Chemical Technology of Materials

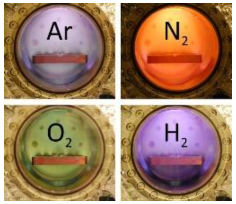
Contents

$$\text{Solid} \underset{\text{freezing}}{\overset{\text{melting}}{\leftrightarrows}} \text{Liquid} \underset{\text{condensing}}{\overset{\text{vaporising}}{\leftrightarrows}} \text{Gas} \underset{\text{recombining}}{\overset{\text{ionising}}{\leftrightarrows}} \text{Plasma}$$

$Lu_3Al_5O_{12}$:Pr(s)

Ga(l) liquid 30-2400 °C (rare in the universe)

I_2(g)



Plasma types (TU Eindhoven)

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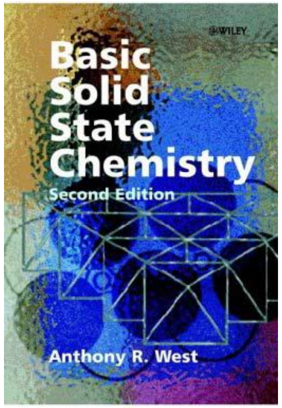
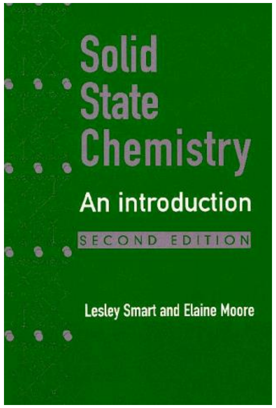
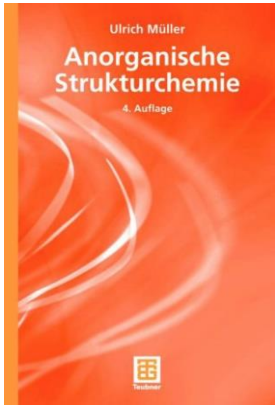
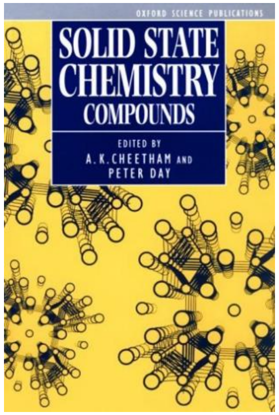
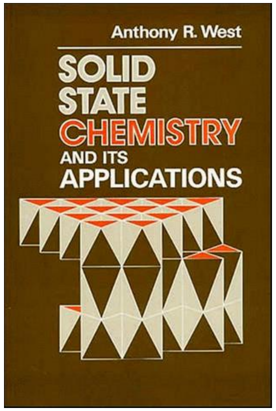










1. Classification of Materials

By the application

- Structural materials (classical materials)
  - Construction materials (gypsum, lime, cement, concrete, mortar, metals, …)
  - Glasses
  - Ceramics (construction elements, containers, porcelain, tiles, bricks, …)
  - Biomimetic materials (surface nanostructures, e.g. lotus flower, shark skin)

- Functional materials (modern materials)
  - Artificial bones and tissue (teeth implants, bone screws, membranes)
  - Electronic ceramic (piezo ceramic, sensors, semi- and superconductors)
  - High temperature resistive ceramic (engine parts, valves)
  - Catalysts (Electro, Photo, Thermal catalysis)
  - Magnetic materials (permanent magnets, tape coatings)
  - Optical materials (pigments, glass fibres, luminescent materials, Laser crystals and ceramics, Faraday rotators)

1. Classification of Materials

By the chemical composition

- **Inorganic materials**
  - **Elements (Fe, Al, Cu, Ag, Au, Si)**
  - **Alloys (steel: Fe-C, brass: Cu-Zn, bronze: Cu-Sn)**
  - **Compounds (Al_2O_3, SiO_2, TiO_2)**
  - **Glasses (quartz glass, soda lime glass, lead glass)**
  - **Ceramics (silicate, oxide, nitride, carbide, or glass ceramics)**

- **Organic materials**
  - **Polymers (polyurethane PU, polyethylene PE, polystyrene PS, teflon PTFE)**

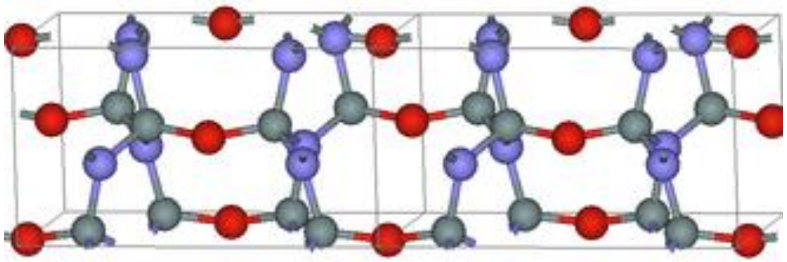
- **Hybrid materials**
  - **Silicone**
  - **ORMOSIL (organically modified silica SiO_2)**
  - **Fibre-reinforced polymers**

1. Classification of Materials

Inorganic solid state compounds

By the type of anions and number of cations or cation (positions)

Anions	Binary	Ternary	Quaternary
Halides	NaF	Na_3AlF_6	$LiCaAlF_6$
Oxides	MgO	$MgAl_2O_4$	$BaMgAl_{10}O_{17}$, $LaMgAl_{11}O_{19}$
Sulphides	SrS	$SrGa_2S_4$	Na_2SrTiS_4
Nitrides	Si_3N_4	$Sr_2Si_5N_8$, $La_3Si_6N_{11}$	$SrYbSi_4N_7$
Carbides	SiC		
Oxy halides	LaOBr		
Oxy sulphides	Y_2O_2S		
Oxy nitrides	Si_2N_2O	$SrSi_2N_2O_2$	
Carbo nitrides		$Y_2Si_4N_6C$	



Crystal structure of Si_2N_2O. Red: O, Blue: N, Gray:Si (*JACS 76 (1993) 2112)*

Lit.: Ceramics Int. 39 (2005) 1097

2. Syntheses Techniques

2.1. Solid State Reactions

2.1.1 Fundamentals of Solid State Reactions

General Principles

Basic Process Steps

2.1.2 Precursor Methods

Co-Precipitation

Other Precursor Methods

2.1.3 Technical Equipment

Container

Furnaces

Synthesis Atmosphere

2.1.4 Special Synthesis Techniques

Fluxes

Melt Salt Method

Carbothermal Reduction

Combustion Methods

Intercalation Reactions

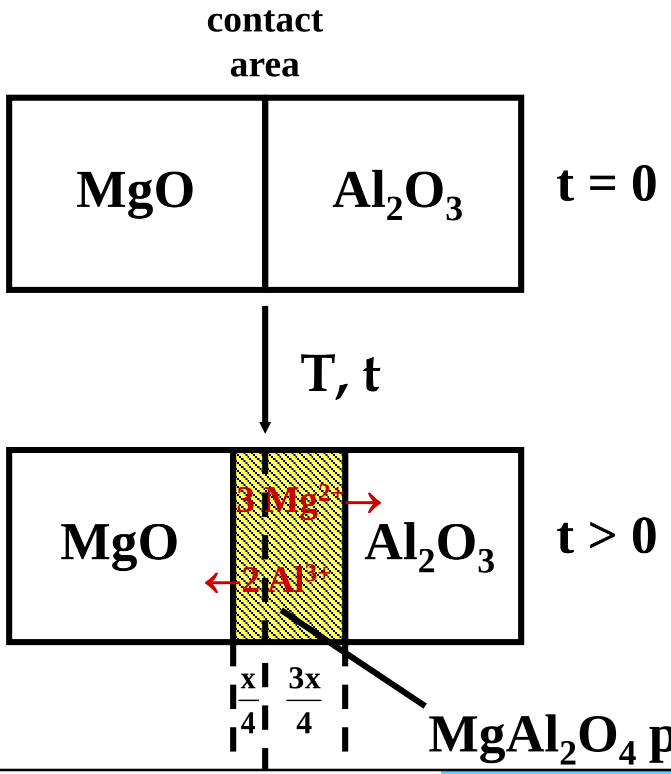
$(Lu_{2,82}Pr_{0,03}Gd_{0,15})Al_5O_{12}$ (Michael Laube)

2.1.1 Fundamentals of Solid State Reactions

General principles

Reactions between solid compounds are driven by diffusion processes (mostly slow)

Example: $MgO + Al_2O_3 \rightarrow MgAl_2O_4$



Reaction at the

interface: $MgO/MgAl_2O_4$

$$2\ Al^{3+} + MgO + 3\ O^{2-} \rightarrow MgAl_2O_4$$

interface: $MgAl_2O_4/Al_2O_3$

$$3\ Mg^{2+} + 3Al_2O_3 + 3\ O^{2-} \rightarrow 3\ MgAl_2O_4$$

Growth rates at both interfaces are given by the ratio 1:3

$MgAl_2O_4$ product layer with thickness x

2.1.1 Fundamentals of Solid State Reactions

General principles

The speed of solid state reactions is

$$\frac{dx}{dt} = k x^{-1}$$

or

$$x = (k't)^{1/2}$$

whereby

x = reaction conversion

t = time

k, k' = speed constants

= f(a, b, c, …)

Which factors determines the speed (constants)?

