  $\Rightarrow$  Exchange interaction between Mn<sup>2+</sup>-ions**

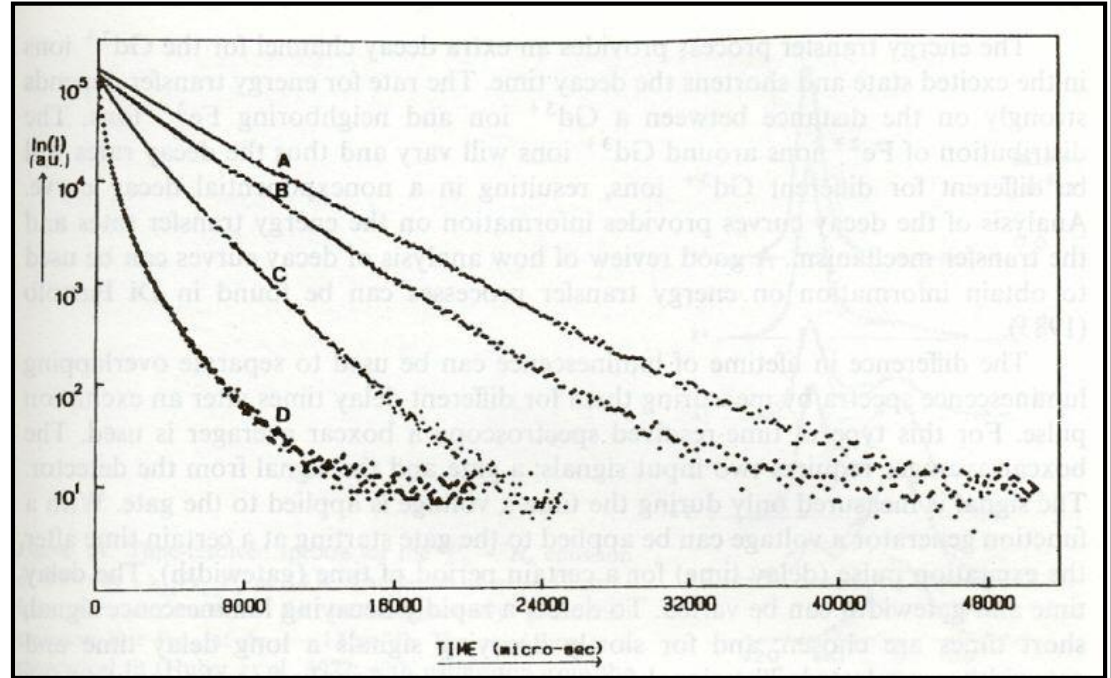
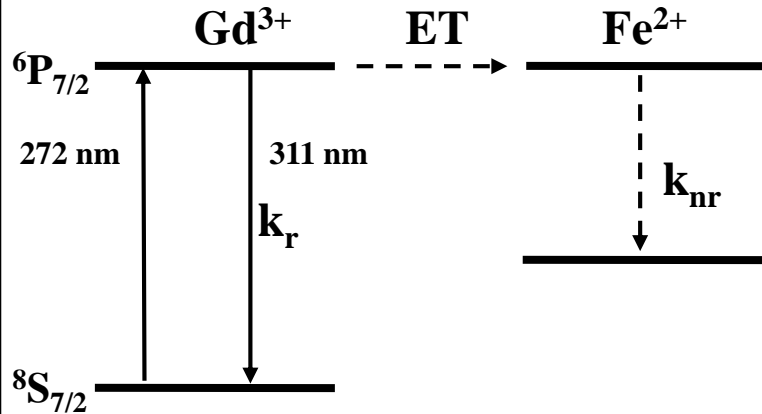
**The decay time is reduced by eliminating the spin selection rule**

**Low excitation density  $\Rightarrow$  Excitation of Mn<sup>2+</sup> pairs  $\Rightarrow$  Short decay time**

**High excitation density  $\Rightarrow$  Excitation of isolated Mn<sup>2+</sup> ions  $\Rightarrow$  Long decay time**

# 4.2.8 Time Resolved Spectroscopy

**Example:  $\text{La}_{0.4}\text{Gd}_{0.6}\text{MgB}_5\text{O}_{10}:x\%\text{Fe}$**



**Decay of the  $\text{Gd}^{3+}$  emission (intraconfigurational transition  $^6\text{P}_{7/2} - ^8\text{S}_{7/2}$ ) at 311 nm**

**A:  $\text{La}_{0.4}\text{Gd}_{0.6}\text{MgB}_5\text{O}_{10}$**

**B:  $\text{La}_{0.4}\text{Gd}_{0.6}\text{MgB}_5\text{O}_{10}:0.01\%\text{Fe}$**

**C:  $\text{La}_{0.4}\text{Gd}_{0.6}\text{MgB}_5\text{O}_{10}:0.1\%\text{Fe}$**

**D:  $\text{La}_{0.4}\text{Gd}_{0.6}\text{MgB}_5\text{O}_{10}:1\%\text{Fe}$   $\Rightarrow$  Energy transfer to  $\text{Fe}^{2+}$  reduces decay time**

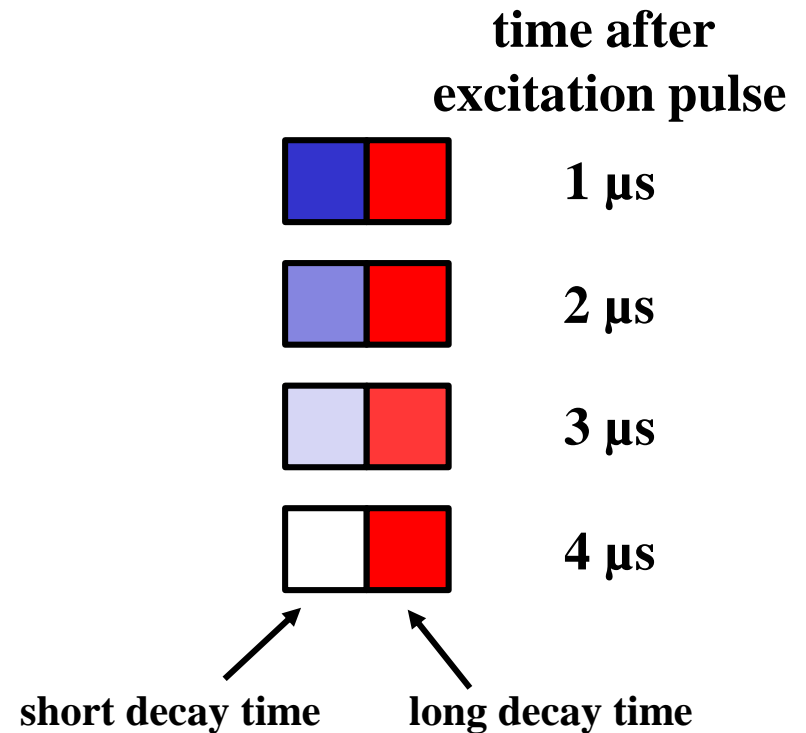
# 4.2.8 Time Resolved Spectroscopy

## Time Resolved Emission Spectra

Emission spectrum and/or intensity can change over time e.g. due to

- Two or more emitting components emission with different decay times
- saturation effects
- energy transfer

In order to observe these effects, the system must not be in equilibrium  
→ Pulsed excitation!



Example for a system comprising a fast and a slow decaying component

e.g.  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$

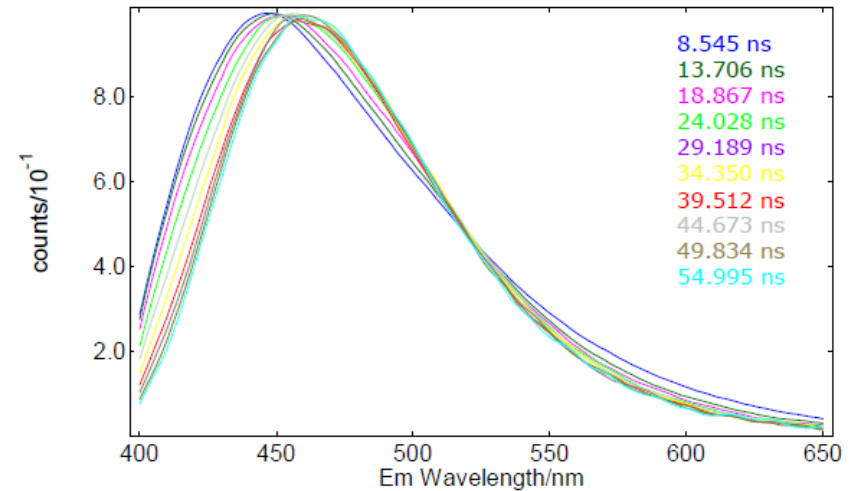


# 4.2.8 Time Resolved Spectroscopy

## Time Resolved Emission Spectra

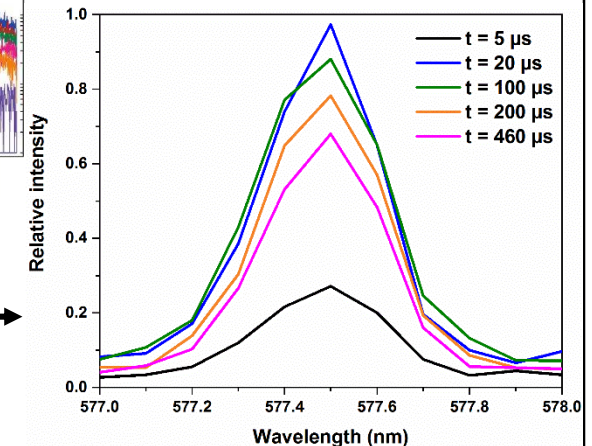
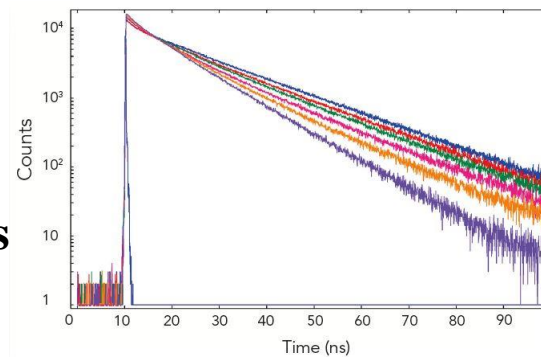
### Recording by ICCD (intensified CCD)

- CCD with amplifier
- all wavelengths are recorded simultaneously
- down to **200 ps** temporal resolution
- wavelength resolution c. **0.5-1 nm**
- **quick** measurement



