3. Inorganic Functional Materials

3.1. Pigments

3.1.1 Definition and Classification

3.1.2 Economic Importance

3.1.3 Production and Synthesis

3.1.4 Catalytic Pigments

3.1.5 Anticorrosive Pigments

3.1.6 Magnetic Pigments

3.1.7 Color Pigments

3.1.8 Effect Pigments

3.1.9 Fillers

Ultramarin Violet   Ultramarin Blue Cr_2O_3 $BiVO_4$ HgO

3.1.1 Definition and Classification

Definition

(Inorganic) pigments (Latin: pigmentum = painter color) consists of micro- or nano-particles, which are practically insoluble in the application system, i.e. suspending Medium (solvents, polymers, glass, …)
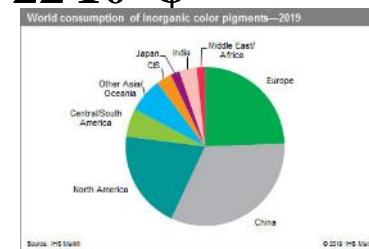
Classification

Application area	Example	Chapter
1. Catalytic pigments	TiO_2	3.1.4
2. Anticorrosive pigments	Pb_3O_4	3.1.5
3. Magnetic pigments	Fe_3O_4	3.1.6
4. Color pigments	$CoAl_2O_4$	3.1.7
5. Nacreous pigments	TiO_2 on Mica, Pearls	3.1.8
6. Luminescent pigments	ZnS:Ag	3.2.
7. Fillers	SiO_2	3.1.9
8. Flame Retardants	MgO	-

3.1.2 Economic Importance

Production of inorganic pigments

	1995	2006	2019
World	$4.85 \cdot 10^6$ t $\Rightarrow 13 \cdot 10^9$ \$	$7.4 \cdot 10^6$ t $\Rightarrow 18 \cdot 10^9$ \$	$22 \cdot 10^9$ \$
Germany	$2.0 \cdot 10^6$ t		

World consumption of inorganic color pigments—2019

Pigment	Percentage	Application areas
TiO_2	66% ($3.2 \cdot 10^6$ t)	White, UV protection + catalytic pigment
Fe_2O_3	14%	Red + magnetic pigment
Carbon Black	10%	Black pigment
$ZnS/BaSO_4$	4%	White pigment
Chromates	3%	Yellow + corrosion protection pigment
Cr_2O_3	1%	Green pigment
$Me^{I}[Fe^{II}Fe^{III}(CN)_6] \cdot H_2O$	< 0.5%	Blue pigment
Ultramarine	< 0.5%	Blue pigment

3.1.3 Production and Synthesis

TiO$_2$ (Titania)

Occurence in nature

FeTiO$_3$ Ilmenite

TiO$_2$ Rutile, anatase
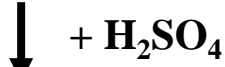
(both contaminated with Fe$_2$O$_3$ and Fe$_3$O$_4$)

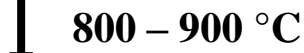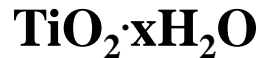$\downarrow$

Mining + Milling process

$\downarrow$

Slurry + Magnetic separation

$\downarrow$

Enriched ore

Sulphate process

Ilmenite

$\downarrow$ + H$_2$SO$_4$

Sulfate cake

$\downarrow$ Leach out

Fe$_2$(SO$_4$)$_3$ + TiOSO$_4$

$\downarrow$ Reduction

FeSO$_4$ + TiOSO$_4$

- FeSO$_4$·7H$_2$O $\downarrow$ Evaporation

TiOSO$_4$

$\downarrow$ + H$_2$O, Boiling

TiO$_2$·xH$_2$O

$\downarrow$ 800 – 900 °C

TiO$_2$
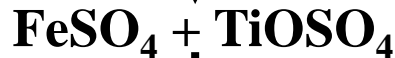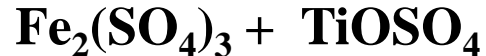
Chloride process

Rutile

$\downarrow$ + Coke+ Cl$_2$
      950 °C

FeCl$_3$ + TiCl$_4$↑

$\downarrow$ Condensation

Purified TiCl$_4$

$\downarrow$ + O$_2$ 1000 °C

TiO$_2$
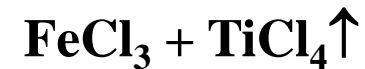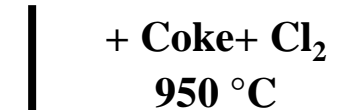
3.1.3 Production and Synthesis

Fe$_2$O$_3$ and Fe$_3$O$_4$

Occurence in nature

α-Fe$_2$O$_3$ **Hematite**

Fe$_3$O$_4$ **Magnetite**

Stability of the metastable γ-Fe$_2$O$_3$

-1/6 O$_2$, 200 °C, vacuum   300 °C, air
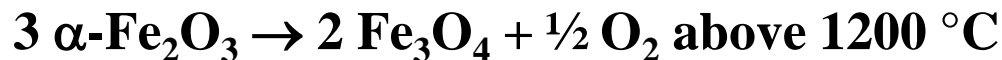
Fe$_3$O$_4$ ⟵——— γ-Fe$_2$O$_3$ ———⟶ α -Fe$_2$O$_3$

Synthesis of the iron oxide pigments (starting from FeSO$_4$)

- **α-Fe$_2$O$_3$**   **(red-brown, antiferromagnetic, corundum structure)**

2 FeSO$_4$ + 4 NaOH + ½ O$_2$ → 2 Na$_2$SO$_4$ + H$_2$O + α-FeOOH → α-Fe$_2$O$_3$ (400 - 500 °C)

- **Fe$_3$O$_4$**   **(black, ferrimagnetic, inverse spinel: [Fe^{III}]$_T$[Fe^{II}Fe^{III}]$_O$O$_4$)**

3 α-Fe$_2$O$_3$ + H$_2$ → 2 Fe$_3$O$_4$+ H$_2$O at 340 - 400 °C

3 α-Fe$_2$O$_3$ → 2 Fe$_3$O$_4$ + ½ O$_2$ above 1200 °C

- **γ-Fe$_2$O$_3$**   **(brown, ferromagnetic, inverse spinel: [Fe^{III}]$_T$[•$_{0.33}$Fe^{III}$_{1.67}$]$_O$O$_4$)**

2 Fe$_3$O$_4$ + ½ O$_2$ → 3 γ-Fe$_2$O$_3$ at 200 - 250 °C in air

3.1.4 Catalytic Pigments

Heterogeneous catalysis

Autocatalyst Pd/Pt/Rh pigment (~ 3 g) onto
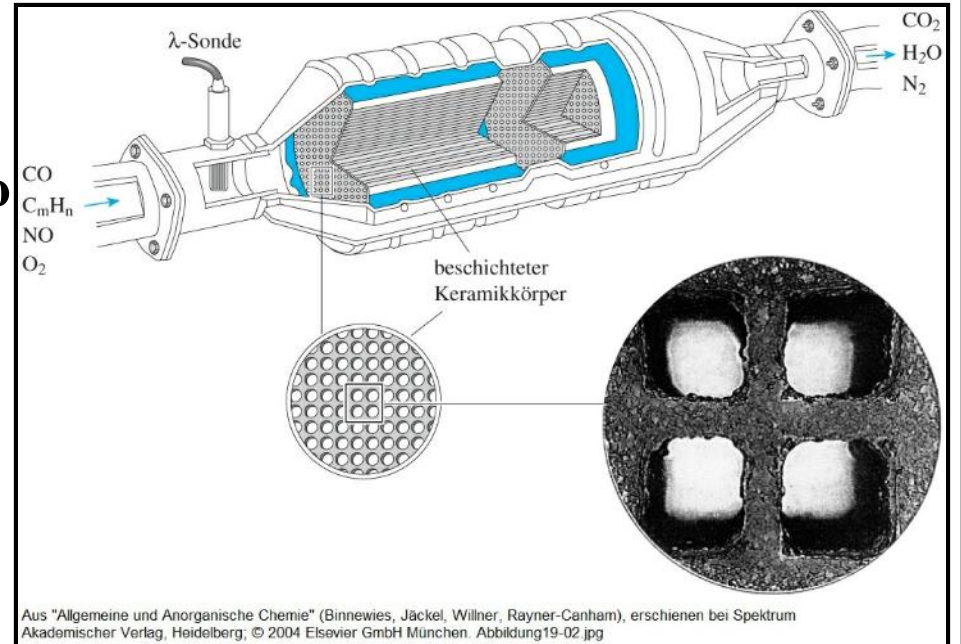a ceramic substrate (value ~ 1000 €/car)

$$2 \text{ CO} + O_2 \rightarrow 2 \text{ CO}_2$$
$$C_8H_{18} + 25 \text{ O}_2 \rightarrow 16 \text{ CO}_2 + 18 \text{ H}_2O$$
$$2 \text{ NO} + 2 \text{ CO} \rightarrow N_2 + 2 \text{ CO}_2$$

Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung19-02.jpg
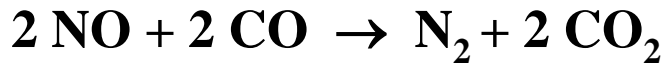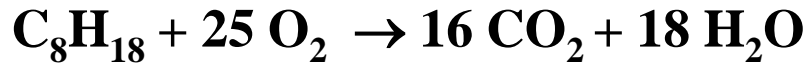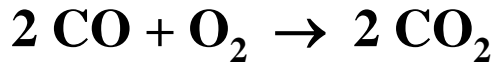
Oxygen regulation by CeO_2

$$2 \text{ CeO}_2 \rightleftarrows Ce_2O_3 + \frac{1}{2} O_2$$

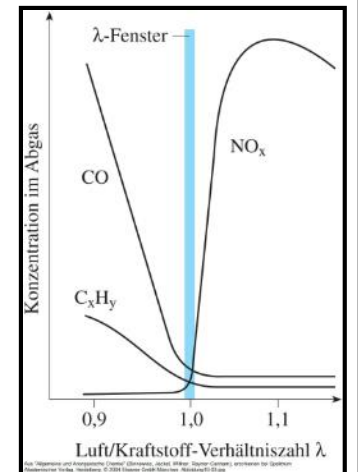Oxidation of soot by CeO_2

$$C + 2 \text{ CeO}_2 \rightarrow CO + Ce_2O_3$$
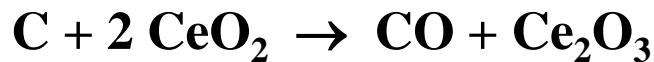
(diesel vehicles)

Oxygen measurement by means of a λ-probe

Electrochemical chain to measure
the O_2 partial pressure in the catalyst
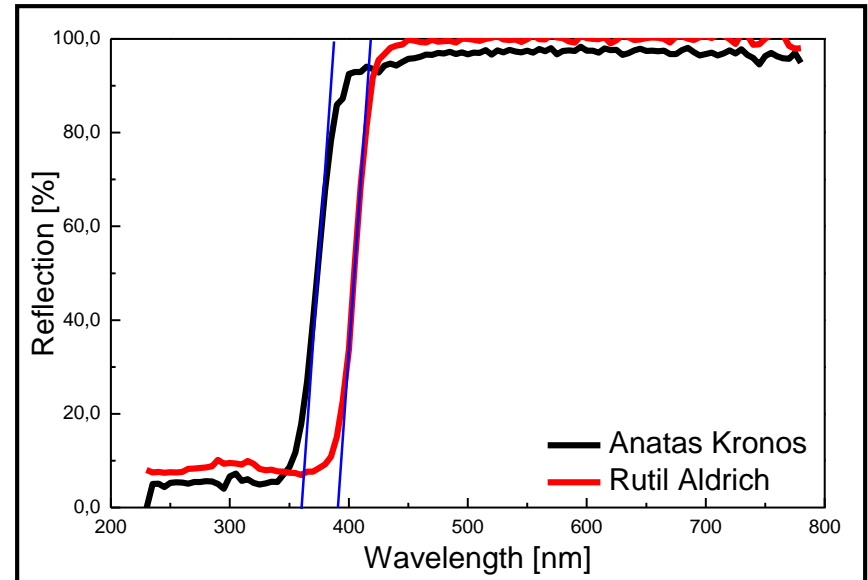
$\Rightarrow$ Oxygen ion conductor $ZrO_2{:}Y^{3+}$

3.1.4 Catalytic Pigments

UV-Absorption and photochemistry

$\Rightarrow$ **TiO$_2$ pigments**

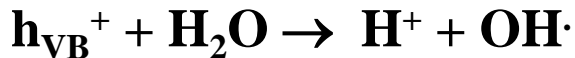| Modification	E$_g$ [eV]	E$_g$ [nm]	n
Anatase	3.5	360	2.55
Rutile	3.2	390	2.79

1. UV-absorption (protective pigment)

$\Rightarrow$ **Use of rutile in sun protective creams, window frames, plastic bags.....**

2. Photochemistry

$\Rightarrow$ **Use of anatase to water and surface cleaning**

$\Rightarrow$ $TiO_2 + h\nu(UV\text{-}A) \rightarrow TiO_2(h_{VB}^+ + e_{CB}^-)$

$h_{VB}^+ + H_2O \rightarrow H^+ + OH\cdot$

$e_{CB}^- + O_2 \rightarrow O_2^{\cdot-}$ (superoxide) $\Rightarrow$ **Mineralisation of organic compounds**

3.1.5 Corrosion Protection Pigments

As corrosion (Latin: corrodere = gnaw away) denotes the decomposition of economically important materials (mostly metals and alloys)

Countermeasure: Coating valuable materials with protective pigments

1. **Cathodic protection (application of a reducing effective pigments)**
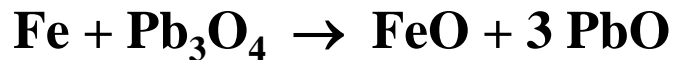Application of Zn on Fe-sheets
Oxidation of base metal according to
$$2\ Zn \rightarrow 2\ Zn^{2+} + 4\ e^- \quad \text{cathodic reaction}$$
$$O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$$
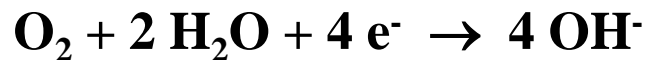
2. **Passivation (formation of impermeable protective oxide layers)**
Application of Pb_3O_4 ($Pb^{II}_2[Pb^{IV}O_4]$), Ca_2PbO_4, or $PbCrO_4$
Oxidation of metal at the boundary layer according to
$$Fe + Pb_3O_4 \rightarrow FeO + 3\ PbO$$
Application of silicate or Al_2O_3 layers to slow down diffusion $\rightarrow$ barrier coatings

3.1.6 Magnetic Pigments

Classification of magnetic materials

```
                        Magnetic materials
                              |
              ┌───────────────┴───────────────┐
        Weakly magnetic                 Strongly magnetic
              |                               |
      ┌───────┴───────┐          ┌────────────┼────────────┐
   Dia-          Para-      Antiferro-     Ferro-      Ferri-
  magnetic      magnetic    magnetic      magnetic    magnetic
```

Dia-magnetic	Para-magnetic	Antiferro-magnetic	Ferro-magnetic	Ferri-magnetic
$CaCO_3$	O_2	MnO	Co	MFe_2O_4, Fe_3O_4
C_6H_6	NO	NiO	Fe	$Y_3Fe_5O_{12}$
(Bio)Polymers	Fremy's Salt	Cr	Ni	$BaFe_{12}O_{19}$
				$Sm_5Co, Nd_2Fe_{14}B$
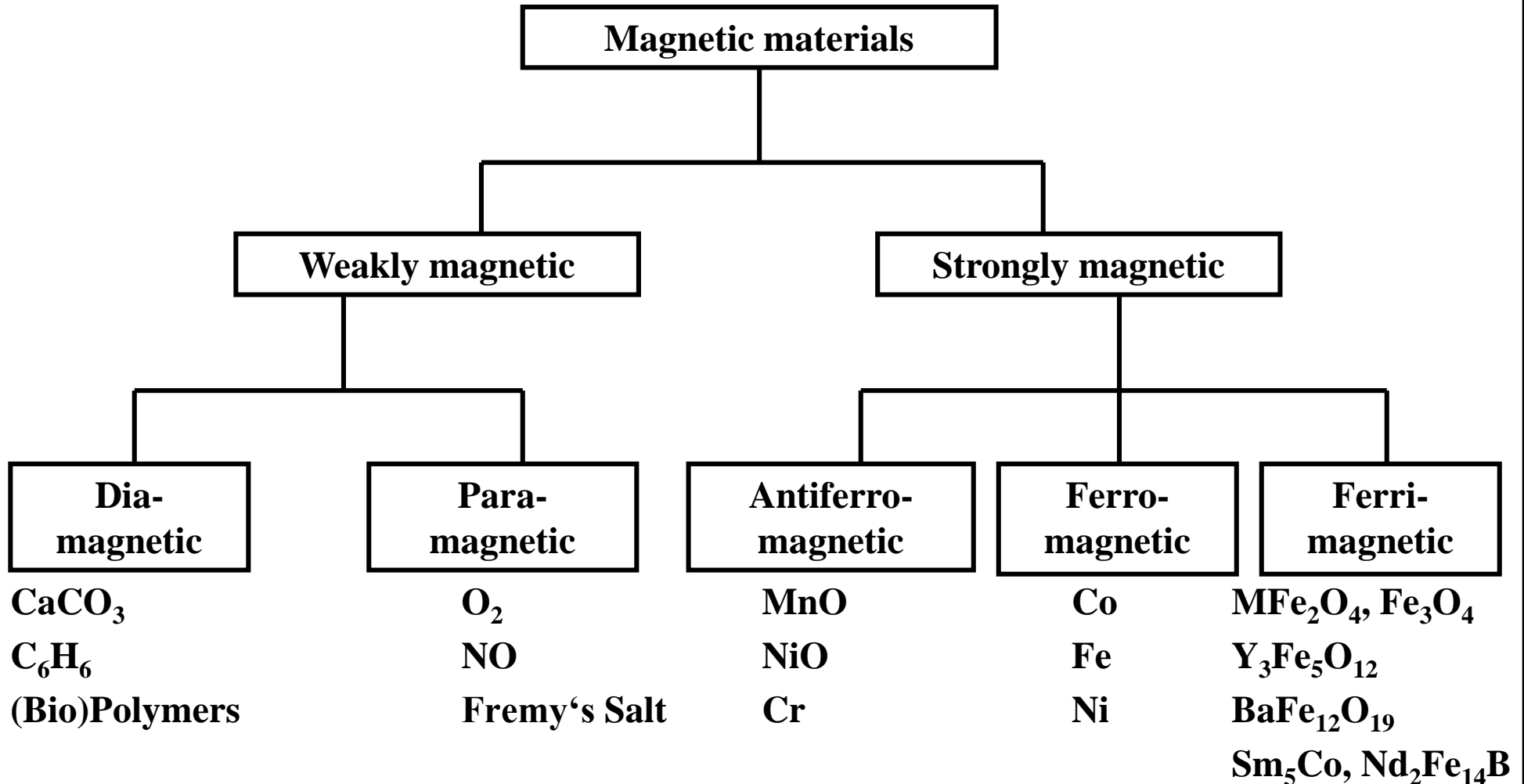
3.1.6 Magnetic Pigments

Magnetic pigments are used for information storage in magnetic or video tapes

Which conditions magnetic pigment has to fulfill?

1. **Cooperative magnetism (the ability for permanent magnetization M)**
   - → **ferromagnetic:** Co, Fe, Ni, CrO_2, γ-Fe_2O_3 (maghemite), $Y_3Fe_5O_{12}$
   - → **antiferromagnetic:** α-Fe_2O_3 (hematite)
   - → **ferrimagnetic:** Fe_3O_4 (magnetite)
   - → **high remanence (residual magnetism after switching off the magnetic field)**
   - → **needle-shaped particles (orientation in the magnetic field)**
2. **No loss of the magnetization M due to heating of the magnetic tape**
   - → **High Curie or Néel temperature**
3. **Good signal/noise ratio**
   - → **Pigment with the smallest possible particle size (single domain/particle)**
4. **Possibility for the complete cancelation of the magnetization**
   - → **Medium coercive field strength H_C (required field strength for demagnetization of the particles)**

3.1.6 Magnetic Pigments

Typical properties of magnetic pigments for

Pigment	Application	Particle size [μm]	Specific surface area [m²/g]	Coercive field strength [kA/m]	Saturation magnetization M_S/δ [μTm³/kg]	M_R/M_S
γ-Fe$_2$O$_3$	Studio radio tapes	0.40	17 – 20	23 – 27	85 – 92	0.80 – 0.85
γ-Fe$_2$O$_3$	Cassette IEC I	0.35	20 – 25	27 – 30	87 - 92	0.80 – 0.90
γ-Fe$_2$O$_3$ (Co-coated)	Cassette IEC II	0.30	30 – 40	52 – 57	94 - 98	0.85 – 0.92
Fe (metallic nanopart.)	8 mm Video	0.25	50 - 60	115 - 127	130 - 160	0.85 – 0.90

3.1.7 Color Pigments

Cause for chromaticity: Selective absorption in the visible spectral range

$\Rightarrow$ **subtractive color blending, i.e. by a color filter**

UV   IR

350   400   450   500   550   600   650   700   750   800

λ [nm]
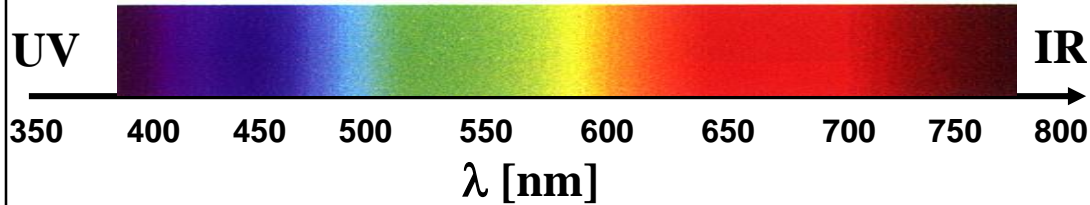
$\Rightarrow$ Yellow

$\Rightarrow$ Magenta

$\Rightarrow$ Cyan

$\Rightarrow$ Red

$\Rightarrow$ Green

$\Rightarrow$ Blue

Green

Yellow   Cyan

White

Red   Blue

Magenta
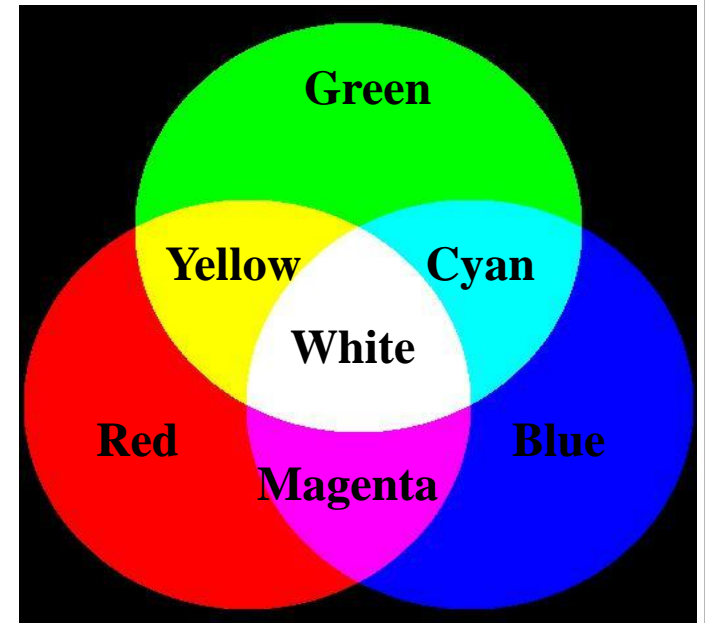
paintings, color printer

3.1.7 Color Pigments

General requirements

Technically desired
- **High saturation: High absorption intensity**
- **High opacity: High refractive index**
- **High light fastness: (Photo) chemical stability**
- **Ecological harmlessness: No toxic elements**

Weißpigment   Buntpigment   Schwarzpigment

Consequence
- **Allowed optical transitions**
  - **VB-CB transitions: CdS**
  - **CT-transitions: CrO_4^{2-}, MnO_4^{-}**
  - **Intervalence transitions (MMCT): Fe^{2+}/Fe^{3+}**
  - **3d-3d-transitions: Co^{2+}**
  - **4f-5d-transitions: Ce^{3+}**
- **High density**
- **Inorganic materials**
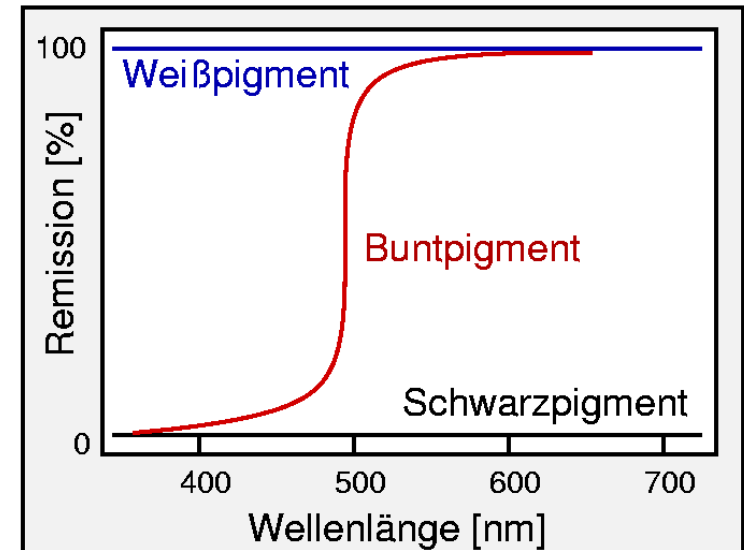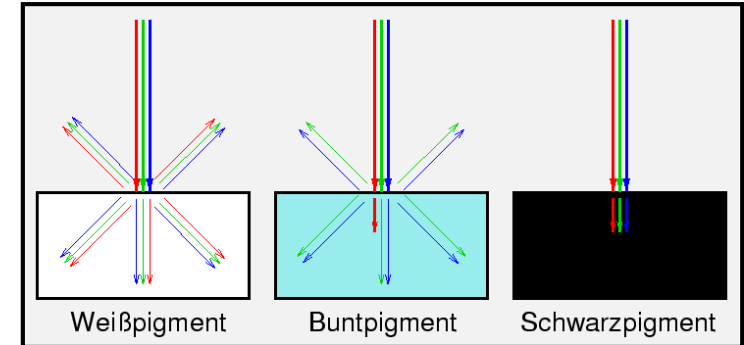
3.1.7 Color Pigments