1. Contact area between starting materials
$\Rightarrow$ Specific surface and particle size (distribution)

2. Speed of seed formation of the product phase (crystal structure of educts and products)

3. Speed of diffusion of involved ions through the different phases, in particular through the product phase (ion charge, crystal structure type)

2.1.1 Fundamentals of Solid State Reactions

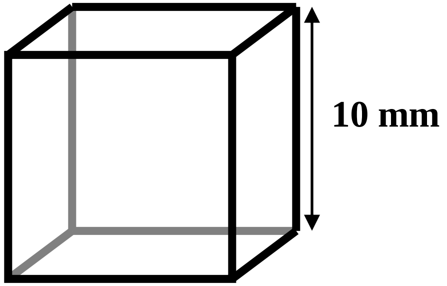
General principles

1. **The specific surface area (particle size distribution) determines the contact area**

Example: MgO with a density of $\rho = 3.58\ g/cm^3$

Single crystal (d = 10 mm)

$V = 1\ cm^3 \Rightarrow 1$ particles

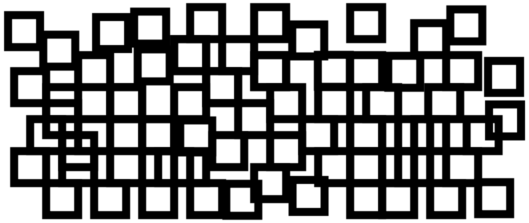


$S = 6 \cdot 1\ cm^2 = 6 \cdot 10^{-4}\ m^2$

$S = 1.68 \cdot 10^{-4}\ m^2/g$

Micro powder (d = 10 µm)

$\Rightarrow 10^9$ particles

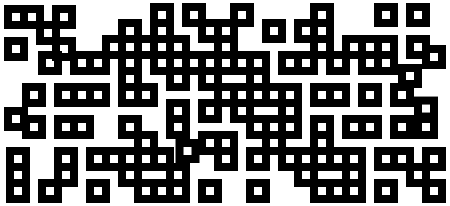


$= 10^9 \cdot 6 \cdot 10^{-10}\ m^2 = 6 \cdot 10^{-1}\ m^2$

$= 0.168\ m^2/g$

Nano powder (d = 10 nm)

$\Rightarrow 10^{18}$ particles



$= 10^{18} \cdot 6 \cdot 10^{-16}\ m^2 = 6 \cdot 10^2$

$= 168\ m^2/g$

2.1.1 Fundamentals of Solid State Reactions

General principles

2. The nucleation rate of the product depends on the degree of similarity of the crystal structure of the reactant and product phase.

Example: $MgO + Al_2O_3 \rightarrow MgAl_2O_4$

MgO (sodium chloride structure)

Cubic close-packed O^{2-} ions, Mg^{2+} ions occupy octahedral gaps

$MgAl_2O_4$ (normal Spinel)

Cubic close-packed O^{2-} ions, Mg^{2+} ions occupy tetrahedral gaps,
Al^{3+} ions occupy octahedral gaps

⇒ simple seed formation of the product phase at the surface of MgO

- Epitactic reaction:	structural similarity at the surface
- Topotactic reaction:	3-dimensional structural similarity

2.1.1 Fundamentals of Solid State Reactions

General principles

3. The speed of diffusion of ions across involved phases and thus the product formation rate depends on the following factors:

- **Annealing temperature and temperature difference to the melting point**
- **Ionic conductivity of involved phases (product phase)**
  - Fluorides > Oxides > Nitrides
  - ß-Al_2O_3 ($NaAl_{11}O_{17}$) >> γ-Al_2O_3 > α-Al_2O_3
- **Formation of eutectic mixtures (melting-point decrease)**
- **Formation of volatile intermediates**
  $SiO_2(s) + 4\ NH_4F(s) \rightarrow SiF_4(g)\uparrow + 4\ NH_3(g) + 2\ H_2O(g)$

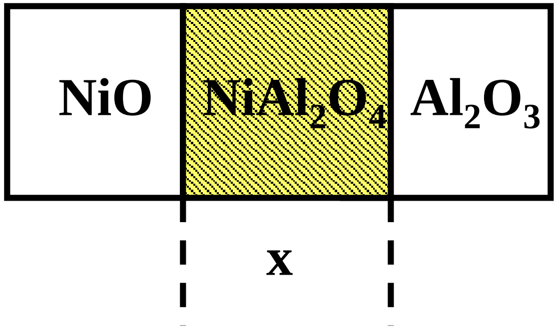
2.1.1 Fundamentals of Solid State Reactions

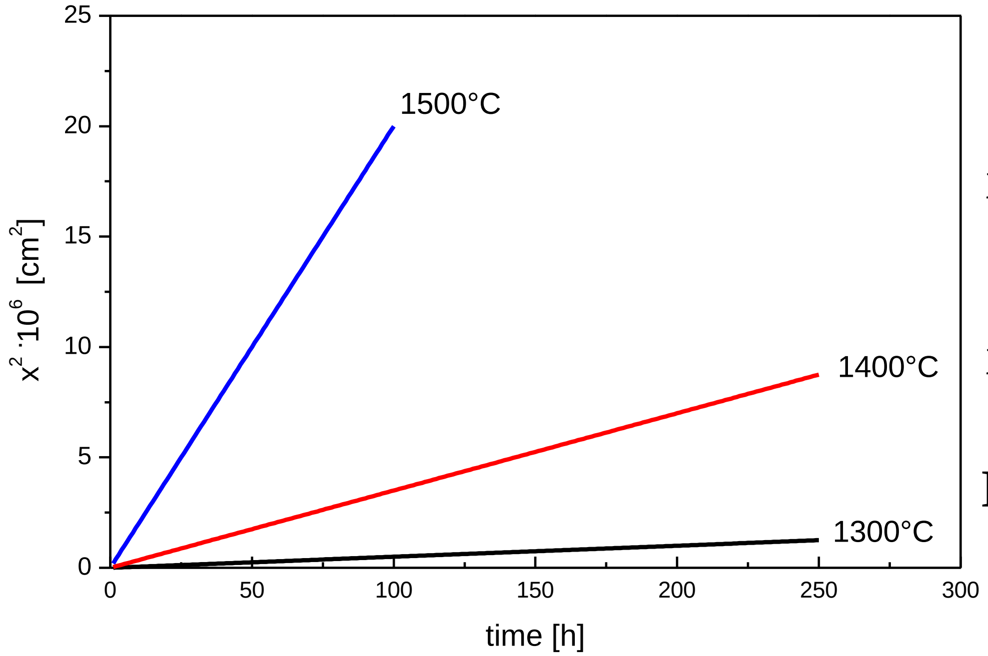
General principles

Influence of the annealing temperature

Example: $NiO(s) + Al_2O_3(s) \rightarrow NiAl_2O_4(s)$

(normal Spinel)





$$x = (k't)^{1/2}$$

$$x^2 = (k't)$$

Mit x = thickness of the product layer
t = time
k‘ = speed constant

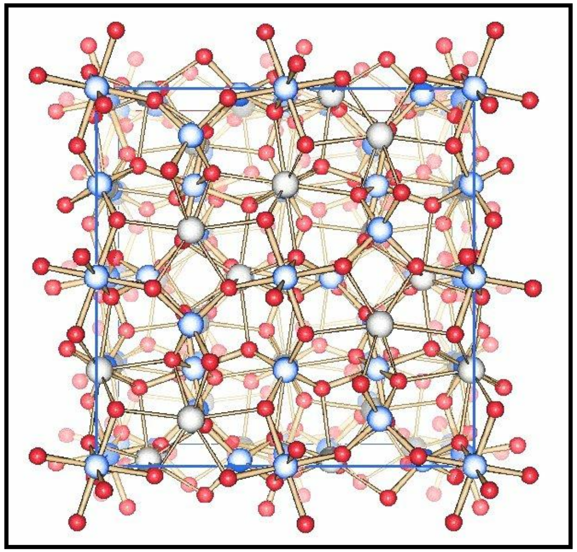
2.1.1 Fundamentals of Solid State Reactions