### Recording via decay curves

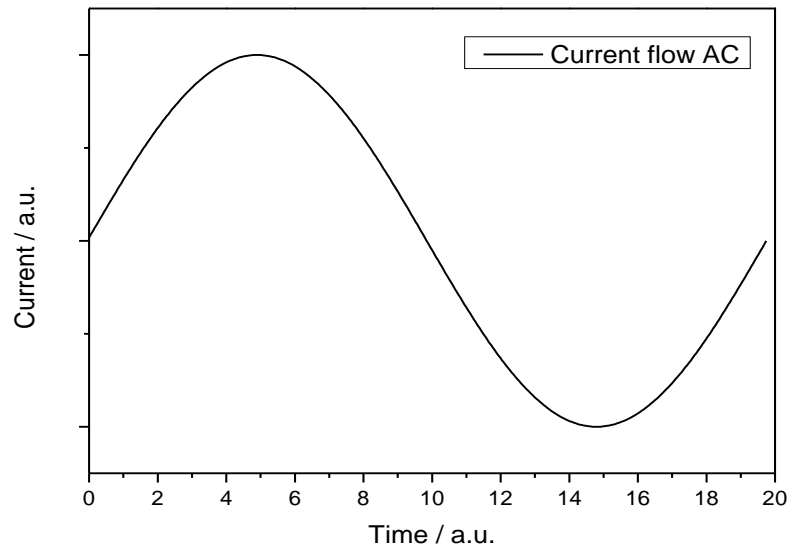
- A decay curve is recorded for each emission wavelength
- A time resolved emission spectrum is constructed from the curves
- down to **few ps** temporal resolution
- wavelength resolution of down to **0.05 nm**
- **(very) slow** measurement



# 4.2.9 Flicker Measurements

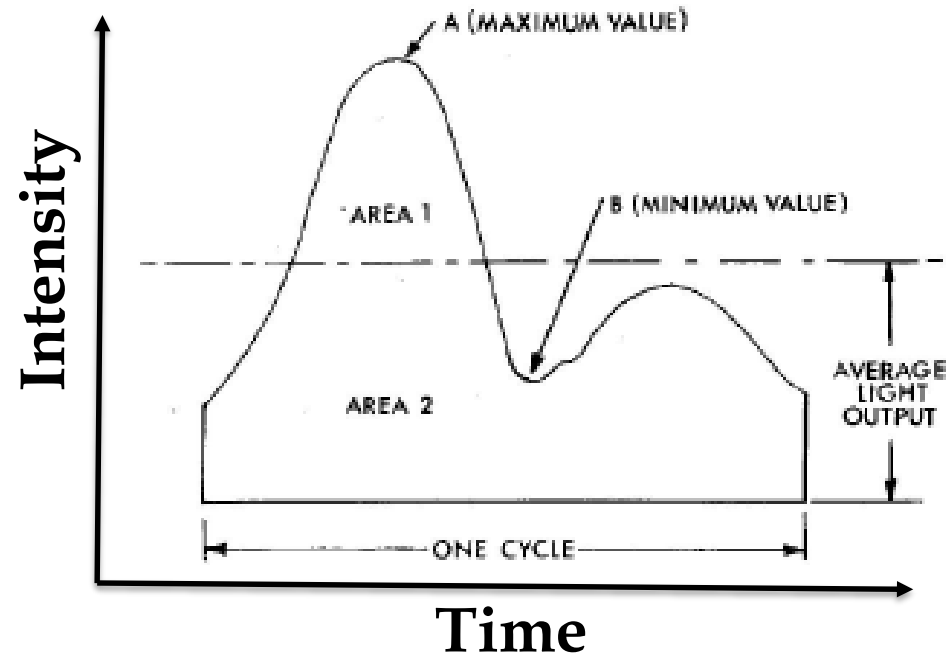
## Definition of flicker

- **Flicker is the fast, periodic change of the intensity of a light source**
- **It is an inherent problem of all kind of electrical light sources**
- **Alternating current (50 Hz) from the electric grid causes flicker of light sources**
- **Incandescent lamps show solely little flicker due to thermal inertia of glowing tungsten**



## 4.2.9 Flicker Measurements

### Quantification of flicker



$$\text{Percent Flicker} = \frac{\text{Max Value} - \text{Min Value}}{\text{Max Value} + \text{Min Value}} \cdot 100\% = \frac{A - B}{A + B} \cdot 100\%$$

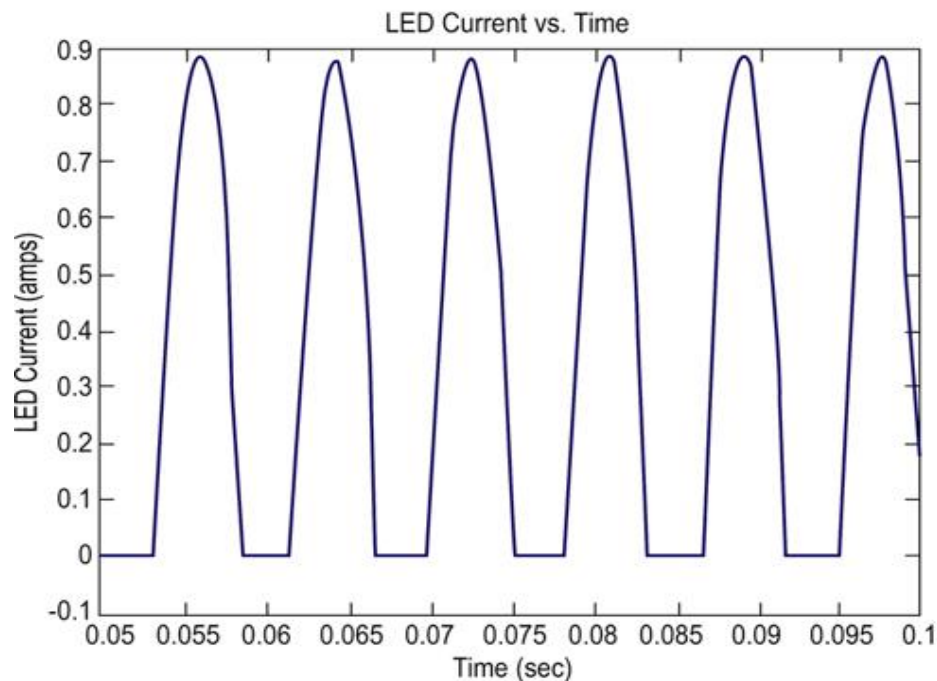
$$\text{Flicker index} = \frac{\text{Area above Mean}}{\text{Total area}} = \frac{\text{Area 1}}{\text{Area 1} + \text{Area 2}}$$

M. Rea, IESNA Lighting Handbook, 9<sup>th</sup> Edition, (2000)

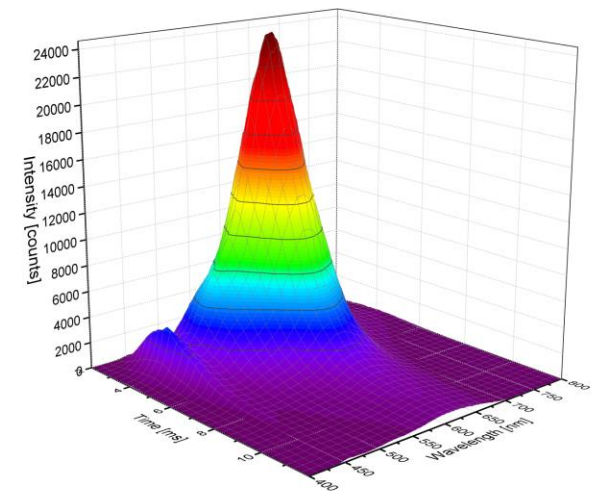
## 4.2.9 Flicker Measurements

**Discharge lamps and particularly LEDs show strong flicker**

- **Flicker with 100 Hz for 50 Hz alternating current**
- **Electronic driver are able to flatten the current and intensity curve**
- **Alternative solution: Phosphors with long decay time  $> 10$  ms**



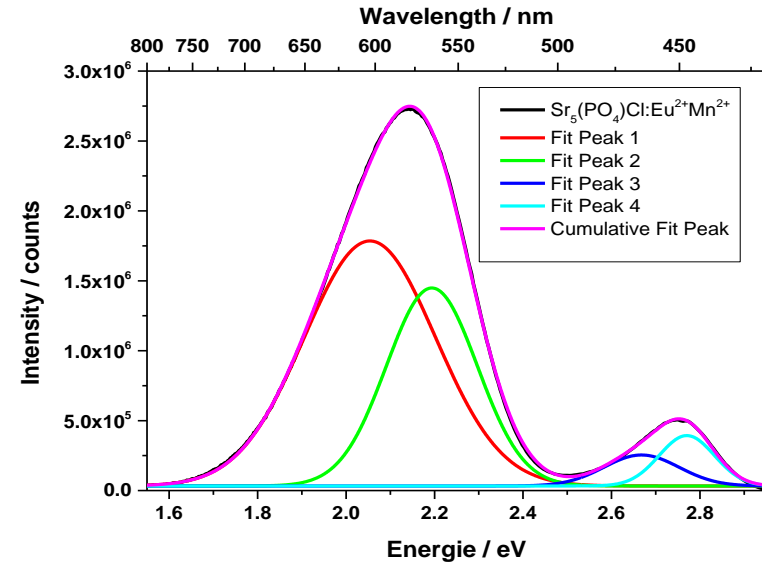
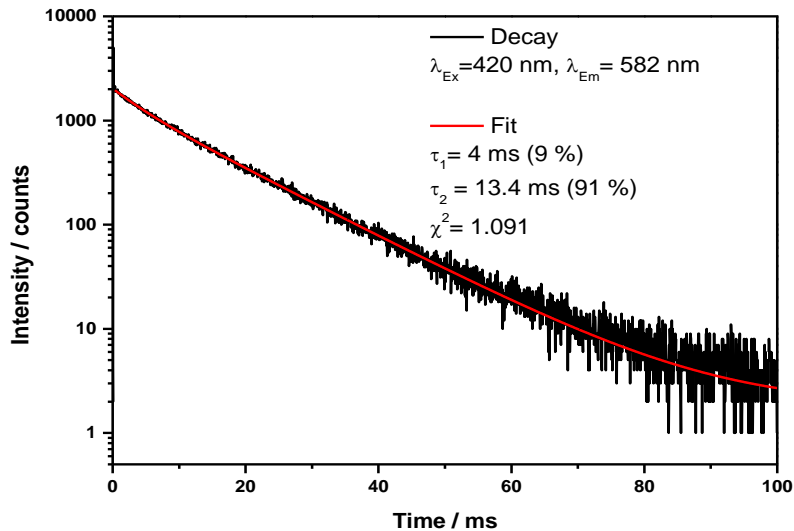
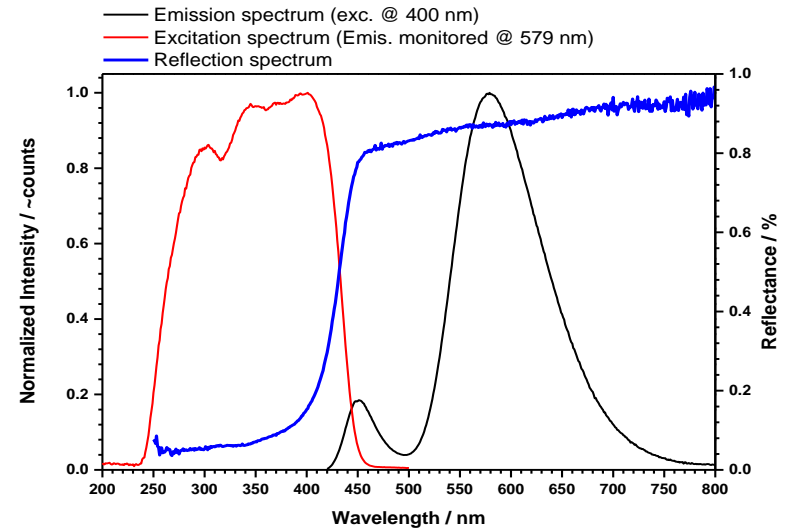
**Example: Osram Parathon E14**  
**Percent Flicker @ 100 Hz = 96%**  
**Flicker Index = 0.45**