Chemical composition of inorganic color pigments

White pigments

$PbCO_3 \cdot Pb(OH)_2$	White lead
ZnO	Zinc white
TiO_2	Titanium white
$BaSO_4$	Barium sulfate
Sb_2O_3	Antimony oxide

Blue pigments

$Na_8Al_6Si_6O_{24}S_2$	Ultramarine
$CoAl_2O_4$	Thenard's blue
$KFe[Fe(CN)_6]$	Prussian blue
$Ca/BaCuSi_4O_{10}$	Egyptian blue / Han blue

Green pigments

Cr_2O_3	Chrome green
$ZnCo_2O_4$	Rinmann's green

Yellow pigments

CdS	Cadmium yellow
$PbCrO_4$	Chrome yellow
$FeO(OH)$	Lepidocrocite
$Pb_3(SbO_4)_2$	Antimony yellow
$BiVO_4$	Bismuth vanadate
$K[Co(NO_2)_6]$	Cobalt yellow

Red pigments

HgS	Cinnabar
Fe_2O_3	Oxide red
Pb_3O_4	Minium
$PbCrO_4 \cdot PbO$	Chrome orange
$CdS \cdot HgS$	Cadmium cinnabar
$LaTaON_2$	La. tantalum oxynitride

Applications: paint, artists paint, porcelain paint, plastic coloring

3.1.7 Color Pigments

Technical applications

- **Colors** $\Rightarrow$ **Micro scale pigments (scattering)**

  Paintings
  Coatings
  Colored plastics (tires, plastic)

- **Color filter** $\Rightarrow$ **Nano scale pigments (no scattering)**

  Incandescent lamps
  Fluorescent lamps
  Cathode ray tubes
  Plasma displays
  LCDs
  FEDs

2 nm   3 nm   4 nm   5 nm   6 nm
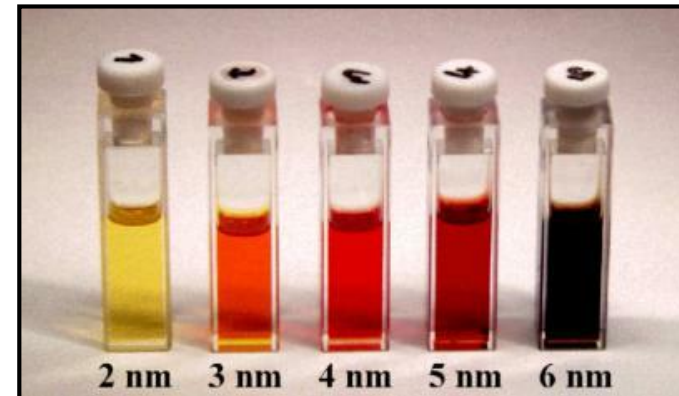
Size dependency of the color of CdSe nanoparticles

3.1.7 Color Pigments

Technical applications

Color filters on light sources: decorative lamps, IR-A emitter, brake and tail lights

Schematic build-up of the color filter

Glass
SiO_2-adhesion layer
Fe_2O_3-nanopigment
Polymer varnish

3.1.7 Color Pigments

Contrast enhancement in cathode ray tubes

(Luminance contrast performance LCP)

$$LCP = \frac{L}{\sqrt{R}}$$

without colour filter

$$LCP = \sqrt{\frac{Luminanz}{Diffuse\ Reflexion}}$$

Tageslicht   Schirmglas

reflektiertes Tageslicht

emittiertes Licht

ZnS: Ag, Al
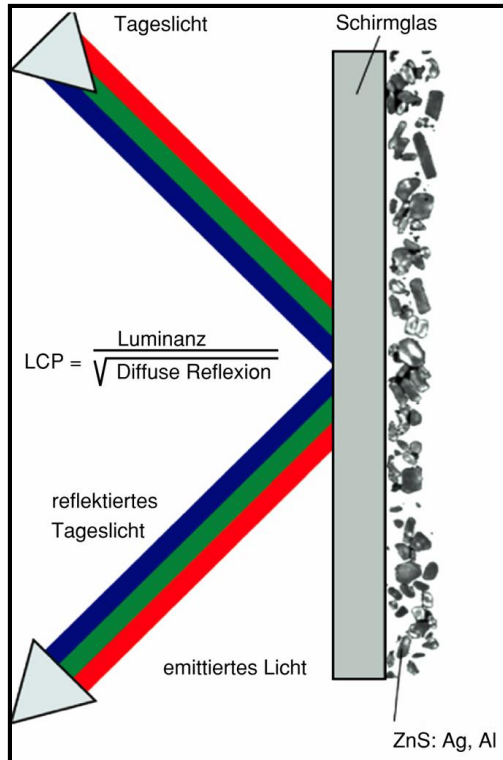
with CoAl$_2$O$_4$ colour filter

$$LCP = \sqrt{\frac{Luminanz}{Diffuse\ Reflexion}}$$

Tageslicht   Schirmglas

reflektiertes Tageslicht

emittiertes Licht

pigmentierter Leuchtstoff
ZnS: Ag, Al
CoAl$_2$O$_4$
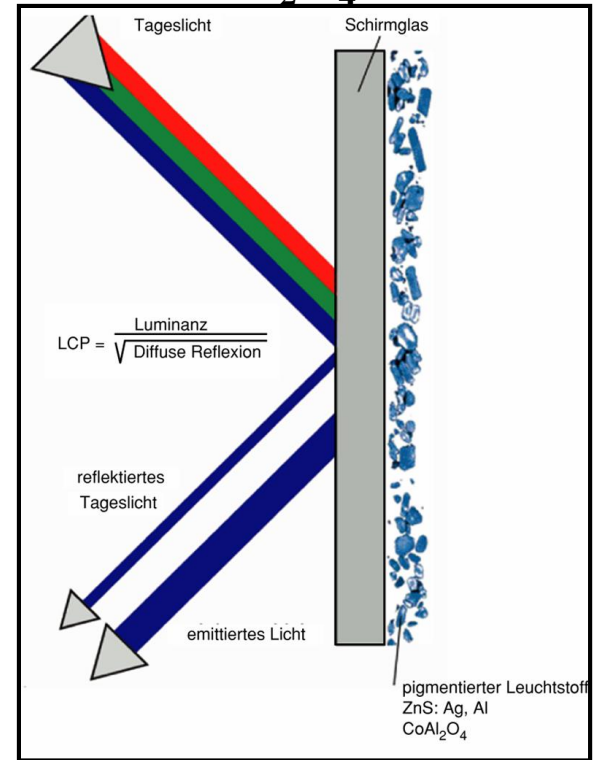
3.1.7 Color Pigments

Technical applications

Emission and reflection spectrum of the pigments in cathode ray tubes

$CoAl_2O_4$ for blue (ZnS:Ag)
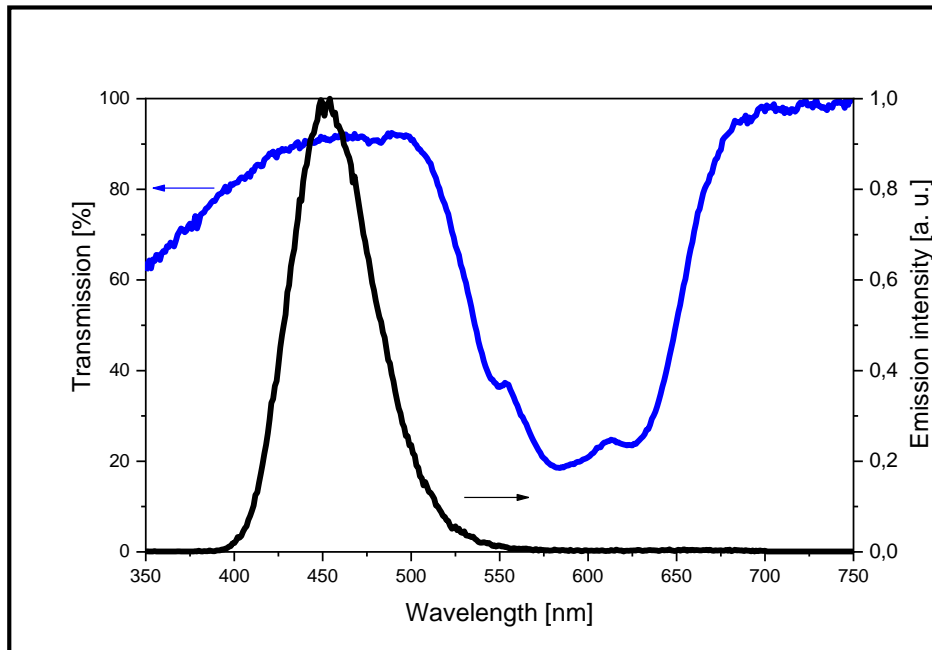
Fe_2O_3 for red ($Y_2O_2S:Eu$)
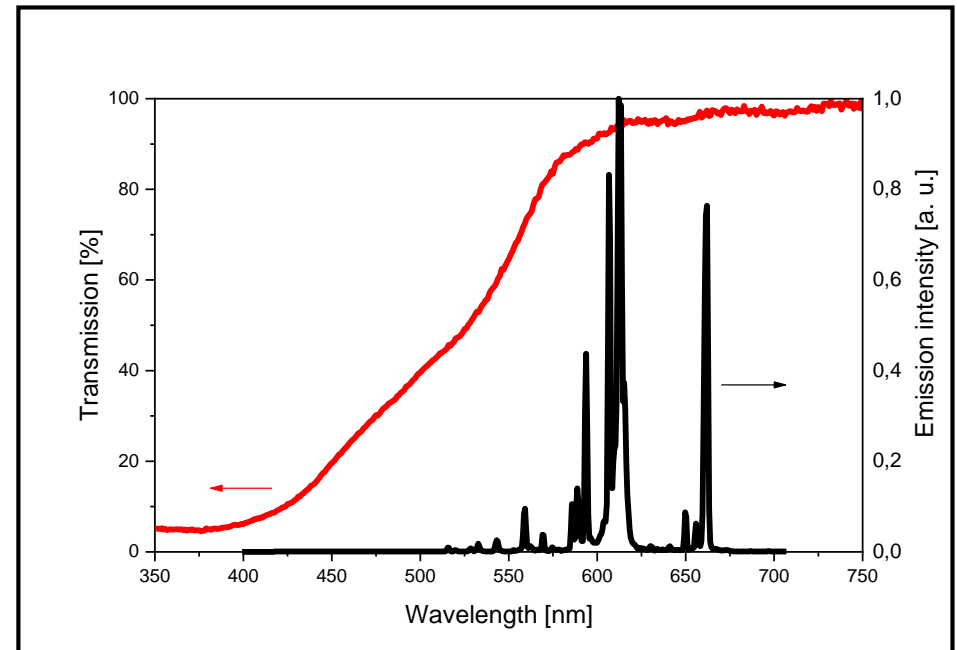
3.1.7 Color Pigments

Technical applications: Pigmentation of ZnS:Ag with CoAl$_2$O$_4$

Procedure

- **Co-precipitation of Co^{2+} and Al^{3+} by hydrolysis of Co(CH$_3$COO)$_2$ and Al(CH$_3$COO)$_3$ in aqueous solution**

- **Calcination: hydroxide mixture → CoAl$_2$O$_4$ (Thenard's blue – a spinel)**

  Nanoscale pigment particles are formed on the microscale phosphor particles
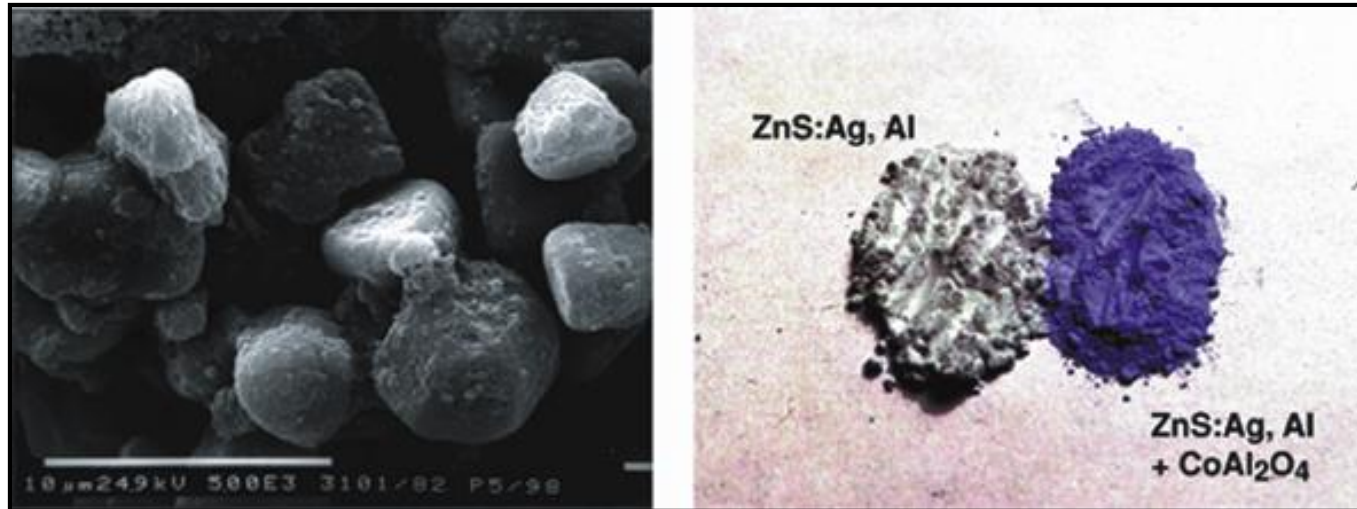
3.1.8 Nacreous Pigments

In Nature

Pearls =
$CaCO_3$ (aragonite)
+ Protein (conchiolin)

i.e. alternating layers
of high and low
refracting materials

Photonic band gap
structures
„Semiconductor
for light"

Nacreous Pigment: An insight into natural pearls

Nucleus

Aragonite crystal and conchiolin layers

$CaCO_3$ — n_1

Protein — n_2
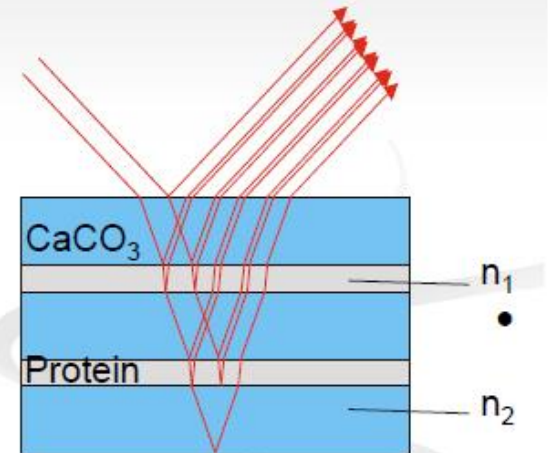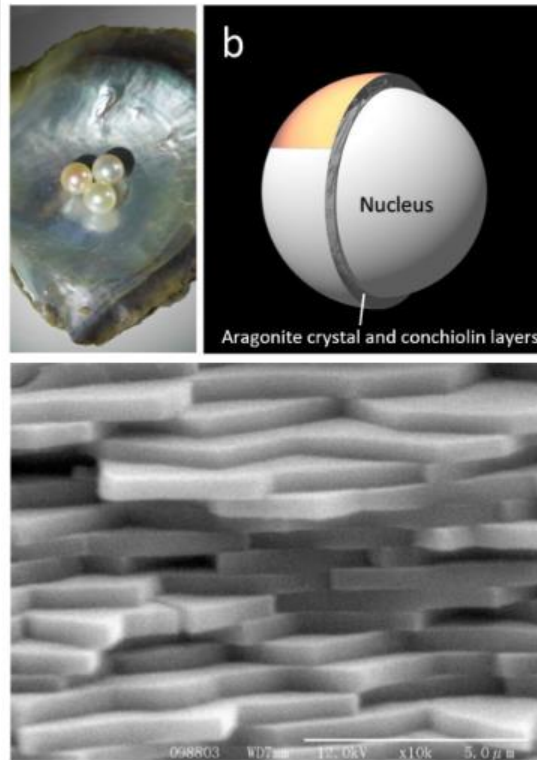
3.1.8 Nacreous Pigments

In Technology (since 1930ties)

- $Pb(OH)_2 \cdot 2PbCO_3$ (Hydrocerussite, lead white)

- $Pb_5(CO_3)_3O(OH)_2$ (Plumbonacrite)

- BiOCl (Bismuth oxychloride)

- $KAl_2(AlSi_3O_{10})(OH)_2$ (Mica), which is a low-refractive layer silicate ($n_1 = 1.563$, $n_2 = 1.604$, $n_3 = 1.599$, $E_g = 7.85$ eV), that can be interlayered by highly refractive oxide, e.g. TiO_2 or ZrO_2

(a) [110] projection   (b) Cleaved surface

1.00 nm

Si   Al   O   K⁺   OH

$a = 0.52$ nm   [110] axis:
$b = 0.90$ nm   axis of symmetry
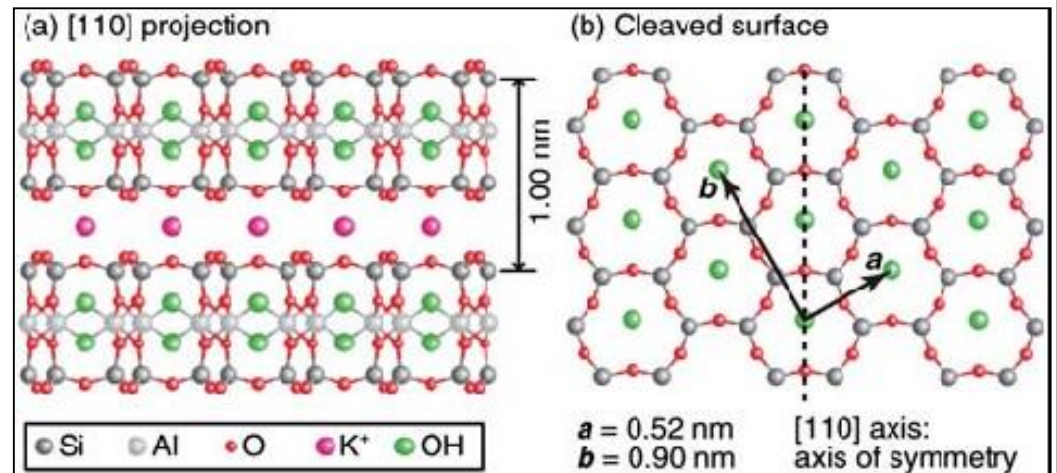
3. Inorganic Functional Materials

3.2 Phosphors (luminescent pigments, luminophores)

3.2.1 Operation

Fundamental steps

Excitation: Absorption of energy from an external source

1. **Energy transfer:**   To activators or defects (storage)

2. **Relaxation:**   Radiative: Emission (luminescence) →   Phosphors

                             Non-radiative: Heat (phonons)   →   Pigments
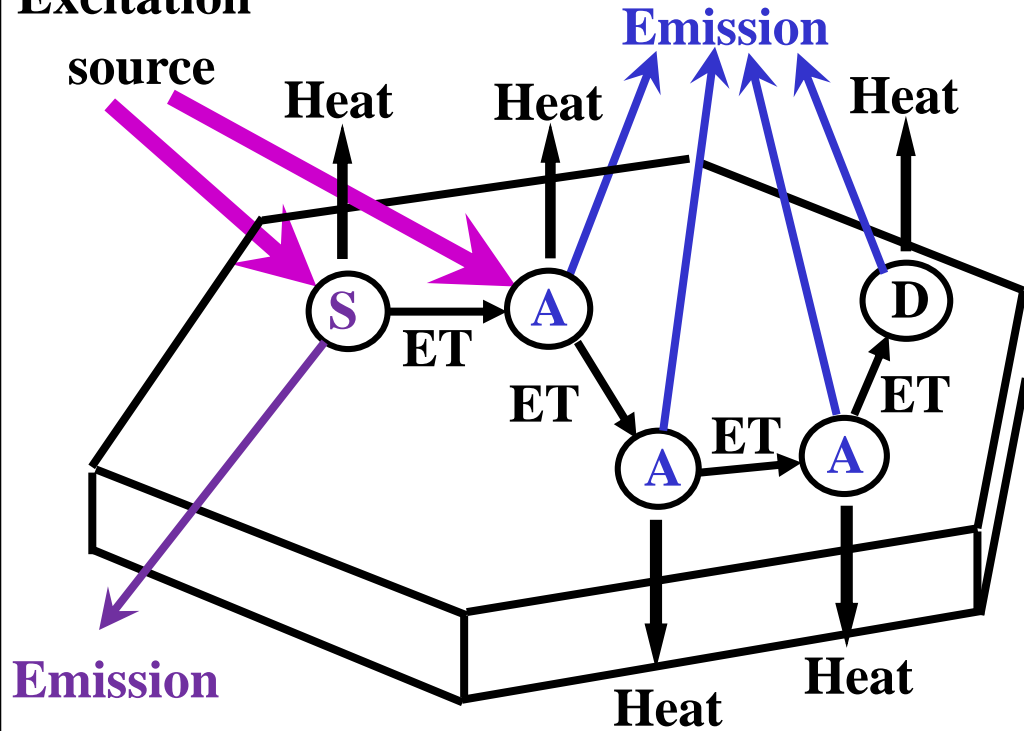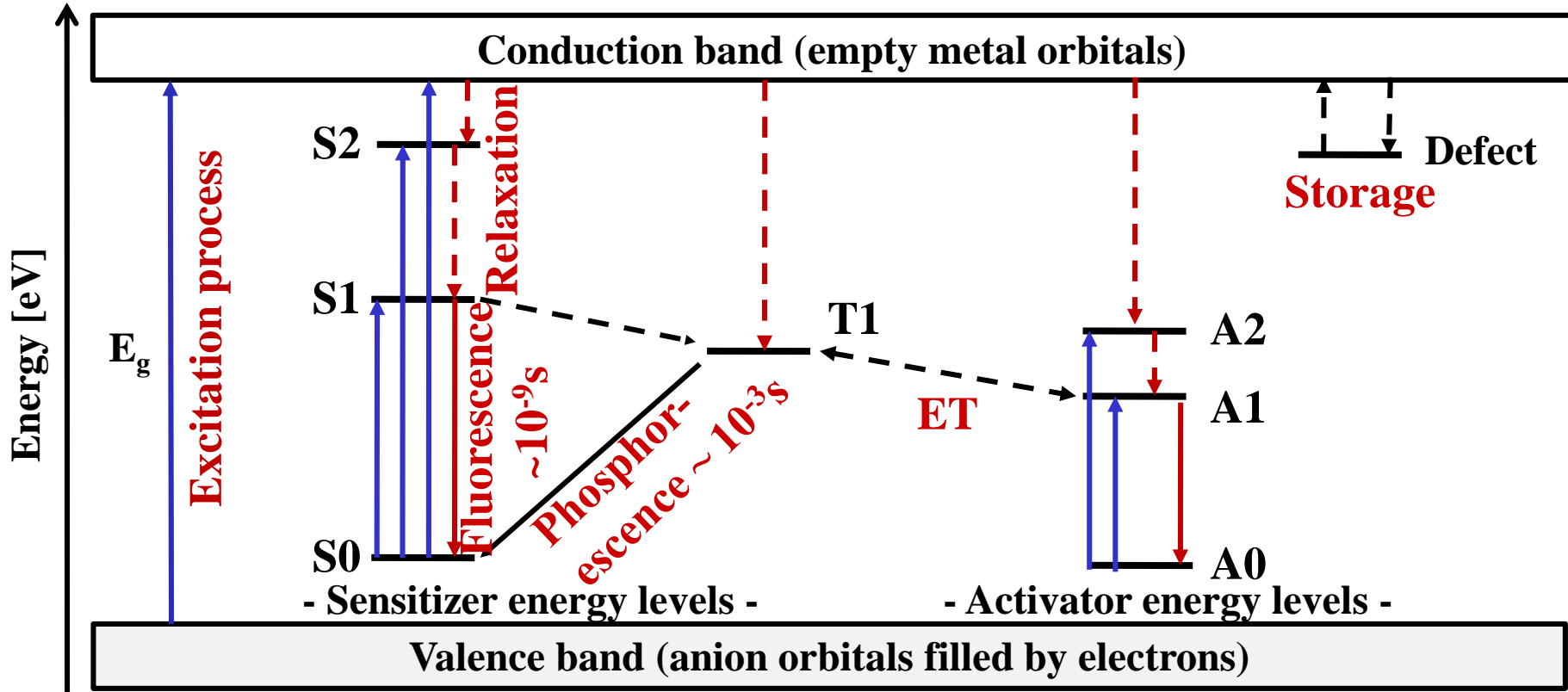

SEM image of $BaMgAl_{10}O_{17}$:Eu
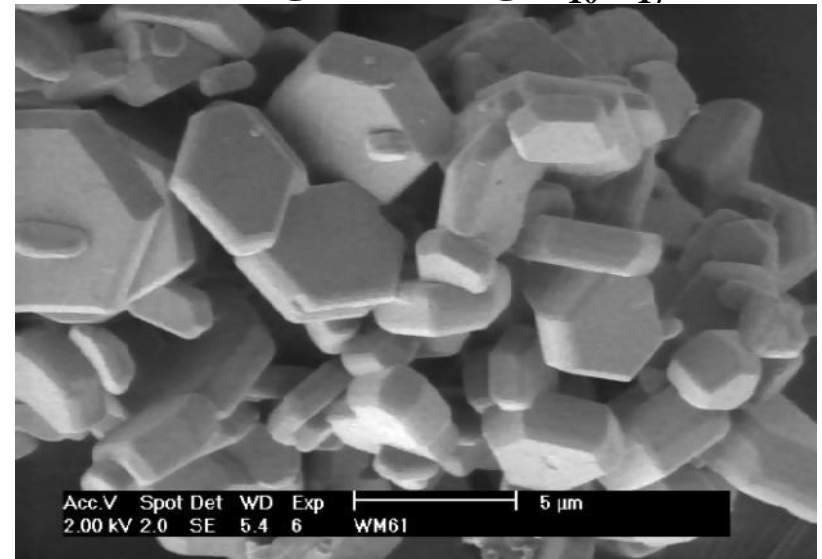
Average particle size ~ 1 - 10 μm

Energy transfer (ET) often occur prior to emission process

3.2.1 Operation

The overall picture

Type	Physical process	time scale
Fluorescence	Spin-allowed transition	ns - μs
Phosphorescence	Spin-forbidden transition	ms
Afterglow	Thermal activation of charge carriers	s – min/h