General principles

Influence of the ionic conductivity of the product phase

$5\ Al_2O_3 + 3\ Y_2O_3 \rightarrow 2\ Y_3Al_5O_{12}$

Product: Garnet structure

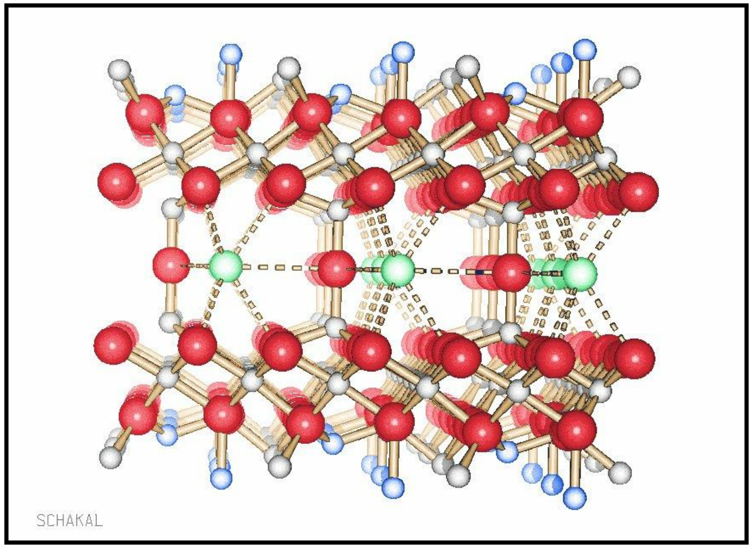


Highly cross-linked structure

Synthesis temperature 1600 - 1700 °C

$5\ Al_2O_3 + BaO + MgO \rightarrow BaMgAl_{10}O_{17}$

Product: ß-Al_2O_3 structure



Spinel block

Conduction layer

Spinel block

Layered structure with conduction planes

Synthesis temperature 1200 – 1300 °C

2.1.1 Fundamentals of Solid State Reactions

Basic process steps

1. Processing of the starting materials
    - Purification
    - Determination of the metal content
2. Homogenisation of the precursor blend (milling)
3. Sintering
4. Post-treatment
    - Washing
    - Milling
    - Eventually tempering: Removal of surface defects
    - Separation
    - Binning

2.1.1 Fundamentals of Solid State Reactions

Basic process steps

1. **Starting material processing – Purification**

Example: Removal of transition metal ions from alkaline earth carbonates $MeCO_3$ (Me = Mg, Ca, Sr, Ba)

- **Dissolution of $Me(NO_3)_2$ or $Me(CH_3COO)_2$ in water**
- **Addition of a $(NH_4)_2S$ solution ⇒ Precipitation of MnS, ZnS, Fe_2S_3, Co_2S_3, etc.**
- **Separation of the precipitate by filtration**
- **Addition of a $(NH_4)_2CO_3$ solution to the filtrate ⇒ Precipitation of**

$$MgCO_3 \xrightarrow{600 – 900\ °C} MgO \qquad CaCO_3 \xrightarrow{1000 – 1200\ °C} CaO \qquad SrCO_3 \xrightarrow{1100 – 1200\ °C} SrO \qquad BaCO_3 \xrightarrow{1000 – 1450\ °C} BaO$$

2.1.1 Fundamentals of Solid State Reactions

Basic process steps

1. Starting material processing – Determination of the metal content

Many starting materials, in particular those being of an alkaline character, react (at least superficially) with H_2O or CO_2, e.g.

$MgO + H_2O \rightarrow Mg(OH)_2$

$La_2O_3 + CO_2 \rightarrow La_2O_2CO_3$

⇒ Effective reduction of the metal content

⇒ Determination of the effective content necessary (by gravimetric analysis)

1. Weigh in

2. Glowing at the intended reaction temperature, e.g. at 1200 °C

3. Weigh out

$F_{\text{Educt}} = m_{\text{weigh-in}}/m_{\text{weigh-out}}$

2.1.1 Fundamentals of Solid State Reactions

Basic process steps

2. Homogenisation of the precursor blend (milling)

- in a agate or porcelain mortar by using a pestle
- in a (planetary) ball mill filled with grinding media (balls)
- in polyethylene flask filled with milling media on a roller bench

  milling media ceramic: Agate, Al_2O_3, BN, SiC, ZrO_2, Si_3N_4, polymer beads

Further „tricks“

- Addition of an organic solvent, e.g. acetone or ethanol to form a paste, whereby the solvent slowly evaporates during milling
- Application of ultra sound to destroy agglomerates
- Precursor methods → chapter 2.1.3

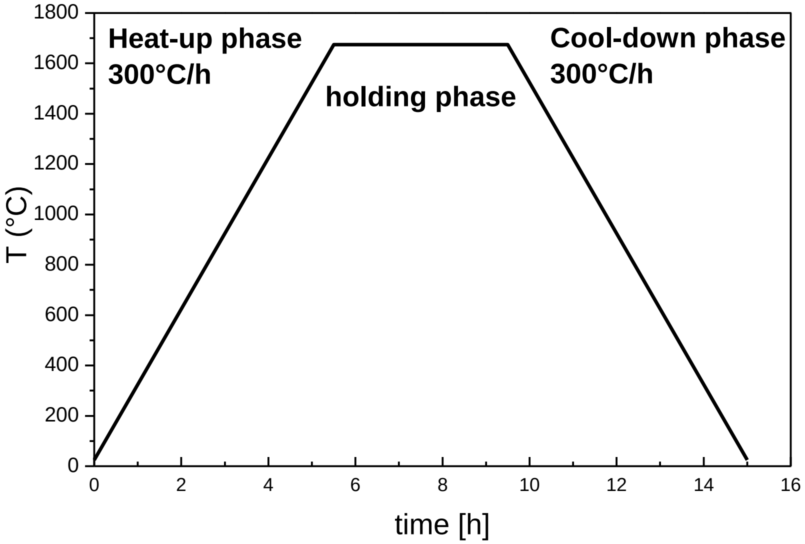
2.1.1 Fundamentals of Solid State Reactions

Basic process steps

3. Sintering

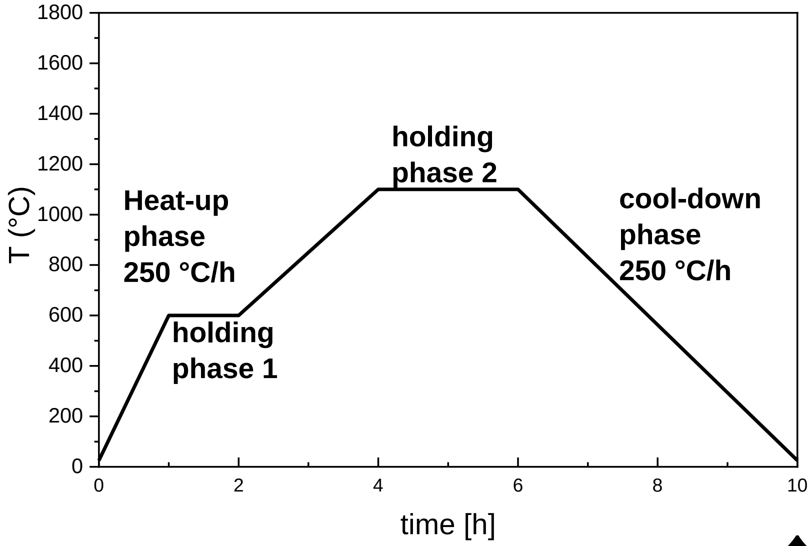
Temperature profile with solely inert precursors

$5\ Al_2O_3 + 3\ Y_2O_3 \rightarrow 2\ Y_3Al_5O_{12}$



Temperature profile for precursor blends comprising at least one reactive material

