Optical Characterisation of Materials

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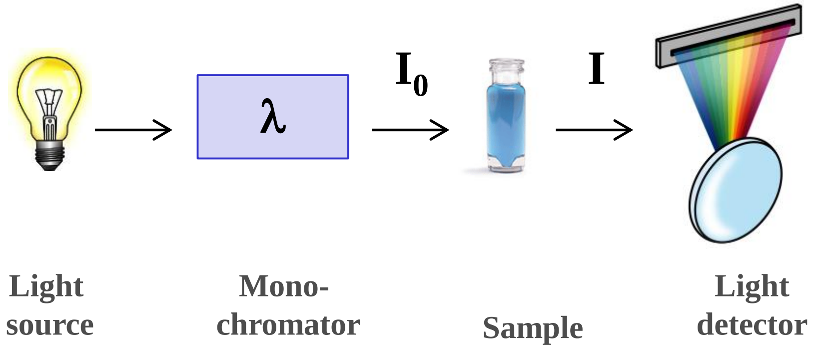

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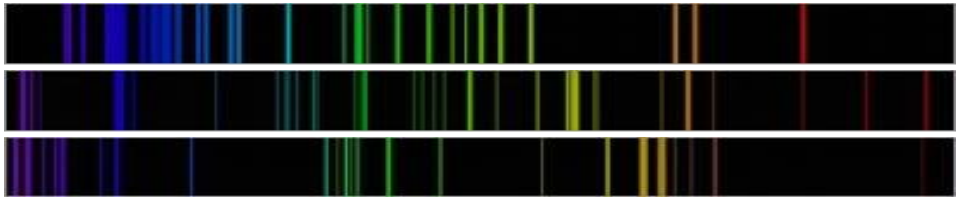
Relevance of Optical Spectroscopy

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

- **Fingerprint of the elements** — **(Astro)physics, analytical chemistry (OES)**



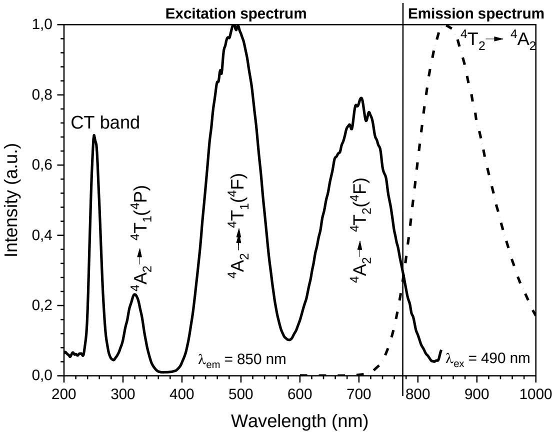
- **Determination of elements or molecules** — **Analytical chemistry: Photometry, AAS, OES**

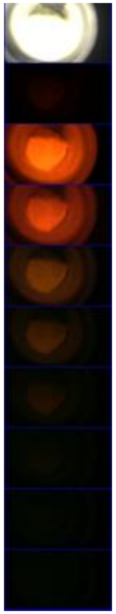
- **Characterisation of molecules** — **Physics, chemistry, biochemistry**

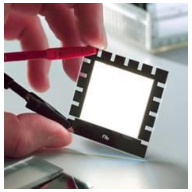
- **Characterisation of materials**
  - **Pigments**
  - **Luminescent materials**
  - **Scintillators**

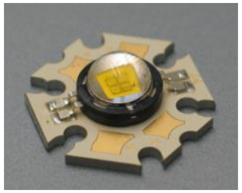
- **Characterisation of devices**
  - **Light sources**
  - **IR and UV sources**
  - **Displays**

$Sr_8MgLa(PO_4)_7:Cr^{3+}$









1. Methods of Material Characterization

1. Chemical composition

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

2. Morphological characterization (micro and nanostructure)

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

1. Methods of Material Characterization

3. Structural characterization

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

4. Surface characterization

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

1. Methods of Material Characterization

5. Determination of physical properties

Electronic properties

Absorption spectroscopy	Electronic ground state
EPR spectroscopy	Oxidation states, electronic ground state
Mössbauer spectroscopy	Oxidation states, coordination geometry
Ultraviolet photoelectron spectroscopy (UPS)	Band structure

Optical properties

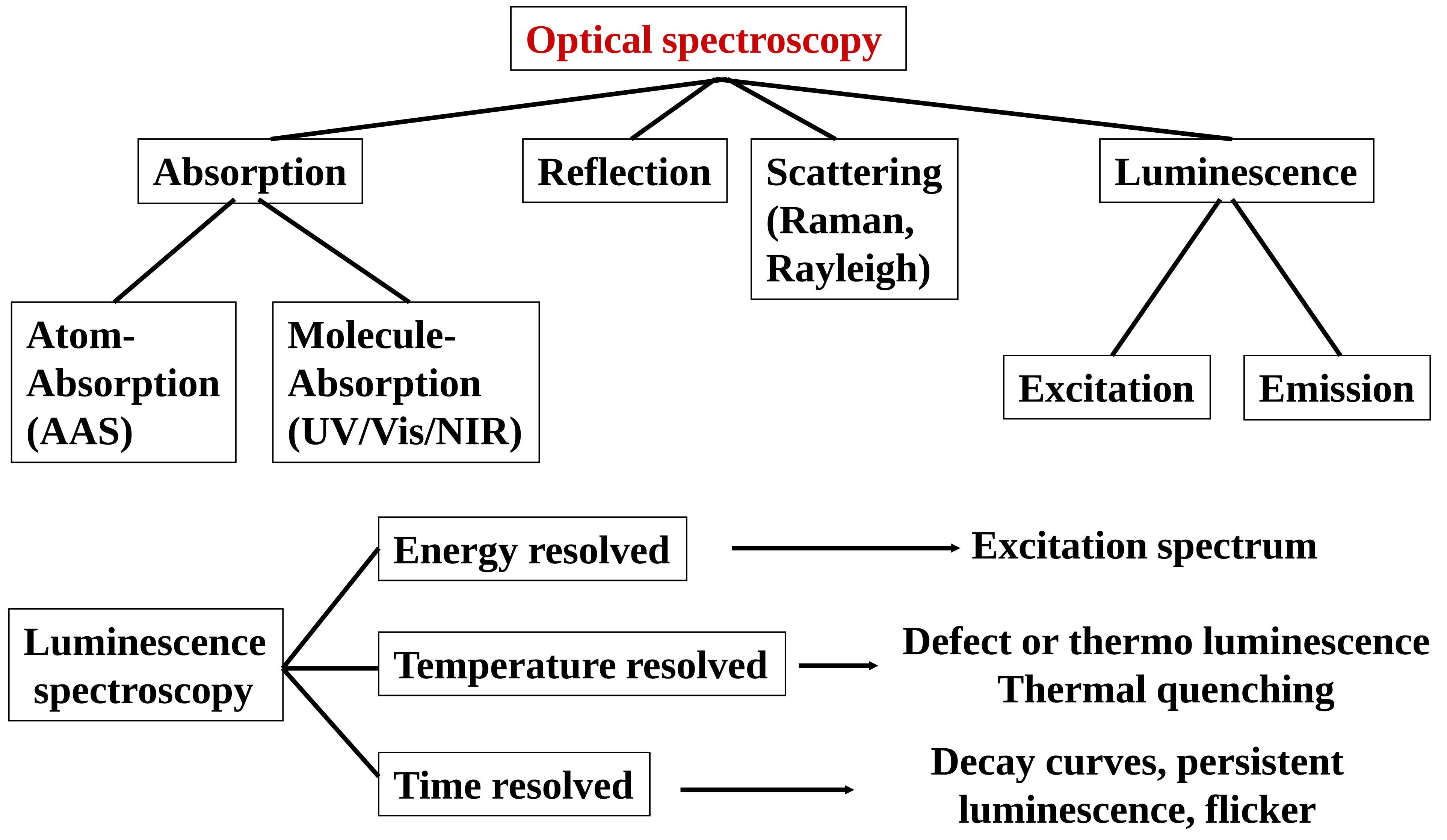
Absorption spectroscopy	Absorption coefficient, electronic ground state
Reflectance spectroscopy	Band gap, color point
Luminescence spectroscopy	Excitation and emission spectrum
	Color point
	Quantum efficiency
	Luminous efficacy
	Thermal quenching

Magnetic properties

Susceptibility measurement	Dia-, para-, ferro-, ferri-, antiferromagnetism
NMR spectroscopy	Ground state

2. Physical Basis

2.1 Classification of Optical Spectroscopy



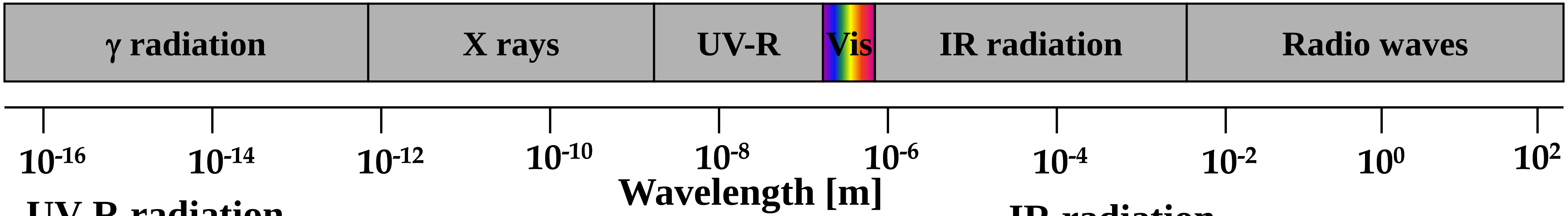
Optical spectroscopy

- 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



UV-R radiation	
EUV	1 - 100 nm
VUV	100 - 200 nm
UV-C	200 - 280 nm
UV-B	280 – 315/320 nm
UV-A	315/320 - 400 nm

IR radiation	
IR-A	780 - 1400 nm
IR-B	1.4 - 3 µm
IR-C	3 - 1000 µm

Radio waves	
Microwaves	1 - 1000 mm
HF-range	1 m - 10 km
NF-range	> 10 km

Visible light		**complementary to**
Violet	380 - 430 nm	Yellow-green
Blue	430 - 480 nm	Yellow
Cyan	480 - 490 nm	Orange
Cyan-green	490 - 500 nm	Red
Green	500 - 560 nm	Purple
Yellow-green	550 - 570 nm	Violet
Yellow	570 - 590 nm	Blue
Orange	590 - 610 nm	Cyan
Red	610 - 780 nm	Cyan-green

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

2.2 The Electromagnetic Spectrum

Energy of photons

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

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

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

The energy is thus proportional to the reciprocal length, to so-called wavenumber $\tilde{\nu}$
with $\tilde{\nu} = 1/\lambda$
$E = h \cdot c \cdot \tilde{\nu}$
$\quad = 1.240 \cdot 10^{-4} \cdot \tilde{\nu}$ [eV]
$\quad = 1240/\lambda$ [eV]
or 1 eV ~ 8065 cm^{-1}

Parameters proportional to energy

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

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

2.3 Time Scale of Physical Processes

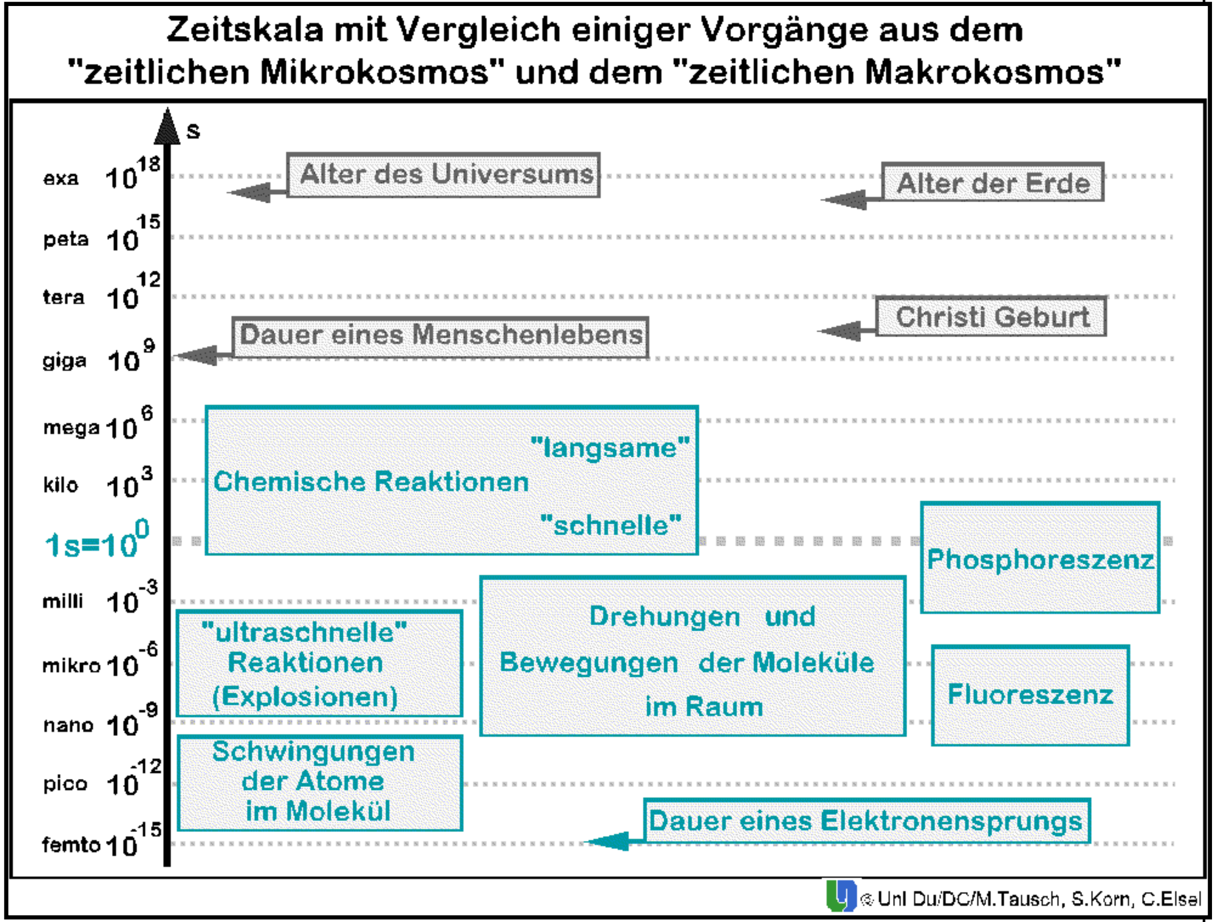
Chemical reactions < molecular rotation < molecular vibration < electron motion

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

The electron continually transitions from one stationary state to the other.



Zeitskala mit Vergleich einiger Vorgänge aus dem "zeitlichen Mikrokosmos" und dem "zeitlichen Makrokosmos"

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2.4 Interaction of Light and Matter

Types of electromagnetic interaction

Radiation type	Interaction with	Physical process
γ-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: $A(\lambda) = E(\lambda)$ (Kirchhoff 1859)

2.4 Interaction of Light and Matter

Electronic states in multi electron atoms

Atom	Electron configuration	Ground state	First excited state
Na^0	$1s^2\ 2s^2\ 2p^6\ 3s^1$	$^2S_{1/2}$	$^2P_{3/2}$, $^2P_{1/2}$

(yellow Na-double line at 589.0 and 589.6 nm ⇒ Spectrometer resolution test)

Cr^{3+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$	^4F	^4P
Ce^{3+}	$[Xe]4f^1$	$^2F_{5/2}$, $^2F_{7/2}$	^2D
Eu^{3+}	$[Xe]4f^6$	$^7F_0$	$^5D_0$
Gd^{3+}	$[Xe]4f^7$	$^8S_{7/2}$	^6P_J

$S = \Sigma s$

$L = |\Sigma l|$

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

Russell-Saunders-Terms (energy levels)

$^{2S+1}L_J$

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 → u, u → g, but not g → g, u → u

With Russell-Saunders (LS) coupling: ΔL, $\Delta J = 0, +/-1$, but not $J = 0 \rightarrow J = 0$

2.4 Interaction of Light and Matter

Electronic transitions in multi electron atoms

Typ		ε [$lmol^{-1}cm^{-1}$]	Example	Electron from	to
s-p transitions	$\Delta l = 1$	10^3-10^4	Na^0	3s	→ 3p
d-d transitions	$\Delta l = 0$	$< 10^2$	Cr^{3+}	3d (t_2)	→ 3d (e)
f-d transitions	$\Delta l = 1$	$10^4 – 10^5$	Ce^{3+}	4f	→ 5d
f-f transitions	$\Delta l = 0$	$< 10^2$	Eu^{3+}	4f	→ 4f
			Gd^{3+}	4f	→ 4f
			Tb^{3+}	4f	→ 4f

Forbidden due to large change in orbital angular momentum:

s-d $\Delta l = 2$

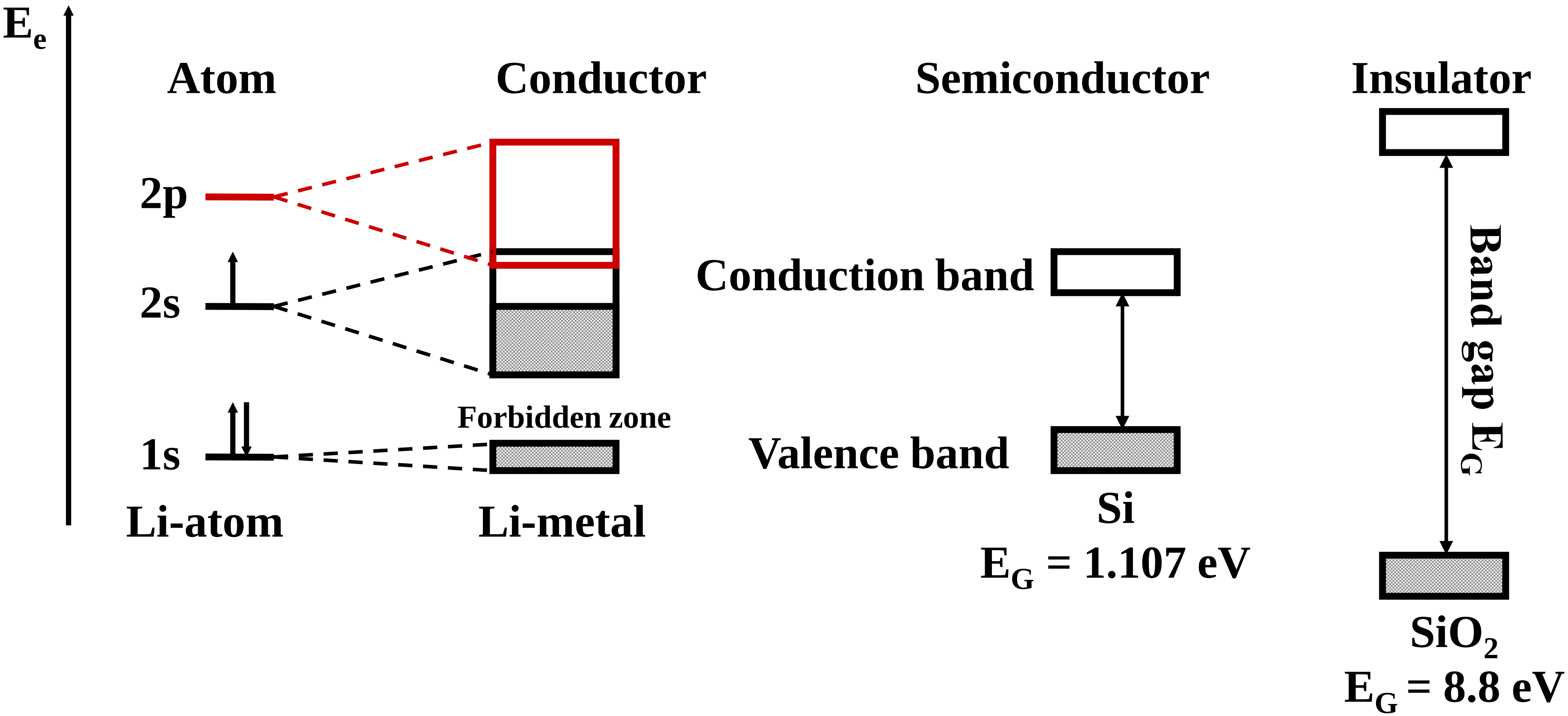
p-f $\Delta l = 2$

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

- these transitions are strongly forbidden!

2.4 Interaction of Light and Matter

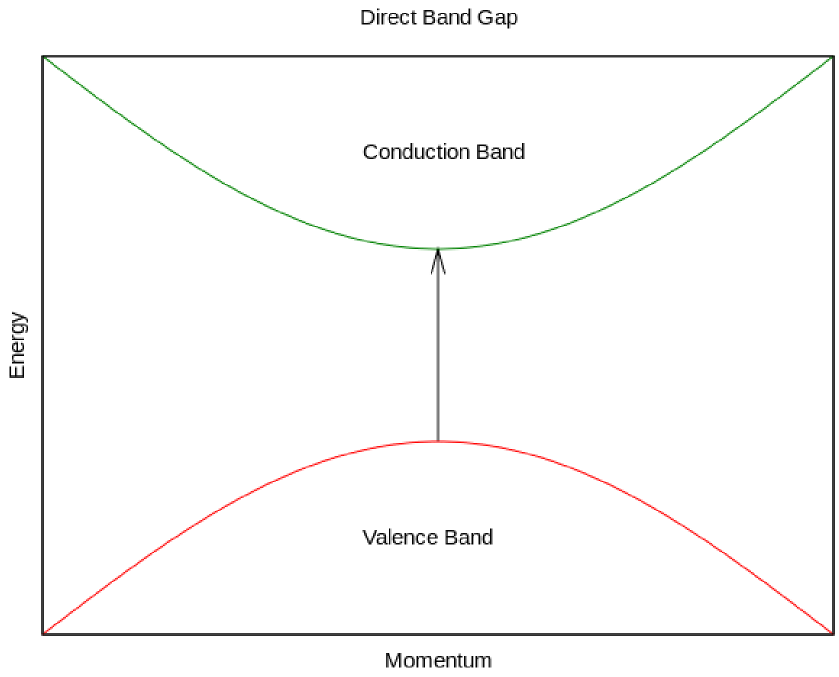
Electronic states in solids (metals, semiconductors, ceramics)

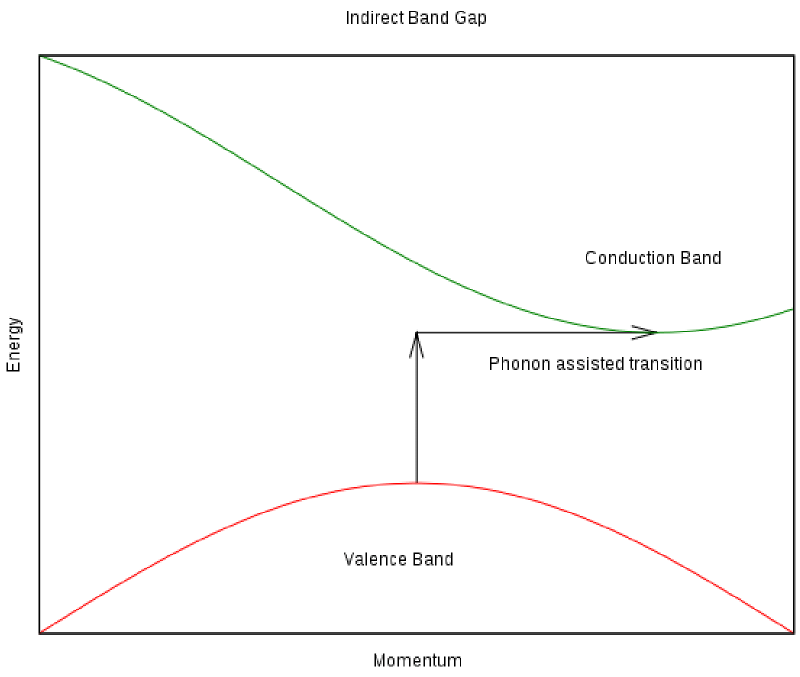


Semiconductors are materials with a small band gap (< 3.0 eV) whose conductivity are increased by structural defects, heating, or by irradiation

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

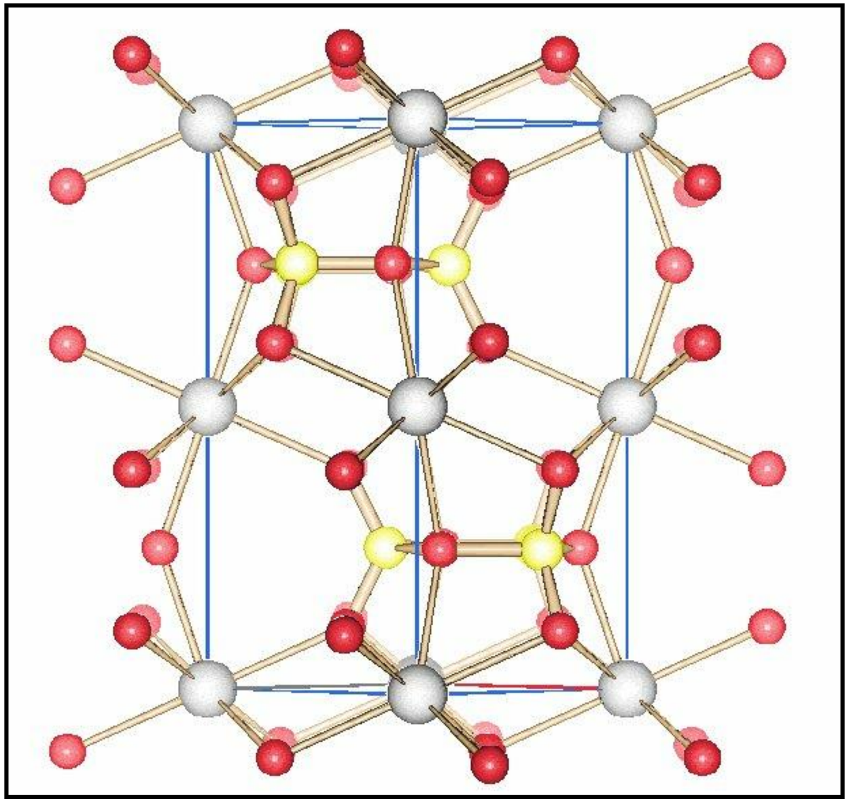
Indirect semiconductors:

Phonon assisted absorption or emission of a photon

→ weak: Si, Ge

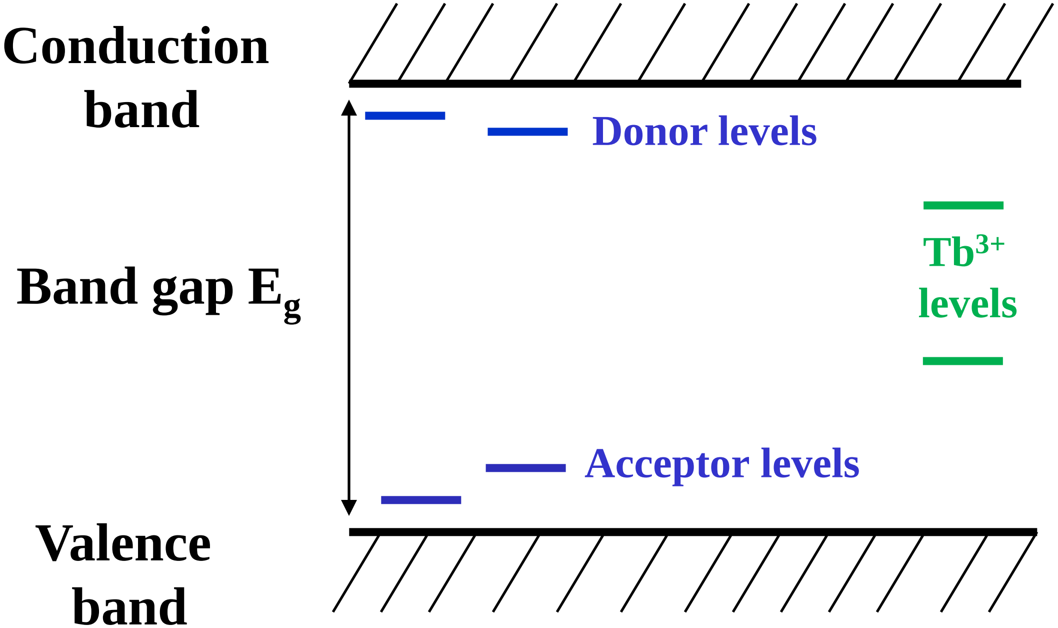
2.4 Interaction of Light and Matter

Electronic states in solids



YBO$_3$ Vaterit

Band gap E_g = 6.5 eV



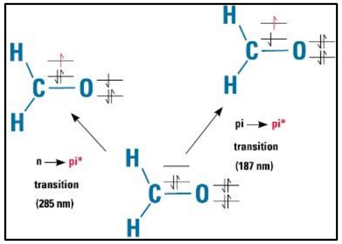
Absorption by

- Excitation band: valence band-conduction band
- Defects (color centers) “blue ice”
- Transitions between energy levels of dopants (Tb^{3+}) or undesired impurities

2.4 Interaction of Light and Matter

Electronic transitions in solids and molecules

Type	ε [$lmol^{-1}cm^{-1}$]	Example	Transition type
Band gap transitions	$10^5 – 10^6$	TiO_2	$O^{2-} \rightarrow Ti^{4+}$ (VB → CB)
CT transitions	$10^4 - 10^6$	WO_4^{2-}	$O^{2-} \rightarrow W^{6+}$ „LMCT“
		$Fe(CO)_5$	$Fe^0 \rightarrow$ CO „MLCT“
		$KFe[Fe(CN)_6]$	$Fe^{2+} \rightarrow Fe^{3+}$ „MMCT“
		$[(cp)_2Zr(biq)]^{2+}$	$cp^- \rightarrow$ biq “LLCT”
$\sigma \rightarrow \sigma^*$	$> 10^3$	CH_4	HOMO → LUMO
$\pi \rightarrow \pi^*$	$10^4 – 10^6$	Butadiene	HOMO → LUMO
$n \rightarrow \pi^*$	$10^1 – 10^2$	$(CH_3)_2C=O$	HOMO → LUMO



In addition

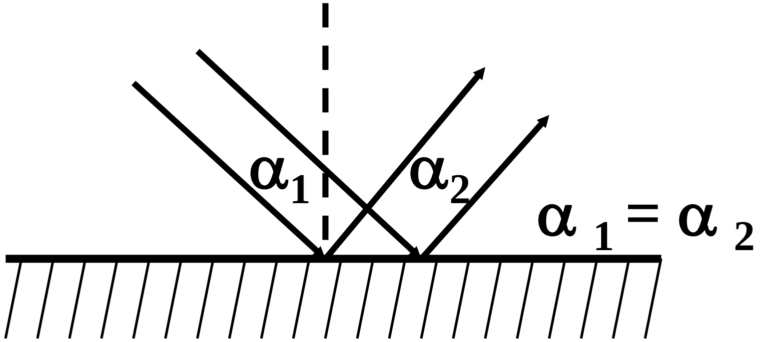
- Excitation of vibrational states, i.e. phonons in the solid state or valence and deformation vibrations in molecules
- Excitation of rotational states (only molecules)

2.4 Interaction of Light and Matter

Reflection

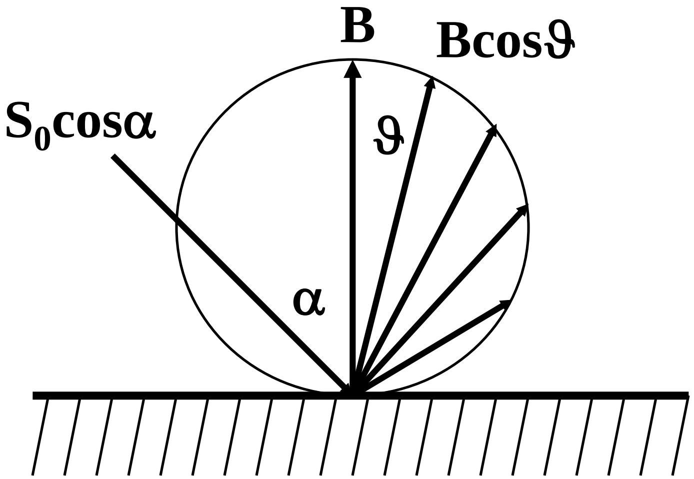
1. Specular reflection (regular)

Reflection from a polished (smooth) surface
in one direction (reflecting surface)
Example: metal, mirror, calm water surface



2. Diffuse reflection (irregular)

Reflection from a non-polished surface
in all directions of the half-space
(matte surface)
Example: paper, powder, white wall

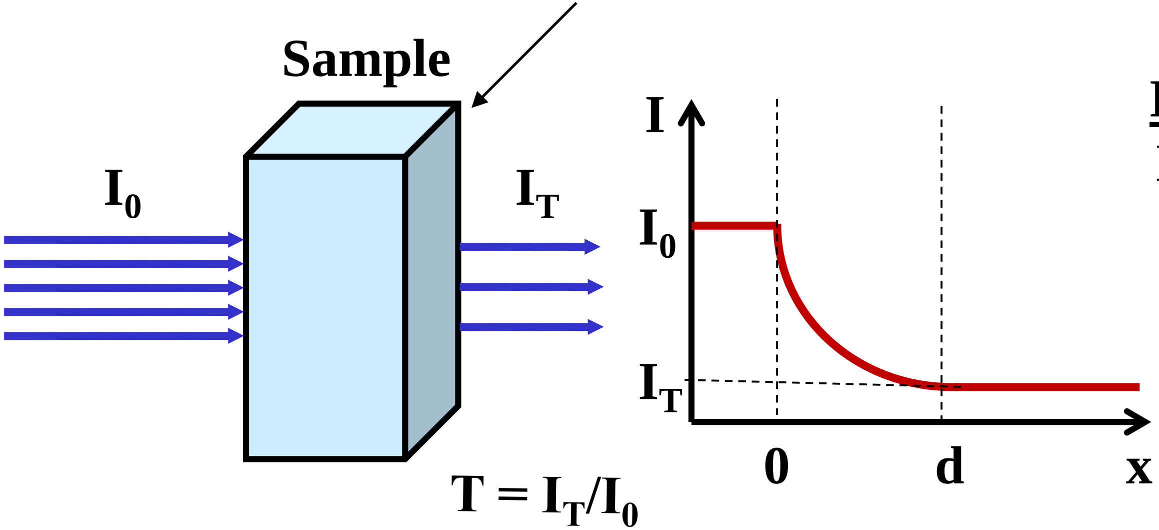


Angular distribution of a
Lambert radiator's

2.4 Interaction of Light and Matter

Absorption

Medium = gas, solution, crystal, transparent ceramics



Lambert-Beer-Bouguer-law

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

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

Absorption: $A = \alpha * c * d$

α = Absorption constant [cm^{-1}]

Fate of the absorbed energy	Physical effect	Application areas
• Vibrations (phonons)	Heat	bolometer
• Charge storage	Color centers	detectors, imaging plate
• Luminescence	Light emission	phosphors, laser gain media
• Charge separation	Current	solar cells

2.4 Interaction of Light and Matter

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

Quantitative description of absorption

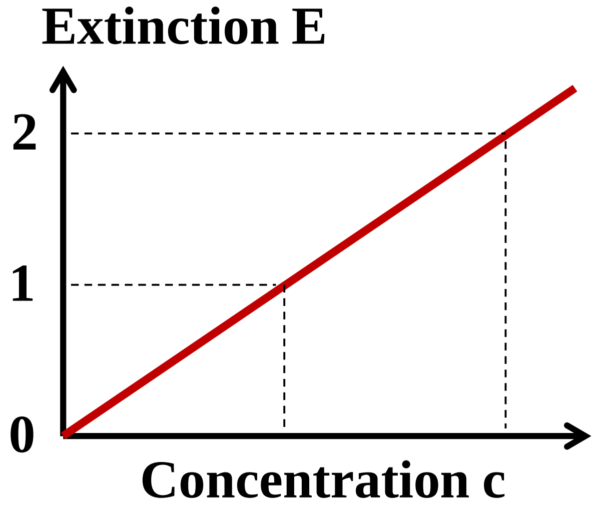
Energy conservation $A + R + T = 1\ (100\%)$

Transmission $T = I_T/I_0 \leq 1\ (100\%)$

Absorption $A = 1 - T = 1 - I_T/I_0 \leq 1\ (100\%)$
(if $R = 0$)

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

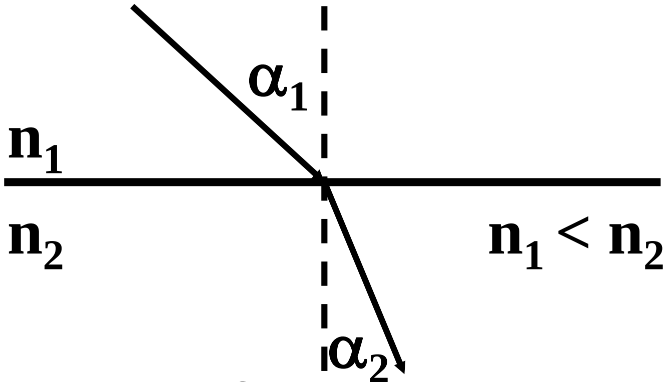
ε = molar extinction coeffizient (material constant, dependent on λ)



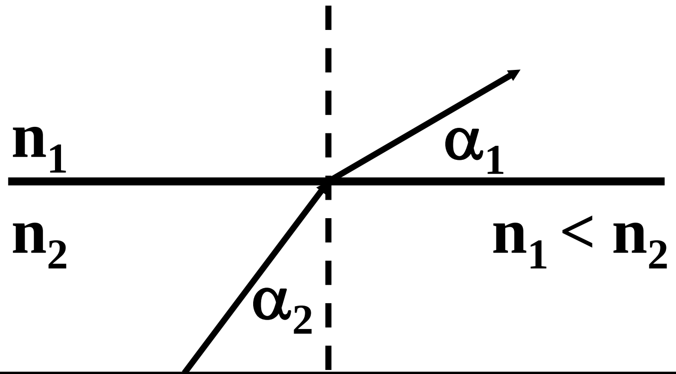
2.4 Interaction of Light and Matter

Refraction

Transition from an optically thin into an optically denser medium



Transition from an optically dense into an optically thinner medium



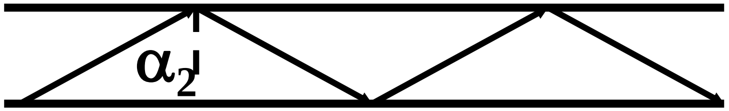
$n_1 \cdot \sin\alpha_1 = n_2 \cdot \sin\alpha_2$ (Snellius equation)

Total reflection occurs at the transition from an optically dense to an optically thinner medium, if the critical angle α_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

Substance	Refractive index n
Vacuum	1.000
Air	1.0003
Water	1.333
Ethanol	1.360
CCl_4	1.460
Benzene	1.501
CS_2	1.628
Ice	1.309
CaF_2	1.434
Quartz glass	1.459
NaCl, α-quartz	1.54
$ZrSiO_4$ (Zircon)	1.923
Diamond	2.417

Critical angle for total reflection

Vacuum/air

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

$= 88.6°$

(air glimmering)

Quartz glass/air

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

$= 43.3°$

(silica fibre)

Diamond/air

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

$= 24.5°$

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

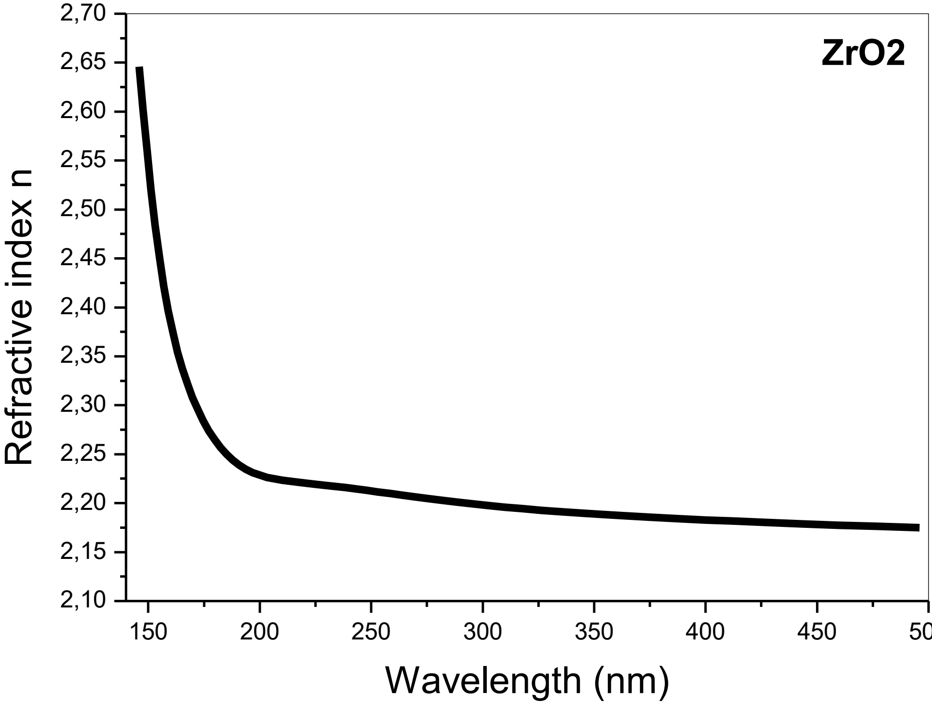
2.4 Interaction of Light and Matter

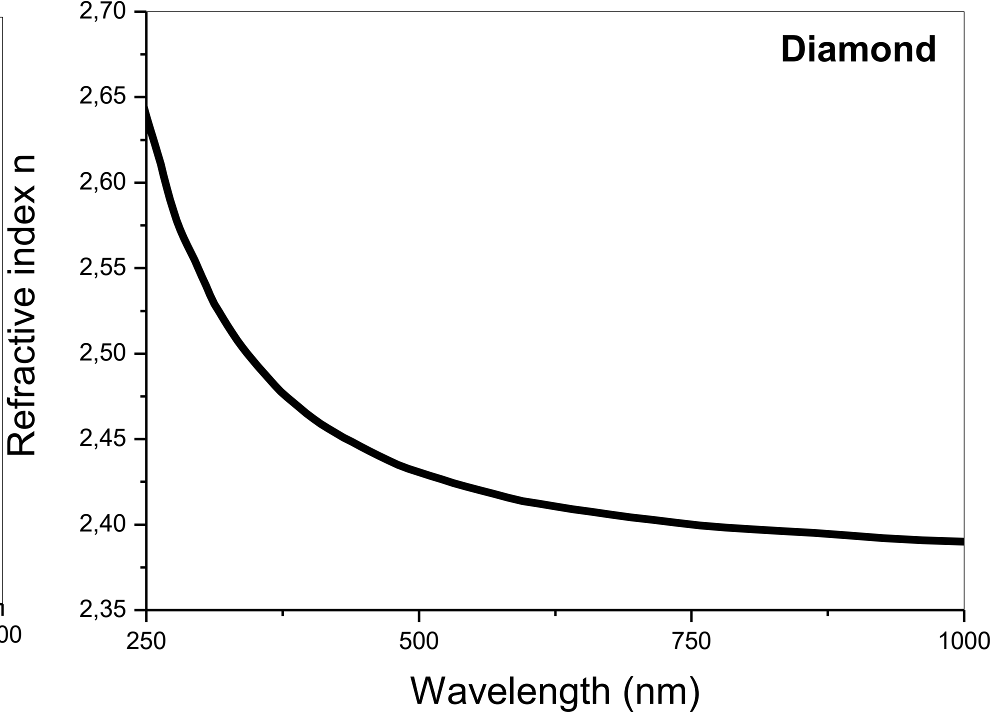
Refractive indices as a function of wavelength (dispersion)

→ **Causes chromatic aberration**

weak dispersion **strong dispersion**

in the visible range





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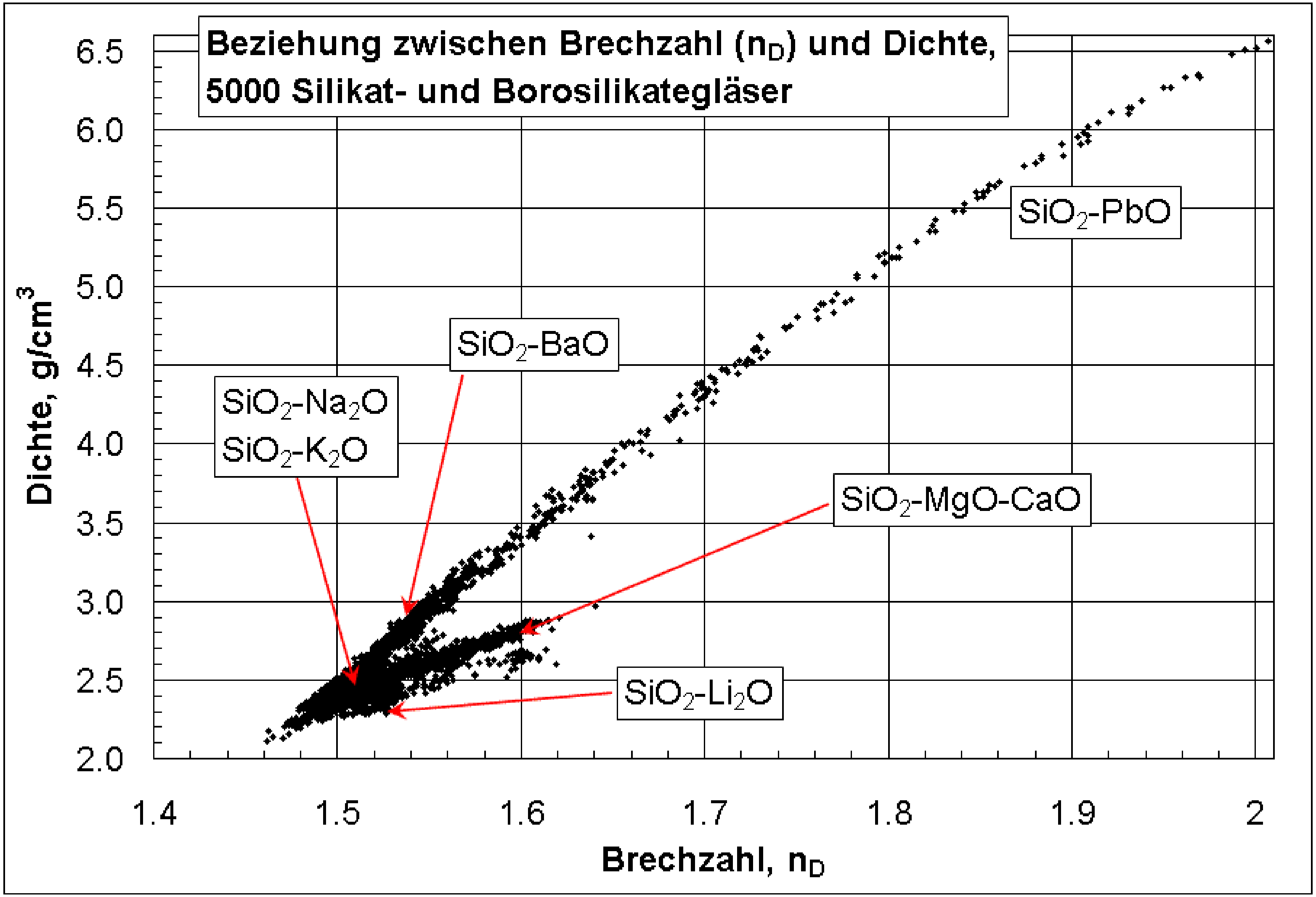
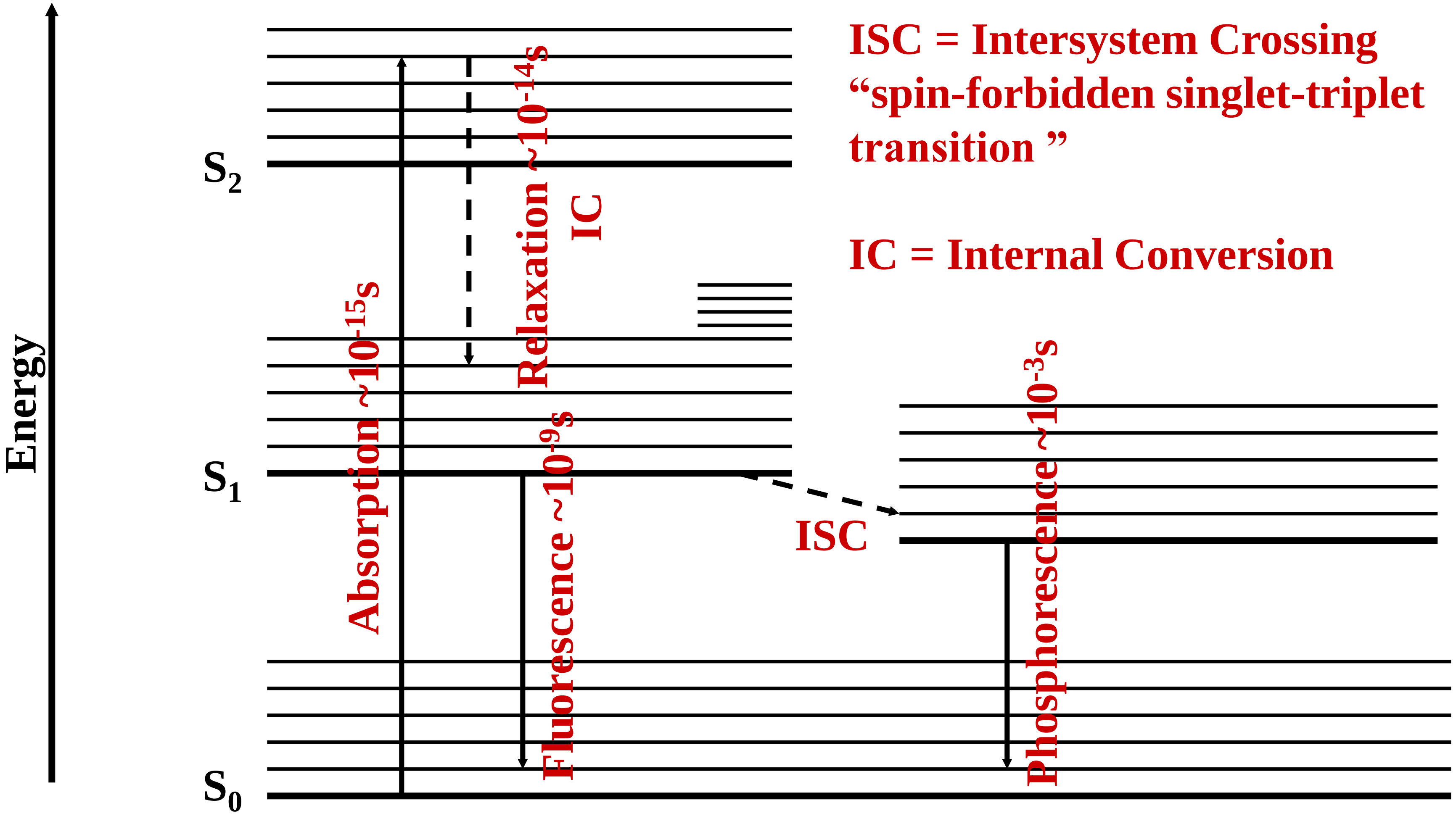
Refractive indices as a function of the density of glasses