# 4.2.9 Flicker Measurements

## Example: $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}\text{Mn}^{2+}$

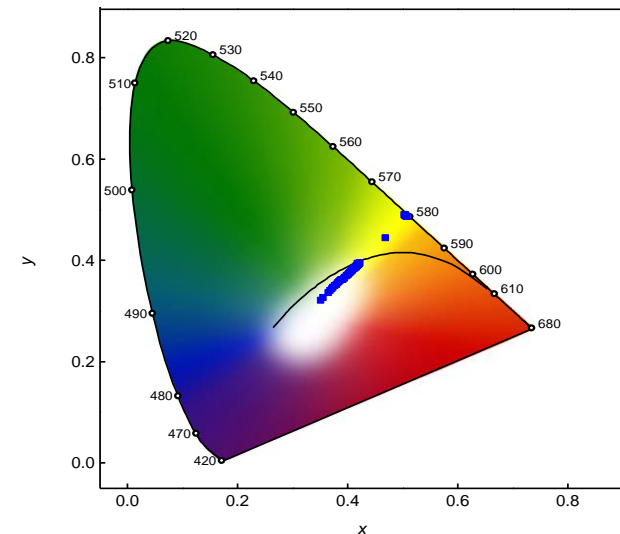
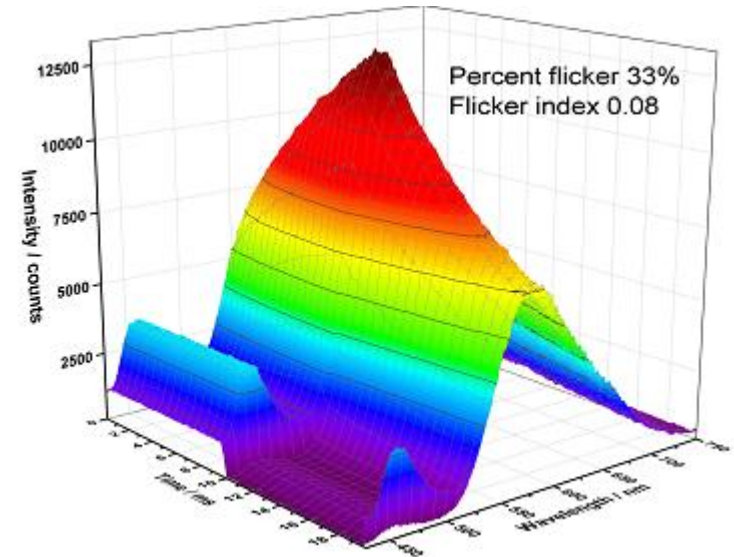
- Excitation 280 – 425 nm
- Emission 579 nm
  - Sr1 451 nm (CN = 9)
  - Sr2 579 nm (CN = 7)
- Decay time ~ 12.5 ms



# 4.2.9 Flicker Measurements

**Example:  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}\text{Mn}^{2+}$**

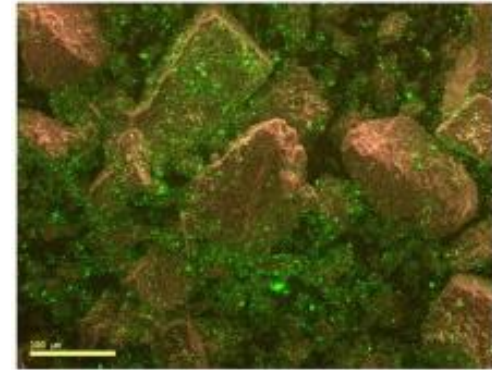
- ▶ **Percent Flicker 33%**
- ▶ **Flicker Index 0.08**
- ▶ **Color point shifts from white to yellow**
- ▶ **Color point (average) :**
  - ▶  **$x = 0.453$ ;  $y = 0.430$ ;  $\text{LE} = 378 \text{ lm/W}_{\text{opt}}$**
- ▶  **$\text{CCT} = 2916 \text{ K}$**



## 4.2.10 X-ray and Cathode Luminescence

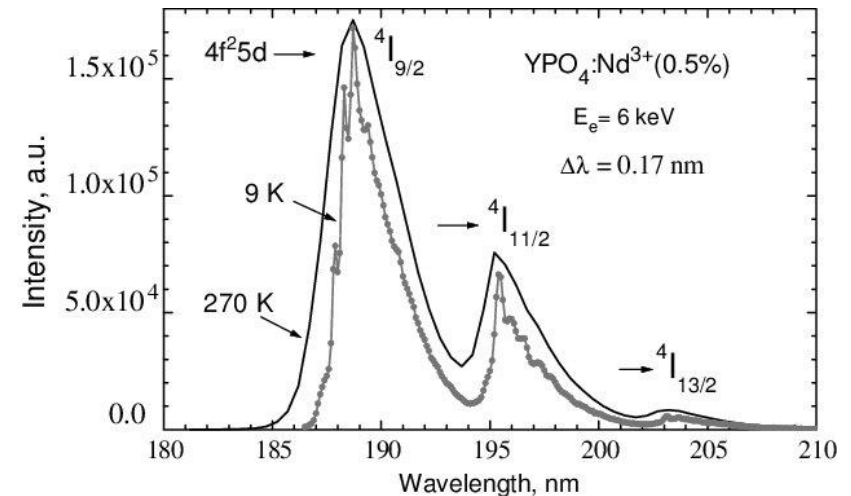
### Excitation with high-energy radiation

- Unspecific excitation of all luminescent species (defects, band transitions, activators)
- Impurities in the ppm range can be determined qualitatively (e. g.  $\text{Gd}^{3+}$  in  $\text{Y}_2\text{O}_3$ )
- The sample can be excited with a spatial resolution in the  $\mu\text{m}$  range
- VUV or UV-C emission can be observed, such as  $\text{Nd}^{3+}$  bands at 190 nm



RGB image revealing the distribution of the API (green) and the lactose (brown) using CL spectroscopic imaging

Lit.: DOI: 10.1016/j.ejps.2011.10.017



Lit.: DOI: 10.1016/S0168-9002(02)00749-0

# 4.3 Reflection Spectroscopy

## 4.3 Reflection Spectroscopy

### 4.3.1 Physical Basis

### 4.3.2 Reflection Spectrometer

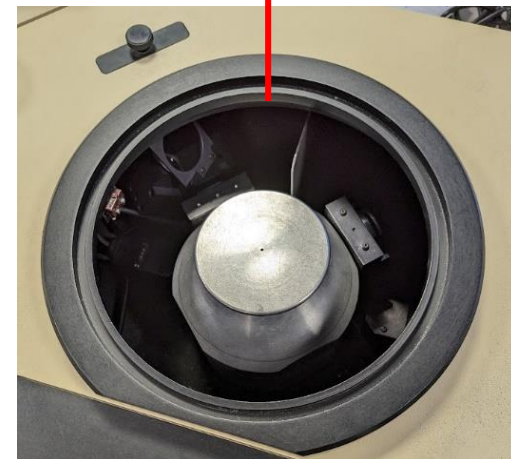
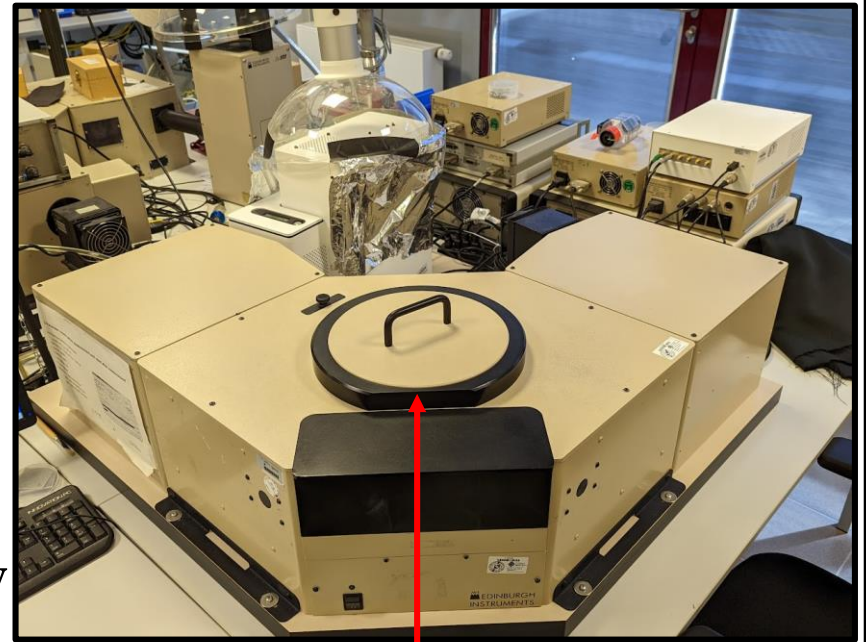
### 4.3.3 The Integrating Sphere

### 4.3.4 VUV Reflection

### 4.3.5 Band Gap Determination

### 4.3.6 The Kubelka-Munk Function

### 4.3.7 Application of Reflection Spectroscopy



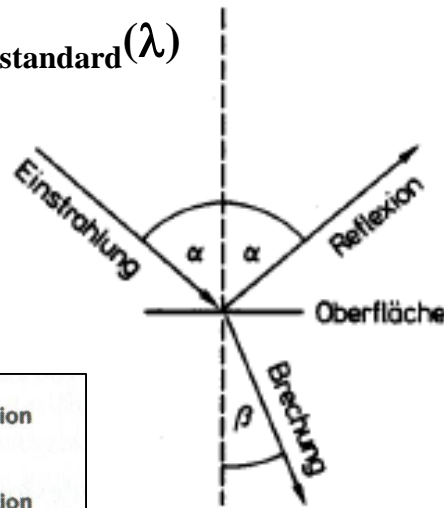


# 4.3.1 Physical Basis

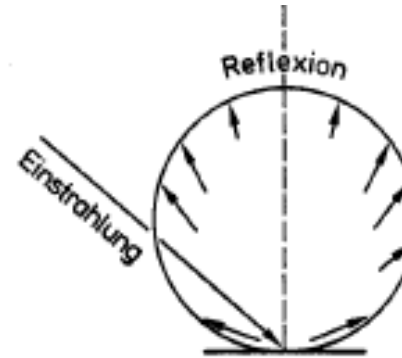
## Types of Reflection

Measurement is made relative to a white standard, e.g. BaSO<sub>4</sub>, CaCO<sub>3</sub>, or Teflon powder

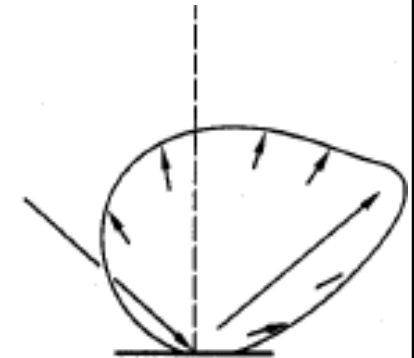
$$R_{\text{diffuse}}(\lambda) = I_{\text{sample}}(\lambda) / I_{\text{white standard}}(\lambda)$$