$Y_2O_3 + 2\ H_3BO_3 \rightarrow 2\ YBO_3 + 3\ H_2O$



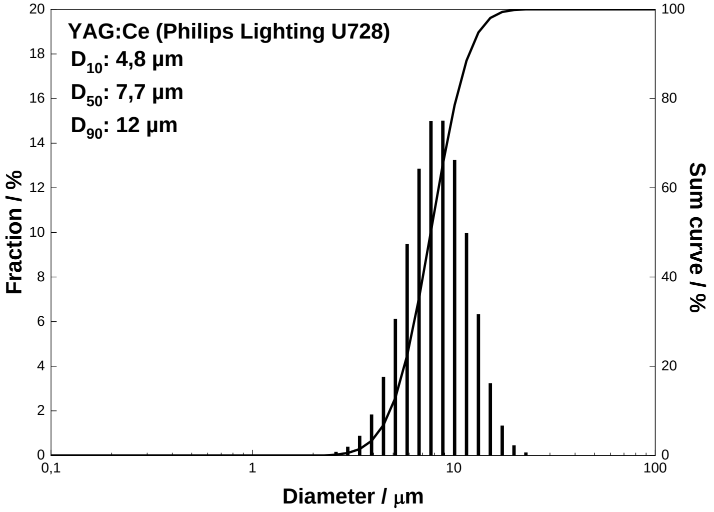
T = 150 °C: $H_3BO_3 \rightarrow HBO_2 + H_2O\uparrow$

T = 500 °C: $2\ HBO_2 \rightarrow B_2O_3 + H_2O\uparrow$

2.1.1 Fundamentals of Solid State Reactions

Basic process steps

4. Post-treatment



Washing

- Removal of flux residues (e.g. fluorides)
- Removal of excess components (e.g. B_2O_3 or P_2O_5)

Milling

- Crushing of the sinter cake
- Optimisation of average particle size distribution (PSD) due to deagglomeration

Separation

- Sieving to remove larger particles and agglomerates
- Sedimentation to remove „dust“
- Centrifugation for the isolation of nanoscale particles

Binning

2.1.2 Precursor Methods

Co-precipitation

- a) Dissolution of metal (transition metals, lanthanides) salts (nitrates) in water
- b) Precipitation as oxalates by addition of sodium oxalate
- c) Conversion into oxides at T = 1000 – 1600 °C

1. Example: Synthesis of Zink Iron spinel

$$Zn^{2+} + 2\,Fe^{3+} + 4\,C_2O_4^{2-} \rightarrow Fe_2(C_2O_4)_3 + ZnC_2O_4$$

$$Fe_2(C_2O_4)_3 + ZnC_2O_4 \xrightarrow{1000\ °C} ZnFe_2O_4 + 4\,CO_2 + 4\,CO$$

2. Example: Synthesis of red emit. phosphor Y_2O_3:Eu

$$2(1-x)\,Y^{3+} + 2x\,Eu^{3+} + 3\,C_2O_4^{2-} \rightarrow (Y_{1-x,}Eu_x)_2(C_2O_4)_3$$

$$(Y_{1-x,}Eu_x)_2(C_2O_4)_3 \xrightarrow{1600\ °C} (Y_{1-x,}Eu_x)_2O_3 + 3\,CO_2 + 3\,CO$$

$x = 0.03 – 0.05$

Compound	k_L [mol^{n}l^{-n}]
FeC_2O_4	$3.2 \cdot 10^{-7}$
ZnC_2O_4	$2.7 \cdot 10^{-8}$
$Y_2(C_2O_4)_3$	$5.3 \cdot 10^{-29}$
$Eu_2(C_2O_4)_3$	$5.0 \cdot 10^{-28}$

2.1.2 Precursor Methods

Co-precipitation: Methods to obtain precipitation reagant

Precipitation of sulphides

Hydrolyis of thio acetamide $CH_3\text{-}CS\text{-}NH_2 + 2\ H_2O \xrightarrow{RT} H_2S + CH_3\text{-}COO^- + NH_4^+$

Precipitation of hydroxides/oxides

Hydrolysis of urea $H_2N\text{-}CO\text{-}NH_2 + H_2O \xrightarrow{80 – 90\ °C} 2\ NH_3 + CO_2$

Hydrolysis of Potassium cyanate $HOCN + 2\ H_2O \rightarrow NH_3 + CO_2$

Hydrolysis of Urotropin $N_4(CH_2)_6 + 6\ H_2O \rightarrow 4\ NH_3 + 6\ CH_2O$

(no formation of carbonates)

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

Precipitation of phosphates

Hydrolysis of trimethyl phosphate $(CH_3O)_3P{=}O + 3\ H_2O \rightarrow 3\ CH_3OH + PO_4^{3-} + 3\ H^+$

Precipitation of sulphates

Hydrolysis of dimethyl sulphate $(CH_3O)_2SO_2 + 2\ H_2O \rightarrow 2\ CH_3OH + SO_4^{2-} + 2\ H^+$

2.1.2 Precursor Methods

Further precursor methods

Precipitation of thermally degradable binary or ternary metal salts:

1st Example: Synthesis of Nickel Iron spinel

$$3\ Ni^{2+} + 6\ Fe^{3+} + 4\ OH^- + 17\ CH_3COO^- + 12\ C_5H_5N \rightarrow Ni_3Fe_6(CH_3COO)_{17}O_3(OH)\cdot 12C_5H_5N + 3\ H^+$$

$$Ni_3Fe_6(CH_3COO)_{17}O_3(OH)\cdot 12C_5H_5N + 109\ O_2 \xrightarrow{1000\ °C} 3\ NiFe_2O_4 + 94\ CO_2 + 56\ H_2O + 6\ N_2$$

2nd Example: Synthesis of ortho-borates

$$H_2N\text{-}CO\text{-}NH_2 + H_2O \rightarrow 2\ NH_3 + CO_2$$

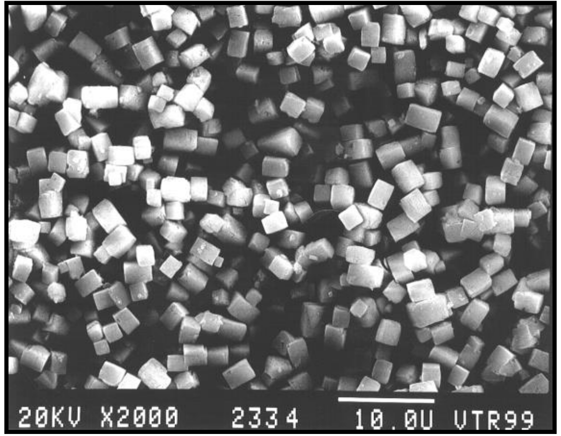
$$Ln^{3+} + H_3BO_3 + 3\ OH^- + CO_2 \rightarrow LnB(OH)_4CO_3 + H_2O$$

(Moydite, orthorhombic)

$$LnB(OH)_4CO_3 \xrightarrow{1100\ °C} LnBO_3 + 2\ H_2O + CO_2$$

(Ln = Sc, Y, La - Lu)