2.4 Interaction of Light and Matter

Luminescence

Jablonski diagram of an arbitrary organic molecule



ISC = Intersystem Crossing
“spin-forbidden singlet-triplet transition ”

IC = Internal Conversion

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 $[N_{h\upsilon}/m^2s]$

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

Physical variable	Symbol	Definition	Unit
Radiant power/flux	Φ_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^2]
Spectral irradiance	L_e	$= dD_e/d\lambda$	[W/m^{2}nm]

Irradiance of the Earth: $E_e = 1.35*10^3$ J/m^{2}s = 1.35 kW/m^2 (= solar constant)

Number of photons: $E = h\nu = hc/\lambda$ and $h\nu_{550} = 4*10^{-19}$ J

$\Rightarrow$ 1 W = 1 J/s = $2.5*10^{18}$ photons per second with wavelength 550 nm

$\Rightarrow$ $3.375*10^{21}$ Photons/m^2 for 1.35 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]

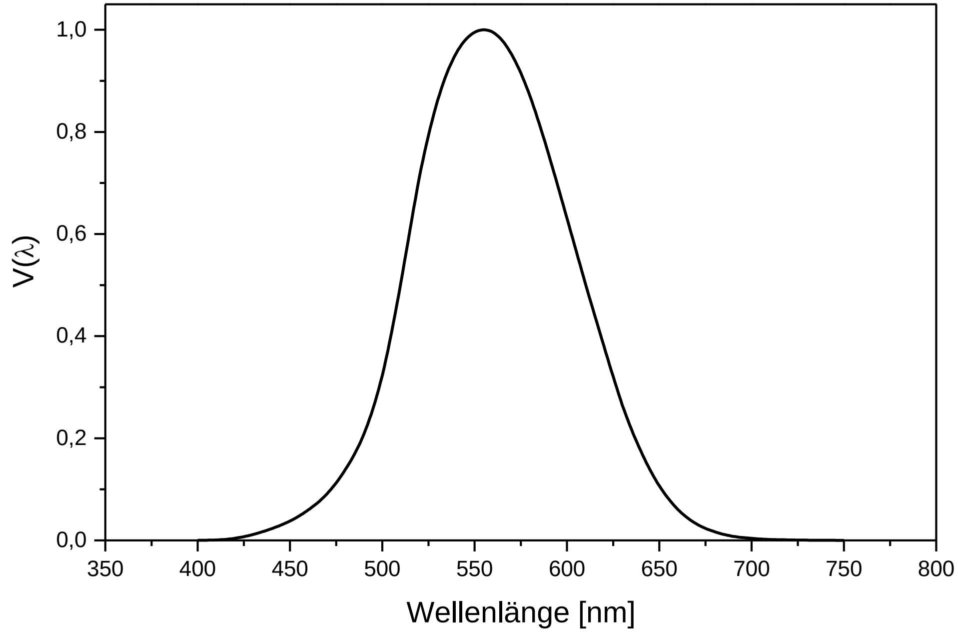
M_0 = Energetic light equivalent

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

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

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

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



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

Ω = Solid angle [sr]
(surface of a sphere = $4\pi r^2$ = 4πsr)

A 1 cd (1 lm / sr) light source emits 4π lm, i.e. 12.57 lm, isotropically in all spatial directions ⇒ Luminance spectrometer

2.6 Photometric Quantities

Origin of the quantity of the energetic light equivalent $M_0 = 0.00146$ W/lm

Reference light source is the candle

Emission spectrum of a diner light (~ 16 g)

<u>P ~ 40 W</u> = 40 J/s (fuel: paraffine ~ 42 MJ/kg)

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

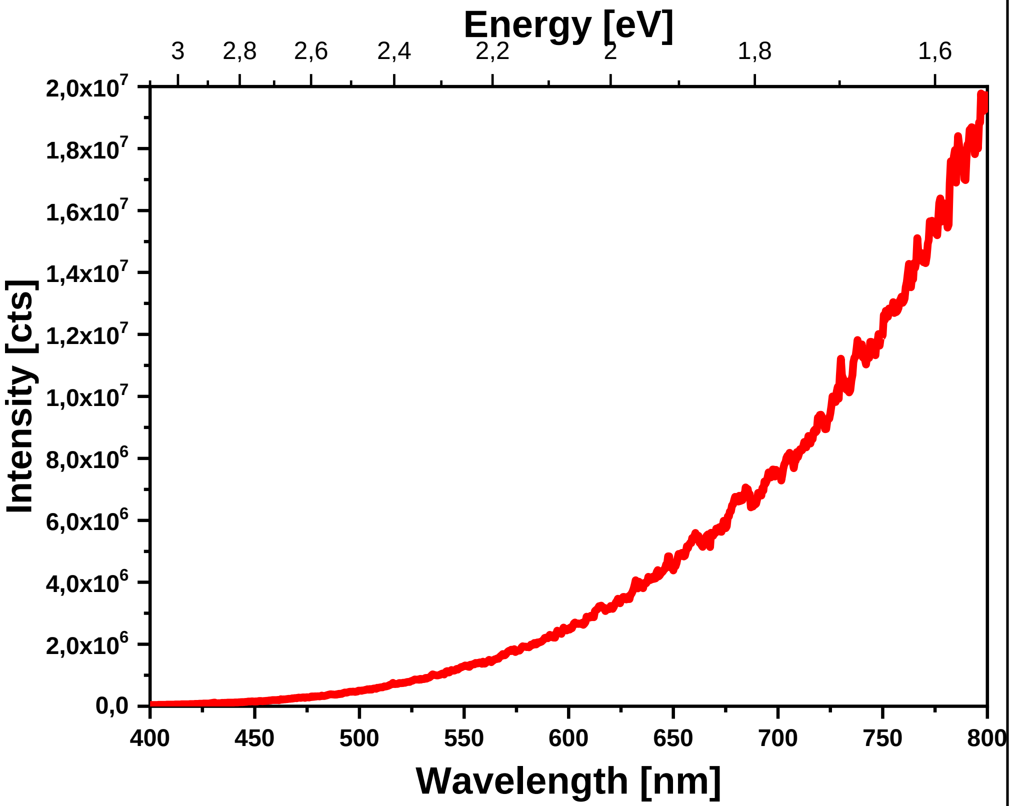
$\eta = 0.00046$ or 0.046%

$I_v = 1$ cd $= 4\pi$ lm ~ 12.566 lm

$\Rightarrow \eta_v = 0.31415$ lm/W $\Rightarrow$ 3.1832 W/lm

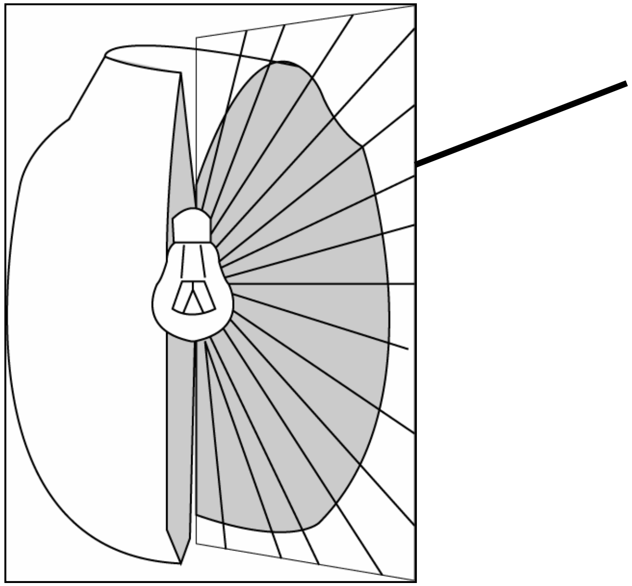
Efficiency $\eta = 0.00046$

$\Rightarrow$ 0.001464 W/lm or 683 lm/W (q.e.d.)



2.6 Photometric Quantities

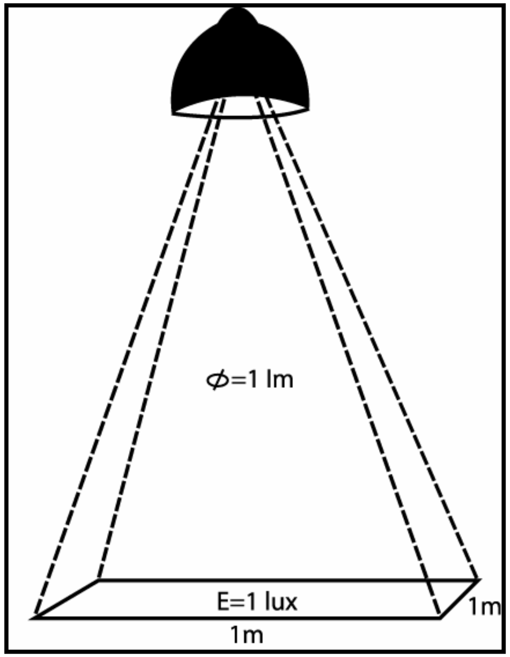
Luminous flux	**Total radiation power emitted from a light source in all spatial directions, which is measured via the sensitivity of the human eye [lm]. It is determined by measurement with an integrating sphere.**
Luminous int.	**Luminous flux emitted per unit solid angle with the value of one steradiant [cd]. For this purpose, the luminous flux detected only in a certain solid angle, typically in the range of the maximum beam intensity.**

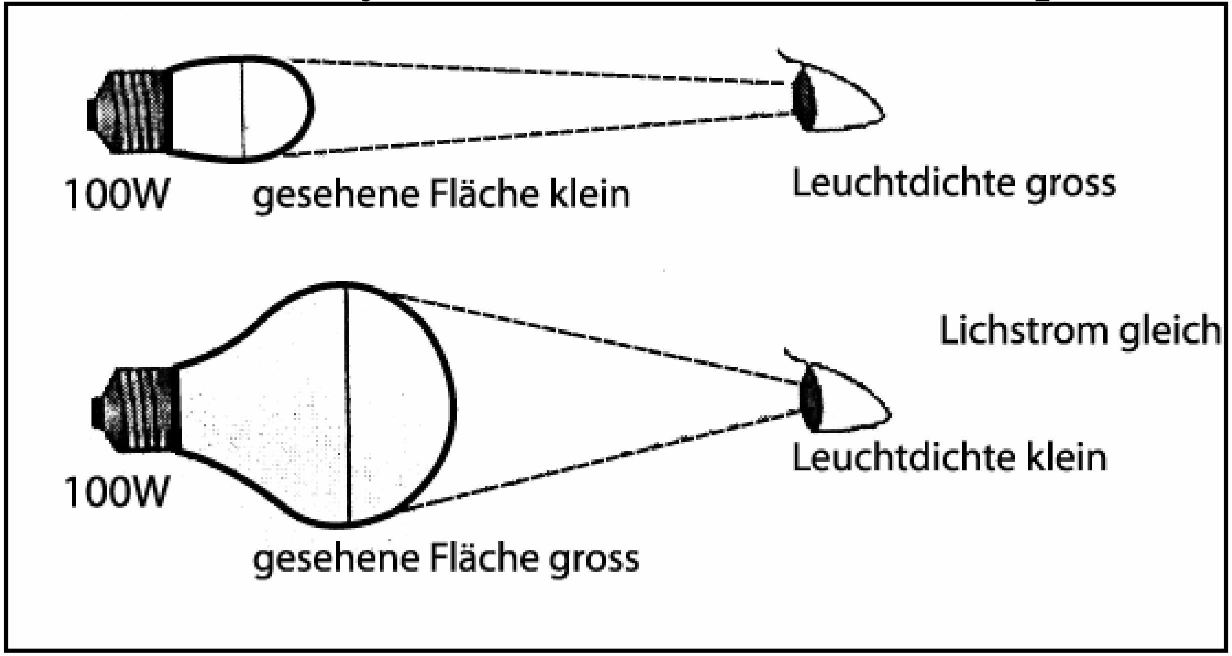


$$\mathit{Luminous\ flux}: \boldsymbol{\Phi}_{\mathrm{v}} = 683 \int_{380}^{780} V_{rel}(\lambda)\Phi_e(\lambda)d\lambda$$

2.6 Photometric Quantities

Illuminance	**Ratio of luminous flux to the illuminated surface [lux = lm/m^2]. It is determined by measurement with a luxmeter.**
Luminance	**Perceived brightness of a light source [cd/m^2]. It is measured with a CCD camera. Vision limit human eye ~ 0.000003 cd/m² ~ 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^2]

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^2] = [nit] (luminance)

Light source	**Light density / Luminance [cd/cm^2]**
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

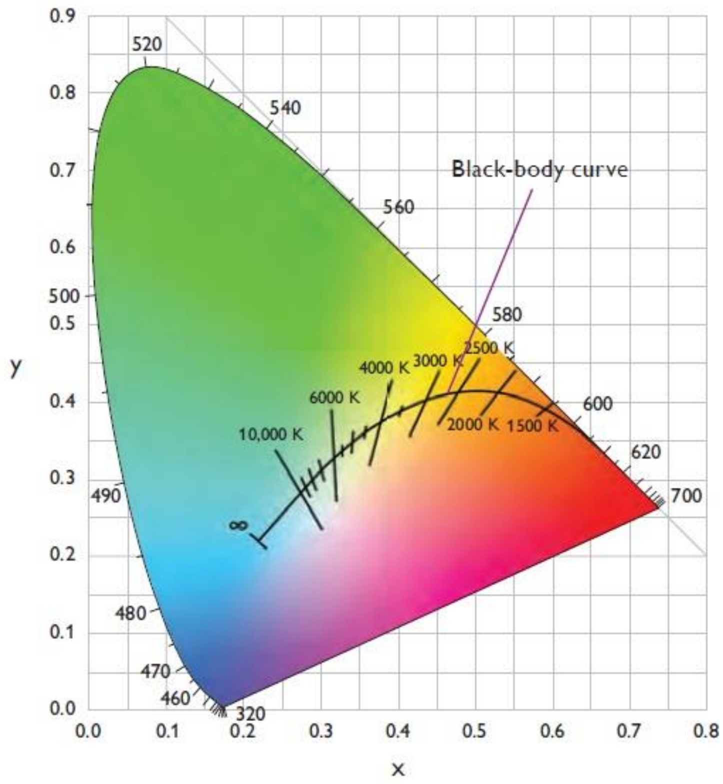
2.6 Photometric Quantities

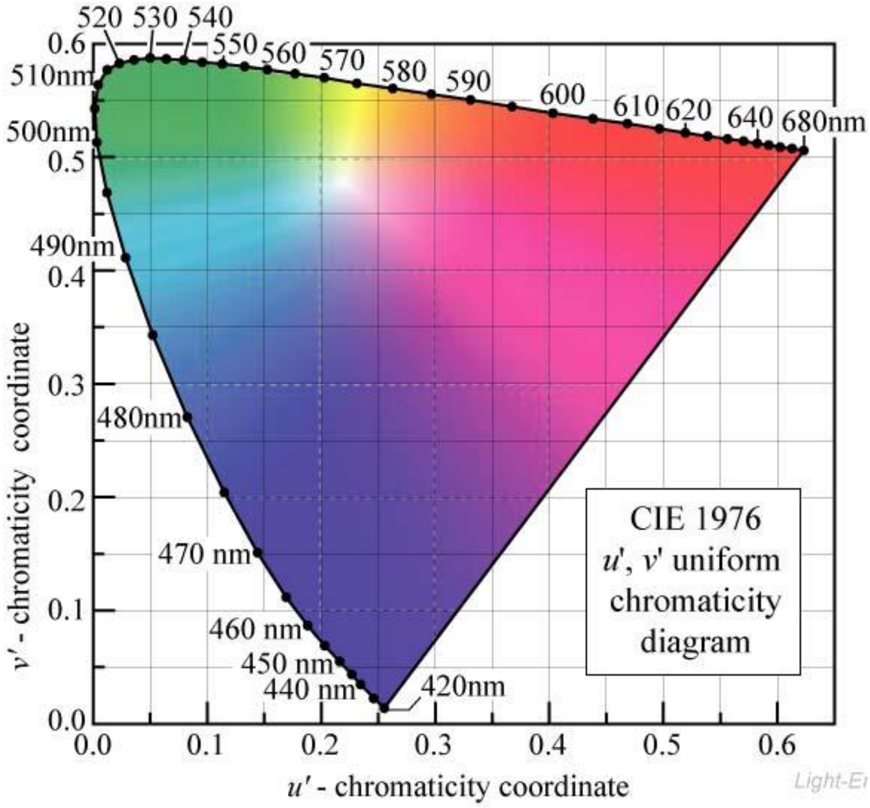
Color Coordinates

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

Various systems exist to represent the color:

CIE1931, CIE1976, CIElab (includes luminance), …

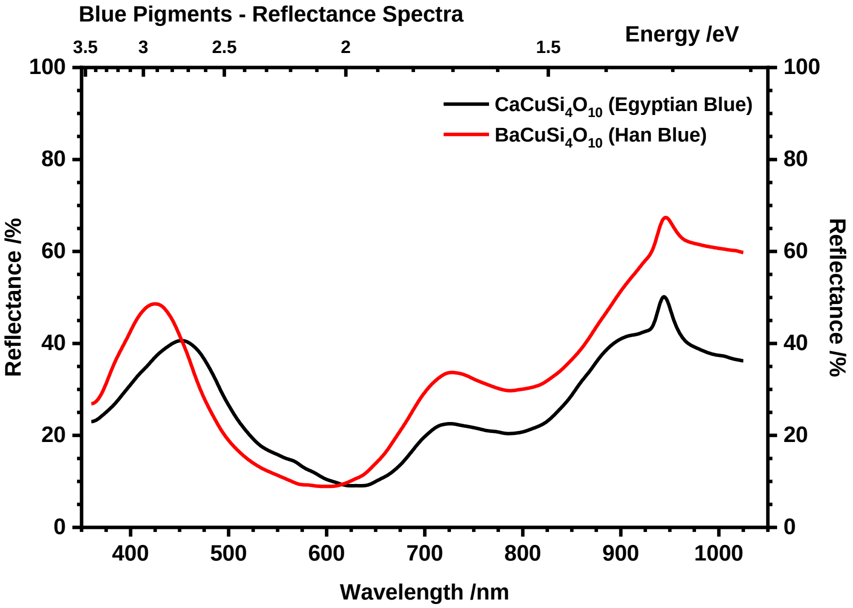




2.6 Photometric Quantities

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 is modeled after sun light
- With very efficient phosphors the body color can be influenced by their luminescence. Absorbed UV radiation is converted into visible light

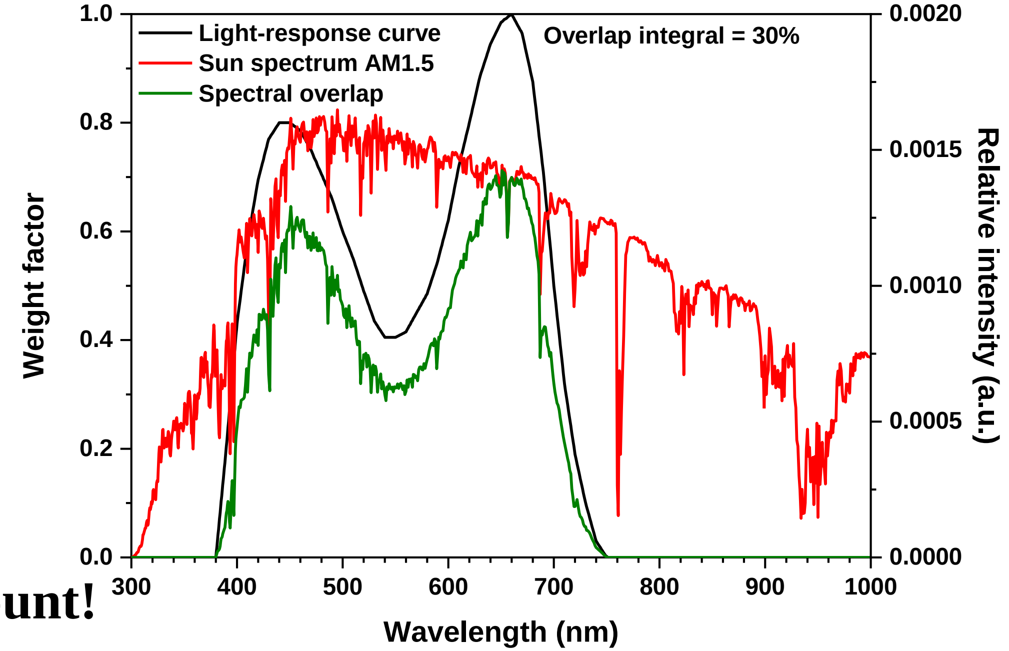


2.7 Photosynthetically Active Radiation

Photosynthetically Active Radiation (PAR)

- Most autotrophic organism use phototosynthesis for energy production and thus utilize photons of specific wavelengths

- Photosynthetic photon flux (PPF) treats all photons in the range of 400-700 nm equally



PPF Density (PPFD)

Number of 400-700 nm photons per irradiated area and time:

Unit: [mol · m^{-2} · s^{-1} = W · m^{-2}]

→ does not take the efficiency into account!

2.7 Photosynthetically Active Radiation

Photosynthetically Active Radiation (PAR)

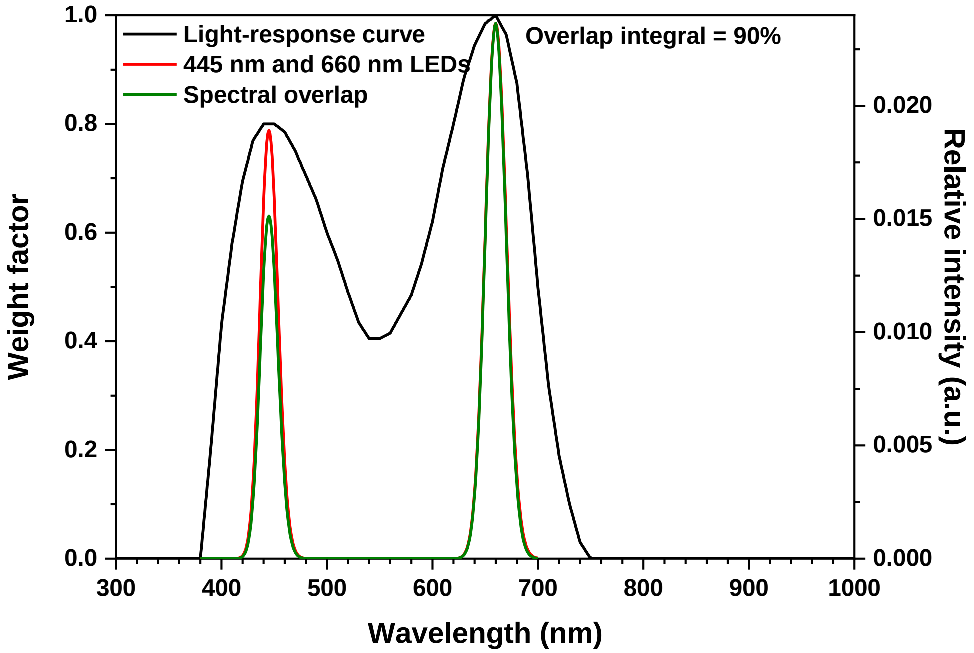
Yield Photon Flux (YPF)

- **Since the photosynthesis efficiency depends on the respective wavelength of the photon, weight factors can be used**

- **The physical unit of PPF and YPF are identical, but their actual value can differ greatly**

- **The spectral overlap integral (OI) quantifies the overall efficiency**

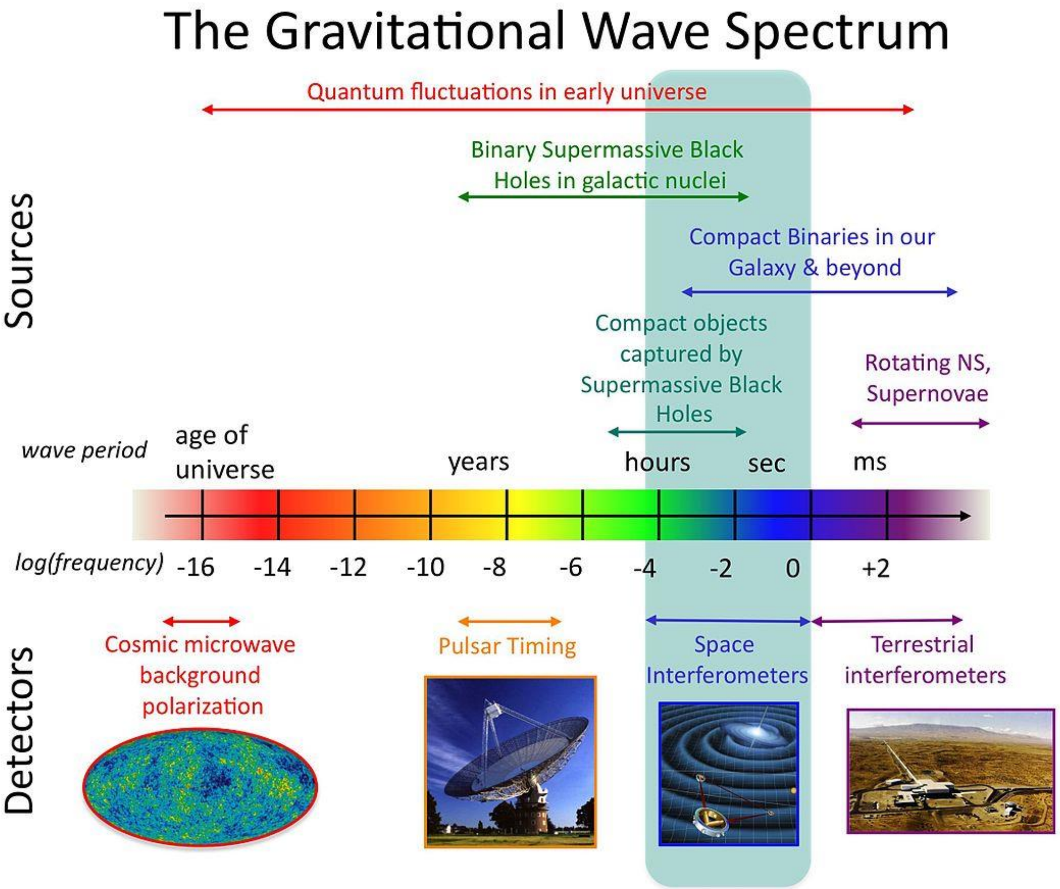
YPF = OI · PPF



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**



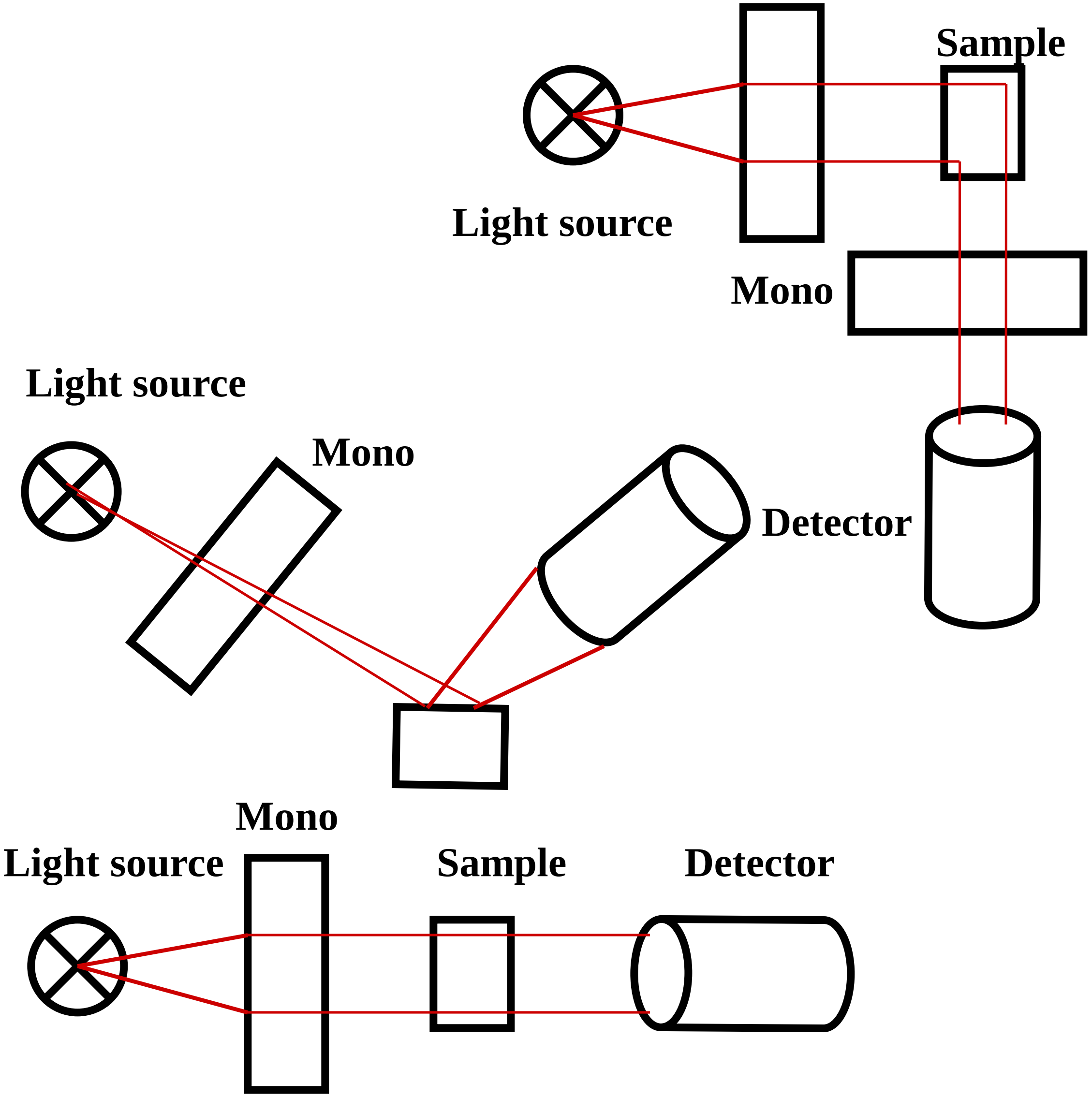
3.1 Construction of a Spectrometer

Geometries

Fluorescence, phosphorescence of solutions (rectangular geometry)

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

Absorption, transmission of solutions, gases (linear geometry)



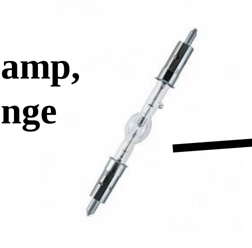
3.2 Excitation Sources

Typical radiation sources

• Celestial objects (only of interest for astrophysics)	Continuous + Lines
• Halogen lamps	Continuous
• Gas discharge lamps	
– Xe-medium pressure lamps	Quasi-continuous
– Low-pressure mercury lamps	Lines
– Medium pressure mercury lamps	Quasi-continuous
– High pressure mercury lamps	Quasi-continuous
– H_2/D_2-lamps	Quasi-continuous
• LEDs	narrow band
• Laser (less suitable for excitation spectra!)	narrow line
– Gas laser (CO_2, N_2, Kr, excimers: ArF*, XeF* etc.)	
– Solid-state laser	
– Dye laser	
– Laser diodes	
• Synchrotrons (BESSY, DELTA, DESY, CERN, …)	White!

3.2 Excitation Sources

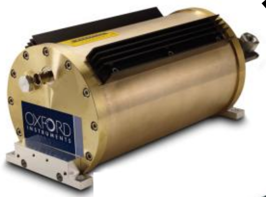
Radiation sources for fluorescence spectroscopy



Xenon disch. lamp, wavelength range 200 - 900 nm

Fianium supercontinuum SC450-4 white light laser, wavelength range 0.46 - 2.4 µm

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



D_2 bulb, wavelength range 120 - 400 nm

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, α- and γ-radiation

3.2 Excitation Sources

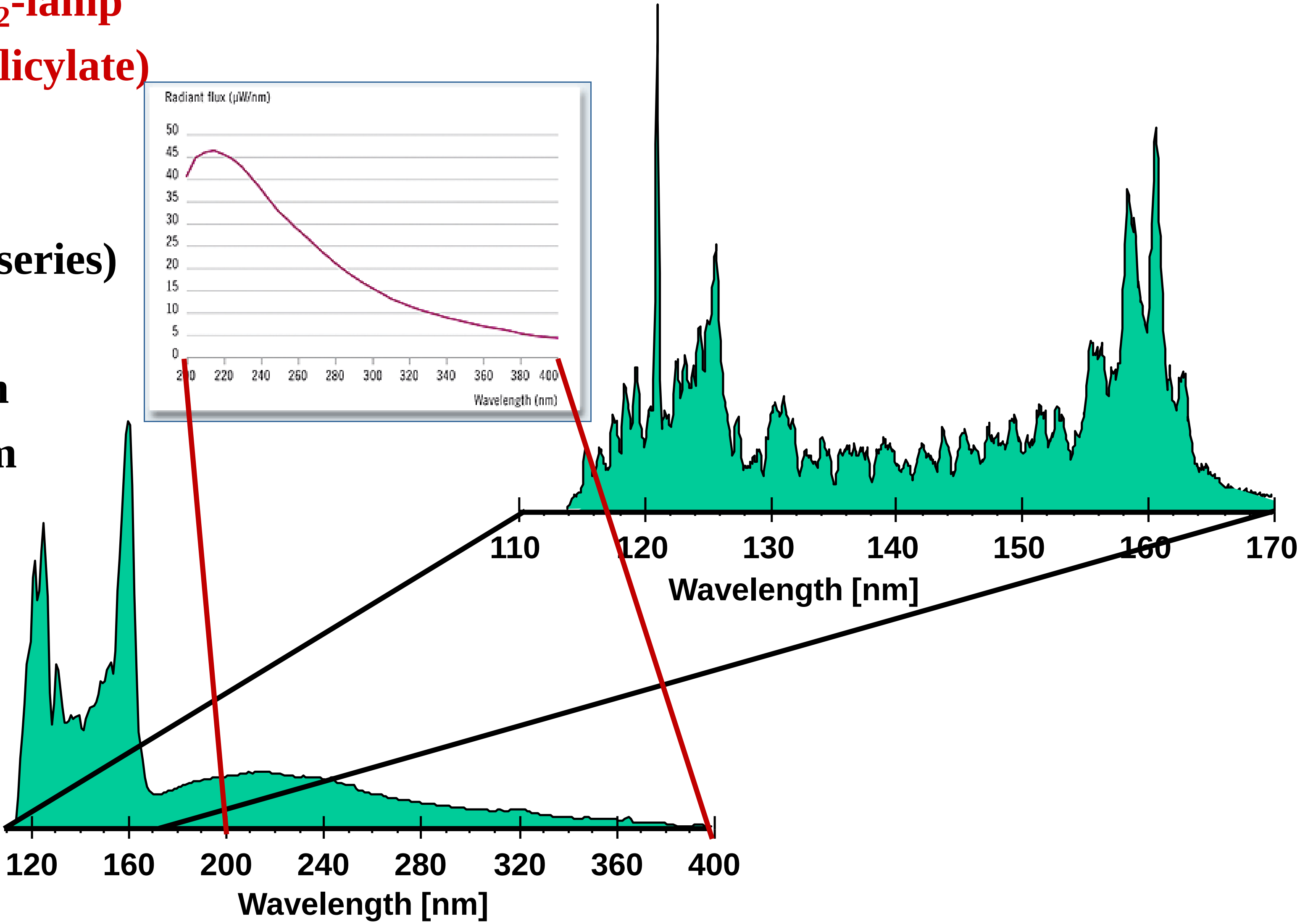
Spectrum of a D_2-lamp (Standard Na-salicylate)

110 – 170 nm

D-lines (Lyman-series)

170 nm – 400 nm

Quasi-continuum



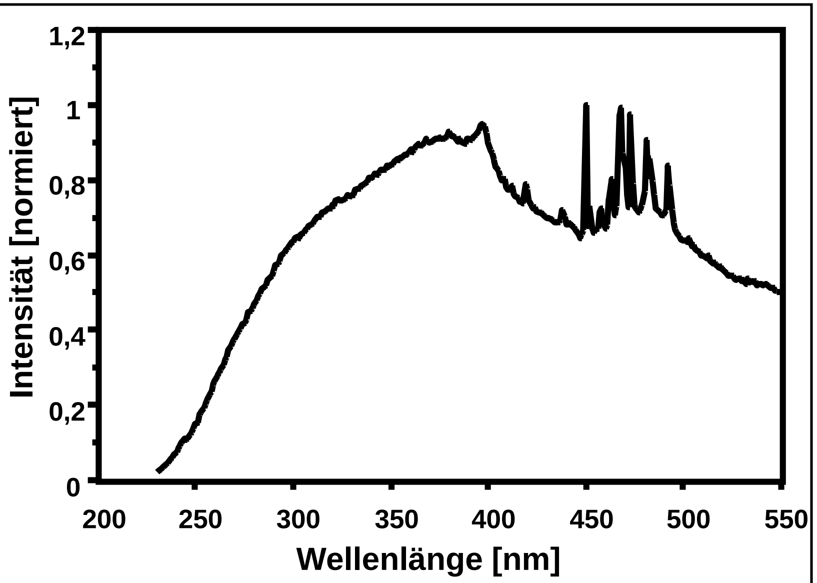
3.2 Excitation Sources

Spectrum of a Xe-medium pressure lamps

- 220 – 450 nm

  Quasi-continuum
- > 450 nm

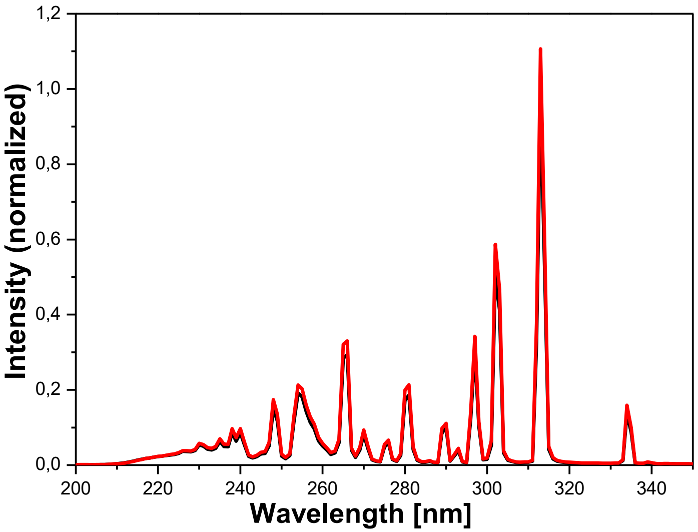
  Quasi-continuum + Xe-lines



Spectrum of a high pressure mercury lamps

- 210 – approx. 300 nm

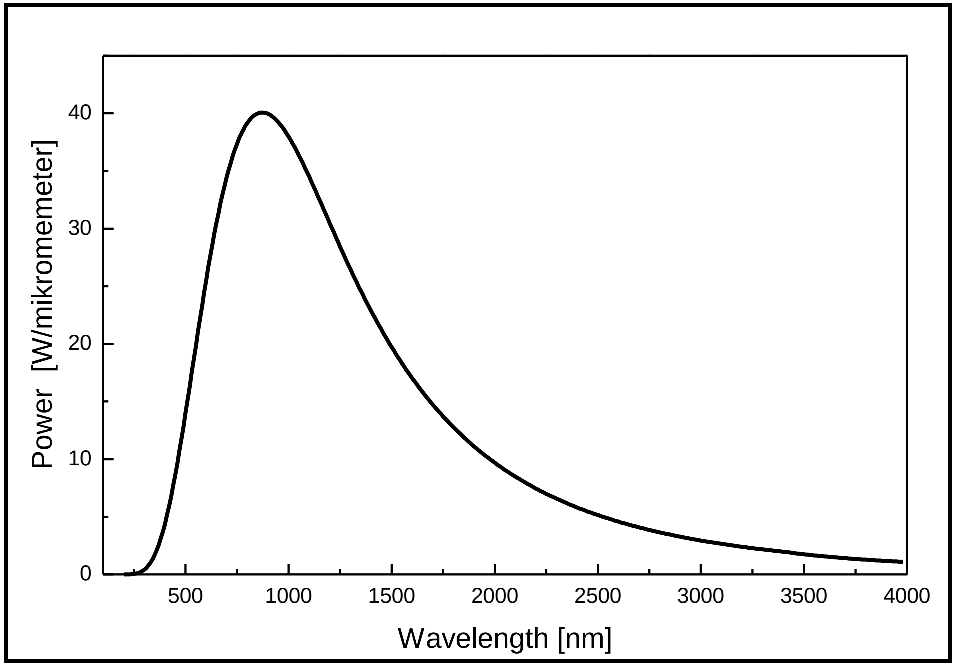
  Quasi-continuum
- Hg-lines at 248, 254, 265, 303, 313, 365, 405, 435, 546 and 579 nm



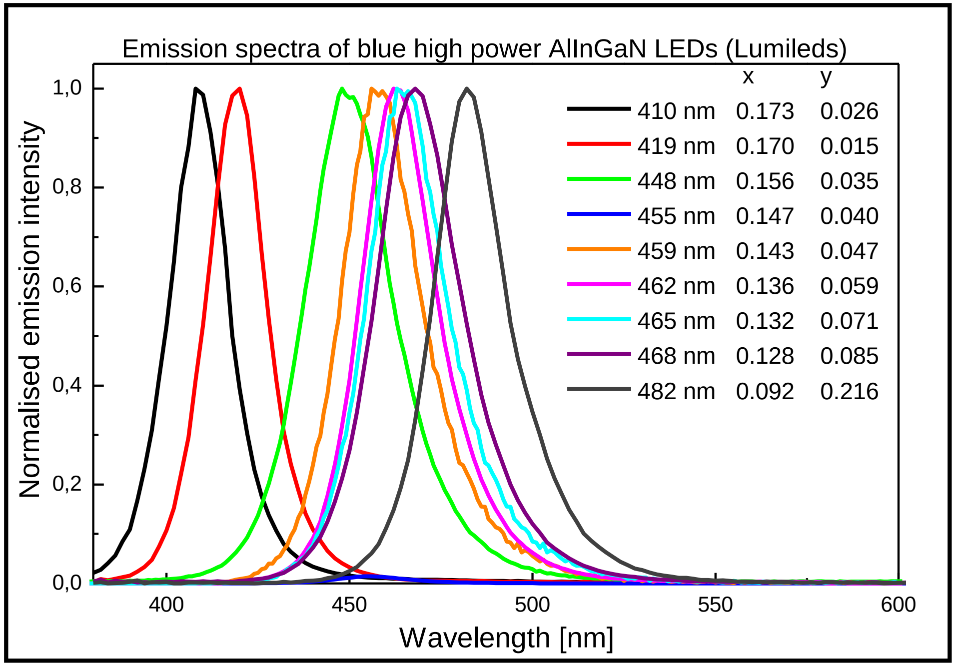
3.2 Excitation Sources

Spectra of halogen lamps and LEDs

Halogen lamp (broad band emitter)



LEDs (narrow band emitter)



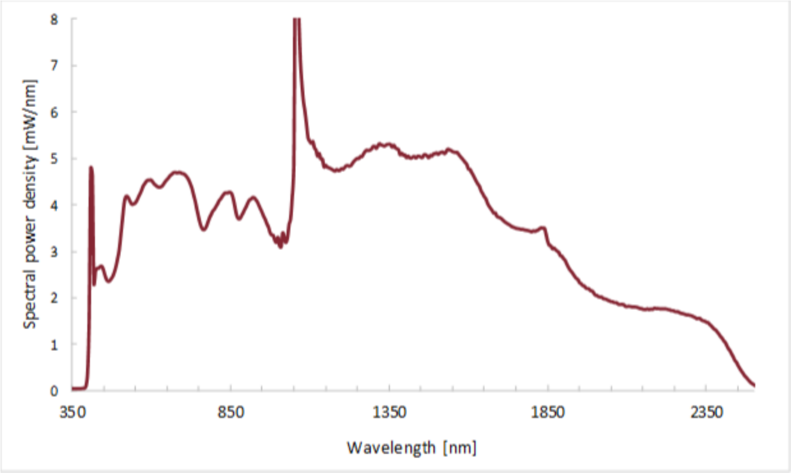
LEDs are very flexible light sources (geometric and spectral)

(In,Ga)N	**365 – 500 nm**	**(Al,In,Ga)P**	**580 – 700 nm**
(Al,Ga)N	**210 – 365 nm**	**Ga(As,P)**	**> 650 nm**

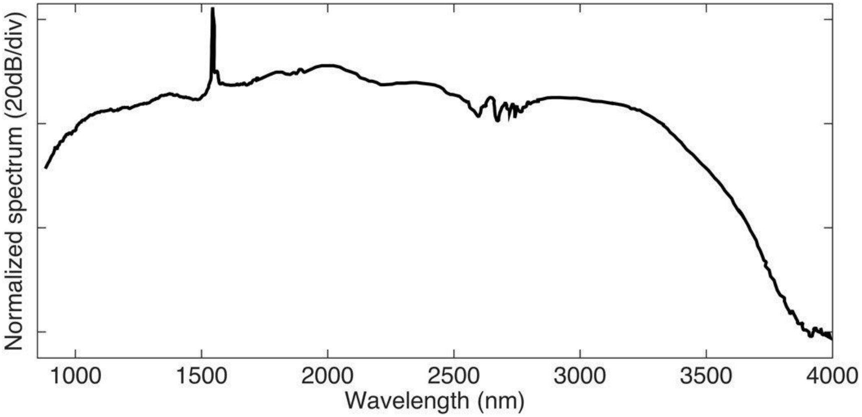
3.2 Excitation Source

Super continuum laser (white laser)

- **Spectral broadening of a laser line via non-linear effects in a glass fiber**
- **In the spectrum the primar laser line can still be observed (e. g. 1064 nm of YAG:Nd)**
- **The optical power in 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

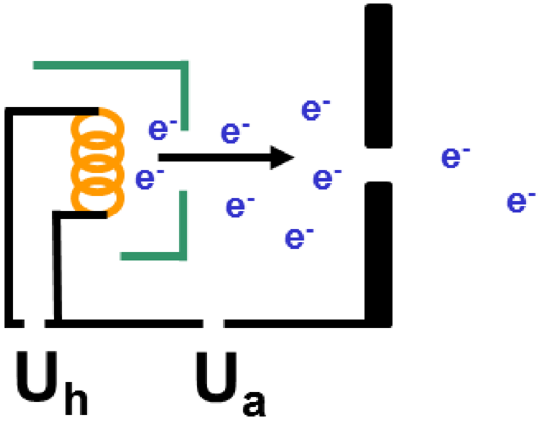


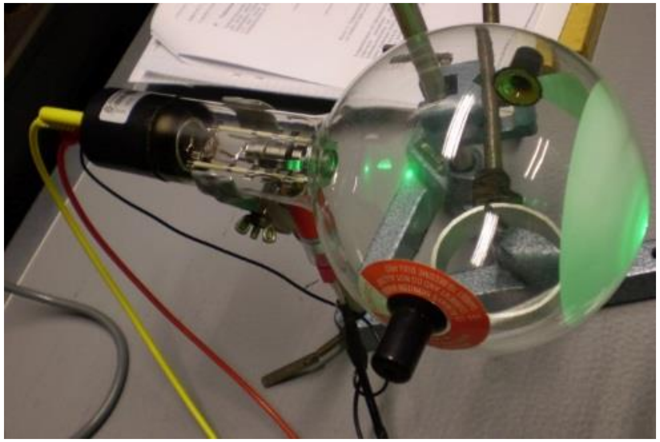
Experimental NIR SC-laser
Ref.: DOI 10.1117/2.1201510.006199

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, the higher is the energy of the electrons.
- The electron beam is focused by a positively charged Wehnelt cylinder