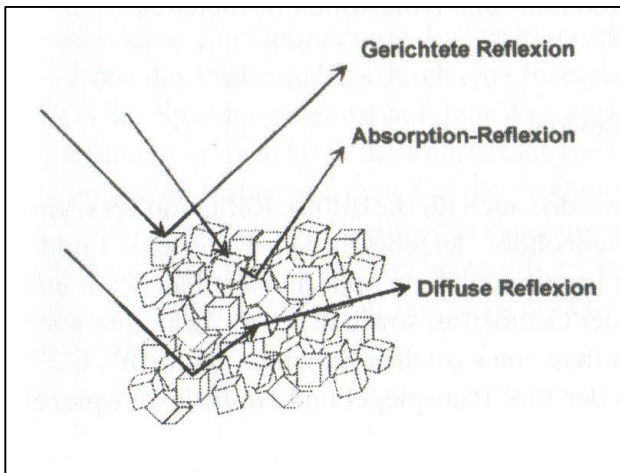
Regular reflection



Diffuse reflection



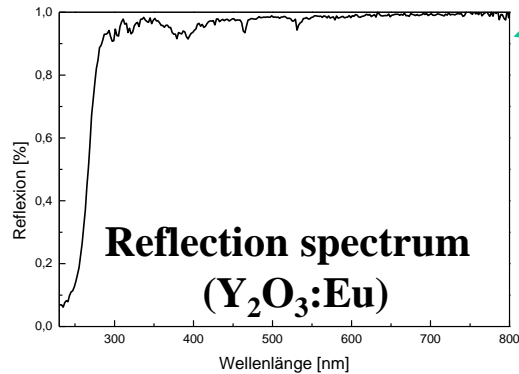
Overlapping of two processes



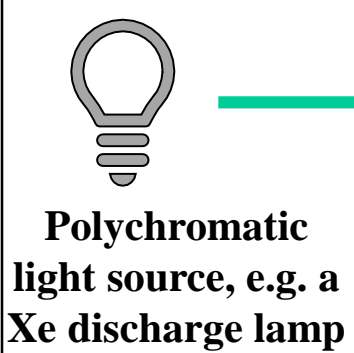
Lit.: D. Oelkrug in H. Naumer, W. Heller, Untersuchungsmethoden in der Chemie, Thieme, 3<sup>rd</sup> edition, 1997

# 4.3.2 Reflection Spectrometer

## Sketch of a typical set-up

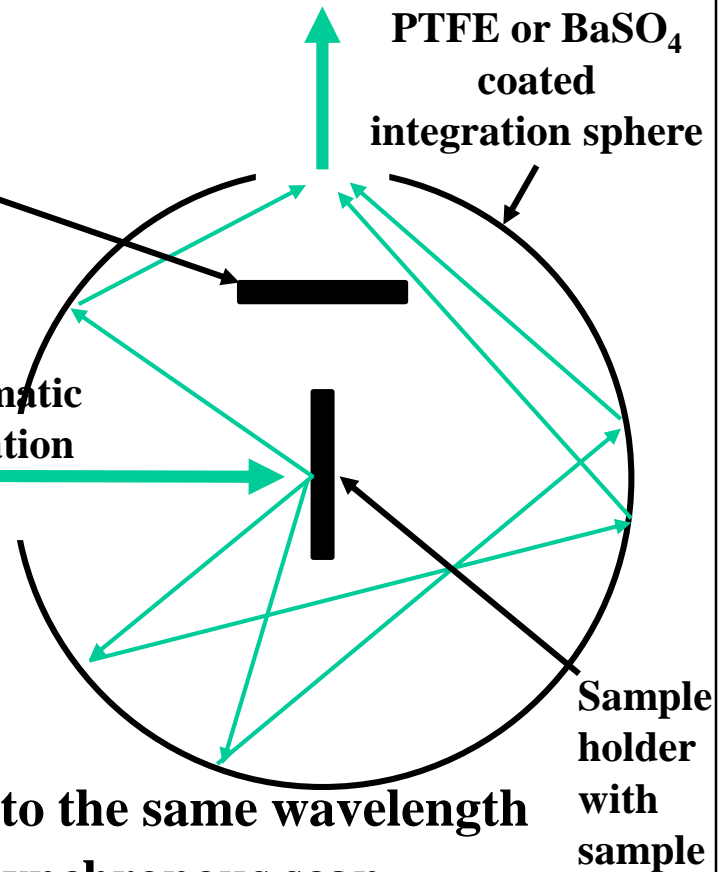


Monochromatic light/radiation



Monochromatic light/radiation

PTFE or BaSO<sub>4</sub> coated shield (baffle)



Excitation and emission monochromator is set to the same wavelength and synchronously tuned ⇒ So-called synchronous scan

# 4.3.3 The Integrating Sphere

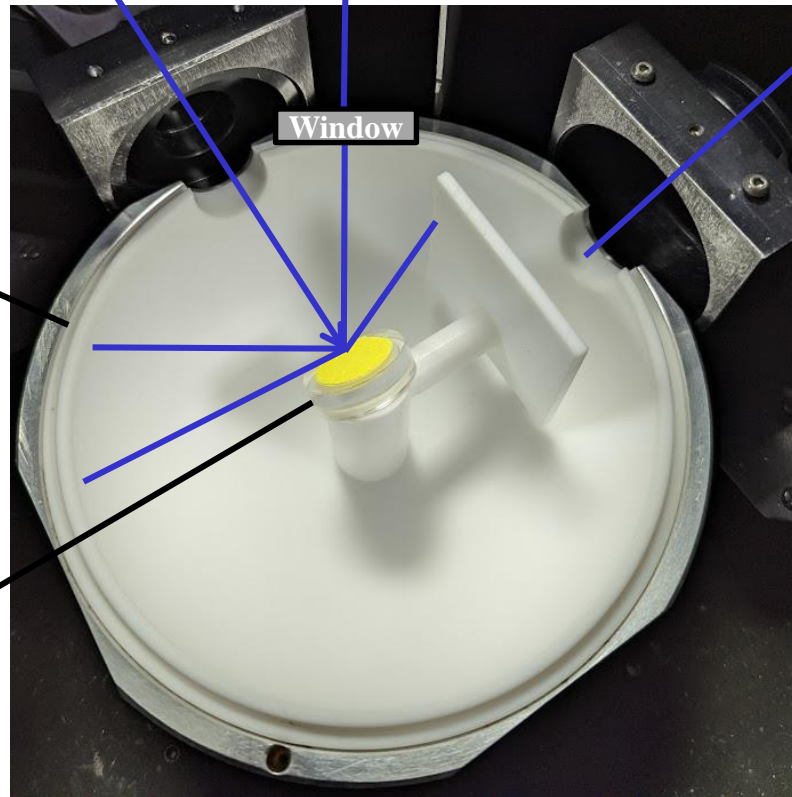
## Image of an Ulbricht Sphere

Light from monochromator 1

Optional output  
to analysis the  
specular reflexes

to mono-  
chromator 2

Coated  
integrating  
sphere  
(BaSO<sub>4</sub>)



Sample holder  
with YAG:Ce

## 4.3.4 VUV Reflection

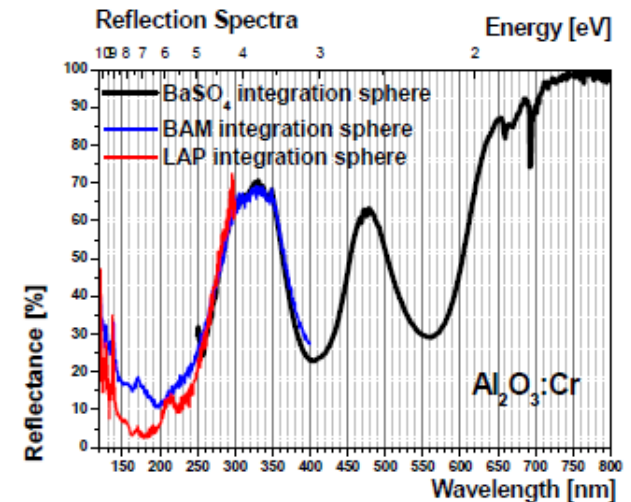
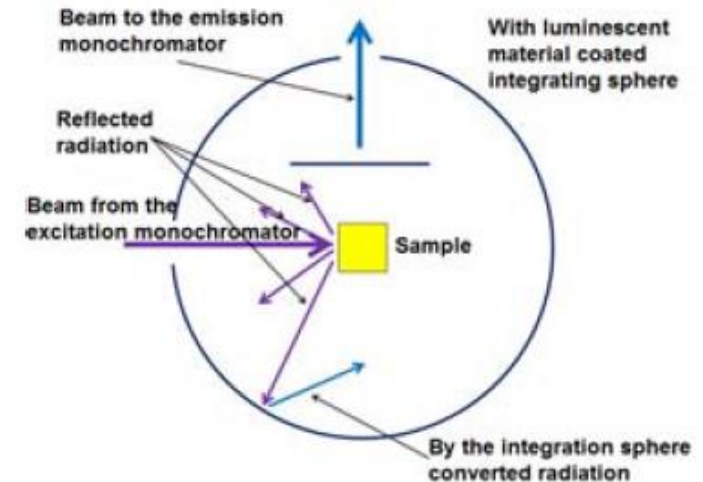
### Specific Challenges in the VUV Range

- PMTs cannot detect VUV radiation
- Teflon and  $\text{BaSO}_4$  absorb VUV ( $< 200 \text{ nm}$ )

→ Scintillation detector + LiF or  $\text{MgF}_2$  coating  
(hygroscopic!)