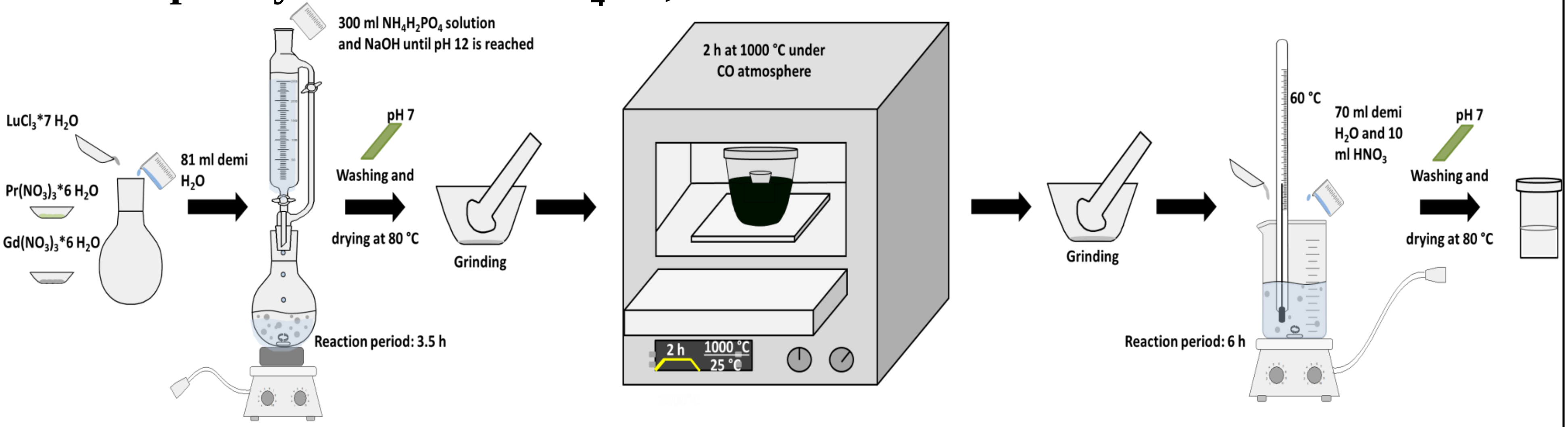
$LnB(OH)_4CO_3$ Precursor



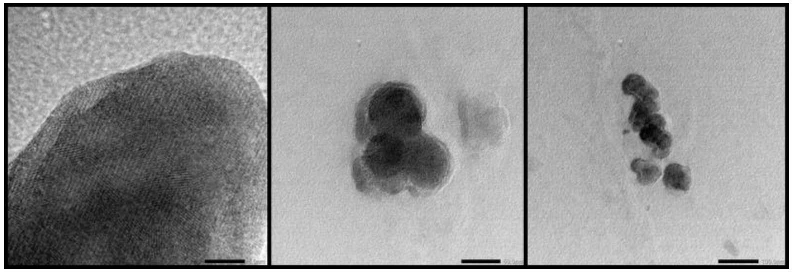
2.1.2 Precursor Methods

Further precursor methods

3rd Example: Synthesis of $LuPO_4$:Pr,Eu

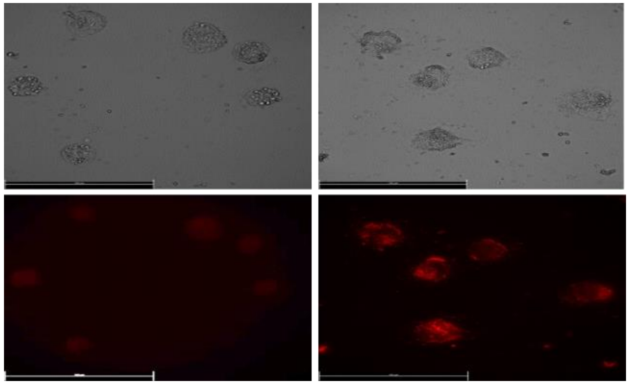


$LuPO_4$:Pr,Eu Nanoparticles



Images by
Jan Kappelhoff
FH münster

$LuPO_4$:Pr,Eu NPs in cell line



2.1.2 Precursor Methods

Further precursor methods

Decomposition of redox active precursor:

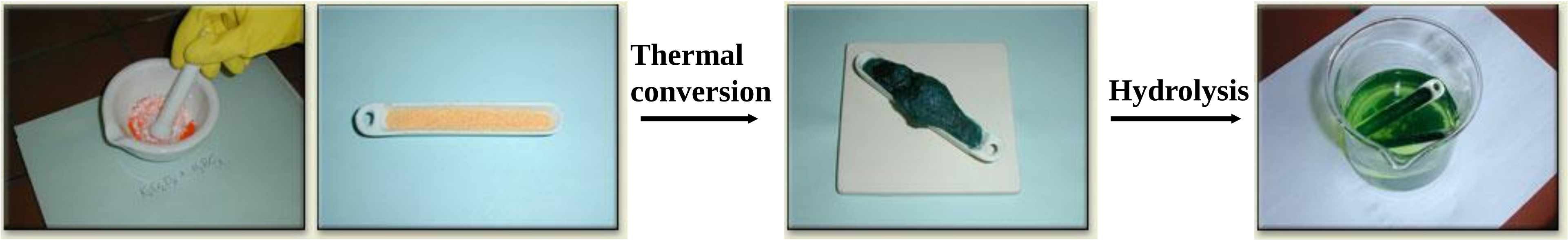
Synthesis of Cr_2O_3 pigment (Viridian)

a) $(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4\ H_2O$ (→ artificial volcano)

b) $2\ K_2Cr_2O_7 + 4\ H_3BO_3 \rightarrow 4\ CrBO_3 + 2\ K_2O + 6\ H_2O + 3\ O_2$

$2\ CrBO_3 + 3\ H_2O \rightarrow 2\ H_3BO_3 + Cr(OH)_3$ (nanoscale particles)

$2\ Cr(OH)_3 \rightarrow Cr_2O_3 + 3\ H_2O$



2.1.3 Technical Equipment

Container

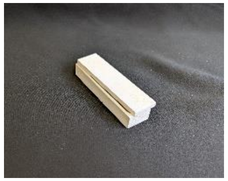
Shape: Boats, Foils, Crucibles

Usage: open Reaction with gases, e.g. CO
covered Prevention of evaporation of volatile compounds, e.g. B_2O_3

Cont. material: Selection according to chemical reactivity toward the reactants

a) Ceramics:
Al_2O_3 (Corundum, “Degussit”)
SiO_2 (Quartz)
ZrO_2 (Zircon)
→ Low stability towards (earth) alkaline metal oxides

SiC (Silicon carbide) → high surface roughness
BN (Boron nitride) → use under reducing conditions



b) Noble Metals:

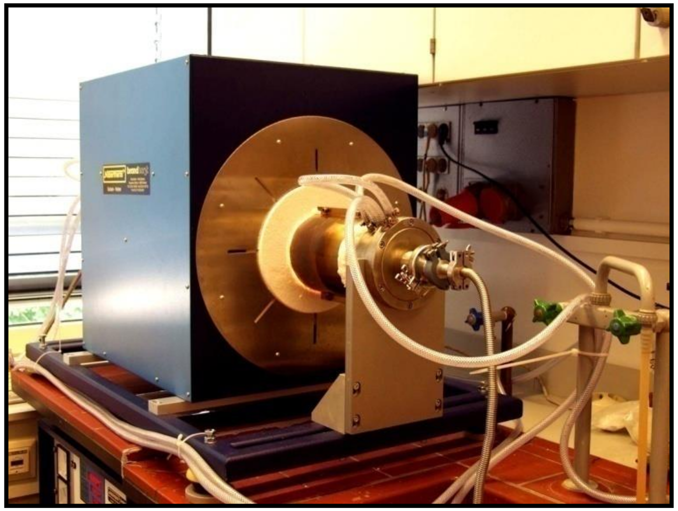
Ni T_m = 1453 °C
Pt T_m = 1772 °C
Ir T_m = 2430 °C
Mo T_m = 2620 °C
W T_m = 3410 °C → synthesis of nitrides and carbides
Nb T_m = 2469 °C
Ta T_m = 2996 °C
Re T_m = 3186 °C

2.1.3 Technical Equipment

Furnaces - laboratory

Chamber furnaces

- „MgO“ chamber furnaces up to 1750 °C
- Graphite furnaces up to 3000 °C (reductive atmosphere)
- Atmosphere is difficult to control



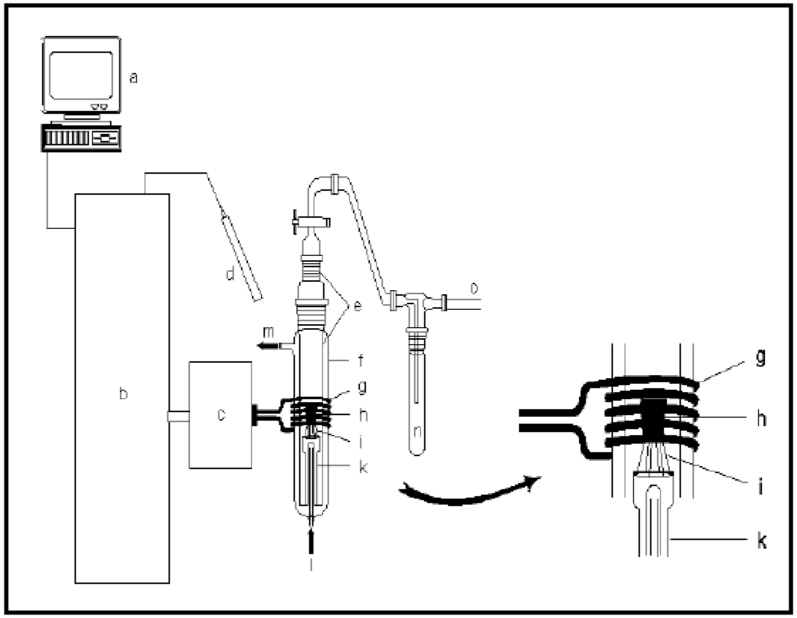
Tube furnaces

- Quartz tubes up to 1200 °C
- Corundum tubes up to 1800 °C
- Multi zone operation
- Atmosphere can be easily controlled