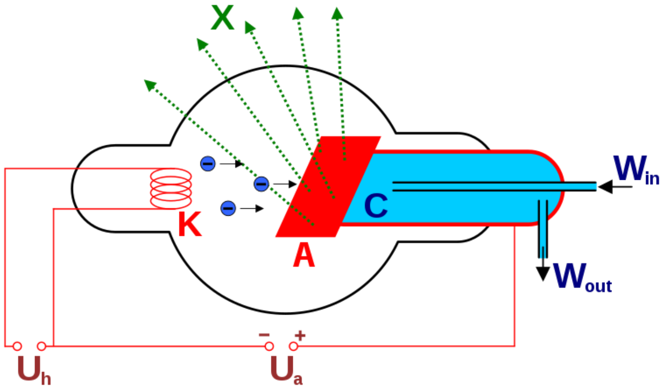




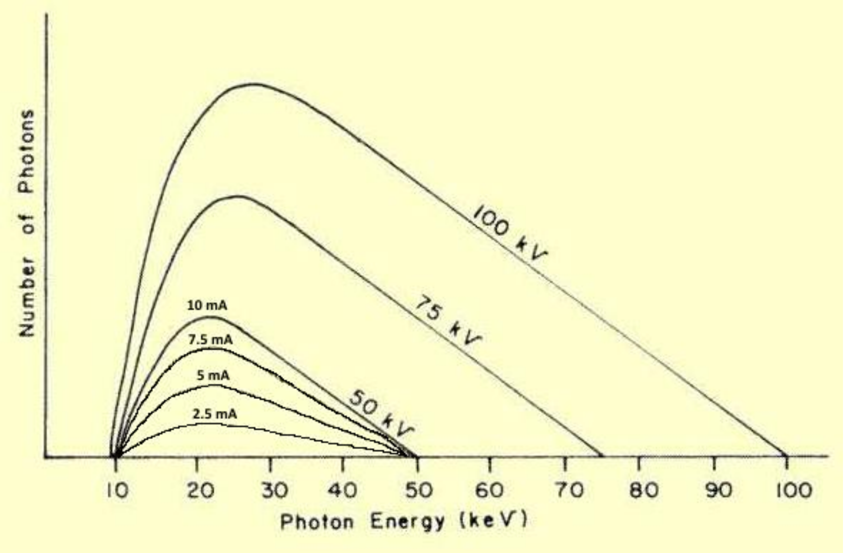
Source: Wikipedia

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



Ref.: Perry Sprawls, “Physical Principles of Medical Imaging”

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

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

3.2 Excitation Sources

α-, β-, γ-emitter

α: He^{2+} cations

- typical α-emitters: ^{241}Am, ^{238}Pu, ^{239}Pu
- penetration depth: 10-15 µm (YAG, 5 MeV)

β: electrons, e$^-$

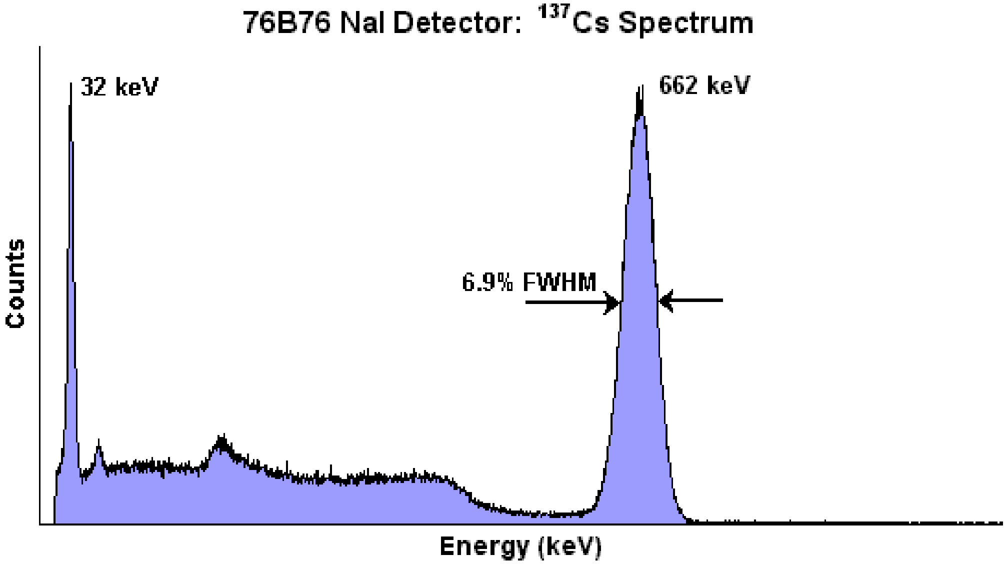
- typical β-emitters: ^{137}Cs, ^{90}Sr, ^{3}H
- penetration depth: < 1 µm (10 keV), 8-10 µm (70 keV)

γ: high-energy photons

- typical γ-emitters: ^{137}Cs, ^{60}Co
- simultaneously emitted α or β particles are stopped by an thin metal absorber
- interacts with the whole particle

Tritium filled tube coated with Zn_2SiO_4:Mn^{2+}

Commercial ß-source

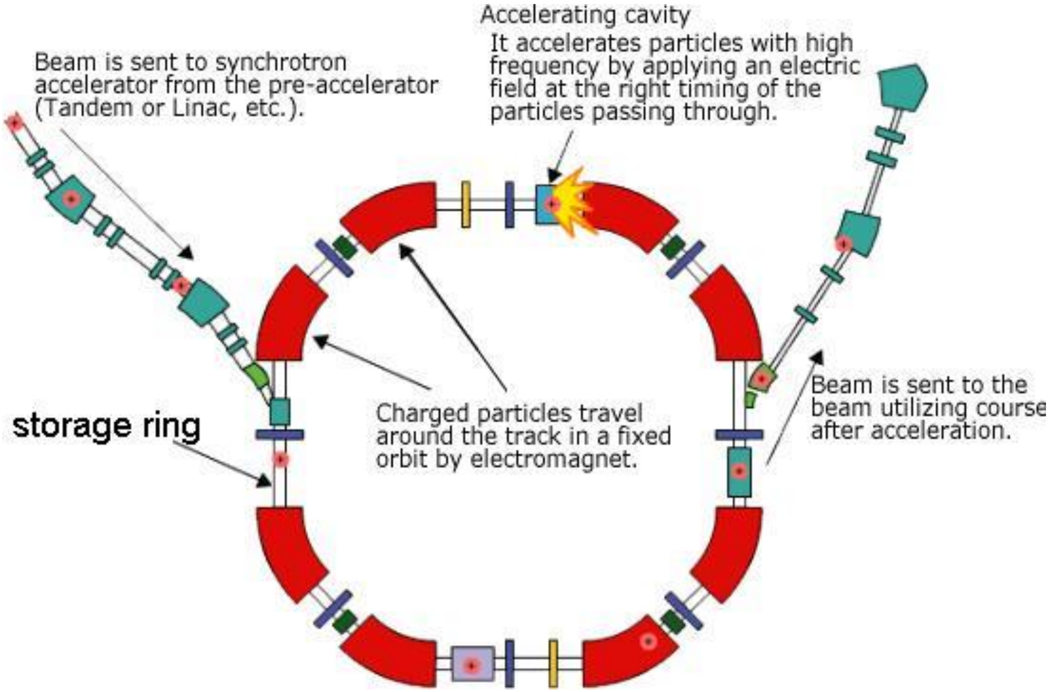


3.2 Excitation Sources

Synchrotron

Generates a continuus spectrum by accelerating electrons

- **Energy (wavelength) depends on the acceleration and can range from < 1 eV (> 1 µm, NIR) to > 1 GeV (< 1 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**

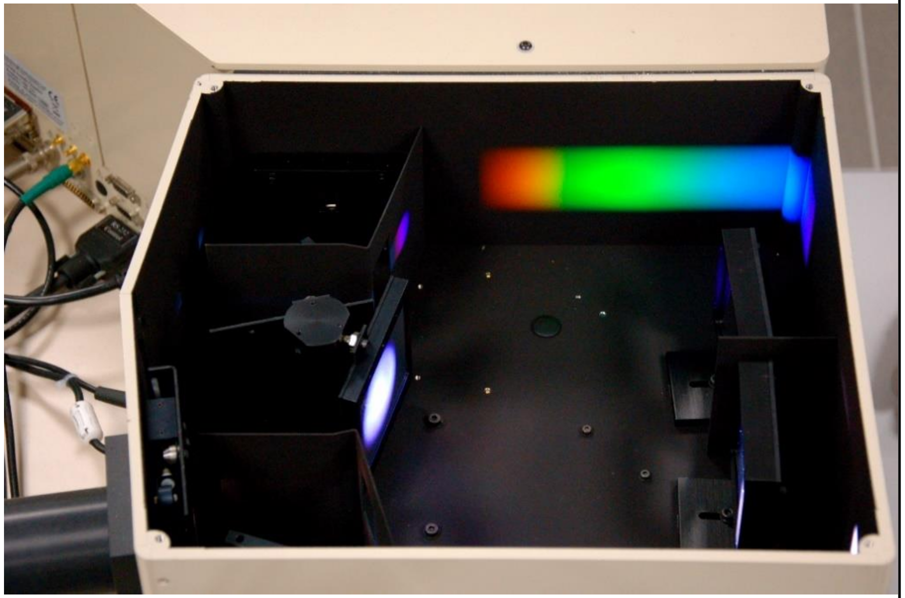


3.3 Dispersive Elements

- **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**

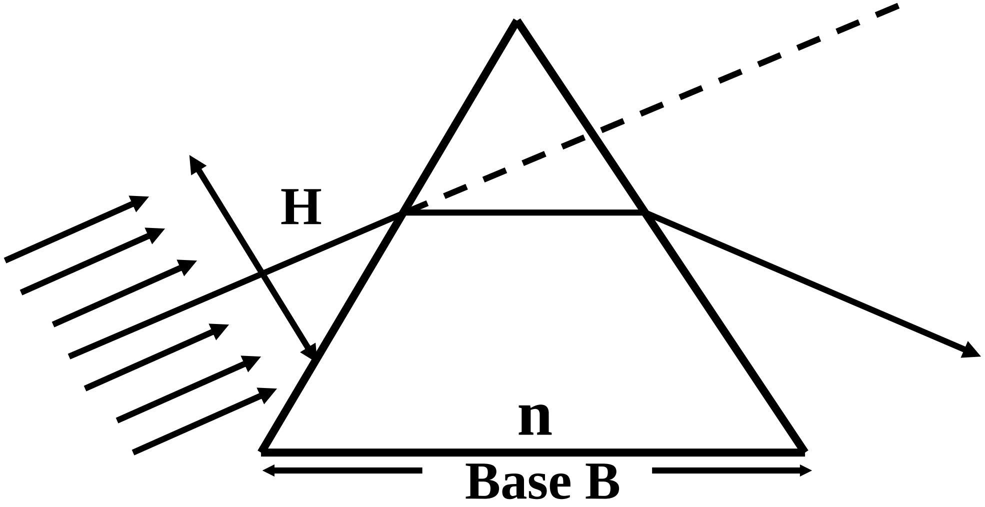
  Angular dispersion:

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

  B = Prism base

  H = Height of beam (slit width)

  n = Refractive index



- **Dispersion gratings**

  Grating constant (lines / mm) determines the usable area ⇒ "Gratings"

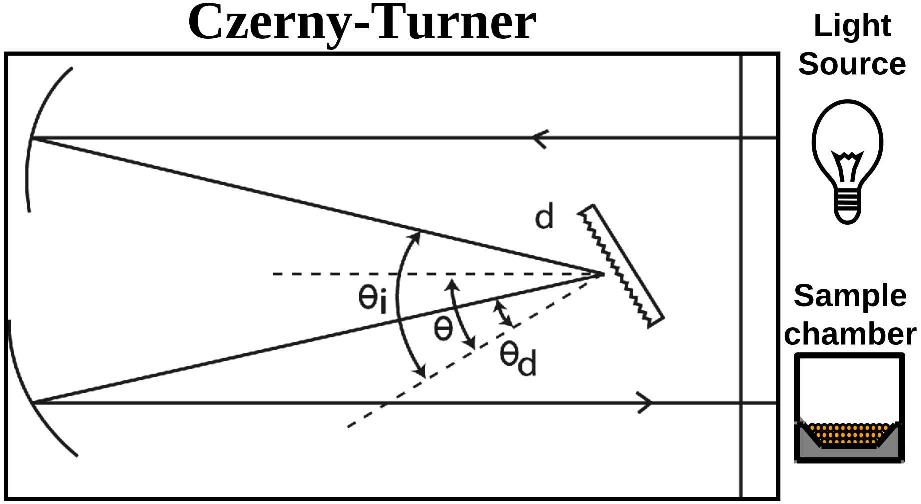
  e.g. 1200 or 2400 lines / mm

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

  m = Order

  N = Slit number

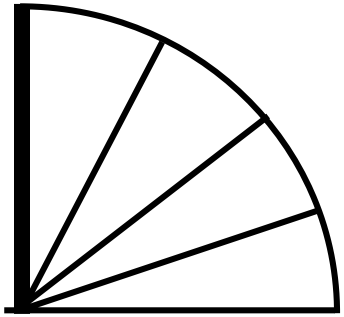
Czerny-Turner



Attention! Reflections of higher order ⇒ Filter

3.3 Dispersive Elements

Higher orders upon use of a grating



1st order 250 nm

1st order 500 nm
2nd order 250 nm (weak)

1st order 750 nm
2nd order 375 nm (weak)
3rd order 250 nm (very weak)

The second order has to be removed with a filter!

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

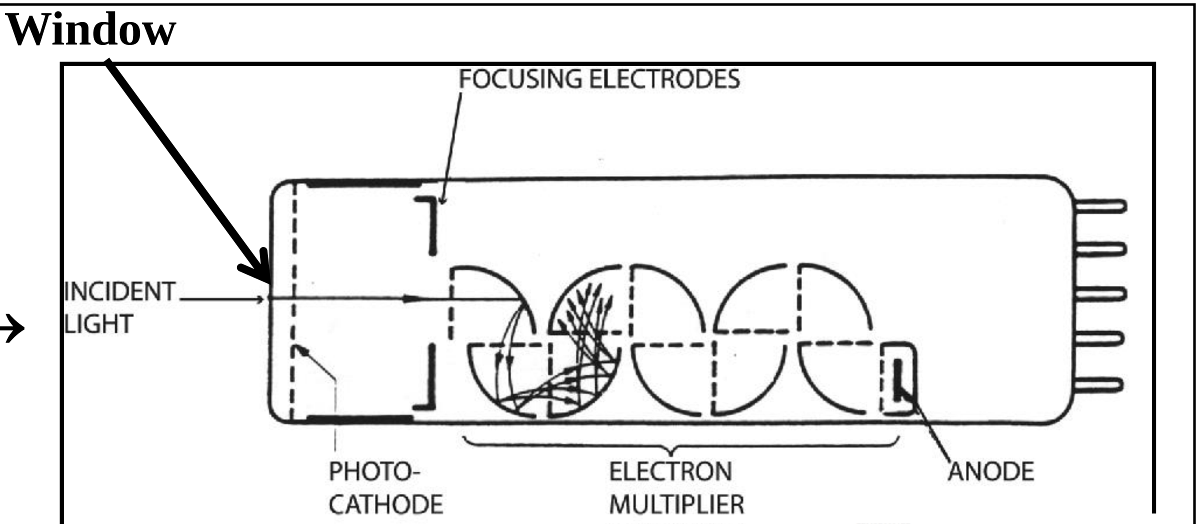
The grating will group 2nd order 350 nm photons from the lamp together with the 1st order 700 nm photons from the sample…..

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

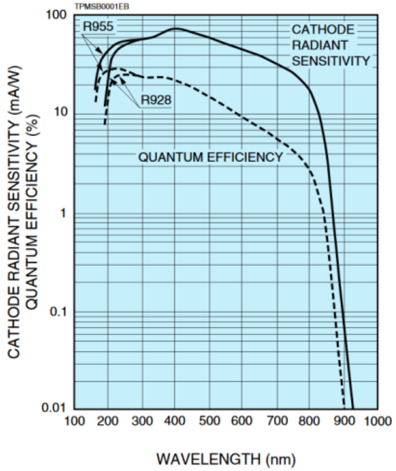
3.4 Detectors

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**
  - $2\,[\mathrm{Fe}^{III}(C_2O_4)_3]^{3-} \rightarrow 2\,\mathrm{Fe}^{II} + 5\,C_2O_4^{2-} + 2\,CO_2\uparrow$
  - **Reaction of Fe^{2+} with phenanthroline + measuring the absorbance at 510 nm**
  - **Photons/s = number of formed product's molecules/(QY*irradiation time)**

3.4 Detectors

Actinometer (Photochemical detectors)

- **Ferrioxalate actinometer (UV – 500 nm)**

$$\text{a) } [\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]^{3-} + 6\ \text{H}_2\text{O} \xrightarrow{h\nu} [\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]^{2+} + 2\ \text{C}_2\text{O}_4^{2-} + \text{C}_2\text{O}_4^{-\cdot}$$

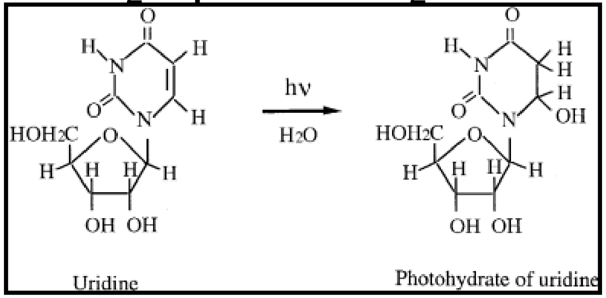
$$\text{b) } [\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]^{3-} + \text{C}_2\text{O}_4^{-\cdot} + 6\ \text{H}_2\text{O} \xrightarrow[\Delta T]{} [\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]^{2+} + + 3\ \text{C}_2\text{O}_4^{2-} + 2\ \text{CO}_2\uparrow$$

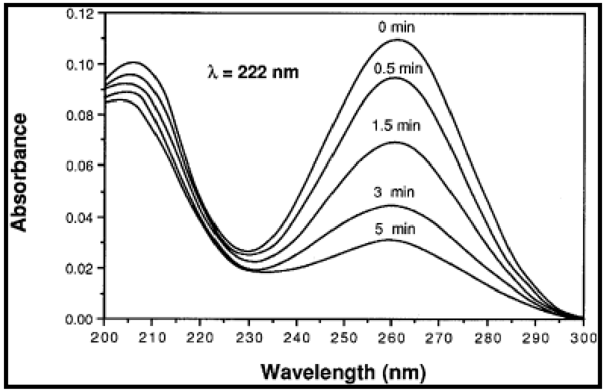
- **Uranyloxalat actinometer (208 – 426 nm)**

$$\text{H}_2\text{C}_2\text{O}_4 \xrightarrow{h\nu,\ \text{UO}_2^{2+}} \text{CO}_2\uparrow + \text{CO}\uparrow + \text{H}_2\text{O}$$

- **KI/KIO$_3$ actinometer (UV/Vis ⇔ Grätzel cell)**

$$8\ \text{KI} + \text{KIO}_3 + 2\ \text{H}_2\text{O} \xrightarrow{h\nu} 3\ \text{I}_3^-(\text{triiodid}) + 6\ \text{OH}^- + 9\ \text{K}^+$$





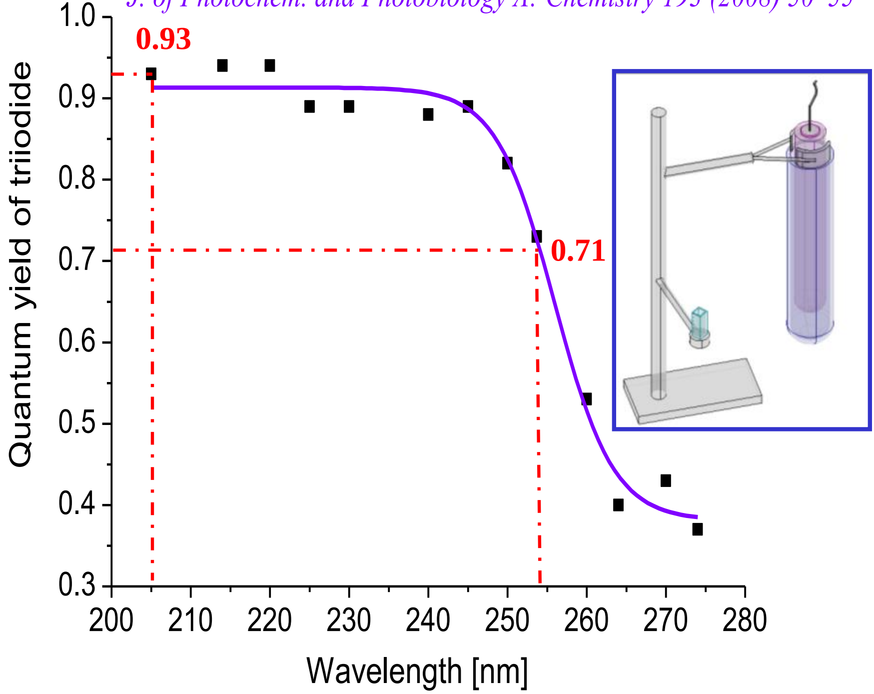
- **Uridine actinometer (200 – 290 nm)**
  Ref.: J.-Y. Zhang et al., Applied Surface Science 109/110, 1997, 482

3.4 Detectors

Triiodid Actinometer: $8\ KI + KIO_3 + 2\ H_2O \rightarrow 3\ I_3^- + 6\ OH^- + 9\ K^+$

QY according S. Goldstein, J. Rabani

J. of Photochem. and Photobiology A: Chemistry 193 (2008) 50–55



A = Absorbance at 352 nm (UV/Vis spectroscopy)
d = 1 cm cuvette
V = $3\ cm^3$
S: Irradiated surface $3\ cm^2$
F: Represent photon energy [$mJ{\cdot}mol^{-1}$] at emission wavelength of radiation source
Φ = Quantum yield of actinometer at emission wavelength of radiation source
ε = 27600 M·cm: molar abs. coeff. of I_3^- at 352 nm

h = Planck constant = $6.626{\cdot}10^{-34}$ Js
c = Speed of light in vacuum = $3{\cdot}10^8\ ms^{-1}$
N_A = Avogadro constant = $6.022{\cdot}10^{23}\ mol^{-1}$
λ = Wavelength of emitted radiation, e.g. 205 or 254 nm

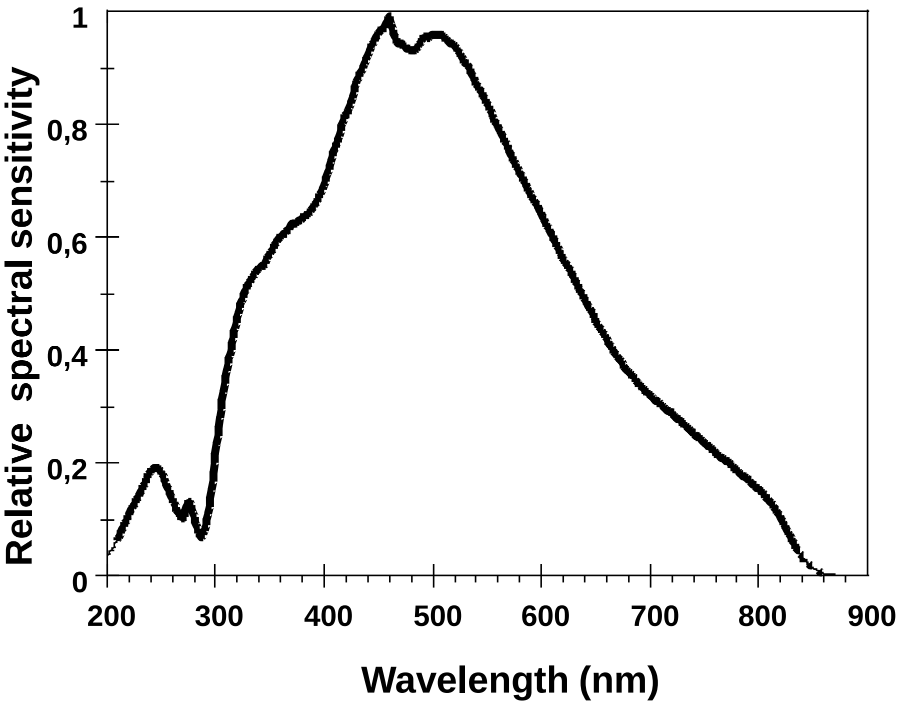
$$\text{Energy of photons/mol F} = \frac{h \cdot c \cdot N_A}{\lambda}$$

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

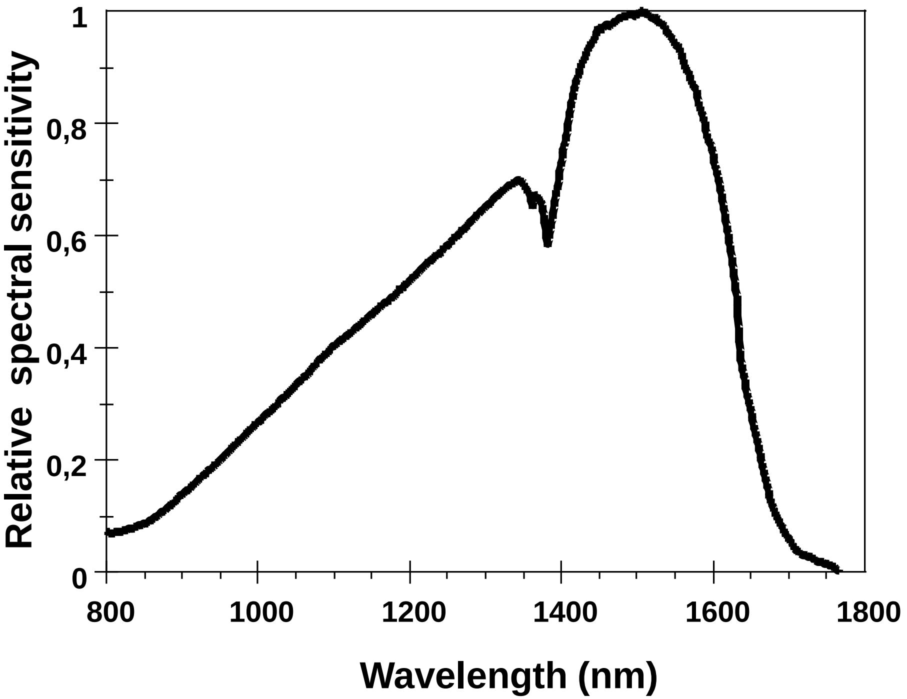
3.4 Detectors

Spectral sensitivity

Photomultiplier tube
200 – 850 nm
(Peltier element-cooling)

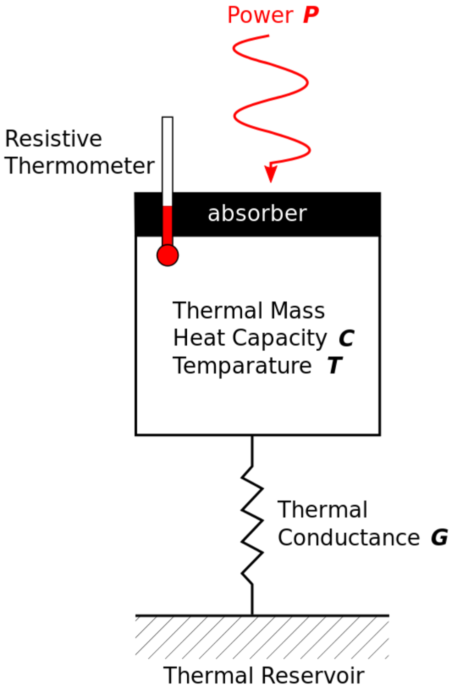


Ge semiconductor detector
800 – 1750 nm
(Liquid N_2-cooling)



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)

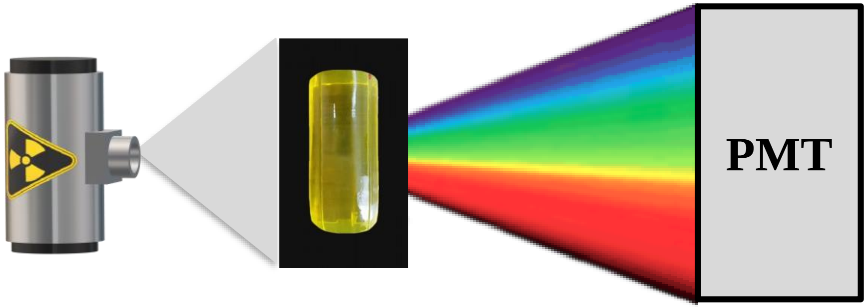
- Ionizing radiation is converted into visible radiation and detected by a common PMT or CCD

- Fast and very high sensitivity

3.4 Detectors

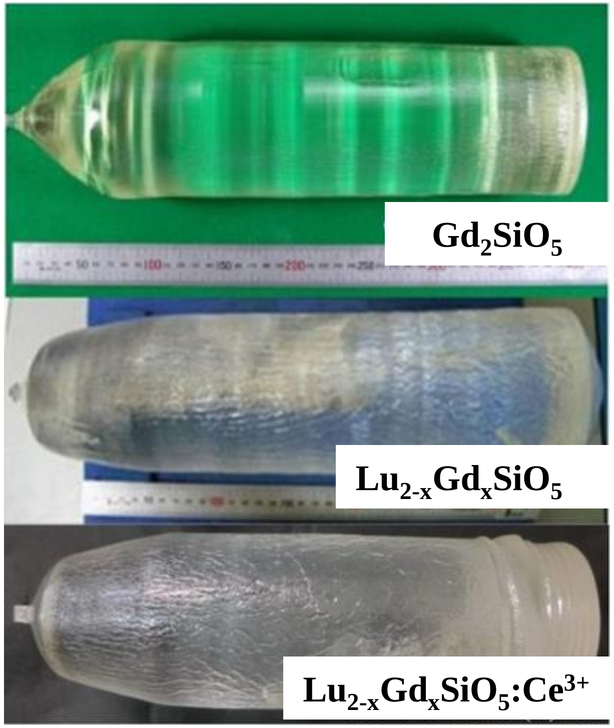
Scintillators

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



Scintillator materials (selection)

– $Lu_3Al_5O_{12}$:Ce	525 nm
– $Bi_4Ge_3O_{12}$	500 nm
– $PbWO_4$	420 nm
– $Lu_{2-x}Gd_xSiO_5$:Ce	420 nm
– NaI:Tl	415 nm
– $Lu_2Si_2O_7$:Ce	380 nm
– $LuPO_4$:Ce	350 nm
– $LuPO_4$:Pr	235 nm



Inorg. scintillators Technological backbone of modern medical diagnostic techniques: CT, SPECT, PET

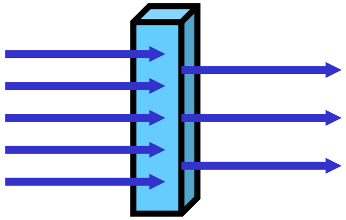
Source: https://www.opt-oxide.com/en/singlecrystals (03.12.2018)

3.5 Sample Chamber

Geometry

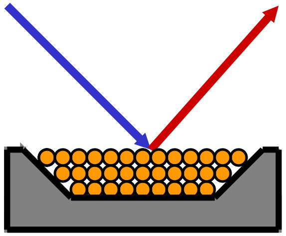
Absorption spectroscopy

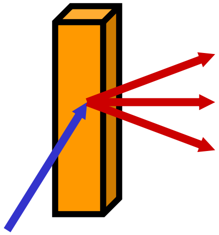
- Linear arrangement: laser source - mono - sample - detector
- One-or two-beam arrangement



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_2O and O_2 absorb radiation below approximately 200 nm

UV/Vis-measurements

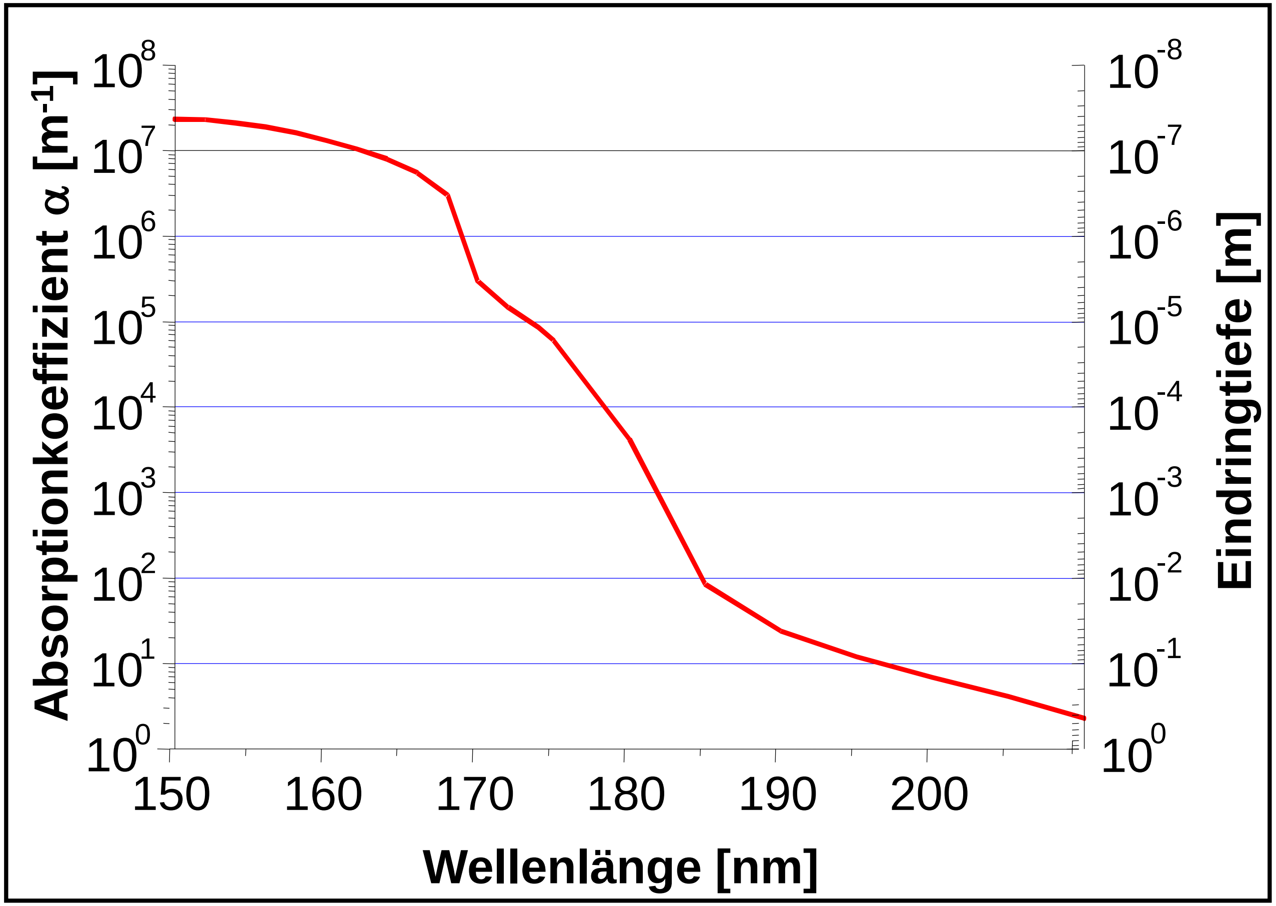
(200 – 800 nm excitation)

⇒ air /water

VUV- measurements

(100 – 200 nm excitation)

⇒ Vacuum, Ar or N_2

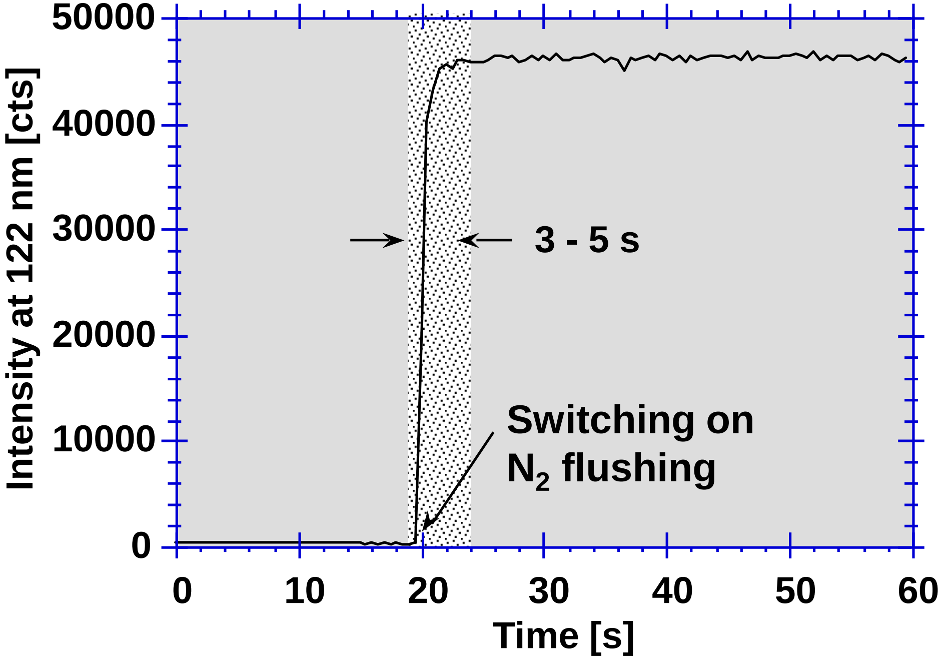


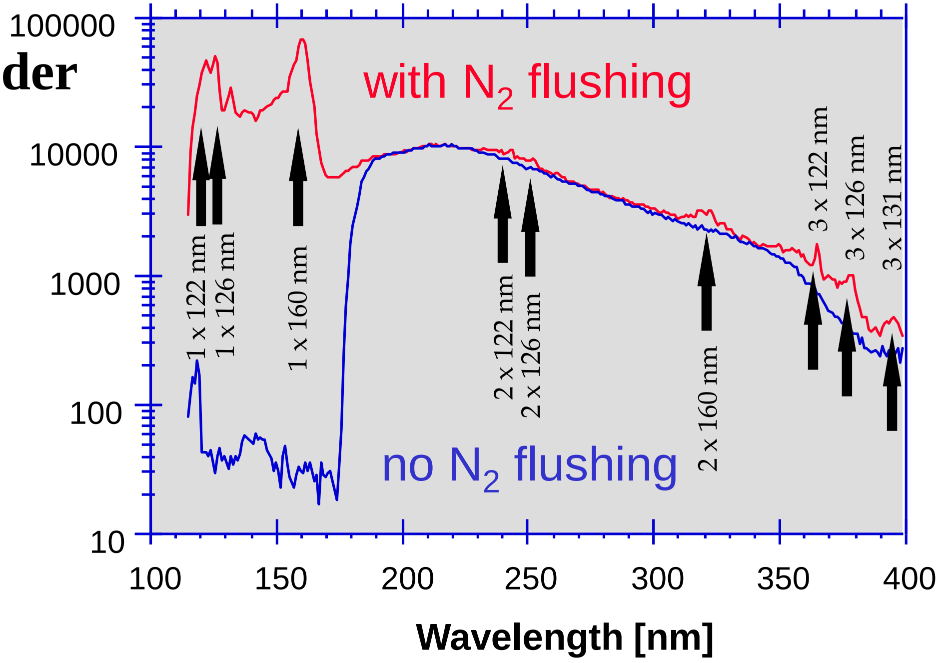
3.5 Sample Chamber

Atmosphere

Effect of flushing with an inert gas, e.g. N_2

1. **Transmission up to approx. 120 nm**
2. **Loss of the filtering effect for higher-order maxima (2. and 3. order)**

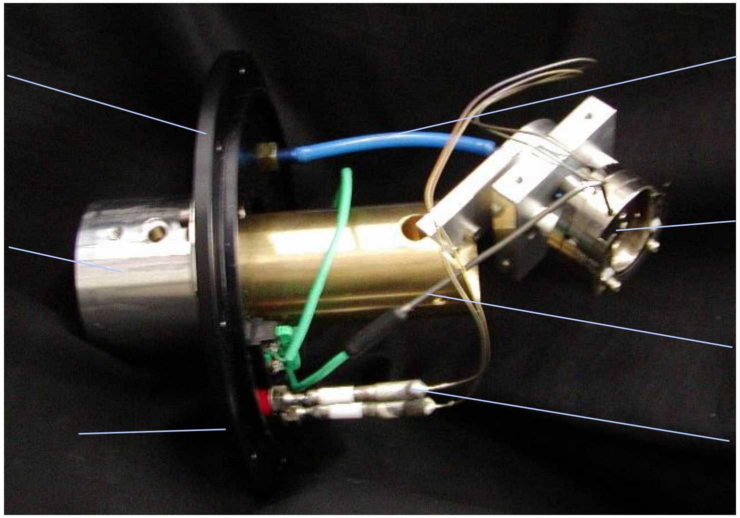




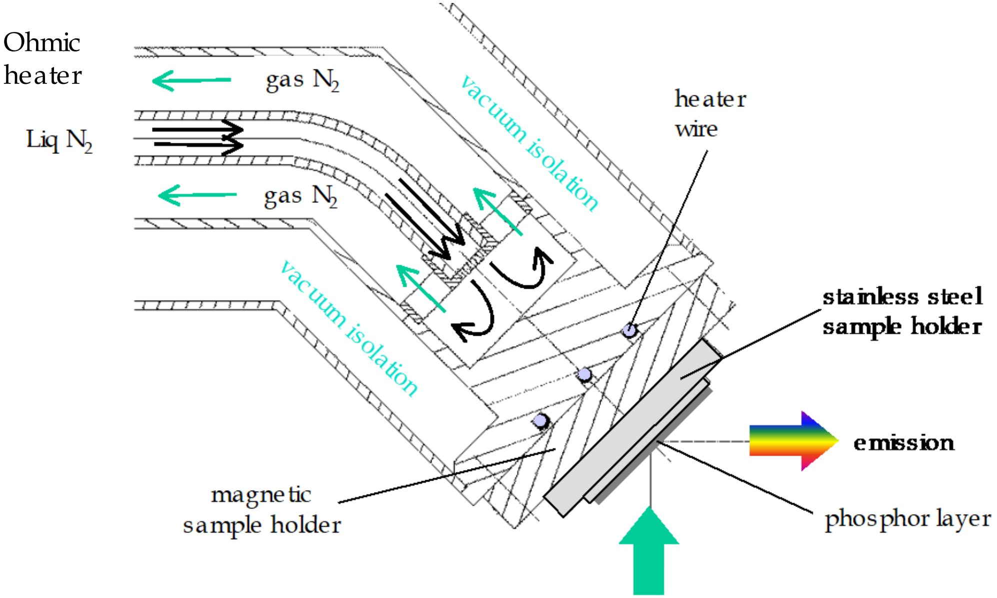
3.5 Sample Chamber

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 about 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

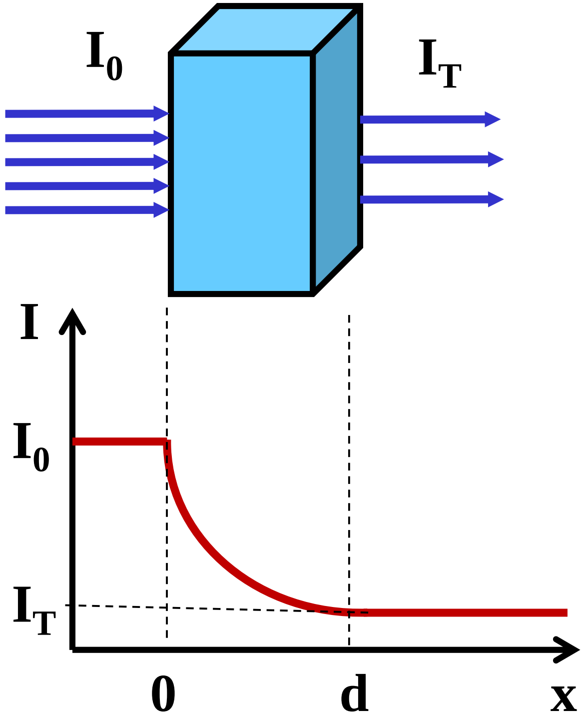
4.1.3 Deviation from the Lambert-Beer-Law

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):

$dI \sim I \cdot dx$ **or** $dI = -\alpha(\lambda) \cdot I \cdot dx$

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 $[l \cdot mol^{-1} cm^{-1}]$

$\boxed{\ln(x) = \log(x) \cdot \ln(10) \text{ or } \log(x) = \ln(x)/\ln(10)}$

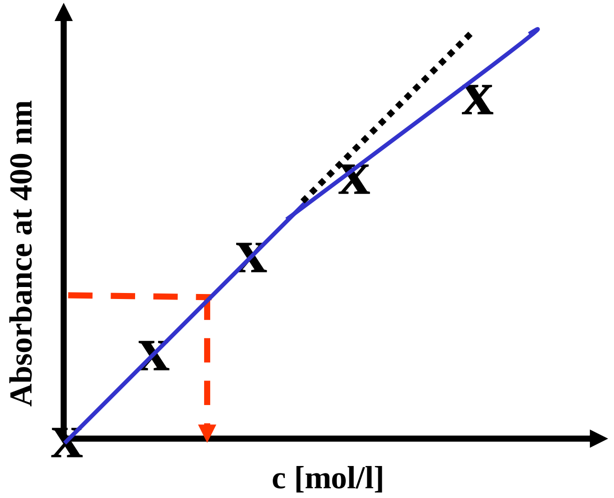
4.1.2 Validity of the Lambert-Beer-Law

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.**

  $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\ CrO_4^{2-} + 2\ H^+$

$$\boxed{A = \log \frac{I_0 + I_S}{I + I_S}}$$

- **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**

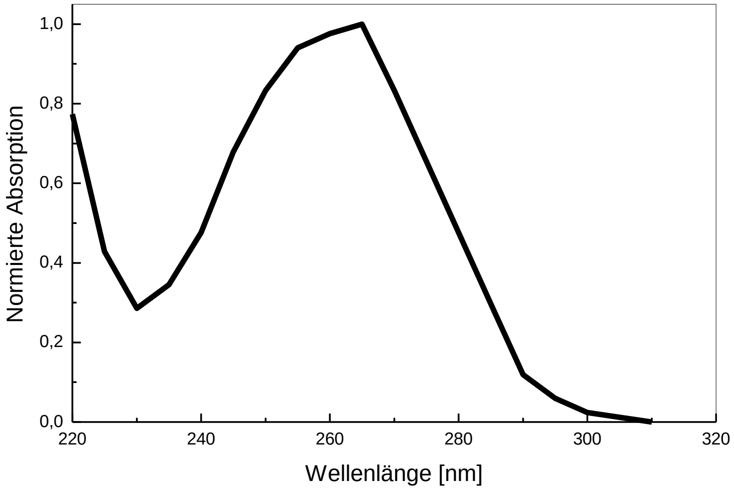
  ⇒ Mutual interaction of the chromophores in the solution

4.1.4 Extinction of Biologically Relevant Molecules

Analysis of biomolecules

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

Absorption spectrum of dTMP



Applications areas

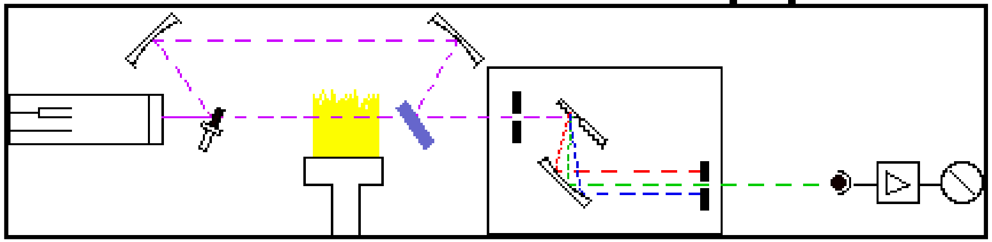
- Fusing of DNA
- Oxidation state of hemoglobin und Cytochrome c

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

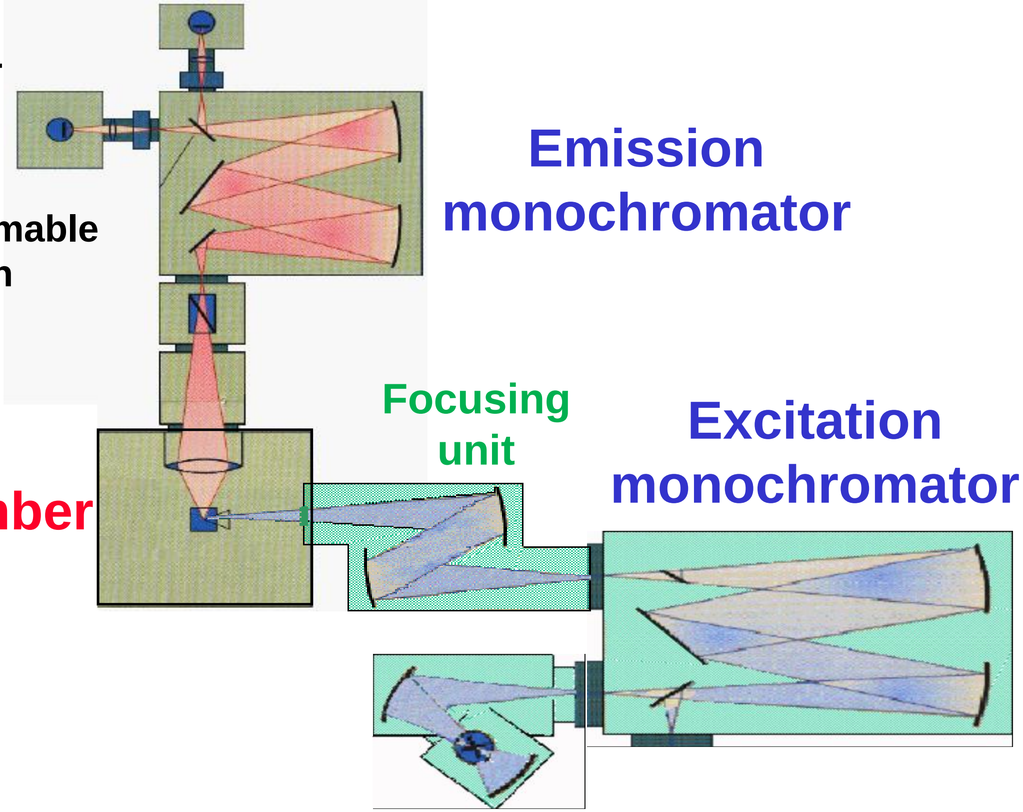
Definition

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



Analog detector

Photon counter PMT (Peltier cooled)