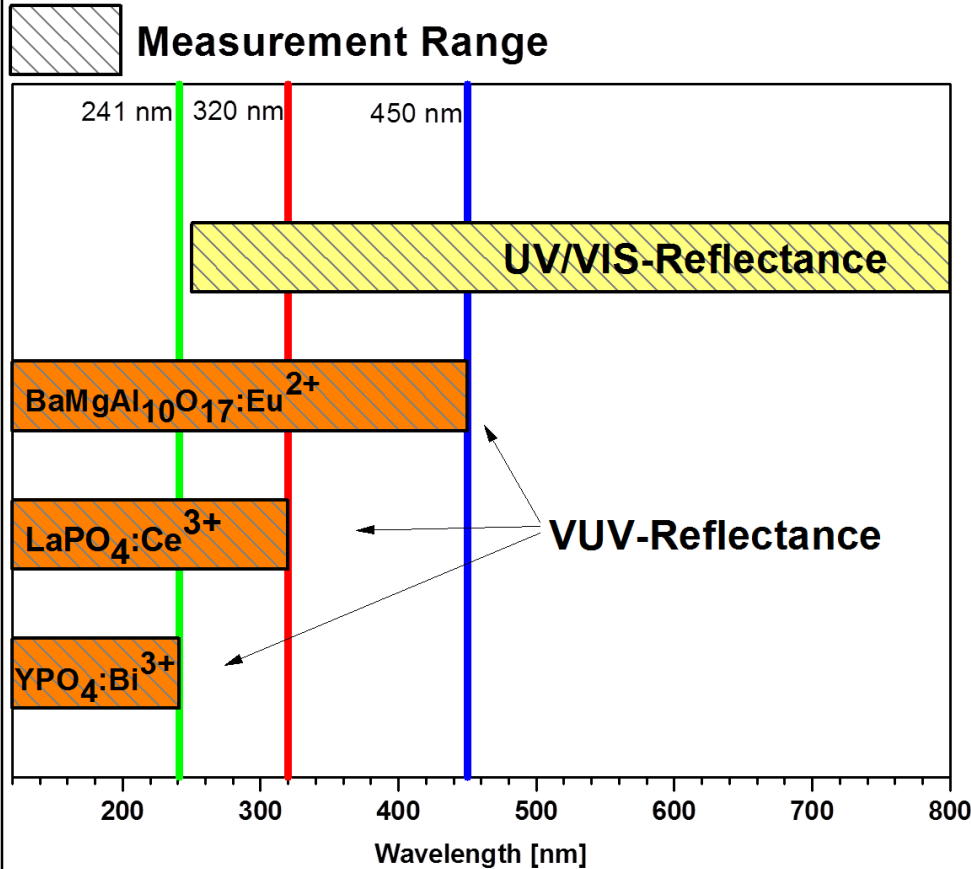
**Alternative:** Coating of the integration sphere with a phosphor which converts the VUV to visible radiation

**Drawbacks:** A phosphor coating is more prone to contamination than a teflon sphere. The converter must not emit in the same range as the sample!



# 4.3.4 VUV Reflection

## Specific Challenges in the VUV Range



$\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$  coated integration sphere under daylight or upon VUV exc.



$\text{LaPO}_4:\text{Ce}$  coated integration sphere

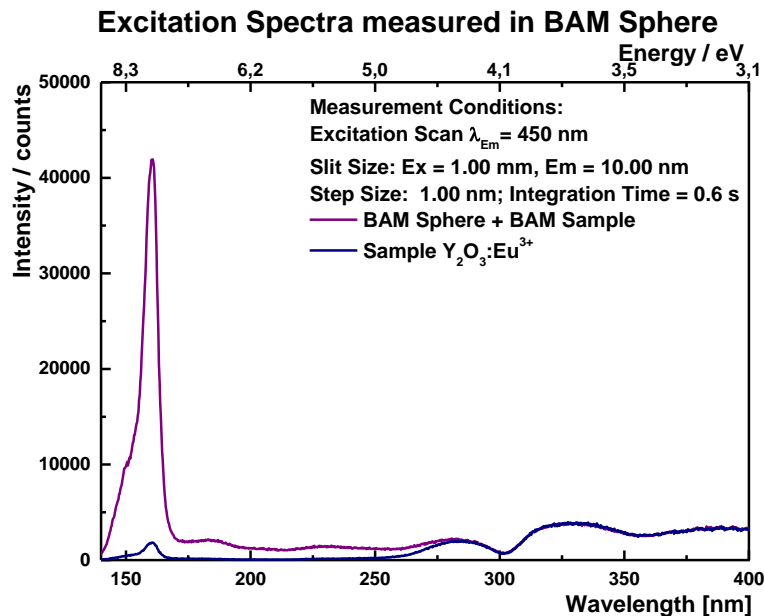
### Reference

B. Herden, A. Katelnikovas, S. Möller, H. Winkler, R. Petry, H.-J. Meyer, T. Jüstel, Powder Reflection Spectroscopy in the Vacuum UV Range, D. Ensling, J. Appl. Spectrosc. 81 (2014) 341-346

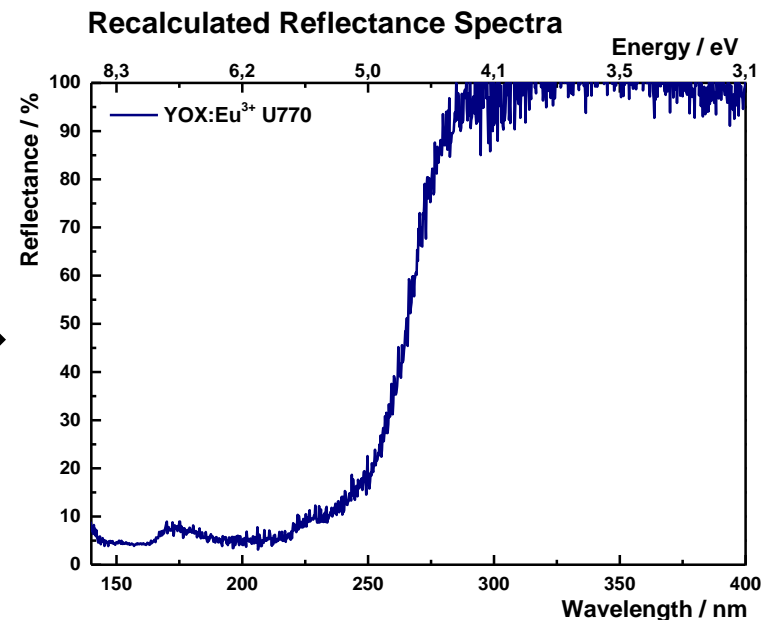
## 4.3.4 VUV Reflection

### Procedure for recording a diffuse reflection spectrum $R_{\text{diffuse}}(\lambda)$ in the VUV range

1. Irradiation of the sample by VUV photons outcoupled from the evacuated excitation monochromator into a  $N_2$  flushed  $BaMgAl_{10}O_{17}:Eu^{2+}$  (BAM:Eu) coated Ulbricht sphere
2. Conversion of reflected VUV photons into blue light by BAM:Eu coating and integration over the sphere
3. Light output is collected by a PMT via the emission monochromator
4. Determination of reflection spectrum by dividing  $I(\text{Sample})/I(\text{BAM:Eu})$



Division



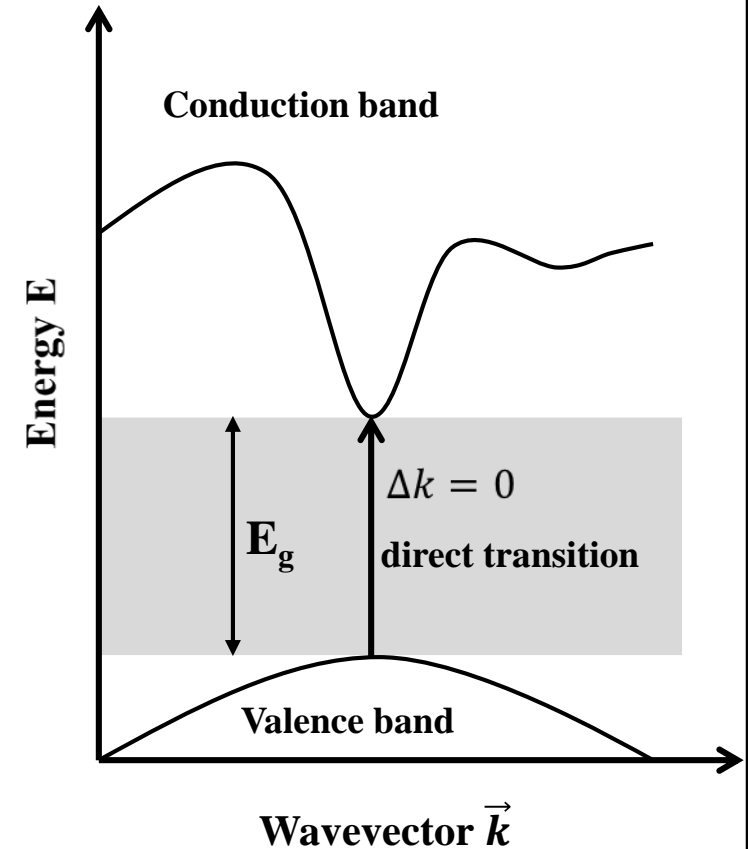
# 4.3.5 Band Gap Determination

## Motivation

- The optical band gap is of large interest to judge potential application areas of optical materials
- It indicates the difference in energy between the top of the valence band filled with electrons and the bottom of the conduction band devoid of electrons