  N_2, N_2/H_2, Ar, H_2S, NH_3, CO, CO_2, ……

2.1.3 Technical Equipment

Furnaces - laboratory



High frequency furnaces (radio frequency RF)

- **50 – 500 kHz**
- **Up to 2000 °C**
- **Extremaly fast heating rate is possible**
- **W- or C-crucible**
- **Intert gas atmosphere is required**

  ⇒ N_2, Ar

Application: Synthesis of high-melting nitrides based on Me (Me = Ca, Sr, Ba), Ln (Ln = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Yb) and $Si(NH)_2$

- **$BaSi_7N_{10}$**	*Chem. Eur. J. 3 (1997) 249*
- **$MeYb[Si_4N_7]$**	*Angew. Chem. 108 (1996) 2115*
- **$Ln_2[Si_4N_6C]$**	*J. Mater. Chem. 2001*
- **$Ba_2Nd_7[Si_{11}N_{23}]$**	*Angew. Chem. 109 (1997) 2765*

2.1.3 Technical Equipment

Furnaces – Industrial production

High pressure furnaces (up to several 1000 bar)

- Hot isostatic presses (HIP)
- Hot uniaxial presses (HUP)
- Multi anvil presses, e.g. for diamond synthesis

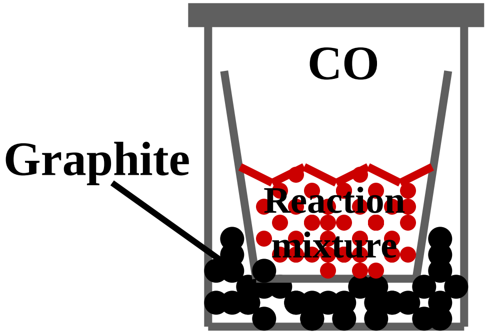
Pusher-type furnaces

- Mass production, e.g. of $BaMgAl_{10}O_{17}:Eu$ production →
- Temperature profile is controlled by the sleeping rate
- Oxidizing or reducing heating is possible

2.1.3 Technical Equipment

Synthesis atmosphere

Type	Gas	Application to the synthesis of
• Inert	N_2, Ar	Zn-, Ga-, In-compounds
• Oxidizing	air, O_2	oxides
• Reducing	N_2/H_2	Mn^{2+}, Eu^{2+}, Yb^{2+} phosphors
	$NH_3 \rightarrow N_2 + 3\ H_2$	nitrides
	H_2S	sulfides
	CO ($C + CO_2 \rightleftharpoons 2\ CO$) (Boudouard equilibrium)	Ce^{3+}, Pr^{3+}, Tb^{3+} phosphors
• Fluorinating	NH_4F, CF_4, NF_3	fluorides
• High pressure	N_2, Ar	nitrides
• Vacuum		ceramics (transparent)



2.1.4 Special Synthesis Techniques

Fluxes (e.g. for synthesis of inorganic pigments)

Fluxes increase the reaction rate by lowering the melting point or by forming reactive intermediate products

The selection of the fluxes depends on the required synthesis temperature (sublimation) and the reactivity toward the reactants and crucible's material

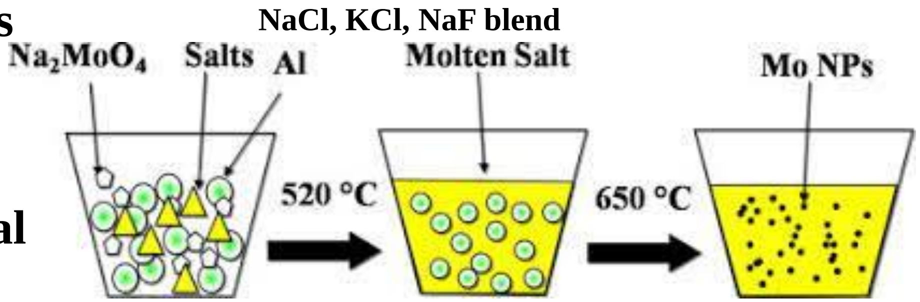
Example	Melting point [°C]	Application to the synthesis of
• NH_4Cl	340 (sublimated)	$BaSi_2O_5$:Pb
• NH_4I	551 (decomposition)	SrS:Eu
• NaCl	801	$CaWO_4$
• Li_2SO_4	845	$GdTaO_4$:Tb
• $Li_2B_4O_7$	930	$LaPO_4$:Ce,Tb
• MgF_2	1261	$BaMgAl_{10}O_{17}$:Eu
• AlF_3	1291 (sublimated)	$(Y,Lu,Gd)_3(Al,Ga)_5O_{12}$:Ce

2.1.4 Special Synthesis Techniques

Melt salt method (e.g. for crystal growth)

The composition of a suitable melt mixture must meet the following criteria

- High solubility of the crystallizing components
- High temperature coefficient of solubility
- No mixed crystal formation
- No or low reactivity toward crucible's material



Example	Melting point (eutectic) [°C]	Application to the crystallization of
BaO/B_2O_3	870	$BaZn_2Fe_{12}O_{22}$, $Y_3Fe_5O_{12}$
$BaO/B_2O_3/Bi_2O_3$	600	$NiFe_2O_4$, $ZnFe_2O_4$
$Na_2B_4O_7$	740	$NiFe_2O_4$, Fe_2O_3
PbF_2	840	$MgAl_2O_4$, Al_2O_3
PbO/B_2O_3	500	$YFeO_3$, In_2O_3
PbO/PbF_2	494	$GdAlO_3$, $Y_3Fe_5O_{12}$
$PbO/PbF_2/B_2O_3$	494	Al_2O_3, $Y_3Al_5O_{12}$
$Pb_2P_2O_7$	824	Fe_2O_3, $GdPO_4$
$Pb_2V_2O_7$	720	Fe_2TiO_5, YVO_4

2.1.4 Special Synthesis Techniques

Carbothermal reduction

Reduction of oxides by carbon (or hydrocarbons), through reactions between solid and gaseous intermediate products

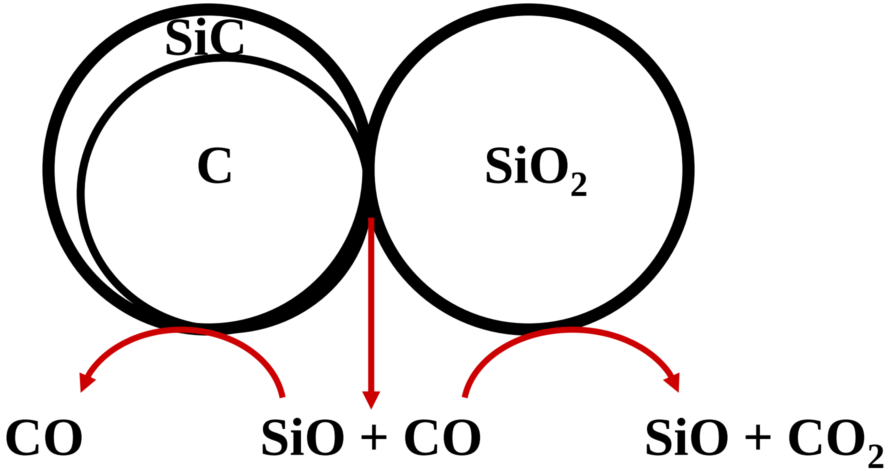
Example: Synthesis of silicon carbide

$C(s) + SiO_2(s) \rightarrow SiO(g) + CO(g)$

$SiO_2(s) + CO(g) \rightarrow SiO(g) + CO_2(g)$

$C(s) + CO_2(g) \rightarrow 2\,CO(g)$

$C(s) + SiO(g) \rightarrow SiC(s) + CO(g)$



Excess of carbon ⇒ Product contaminated with carbon

2.1.4 Special Synthesis Techniques

Carbothermal reduction

The carbothermal reduction is used for the synthesis of carbides, nitrides and borides, in which CO is a by-product and acts as a reducing agent