3.2.1 Operation

Excitation by UV or visible radiation

Excitation energy $< E_G$ of the host compound $\Rightarrow$ Excitation of optical centres

activator excitation

CB ———————————————

A**

A* η_{Escape}

$h\nu$

k_r ⫶ k_{nr}

A

VB ///////////////////////

sensitizer excitation

CB ———————————————

S* ET   A**

$\eta_{Transfer}$ A* η_{Escape}

$h\nu$

S

A

VB ///////////////////////

$$\text{IQE} = \eta_{Act} = k_r/(k_r + k_{nr}) = \tau/\tau_r$$
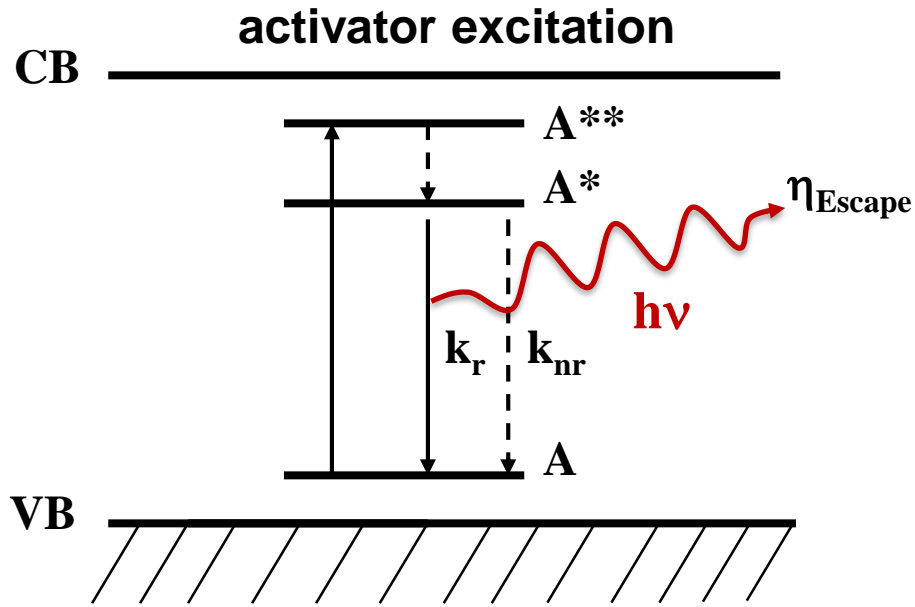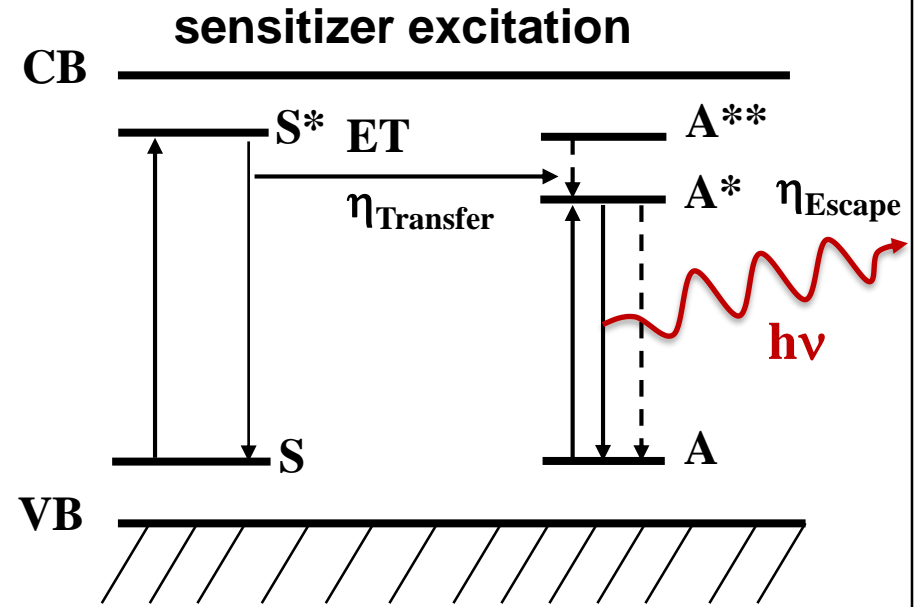
$$\text{EQE} = \eta_{Act} * \eta_{Transfer} * \eta_{Escape}$$

with $1/(k_r + k_{nr}) = \tau$ and $k_r = 1/\tau_r$

3.2.1 Operation

Excitation by VUV, EUV, or ionising radiation (x-ray, high energy particles)

Excitation energy > or ~ E_G of the host lattice $\Rightarrow$ Band-to-band excitation
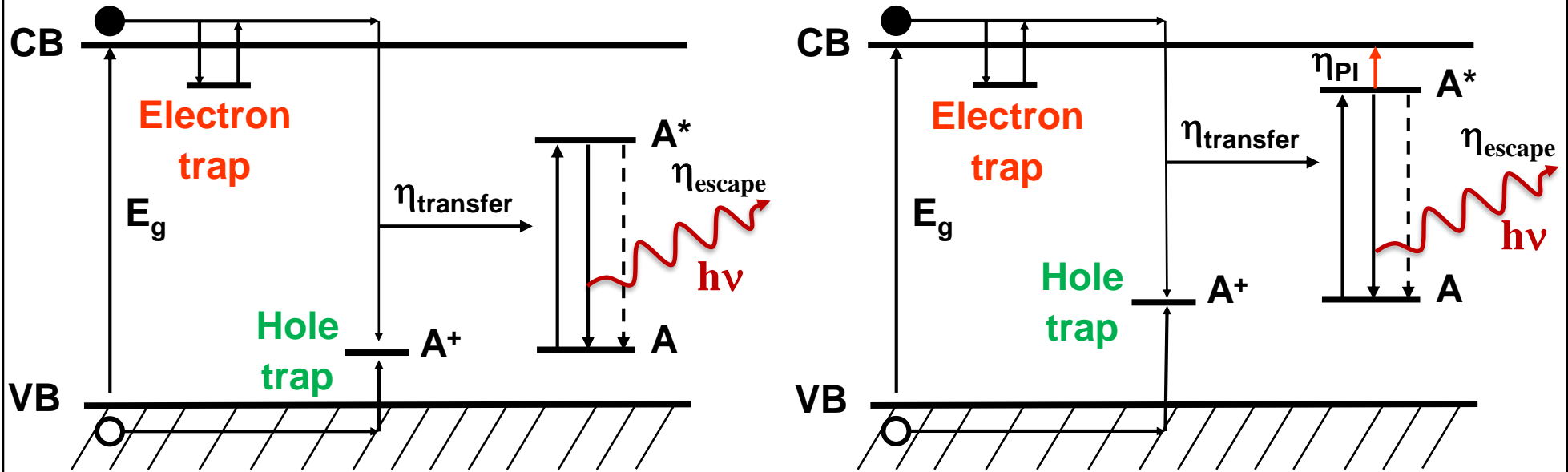
$$EQE = \eta_{activator} * \eta_{transfer} * \eta_{escape} * (1 - \eta_{PI})$$

Probability of photoionisation (PI) depends on energy distance of the excited state to the conduction band edge

3.2.2 Composition

An (inorganic) luminescent material is a material which converts energy absorbed from an external source into electromagnetic radiation beyond thermal equilibrium …..
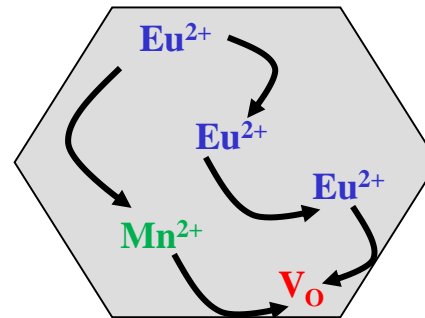
Host matrix

- Number of sites, coordination number and CFS
- Symmetry of lattice sites suitable to host activator
- Optical band gap
- Phonon spectrum
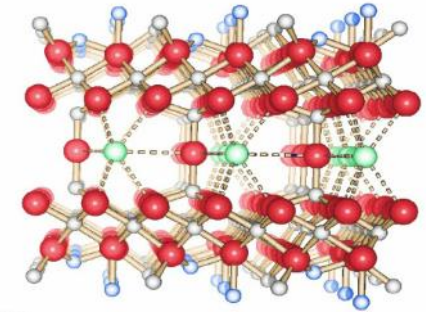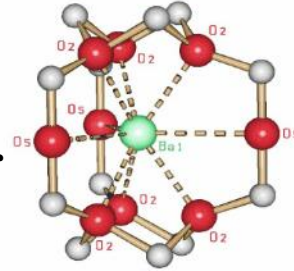
Dopants, impurities, and defects

- Concentration quenching
- Form solid solution → change of T_m
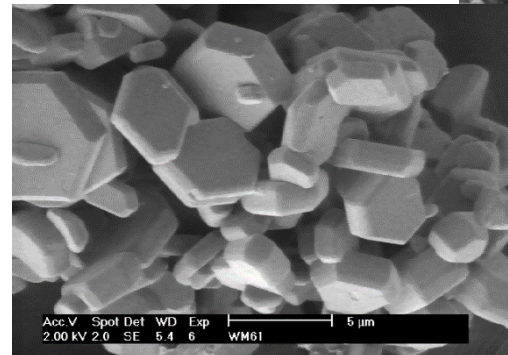- Energy level diagram
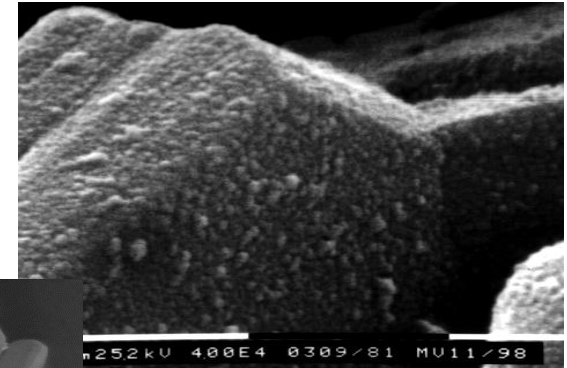
Particle size distribution and surface

- Surface potential and morphology
- Coatings → Light in- and out-coupling

⇒ Impact on
PL spectra, thermal and photo stability, quantum efficiency, linearity, decay time, and thermal quenching
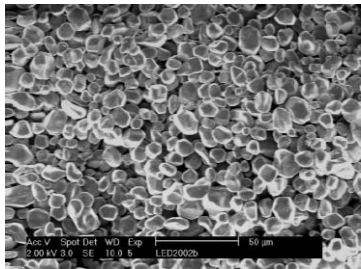
3.2.2 Composition

Phosphor = host matrix + dopants + impurities + defects

Host matrix = halides, oxides, sulfides, nitrides, phosphides, ...

Dopants = activators/sensitizers = RE-ions, transition metal ions, s²-ions

3.2.2 Composition

Host matrix

- **Oxides** Y_2O_3, $Y_3Al_5O_{12}$, YBO_3, YVO_4, YPO_4, $LaPO_4$, $BaMgAl_{10}O_{17}$, …

- **Fluorides** CaF_2, YF_3, $LiYF_4$, K_2SiF_6, KYF_4, KY_3F_{10}, K_2NbF_7, YOF, …

- **Nitrides** $CaSiN_2$, $CaAlSiN_3$, $Sr_2Si_5N_8$, $La_3Si_6N_{11}$, $SrLiAl_3N_4$, $SrSi_2N_2O_2$, …

- **Sulphides** ZnS, CdS, MgS, CaS, SrS, $SrGa_2S_4$, $SrIn_2S_4$, Y_2O_2S, Gd_2O_2S, …

- **Selenides** $ZnSe$, $CdSe$

| La_2O_3 | CeO_2 | $PrPO_4$ | Nd_2O_3 | $NdPO_4$ | Sm_2O_3 | Eu_2O_3 |
| Gd_2O_3 | Dy_2O_3 | Ho_2O_3 | Er_2O_3 | Tm_2O_3 | Yb_2O_3 | Lu_2O_3 |
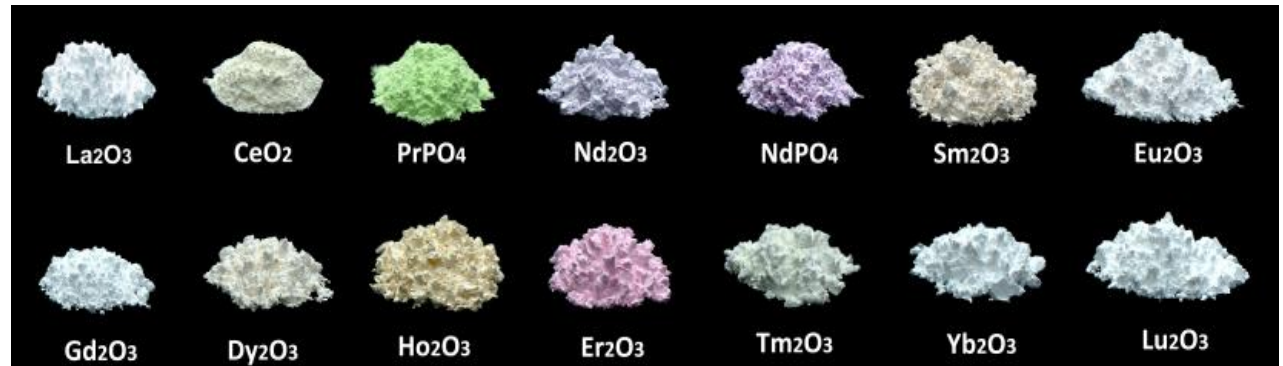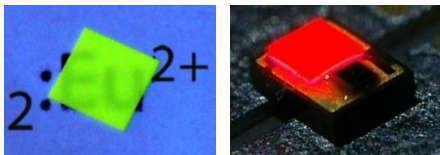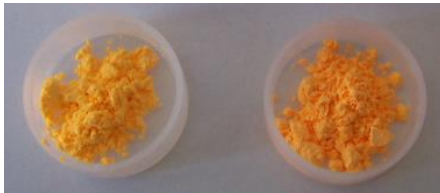
3.2.2 Composition

Dopants

	Examples	Optical transitions
• **Activators**		
– **Lanthanide ions**	Ce^{3+}, Eu^{2+}, Yb^{2+}	$[Xe]4f^n - [Xe]5d^14f^{n-1}$
	Nd^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}	$[Xe]4f^n - [Xe]4f^n$
– **Transition metal ions**	$Cr^{3+/4+}$, $Mn^{2+/4+}$, Fe^{3+}, Cu^{2+}	$3d^n - 3d^n$
	Ru^{2+}	$4d^n - 4d^n$
– **s^2-ions**	Sn^{2+}, Sb^{3+}	$[Kr]4d^{10}5s^2 - 5s^15p^1$
	Tl^+, Pb^{2+}, Bi^{3+}	$[Xe]4f^{14}5d^{10}6s^2 - 6s^16p^1$
• **Sensitizers**		
– **Lanthanide ions**	Ce^{3+}	$[Xe]4f^1 - [Xe]5d^1$
– **Complex anions**	VO_4^{3-}, MoO_4^{2-}, WO_4^{2-}, UO_2^{2+}	LMCT
– **Organic ligands**	bpy, phen, …..	π-π*

Impurities

	Examples	
• **Transition metal ions**	Fe^{3+}, Cr^{3+}, Co^{2+}, Cu^{2+}	$\rightarrow$ competitive absorption
• **Lanthanide ions**	Eu^{3+} in Tb^{3+} phosphors	$\rightarrow$ energy transfer
• **Fluxing agent residuals**	Cl^-, F^-, BO_3^{3-}, ...	$\rightarrow$ defect formation

3.2.2 Composition

Defects

<u>Types</u>
- **Surface defects**
- **Anion or cation vacancies V_K, V_A**
- **Ions on interstitial sites I**

Interstitial atom

Strained lattice region

<u>Effect on the physical properties</u>
- **Afterglow**
- **Quenching of the luminescence**
  - **Competitive absorption**
  - **Energy transfer to defects + non-radiative relaxation**
  - **Re-absorption of emission**
- **Color point shift**
- **Stability reduction**
  - **Formation of color centers by electron capture**
  - **Reduction of thermal conductivity ($\rightarrow$ challenge for LED phosphors)**
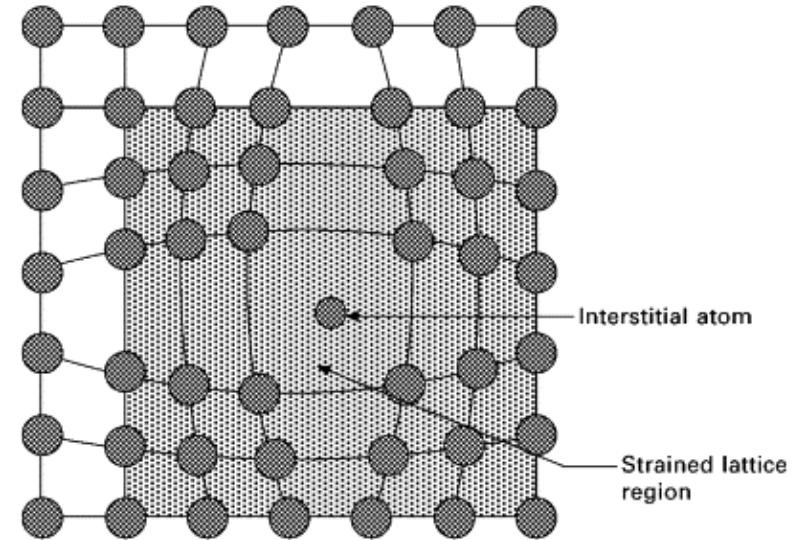
3.2.2 Composition

Deviation from the ideal composition: Loss mechanisms reduce IQE and EQE

1. The absorbed energy does not reach the activator ion $(\eta_{Transfer})$
   a) Competitive absorption
   b) ET to defects or non-luminescent impurity ions
   c) Excited state absorption (ESA)
   d) Auger processes

2. The absorbed energy reaches the activator ion, but non-radiative (η_{Act})
   channels exists at the cost of radiative return to the ground state
   a) Crossing of excited and ground state parabola
   b) Multi-phonon relaxation (MPR)
   c) Cross-relaxation (CR)
   d) Photoionisation (PI)
   e) Energy transfer to quenching sites $\eta_{transfer} = f$(spectral overlap, p, T, …)

3. Emitted radiation is re-absorbed by the luminescent material (η_{Esc})
   a) Self-absorption due to spectral overlap between excitation
   and emission band
   b) Additional absorption bands due to degradation of the material,
   e.g. by colour centre formation

3.2.2 Composition

Relevant optical properties

Quantum efficiency (IQE and EQE)

Decay curve

Photoluminescence spectra

Colour point (consistency)
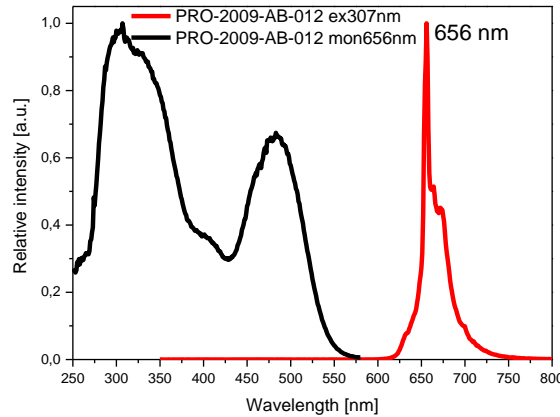
Lumen equivalent

Reflection spectrum

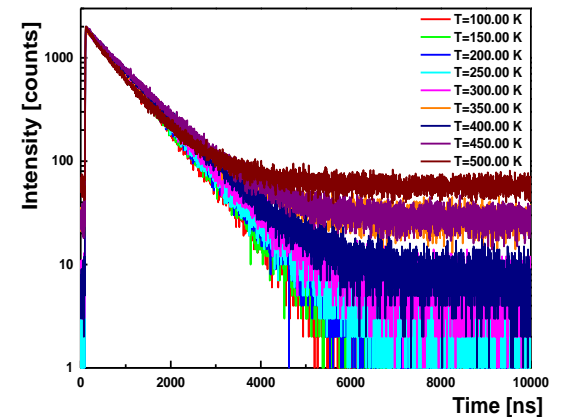Thermal quenching

Linearity (saturation)

Refractive index (dispersion)
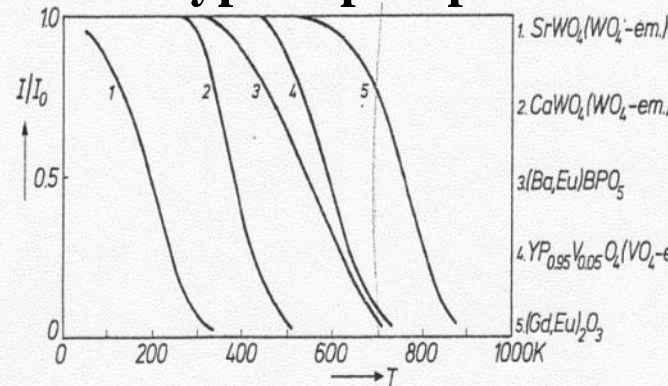
Photochemical and thermal stability

Photoluminescence (PL) spectra of $Mg_2TiO_4:Mn$

Decay curves of $SrSi_2N_2O_2:Eu$

T-Dependence of integral PL of some typical phosphors

1. $SrWO_4 (WO_4^{-}$-em.)
2. $CaWO_4 (WO_4^{-}$-em.)
3. $(Ba,Eu)BPO_5$
4. $YP_{0.95}V_{0.05}O_4 (VO_4^{-}$-em.)
5. $(Gd,Eu)_2O_3$

### Linearity of YAG:Ce and $LiEuMo_2O_8$
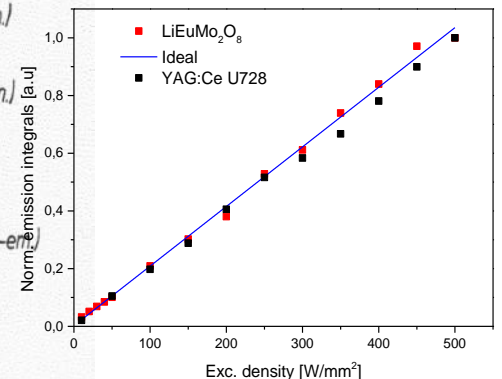
3.2.3 Synthesis of Phosphors

Ceramic method: General procedure (see also chapter 2.1)

1. Preparation and purification of the reactants

2. Homogenization of the reactants

3. Pre-sintering (Decomposition of precursors)

4. Sintering: Conversion into the product (phase formation)

5. Washing

6. Grinding

7. (Thermal post-treatment)

8. Fractioning (Binning)

3.2.3 Synthesis of Phosphors

Ceramic method: Synthesis of Zn_2SiO_4:Mn^{2+}

$$SiO_2 + 1.9\ ZnO + 0.1\ MnCO_3 \rightarrow (Zn_{0.95}Mn_{0.05})_2SiO_4 + 0.1\ CO_2\uparrow$$
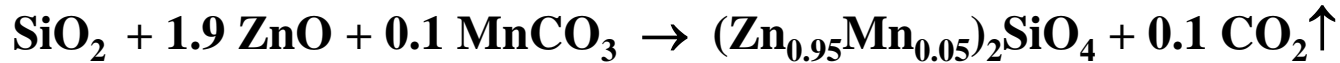
Synthesis procedure

- **Determination of the (metal) content of the reactants**
- **Starting materials water or ethanol suspension**
- **10 minutes ultrasonic bath treatment**
- **Concentrate on the rotary evaporator**
- **Drying residue at 100 °C**
- **2 h sintering under nitrogen /hydrogen (5%) atmosphere at 1200 °C (fluxing agent NH_4Cl)**
- **Grinding**
- **Sieving**

Sample: Philips LightingG210
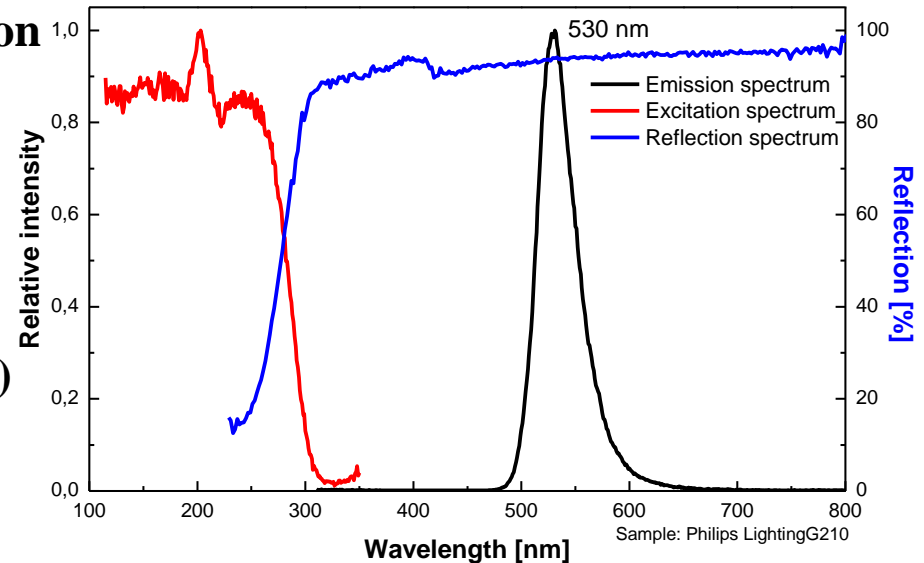
Problem: Evaporation of ZnO resulting in Zn-deficient phosphor $(Zn_{0.95-x}Mn^{II/III}_{0.05})_2SiO_4$
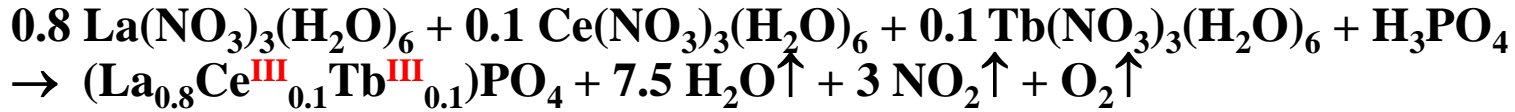
3.2.3 Synthesis of Phosphors