Material class	$E_g$ [eV]
Metals	0.0
Semiconductors	0.0 - ~3.0
Insulators	> ~3.0

$$\mathbf{p} = \hbar \cdot \mathbf{k}$$

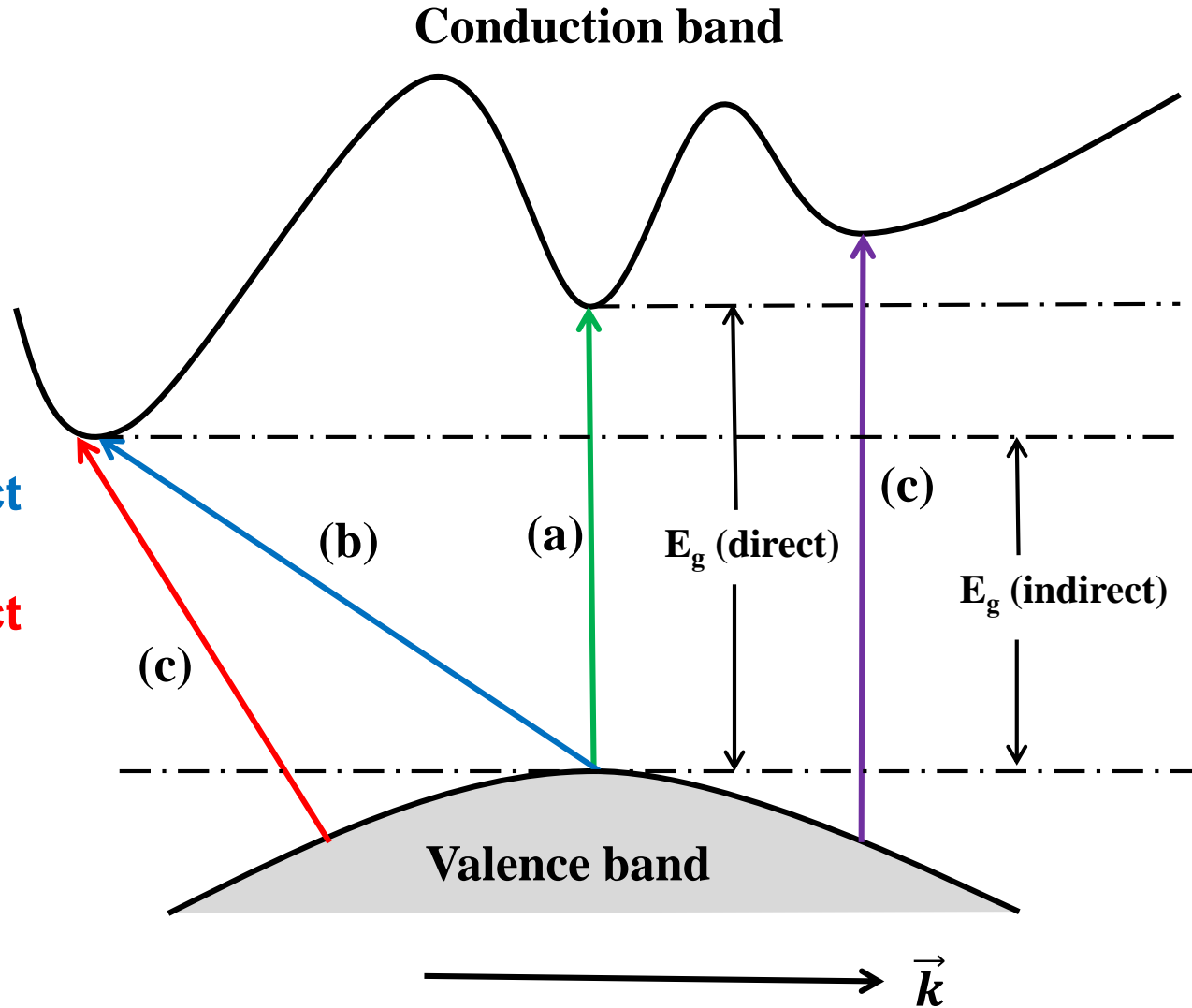


# 4.3.5 Band Gap Determination

## Motivation

### Types of transitions

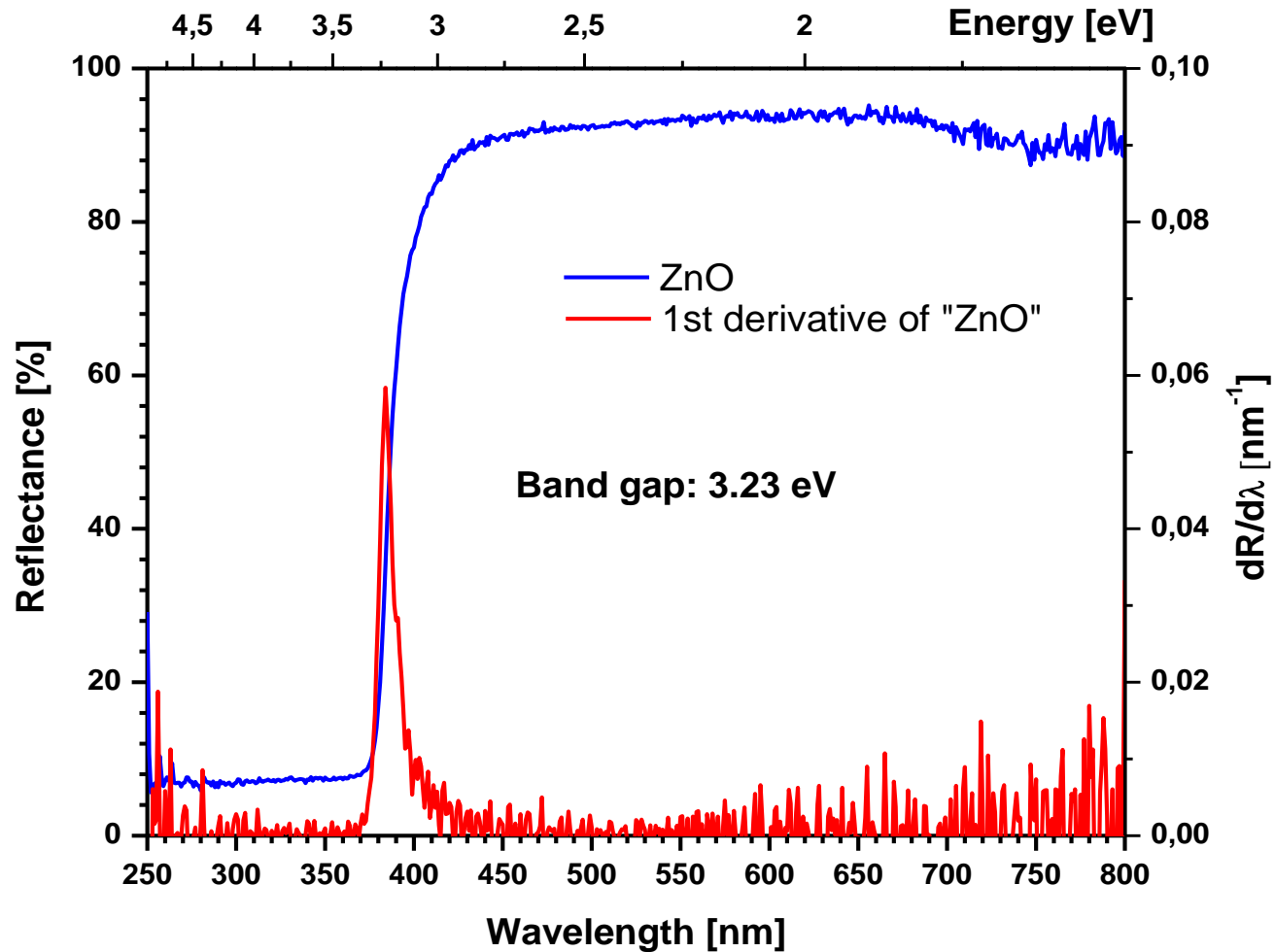
- (a) **Allowed**    **direct**
- (b) **Allowed**    **indirect**
- (c) **Forbidden**   **direct**
- (d) **Forbidden**   **indirect**





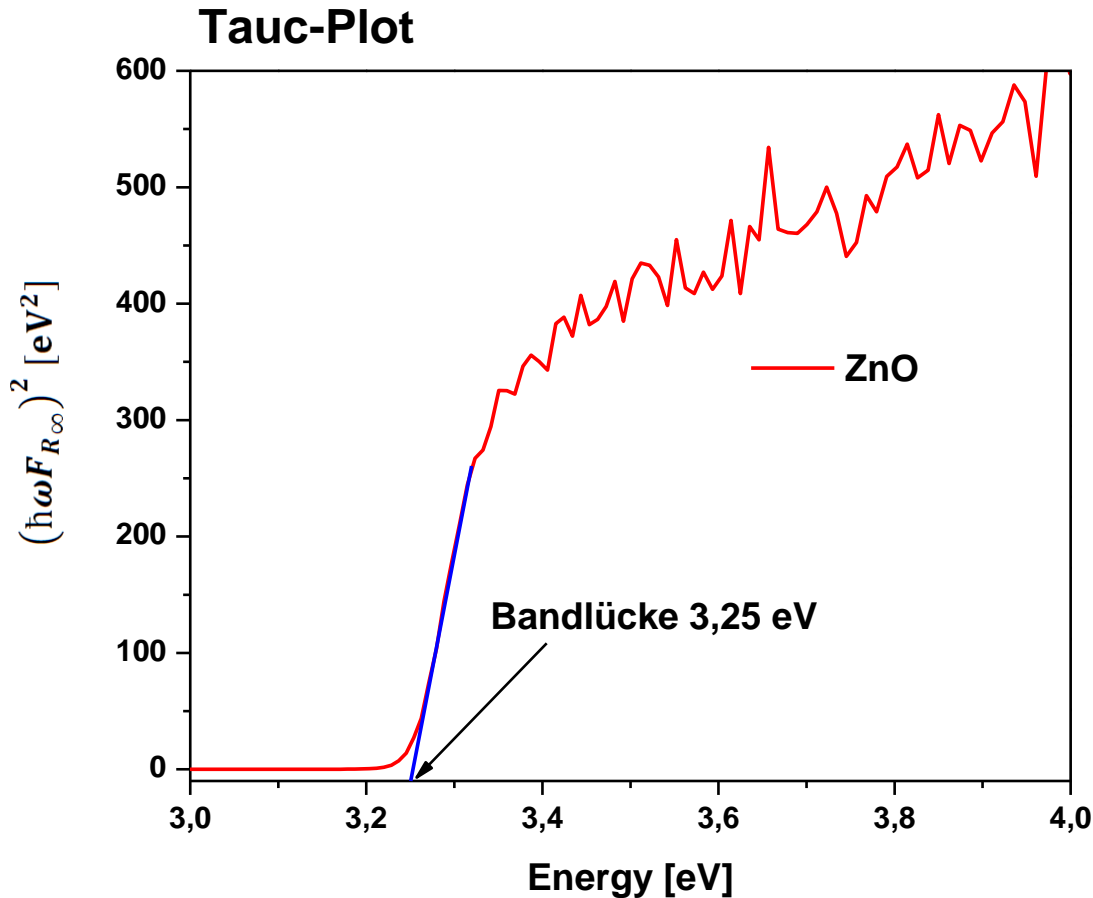
# 4.3.5 Band Gap Determination

## Method by the turning point



# 4.3.5 Band Gap Determination

## Method by the Tauc plot



### Tauc's equation

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$

For allowed direct transitions.....n = 1/2

For forbidden direct transitions.....n = 3/2

For allowed indirect transitions.....n = 2

For forbidden indirect transitions..... ..n = 3

Lit.: J. Tauc (F. Abeles ed.), Optical Properties of Solids, North-Holland (1972)

## 4.3.6 The Kubelka-Munk Function

### Diffuse Reflection of Powder Samples Depend on Ratio of Absorption to Scattering

Under certain assumptions, i.e.

- Diffuse radiation
- Suppression of the regular reflection
- Approximately spherical particles with  $d \gg$  than the wavelength of the incident light
- Weak bands in a non-absorbing matrix
- No overlapping of bands
- Infinite layer thickness

there is a mathematical relationship between absorption, scattering and reflection

⇒ The Kubelka-Munk-function:

$$F(R_\infty) = \frac{A}{S} = \frac{(1 - R_\infty)^2}{2 \cdot R_\infty}$$

**S** = Scattering coefficient

**R<sub>∞</sub>** = Diffuse scattering

**A** = Absorption =  $\epsilon \cdot c$

An ideally black surface  $R_\infty = 0$  is therefore difficult to realize, because for  $R_\infty = 0$  applies  $A/S = \infty$ , i.e. extremely high absorption or virtually no scattering

The scattering coefficient **S** can be estimated from the particle size of the powder:

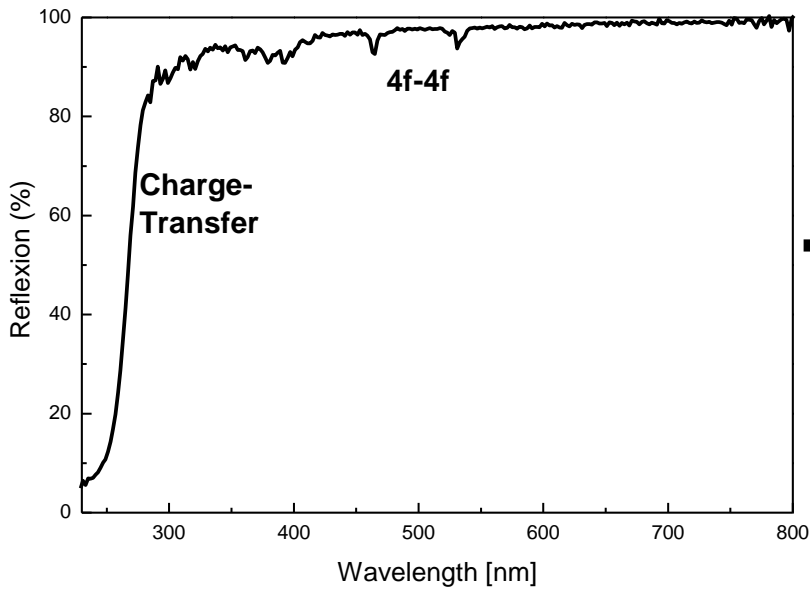
$$S \sim 1/\text{grain size} \sim 1/d_{50} [\text{cm}^{-1}]$$