Reaction	Minimum reaction temperature [°C]	
$SiO_2 + 3\,C \rightarrow SiC + 2\,CO$	1500	
$TiO_2 + 3\,C \rightarrow TiC + 2\,CO$	1300	
$WO_3 + 4\,C \rightarrow WC + 3\,CO$	700	
$TiO_2 + B_2O_3 + 5\,C \rightarrow TiB_2 + 5\,CO$	1300	
$Al_2O_3 + 3\,C + N_2 \rightarrow 2\,AlN + 3\,CO$	1700	„carbothermal nitridation“
$3\,SiO_2 + 6\,C + 2\,N_2 \rightarrow Si_3N_4 + 6\,CO$	1550	
$2\,TiO_2 + 4\,C + N_2 \rightarrow 2\,TiN + 4\,CO$	1200	

2.1.4 Special Synthesis Techniques

Combustion methods

Thermit method: Use of a fuel, e.g. Al, Mg, or organic

General procedure:

Reduction of metal oxides with Mg or Al (strongly exothermic)

First example (Goldschmidt process: aluminothermic)

$3\ Fe_3O_4(s) + 8\ Al(s) \rightarrow 9\ Fe(l) + 4\ Al_2O_3(s)$

Application: Seamless welding of rails (see image)

Further examples:

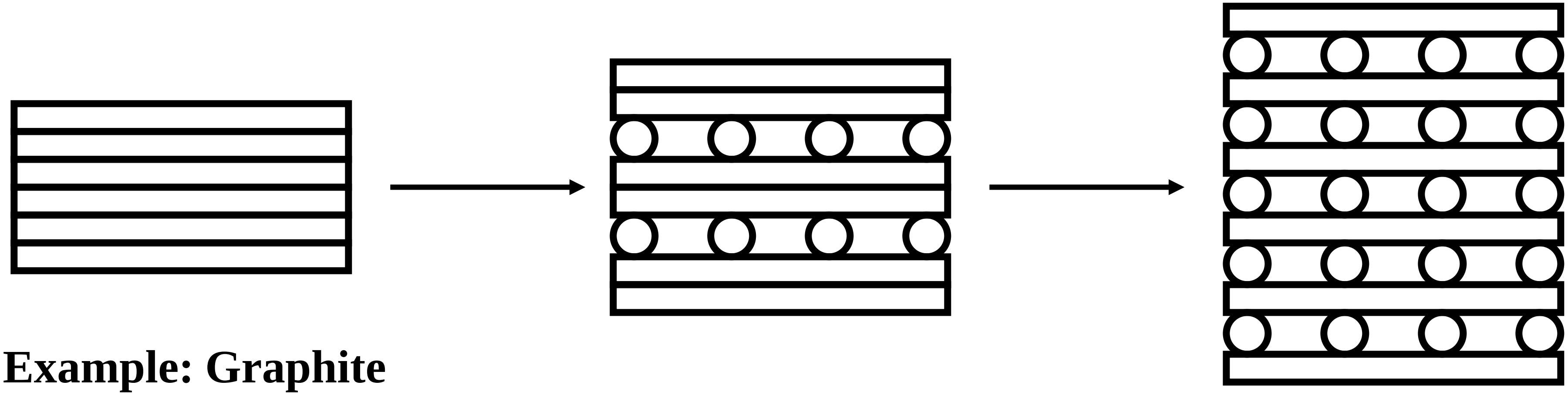
$SiO_2(s) + C(s) + Mg(s) \rightarrow SiC(s) + 2\ MgO(s)$

$TiO_2(s) + B_2O_3(s) + 5\ Mg(s) \rightarrow TiB_2(s) + 5\ MgO(s)$

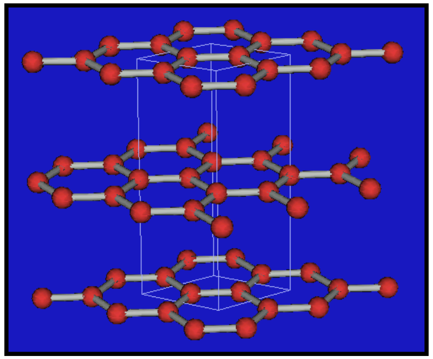
2.1.4 Special Synthesis Techniques

Intercalation reactions

Modification of an existing structure by intercalation of ions/atoms ⇒ in layered structures: graphite, TiS_2, ß-Alumina, FeOCl, $LiCoO_2$



Example: Graphite



Reversible intercalation of atoms or small molecules

+ K $\rightarrow$ C_8K (brown) $\rightarrow$ $C_{24}K$ (blue) $\rightarrow$ $C_{36}K$ $\rightarrow$ $C_{60}K$
+ Br_2 $\rightarrow$ C_8Br
+ $FeCl_3$ $\rightarrow$ Graphite/$FeCl_3$ intercalate

2.1.4 Special Synthesis Techniques

Intercalation reactions

Further examples:

- **Na in WO_3: Na + WO_3 → Na_xWO_3 (tungsten bronze)**
- **Li in TiS_2 (CdI_2-type, layer structure):**

a) Preparation with n- butyl lithium

$$x\ C_4H_9Li + TiS_2 \rightarrow Li_xTiS_2 + x/2\ C_8H_{18}$$

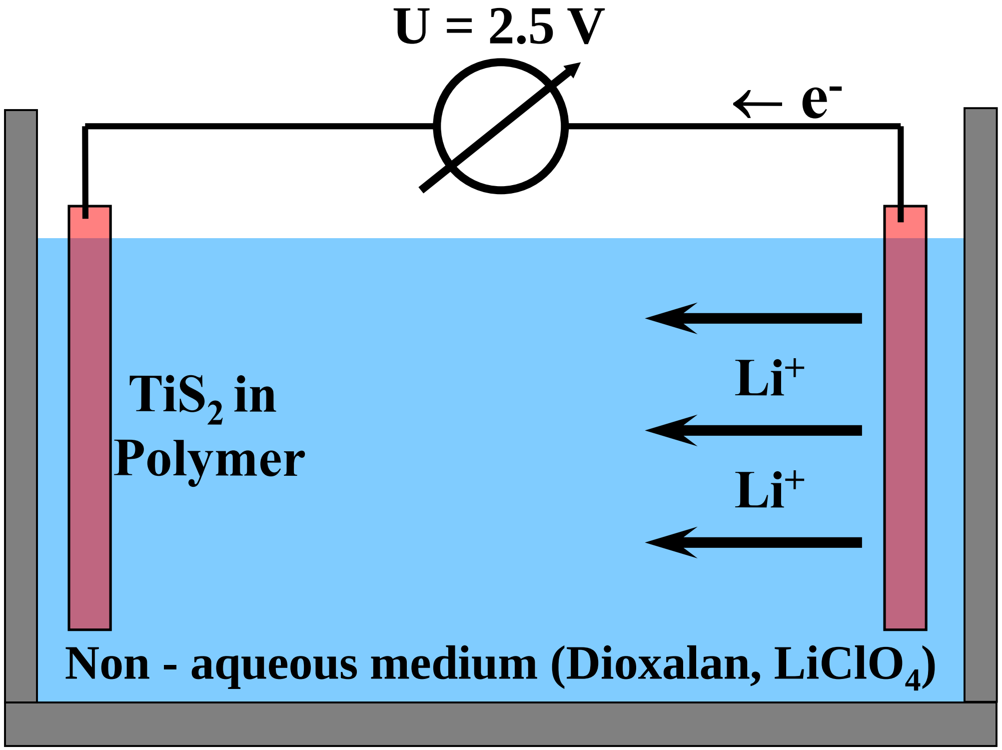
b) Electrochemical synthesis

Anode: $x\ Li \rightarrow x\ Li^+ + x\ e^-$

Cathode: $x\ Li^+ + x\ e^- + TiS_2 \rightarrow Li_xTiS_2$

⇒ **Energy storage**

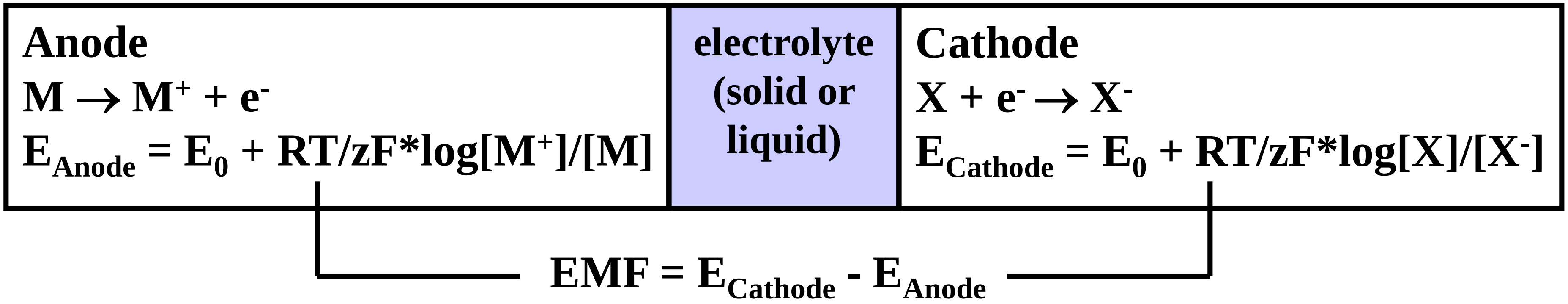
⇒ **Application: Li-TiS_2-battery**



2.1.4 Special Synthesis Techniques

Excursion: Electrochemical cells (batteries)