Programmable deflection mirror

Emission monochromator

Focusing unit

Excitation monochromator

Sample chamber

Programmable deflection mirror

Light source

Typical excitation wavelengths : 100 - 600 nm

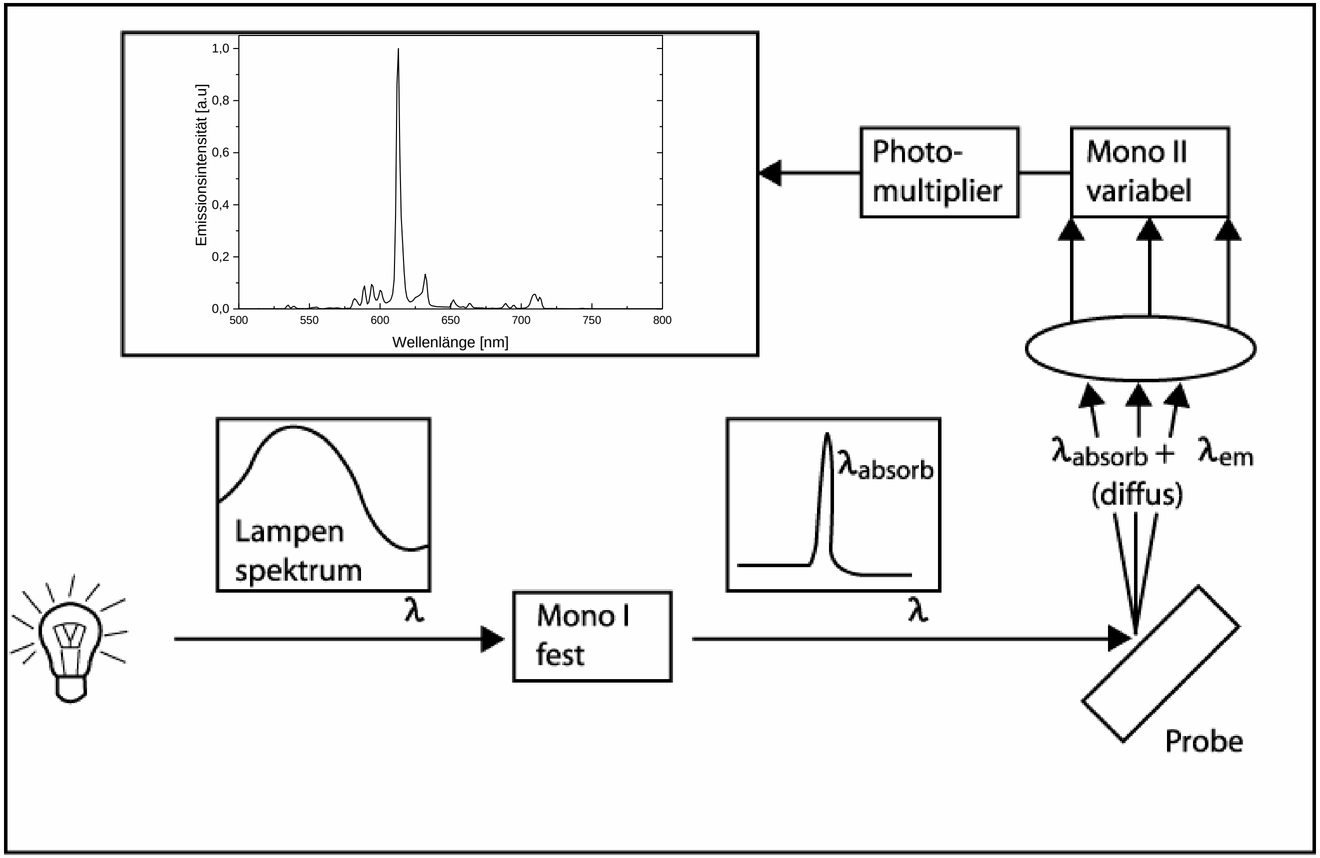
4.2.3 Emission Spectroscopy

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

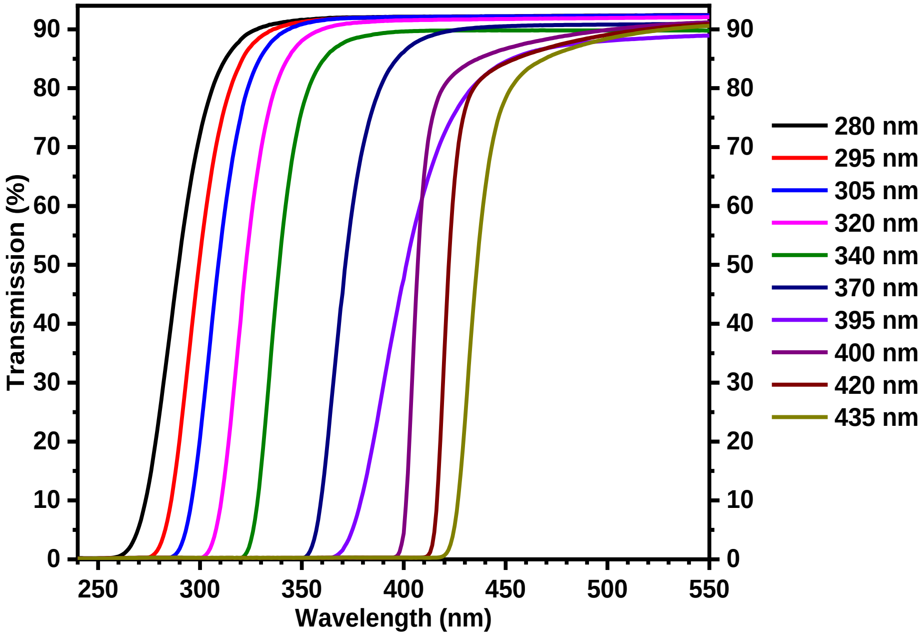


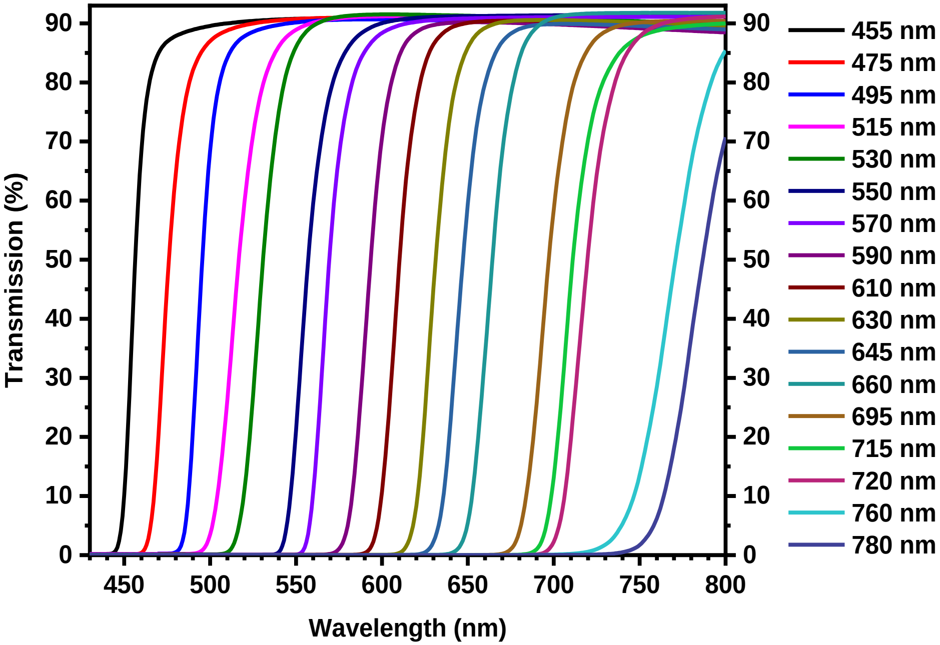
I(λ) must be compensated for the fluctuations of the light source, for example, by a quantum counter, reflected monochromatic light of excitation beam must be filtered

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

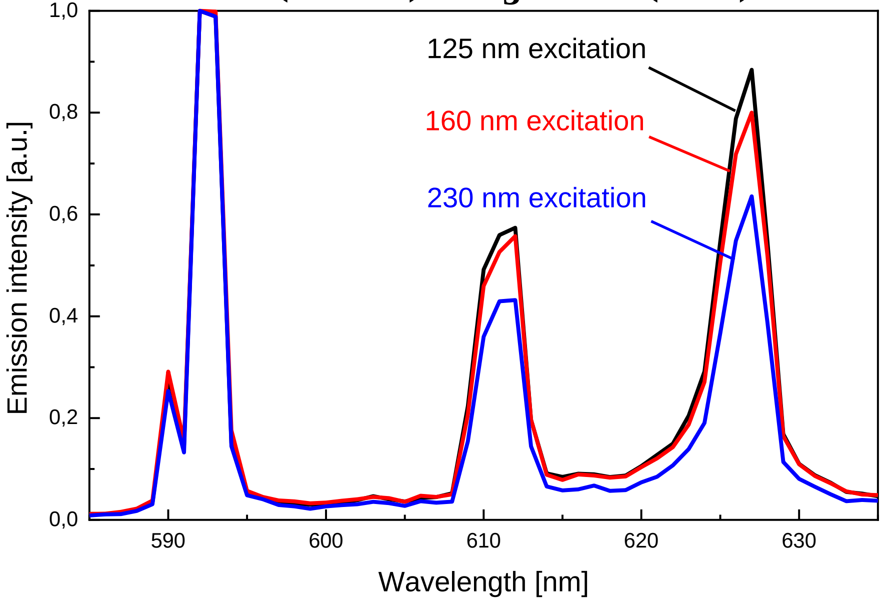




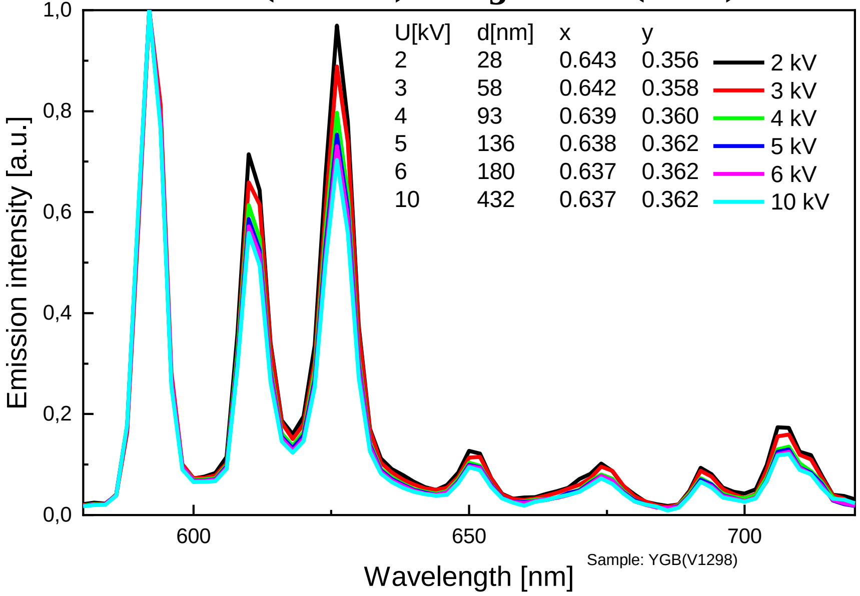
4.2.3 Emission Spectroscopy

The emission spectrum of a sample depends on the excitation energy

Photoluminescence of $(Y,Gd)BO_3:Eu^{3+}(5\%)$



Cathodoluminescence of $(Y,Gd)BO_3:Eu^{3+}(5\%)$



U[kV]	d[nm]	x	y
2	28	0.643	0.356
3	58	0.642	0.358
4	93	0.639	0.360
5	136	0.638	0.362
6	180	0.637	0.362
10	432	0.637	0.362

Sample: YGB(V1298)

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

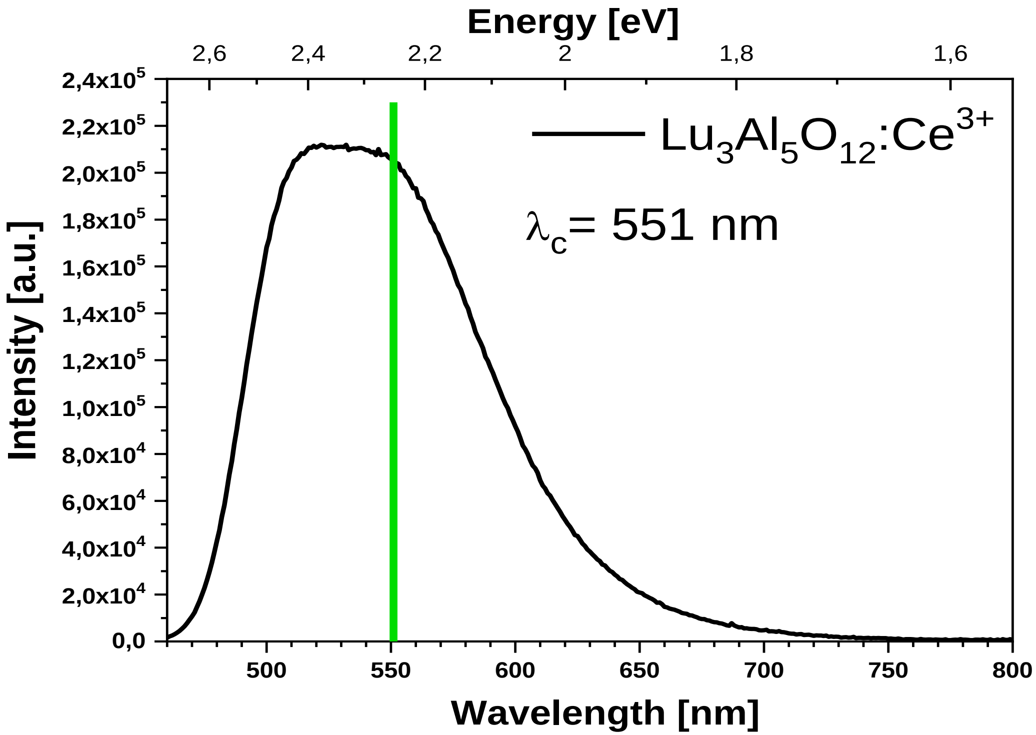
Penetration depth of electrons: $r \sim 0.046*U^{5/3}/\rho$ [µm] → 2 kV: 30 nm, 10 kV: 400 nm

4.2.3 Emission Spectroscopy

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

The centroid wavelength λ_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.

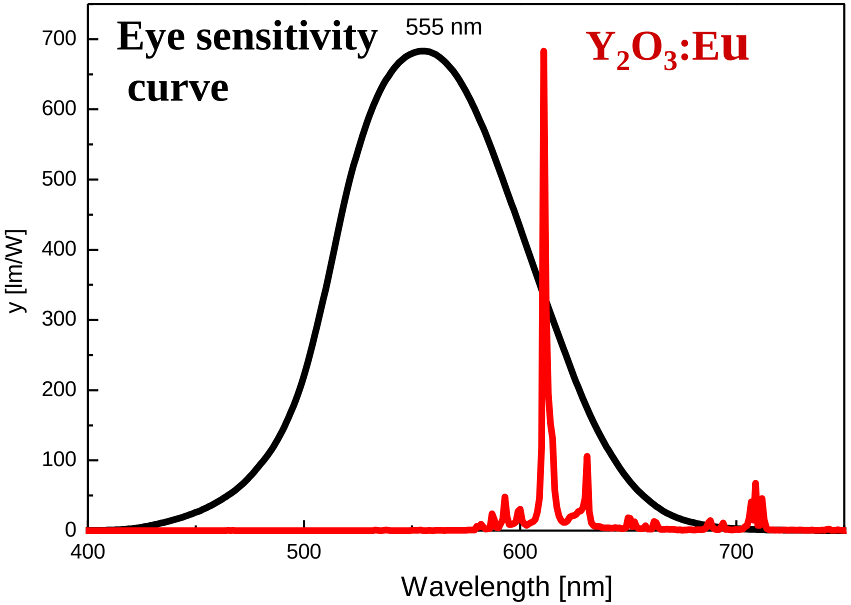
$$\lambda_c = \frac{\int_{\lambda_1}^{\lambda_2} \lambda \cdot S(\lambda) \cdot d\lambda}{\int_{\lambda_1}^{\lambda_2} S(\lambda)\, d\lambda}$$



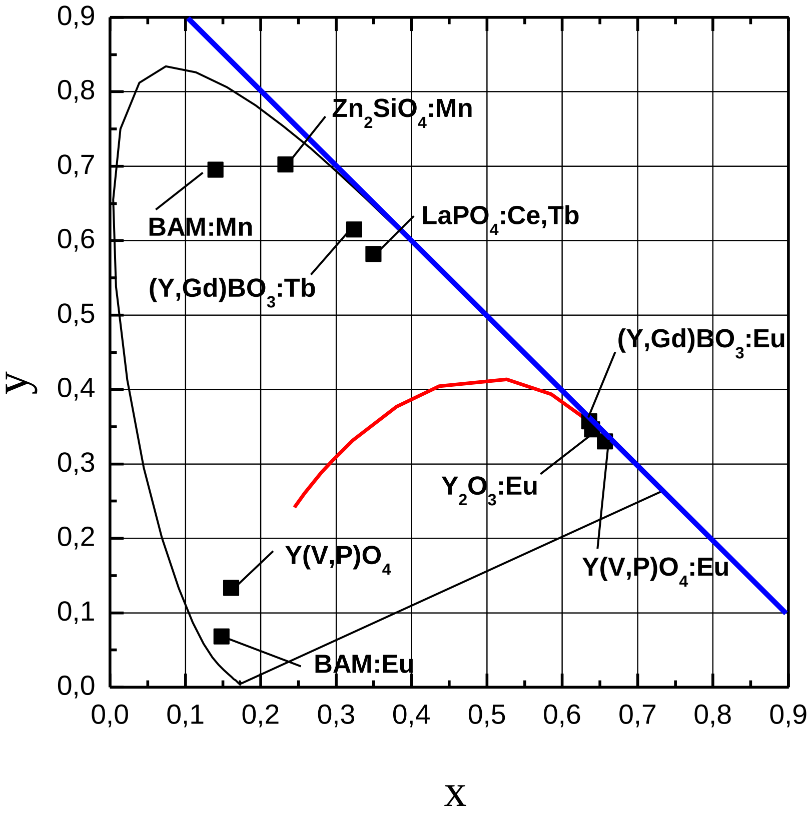
4.2.3 Emission Spectroscopy

From the emission spectrum of light physiological figures can be calculated

Lumen equivalent LE [lm/W]



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



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

4.2.3 Emission Spectroscopy

VUV Spectroscopy

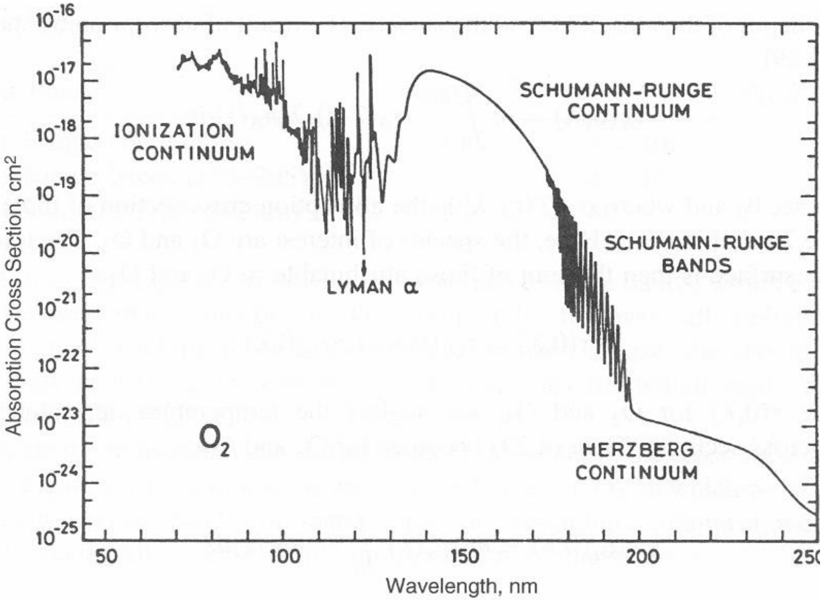
VUV spectroscopy requires a special instrumental setup, as VUV radiation is absorbed by O_2 and H_2O. CO_2 will be split photochemically into C and O_2 (dark layer on mirrors)

- **Lamp (deuterium), monochromator and detector in high vacuum (10^{-6} mbar)**

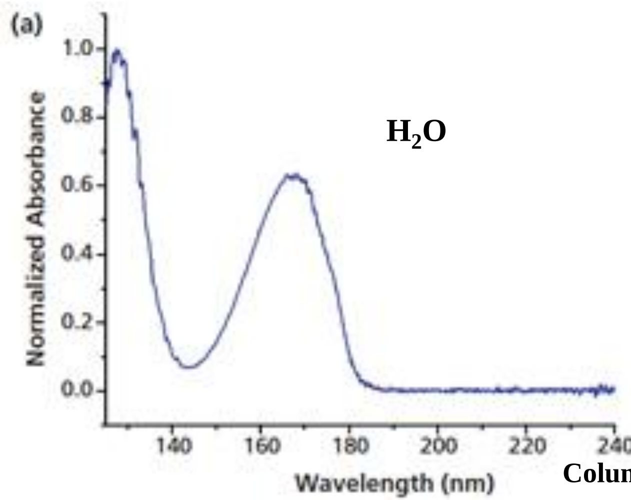
- **The sample chamber can be flooded with N_2. This facilitates changing of the sample. The sample chamber is connected to the rest of the system via LiF or MgF_2 windows**

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*



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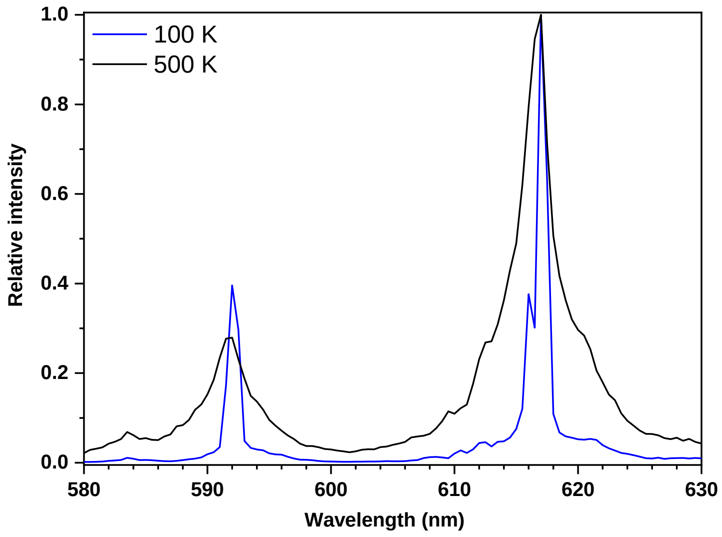
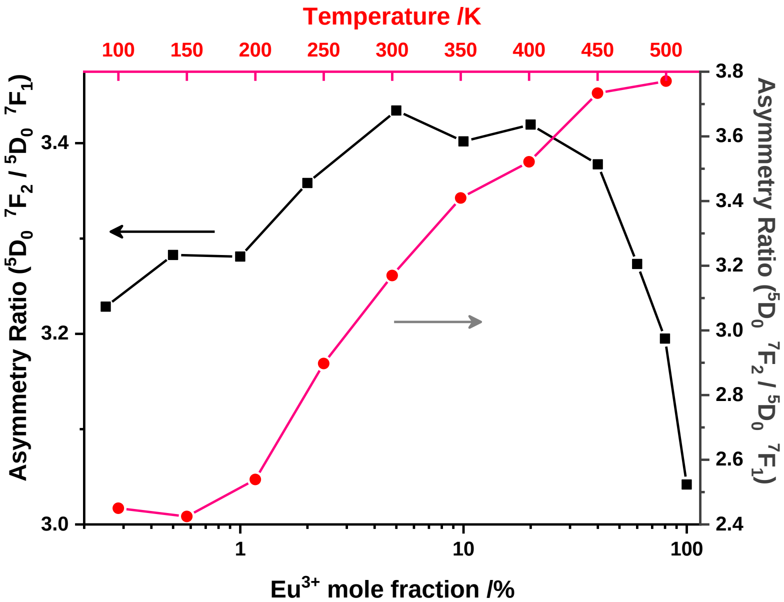
4.2.3 Emission Spectroscopy

Impact of temperature and site symmetry



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

Some 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.

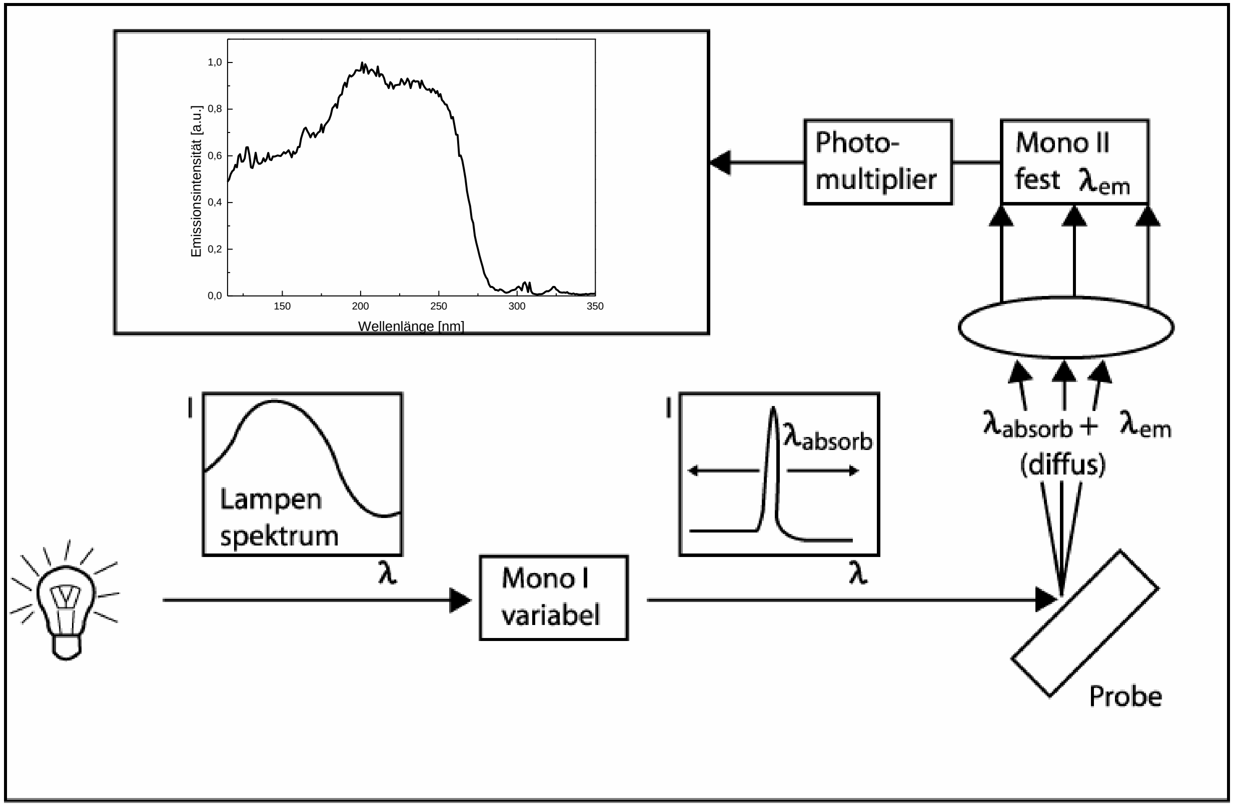
The asymmetry ratio can change depending on temperature, pressure or other parameters

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 (Y_2O_3:Eu)



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

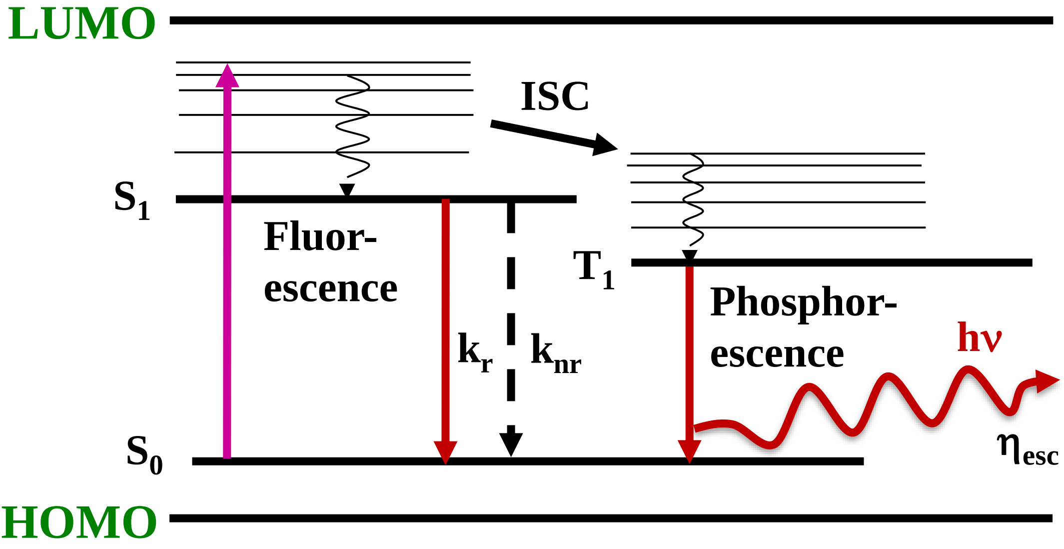
$$I(\lambda_{exc}) = I^{sample}(\lambda_{exc}) / I^{set}(\lambda_{exc})$$

4.2.5 Quantum Yield

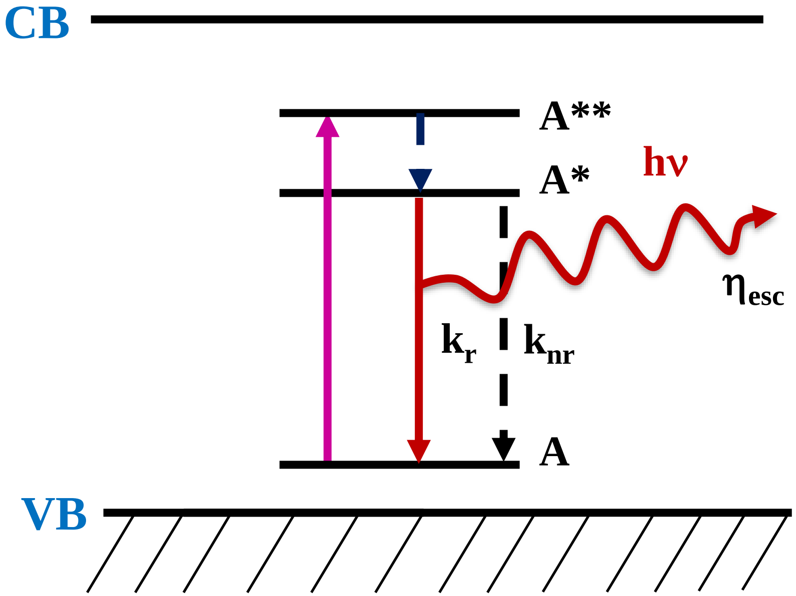
Absorption of radiation yields excited states, which then return to the ground state

Excitation energy < E_G of solvent or host crystal ~ ΔE of optical centres

Organic materials (luminophores, dyes)



Inorganic materials (phosphors)



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

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**

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

4.2.5 Quantum Yield

Relative measurements in comparison to references

Typical reference materials (determined by PTB, Germany)

Spectral region	Material	QY at 254 nm (a Hg line)
UV-B	$LaPO_4$:Ce	90%
UV-A	$BaSi_2O_5$:Pb	88%
Blue	$BaMgAl_{10}O_{17}$:Eu	89%
Green	Zn_2SiO_4:Mn	80%
Red	Y_2O_3:Eu	84%

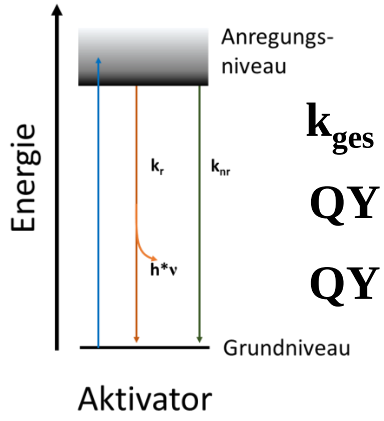
For the determination of the quantum yield one determines the integral I of the emission spectrum (proportional to the number of emitted photons) and the reflectance R of thesubstance or the reference at the excitation wavelength λ_{exc}

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

4.2.5 Quantum Yield

Absolute methods for the determination of QY

- **Internal quantum yield:** **decay time**

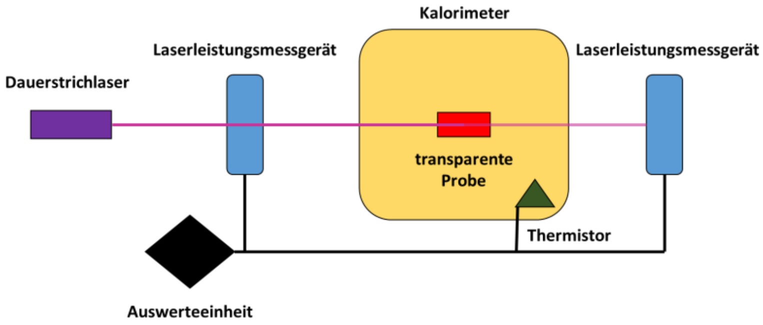


$$k_{ges} = k_r + k_{nr}$$

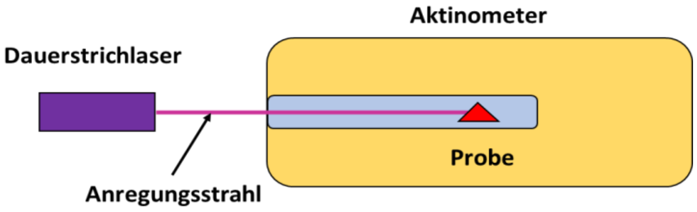
$$QY = k_r / k_{ges}$$

$$QY = \tau / \tau_r$$

- **External quantum yield:** **calorimetric**

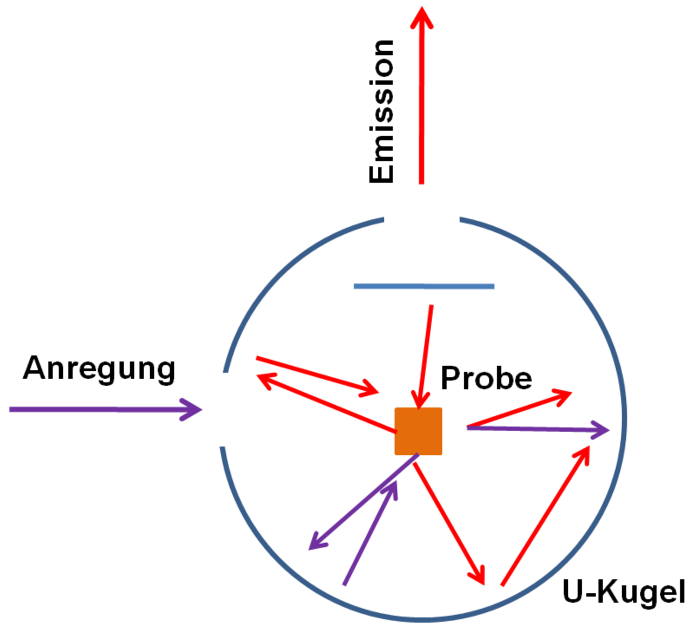


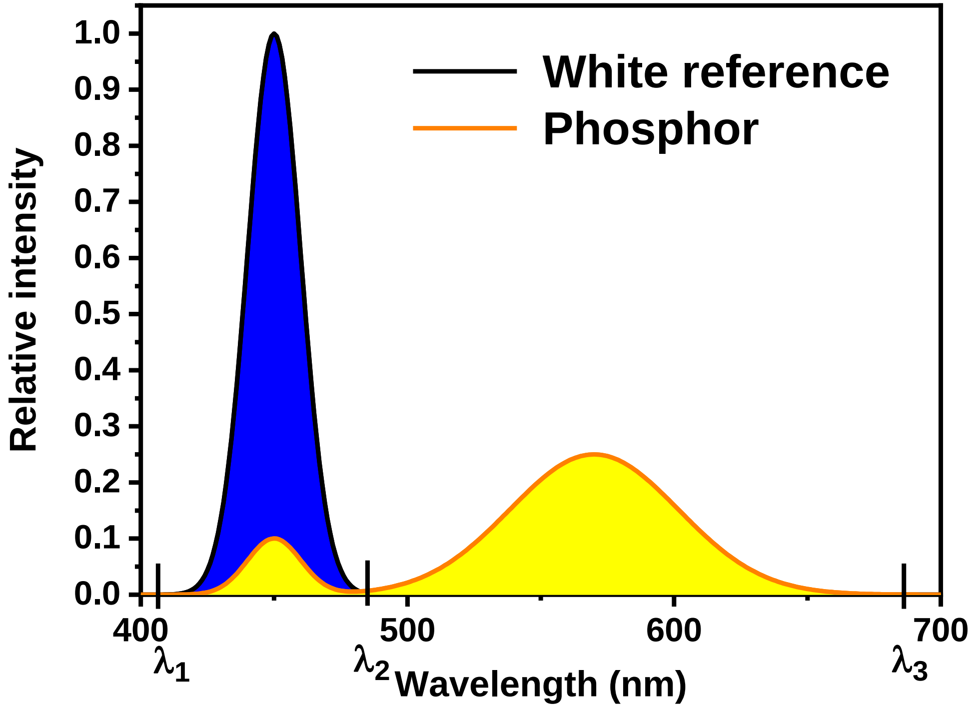
- **External quantum yield:** **actinometric**



4.2.5 Quantum Yield

External quantum yield: absolute methods by using an integration sphere





$$\mathbf{EQA_{sample}} = \frac{\mathbf{nE}}{\mathbf{nA}} = \frac{\int_{\lambda_2}^{\lambda_3} \frac{\lambda}{hc}\left[I_{emission}^{sample}(\lambda) - I_{emission}^{reference}(\lambda)\right] d\lambda}{\int_{\lambda_1}^{\lambda_2} \frac{\lambda}{hc}\left[I_{excitation}^{reference}(\lambda) - I_{excitation}^{sample}(\lambda)\right] d\lambda}$$

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 Σk is the sum of the rate constants for
  all processes that depopulate the excited state

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

- Radiative lifetime τ_r is related to k_r

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

- Measured lifetime τ depends on the sum of the rate constants

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

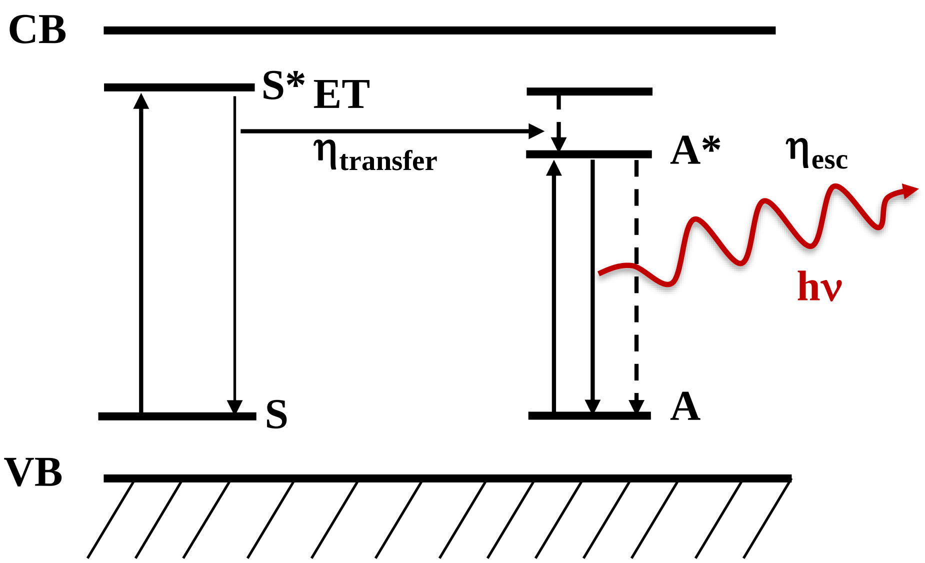
- The observed fluorescence lifetime τ, is the average
  time the molecule spends in the excited state
  $\Rightarrow$ Measured lifetime is proportional to quantum yield

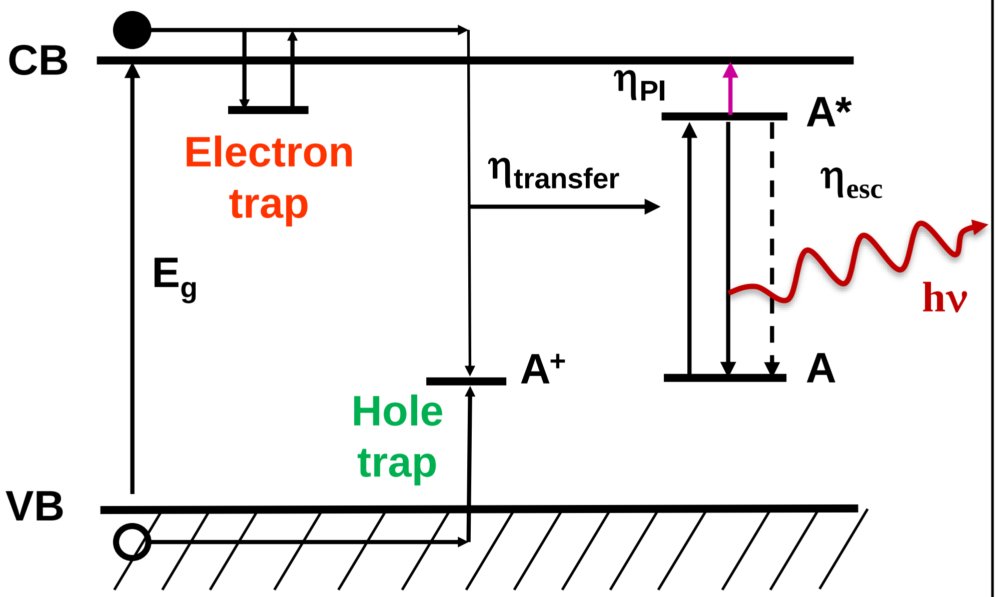
$$\boxed{QY = \frac{\tau}{\tau_r}}$$

4.2.5 Quantum Yield

Excitation by VUV or EUV radiation

Excitation energy ~ ΔE of sensitisers or E_G of the host matrix/solvent





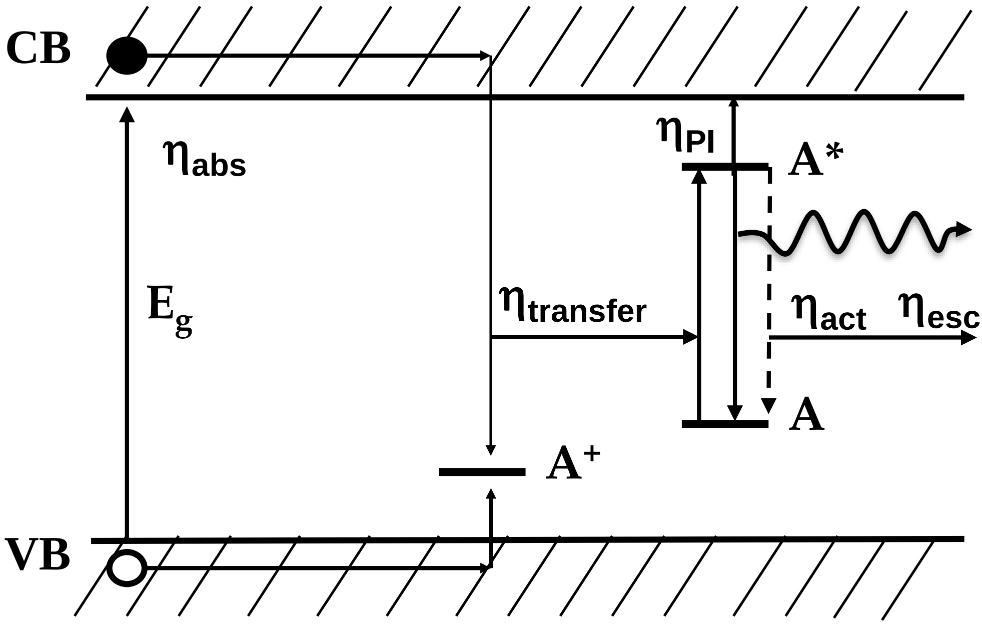
$$\eta_{total} = \eta_{act} * \eta_{transfer} * \eta_{esc} * (1 - \eta_{PI})$$ with PI = Photoionisation

η_{total} = External Quantum Yield (EQY) or External Quantum Efficiency (EQE)

η_{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)

IQY $= \eta_{act}$

$= k_r/(k_r + k_{nr})$

$= \tau/\tau_r$

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)

EQY $= N_{h\nu(\text{emitted})}/N_{h\nu(\text{absorbed})}$

$= \eta_{transfer} * \eta_{act} * \eta_{esc} * (1- \eta_{PI})$

(No correlation to decay time!)

Emission spectrum (Ulbricht sphere)

Light Yield (Fluorescence Intensity)

LY $= EQY * \eta_{abs}$

(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)	External Quantum Yield (Efficiency)
Efficiency of a luminescent center	Efficiency of a luminescent powder or solution
Microscopic view	Macroscopic view
Decay time measurement	Emission spectrum measurement
Fluorescence spectrometer	Ulbricht (integrating) sphere

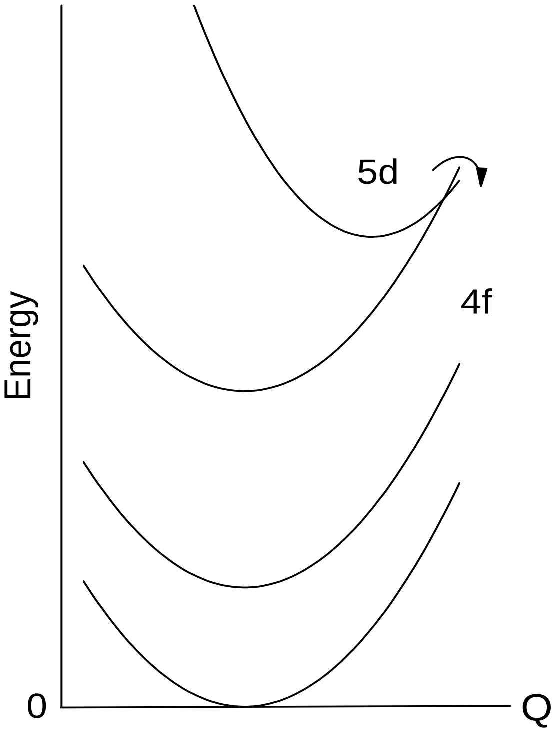
$$\boxed{\mathrm{IQY} = \frac{\tau}{\tau_r}}$$

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

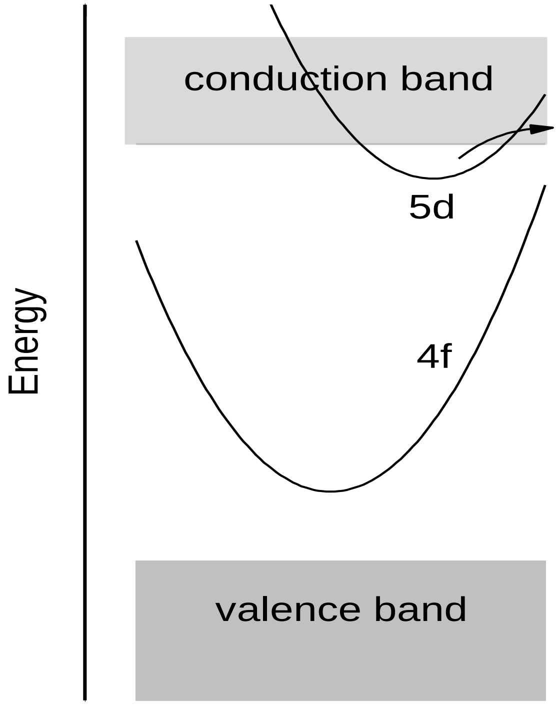
with τ = experimental lifetime and τ_r = radiative lifetime

4.2.5 Quantum Yield

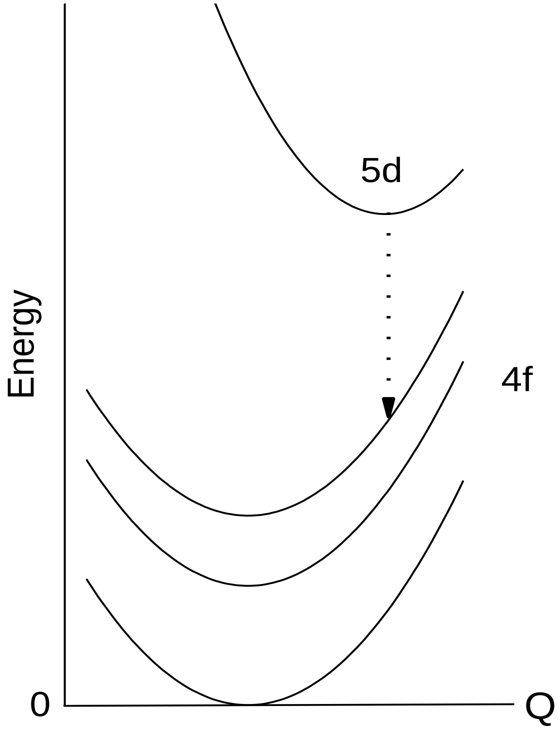
Several mechanisms for the quenching of luminescent materials results in the reduction of the photoluminescence quantum yield, e.g.