# 4.3.6 The Kubelka-Munk Function

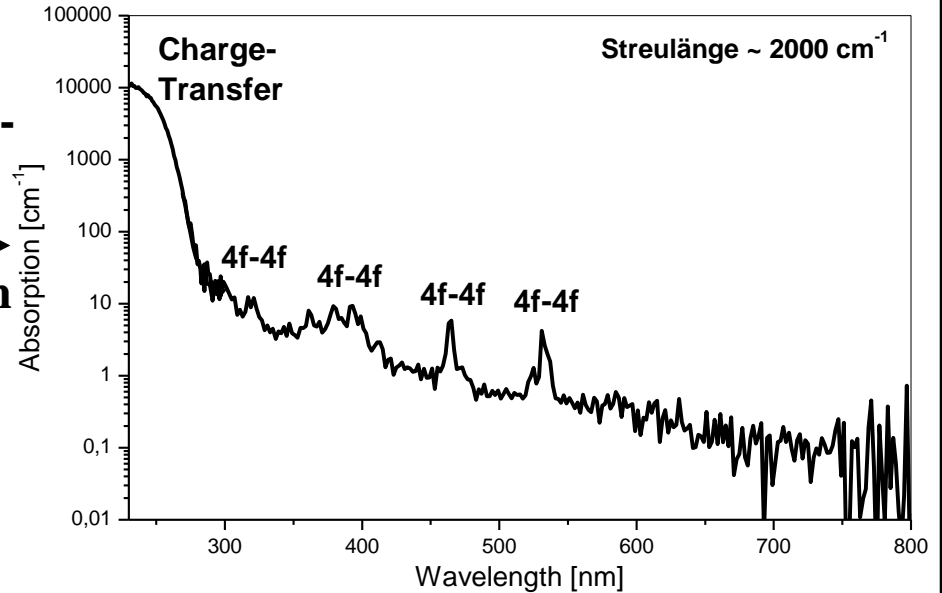
## Determination of Qualitative Absorption Spectra of Powder Samples

Boundary condition:  $T = 0$  „ semi-infinitely thick layer“  $\Rightarrow R + A = 1$

Example: Phosphor  $Y_2O_3:Eu^{3+}(5\%)$  with  $d_{50} = 5 \mu m \Rightarrow S \sim 0.2 \mu m^{-1} = 2000 cm^{-1}$



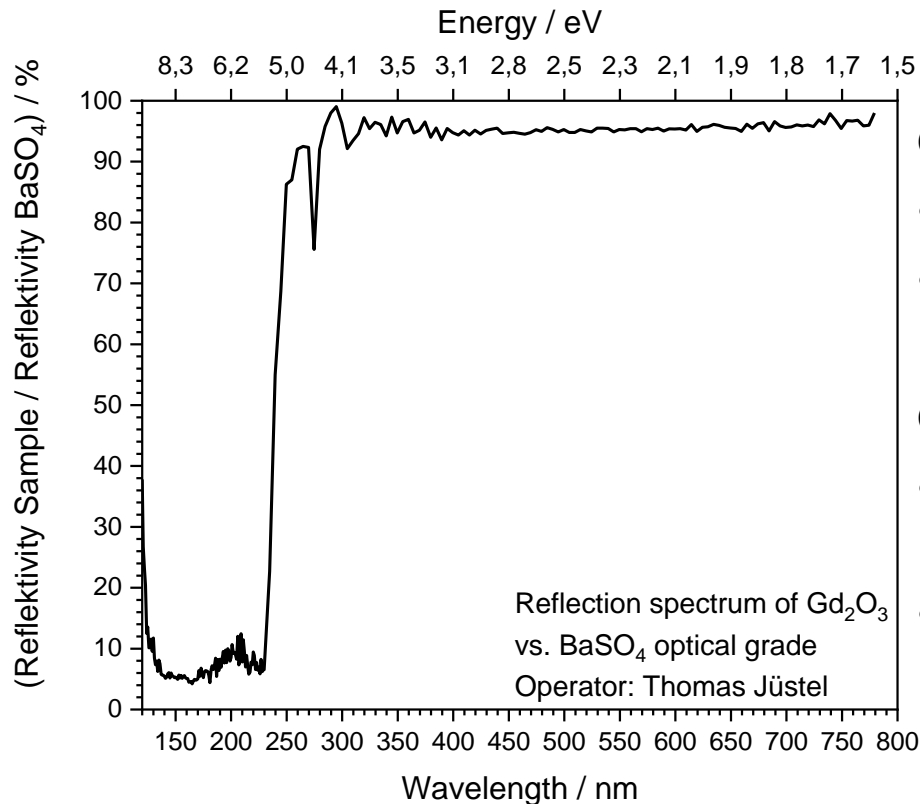
Kubelka-  
Munk  
Function



# 4.3.7 Application of Reflection Spectroscopy

## Determination of Optical Transitions of Powder Samples

Example:  $\text{Gd}_2\text{O}_3$



### Optical transitions

- Band-to-band transition  $\sim 225 \text{ nm}$  (5.5 eV)
- $[\text{Xe}]4f^7 (^8\text{S}_{7/2}) - [\text{Xe}]4f^7 (^6\text{P}_{5/2}) \sim 275 \text{ nm}$

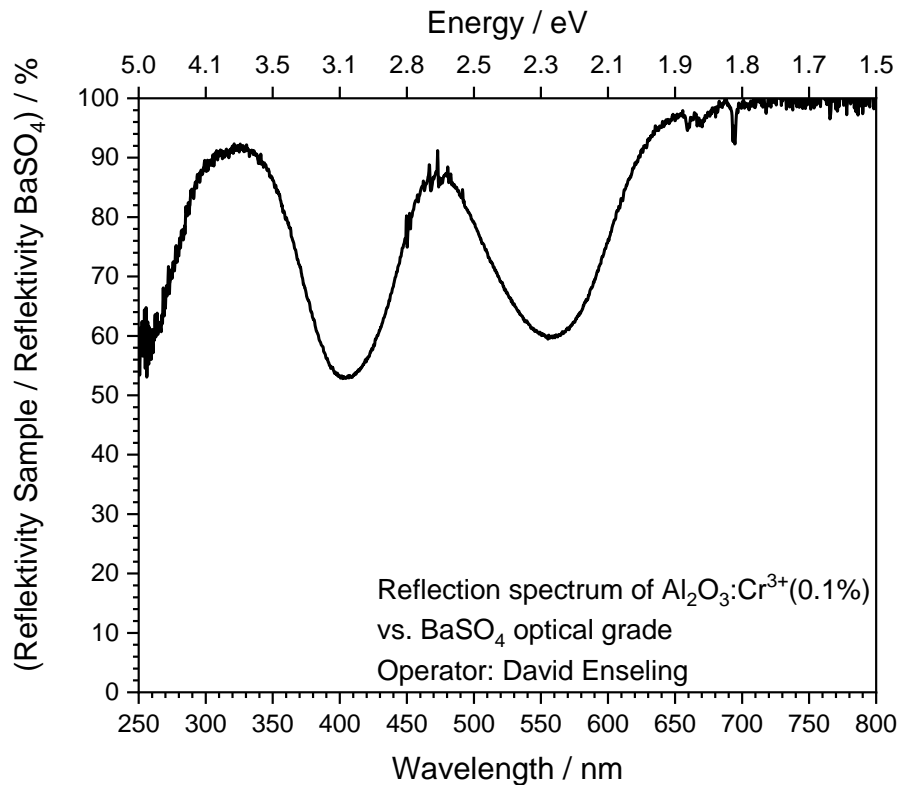
### Optical band gap according to literature

- 5.5 eV (IOP Conf. Series: Journal of Physics: Conf. Series 917 (2017) 062001)
- 5.4 eV (J. All. Comp. 242 (1996) 41)

# 4.3.7 Application of Reflection Spectroscopy

## Determination of Optical Transitions of Powder Samples

Example:  $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$



### Optical transitions

- Band-to-band transition  $< 200$  nm
- $\text{Cr}^{3+}$ :  $[\text{Ar}]3d^3$  ( $^4\text{F}$ ) to  $[\text{Ar}]3d^3$  ( $^4\text{F}$ ,  $^4\text{P}$ )
  - $^4\text{A}_2 - ^4\text{T}_2$       405 nm band
  - $^4\text{A}_2 - ^4\text{T}_1$       560 nm band
  - $^4\text{A}_2 - ^2\text{E}$       694 nm lines

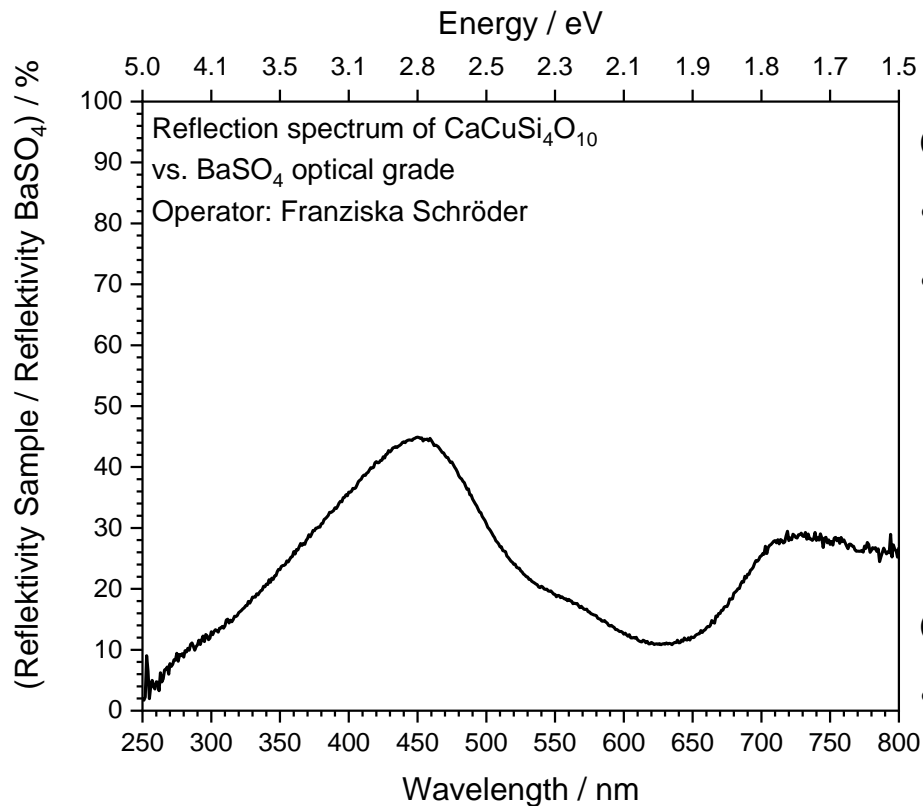
### Optical band gap

- 8.7 eV (Appl. Phys. Lett. 55 (1989) 1955)
- 8.8 eV (Chem. Phys. Lett. 637 (2015) 172)
- 8.9 eV (JETP Letters 85 (2007) 165)