Precursor method: Synthesis procedure

1. **Preparation of a precursor solution**

2. **Precipitation as hydroxides, carbonates, sulfates, phosphates, …**

3. **Regenerating the precipitate**

4. **Sintering: Conversion into the product (phase formation)**

5. **Sintering: Crystallization (particle growth)**

6. **Grinding**

7. **Fractionation (Binning)**

3.2.3 Synthesis of Phosphors

Precursor method: Synthesis of LaPO$_4$:Ce^{3+}Tb^{3+}

0.8 La(NO$_3$)$_3$(H$_2$O)$_6$ + 0.1 Ce(NO$_3$)$_3$(H$_2$O)$_6$ + 0.1 Tb(NO$_3$)$_3$(H$_2$O)$_6$ + H$_3$PO$_4$
$\rightarrow$ (La$_{0.8}$Ce$^{III}_{0.1}$Tb$^{III}_{0.1}$)PO$_4$ + 7.5 H$_2$O$\uparrow$ + 3 NO$_2\uparrow$ + O$_2\uparrow$
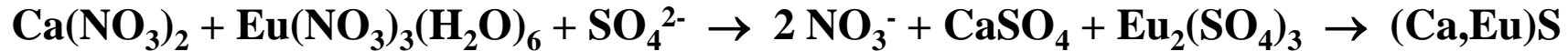
Synthesis procedure

- **Dissolving nitrates in H$_2$O**
- **Addition of phosphoric acid + overnight stirring**
- **Concentrate on the rotary evaporator**
- **2 h sintering at 800 °C under CO**
- **Addition of LiF and grinding**
- **2 h sintering at 1000 °C under CO**
- **Cooling to room T in 4h**
- **Washing of phosphor in diluted HNO$_3$**
- **Extraction by suction, acid-free washing**
- **Drying at 100 °C**
- **Grinding and sieving**
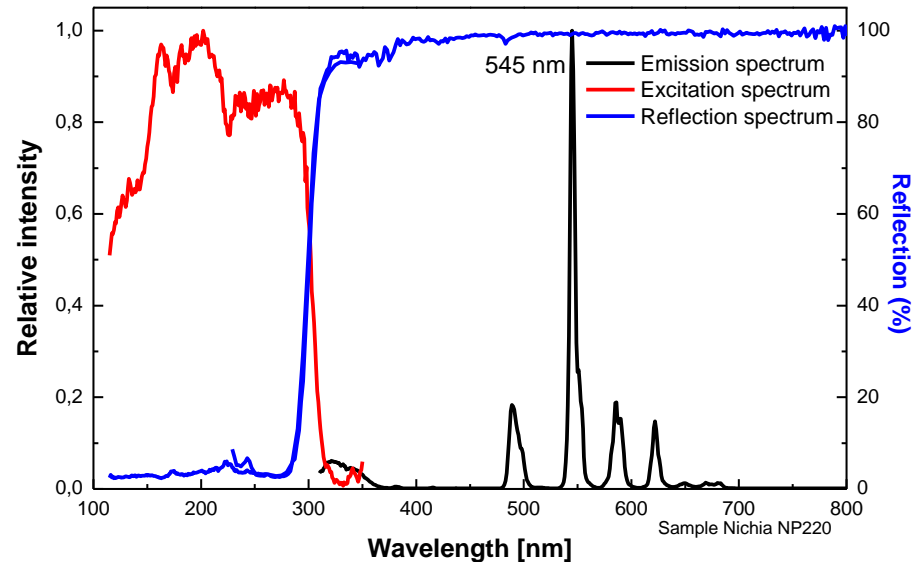
3.2.3 Synthesis of Phosphors

Precursor method: Synthesis of CaS:Eu^{2+}

$$Ca(NO_3)_2 + Eu(NO_3)_3(H_2O)_6 + SO_4^{2-} \rightarrow 2\ NO_3^- + CaSO_4 + Eu_2(SO_4)_3 \rightarrow (Ca,Eu)S$$

Synthesis procedure
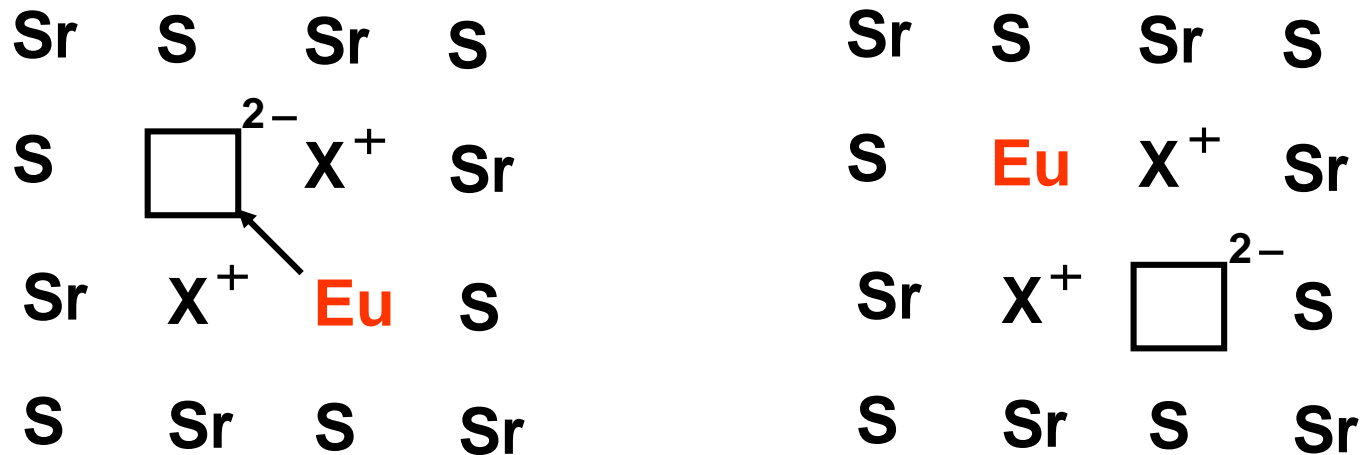
- **Dissolving nitrates in H$_2$O**
- **Precipitation as sulfates**
- **Washing**
- **2 h sintering at 500 °C in air**
- **24 h sintering at 1000 °C under N$_2$/H$_2$/H$_2$S**
- **Addition of NH$_4$I and grinding**
- **4 h sintering at 1100 °C under N$_2$**
- **Milling in cyclohexane**
- **Extraction by suction**
- **Drying**
- **Grinding and sieving**
- **Packaging (under inert gas)**
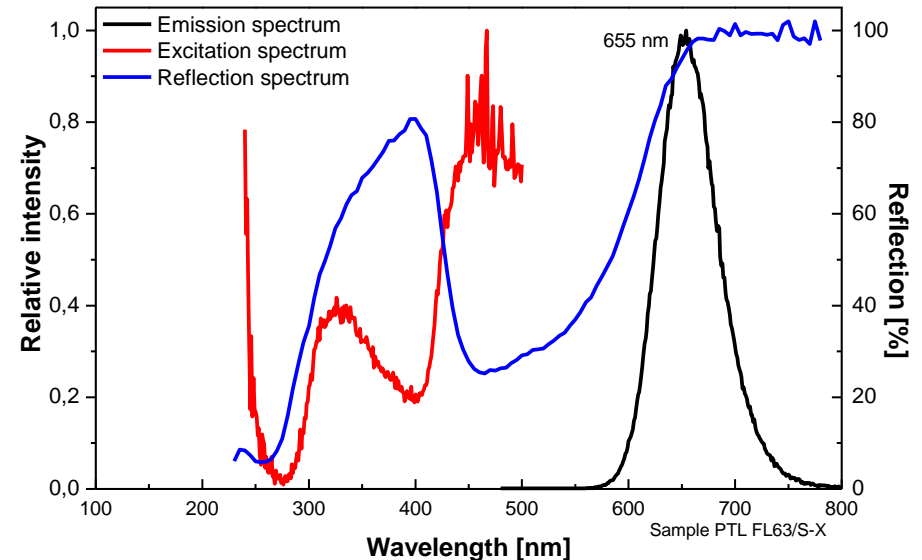
3.2.3 Synthesis of Phosphors

Influence of a halide fluxing agent

- Increase of the Eu^{2+} ions (activators) mobility in the host material
- No clustering of Eu^{2+} ions $\Rightarrow$ Reduction of concentration quenching

$$
\begin{array}{cccc}
Sr & S & Sr & S \\
S & \square^{2-}\ X^{+} & Sr \\
Sr & X^{+}\ Eu & S \\
S & Sr & S & Sr
\end{array}
\qquad
\begin{array}{cccc}
Sr & S & Sr & S \\
S & Eu\ X^{+} & Sr \\
Sr & X^{+}\ \square^{2-} & S \\
S & Sr & S & Sr
\end{array}
$$

Defect equation: $4\ HX + 2\ S_S{}^x + Sr_{Sr}{}^x \Leftrightarrow 2\ H_2S + 2\ X_S{}^{\bullet} + V_{Sr}{}'' + SrX_2$

3.2.4 Areas of Application

Technical area	Applications
Lighting	
Low-pressure mercury lamps	Fluorescent tubes, energy saving lamps
High-pressure mercury lamps	Street lighting, Shop lighting
Ne-discharge lamps	Indicator signal lighting
Xe-excimer lamps	Backlighting, UV irradiation
Inorganic LEDs	White and colored LEDs
OLED light sources	Flat and flexible light sources
Imaging	
Cathode ray tubes	RGB + B/W TV or monitors
Plasma panels	RGB + B/W TV
Electroluminescent screens	Radar screens, EL foils
(Emissive) LCDs	Monitors
OLED screens	Mobile phones, digital cameras, razors

3.2.4 Areas of Application

Technical area	Sample applications
Optical brighteners	Paint, paper, clothes, detergents
Product anticounter feiting	Banknotes, stamps, credit cards, certificates, tickets, documents,
Security	Emergency lighting
Advertising	Ne discharge lamps
Medicine	Computer and positron emission tomographs x-ray films, psoriasis lamps, bilirubin lamps
Dentistry	Dental ceramics
Astronomy	EUV/VUV-amplifier
Biochemistry	Fluorescence markers for DNA, RNA, proteins
Analysis	Immunoassays
Lithography	Photocopier
Cosmetics	Tanning lamps
Water purification	Xe excimer lamps, UV LEDs

3.2.5 Processing of Phosphors

Powder → Suspension, paste, ceramics → Phosphor layer ("luminescent screen")

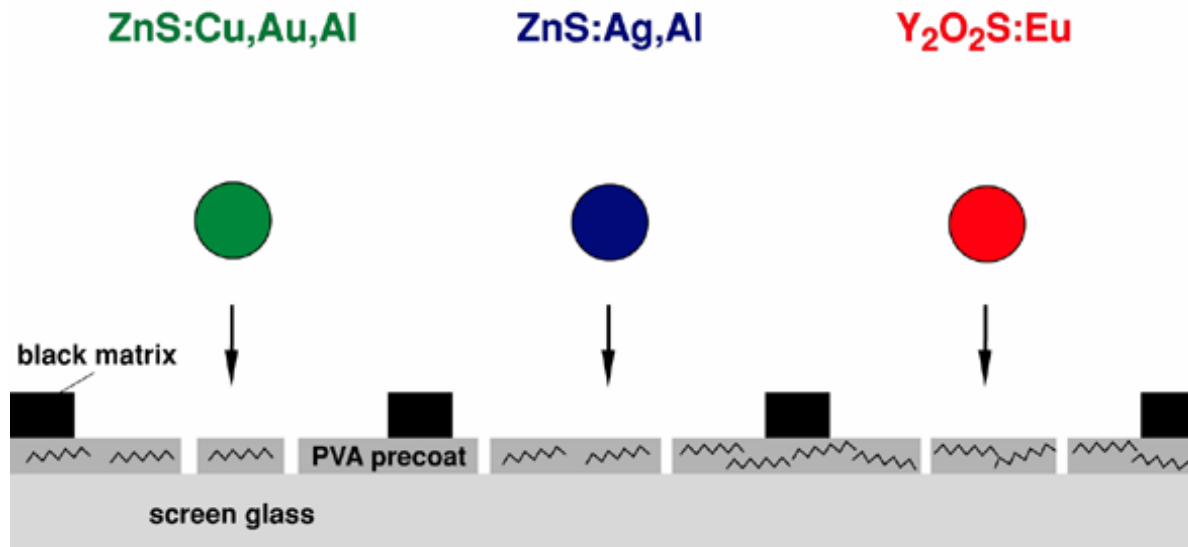1. **Phosphor powder → suspension, printing paste, luminescent ceramic or crystal**

Solvent	butyl acetate	distilled water
Binder	nitrocellulose	polyethylene oxide
Adhesion medium	Alon-C (Al_2O_3)	$Ca_2P_2O_7$
Dispersing agent	2-Methoxy-1-propanol	poly acrylic acid
		$[- CH_2-CH(COOH)-]_n$

2. **Phosphor suspension → Phosphor layer**

Screens: Flow-coating

           Printing process (screen printing, flexi printing, etc.)

Light sources: Sedimentation

           Up-Flushing

           Electrophoretic deposition (EPD)

3.2.5 Processing of Phosphors

Flow-coating: Coating of RGB cathode ray tubes

ZnS:Cu,Au,Al   ZnS:Ag,Al   Y$_2$O$_2$S:Eu

black matrix

PVA precoat

screen glass

$$PVA + Cr_2O_7^{2-} \xrightarrow{h\nu} Polymerization/cross\text{-}linking$$

PVA = Polyvinyl alcohol $[- CH_2\text{-}CHOH\text{-}]_n$

Process cycle

- **Applying green phosphor suspension**
- **Exposure to UV radiation**
- **Rinsing**
- **Applying blue phosphor suspension**
- **Exposure to UV radiation**
- **Rinsing**
- **Applying red phosphor suspension**
- **Exposure to UV radiation**
- **Rinsing**

3.2.6 Degradation of Phosphors

Degradation mechanisms	Example
• Thermal oxidation or reduction of the activator	$BaSi_2O_5:Pb^{2+}$
• Photo-oxidation or reduction of the activator	$BaMgAl_{10}O_{17}:Eu^{2+}$
• Dissolution/decomposition in suspension	$BaSi_2O_5:Pb^{2+}$
• Reactions with the glass wall	$(Ce,Gd)MgB_5O_{10}:Tb^{3+}$
• Hg-take up in fluorescent lamps	$Zn_2SiO_4:Mn^{2+}$
• Hydrolysis by moisture	$(Mg,Ca,Sr,Ba)S:Eu^{2+}$ $(Ca,Sr,Ba)SiN_2:Eu^{2+}$

$\Rightarrow$ **Protection by particle coatings, also useful for color pigments: Core-Shell-Part.**

3.2.7 Particle Coatings

Technologies

- **Encapsulation with polymers**

- **Precipitation methods**
  - **Homogeneous**
  - **Inhomogeneous**

- **Pigmentation with nanoscale particles**
  - **By adhesion in suspension**
  - **By addition to the dry phosphor powder**

- **Fluidised Bed Chemical Vapour Deposition (FB-CVD)**
  - **Oxidation of metal organic compounds, e.g. $Al(CH_3)_3$**
  - **Deposition of elements, e.g. diamond-like carbon (DLC)**

3.2.7 Particle Coatings

Process of a homogeneous precipitation for particle coatings

- **Preparation of the phosphor suspension and fixing the pH value (buffer)**

- **Dissolution of the coating material precursor (nitrates), possibly addition of a complexing agent**

- **Precipitation**
    - **by homogeneous pH value increase, e.g. hydrolysis of urea**
      $$(H_2N)_2CO + H_2O \rightarrow 2\,NH_3 + CO_2$$

- **Separation**
    - **Filtration**
    - **Centrifugation**
    - **Sedimentation**

- **Densification of the particle coating**
    - **Calcination (e.g. to convert hydroxides → oxides)**

3.2.7 Particle Coatings

Inorganic materials for particle coatings (shell materials)

Requirements
- Chemical and thermal stability
- Low phonon frequency
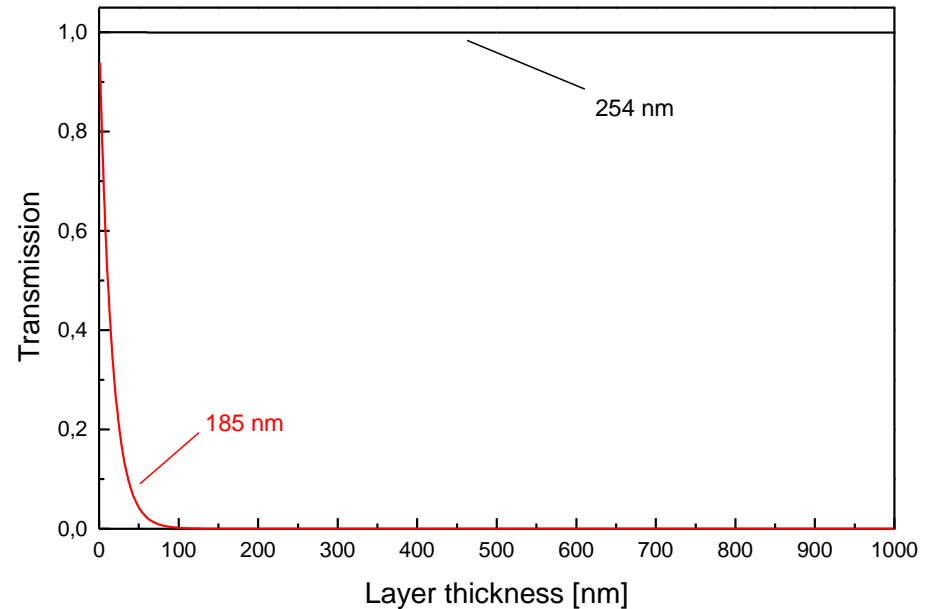- Optical transparency ($\rightarrow$ wide band gap)
- Appropriate isoelectric point

Protective-coating	Band gap [eV]
α-Al_2O_3	8.7
$LaPO_4$	8.6
SiO_2	8.4
$Ca_2P_2O_7$	8.3
MgO	8.0
γ-Al_2O_3	7.3
Y_2O_3	5.6
La_2O_3	5.5
C (diamond)	5.4

Color filter

- Fe_2O_3 red
- $CoAl_2O_4$ blue

Transmission of Y_2O_3 at 185 and 254 nm

3.2.7 Particle Coatings

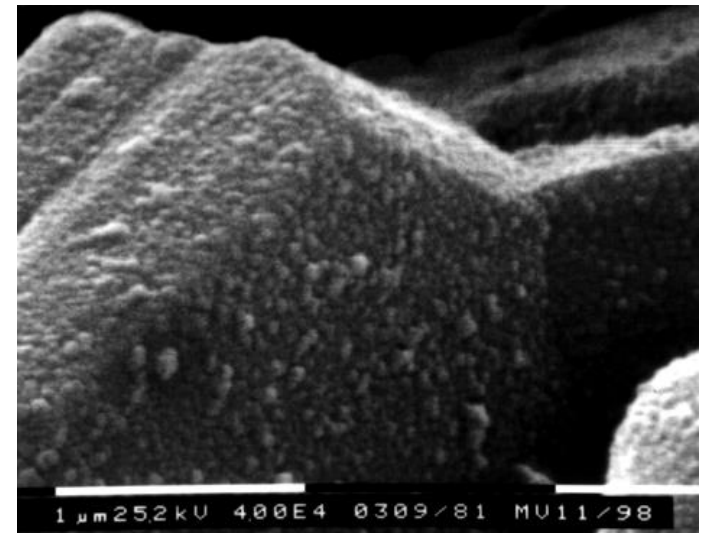**Example of use: Coating of BaMgAl$_{10}$O$_{17}$:Eu with MgO**

Coating process

- **Dissolving Mg(NO$_3$)$_2$ in demi water**
- **pH-value increase: Mg^{2+} + 2 NH$_3$ + 2 H$_2$O $\rightarrow$ Mg(OH)$_2$ + 2 NH$_4^+$**
- **Calcination at 600 °C: Mg(OH)$_2$ $\rightarrow$ MgO + H$_2$O**
- $\Rightarrow$ **MgO nanoparticle onto the phosphor particles**

SEM image of BaMgAl$_{10}$O$_{17}$:Eu

1 µm 30.0 kV 3.66E4 1509/8; U771/98

SEM image of BaMgAl$_{10}$O$_{17}$:Eu (MgO)

1 µm 25.2 kV 4.00E4 0309/81 MV11/98
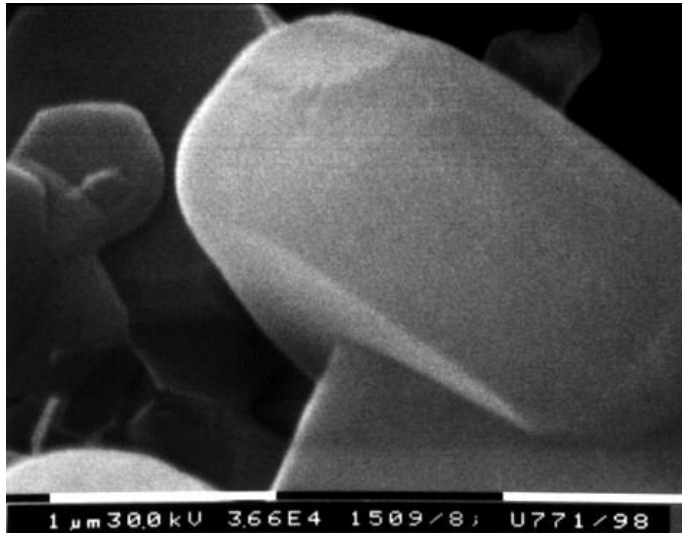
3.2.7 Particle Coatings

Example of use: Coating of BaSi₂O₅:Pb (BSP) with La₂O₃

Problem: Hydrolysis in water to the hydroxide

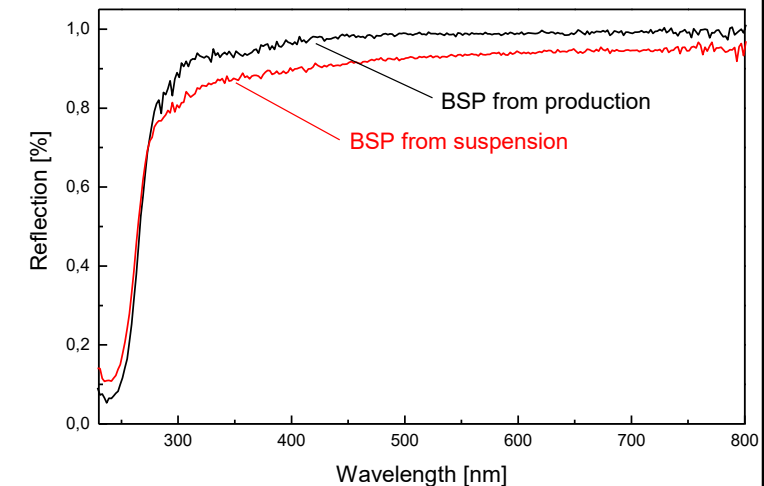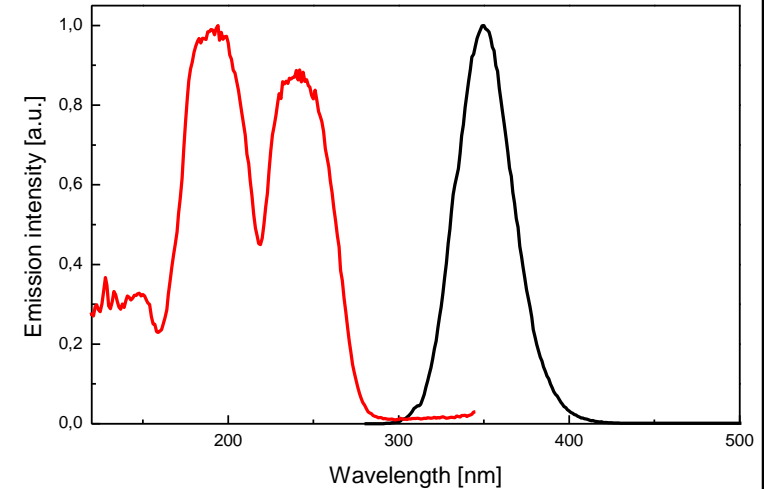- $BaSi_2O_5 + H_2O \rightarrow Ba(OH)_2 + 2\ SiO_2$

  $\Rightarrow$ pH 9 - 10

- Hydrolysis of Ln^{3+} at pH > 4-5 $\rightarrow$ La(OH)₃

Consequences

- Surface becomes porous
- Activator Pb^{2+} is washed out
- Coating at low pH is not possible
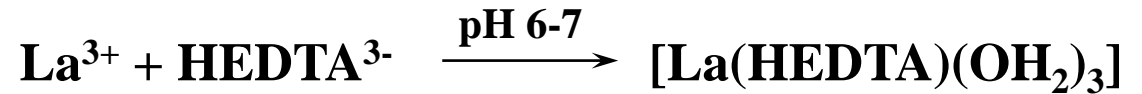
The coating process

- Neutralization to alkaline suspension
- Precipitation at pH 8 - 10
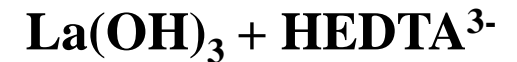- Masking of La^{3+} is required

3.2.7 Particle Coatings

Example of use: Coating of $BaSi_2O_5$:Pb with La_2O_3

Masking of La^{3+} with EDTA and precipitation in the alkaline solution

$$La^{3+} + HEDTA^{3-} \xrightarrow{\text{pH 6-7}} [La(HEDTA)(OH_2)_3]$$

TEM image (magnification: 125000x)

Precipitation at pH 9

$$La(OH)_3 + HEDTA^{3-}$$

1) Washing
2) ΔT

$$La_2O_3$$

TEM image (magnification: 260000x)

Surface is coated with La_2O_3 „nanostructured"

3.2.7 Particle Coatings

Example of use: Coating of SrS:Eu with SiO$_2$

SrS is very hydrolysis sensitive: $SrS + 2\,H_2O \rightarrow H_2S\uparrow + Sr(OH)_2 \xrightarrow{CO_2} SrCO_3\downarrow + H_2O$

$\Rightarrow$ Coating can not be carried out in an aqueous suspension

$\Rightarrow$ Coating process in ethanol or propanol

$Si(OEt)_4 + 2\,H_2O \rightarrow SiO_2 + 4\,EtOH$
"TEOS"

The coating is impermeable and thus increases the resistance towards hydrolysis

The coating is nanostructured and increases the light output of the phosphor by about 5% by refractive index fitting (antireflection coating)