Thermally activated InterSystem Crossing (ISC)



Thermally activated PhotoIonization (PI)

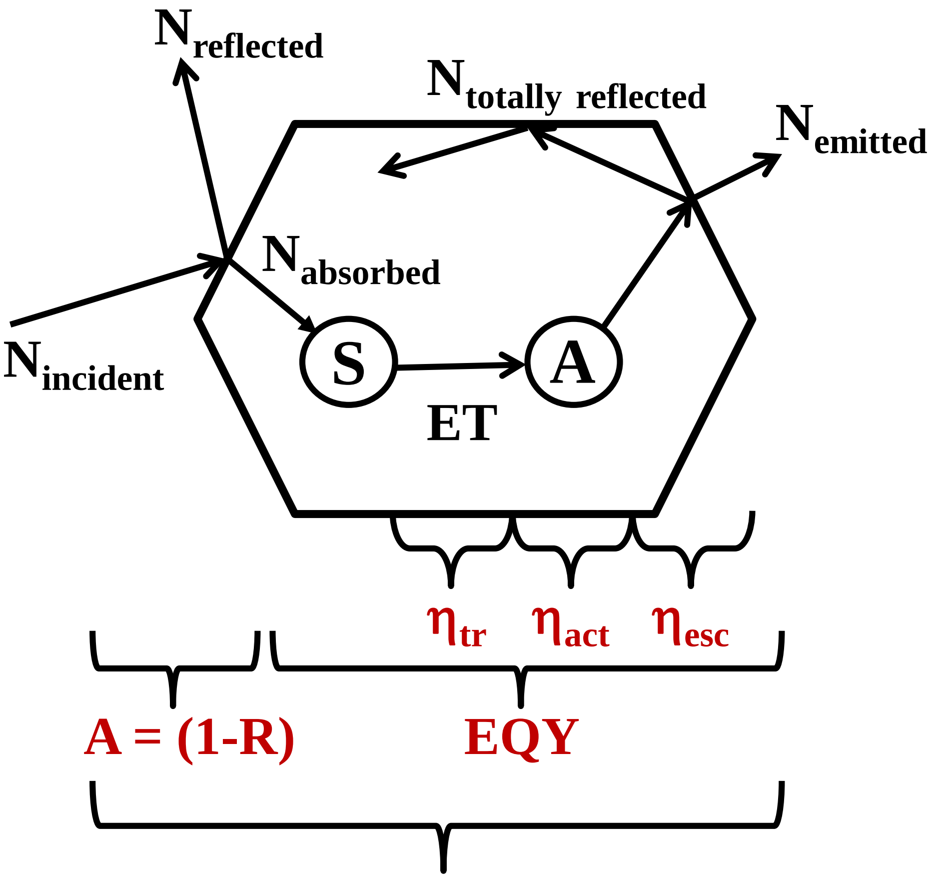


Multi Phonon Relaxation (MPR)

4.2.6 Light Yield

Light Yield LY = Fluorescence Intensity ~ I(λ_{exc}) (or integral lamp output)

Light conversion at a phosphor particle



LY = EQY * A = EQY * (1-R) [0.....1]

External Quantum Yield (EQY)

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

Absorption A

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

Reflectance R

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

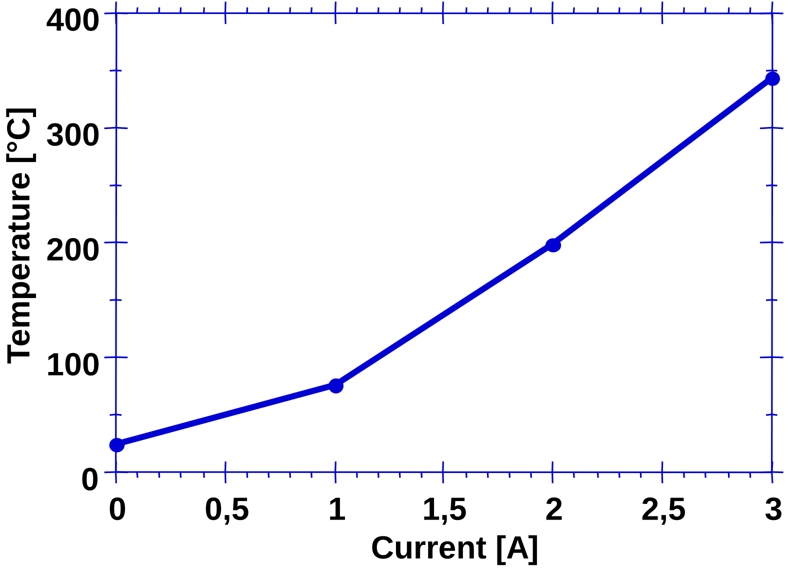
Light Yield LY

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

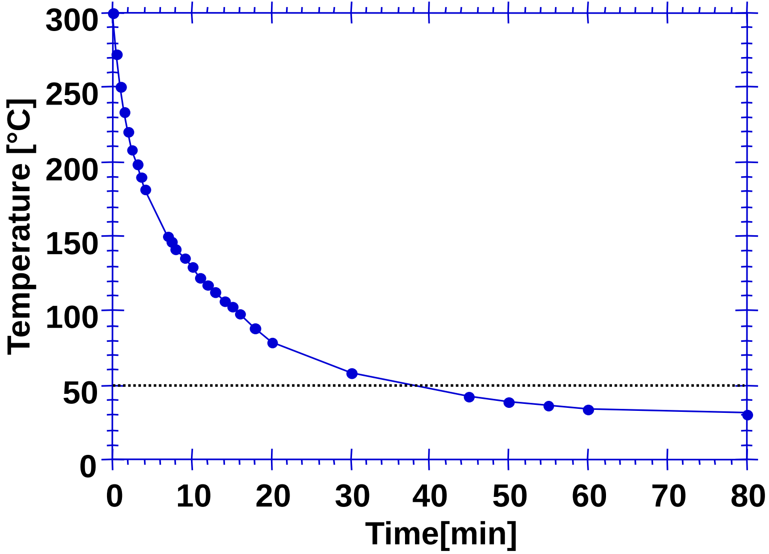
4.2.7 Temperature Resolved Spectroscopy

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

Heating characteristics



Cooling characteristics



Heating the sample

N_2-flushing cools the sample

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

Cooling the sample

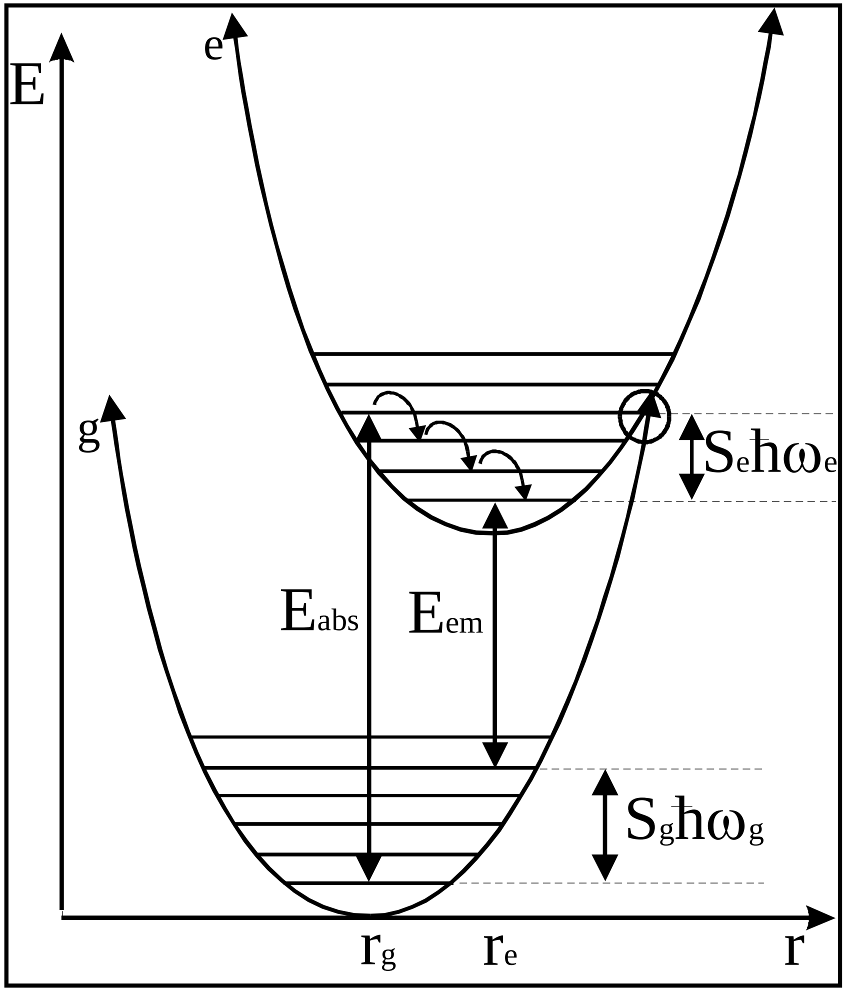
< 0 °C: H_2O Resublimation

< -78 °C: CO_2 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

  $S = S_e h\omega_e + S_g h\omega_g$

- **Full width at half maximum of the emission band**

  FWHM ~ $\sqrt{S}$

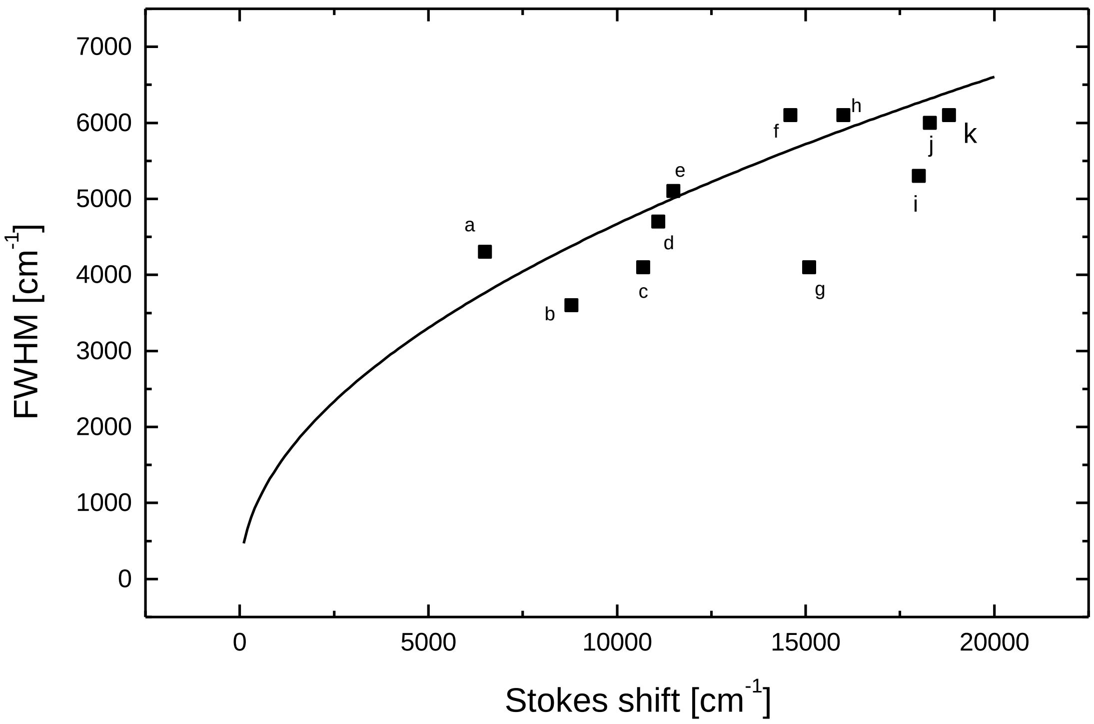
- **Thermal quenching decreases with increasing $\Delta R = r_e - r_g$**

- **ΔR depends on the activator-host lattice interaction**

4.2.7 Temperature Resolved Spectroscopy

Thermal quenching of luminescence processes: FWHM = f(Stokes Shift)

h

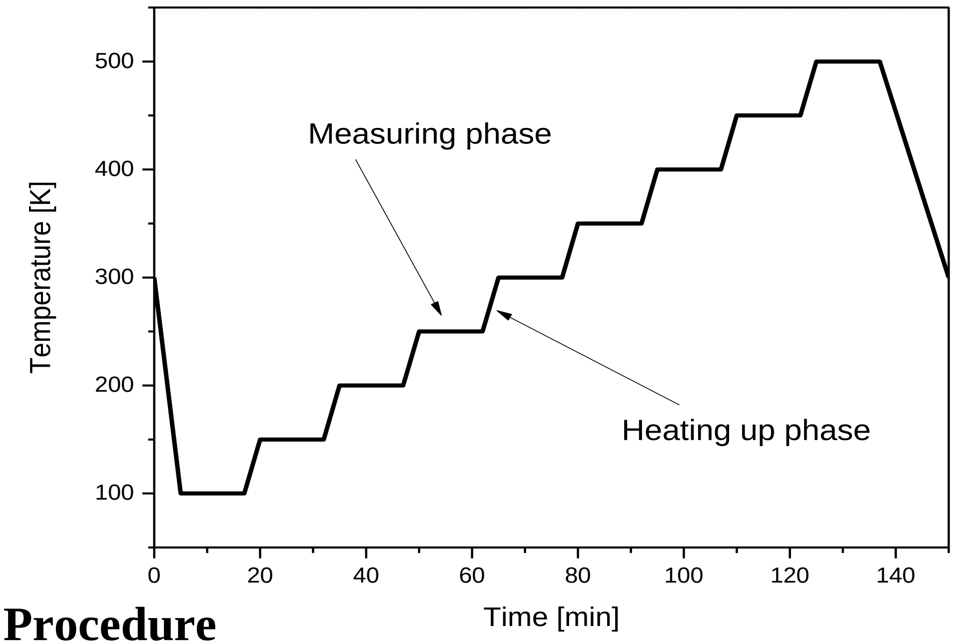


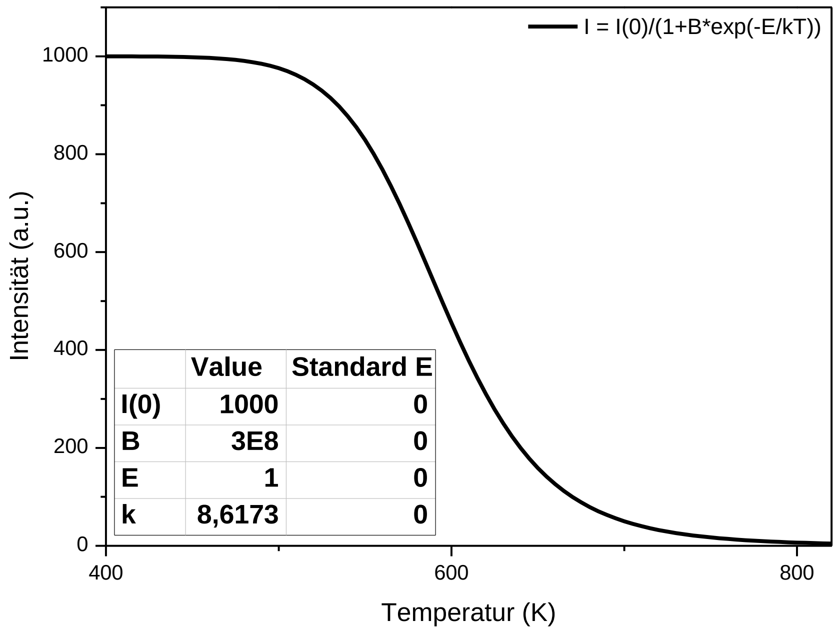
- **a** $Ba_2MgGe_2O_7$:Bi
- **b** $Ca_3Si_2O_7$:Pb
- **c** LaOCl:Bi
- **d** $BaLaYB_9O_{16}$:Sb
- **e** $Y_2Si_2O_7$:Bi
- **f** $CaZrB_2O_6$:Pb
- **g** LaOCl:Sb
- **h** $CaWO_4$
- **i** $SrLaBO_4$:Pb
- **j** $YTaO_4$:Nb
- **k** $CaMgSi_2O_6$:Ti

Extent of Thermal Quenching ↓

4.2.7 Temperature Resolved Spectroscopy

Thermal quenching experiments ⇒ Intensity/integral as f(T)





	Value	Standard E
I(0)	1000	0
B	3E8	0
E	1	0
k	8,6173	0

Procedure

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

$$I(T) = A_0 + I_0/(1 + B\exp(-\Delta E/k_BT))$$ **„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}, …)

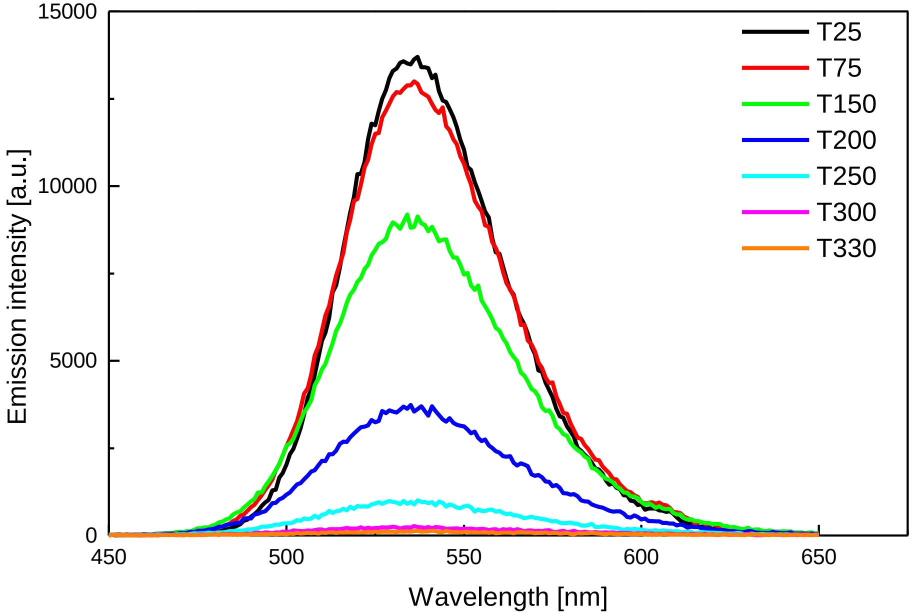
$$N_{\mathrm{NR}} = N_{\mathrm{NR,max}} * e^{-\frac{E}{kT}}$$

$$IQE = \frac{N_{\mathrm{R}}}{N_{\mathrm{R}} + N_{\mathrm{NR}}} = \frac{1}{1 + \frac{N_{\mathrm{NR}}}{N_{\mathrm{R}}}}$$

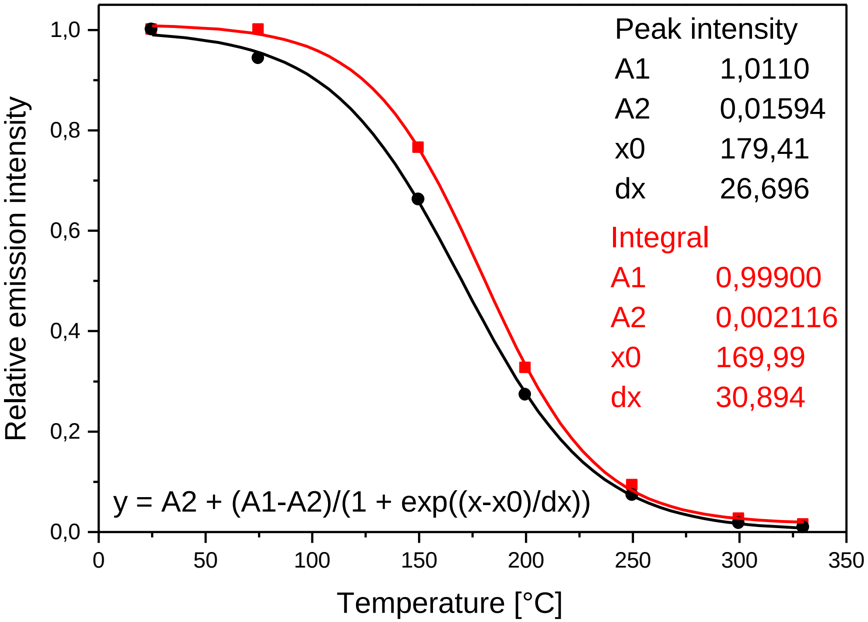
4.2.7 Temperature Resolved Spectroscopy

Example of $SrGa_2S_4:Eu$

Emission spectrum (460 nm excitation)



Emission intensity

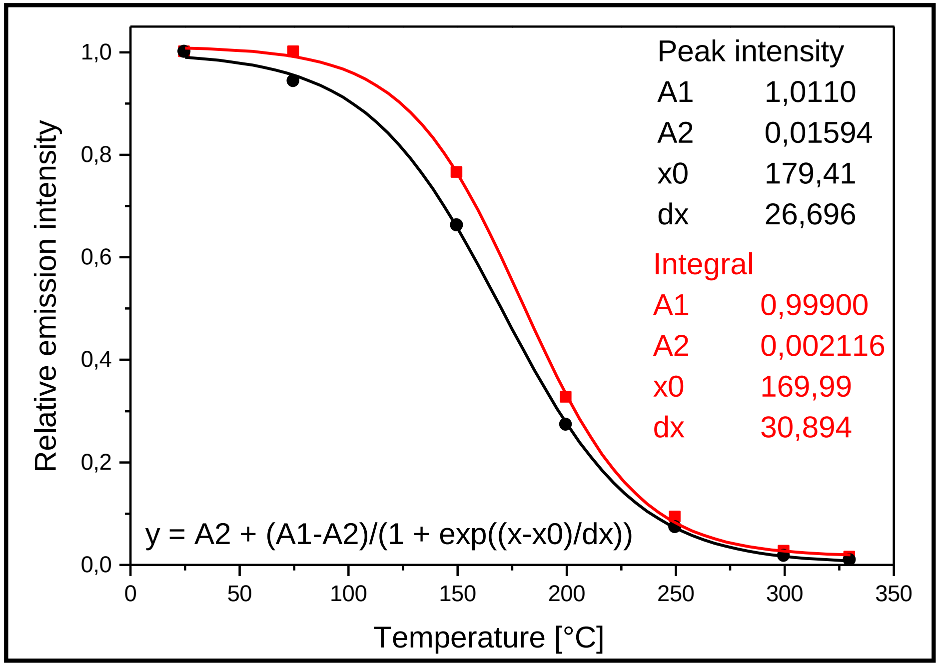


- $T_{1/2}$ = Temperature at which the luminescence process declines by 50% of its low temperature emission intensity ($SrGa_2S_4:Eu$ ~ 170 °C)
- In many applied inorganic phosphors the quantum yield starts increasing distinctly from 100 – 150 °C upwards

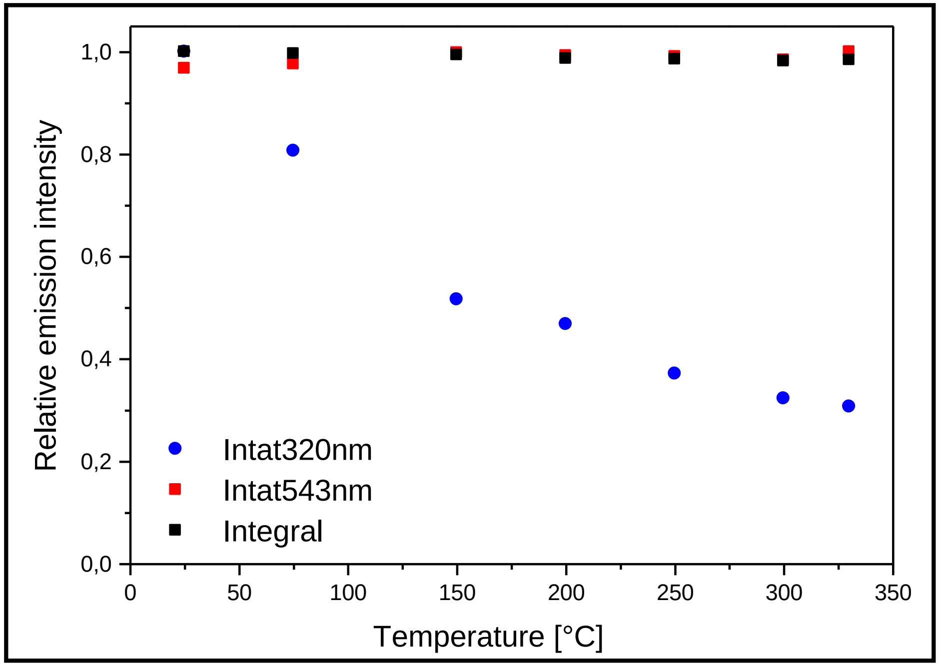
4.2.7 Temperature Resolved Spectroscopy

Comparison between a line and a band emitter

$SrGa_2S_4$:Eu (460 nm excitation)



$LaPO_4$:Ce,Tb (254 nm excitation)



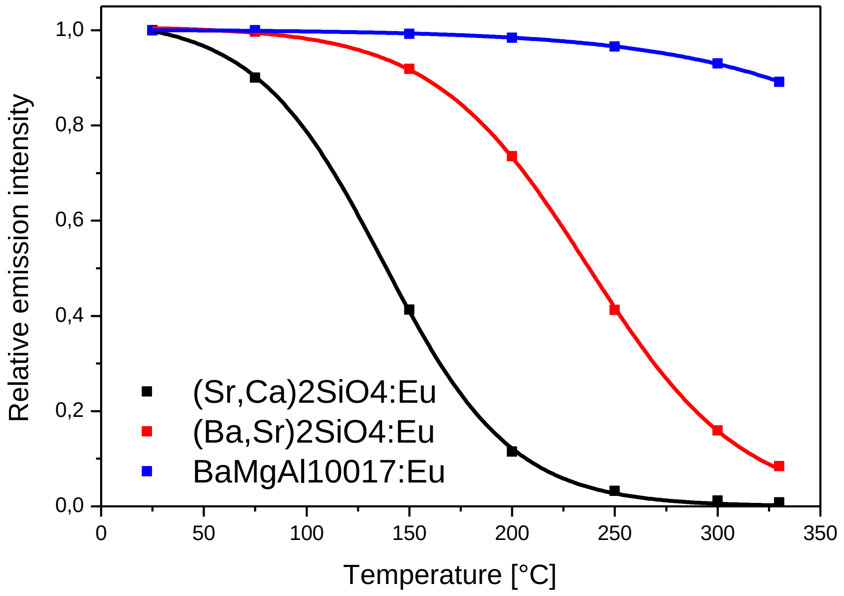
Temperature resolved spectra for the investigation of

- **Thermal quenching of the luminescence**
- **Energy transfer, e.g. in $LaPO_4$:Ce,Tb** $Ce^{3+} \rightarrow Tb^{3+}$

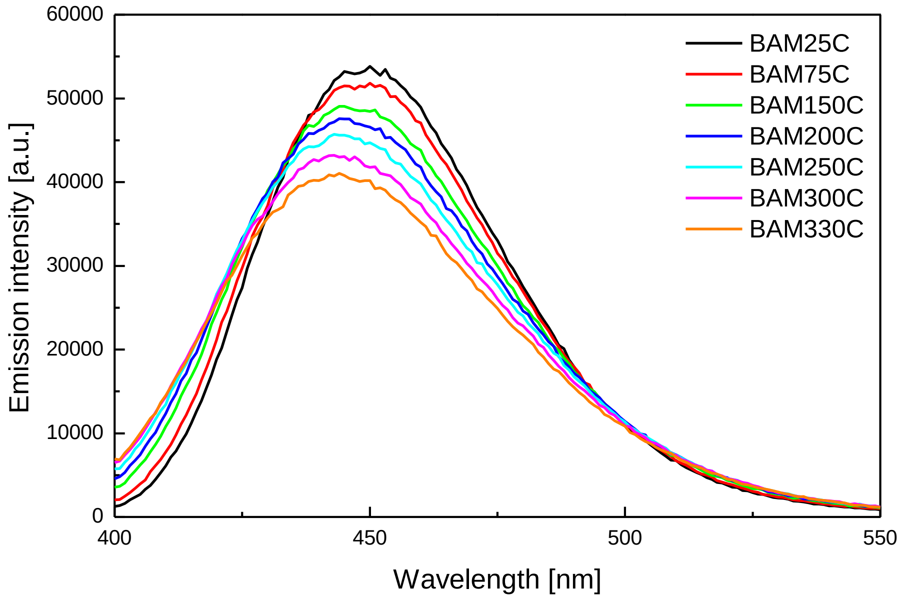
4.2.7 Temperature Resolved Spectroscopy

Thermal quenching of Eu^{2+} phosphors

Quantum yield as a function of temperature



Spectral width of the emission band of $BaMgAl_{10}O_{17}$:Eu as a function of T



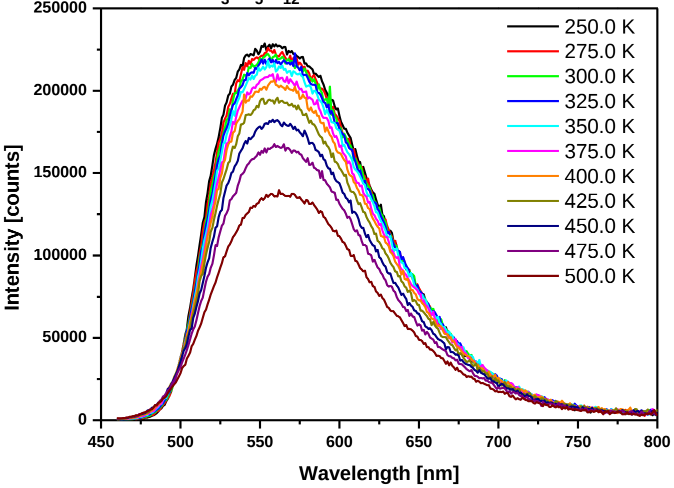
Stokes shift: $BaMgAl_{10}O_{17}$:Eu < $(Ba,Sr)_2SiO_4$:Eu < $(Sr,Ca)_2SiO_4$:Eu

Thermal quenching: $BaMgAl_{10}O_{17}$:Eu < $(Ba,Sr)_2SiO_4$:Eu < $(Sr,Ca)_2SiO_4$:Eu

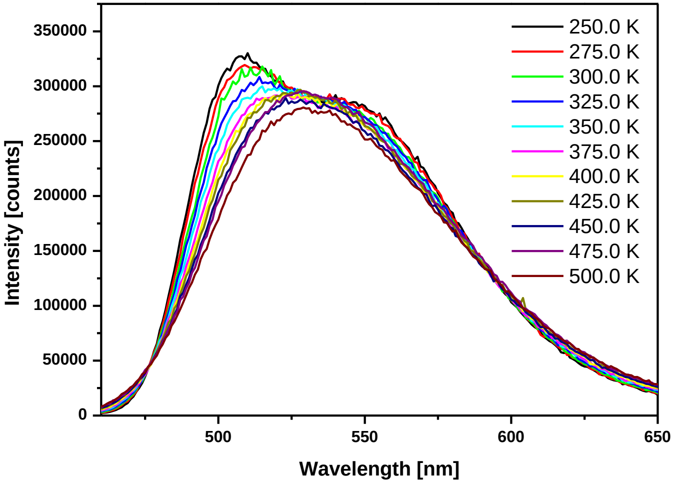
4.2.7 Temperature Resolved Spectroscopy

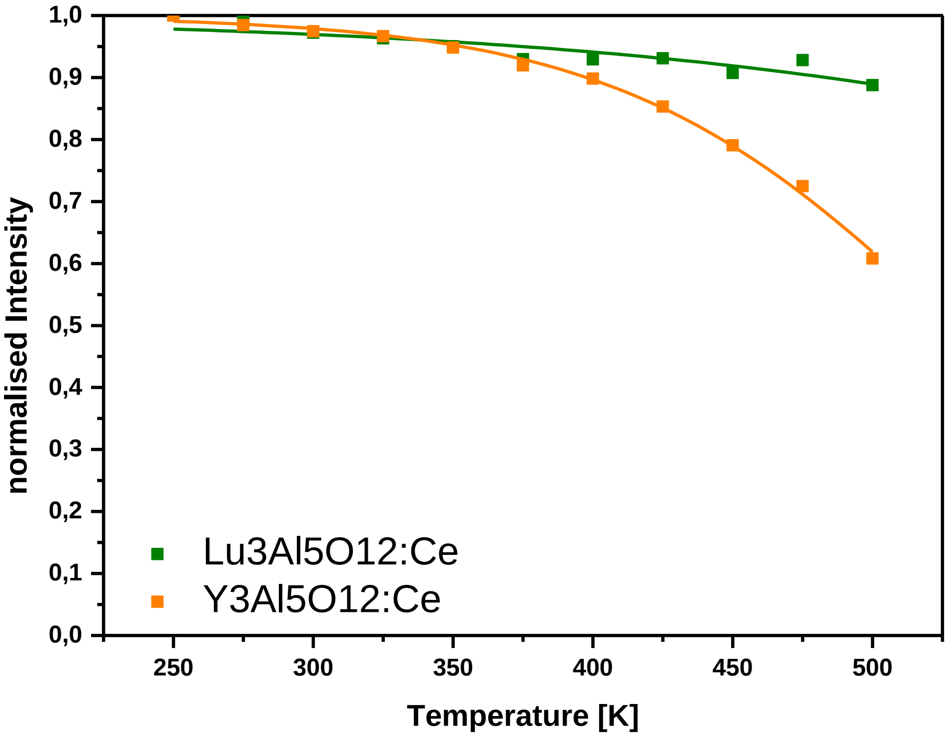
Thermal quenching of Ce^{3+} phosphors

Sample: $Y_3Al_5O_{12}:Ce^{3+}$



Sample: $Lu_3Al_5O_{12}:Ce^{3+}$





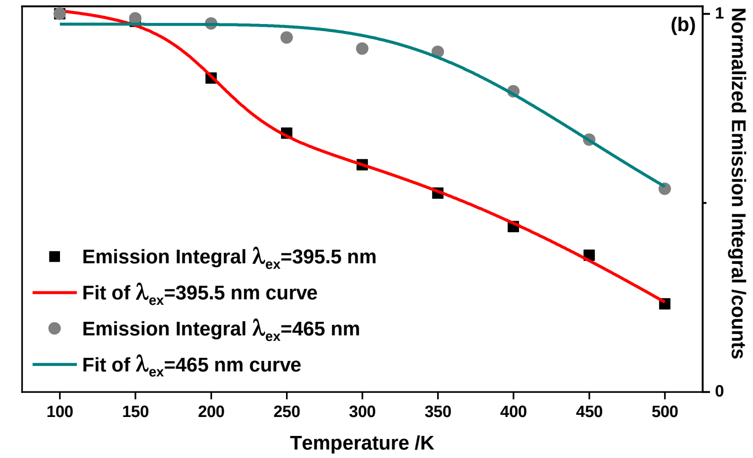
Stokes shift: $Lu_3Al_5O_{12}:Ce < Y_3Al_5O_{12}:Ce$

Thermal quenching: $Lu_3Al_5O_{12}:Ce < Y_3Al_5O_{12}:Ce$

Re-absorption leads to the observed color point shift!

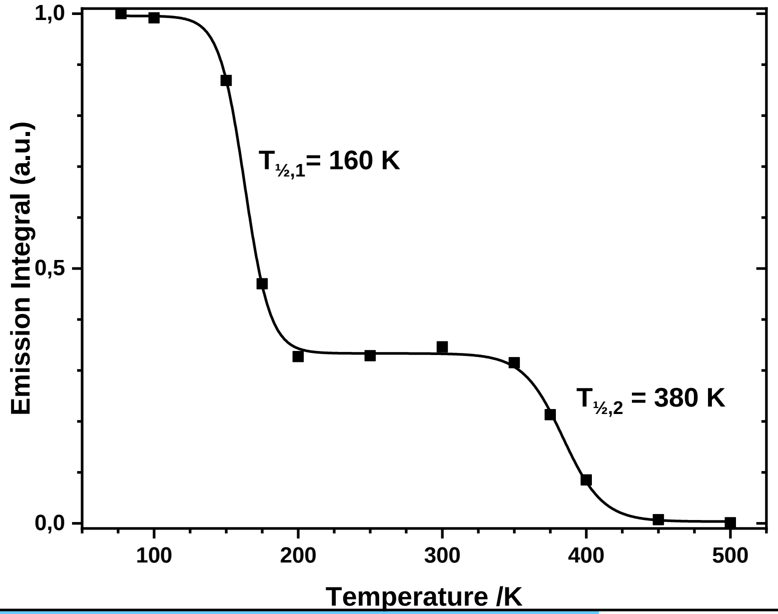
4.2.7 Temperature Resolved Spectroscopy

Special cases



- **Simultaneous excitation via band gap and direct excitation of the activator can result in a bi-sigmoidal curve (example: $LiEuMo_2O_8$)**
- **Simultaneous emission of two luminescent centers in the same spectral region can also result in a bi-sigmoidal curve (example: $Rb_2Ge_4O_9:Mn^{4+}$)**
- **The curve can be fitted via weighted addition of two fitting functions. This yield two $T_{1/2}$ values:**

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

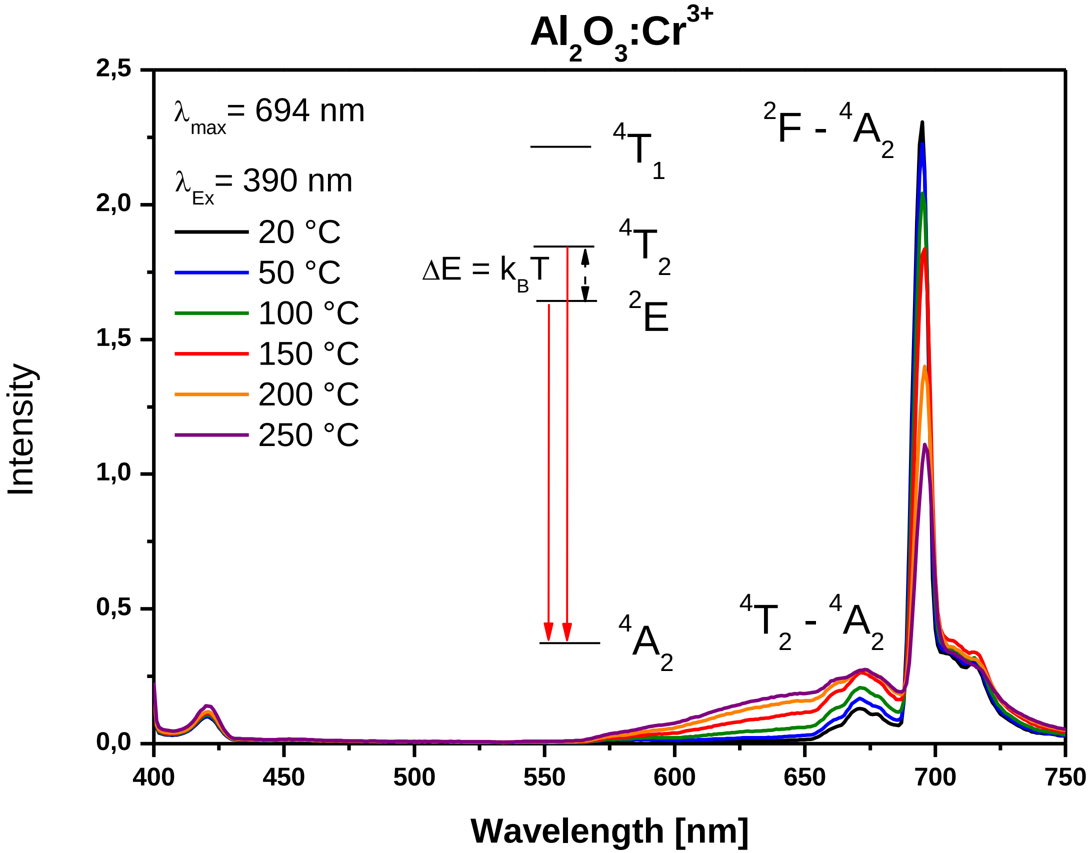


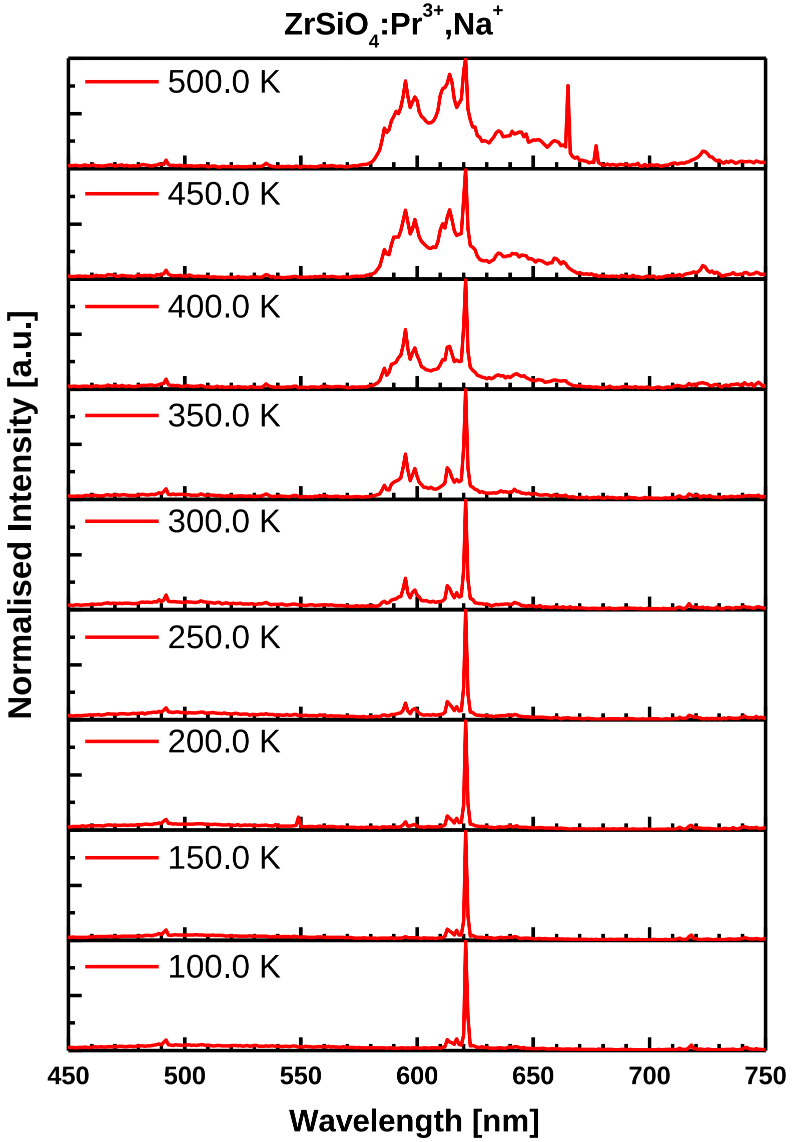
Lit.:

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

4.2.7 Temperature Resolved Spectroscopy

Thermal excitation of higher radiative states

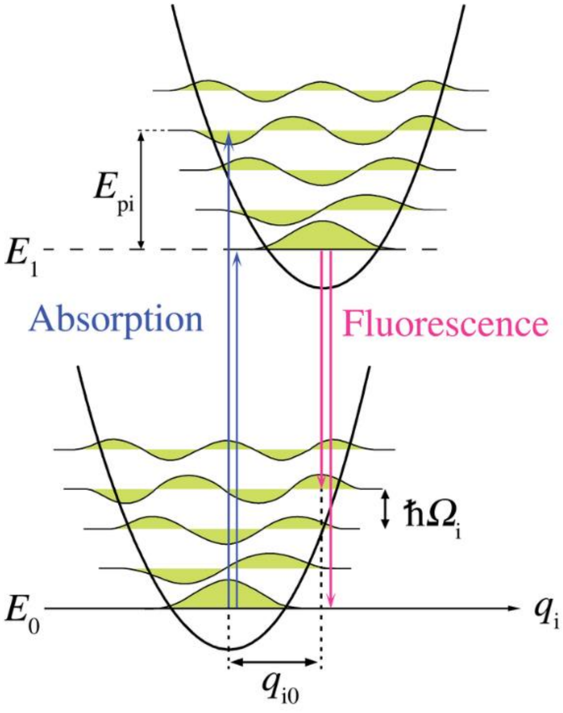


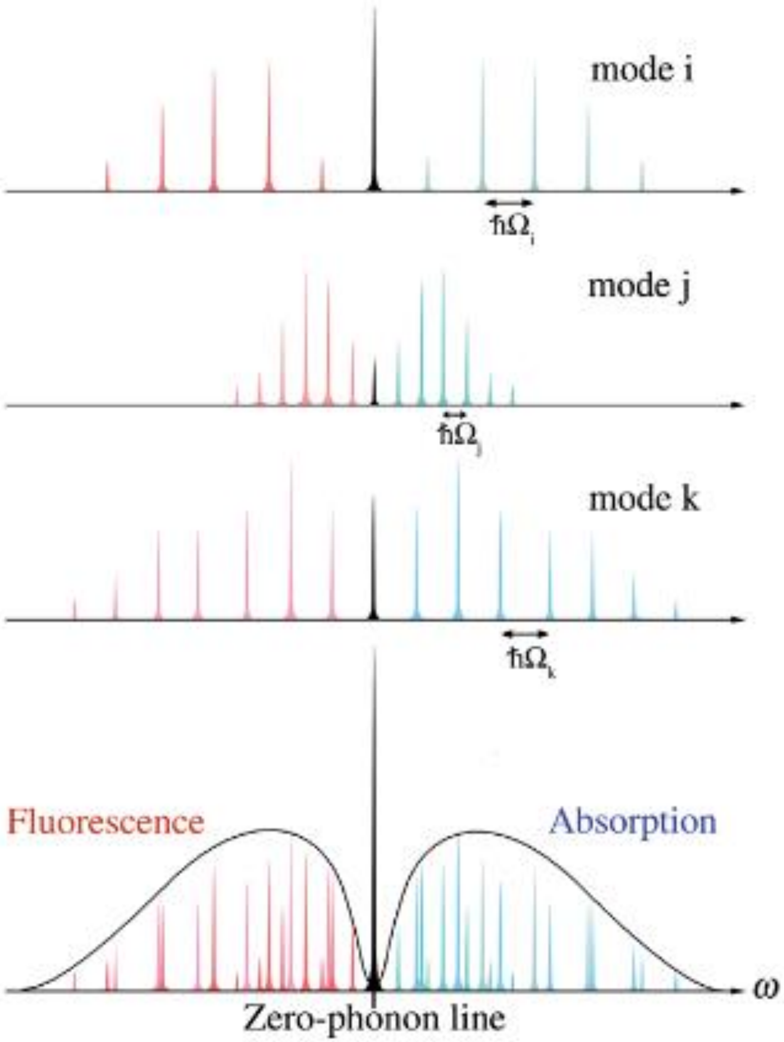


4.2.7 Temperature Resolved Spectroscopy

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



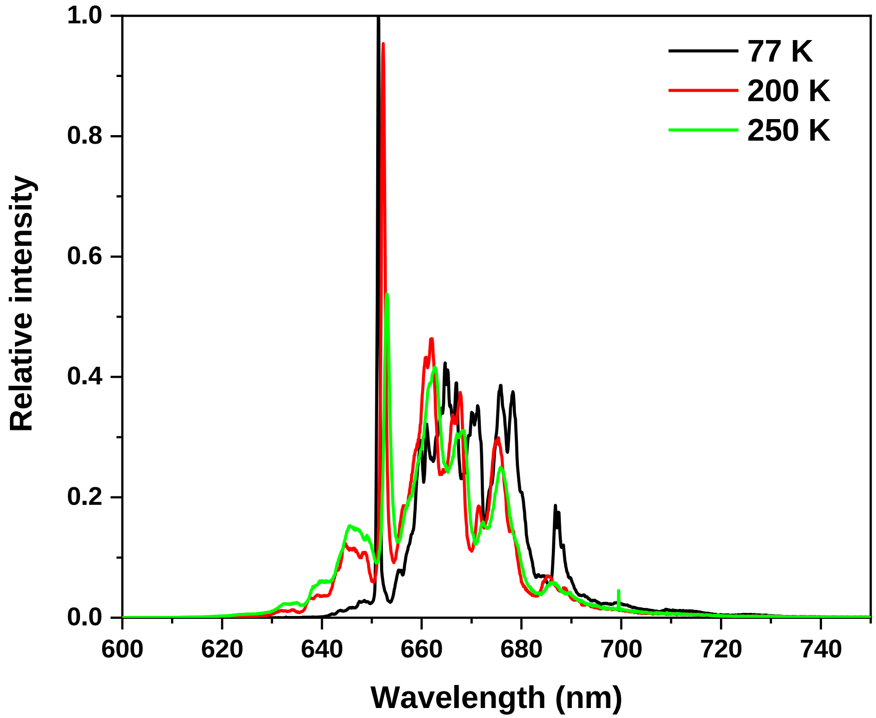


4.2.7 Temperature Resolved Spectroscopy

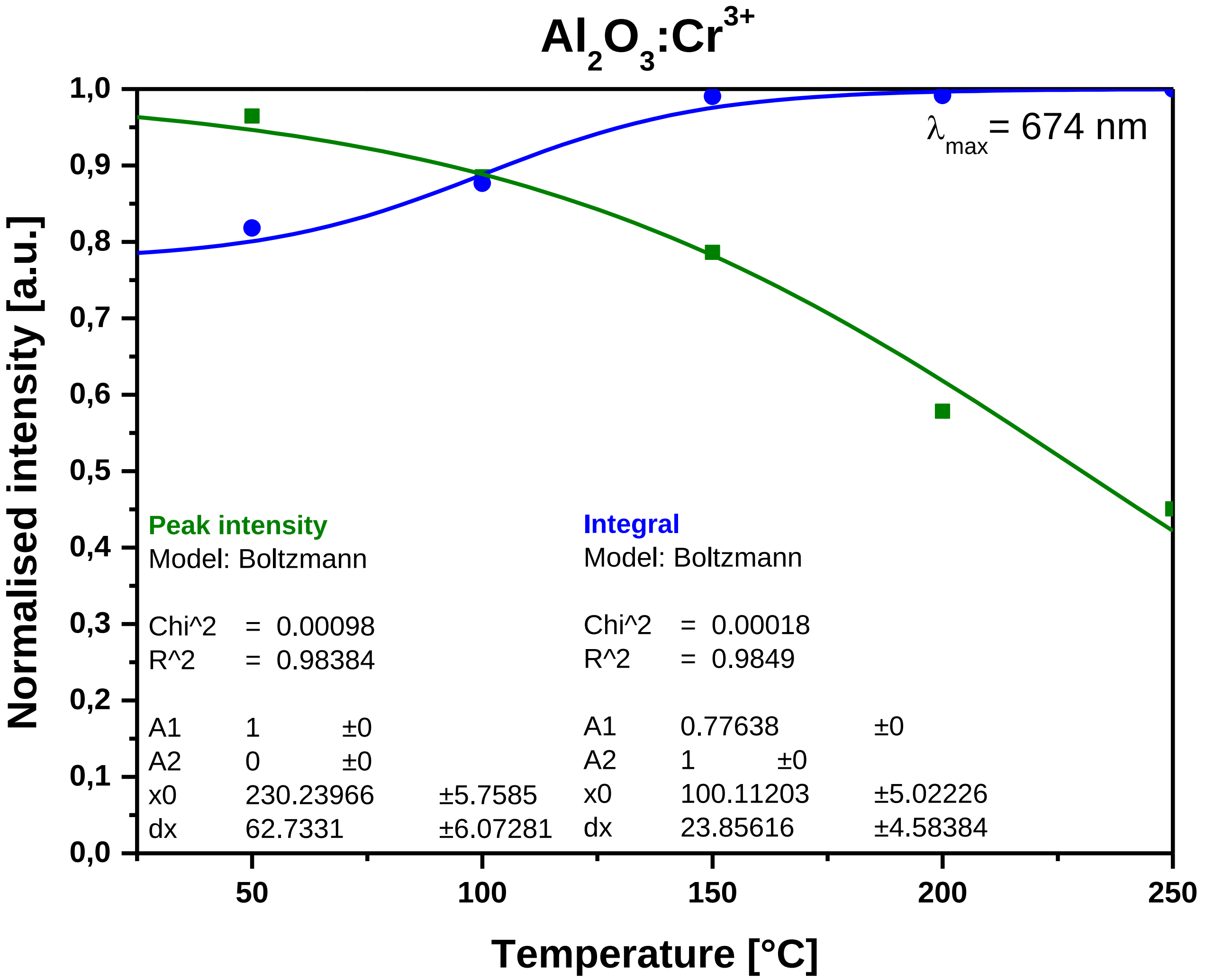
Zero Phonon Line

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



Peak intensity
Model: Boltzmann

Chi^2 = 0.00098
R^2 = 0.98384

A1	1	±0
A2	0	±0
x0	230.23966	±5.7585
dx	62.7331	±6.07281

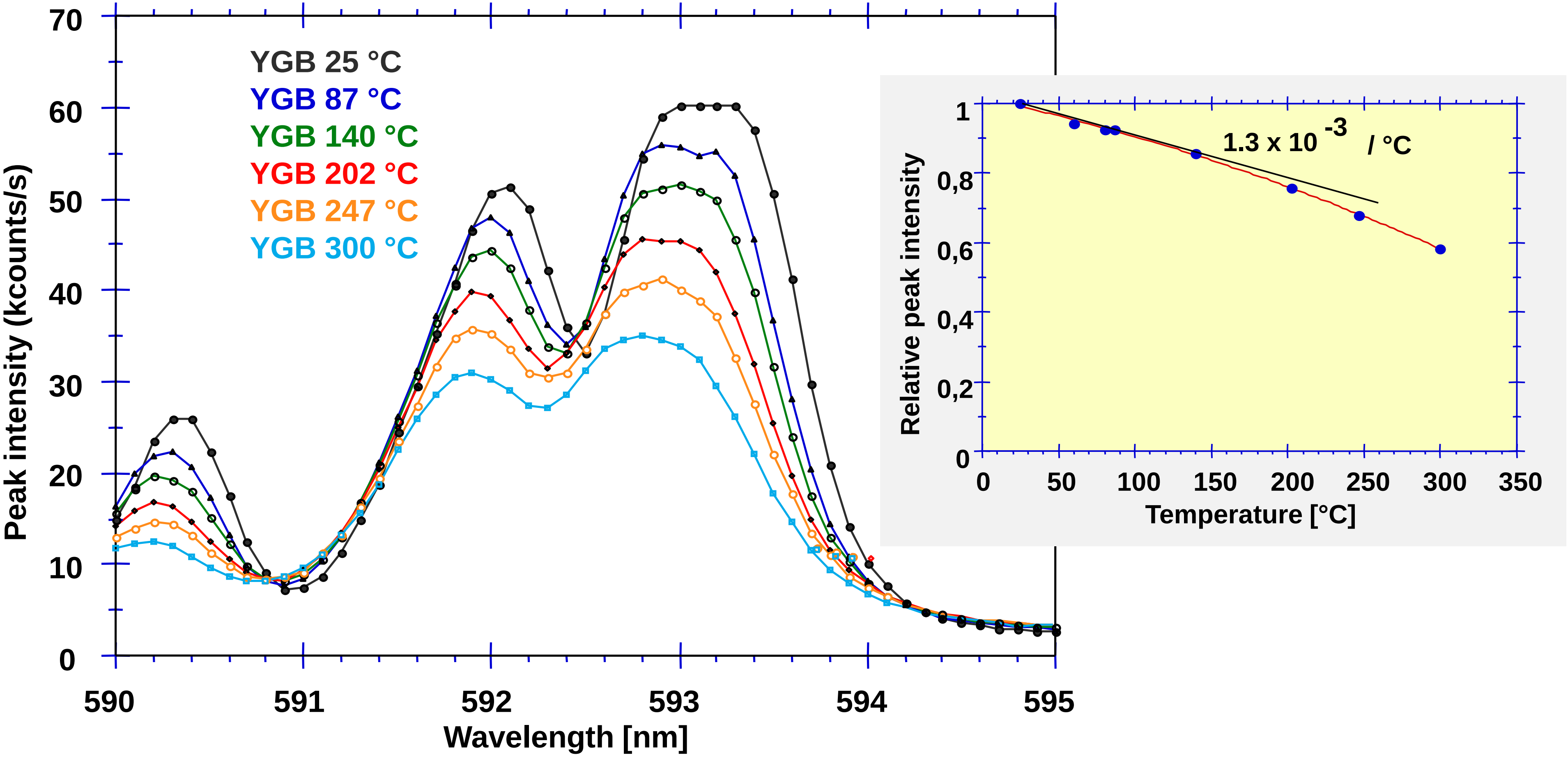
Integral
Model: Boltzmann

Chi^2 = 0.00018
R^2 = 0.9849

A1	0.77638	±0
A2	1	±0
x0	100.11203	±5.02226
dx	23.85616	±4.58384

4.2.7 Temperature Resolved Spectroscopy

Red PDP phosphor (Y,Gd)BO$_3$:Eu^{3+}(YGB:Eu) → $^5D_0 \rightarrow {}^7F_1$ transition as a temperature sensor since it shows reversible change of the emission spectrum



4.2.7 Temperature Resolved Spectroscopy

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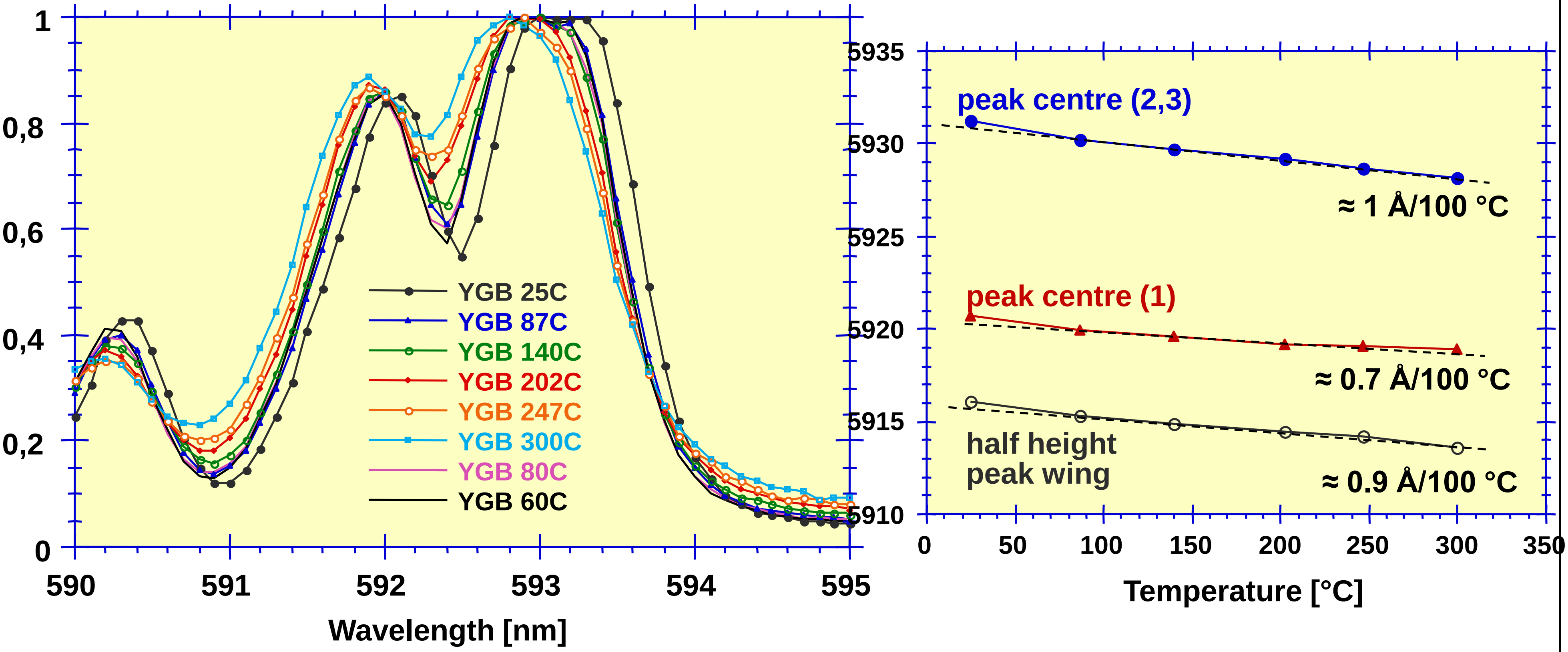


Optical temperature sensing:
- Line/band shift
- Line/band broadening
- Line/band intensity (ratio)

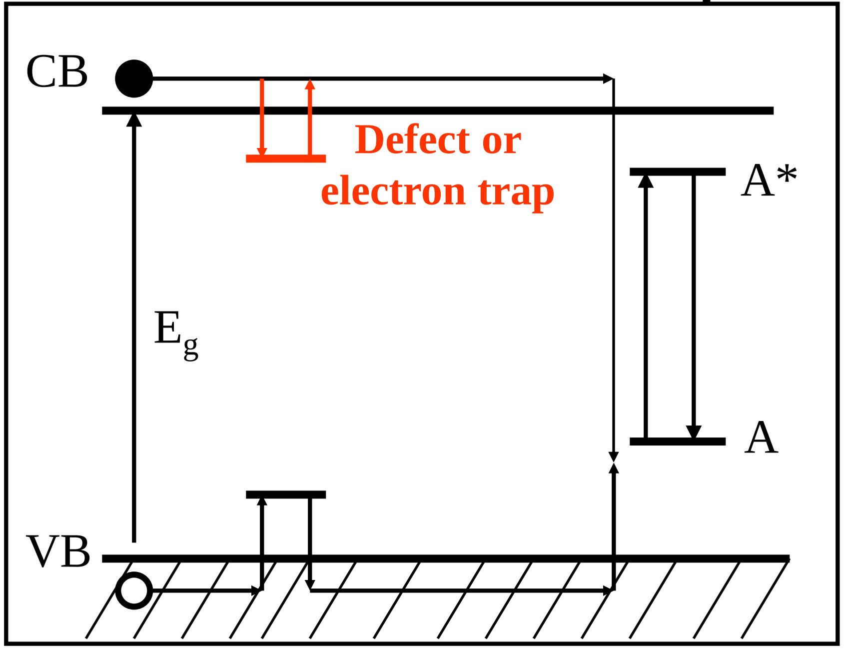
4.2.7 Temperature Resolved Spectroscopy

Thermoluminescence

Technology

- Sample is cooled e.g. down to -196 °C (77 K) or -269 °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

Band model of a solid state compound



Thermoluminescence (TL) (glow curves)

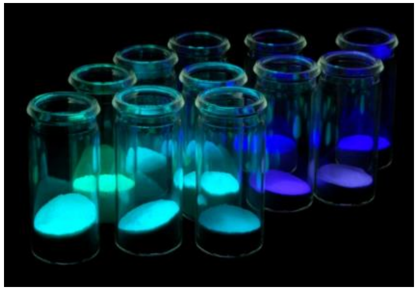
- Integral of the bands: Defect density
- Position of the bands: Energetic position of the defects
- Number of bands: Number of defect types

⇒ Insights in charge carrier trapping and luminescence quenching mechanisms

4.2.7 Temperature Resolved Spectroscopy

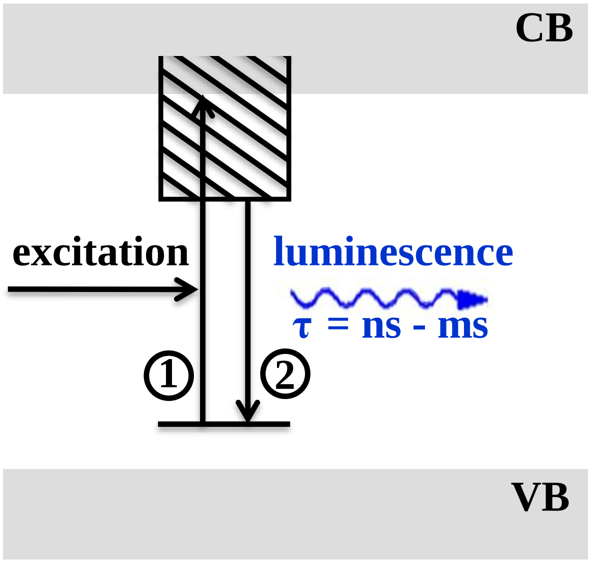
Thermoluminescence: Application Areas

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



$Sr_4Al_{14}O_{25}$:Eu^{2+},Dy^{3+} samples

Luminescence



CB

excitation

luminescence

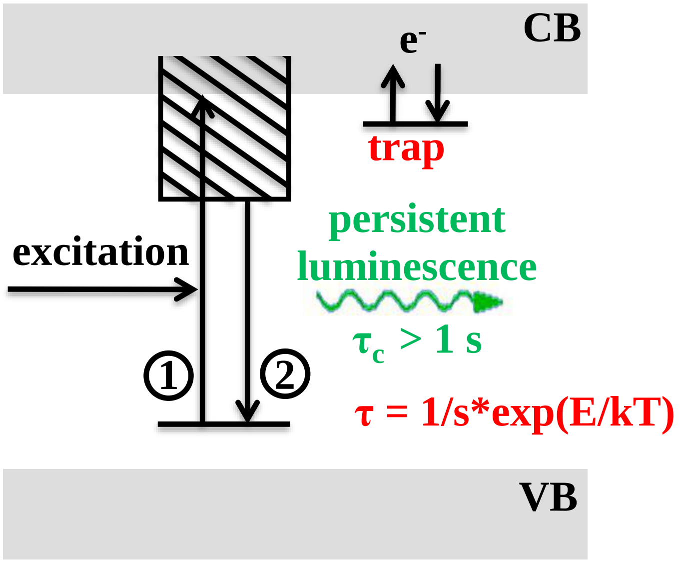
τ = ns - ms

①

②

VB

Persistent luminescence



e^-

CB

trap

excitation

persistent luminescence

τ_c > 1 s

τ = 1/s*exp(E/kT)

①

②

VB

4.2.7 Temperature Resolved Spectroscopy

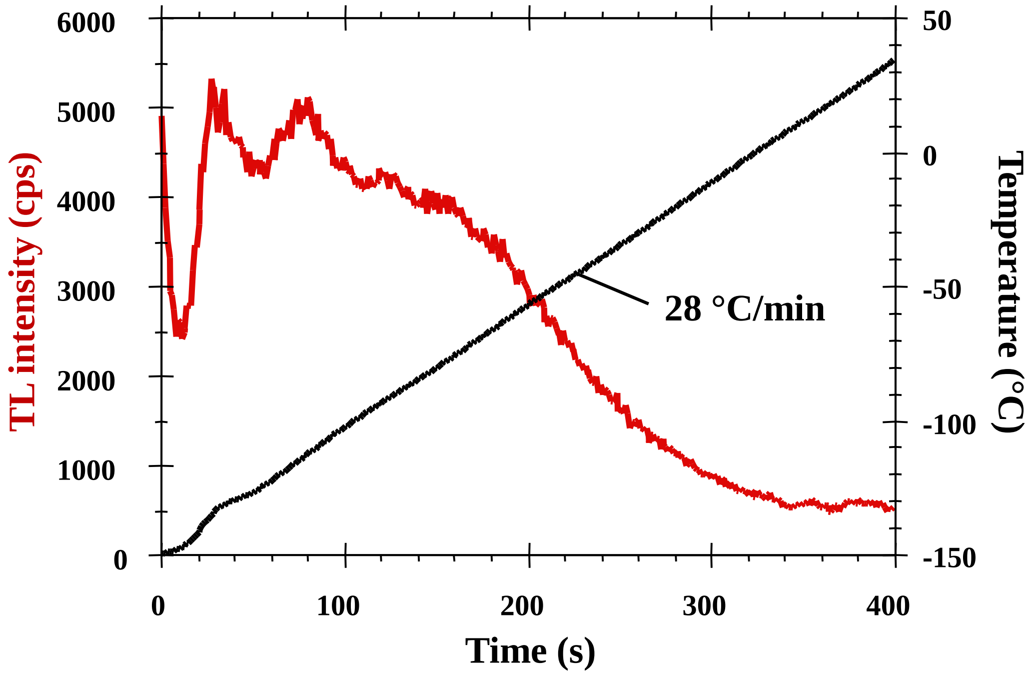
Thermoluminescence: Persistent luminescent materials

Host matrix	Luminescence center	Co-dopant	Emission maximum [nm]	Afterglow duration
$MgAl_2O_4$	Eu^{2+}	Dy^{3+}	480	> 1 min
$CaAl_2O_4$	Eu^{2+}	Nd^{3+}	440	> 5 h
$Ca_{12}Al_{14}O_{33}$	Eu^{2+}	Nd^{3+}	440	> 5 min
$SrAl_{12}O_{19}$	Eu^{2+}	Dy^{3+}	400	> 2 h
$SrAl_4O_7$	Eu^{2+}	Dy^{3+}	480	> 1 h
$Sr_4Al_{14}O_{25}$	Eu^{2+}	Dy^{3+}	405, 490	> 10 h
$SrAl_2O_4$	Eu^{2+}	Dy^{3+}	445, 520	> 10 h
$Sr_3Al_2O_6$	Eu^{2+}	Dy^{3+}	535, 620	> 10 min
$BaAl_2O_4$	Eu^{2+}	Dy^{3+}	505	> 2 h
$SrMgAl_{10}O_{17}$	Eu^{2+}	Dy^{3+}	460, 515	> 3 min
$BaMgAl_{10}O_{17}$	Eu^{2+}	Co^{3+}	450	> 5 min
$BaCa_2Al_8O_{15}$	Eu^{2+}	Dy^{3+}	435	> 5 min
$Ca_2Si_5N_8$	Eu^{2+}	Tm^{3+}	610	> 1 h
$CaAl_2B_2O_7$	Eu^{2+}	Nd^{3+}	464	> 1 h
$SrAl_{1.7}B_{0.3}O_4$	Eu^{2+}	-	520	> 2 h
$Ca_2P_2O_7$	Eu^{2+}	Y^{3+}	415	> 6 h
$Sr_2P_2O_7$	Eu^{2+}	Y^{3+}	420	> 8 h
$SrMg_2P_2O_8$	Eu^{2+}	Ce^{3+}/Gd^{3+}	400	> 2 h
CaS	Eu^{2+}	Tm^{3+}/Pr^{3+}	650	> 1 h
$CaGa_2S_4$	Eu^{2+}	Ho^{3+}	555	> 30 min
Ca_2SiS_4	Eu^{2+}	Nd^{3+}	660	> 30 min
$Sr_3Al_2O_5Cl_2$	Eu^{2+}	Tm^{3+}/Dy^{3+}	620	> 5 min

4.2.7 Temperature Resolved Spectroscopy

Thermoluminescence

Example: $BaMgAl_{10}O_{17}$:Eu



Arrhenius equation

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

s = frequency factor [s^{-1}]

E = trap depth [eV]

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

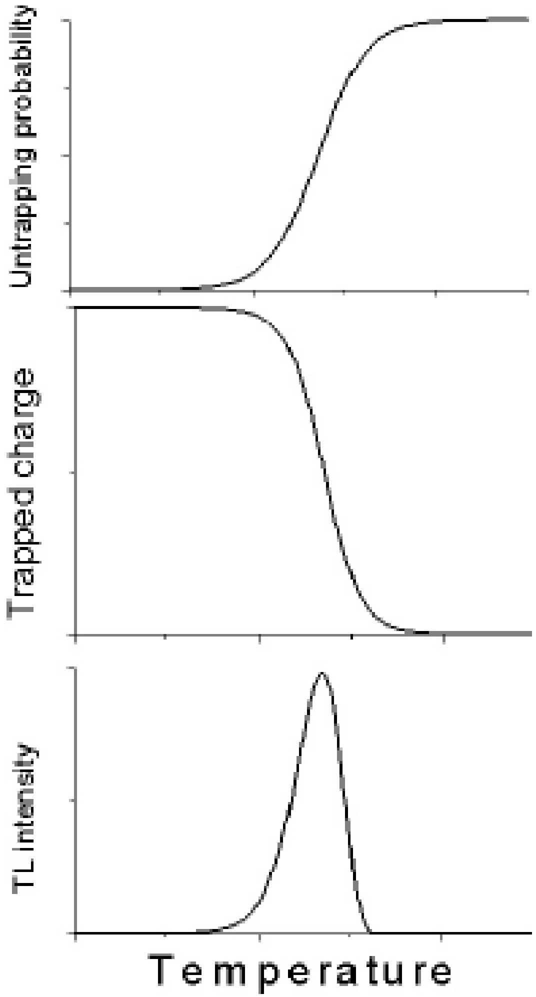
First order kinetics i.e., no retrapping:

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

"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

$T(t) = T_0 + ß \cdot T$

T_0 = start temperature

ß = heating rate

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

4.2.7 Temperature Resolved Spectroscopy

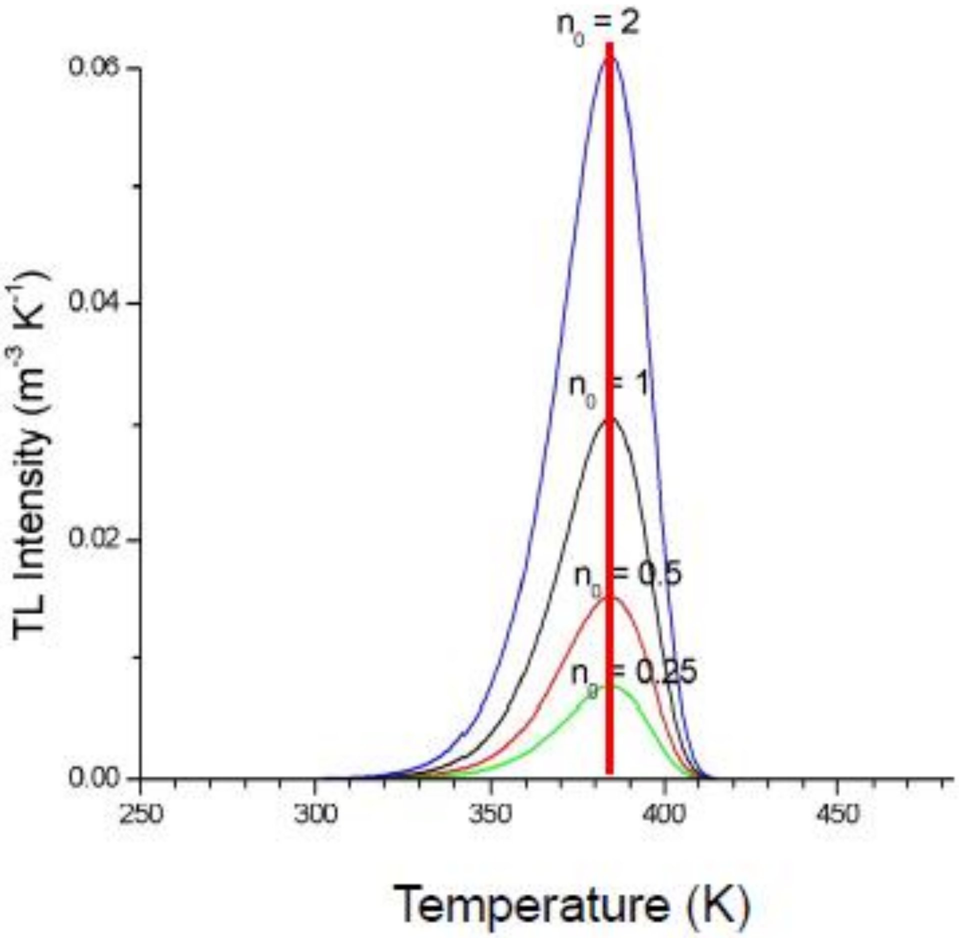
First-order glow peak - Variation in n_0 (Number of traps)

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

Findings for n_0

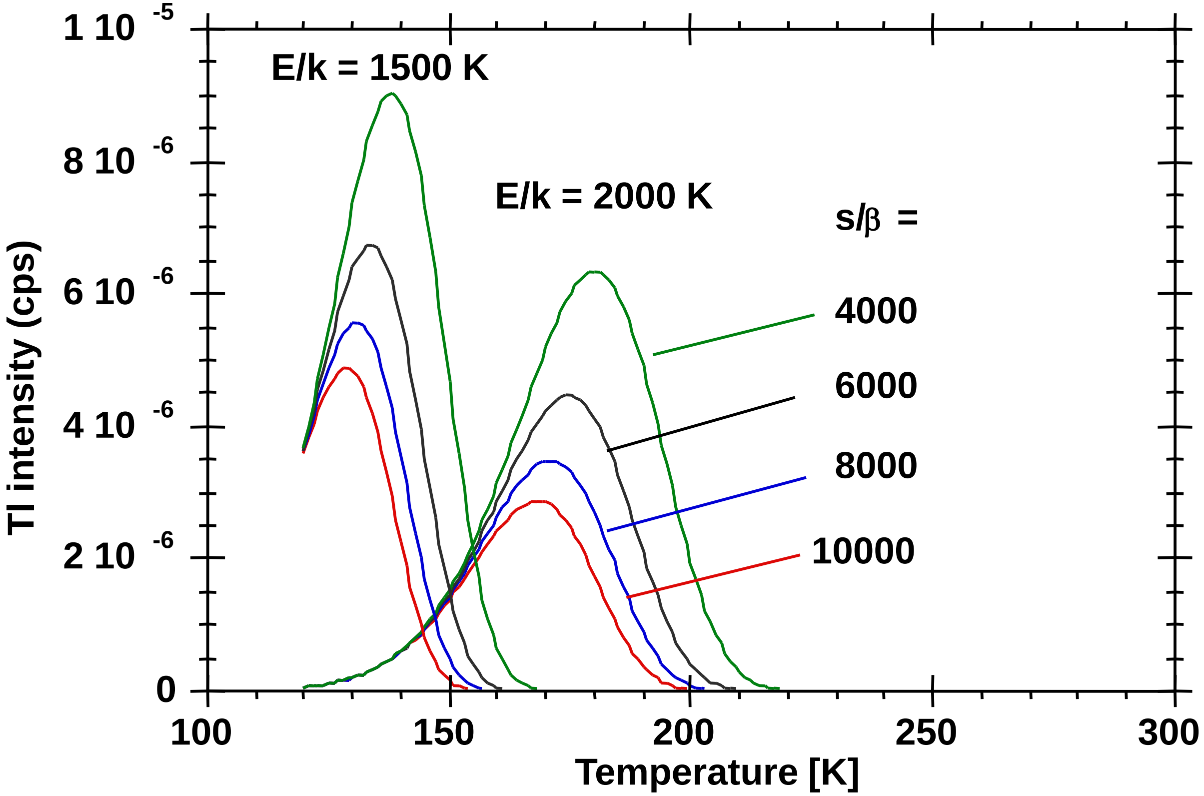
- **~ Peak area**
- **~ Peak height**
- **Independent of peak maximum**

→ relates to defect density of material



4.2.7 Temperature Resolved Spectroscopy

First-order glow peak - Variation in E and s or ß



Assumption: 1st order kinetics

N_{T0} : Number of traps

s : Frequency factor

ß : Heating rate

E : trap depth

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

Randall, Wilkins 1945

4.2.7 Temperature Resolved Spectroscopy

Analysis of thermoluminescence measurements

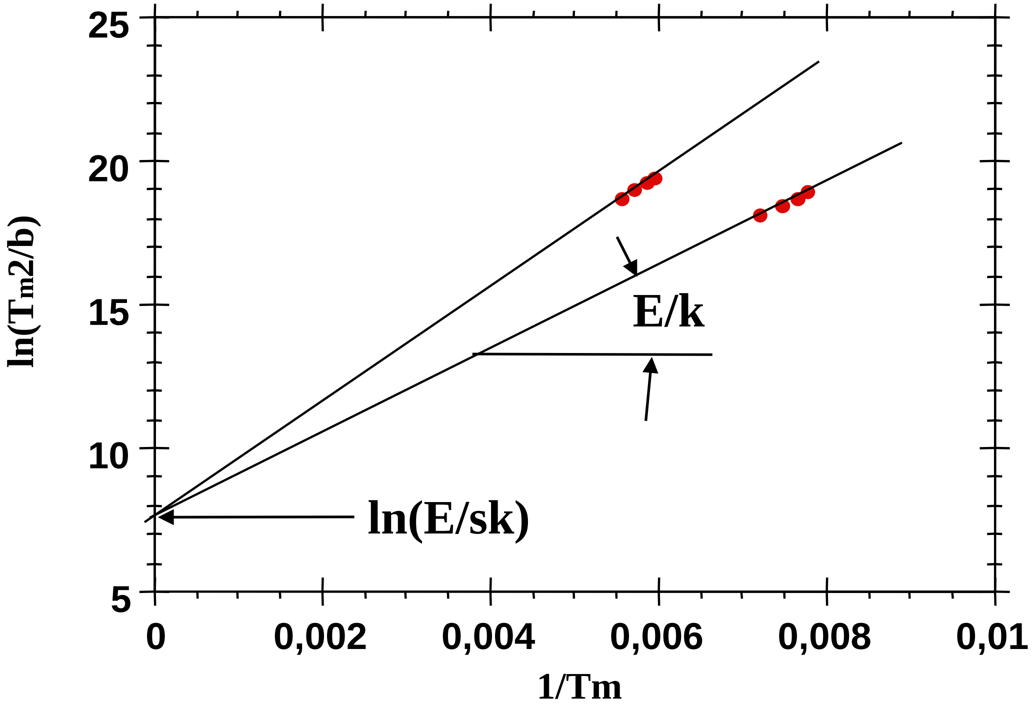
$$\boxed{I_{TL} = N_{T_0} s \exp(-E/kT) \cdot \exp\left[-s/\beta \int_{T_0}^{T} \exp(-E/kT)\, dT\right]}$$

First order kinetics

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

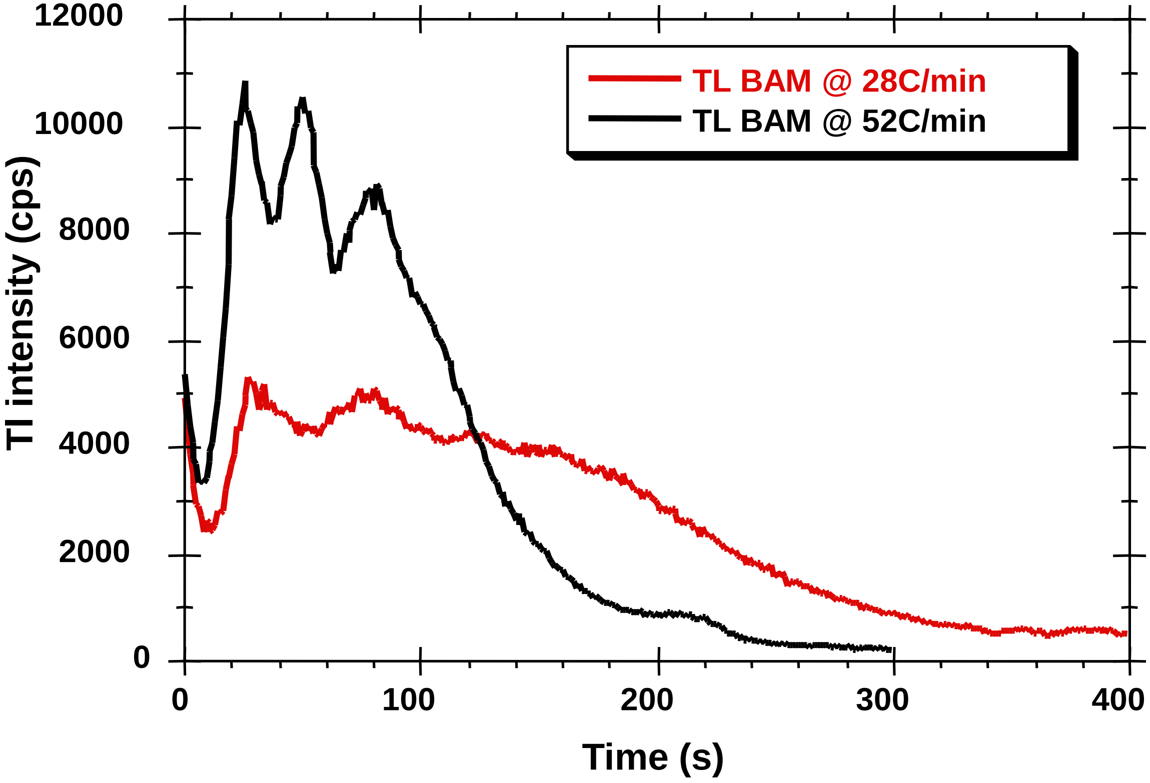
⬇

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



4.2.7 Temperature Resolved Spectroscopy

a) Thermoluminescence analysis of $BaMgAl_{10}O_{17}$:Eu (BAM:Eu)



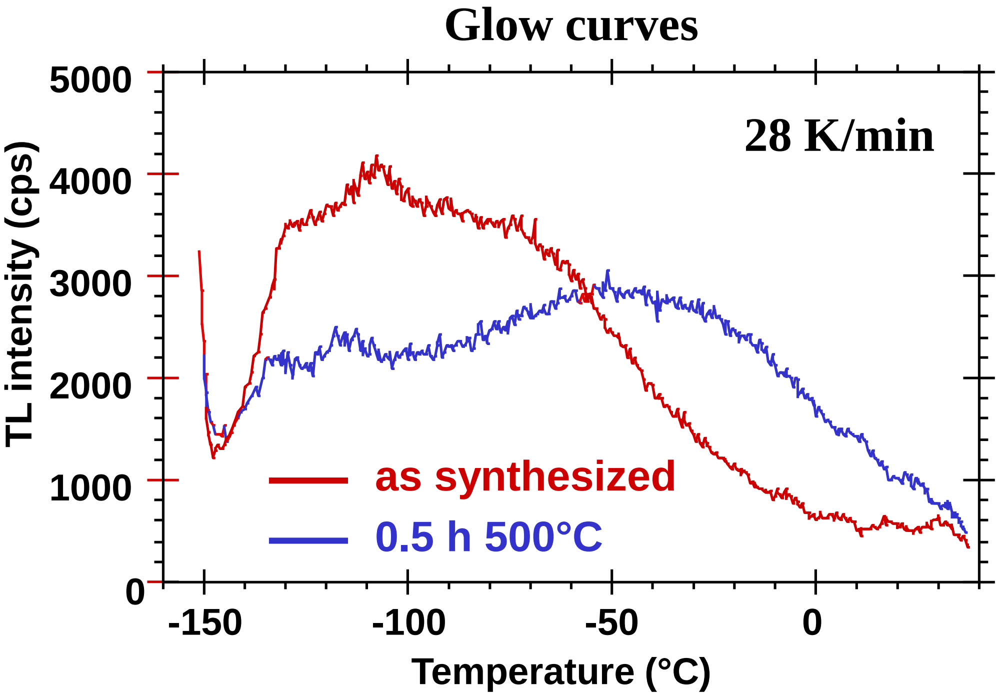
As a function of heating rate

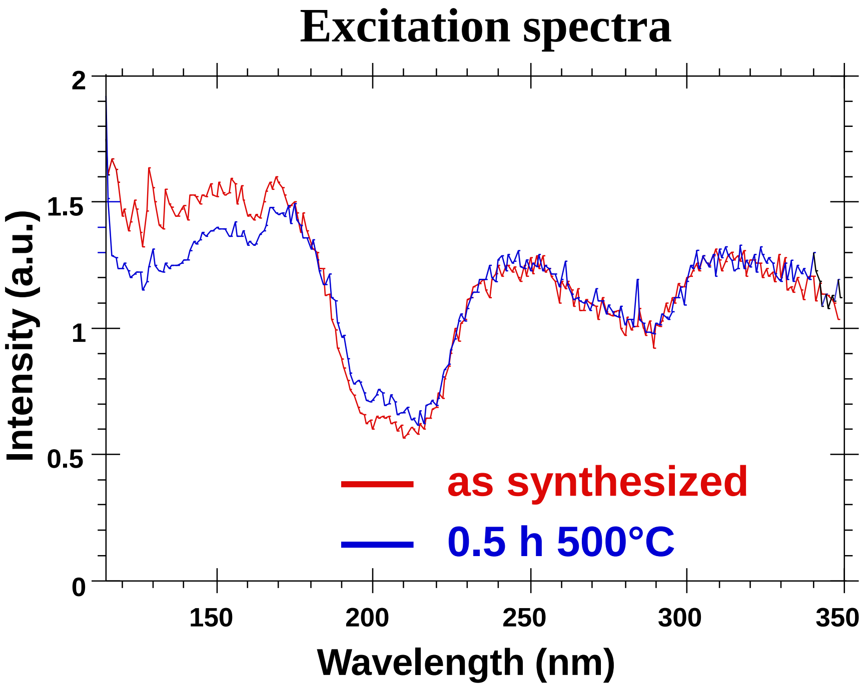
ß [°C/min]	$\int I_{TL}\,dt$ [Mcps*s]
11	0.898
15	1.117
22	1.104
28	1.050
45	1.027
52	1.078

4.2.7 Temperature Resolved Spectroscopy

a) Thermoluminescence analysis of $BaMgAl_{10}O_{17}$:Eu (BAM:Eu)

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

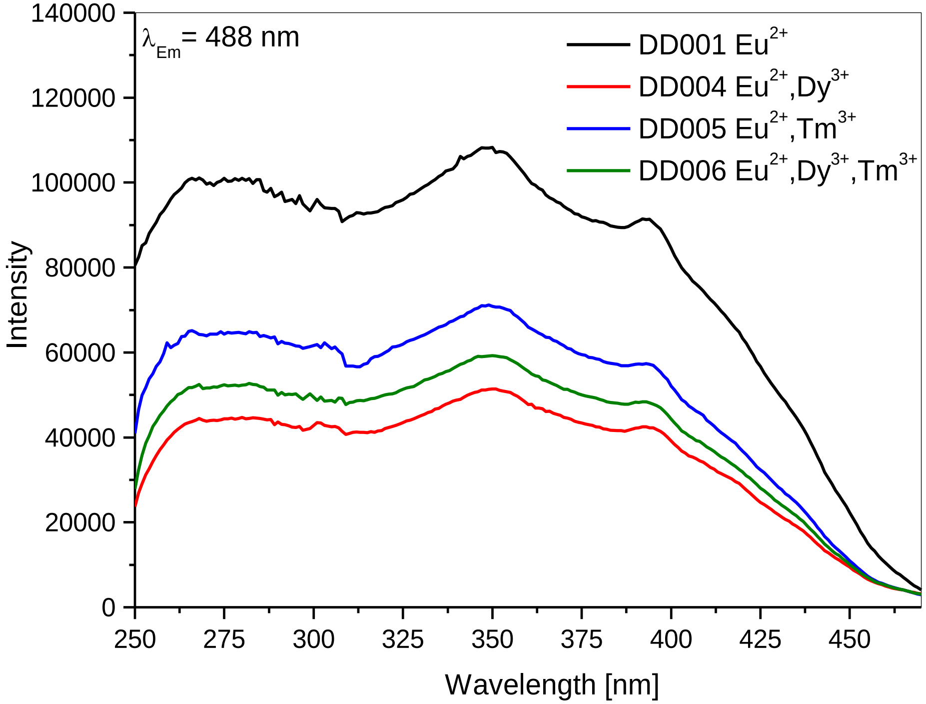


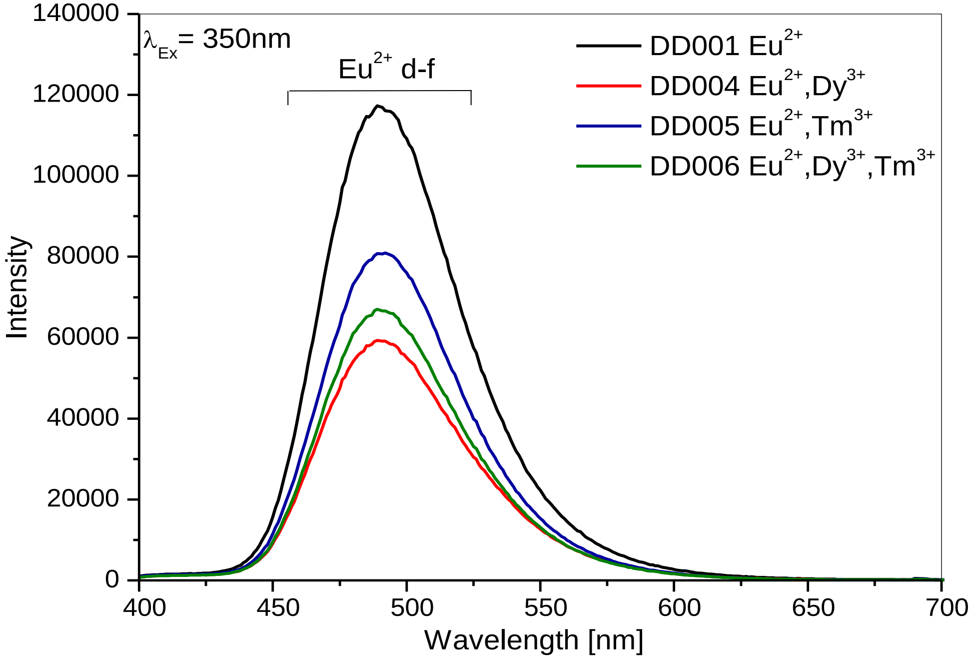


"High temperature" TL traps are generated by the oxidation (direct evidence for the formation of Eu^{3+})

4.2.7 Temperature Resolved Spectroscopy

b) Luminescence spectra of $Sr_4Al_{14}O_{25}$:Eu





Excitation spectrum of $Sr_4Al_{14}O_{25}$:Eu^{2+},X

Emission spectrum of $Sr_4Al_{14}O_{25}$:Eu^{2+},X

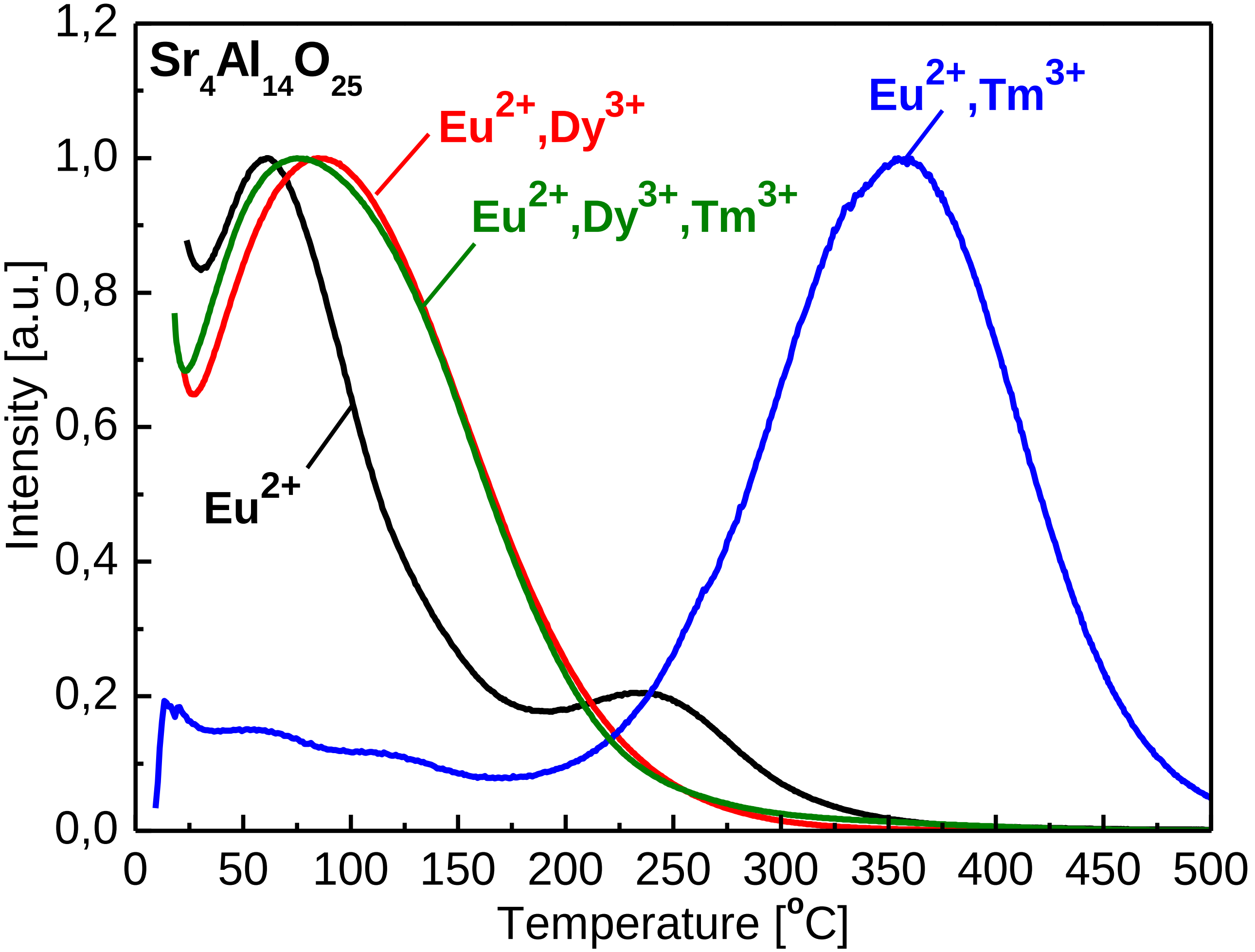
4.2.7 Temperature Resolved Spectroscopy

b) Thermoluminescence analysis of $Sr_4Al_{14}O_{25}$:Eu

Co-doping with Dy^{3+} results in „afterglow" at room temperature

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

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

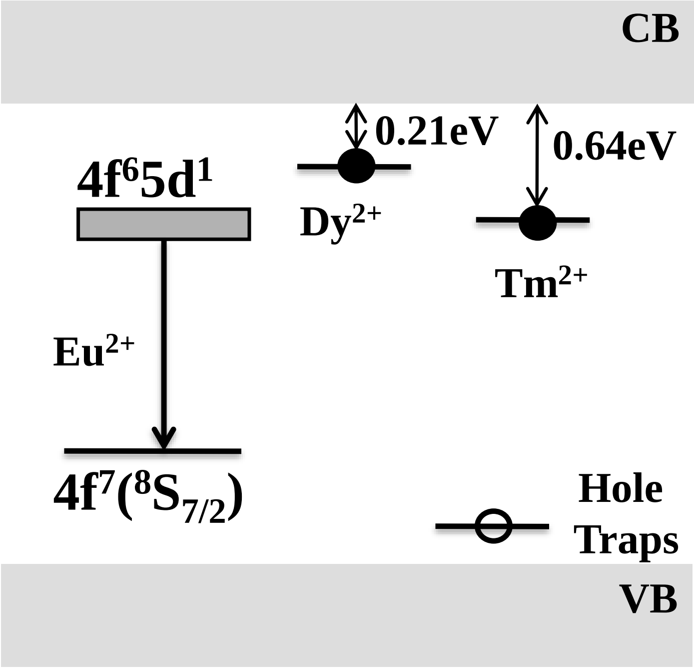


4.2.7 Temperature Resolved Spectroscopy

b) Thermoluminescence analysis of $Sr_4Al_{14}O_{25}$:Eu

Data from the "peak shape" method

Compound	„Trap“ depth [eV]
$Sr_4Al_{14}O_{25}:Eu^{2+}$	0.26, 0.55
$Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$	0.21
$Sr_4Al_{14}O_{25}:Eu^{2+},Tm^{3+}$	0.64
$Sr_4Al_{14}O_{25}:Eu^{2+}, Dy^{3+},Tm^{3+}$	0.23



- $Dy^{2+/3+}$ is energetically closer to the conduction band than $Tm^{2+/3+}$
- Energy gap between Dy and Tm is about 0.4 eV

(see also publications by Pieter Dorenbos, TU Delft)

4.2.8 Time Resolved Spectroscopy

Requirement: Pulsed, highly intense light source

- µs-flash lamps
- ns-flash lamps
- Laser: N_2, excimer, Al_2O_3:Cr, YAG:Nd, …..
- LEDs: (Al,In,Ga)N, (Al,In,Ga)P, Ga(As,P), …..