# 4.3.7 Application of Reflection Spectroscopy

## Determination of Optical Transitions of Inorganic Pigments

Example:  $\text{CaCuSi}_4\text{O}_{10}$



### Optical transitions

- Band-to-band transition  $\sim 340$  nm (3.6 eV)
- $\text{Cu}^{2+}$ :  $[\text{Ar}]3d^9 \rightarrow [\text{Ar}]3d^9$  transitions
  - ${}^2E_g \rightarrow {}^2B_{1g}$  500 nm
  - ${}^2A_{1g} \rightarrow {}^2B_{1g}$  625 nm
  - ${}^4A_{2g} \rightarrow {}^2T_{1g}$  750 nm

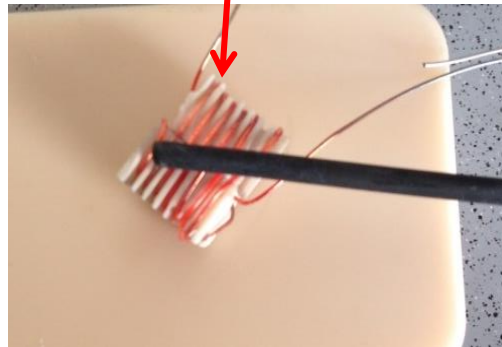
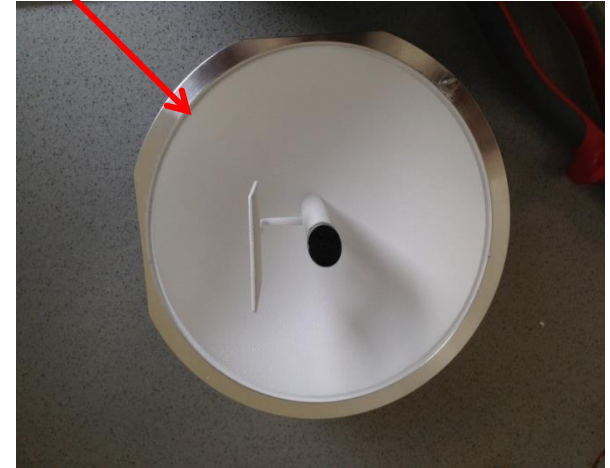
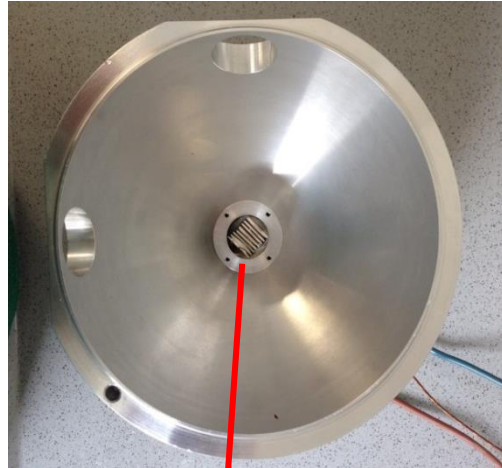
### Optical band gap according to literature

- 3.6 eV (J. Phys. Chem. Lett. 7 (2016) 399)

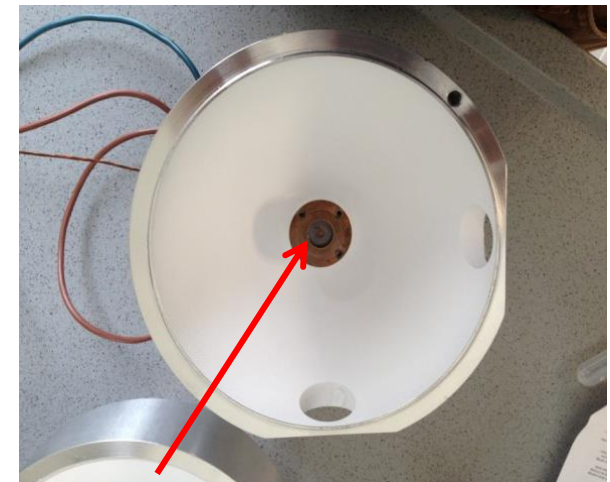
# 4.3.7 Application of Reflection Spectroscopy

## Thermochromic Properties of Inorganic Pigments

BaSO<sub>4</sub> coated Ulbricht sphere



Heating element  
up to 300 °C



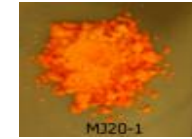
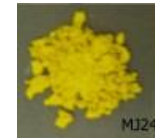
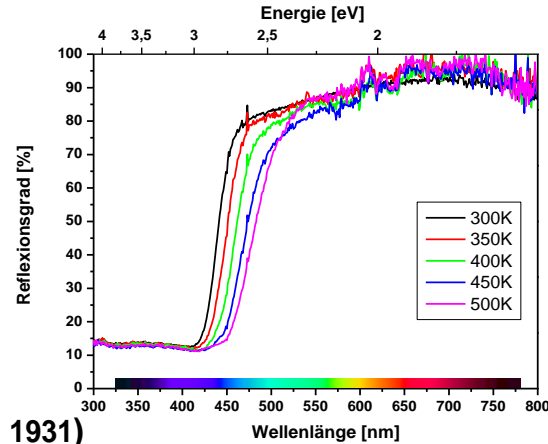
Cu sample holder



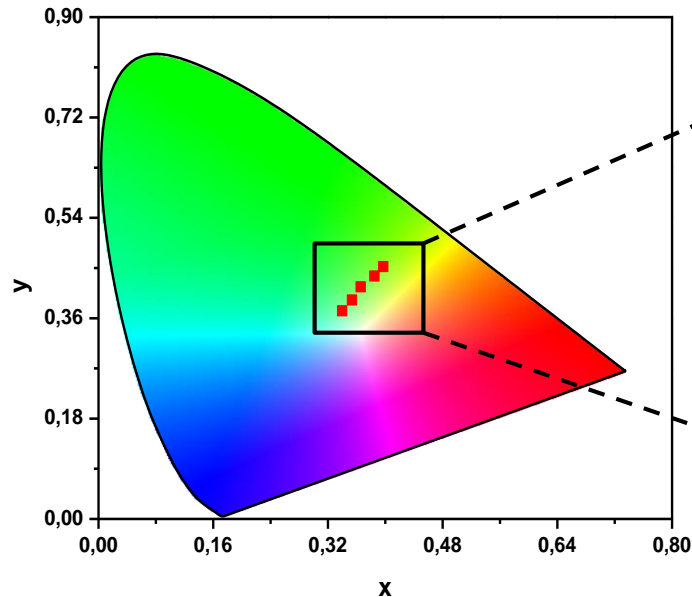
# 4.3.7 Application of Reflection Spectroscopy

## Thermochromic Properties of Inorganic Pigments

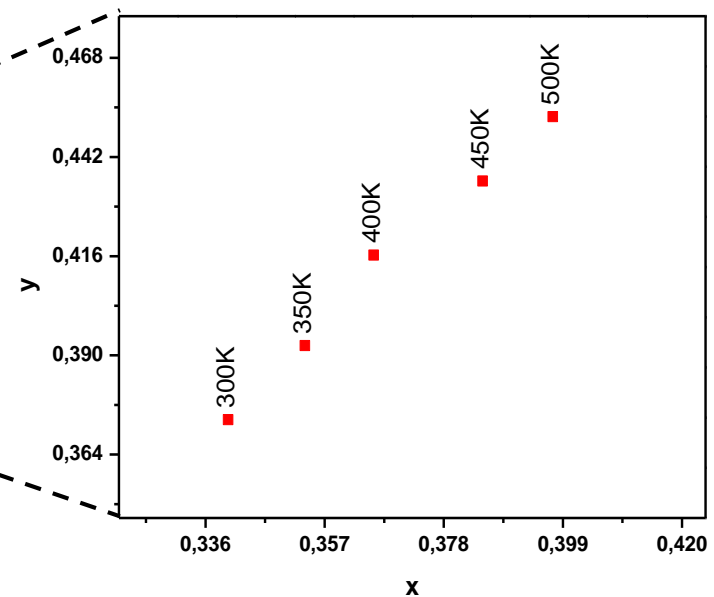
Example:  
Yellow pigment  $\text{BiVO}_4$



Colour Points (C.I.E. 1931)



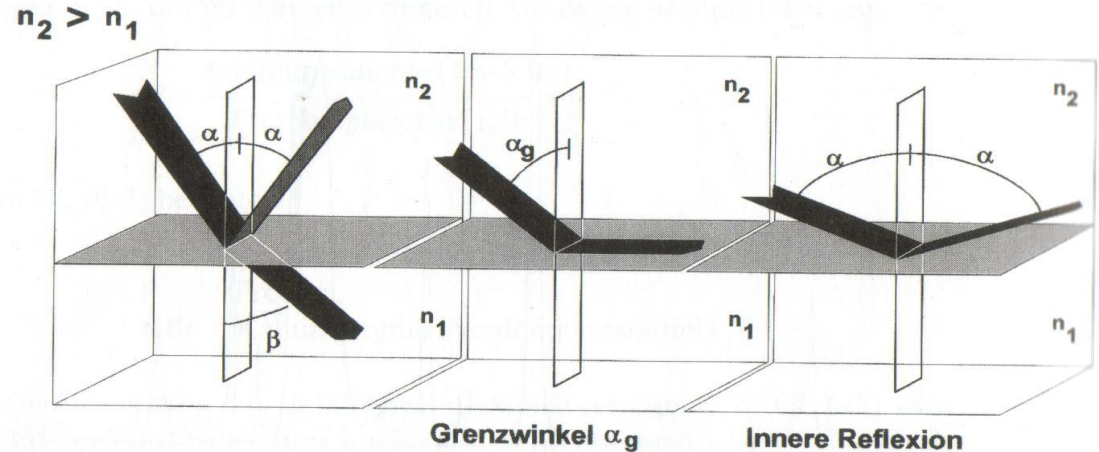
Colour Points (C.I.E. 1931)



# 4.3.7 Application of Reflection Spectroscopy

## Attenuated Total Reflection (ATR)

### Phenomenon of total reflection



**But:** The total reflected radiation also penetrates into the optically less dense medium (Goos, Hänchen 1947) and can be weakened by absorption  
→ ATR-spectroscopy

**Note:** The penetration depth of radiation is wavelength dependent:  
The larger the wavelength, the more intensive bands appear, furthermore their positions are changed.  
→ ATR correction is required (e.g. OPUS software from Bruker)

$$d_p = \frac{\lambda}{2\pi \sqrt{(n_K^2 \sin^2 \Theta - n_P^2)}}$$

# 4.3.7 Application of Reflection Spectroscopy

## Attenuated Total Reflection (ATR)



ATR Unit for FT-IR Spectroscopy

### Advantages

- No sample preparation is necessary for powders or thin crystals and liquids

### Disadvantages

- Intimate contact between the material and crystal is necessary
- Crystal may be neither chemically or mechanically damaged
- Only room temperature
- Range of application is limited by the crystal material, e.g.  $17000 - 650 \text{ cm}^{-1}$  for ZnSe