Acc.V Spot Det WD Exp   1 µm
2.00 kV 3.0 SE 5.2 4   PSC3-27
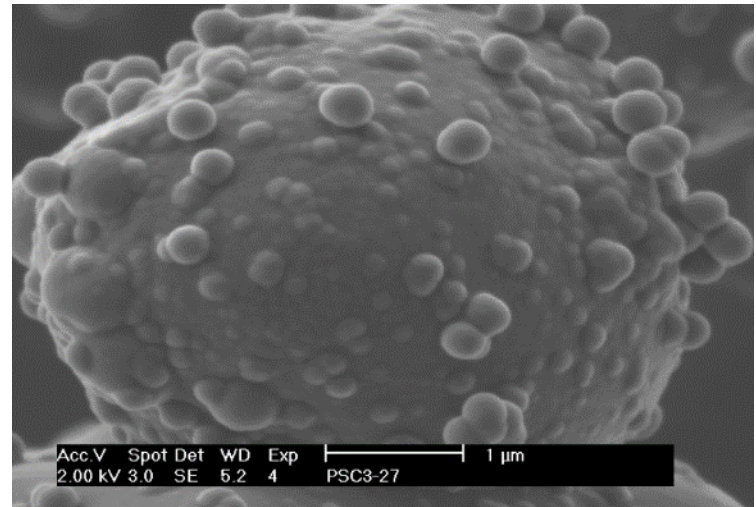
3.2.8 Recycling

Fluorescent lamps

Due to the relatively high price of rare earths their recycling is worthwhile

Status 2010: Y_2O_3: 150 €/kg Lu_2O_3: 900 €/kg Eu_2O_3 & Tb_4O_7: ~ 1200 €/kg

Status 2021: Y_2O_3: 60 €/kg Lu_2O_3: 5400 €/kg Eu_2O_3: 195 €/kg, Tb_4O_7: 11200 €/kg

$\Rightarrow$ Recycling of fluorescent lamps (linear and compact lamps) $\rightarrow$ WEEE regulation (2012/19)
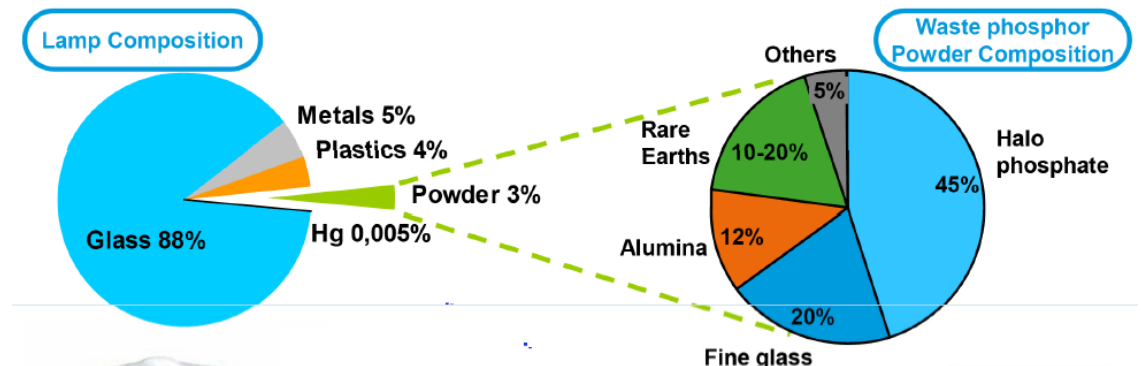
Procedure

1. Removal of Al- or plastic caps including electrodes
2. Washing out of the phosphor
3. Removal of Hg by sublimation
4. Regeneration of the phosphor

   Halophosphates

   $\Rightarrow$ Disposal

   Trichromatic phosphor mixtures

   $\Rightarrow$ Direct reuse or recovery of rare earths using digestion methods

3.2.8 Recycling

Fluorescent lamps

At present in Germany approximately 100 million discharge lamps are used. Therefore the recycling have a high environmental relevance regarding the mercury content:

Mercury content in used discharge lamps	Typical content
• Standard fluorescent tubes	< 15.0 mg
• Three bands fluorescent tubes	< 7.5 mg
• Compact fluorescent lamps	< 7.0 mg
• High pressure discharge lamps	< 30.0 mg
• Special emitter	1.5 g

Hg diffuses mainly into the lamp glass (in exchange for Na)

⇒ The mercury content in recycled glass from used fluorescent lamps usually lies between 4 and 6 mg/kg of glass

3.2.9 Nanoscale Phosphors

Phosphors with an average particle size between 1 and 100 nm

<u>Applications of nanoscale phosphors</u>
1. Transparent dispersions, layers, and ceramic converters
2. Security labeling (precious documents)
3. Color converter in ILEDs and OLEDs
4. Phosphors in fluorescent lamps
5. Emissive displays (CRTs, PDPs, emissive LCDs)

<u>Problems in the application</u>
- Plasma-phosphor interaction (Ar^+, Ne^+, Xe^+, e^-)
- Hg/Hg^+- uptake
- Chemical stability in suspension
- Agglomeration in suspension
- Adsorption of hydrocarbons and H_2O
- Strong scattering / low absorption strength
- Quenching of the luminescence due to surface defects
  $\Rightarrow$ Lower quantum yield compared to microscale phosphors
- Production costs

3.2.9 Nanoscale Phosphors

Nanoscale phosphors

Luminescence deletion occurs by energy transfer (ET) to the surface:
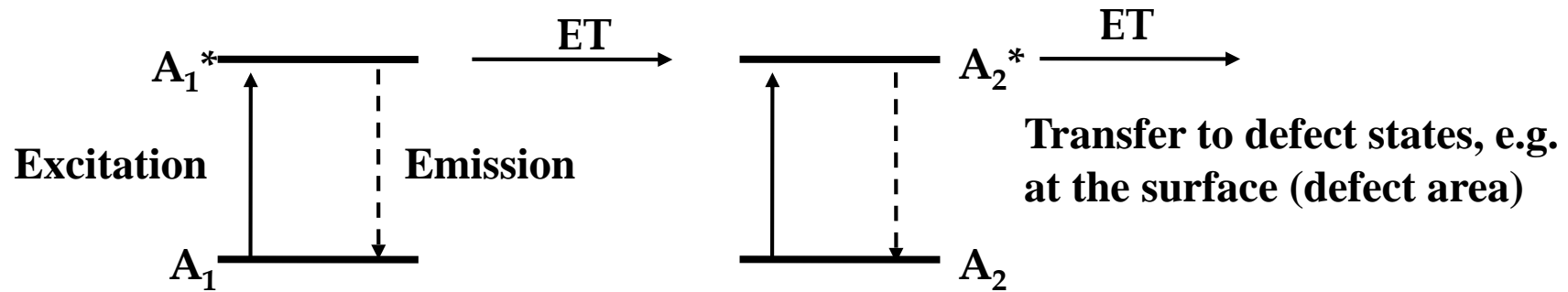
Typical transition time scale ~ $1*10^{-7}....10^{-8}$ s

Phosphors, which exhibit short intrinsic decay times ($\tau < 1 \cdot 10^{-7}$ s), can also be very efficiently nanoscale materials

$\Rightarrow$ Quantum Dots (GaN, GaP, GaAs, ZnSe, ZnTe, CdS, CdSe, CdTe, Si, …)

$\Rightarrow$ Activators with fast 4f-5d transitions, such as Pr^{3+}, Nd^{3+}, Eu^{2+}, Ce^{3+}

However, surface quenching can be suppressed by surface modifications

3.2.9 Nanoscale Phosphors
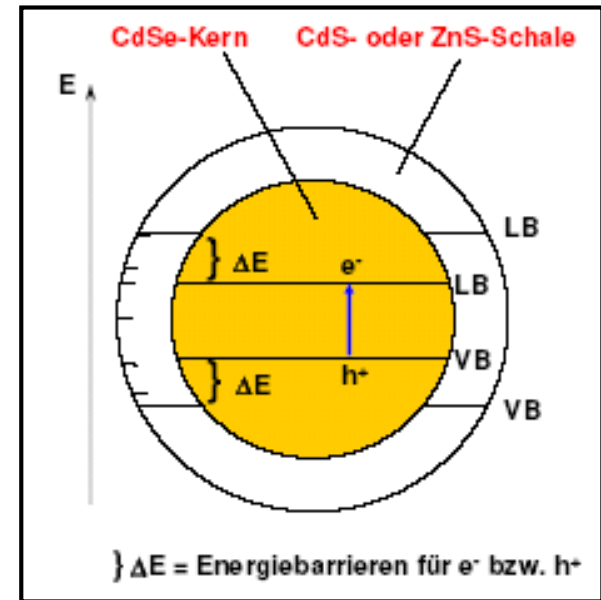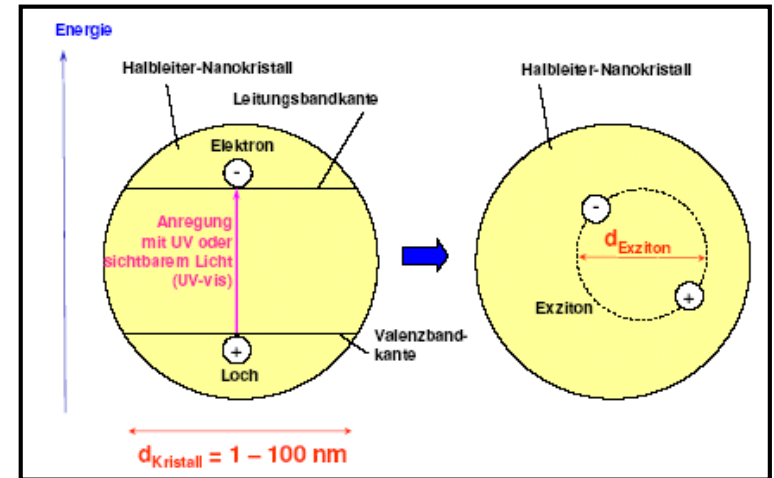
Nanoscale semiconductor phosphors

Problem:

Surface quenching of the excited states, as excitons in semiconductors have substantial radius

Semiconductor	Bohr radius [nm]	Band gap [eV]
CuCl	1.3	3.4
ZnSe	8.4	2.58
CdS	5.6	2.53
CdSe	10.6	1.74
CdTe	15.0	1.50
GaAs	28.0	1.43
PbS	40.0	0.41

Solution:

Epitaxial coating with a material with a higher band gap (Exciton Reflective Coating)

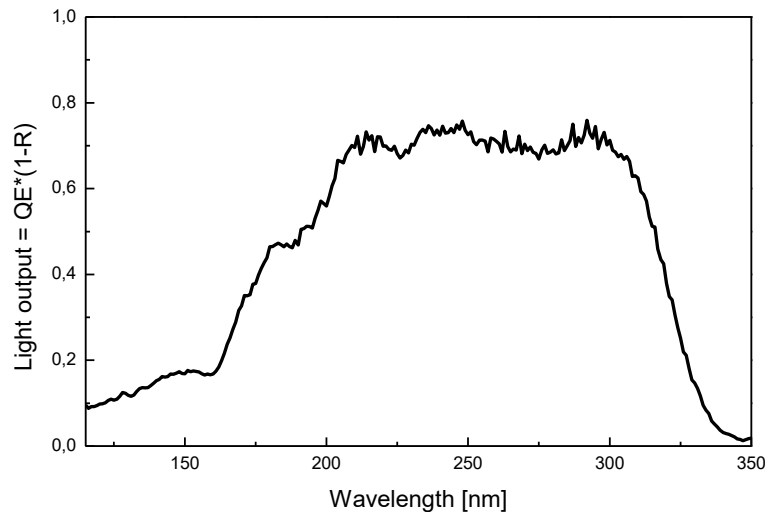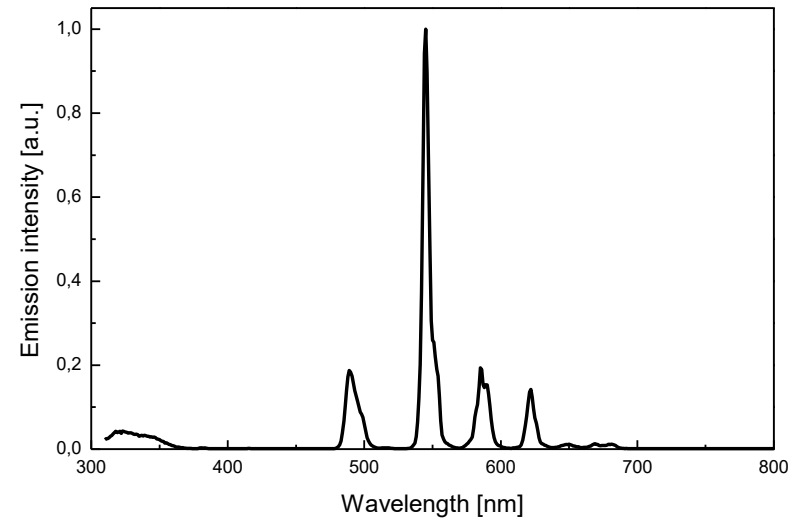# 3.2.9 Nanoscale Phosphors

Colloidal phosphors, which form stable suspensions

Example: $CePO_4$:Tb as a nanoscale phosphor (d_{50} ~ 10 nm)

Light output ~ $I(\lambda_{exc})$

Emission spectrum

- **QE ~ 60% (40% Tb^{3+} + 20% Ce^{3+})**
- **Ce^{3+} is an [Xe]$4f^1$ - [Xe]$5d^1$ emitter with a decay time of about 20 - 100 ns**
- **Efficient ET to Tb^{3+}, but not between the Tb^{3+} ions**

3.2.9 Nanoscale Phosphors
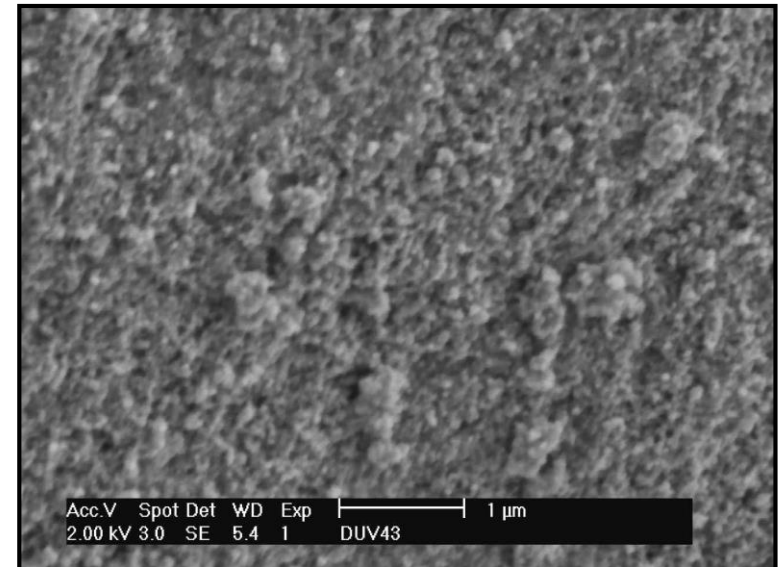
Synthesis of nanoscale garnets and oxides

Example: Hydrogencarbonate precipitation for the synthesis of $Ln_3Al_5O_{12}$-nanoparticles

- **Precipitation of Ln^{3+} and Al^{3+} by addition of NH_4HCO_3**

  $$3\ Ln^{3+} + 5\ Al^{3+} + 12\ OH^- + H_2O + 3\ CO_3^{2-} \rightarrow [3\ LnOHCO_3 / 5\ AlOOH]_{Gel} + 3\ H_2O$$

- **Sintering at 900 °C**

  $$[3\ LnOHCO_3 / 5\ AlOOH]_{Gel} \rightarrow Ln_3Al_5O_{12} + 3\ CO_2 + 4\ H_2O$$

XRD of $Lu_3Al_5O_{12}$
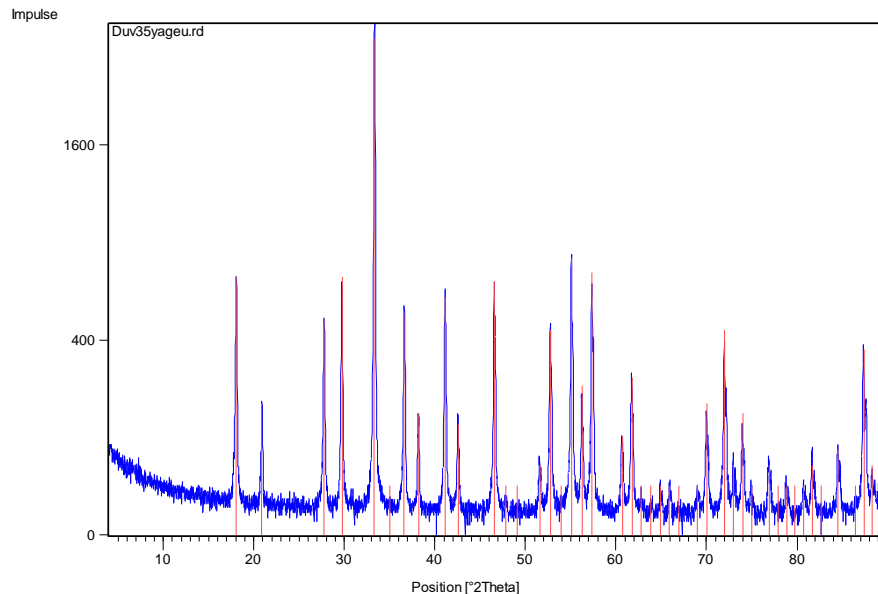
SEM Image of $Lu_3Al_5O_{12}$

3.2.10 Nitride Phosphors

Phosphors on the basis of the host lattice, which contain the nitride anion N^{3-}

<u>Advantages over oxide and sulphide phosphors</u>
- **Highly compact network (N bond order: 3-4)**
    - $\Rightarrow$ **high density**
    - $\Rightarrow$ **high chemical stability**
    - $\Rightarrow$ **high hardness**
    - $\Rightarrow$ **high thermal quenching temperature**

- **High charge density between the activator and the nitride anions**
  Oxides < Oxynitrides < Nitrides < Nitridocarbide
    - $\Rightarrow$ **Strong red shift of the band gap or the emission band**

	Si	$X = O^{2-}$	$X = N^{3-}$	$X = C^{4-}$
r [pm]	26	138	146	160
Electronegativity χ	1.92	3.61	3.07	2.54
Ionic bonding Si-X [%]	-	51	28	9

3.2.10 Nitride Phosphors

Very efficient, long-wavelength absorbing emitters $\Rightarrow$ Application in light emitting Diodes (LEDs)

$(Sr,Ba)SiN_2:Eu^{2+}$	$\lambda_{em} = 620 - 700$ nm	H.T. Hintzen et al.
$(Ca,Sr)AlSiN_3:Eu^{2+}$	$\lambda_{em} = 610 - 650$ nm	K. Uheda et al.
$SrLi[Al_3N_4]:Eu^{2+}$	$\lambda_{em} = 650$ nm	W.S. Schnick et al.
$SrAlSi_4N_7:Eu^{2+}$	$\lambda_{em} = 630$ nm	W.S. Schnick et al.
$(Ca,Sr,Ba)_2Si_5N_8:Eu^{2+}$	$\lambda_{em} = 580 - 630$ nm	W.S. Schnick et al.
$YSiO_2N:Tb^{3+}$	$\lambda_{em} = 545$ nm	B. Hintzen et al.
$Y_2Si_3O_3N_4:Tb^{3+}$		
$Gd_2Si_3O_3N_4:Tb^{3+}$		
$(Ca,Sr,Ba)Si_2N_2O_2:Eu^{2+}$	$\lambda_{em} = 505 - 565$ nm	P.J. Schmidt et al.
$SrSiAl_2O_3N_2:Eu^{2+}$	$\lambda_{em} = 480$ nm	Osram AG, US 6670748

Warm-white pcLEDs with a yellow-emitting, e.g. $(Y,Gd,Tb)_3Al_5O_{12}:Ce$, and a red-emitting nitride phosphor, mainly $(Ca,Sr)AlSiN_3:Eu$ or $(Ca,Sr,Ba)_2Si_5N_8:Eu$, are on the market since end of 2003
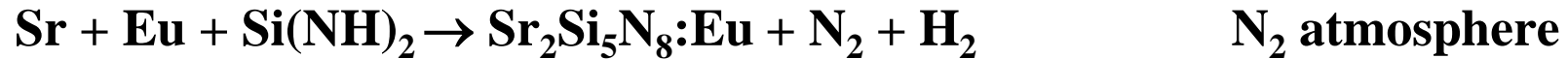
Lit.: Nitride Phosphors and Solid State Lighting, CRC Press, 2011

3.2.10 Nitride Phosphors

Synthesis of nitride phosphors

Selected routes

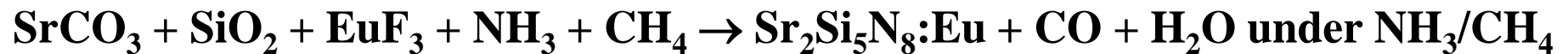1. **Conversion of the metals with imides/amides (high frequency furnace)**

$$Sr + Eu + Si(NH)_2 \rightarrow Sr_2Si_5N_8{:}Eu + N_2 + H_2 \qquad N_2 \text{ atmosphere}$$

2. **Classic solid-state reaction (in Nb or Ta-ampoules)**

$$2\ Ca_3N_2 + 5\ Si_3N_4 + N_2 + Eu \rightarrow 3\ Ca_2Si_5N_8{:}Eu \qquad N_2 \text{ atmosphere}$$

3. **Carbothermal reduction/nitridation, CRN method (tube furnace)**

$$SrCO_3 + EuF_3 + Si_3N_4 + C \rightarrow Sr_2Si_5N_8{:}Eu + CO \qquad N_2/H_2 \text{ atmosphere}$$

4. **Gas-reduction/nitridation (GRN) method (tube furnace)**

$$SrCO_3 + SiO_2 + EuF_3 + NH_3 + CH_4 \rightarrow Sr_2Si_5N_8{:}Eu + CO + H_2O \text{ under } NH_3/CH_4$$

3. Inorganic Functional Materials

3.3. Ceramics
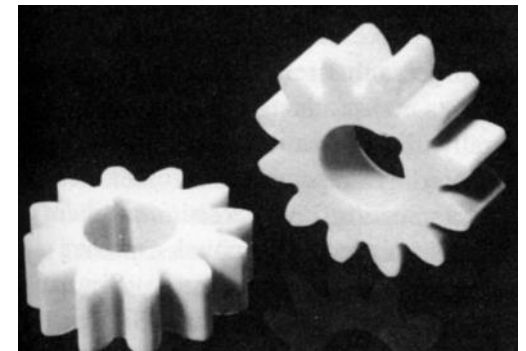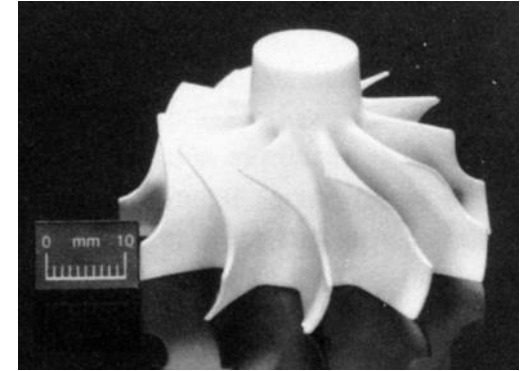
3.3.1 Definition and Classification

By ceramics one understands solid materials, which are inorganic and non metallic, and which from a structure consisting of one or more phases (crystalline, glass-like)

Structural or construction ceramics
Ceramics, which have to withstand mechanical stresses and strains.

High-performance ceramics
Highly developed, high-performance ceramic material.

Functional ceramics
High performance ceramics, which are used in the inherent properties of the material for an Active function, e.g. ceramic components, which exhibit electrical, magnetic, dielectric or optical properties.

Cutting ceramics
High performance ceramics, which are suitable due to outstanding abrasion and thermal resistance quality as a tool for cutting processing (tricks, drilling, milling).

Bio ceramics
High performance ceramics for the application in the medical filed i.e. in the human body. This concerns products, which replace bones, teeth or hard tissue.