Measurement Procedure

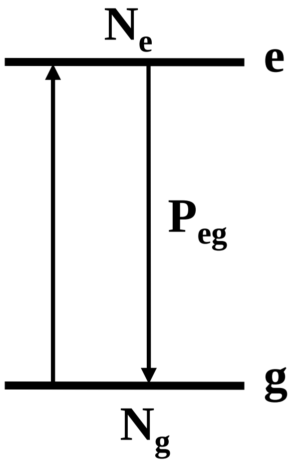
- Pulsed or continuous wave excitation of the sample
- Measurement of the luminescence intensity as the function of time after the excitation source has been switched off (or single photon counting)
- Fitting of the obtained decay curve with one or several e-functions:

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

4.2.8 Time Resolved Spectroscopy

Lifetime of the excited state

First order kinetics (two level system, no quenching)



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

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

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

$\Rightarrow N_e(t) = N_e(0)*\exp(-t/\tau)$ $\tau = 1/P_{eg}$

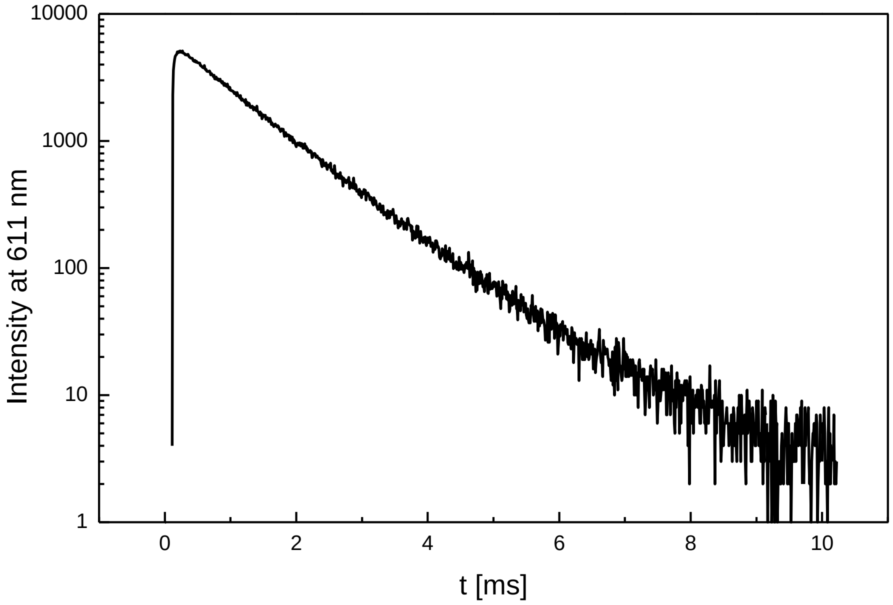
Allowed transitions	10^{-6} to 10^{-9} s (4f - 5d, 6s - 6p)	Eu^{2+}
Forbidden transitions	~ 10^{-3} s (4f - 4f, 5d - 5d)	Eu^{3+}

4.2.8 Time Resolved Spectroscopy

Mono- and bi-exponential decay

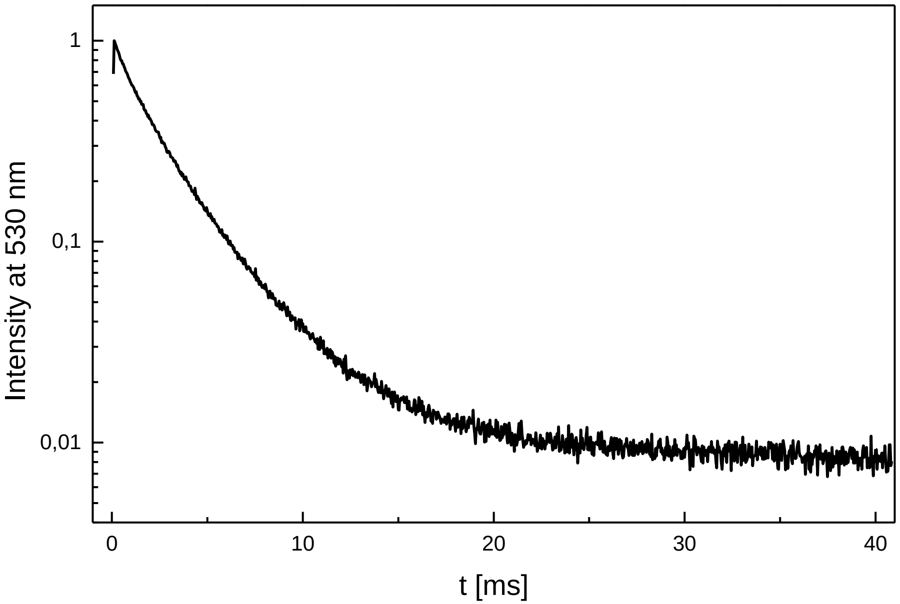
mono-exponential behavior, e.g. Eu^{3+}, Gd^{3+}, Tb^{3+}
bi-exponential behavior, e.g. Mn^{2+} due to Mn^{2+}-O-Mn^{2+} antiferromagnetic coupling

$(Y,Gd)_2O_3:Eu^{3+}$



$B_1 = 1.0$ $\tau_1 = 1.1$ ms

$Zn_2SiO_4:Mn^{2+}$

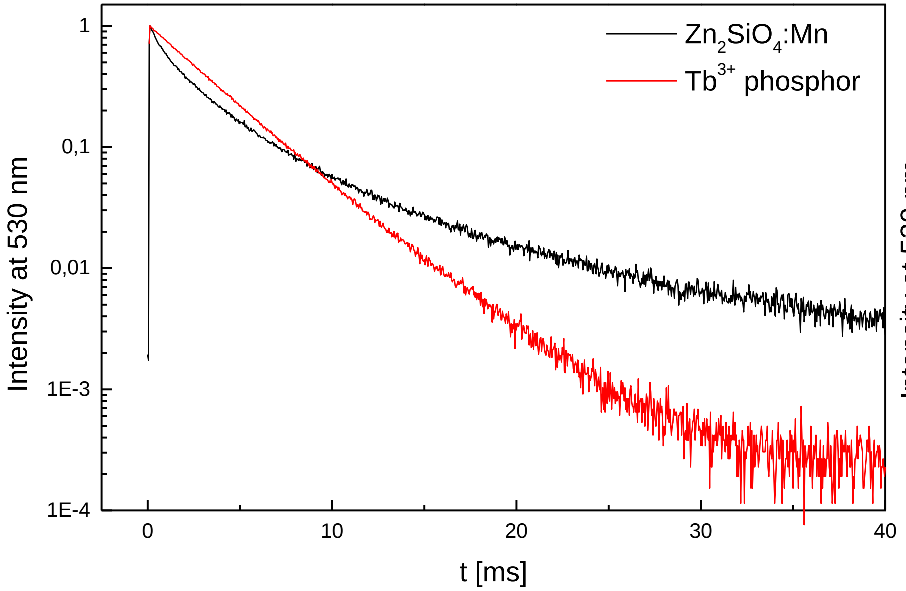


$B_1 = 0.44$ $\tau_1 = 5.6$ ms
$B_2 = 0.56$ $\tau_2 = 2.3$ ms

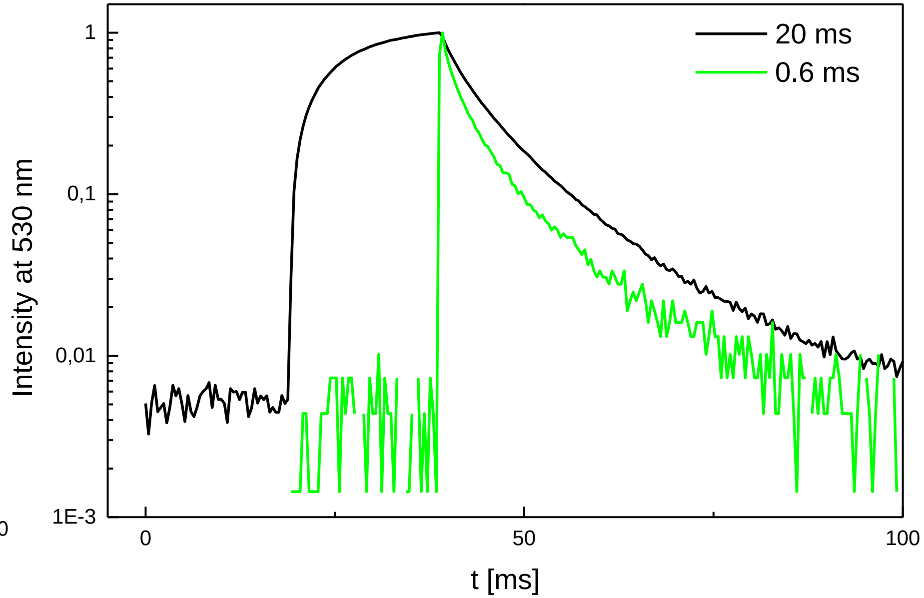
4.2.8 Time Resolved Spectroscopy

Mono- and bi-exponential decay

Single-pulse excitation of $Zn_2SiO_4:Mn^{2+}$ and $(Y,Gd)BO_3:Tb^{3+}$



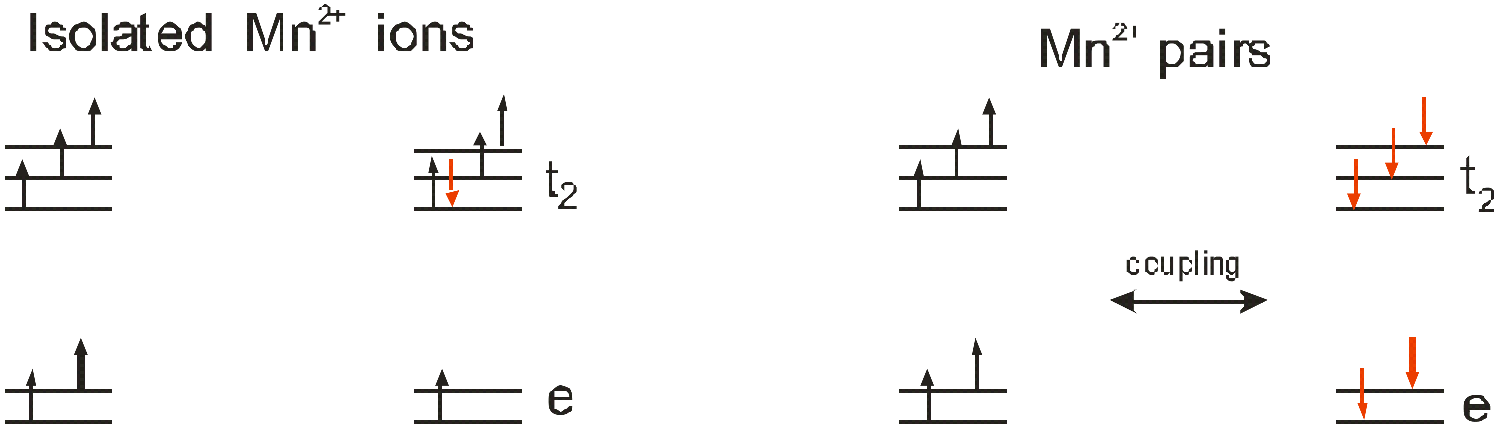
Decay curve of $Zn_2SiO_4:Mn^{2+}$ (Single pulse and continuous wave excitation)



Phosphor	Decay curve	Single pulse	Continuous wave
• $(Y,Gd)BO_3:Tb^{3+}$	mono-exponential	9 ms	10 ms
• $Zn_2SiO_4:Mn^{2+}$	bi-exponential	11 ms	17 ms

4.2.8 Time Resolved Spectroscopy

Exchange interaction in Mn^{2+} phosphors



ground state S = 5/2 | ground state S = 0,1,2,3,4,5

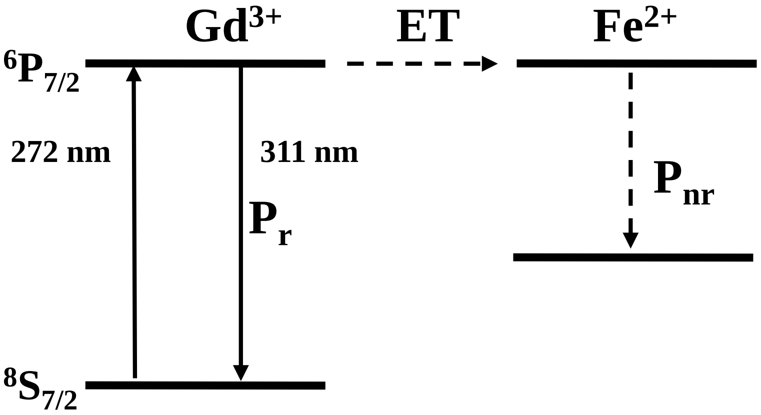
excited state S = 3/2 | excited state S = 1,2,3,4

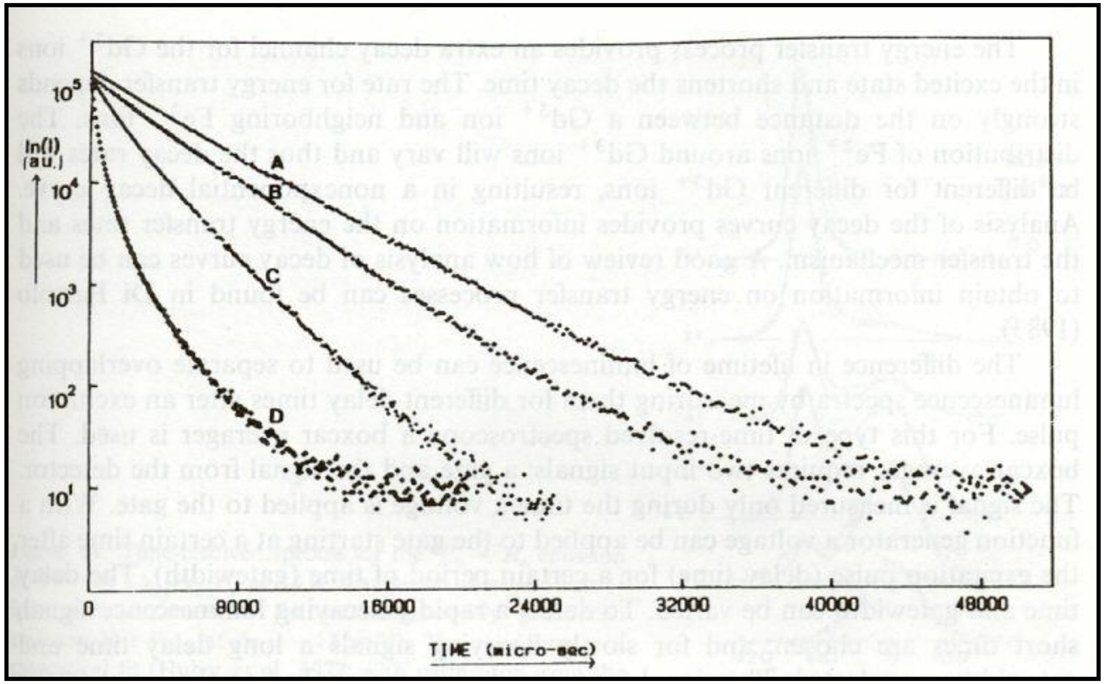
High Mn^{2+} concentration ⇒ Exchange interaction between Mn^{2+}-ions
The decay time is reduced by eliminating the spin selection rule

Low excitation density ⇒ Excitation of Mn^{2+} pairs ⇒ Short decay time
High excitation density ⇒ Excitation of isolated Mn^{2+} ions ⇒ Long decay time

4.2.8 Time Resolved Spectroscopy

Example: $La_{0.4}Gd_{0.6}MgB_5O_{10}$:x%Fe





Decay of the Gd^{3+} emission (intraconfigurational transition $^6P_{7/2}$ – $^8S_{7/2}$) at 311 nm

A: $La_{0.4}Gd_{0.6}MgB_5O_{10}$

B: $La_{0.4}Gd_{0.6}MgB_5O_{10}$:0.01% Fe

C: $La_{0.4}Gd_{0.6}MgB_5O_{10}$:0.1% Fe

D: $La_{0.4}Gd_{0.6}MgB_5O_{10}$:1% Fe ⇒ Energy transfer to Fe^{2+} reduces decay time

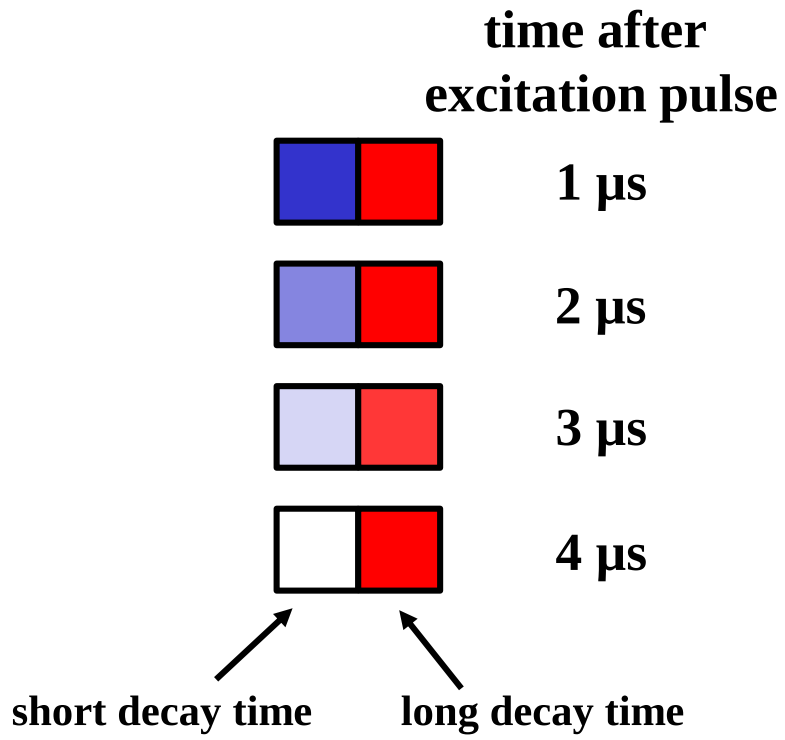
4.2.8 Time Resolved Spectroscopy

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!

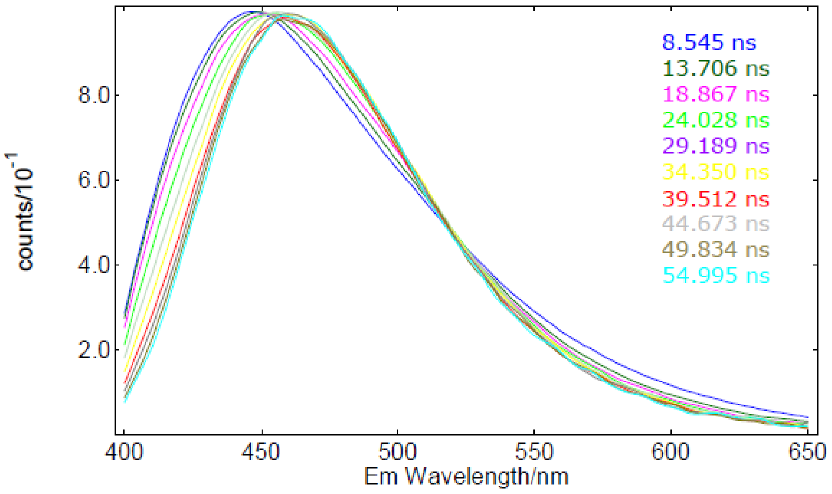


Example for a system comprising a fast and a slow decaying component

e.g. Eu^{2+} and Eu^{3+}

4.2.8 Time Resolved Spectroscopy

Time Resolved Emission Spectra

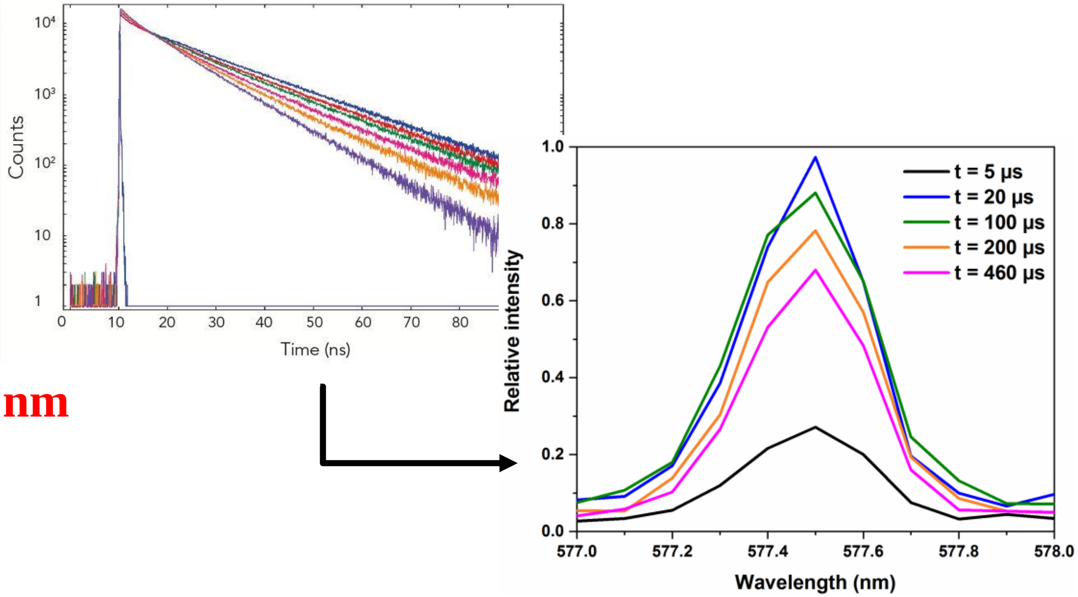


Recording by ICCD (intensified CCD)

- **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

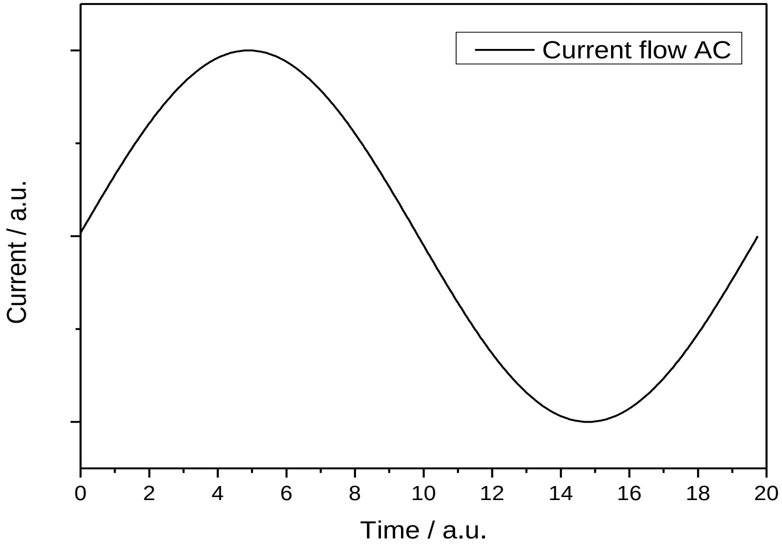
- **A decay curve is recorded for each emission wavelength**
- **A time resolved emission spectrum is constructed from the curves**
- **down to few ps temporal resolution**
- **wavelength resolution of down to 0.05 nm**
- **(very) slow measurement**

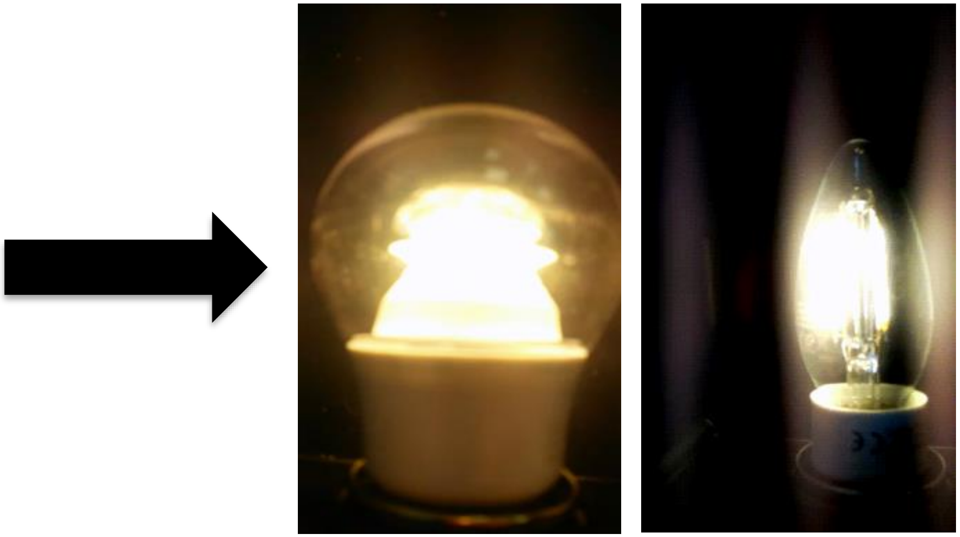


4.2.9 Flicker Measurements

Definition of flicker

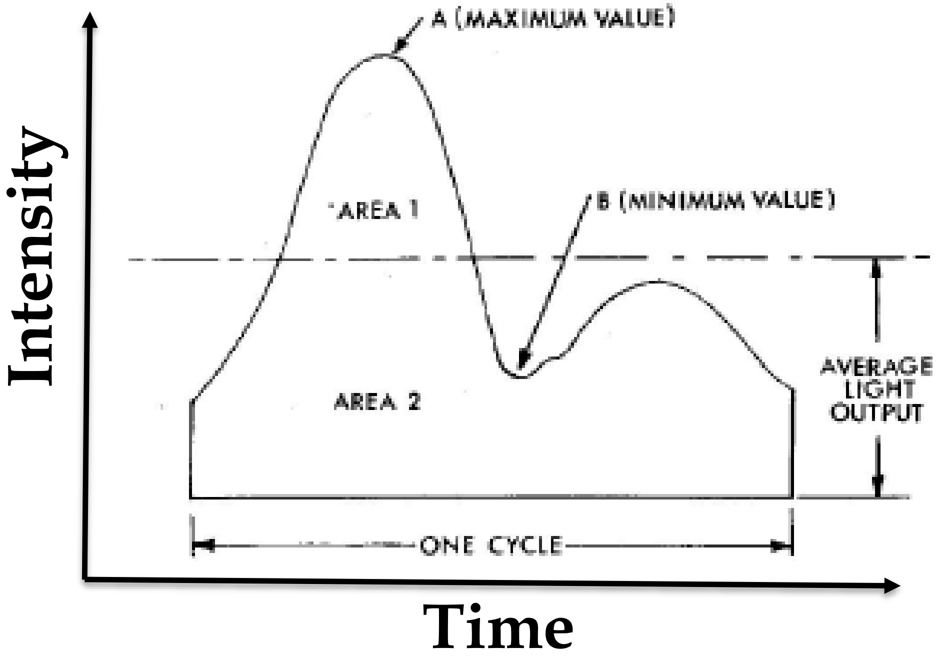
- **Flicker is the fast, periodic change of the intensity of a light source**
- **It is an inherent problem of all kind of electrical light sources**
- **Alternating current (50 Hz) from the electric grid causes flicker of light sources**
- **Incandescent lamps show solely little flicker due to thermal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





4.2.9 Flicker Measurements

Quantification of flicker



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

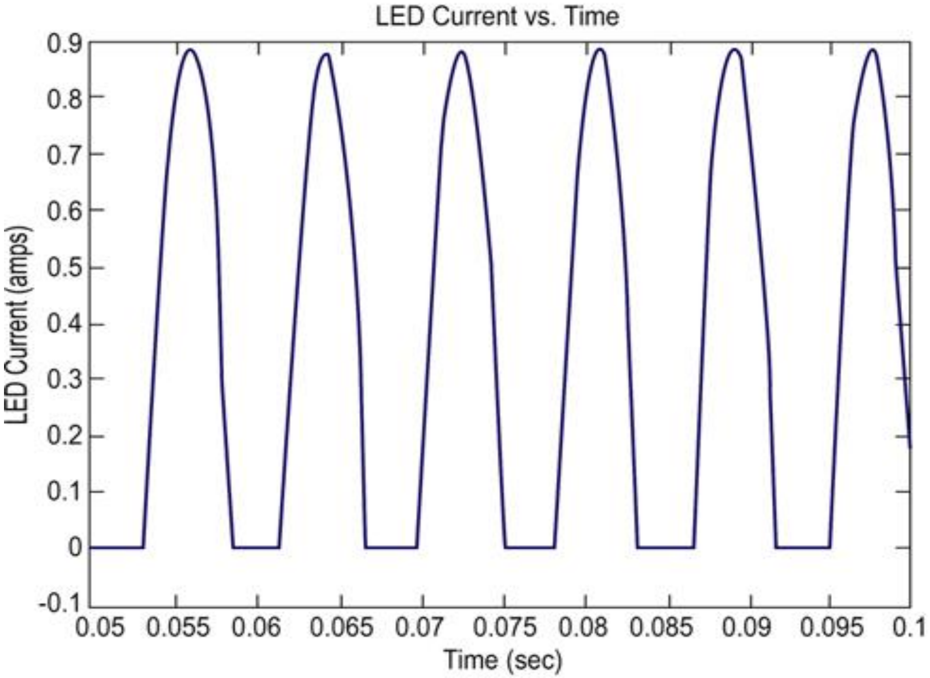
$$Flicker\ index = \frac{Area\ above\ Mean}{Total\ area} = \frac{Area\ 1}{Area\ 1 + Area\ 2}$$

M. Rea, IESNA Lighting Handbook, 9th Edition, (2000)

4.2.9 Flicker Measurements

Discharge lamps and particularly LEDs show strong flicker

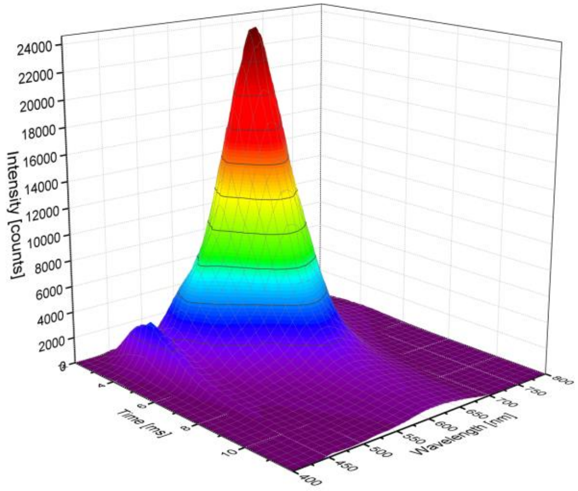
- **Flicker with 100 Hz for 50 Hz alternating current**
- **Electronic driver are able to flatten the current and intensity curve**
- **Alternative solution: Phosphors with long decay time > 10 ms**



Example: Osram Parathon E14

Percent Flicker @ 100 Hz = 96%

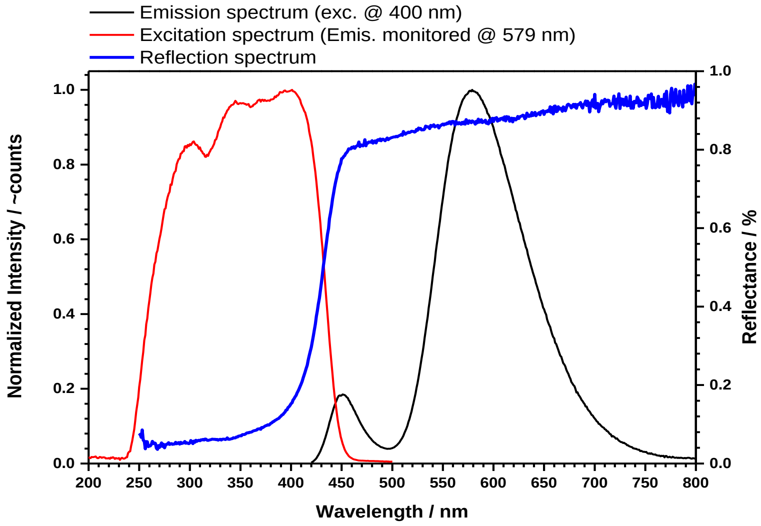
Flicker Index = 0.45

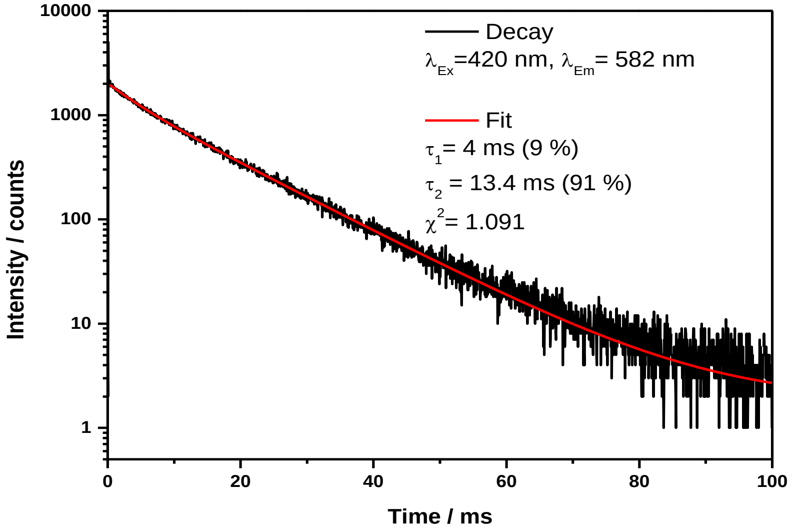


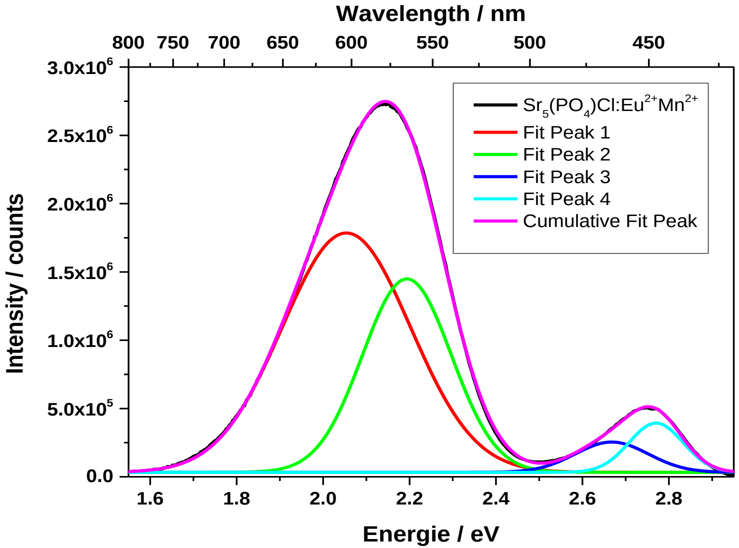
4.2.9 Flicker Measurements

Example: $Sr_5(PO_4)_3Cl:Eu^{2+}Mn^{2+}$

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

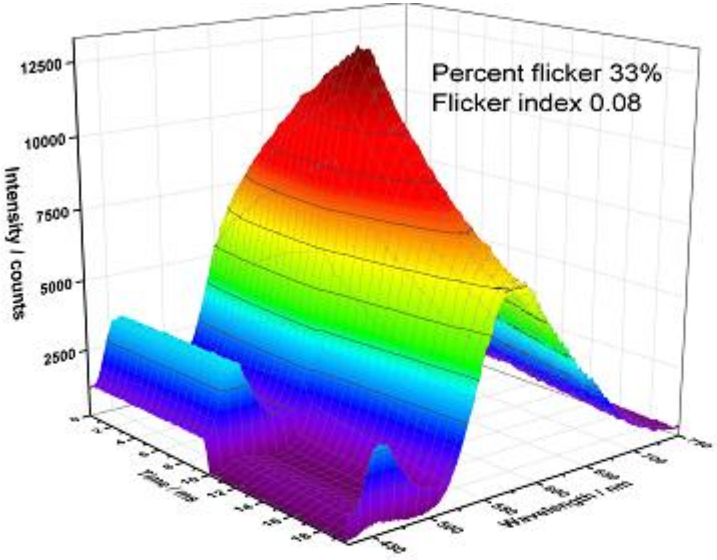




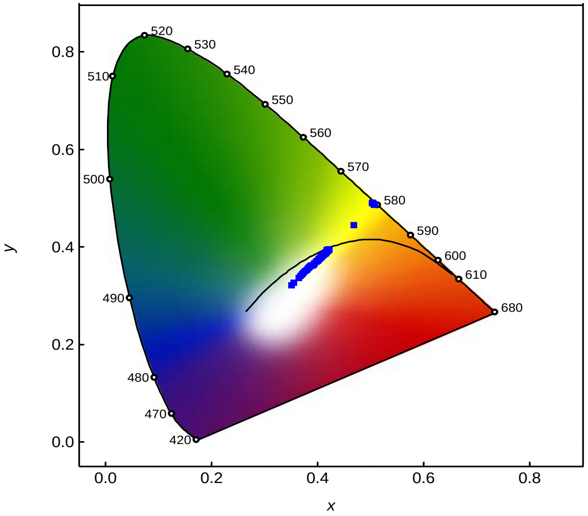


4.2.9 Flicker Measurements

Example: $Sr_5(PO_4)_3Cl:Eu^{2+}Mn^{2+}$



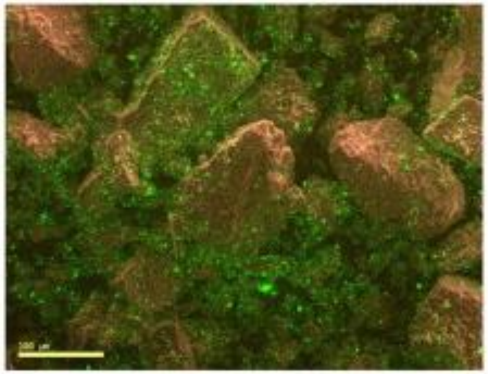
- **Percent Flicker 33%**
- **Flicker Index 0.08**
- **Color point shifts from white to yellow**
- **Color point (average) :**
  - **x = 0.453; y = 0.430; LE = 378 lm/W_{opt}**
- **CCT = 2916 K**



4.2.10 X-ray and Cathode Luminescence

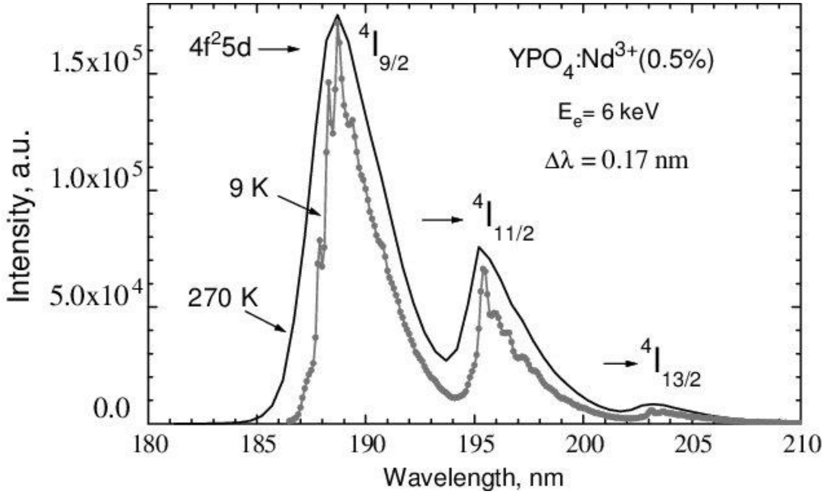
Excitation with high-energy radiation

- **Unspecific excitation of all luminescent species (defects, band transitions, activators)**
- **Impurities in the ppm range can be determined qualitatively (e. g. Gd^{3+} in Y_2O_3)**
- **The sample can be excited with a spatial resolution in the µm range**
- **VUV or UV-C emission can be observed, such as Nd^{3+} bands at 190 nm**



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

DOI: 10.1016/j.ejps.2011.10.017

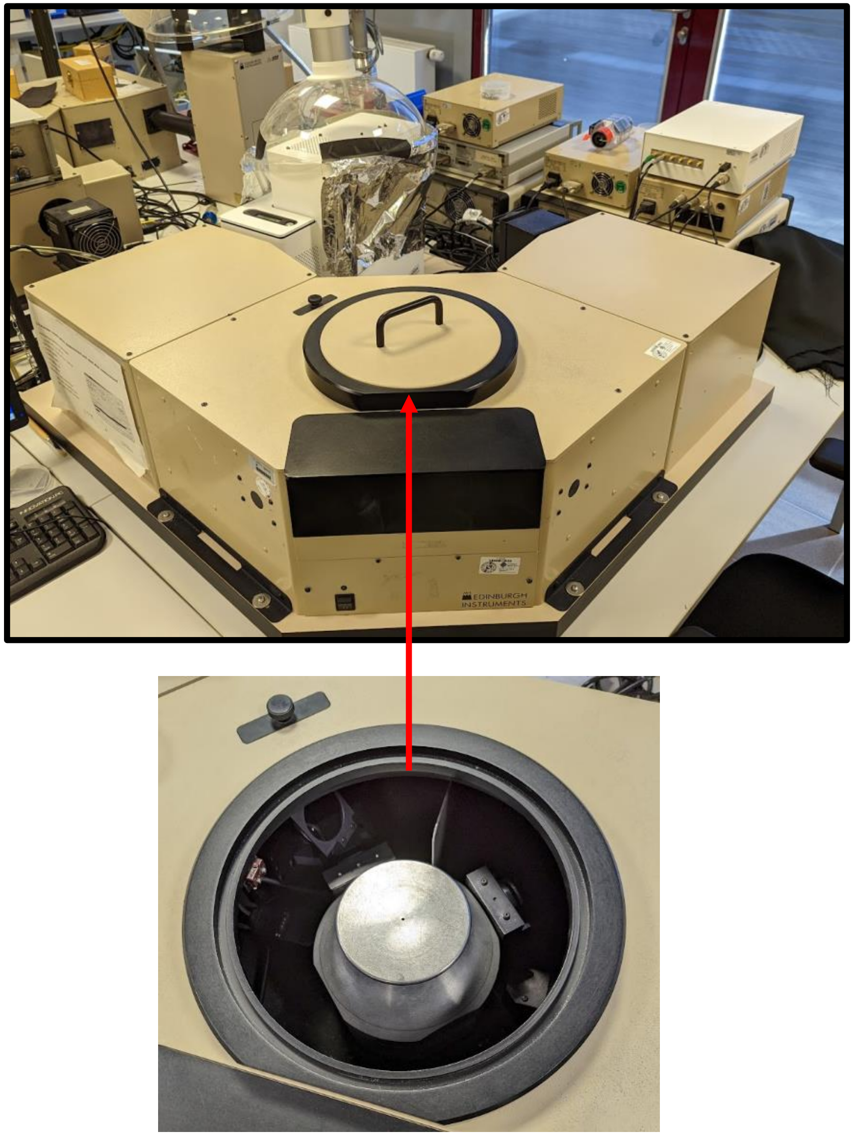


DOI: 10.1016/S0168-9002(02)00749-0

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**

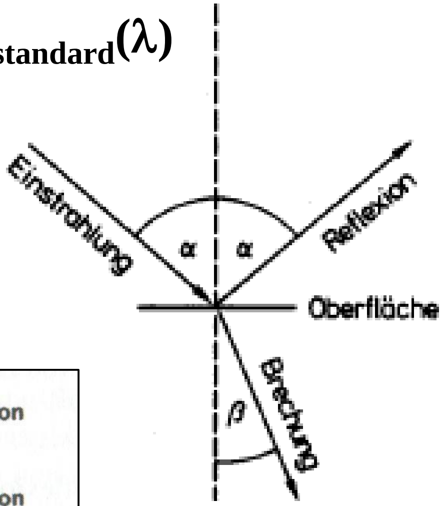


4.3.1 Physical Basis

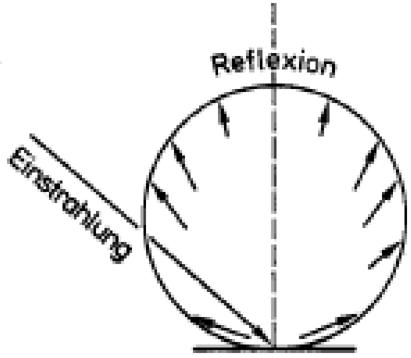
Types of Reflection

Measurement is made relative to a white standard, e.g. $BaSO_4$, $CaCO_3$, or Teflon powder

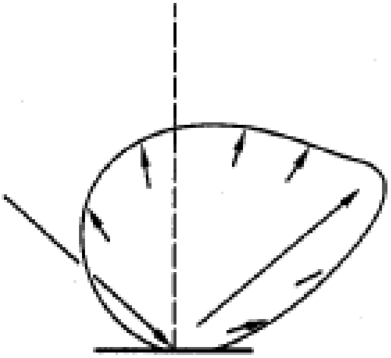
$$R_{diffuse}(\lambda) = I_{sample}(\lambda)/I_{white\ standard}(\lambda)$$



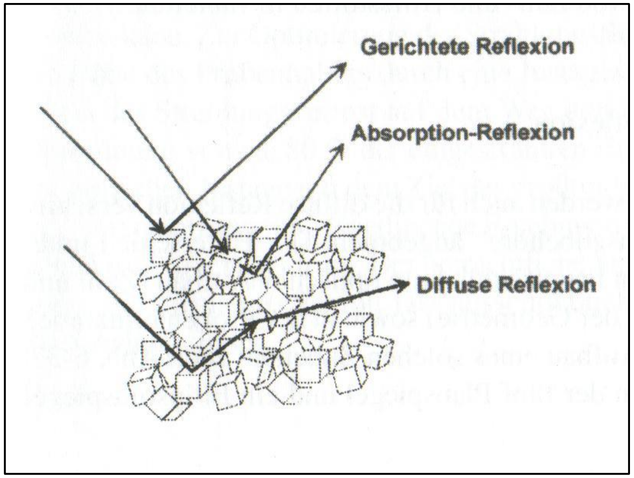
Regular reflection



Diffuse reflection



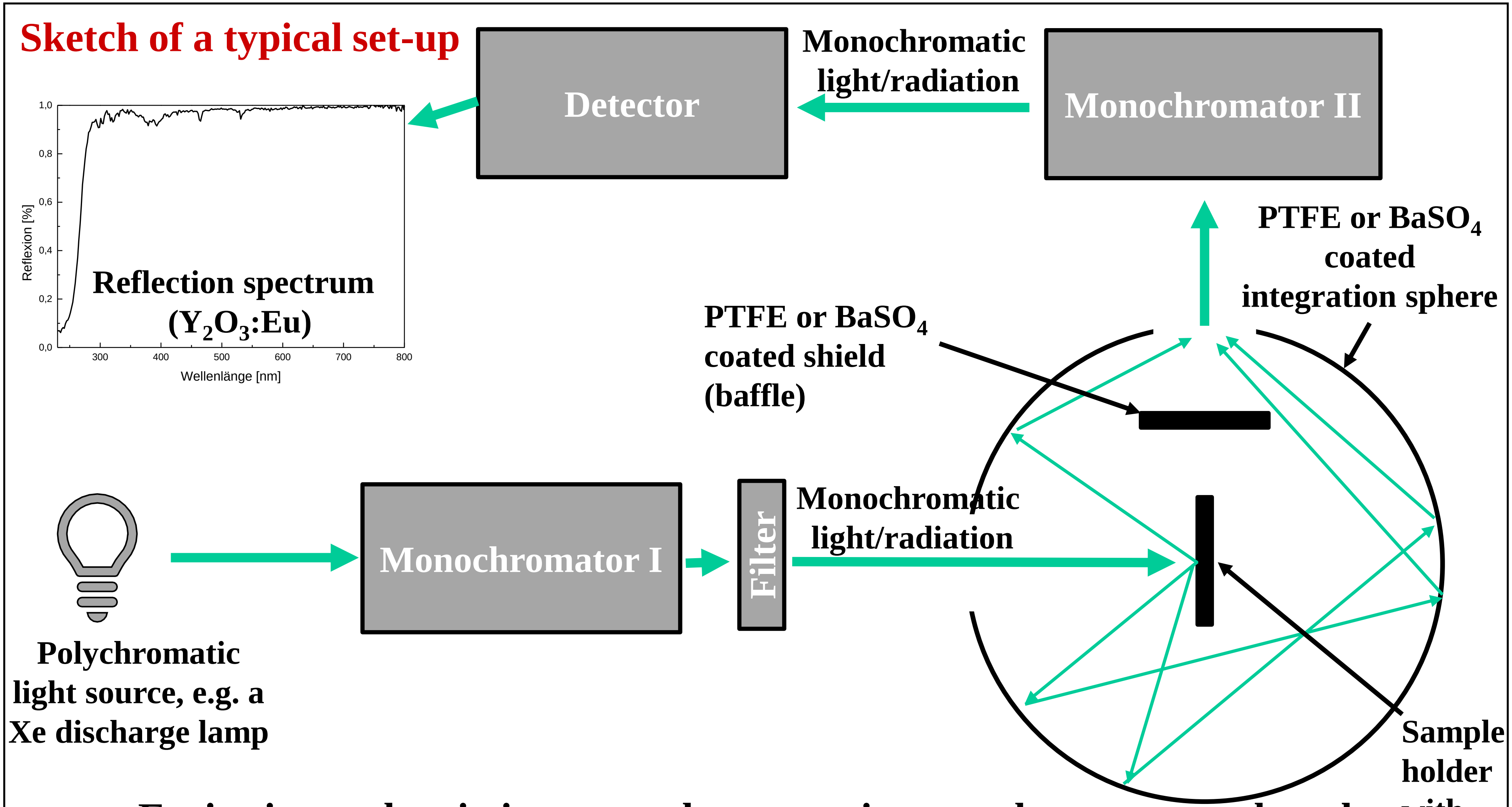
Overlapping of two processes



Ref.:D. Oelkrug in H. Naumer, W. Heller, Untersuchungsmethoden in der Chemie, Thieme, 3rd edition, 1997

4.3.2 Reflection Spectrometer

Sketch of a typical set-up



Reflection spectrum (Y_2O_3:Eu)

Detector

Monochromatic light/radiation

Monochromator II

PTFE or $BaSO_4$ coated integration sphere

PTFE or $BaSO_4$ coated shield (baffle)

Monochromator I

Filter

Monochromatic light/radiation

Polychromatic light source, e.g. a Xe discharge lamp

Sample holder with sample

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

4.3.3 The Integrating Sphere

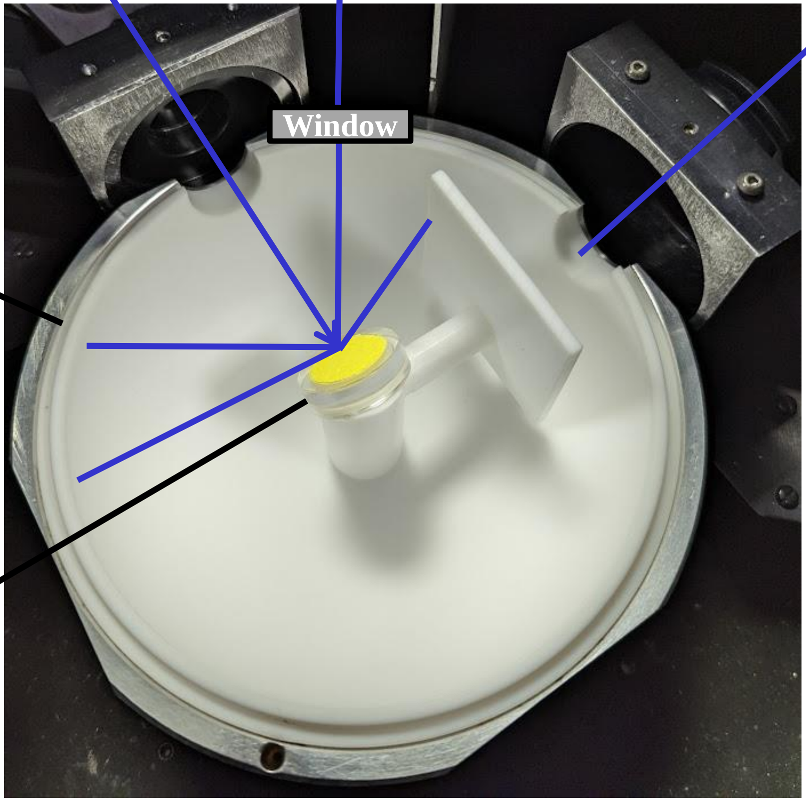
Image of an Ulbricht Sphere

Light from monochromator 1

Optional output
to analysis the
specular reflexes

to mono-
chromator 2

Coated
integrating
sphere
($BaSO_4$)



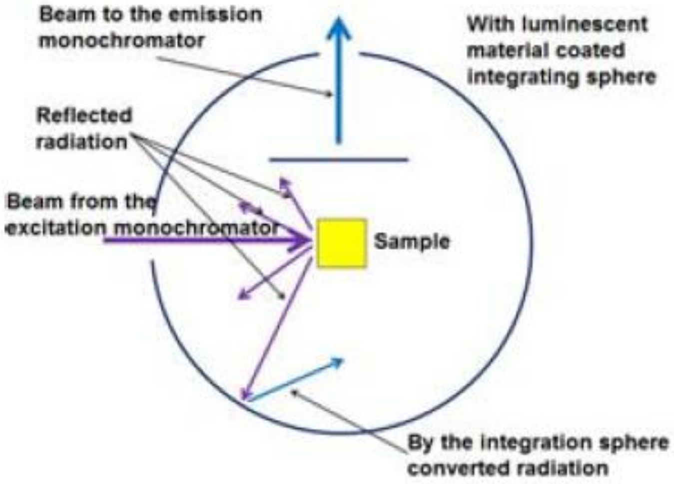
Sample holder
with YAG:Ce

4.3.4 VUV Reflection

Specific Challenges in the VUV Range

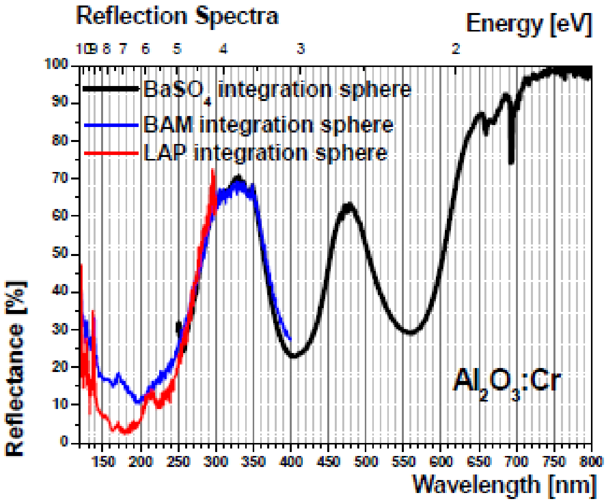
- PMTs cannot detect VUV radiation
- Teflon and $BaSO_4$ absorb VUV (< 200 nm)

→ Scintillation detector + LiF or MgF_2 coating (hygroscopic!)