3.3.1 Definition and Classification

Classification of the ceramics based on their chemical or mineralogical composition

Silicate or clay ceramics (classical structural ceramics)
- Arrangement of several crystalline phases and glass phases (silicate)
- Most important components:
  Silicates $\Rightarrow$ kaolinite $Al_4[Si_4O_{10}](OH)_8$, talc $Mg_3Si_4O_{10}(OH)_2$, montmorillonite, feldspar
  Additive $\Rightarrow$ corundum Al_2O_3, zircon $ZrSiO_4$

Oxide ceramics
- Fine-grained structure consisting of crystalline and usually binary oxide phase and only small amounts of glass phase
- Binary oxides: Al_2O_3, MgO, ZrO_2, TiO_2
- Mixed oxide ceramics: $(Ba,Pb)(Ti,Zr)O_3$, Al_2O_3/ZrO_2

Non-oxide ceramics
- Ceramic materials based on compounds of boron, carbon, nitrogen, and silicon
- SiC, Si_3N_4, AlN, BN, …

3.3.2 General Structure

Ceramics consist of more or less randomly oriented crystalline grains (crystallites), amorphous areas (glass phase), and cracks or pores

(Micro)structure = crystallites + gas phases + pores + cracks

Structure of a mix-carbide ceramics consists of crystallites (dark) and pores (light areas)
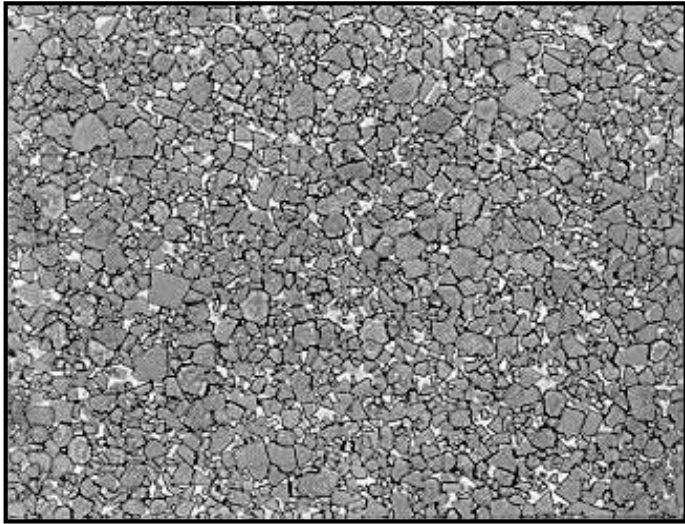
Microstructure of a dense Al_2O_3 ceramics consisting of microcrystallites

20 µm
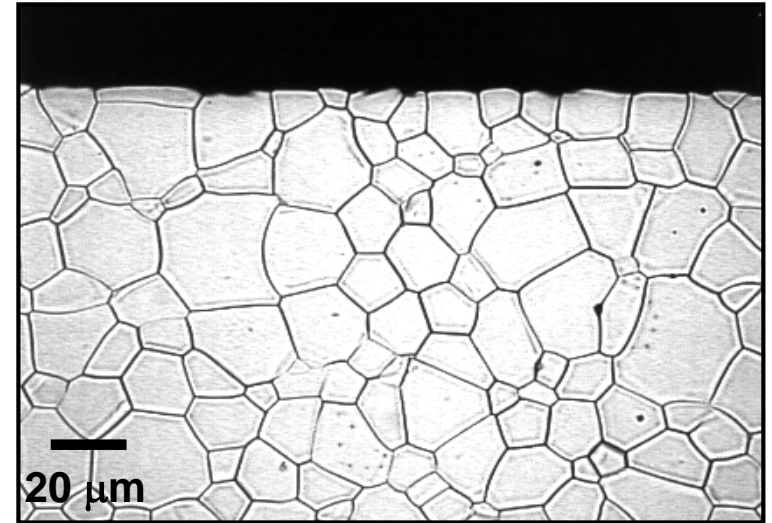
The structural composition is of crucial importance for the mechanical and physical properties of a ceramic component

3.3.3 Properties

**Due to their ionic or covalent bonds ceramic materials possess a number of characteristic properties**

- low thermal and electrical conductivity
- high hardness and brittleness
- high melting point (> 1500 °C)
- high chem. and therm. stability
- low density

Material	Density[g/cm^3]	Tensile strength [N/mm^2]
Al_2O_3	4.0	210
SiC	3.1	175
Si_3N_4	3.2	560
SiAlON	3.2	420
ZrO_2	5.8	455

SiAlON = $Si_{3-x}Al_xN_{4-x}O_x$

Ceramics, which functional and non-mechanical properties are not in the foreground, exhibit however different properties, like e.g.
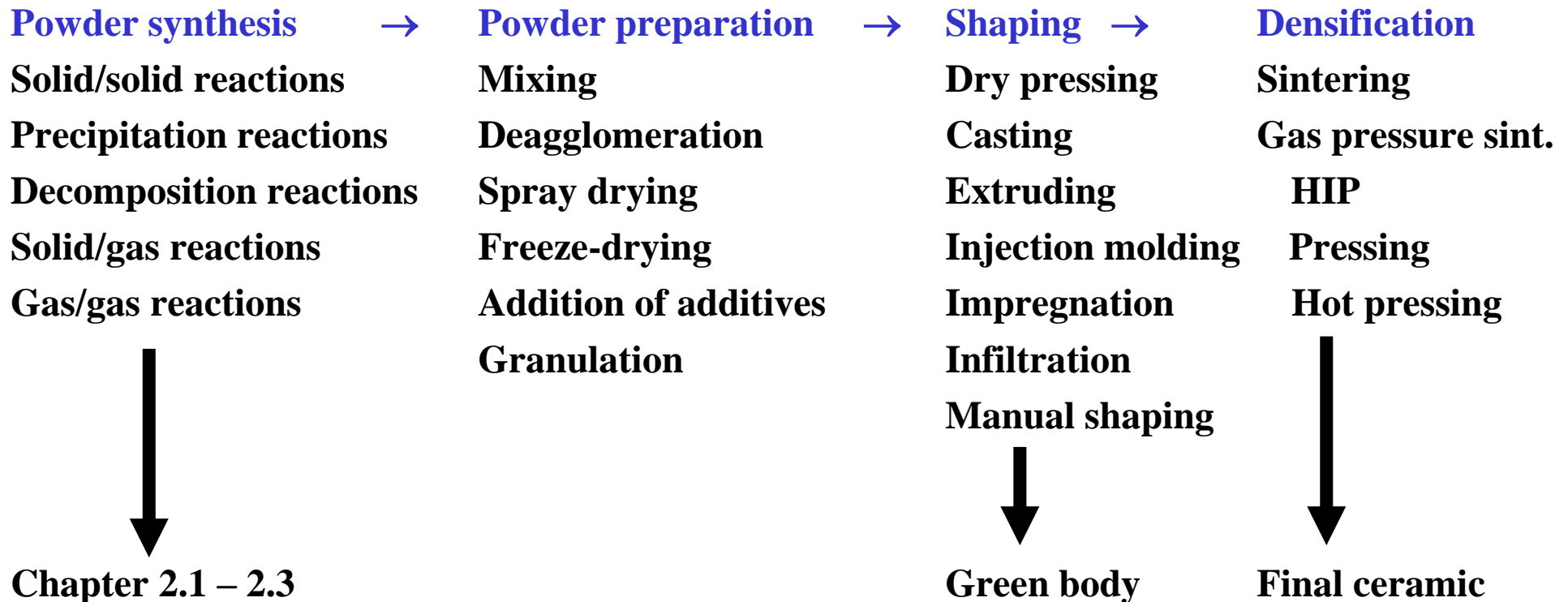
FeO, ZnO	Semiconductor
$YBa_2Cu_3O_{7-x}$	Superconductor
ß-$NaAl_{11}O_{17}$	Ion conductor
CrO_2, $Y_3Fe_5O_{12}$	Magnets
(Pb,La)(Zr,Ti)O_3	Pressure sensors
Gd_2O_2S:Pr	Scintillators for CT
$Y_3Al_5O_{12}$:Ce	Luminescence converter for LEDs
$Lu_3Al_5O_{12}$:Nd	Solid state laser
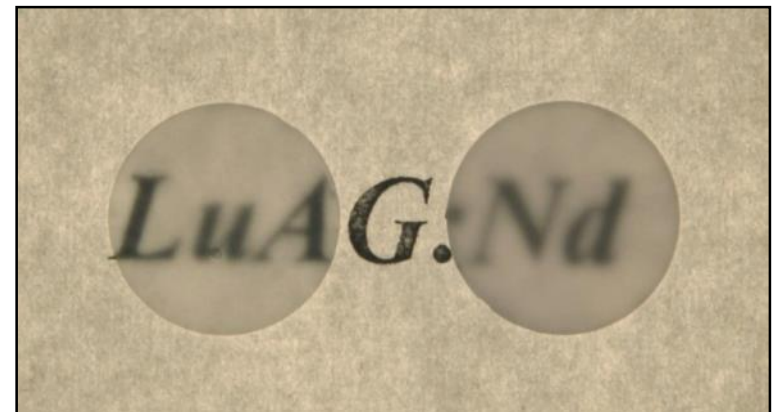
3.3.4 Preparation of Crystalline Ceramics

The basic characteristics or the microstructure of a ceramic component depend on selected raw materials and on the production process
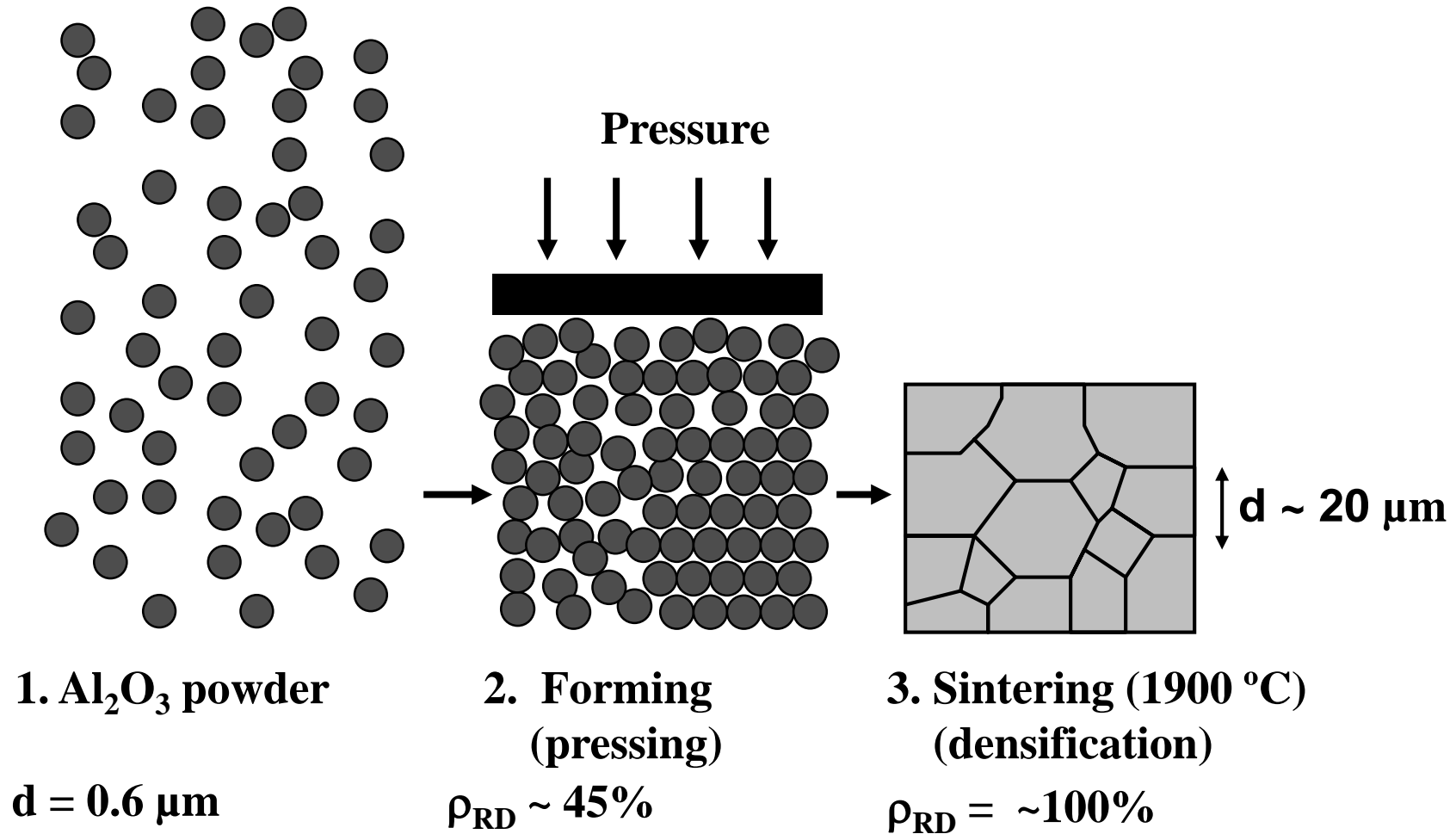
General flow chart

Powder synthesis →	Powder preparation →	Shaping →	Densification
Solid/solid reactions	Mixing	Dry pressing	Sintering
Precipitation reactions	Deagglomeration	Casting	Gas pressure sint.
Decomposition reactions	Spray drying	Extruding	HIP
Solid/gas reactions	Freeze-drying	Injection molding	Pressing
Gas/gas reactions	Addition of additives	Impregnation	Hot pressing
	Granulation	Infiltration	
		Manual shaping	
Chapter 2.1 – 2.3		Green body	Final ceramic

3.3.4 Preparation of Crystalline Ceramics

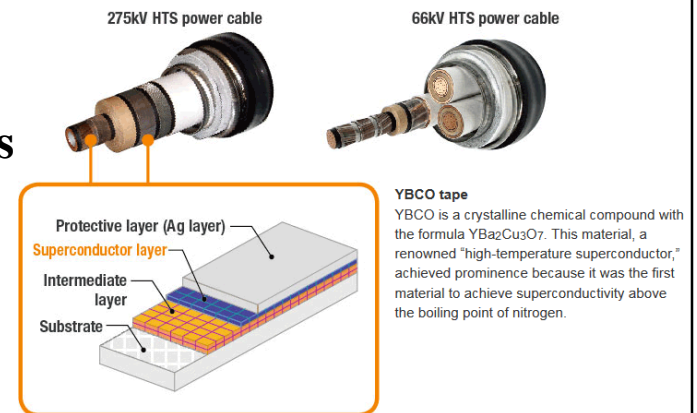**Production of oxide ceramics for ceramic light sources (CDM light sources)**

Pressure

1. Al_2O_3 powder

$d = 0.6\ \mu m$

2. Forming
(pressing)

$\rho_{RD} \sim 45\%$

3. Sintering (1900 °C)
(densification)

$\rho_{RD} = \sim 100\%$

$d \sim 20\ \mu m$

3.3.4 Preparation of Crystalline Ceramics

Production of a high temperature superconductor ceramics from „YBaCu"

$$Y_2O_3 + 4\ BaCO_3 + 6\ CuO \rightarrow 2\ YBa_2Cu^{II/III}_3O_{7-x} + 4\ CO_2\uparrow$$
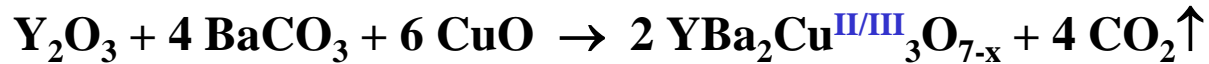
Manufacturing process

1. Mixing and grinding of the starting materials $BaCO_3$, Y_2O_3, CuO in acetone
2. Sintering at 890 °C in air
3. Pulverization
4. Sintering bei 930 °C in air
5. Powderization $\Rightarrow$ YBaCu-powder
6. Forming $\Rightarrow$ YBaCu-green body
7. Sintering $\Rightarrow$ YBaCu-ceramic
   $\rightarrow$ Further processing into cables

275kV HTS power cable

66kV HTS power cable

Protective layer (Ag layer)
Superconductor layer
Intermediate layer
Substrate

YBCO tape
YBCO is a crystalline chemical compound with the formula YBa2Cu3O7. This material, a renowned "high-temperature superconductor," achieved prominence because it was the first material to achieve superconductivity above the boiling point of nitrogen.

3.3.5 Raw Materials

For the ceramics production either naturally occurring raw materials, further treated raw materials or inorganic chemicals are used

Group	Substances	
Non-processed	Rock clay	Clay minerals
Raw materials	Raw bauxite	$AlO(OH) \cdot xFe_2O_3 \cdot ySiO_2$
Industrially processed	Wollastonite	$CaSiO_3$ „chain silicate"
Raw materials	Zircon	$ZrSiO_4$
	Rutile	TiO_2
	Kaolinite	$Al_4[Si_4O_{10}](OH)_8$
	Dolomite	$(Ca,Mg)CO_3$
Industrial inorganic	Al_2O_3, MgO, SiC, ZrO_2, UO_2, Y_2O_3, Gd_2O_3, BeO, Ta_2O_5	
Chemicals	$BaTiO_3$, $Pb(Ti,Zr)O_3$, Al_2TiO_5, MFe_2O_4 (M = Mn, Ni, ...)	
	Si_3N_4, BN, AlN, B_4C, TiB_2, TiN, $MoSi_2$	

3.3.6 Technology of Clay Products

Tone products are used for the production of pipes, bricks, tiles, pottery etc

Raw materials

- Clay, e.g. kaolinite $Al_4[Si_4O_{10}](OH)_8$
- Initial bonding agent (mostly water)
- Ceramic particle (mostly SiO_2-quartz powder)
- Fluxing agent during the following thermal treatment, e.g. felspar $[(K,Na)_2O \cdot Al_2O_3 \cdot 6SiO_2]$

Forming technology
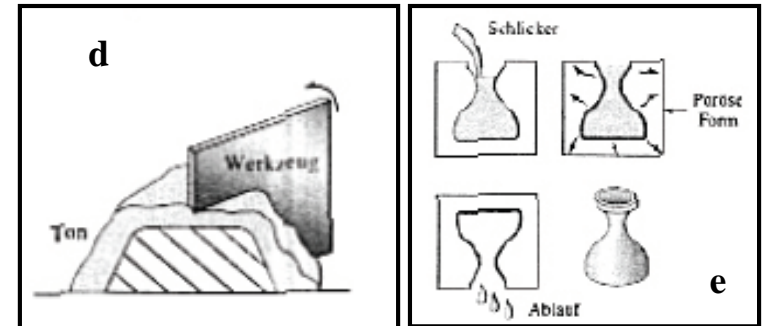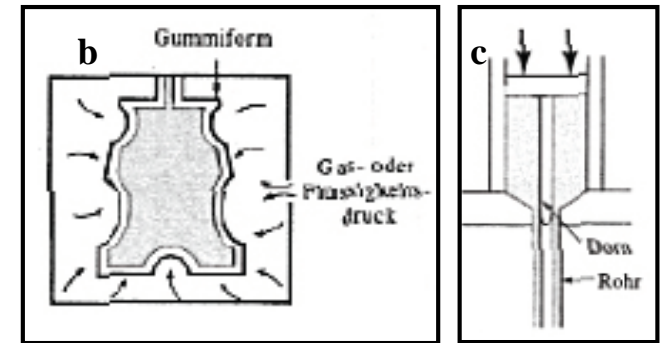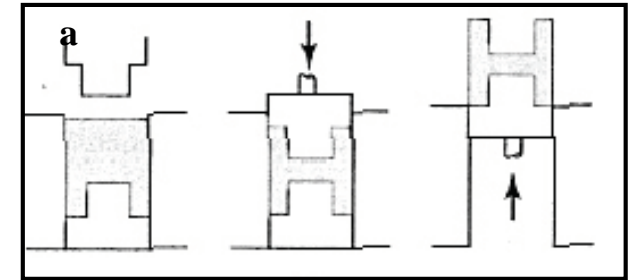
a. Pressing
b. Isostatic pressing
c. Extrusion
d. Manual forming
e. Slip casting

Ref.: D.R. Askeland, Materialwissenschaften, Spektrum Akademischer Verlag GmbH, Heidelberg, Berlin, Oxford, 1996

3.3.6 Technology of Clay Products

Drying and firing of clay products

a)   **Decrease in volume during drying**
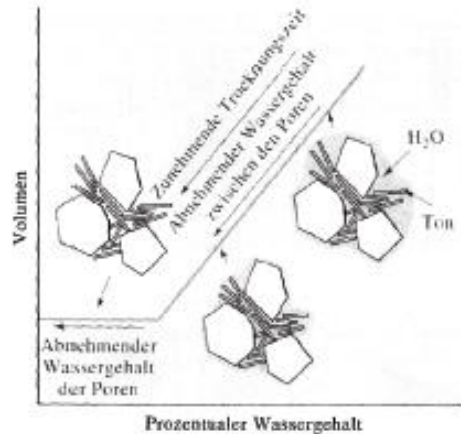
Evaporation of water stored between clay plates

b)   **Density increase upon burning**
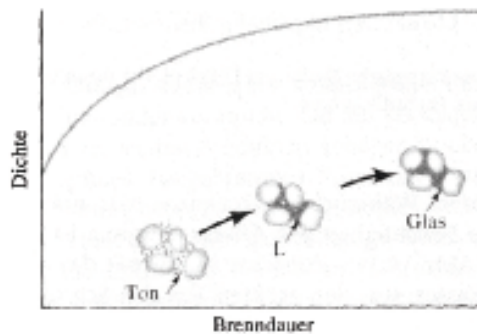
1.   **Dehydrogenation of the bonded water in kaolinite**
2.   **Melting of the flux and the silicate**
3.   **Formation of a glass phase in the clay mineral gaps**

Ref.: D.R. Askeland, Materialwissenschaften, Spektrum Akademischer Verlag GmbH, Heidelberg, Berlin, Oxford, 1996

3.3.7 Refractory Ceramic Materials

Lining of furnaces and other high temperature equipment

Classification of materials is done according to their chemical behavior ($\rightarrow$ PZC)

Material class	SiO$_2$ [%]	Al$_2$O$_3$ [%]	MgO [%]	Fe$_2$O$_3$ [%]	Cr$_2$O$_3$ [%]	
Silica brick	**95 - 97**					**acid**
Fire brick	**10 - 45**	**50 – 80**				
Magnesite			83 - 93	2 – 7		**neutral**
Olivine	43		57			
Chromite	3 - 13	12 - 30	10 - 20	12 - 25	30 – 50	**basic**
Chromite magnesite	2 - 8	20 - 24	30 - 39	9 - 12	30 - 50	

Special refractory materials

- Graphite (stable under oxygen exposure) $\rightarrow$ Graphite furnaces
- Zirconium compounds: ZrO$_2$, ZrO$_2$·SiO$_2$
- Silicon carbide: SiC reacts at the surface of SiO$_2$ $\rightarrow$ Passivation to about 1500 °C

3.3.9 Ceramic Cover Layers

Ceramic substances serve frequently also as a protective coating → Glazes and enamel

Glaze: **Protective layer for ceramic**

Enamel: **Protective layer for metallic**

This concerns clay products, which easily glass during sintering, e.g. $CaO \cdot Al_2O_3 \cdot 2SiO_2$
→ Transparent glaze/enamel

Additive of further minerals leads to colored protective coating

Color	Additive
White	$ZrSiO_4$
Blue	Co_2O_3
Green	Cr_2O_3
Yellow	PbO
Red	Se, CdS

3.3.10 Modern Forming Technology

For the production of modern ceramics from high purity raw materials one uses special forming technology

- **Pressing and sintering (hot pressing)**
  HIP-technique (Hot Isostatic Pressing): green body is sintered in a pressure chamber under inert gas (N_2)

- **Reaction sintering**
  3 Si (powder or green body) + 2 N_2 → Si_3N_4

- **Sol-Gel-technique**
  → Chapter 2.3.2

Mechanical properties of Si_3N_4-ceramic

Production process	Compression strength [N/mm²]	Bending strength [N/mm²]
Slip casting	140	70
Reaction sintering	770	210
Hot pressing	3500	875

3. Inorganic Functional Materials

3.4. Ion Conductors
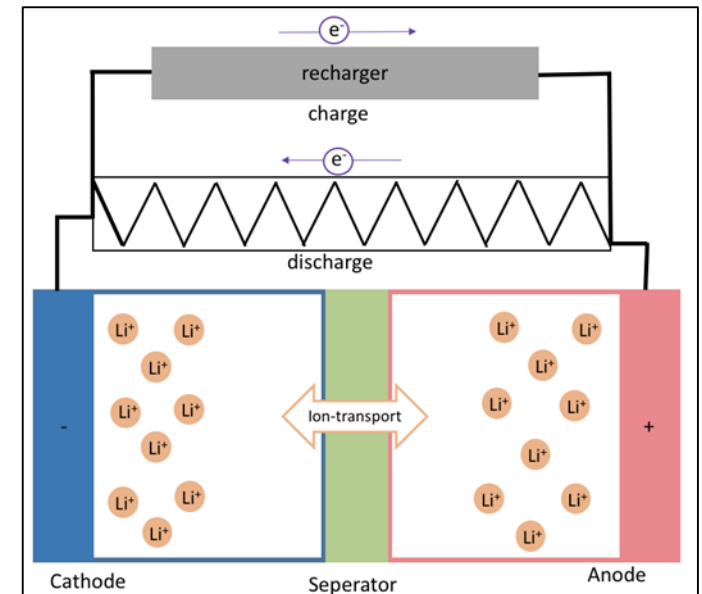
3.4.1 Ion Conduction in the Solid State

Conductivity in the solid requires the mobility of the cations or anions

At room T, majority of solid compounds are very poor conductors, i.e. insulators

Increased ion conductivity

- **in certain crystal structures (mostly layer structures)**
  Example: $NaAl_{11}O_{17}$ (ß-Al_2O_3)

- **by generation of defects due to temperature increase (intrinsic): $N_V = N_0 \cdot exp[-E_V/k_BT]$**
  Example: NaCl

  RT $\sigma < 10^{-12} \, \Omega^{-1}cm^{-1}$ $\sigma_{ion} = N_V \cdot q \cdot \mu_{ion}$

  800 °C $\sigma \sim 10^{-3} \, \Omega^{-1}cm^{-1}$ μ_{ion} = ion mobility $[cm^2s^{-1}V^{-1}]$

  Just below the melting point of a solid, the conductivity increases strongly

- **by the insertion of dopings (extrinsic)**

log σ — intrinsic — extrinsic — Increasing doping level — 1/T [K^{-1}]
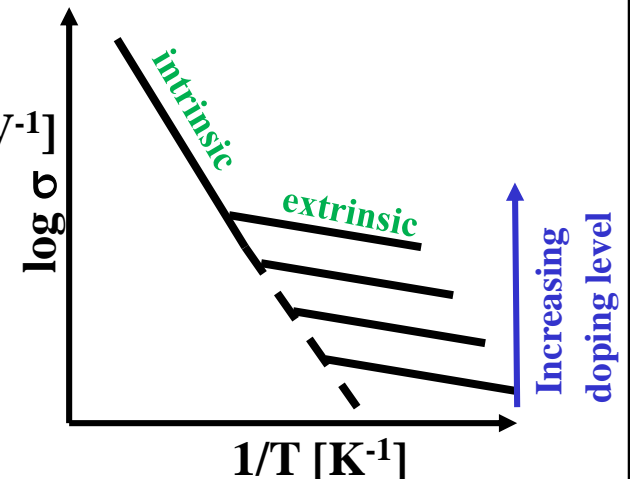
3.4.1 Ion Conduction in the Solid State

Ion mobility

$\mu_{total} = \mu_{cation} + \mu_{anion}$ $[cm^2s^{-1}V^{-1}]$

Nature & amplitude of the energy barrier to shift an ion from one site to the other of the energy barrier

- **Structure**   Geometry constraint to enter the site, free volume, ion size
- **Electrostatics**   Interaction with adjacent ions
- **Polarizability**   Lattice type, charge of the ion ($Na^+ > Ca^{2+}$)
                              $\rightarrow$ **Advantage of less polarizing ions (Cu^+, Ag^+)**

$$\sigma_{ion} = \frac{\sigma_0}{T} \exp\left(-\frac{\Delta_{act}H}{kT}\right)$$ with $\Delta_{act.}H = \Delta_{defect\ creation}H + \Delta_{migration}H$

Conclusion: Temperature increase enhances mobility, though thermal vibration also rises!

3.4.2 Solid Electrolytes

Solid electrolytes concerns usually halides or oxides

Solid electrolytes can be interpreted as a phase between the crystalline and liquid phase due to the mobility of ions

NaCl dissolved in water: $\sigma = 10^{-1}$ Scm^{-1}
Solid NaCl: $\sigma = 10^{-12}$ Scm^{-1}

Crystalline solid $\rightarrow$ Solid electrolyte $\rightarrow$ Liquid

TemperatureT $\uparrow$
Defect concentration c(vacancies) $\uparrow$
Conductivity σ $\uparrow$
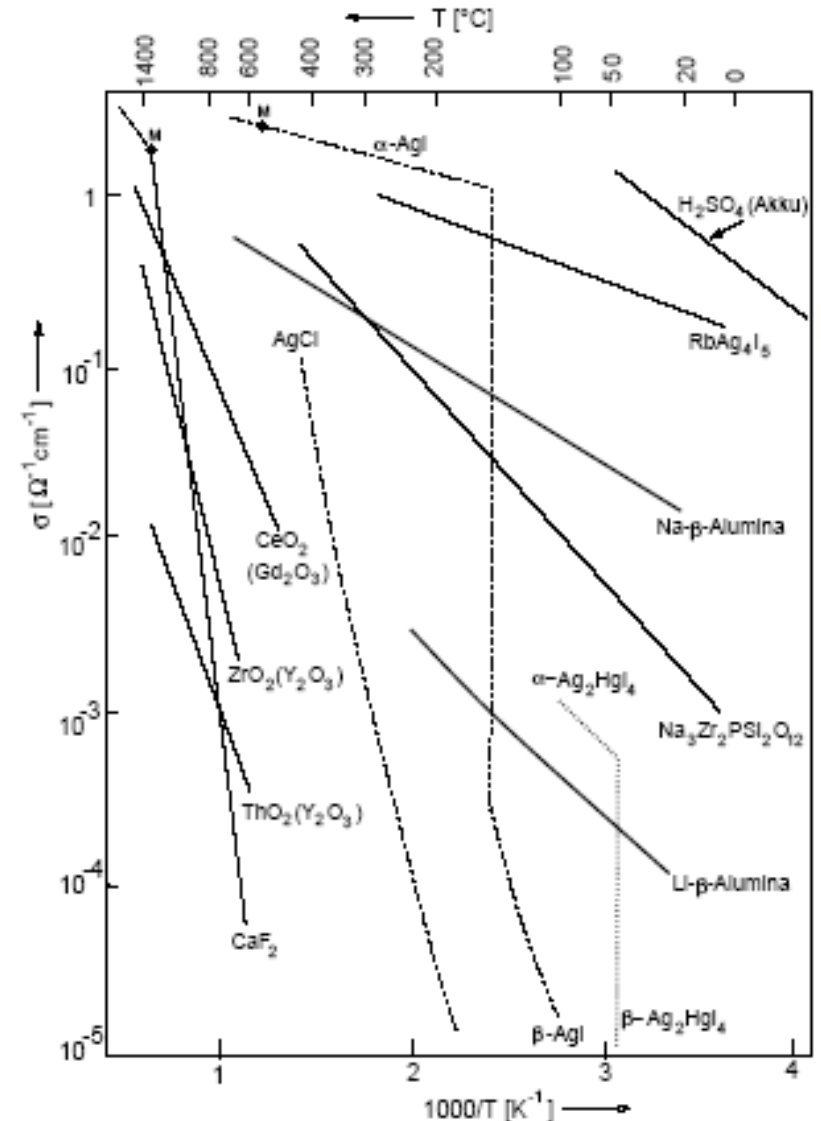
3.4.3 Cation Conductors

Cation conductors are defect semiconductor with defects in the cationic sublattice!

- **Ag^+ based**
  - **AgI**

- **Li^+ based**
  - **$Li_{10}GePS_{12}$**
  - **$Li_{3x}La_{2/3-x}V_{1/3-2x}TiO_3$ with V = Vacancy**
  - **$Li_4P_2S_6$, $Li_7P_3S_{11}$, Li_6PS_5X with X = F, Cl, Br, I**

- **Na^+ based**
  - **$NaAl_{11}O_{17}$ (ß-Alumina)**
  - **$Na_3Zr_2PSi_2O_{12}$ (NaSiCON)**

Phase diagram of $70Li_2S$-$30P_2S_5$ based on XRD
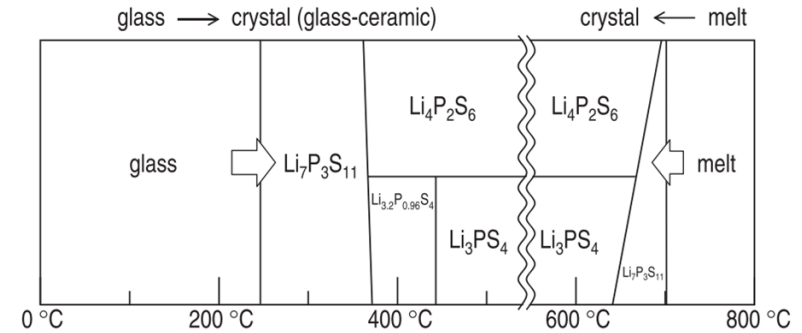
Unit cell of $Li_7P_3S_{11}$ Li (gray), S (yellow), P (red)
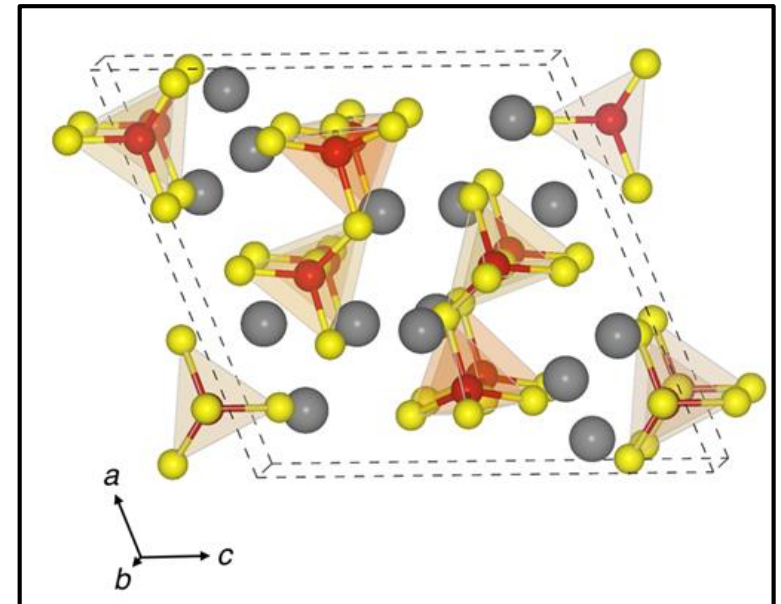
3.4.4 Anion Conductors

Anion conductors are defect semiconductor with defects in the anionic sublattice!

- **Halides**
  - AX, AEX, PbX_2 with A = Li, Na, K, Rb, Cs, AE = Mg, Ca, Sr, Ba, and X = F, Cl, Br, I

- **Oxides with fluoride structure**
  - CeO_2, HfO_2, ThO_2
  - TiO_{2-x}, VO_{2-x}
  - WO_{3-x}, MoO_{3-x}

- **Oxides with perovskite structure**
  - $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-0.5(x+y)}$

- **Oxides with ß-$SnWO_4$ structure**
  - $La_2Mo_2O_9$

Fluorite structure (CaF_2-type)
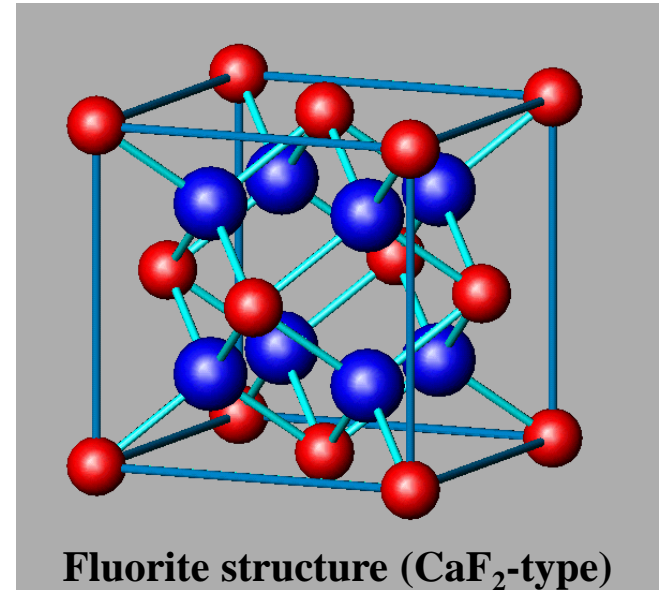
3.4.4 Oxides with Fluoride Structure

Oxide anion conductors: Zirconia ZrO_2

$$\underset{1100\,°C}{ZrO_2 \text{ (monoclinic)}} \rightleftharpoons \underset{2350\,°C}{ZrO_2 \text{ (tetragonal)}} \rightleftharpoons \underset{2680\,°C}{ZrO_2 \text{ (cubic)}} \rightleftharpoons melt$$

Stabilization of cubic zirconia and formation of anion lattice vacancies by Ca^{2+} or Y^{3+} doping:
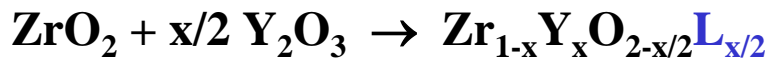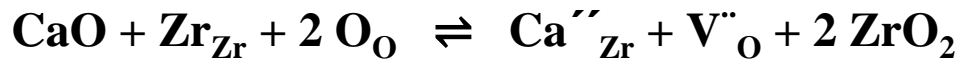
$$ZrO_2 + x\,CaO \rightarrow Zr_{1-x}Ca_xO_{2-x}L_x \quad (0.1 < x < 0.2)$$

Kröger-Vink notation:

$$CaO + Zr_{Zr} + 2\,O_O \rightleftharpoons Ca''_{Zr} + V^{\cdot\cdot}_O + 2\,ZrO_2$$

$$ZrO_2 + x/2\,Y_2O_3 \rightarrow Zr_{1-x}Y_xO_{2-x/2}L_{x/2}$$

Kröger-Vink notation:

$$Y_2O_3 + 2\,Zr_{Zr} + O_O \rightleftharpoons 2\,Y'_{Zr} + V^{\cdot\cdot}_O + 2\,ZrO_2$$

$$\rightarrow \sigma_{RT} = 10^{-4}\,Scm^{-1}$$

Phase diagram of the system ZrO_2-CaO
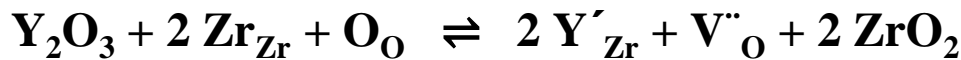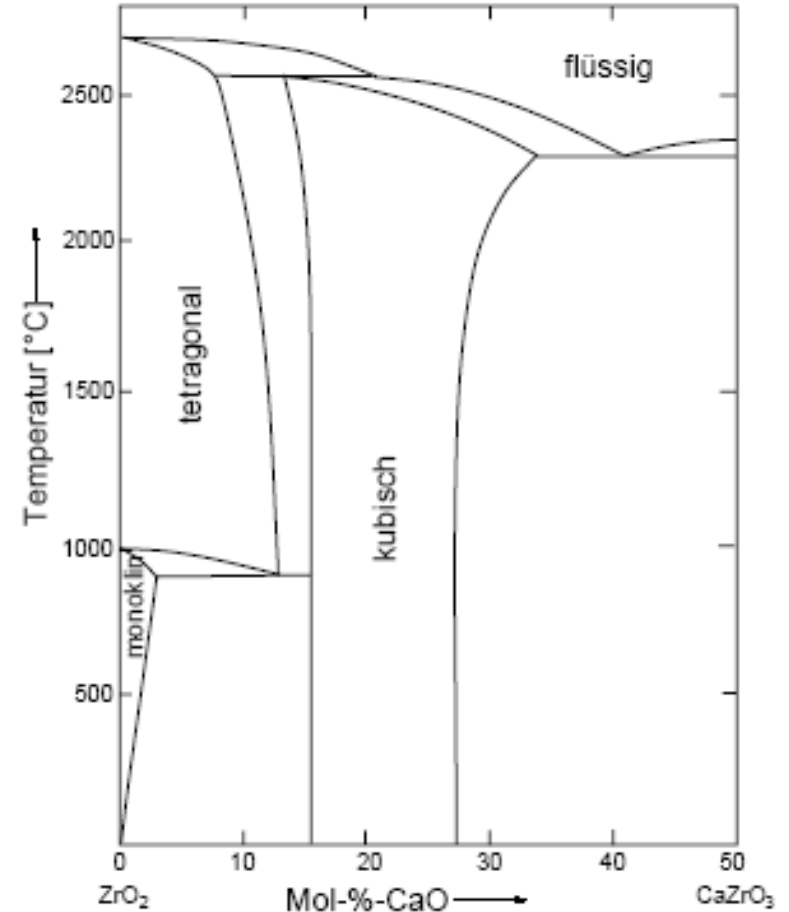
3.4.5 Oxides with ß-Alumina Structure

Cation ion conductors: ß-alumina possesses by inclusion of Na^+ cations a layered structure and thus is a two-dimensional conductor

α-alumina	Al_2O_3
"ß-alumina"	$NaAl_{11}O_{17}$
γ-alumina	Al_2O_3

Na^+ can also be substituted by Li^+, K^+, Ag^+, and Tl^+

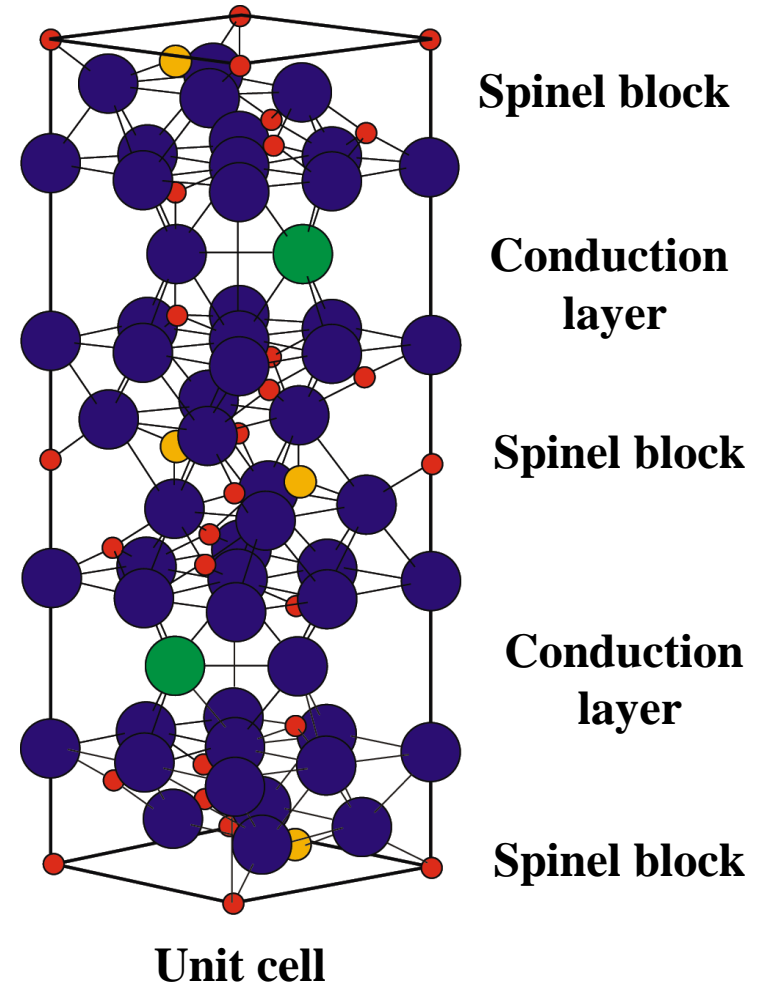The cations in the conduction layer have a high ion mobility (especially small cations)
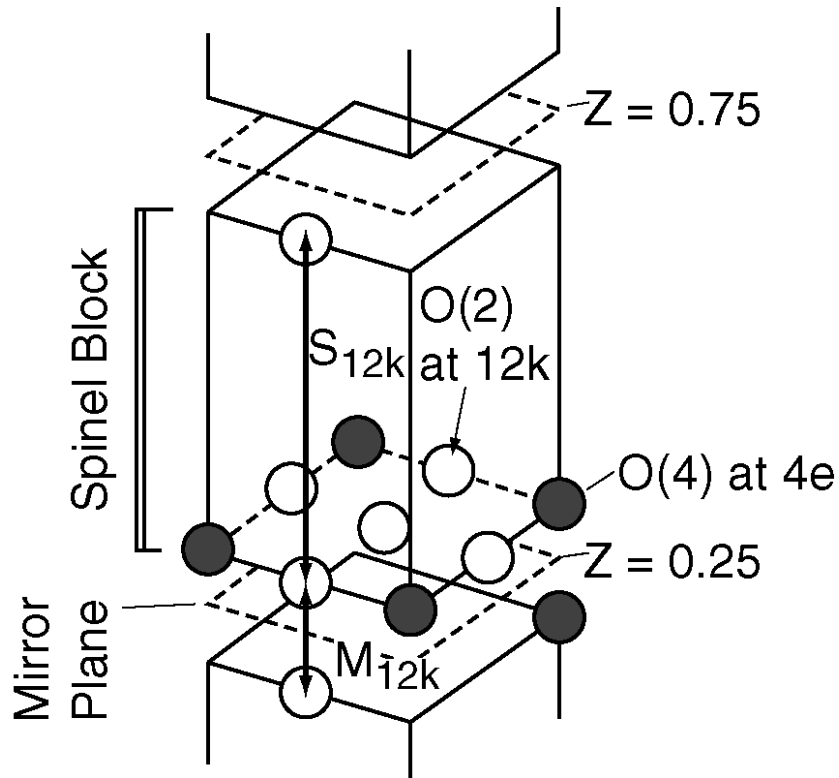
Cation	Activation energy [eV]
Na^+	0.16
Ag^+	0.17
K^+	0.30
Tl^+	0.36

Spinel block

Conduction layer

Spinel block

Conduction layer

Spinel block

Unit cell

3.4.5 Oxides with ß-Alumina Structure

Cation ion conductors: Thermodynamic stability of β-alumina

Z = 0.75

Spinel Block

O(2)
S_{12k} at 12k

O(4) at 4e

Z = 0.25

Mirror Plane

$M_{\overline{12k}}$

Structural influence of cations in the intermediate layer

ß-Alumina

Magnetoplumbite

Conduction layer thickness M_{12k}

Ionic radius [A]
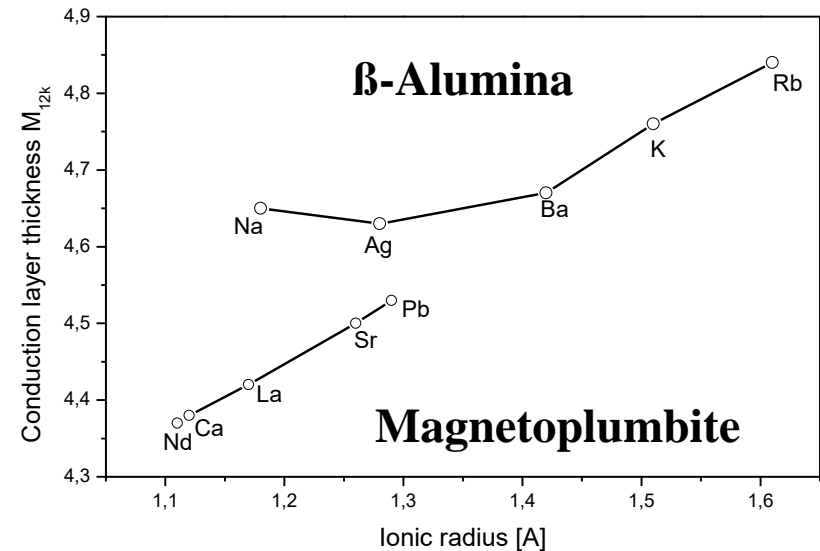
- Stability limit of the β-Alumina phase is $M_{12k} > 4.6$ Å
- Incorporation of small cations destabilizes the ß-alumina phase (Sr^{2+}, Ca^{2+})
- Incorporation of large cations stabilizes the ß-alumina phase (Rb^+, K^+)

3.4.6 Alkali Halides: Hole Transport

In alkali halides the smaller cations are more mobile than the anions

→ Hole transport

Hole transport = Migration of cation lattice vacancies V

Conductivity $\sigma = A \cdot c(V)$

The number of cation vacancies V can be increased by increasing the temperature or by the incorporation of extrinsic cations with a higher charge than those of the Na^+ ions:

$NaCl + x\ MnCl_2 \rightarrow Na_{1-2x}Mn_xV_{Nax}Cl\ (x = 0.0 - 0.5)$

Kröger-Vink notation:

$MnCl_2 + 3\ Na_{Na} + Cl_{Cl} \rightleftharpoons Mn^{\cdot}_{Na} + V^{\cdot}_{Cl} + 3\ NaCl$
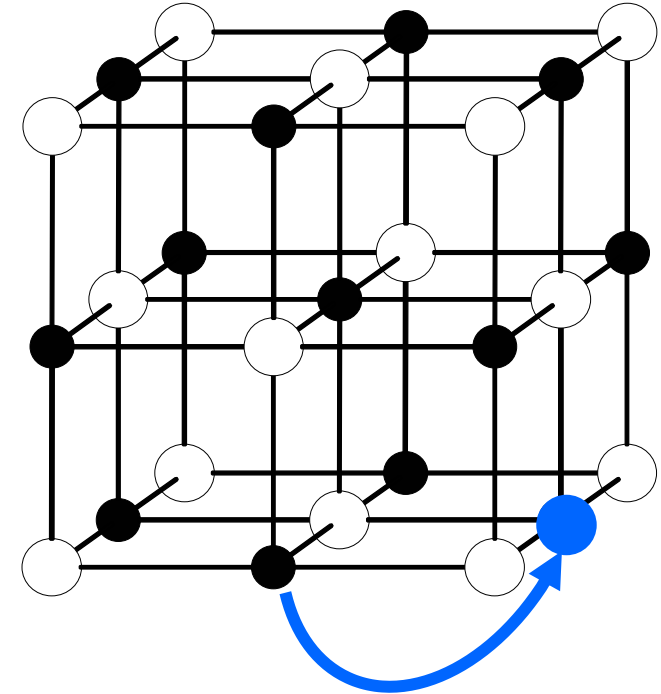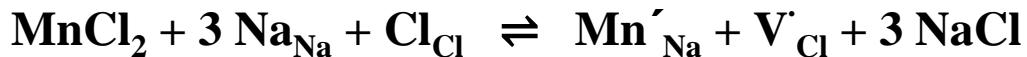
Process	Activation energy A [eV]
Migration of Na^+	0.65 – 0.85
Migration of Cl^-	0.90 – 1.10

3.4.7 Silver Chloride: Interstitial Conduction

In AgCl Frenkel defects are decisive, i.e. silver ions are located at interstitial sites and are coupled to corresponding lattice vacancies

→ Cation migration via interstitial sites **i**

Formation of Frenkel defects

$AgCl \rightarrow Ag_{1-x}L_xAg_{ix}Cl$

Process	Activation energy [eV]
Formation of Frenkel defects	1.24
Migration of the cation vacancies	0.27 – 0.34
Migration of the Ag^+ ions	0.05 – 0.16

Ag Cl Ag Cl

Cl Ag Cl Ag

Ag Cl **Ag** Cl

Cl Ag Cl Ag

Ag Cl Ag Cl

Cl Ag Cl Ag

Ag Cl ☐ Cl

Cl Ag Cl **Ag$_i$** Ag
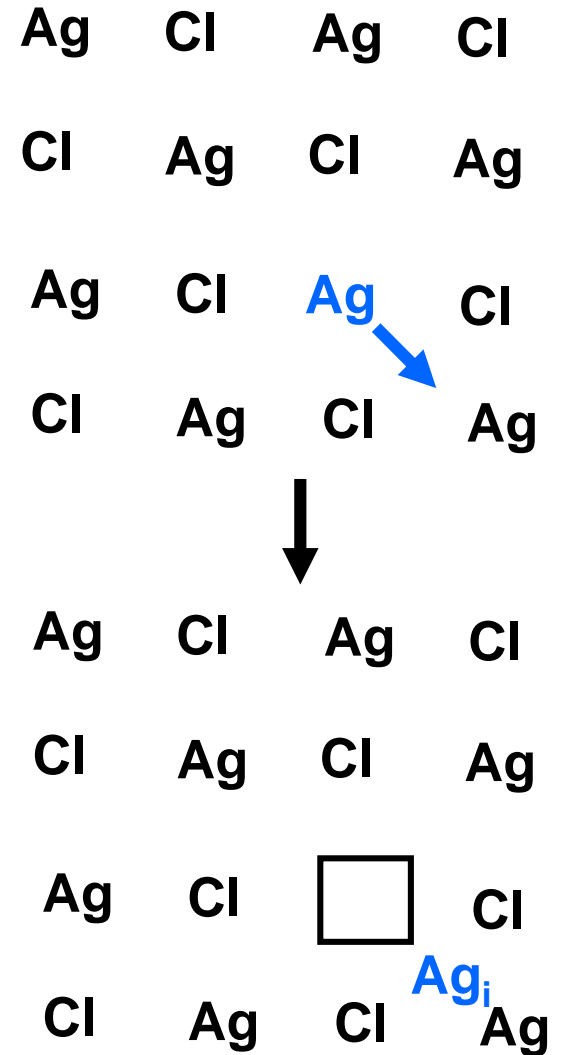
3.4.8 Silver Ion Solid Electrolytes

α-AgI and RbAg₄I₅ are extraordinarily good ion conductors

$$\text{ß-AgI} \overset{146\,°C}{\rightleftharpoons} \text{α-AgI}$$
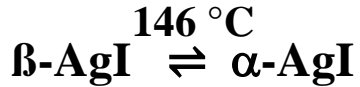
$\sigma(\text{α-AgI}) \sim 1\ \Omega^{-1}\text{cm}^{-1}$!