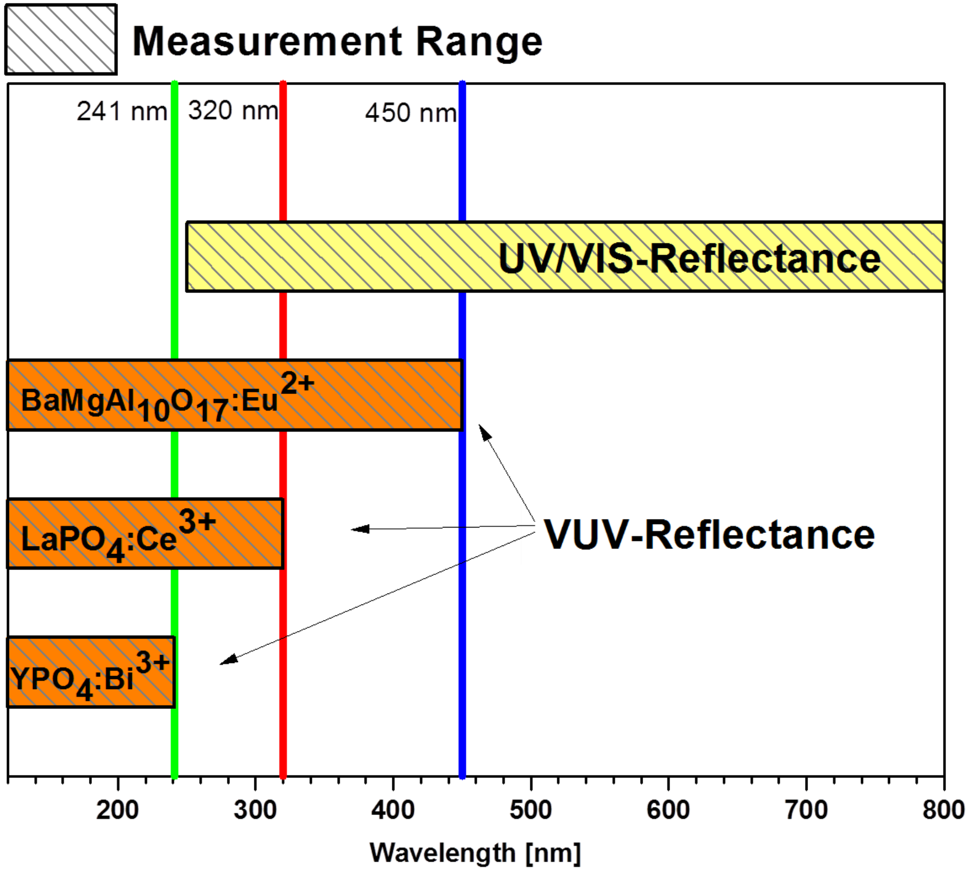
Alternative: Coating of the integration sphere with a phosphor which converts the VUV to visible radiation

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!

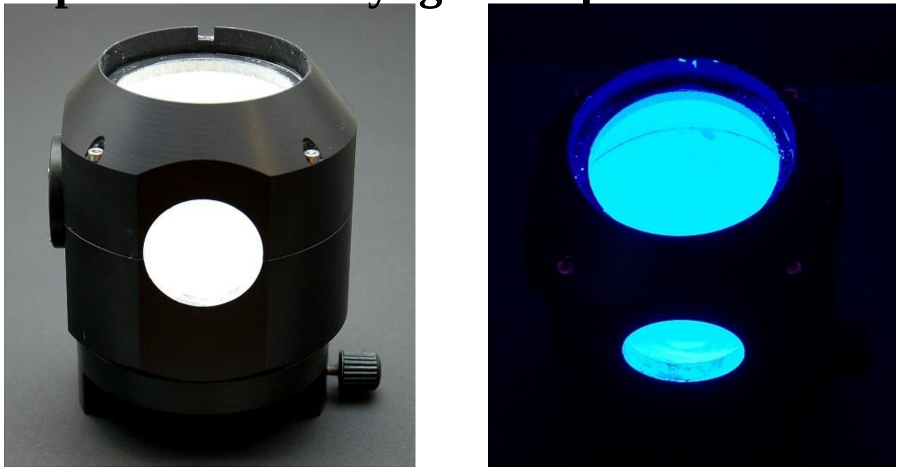


4.3.4 VUV Reflection

Specific Challenges in the VUV Range



$BaMgAl_{10}O_{17}$:Eu coated integration sphere under daylight or upon VUV exc.



$LaPO_4$:Ce coated integration sphere

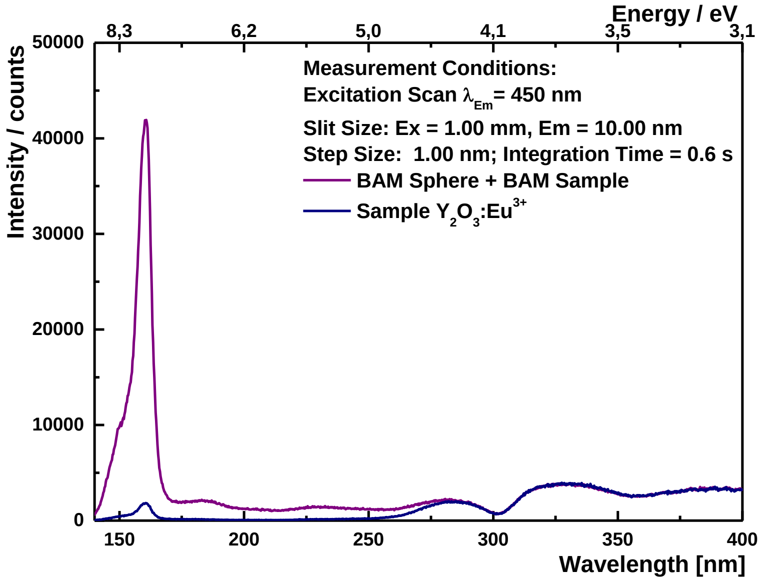
Reference

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

4.3.4 VUV Reflection

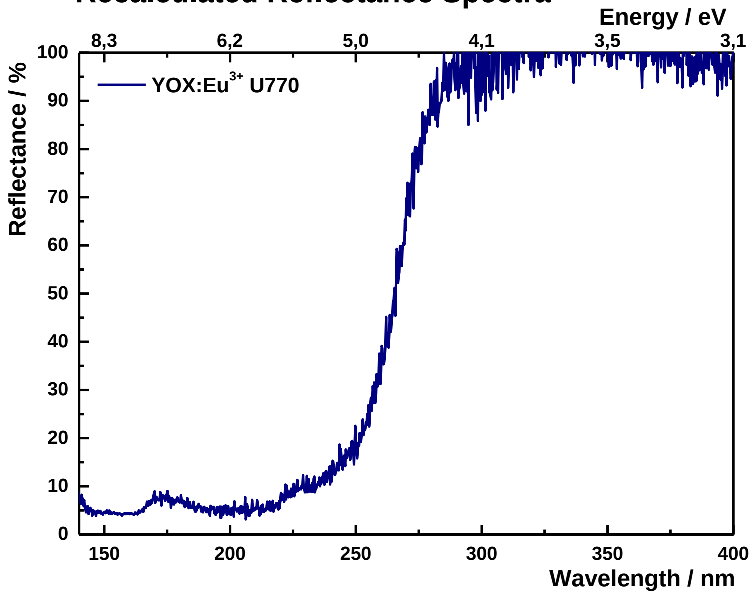
Procedure for recording a diffuse reflection spectrum $R_{diffuse}(\lambda)$ in the VUV range

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(Sample)/I(BAM:Eu)



Excitation Spectra measured in BAM Sphere

Division



Recalculated Reflectance Spectra

4.3.5 Band Gap Determination

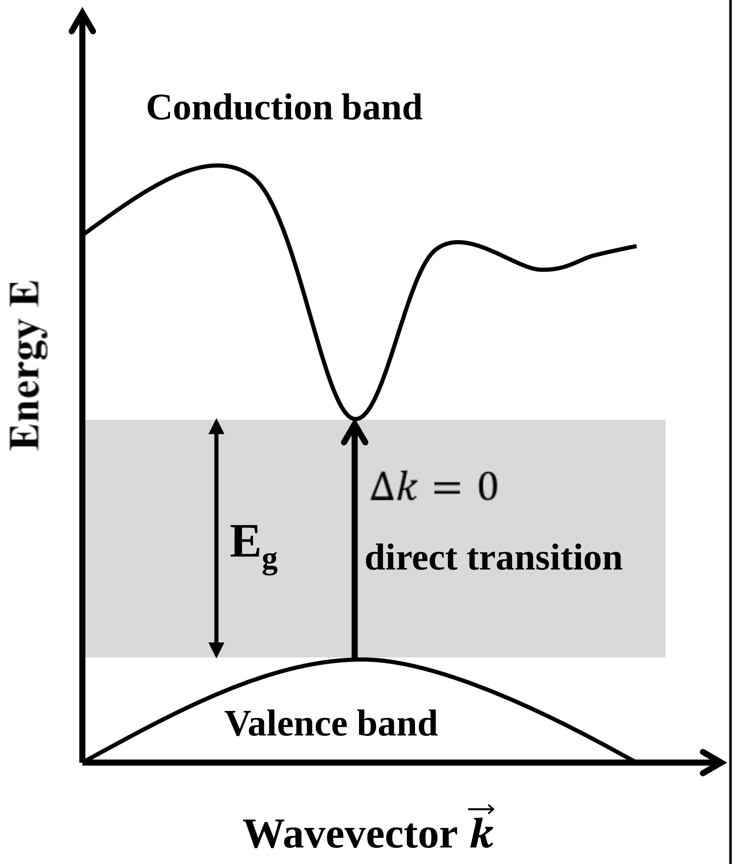
Motivation

- **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

p = ħ·k

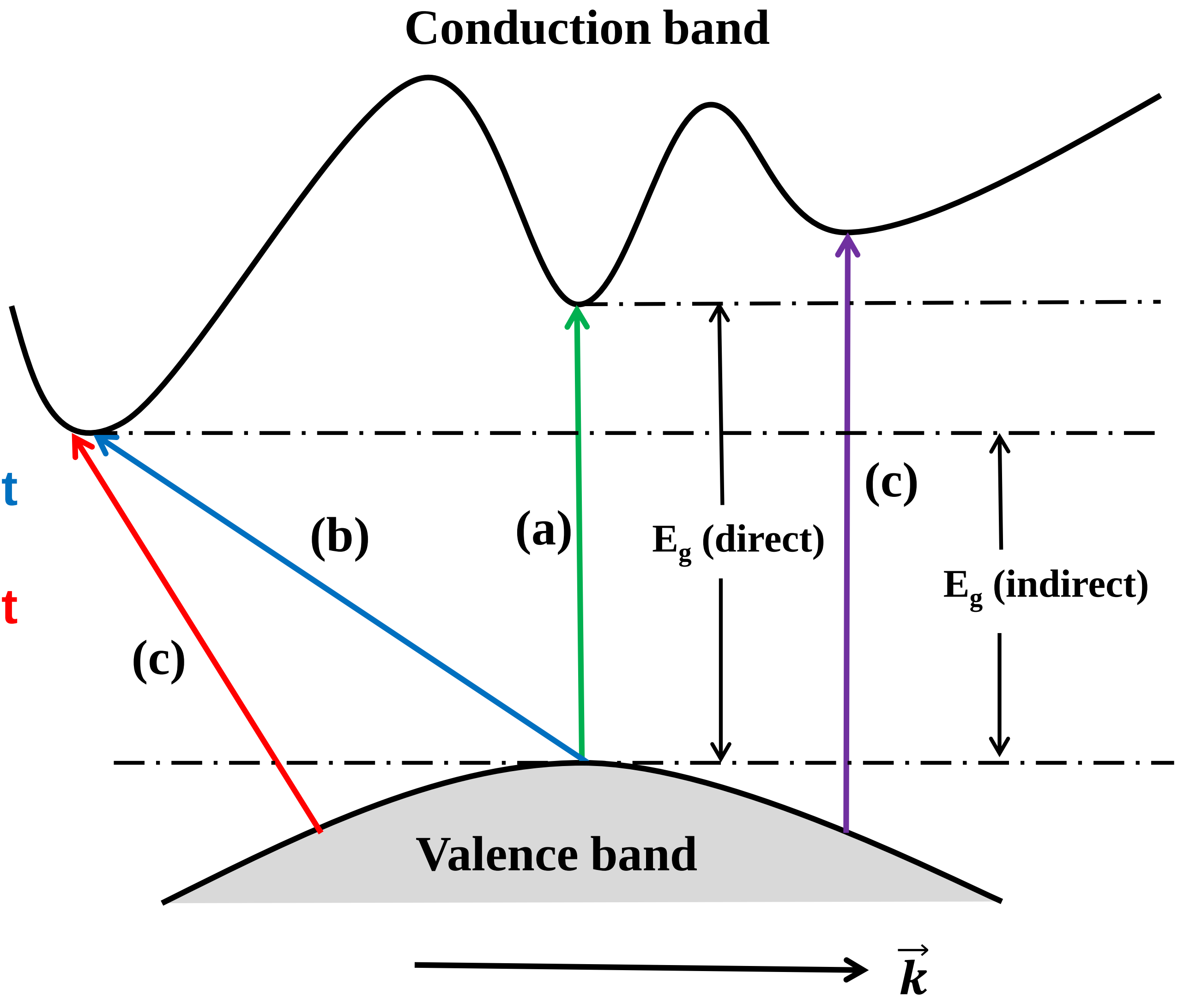


4.3.5 Band Gap Determination

Motivation

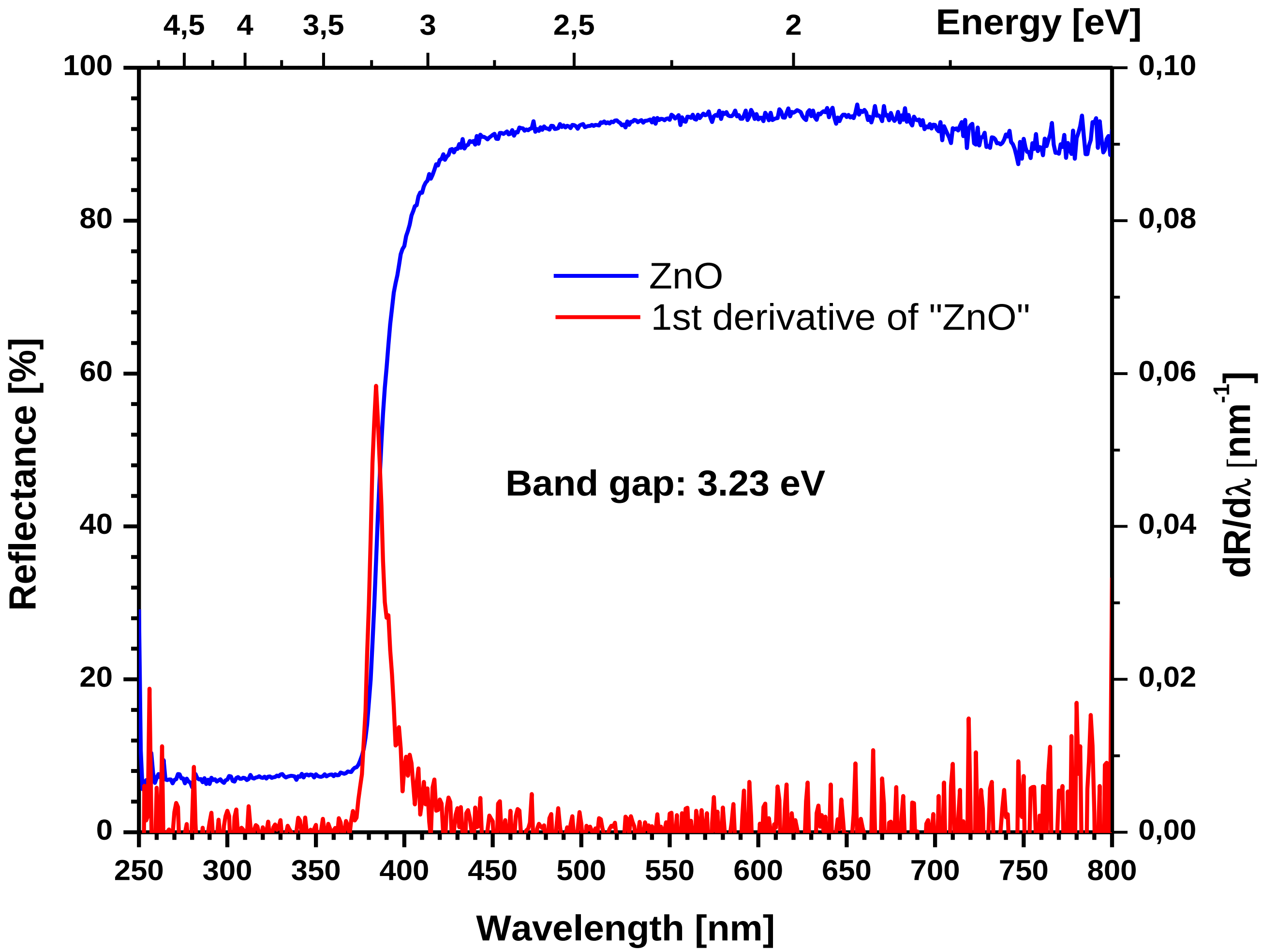
Types of transitions

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



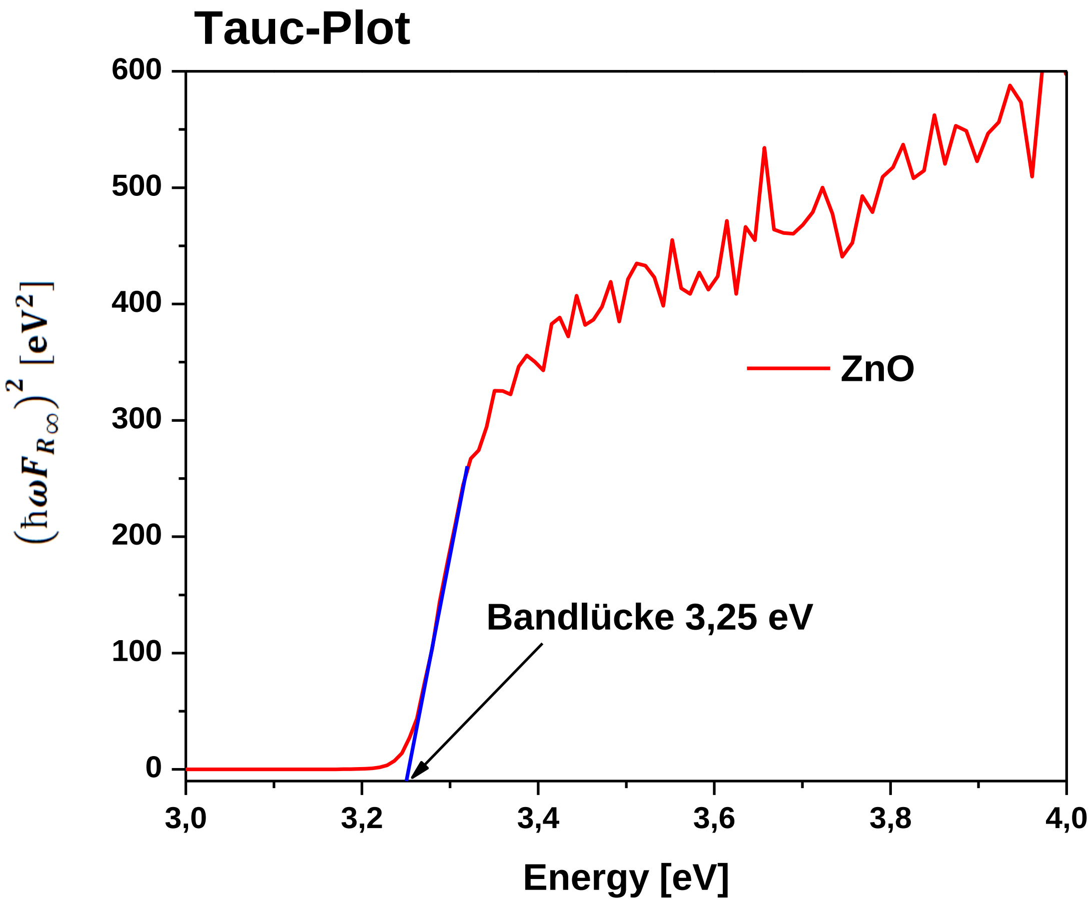
4.3.5 Band Gap Determination

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

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 >> 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:

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

S = Scattering coefficient
$R_\propto$ = Diffuse scattering
A = Absorption = $\varepsilon \cdot c$

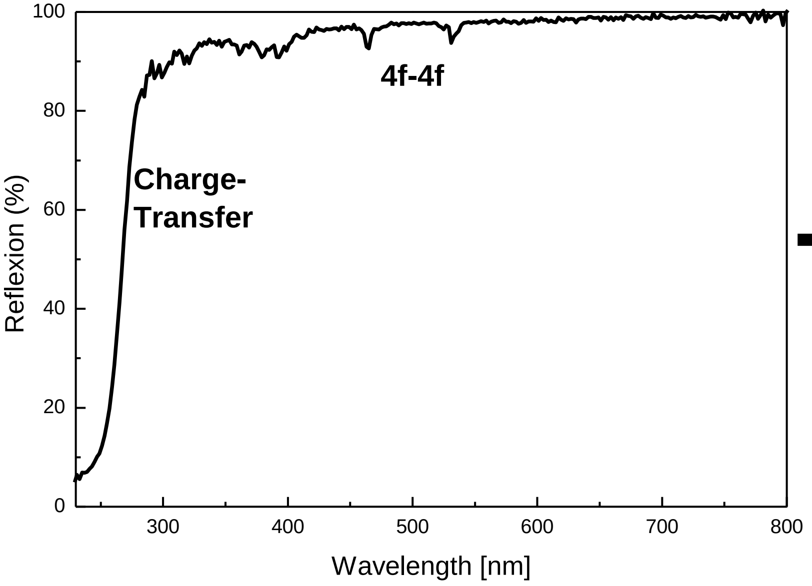
An ideally black surface $R_\propto = 0$ is therefore difficult to realize, because for $R_\propto = 0$ applies $A/S = \propto$, i.e. extremely high absorption or virtually no scattering
The scattering coefficient S can be estimated from the particle size of the powder:
$S \sim 1/\text{grain size} \sim 1/d_{50}$ [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“ ⇒ R + A = 1

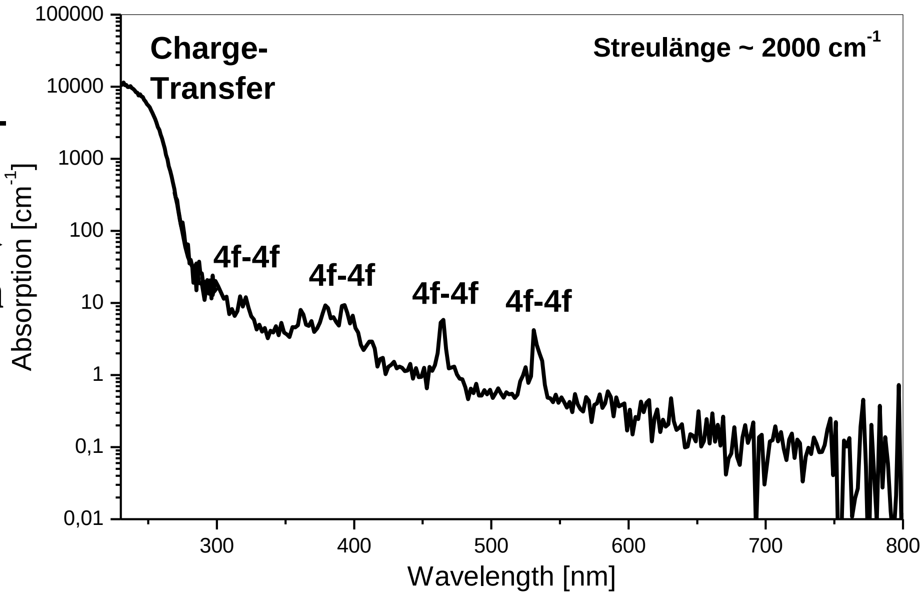
Example: Phosphor $Y_2O_3:Eu^{3+}$(5%) with d_{50} = 5 µm ⇒ S ~ 0.2 µm^{-1} = 2000 cm^{-1}



Kubelka-

Munk

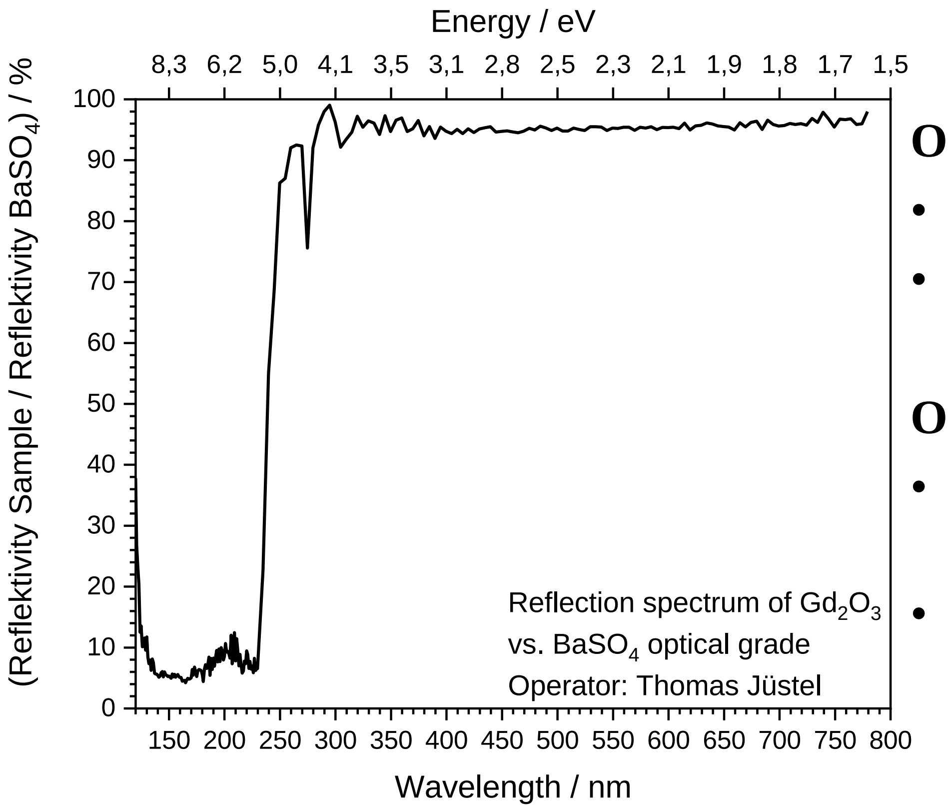
Function



4.3.7 Application of Reflection Spectroscopy

Determination of Optical Transitions of Powder Samples

Example: Gd_2O_3



Optical transitions

- **Band-to-band transition ~ 225 nm (5.5 eV)**
- **[Xe]$4f^7$ ($^8S_{7/2}$) – [Xe]$4f^7$ ($^6P_{5/2}$) ~ 275 nm**

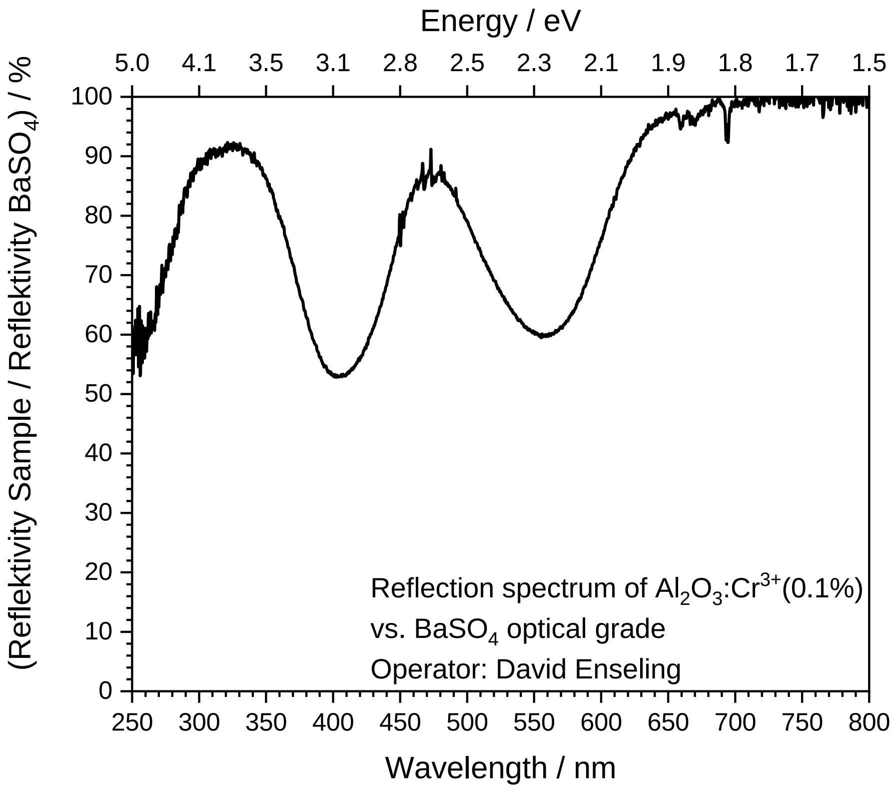
Optical band gap according to literature

- **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: $Al_2O_3:Cr^{3+}$



Reflection spectrum of $Al_2O_3:Cr^{3+}$(0.1%)
vs. $BaSO_4$ optical grade
Operator: David Enseling

Optical transitions

- **Band-to-band transition < 200 nm**
- **Cr^{3+}: [Ar]$3d^3$ (^4F) to [Ar]$3d^3$ (^4F, ^4P)**

– **$^4A_2 - {}^4T_2$**	**405 nm**	**band**
– **$^4A_2 - {}^4T_1$**	**560 nm**	**band**
– **$^4A_2 - {}^2E$**	**694 nm**	**lines**

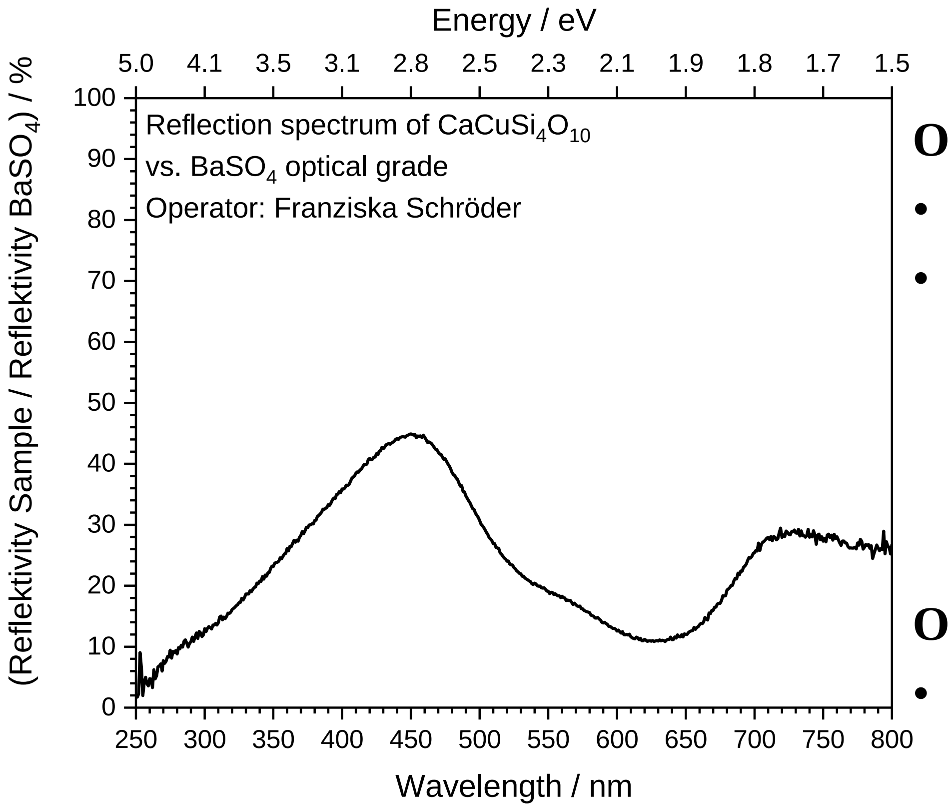
Optical band gap

- **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: $CaCuSi_4O_{10}$



Optical transitions

- **Band-to-band transition ~ 340 nm (3.6 eV)**
- **Cu^{2+}: [Ar]$3d^9$ → [Ar]$3d^9$ transitions**

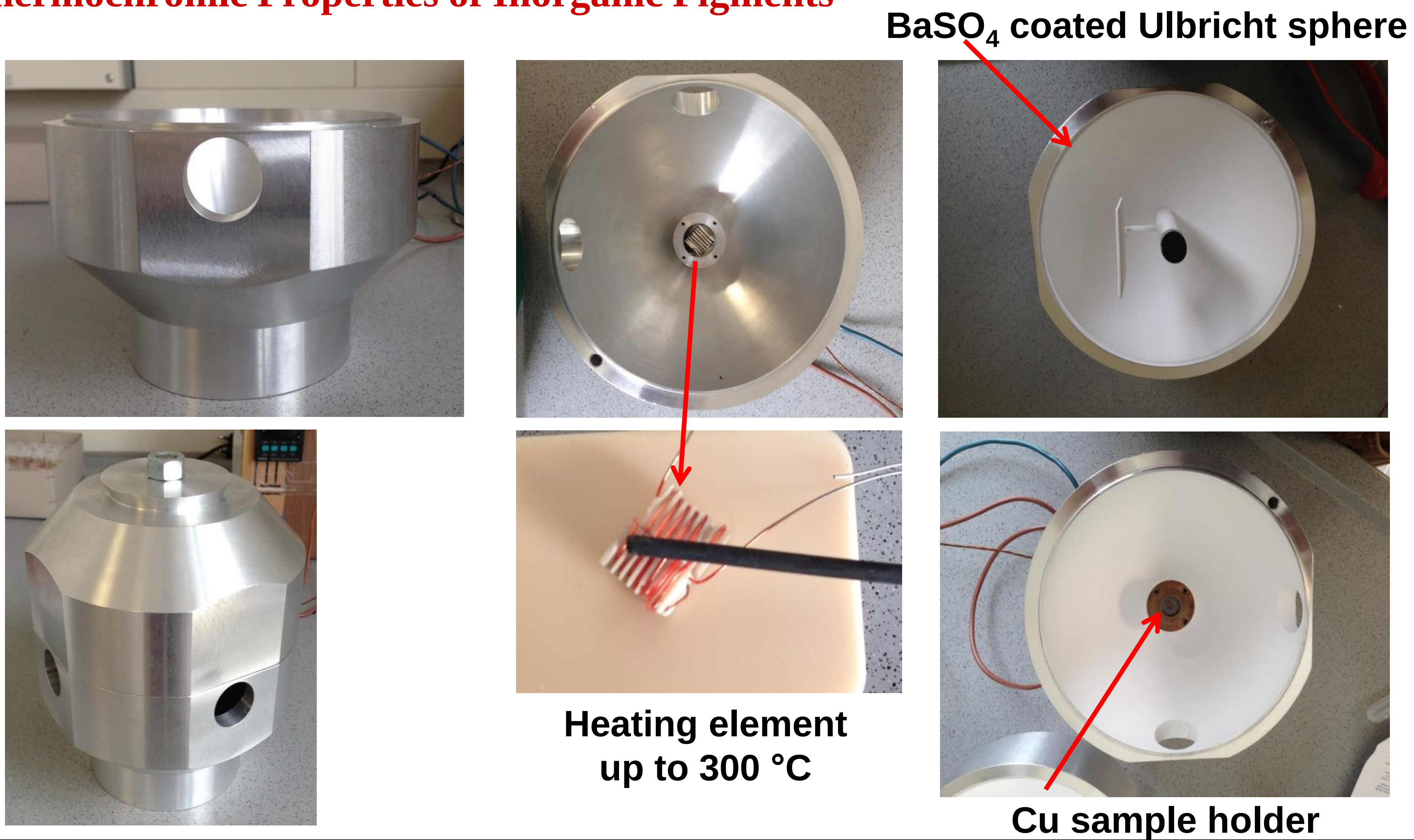
$^2E_g \rightarrow {}^2B_{1g}$	**500 nm**
$^2A_{1g} \rightarrow {}^2B_{1g}$	**625 nm**
$^4A_{2g} \rightarrow {}^2T_{1g}$	**750 nm**

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



$BaSO_4$ coated Ulbricht sphere

Heating element up to 300 °C

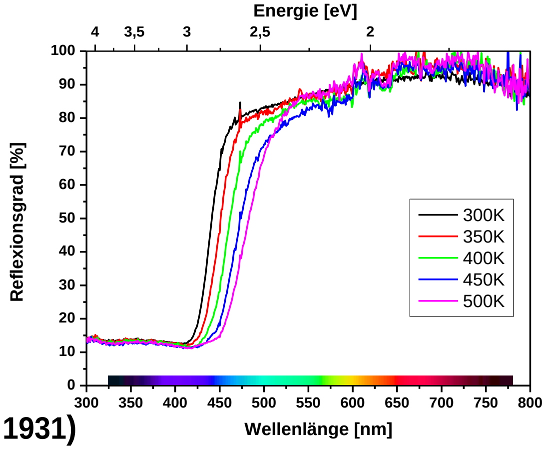
Cu sample holder

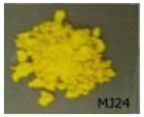
4.3.7 Application of Reflection Spectroscopy

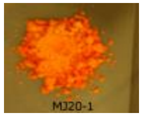
Thermochromic Properties of Inorganic Pigments

Example:

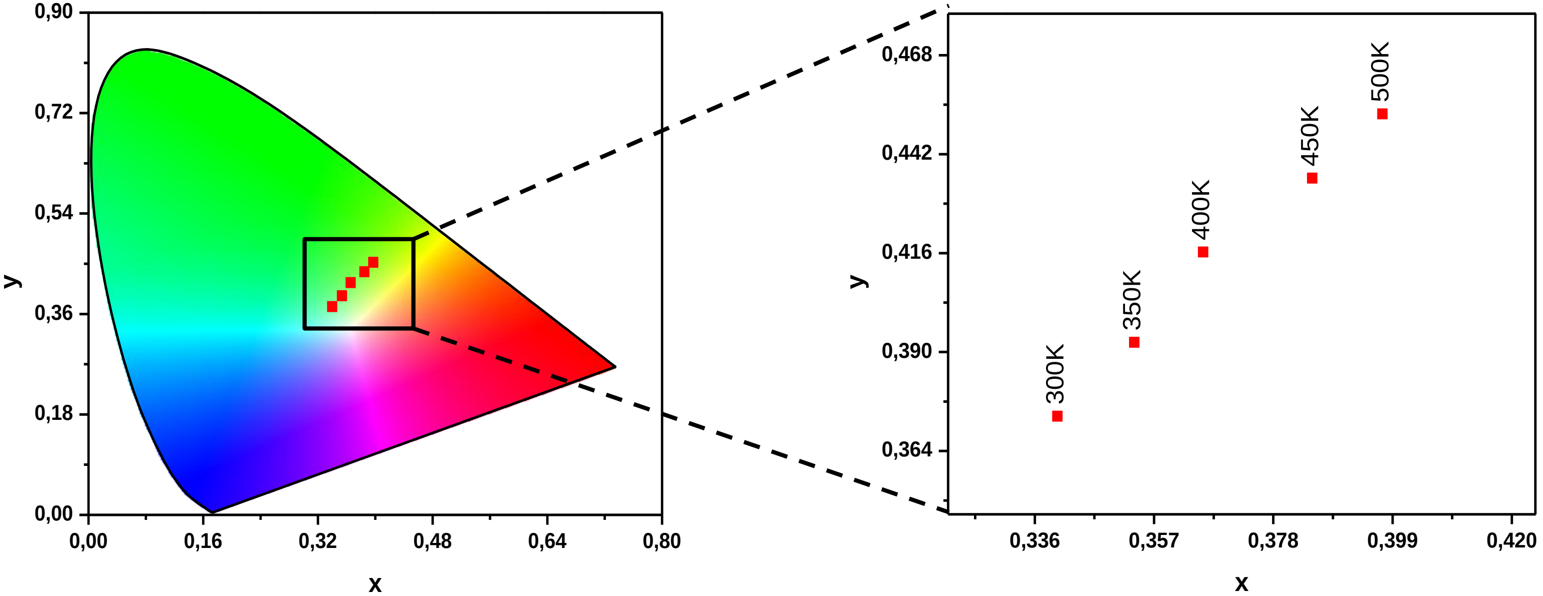
Yellow pigment $BiVO_4$







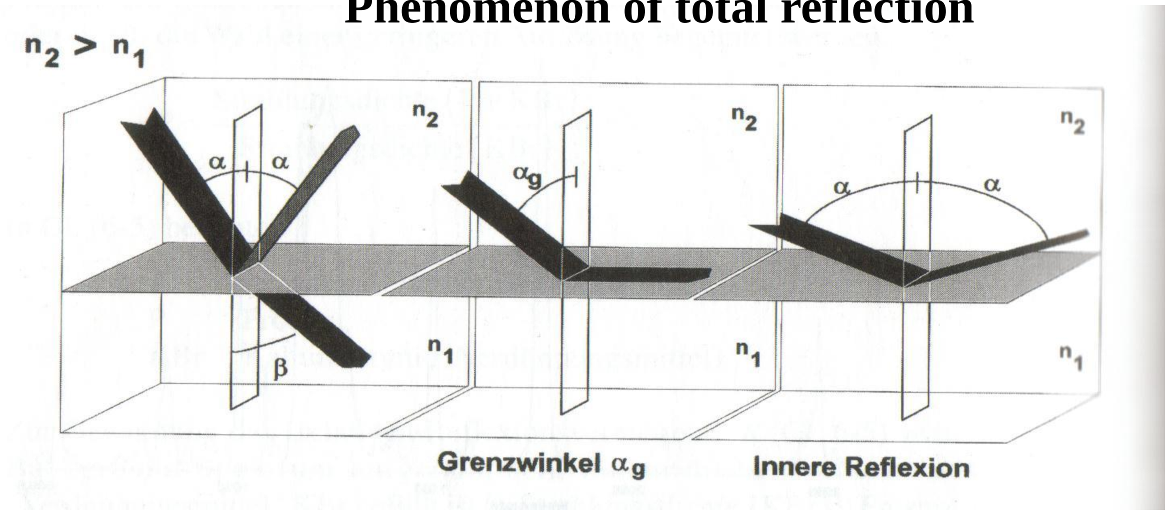
Colour Points (C.I.E. 1931) Colour Points (C.I.E. 1931)



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

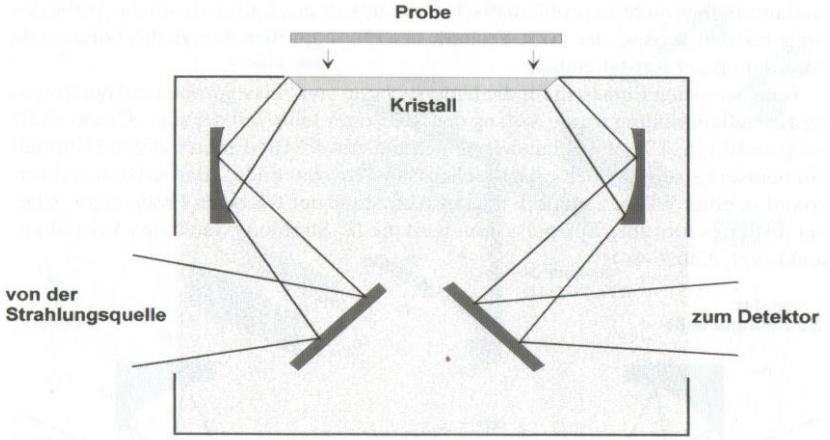
Keep in mind: The penetration depth of radiation is wavelength dependent:
The larger the wavelength, the more intensive bands appear, furthermore their positions are changed.
→ ATR correction is required (e.g. OPUS software from Bruker)

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

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 cm^{-1} for ZnSe