Structure of α-AgI

- Body-centered cubic (bcc) arrangement of anions
- The Ag⁺ ions are statistically distributed over 36 trigonal and tetrahedral positions
- ⇒ High mobility of Ag⁺ anions

Material with the highest conductivity at RT is so far RbAg₄I₅

⇒ $\sigma(\text{RbAg}_4\text{I}_5) \sim 0.25\ \Omega^{-1}\text{cm}^{-1}$

AgI

RbAg₄I₅

Graph: log σ [Ω⁻¹cm⁻¹] vs 1/T [K⁻¹], showing curves labeled α-AgI, β-AgI, and RbAg₄I₅
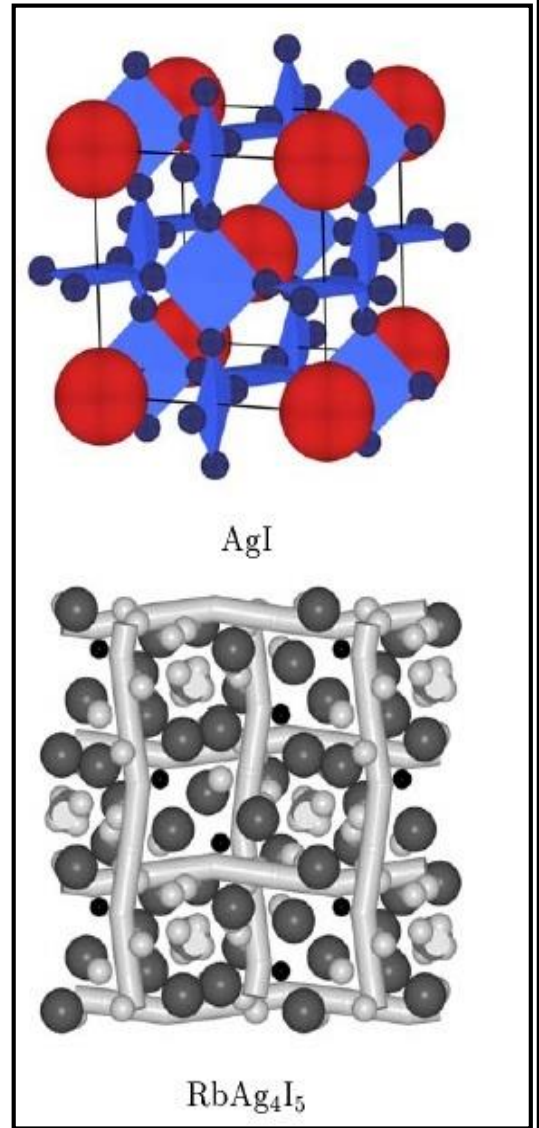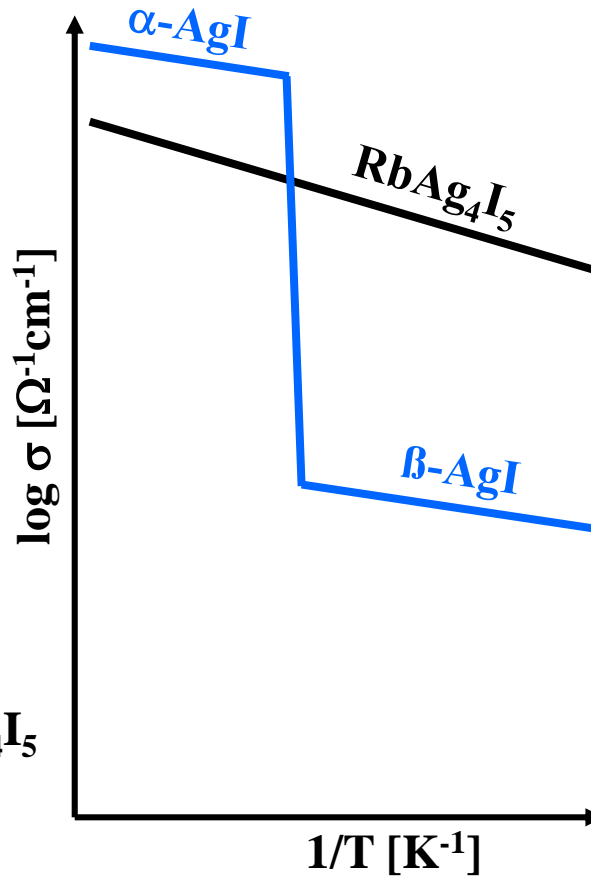
3.4.9 Application Areas

Requirements to obtain a good ion conductor

- **Many similar ions must be mobile**

- **For the mobile ions many empty sites, which can be occupied, must be available**

- **The empty and the occupied positions must have a comparable potential energy**

- **The structure must possess 3D framework with open channels, through which mobile ions can move**

- **The anion network must be easily polarizable**
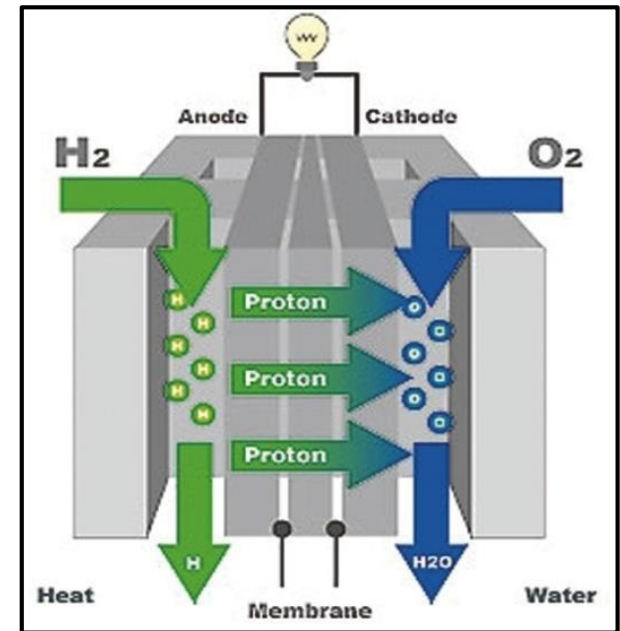
Technical applications

- **Fuel cells and water electrolysis**

- **Water desalination**

- **Sensors, e.g. to measure oxygen partial pressure (-probe)**

- **Batteries, e.g.**
  - **Na(l)|Na-ß-Al$_2$O$_3$|S(l)**
  - **Li(l)|LiI|I$_2$-PVP(Iodpoly-2-vinylpyridine)**

Dessalement de l'eau de mer à 35 g/litre
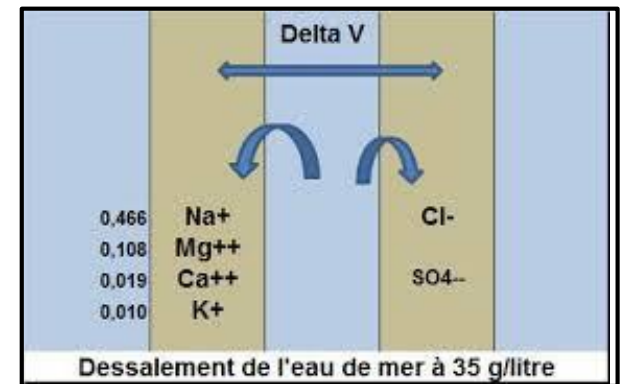
3.5 Biomaterials

Definitions

Biological materials: Materials, which are used naturally by living organisms.

Bio(compatible) materials : Artificial (man-made) materials that are used in place of biological materials, e.g. implant materials

Biomimetic materials: Artificial materials, which recreate the structure of the biological materials

Why is the research concerning biological materials of great importance?

1. **Generate understanding**
   How living things are using materials to adapt to the environment?
2. **Application in the material science**
   Which construction ideas can be derived? $\Rightarrow$ **Biomimetic materials**
3. **Application in the medicine**
   How can biological materials be handled or replaced?

3.5 Biomaterials

Classification

Static structural materials

- **Internal and external skeleton (support function)**
- **Cell walls, fibers, hair, nails, tendons, spider silk, nacre, and so on**

Membranes

- **Structural material with passive mass transport: cell membranes**
- **intracellular membranes of organelles: nuclear membrane, thylakoid membrane**

Active functional materials
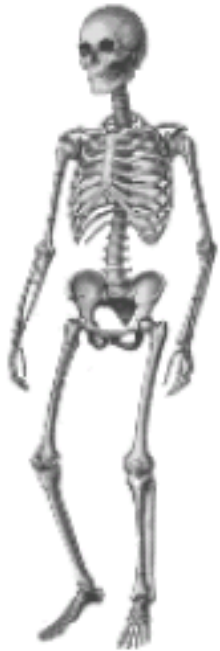
- **Muscles, composed of filaments**

<u>Alternative classifications</u>

- **animal or vegetable**
- **chemical composition**

3.5 Biomaterials

Static structural materials

Endoskeleton

Exoskeleton

Fibers (silk)

Cell walls (wood)

3.5 Biomaterials

Membranes and active functional structural materials
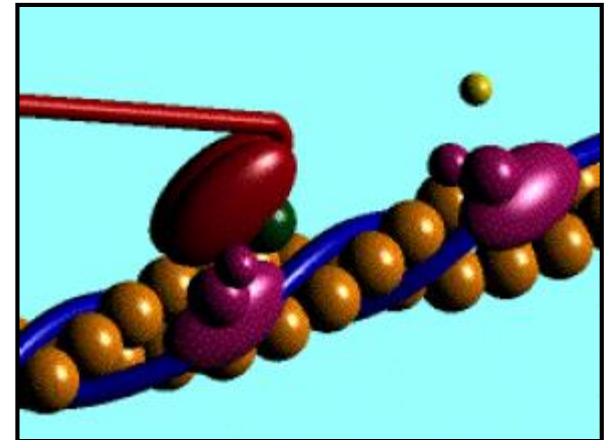
Cell membrane
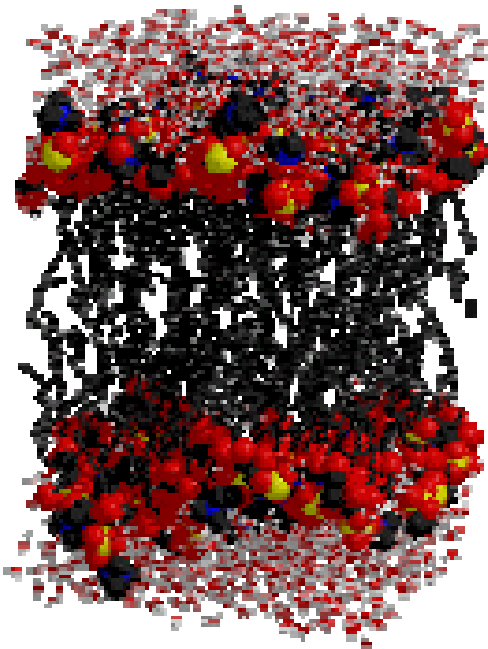
Muscles

Muscles (active)
Tendons (passive)
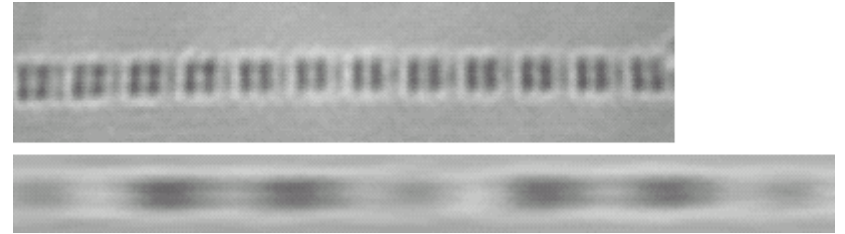
Muscle fibers in the SEM
unstretched (top) and stretched (bottom)

The molecular
Actin-myosin engine

3.5 Biomaterials

Hierarchical structure (bottom-up)

1.   **Nanoscopic (0.1 - 1 nm)**

Molecules: **common polymers and inorganic substances**

- **Carbohydrates: cellulose, chitin**
- **Proteins: polyalanine (spider silk), collagen, keratin, actin and myosin (muscle fibril)**
- **Inorganic compounds: hydroxyapatite (bone), calcite (nacre) $CaCO_3$, SiO_2, Fe_2O_3**
- **Complex compounds: lignin (various types)**

2.   **Mesoscopic (1 – 100 nm)**

Structural units: **order, such as helices or crystals**

- **hard, ordered units (crystals) in a softer, disordered Matrix $\Rightarrow$ Composite materials: mechanical properties change**
- **Cellulose microfibrils, mineralization of bone and tendon**
- **Protein crystals in spider silk, lamellar phase of membranes**
- **Helices as the basic unit of many fibers, such as tendons (collagen)**

3.5 Biomaterials

Hierarchical structure (bottom-up)

3.   **Microscopic (0.1 - 100 µm)**

Cells, tissues

- **Plant cell walls, fiber cells, wood cells**
- **Muscle filaments**

4.   **Macroscopic (from 0.1 mm upwards)**

Architecture

- **Annual rings of trees**
- **Bones**
- **Shells**

Ca^{2+} is the ion of structure formation and thus strongly regulated by "Calmodulin" = calcium modulating protein in living systems
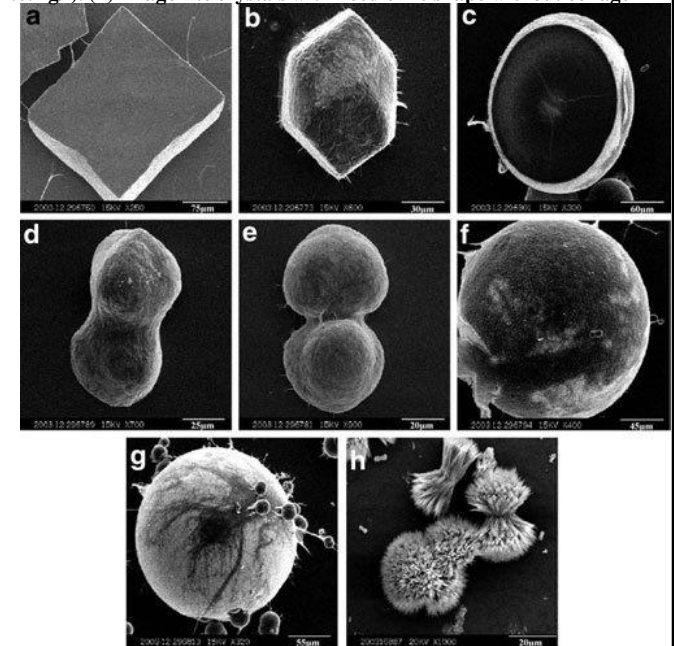
3.5 Biomaterials

Ca²⁺ Chemistry

Biomineralisation (CaCO₃)

- **In mussels, snails, otoliths, ...**
- **Morphological control and orientation by organic ligands**
    – **Carboxyl groups (glu, asp, ...)**
    – **Oxidised carbohydrates**
    – **Collagen**
- **Lab examples**
    – **Spindle-shaped calcite crystals in presence of malonic acid**
    – **Disc-shaped vaterite crystals through stearic acid**

Modification	CaCO₃ (aragonite)	CaCO₃ (calcite)	CaCO₃ (vaterite)
Crystal system	Orthorhombic	Trigonal	Hexagonal
Space group	Pnma (#62)	R-3ch (#167)	P63/mmc (#194)
Coordination number	9	6	8
Formula unit/unit cell	4	6	2

3.5 Biomaterials

Ca²⁺ Chemistry

Biomineralisation of CaCO₃
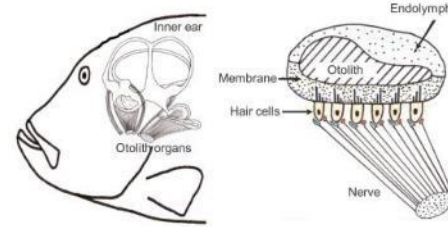
| **Aragonite (meta-stable)**	**Calcite (stable)**	**Vaterite (meta-stable)**
Fish-otholiths, corals, pearls	**Mussel shells**	**Spheroliths**
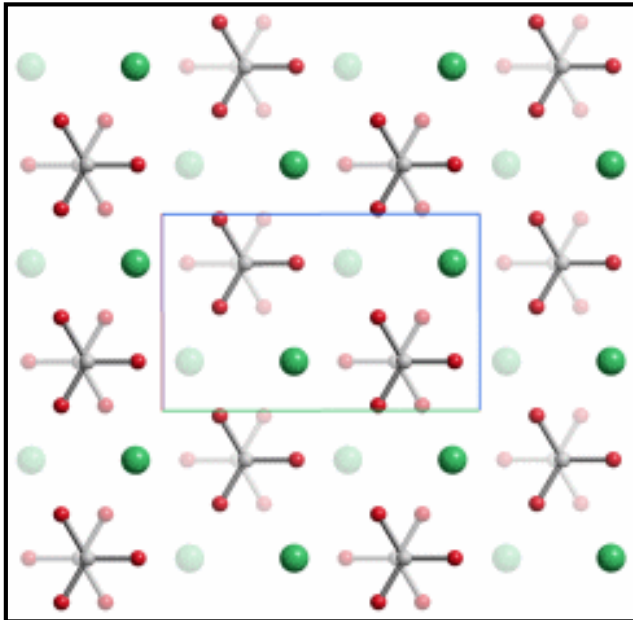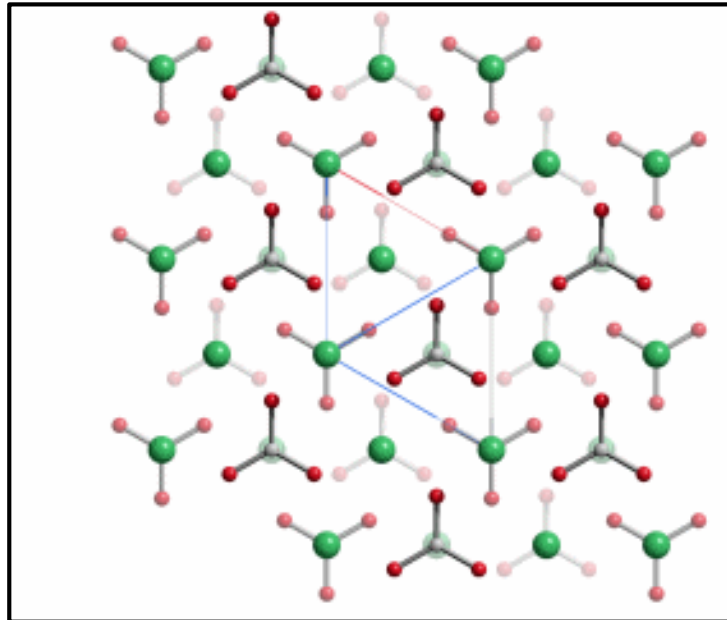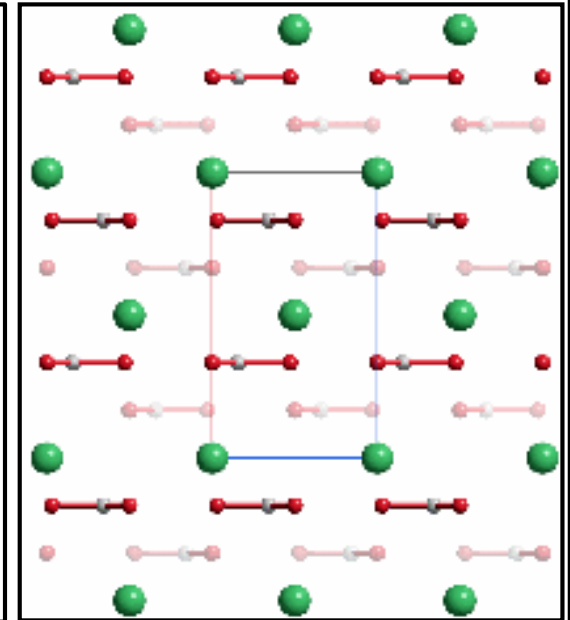
3.5 Biomaterials

Ca²⁺ Chemistry

Biomineralisation of $Ca_5[PO_4]_3X$ with X = OH

- **In bones of vertebra and cephalopods**
- **Collagen serves as template, i.e. it defines the orientation of the apatite crystals**
- **Binding of Ca^{2+} via carboxylates groups of osteocalcin and via phosphoproteins**

Hydroxyapatite $Ca_5[PO_4]_3OH$

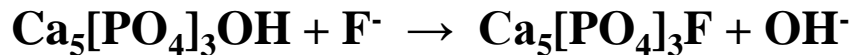| Crystal system	Trigonal
Space group	Pnma (#176)
Coordination number	8 and 9
Formula unit per unit cell	2
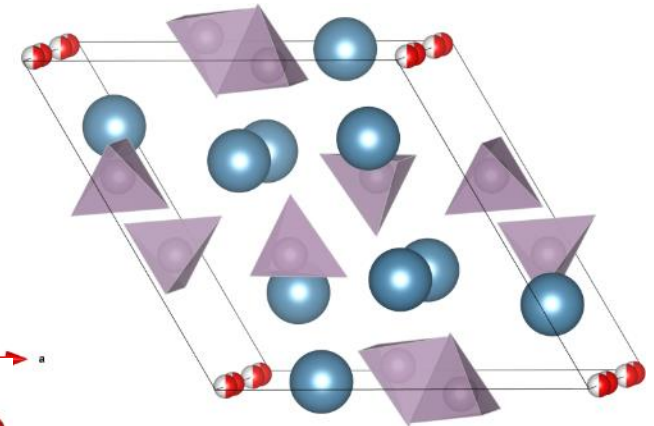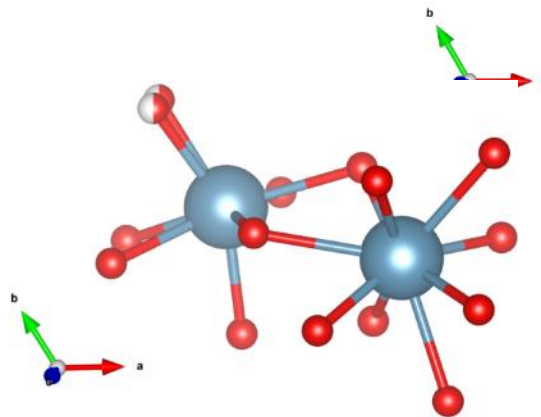
3.5 Biomaterials

Ca²⁺ Chemistry

Biomineralisation of $Ca_5[PO_4]_3X$ with X = F

- In teeth (enamel) of vertebrates and cephalopods
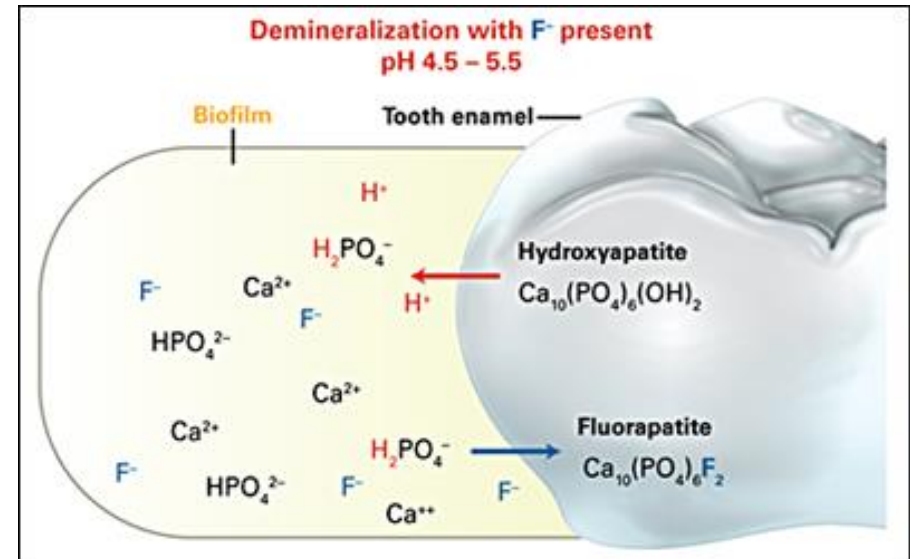- Is formed by fluorination of hydroxyapatite (toothpaste contains Na_2PO_3F)

  $Ca_5[PO_4]_3OH + F^- \rightarrow Ca_5[PO_4]_3F + OH^-$

Fluoroapatite $Ca_5[PO_4]_3F$

Crystal system	Trigonal
Space group	Pnma (#176)
Coordination number	7 and 9
Formula unit per unit cell	2

Pyrophosphates α-$Ca_2P_2O_7$ and ß-$Ca_2P_2O_7$

- Crystal-induced arthropathy

Demineralization with F⁻ present
pH 4.5 – 5.5

Biofilm   Tooth enamel——

H⁺

$H_2PO_4^-$

Hydroxyapatite
$Ca_{10}(PO_4)_6(OH)_2$

F⁻   Ca²⁺   H⁺
F⁻
HPO_4^{2-}

Ca²⁺

Fluorapatite
$Ca_{10}(PO_4)_6F_2$

Ca²⁺ $H_2PO_4^-$
F⁻ HPO_4^{2-} F⁻   F⁻
Ca⁺⁺

3.5 Biomaterials
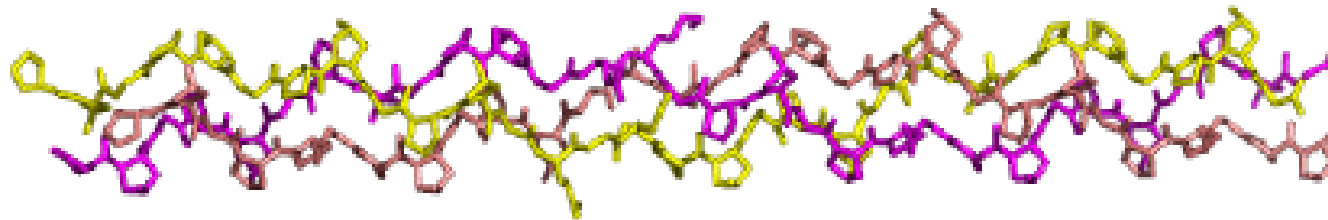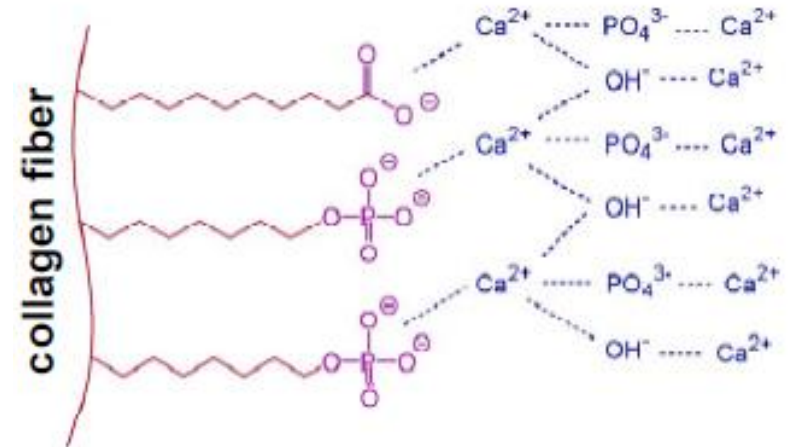
Ca²⁺ Chemistry

Osteocalcin

- **Fixates apatite**

Collagen

- **Three left-handed helices, combined to a right-handed super-helix**

- **Composite material without binding sites for Ca²⁺**

- **Apatite crystals are incorporated parallel to the collagen helix**

3.5 Biomaterials

Ca^{2+} Chemistry

Calciumpyrophosphates

Formula	Ca$_2$P$_2$O$_7\cdot$2H$_2$O (CPPD)	Ca$_2$P$_2$O$_7\cdot$H$_2$O
Crystal system	triclinic	monoclinic
Space group	P1	P2$_1$/n
Formula units Z	2	4
Coordination number Ca^{2+}		7 (Ca1), 6 (Ca2)

Causes "Crowned Dens Syndrome": Severe neck pain

Literature

- Acta Cryst. B31 (1975) 1730
- J. Bone Joint Surg. Am. 89 (2007) 2732
- Acta Cryst. C70 (2014) 862