Schematic design of an electrochemical cell



Anode

$M \rightarrow M^+ + e^-$

$E_{Anode} = E_0 + RT/zF*\log[M^+]/[M]$

electrolyte (solid or liquid)

Cathode

$X + e^- \rightarrow X^-$

$E_{Cathode} = E_0 + RT/zF*\log[X]/[X^-]$

$EMF = E_{Cathode} - E_{Anode}$

Requirements on batteries

- High charge density and low weight
- Sufficiently high cell voltage

  $\Rightarrow$ Pb accumulator: $Pb + PbO_2 + 2\ H_2SO_4 \leftrightarrows 2\ PbSO_4 + 2\ H_2O$: EMK = 2.04 V

  $\Rightarrow$ Na-S cell: $2\ Na + 5\ S \leftrightarrows Na_2S_5$: EMF = 2.08 V, charge density: 720 $Whkg^{-1}$
- Long lifetime

  $\Rightarrow 2\ Li + I_2 \leftrightarrows 2\ LiI$: EMF = 2.8 V (e.g. heart pacemakers)

2.1.4 Special Synthesis Techniques

Excursion: Akkumulators (Li ion based)

Benefits

- High charge density
- Long lifetime
- Low weight (mobile electric devices)

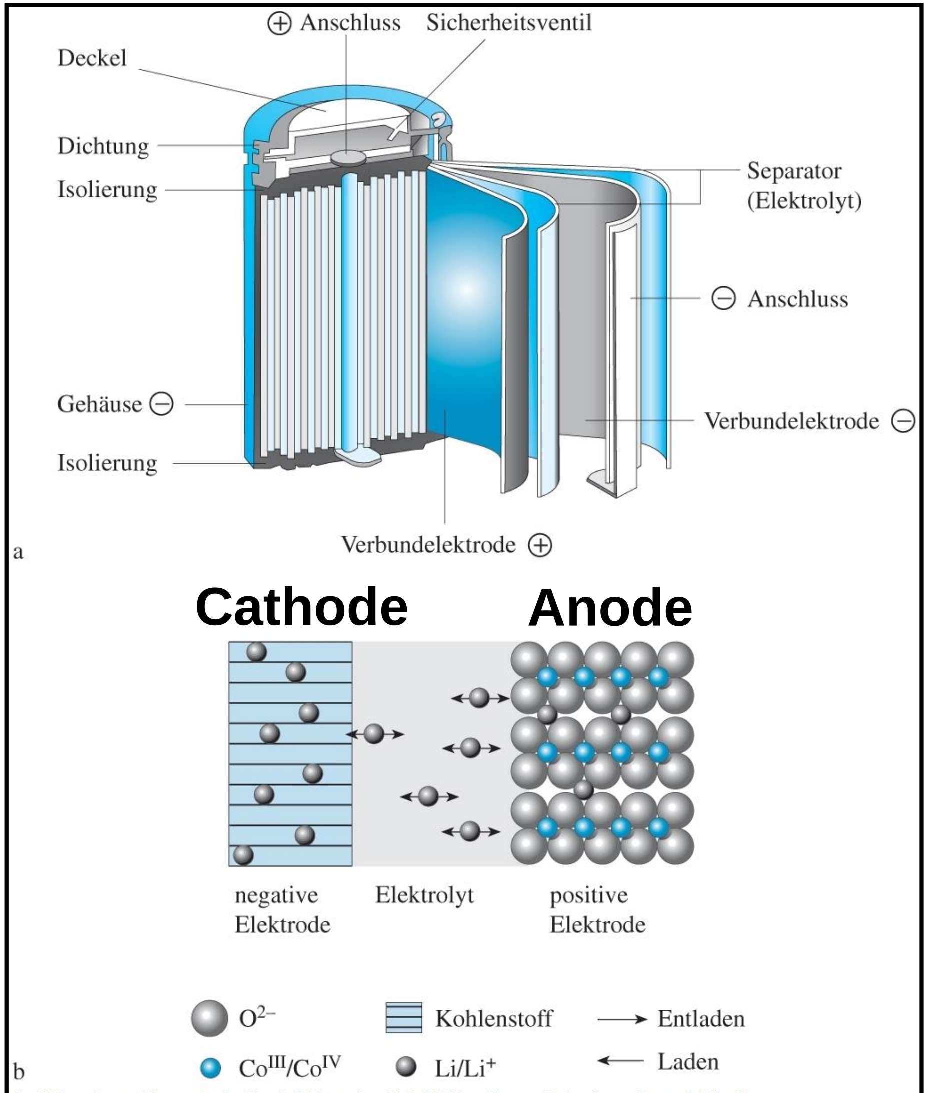
Anode reaction:

$$LiCoO_2 \underset{\textit{Discharge}}{\overset{\textit{Loading}}{\rightleftarrows}} Li_{0.35}CoO_2 + 0.65\ Li + 0.65\ e^-$$

Cathode reaction:

$$C_n + y\ Li + y\ e^- \underset{\textit{Discharge}}{\overset{\textit{Loading}}{\rightleftarrows}} C_nLi_y$$

⇒ Intercalation of Li into graphite structure



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung15-06.jpg

2. Synthesis Techniques of Material Technology

2.2. Gas-Phase Processes

2.2.1 Chemical Transport Reactions

- Basics
- Application in Purification and Preparation
- Excursion: Halogen and Halide Lamps

2.2.2 Chemical Vapor Deposition

- General Aspects
- CVD Diamond
- Deposition of Metals
- Deposition of Metal Oxides
- Deposition of III-V Semiconductors

2.2.3 Aerosol Processes

- Definition and Advantages
- Synthesis of Aerosil ®
- Gas-Particle Conversion
- Spray Pyrolysis

2.2.1 Chemical Transport Reactions

Some fundamentals

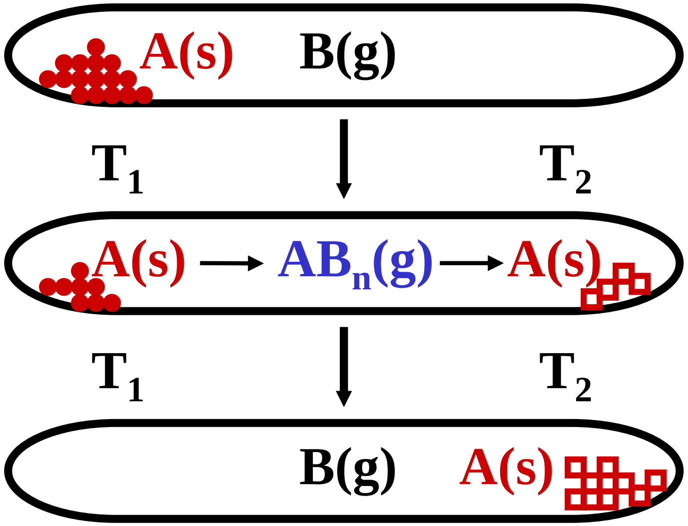
Definition

Reactions in which reversible solid/gas reactions occur, whereby a solid compound is transported via the gas phase along a temperature gradient since the chemical equilibrium is temperature dependent

Process steps

1. **Reaction between gas phase compound and a solid**
2. **Mass transport in the gas phase along a temperature gradient**
3. **Deposition of the solid from the gas phase**

$$A(s) + n\,B(g) \underset{T_2}{\overset{T_1}{\rightleftarrows}} AB_n(g)$$



2.2.1 Chemical Transport Reactions

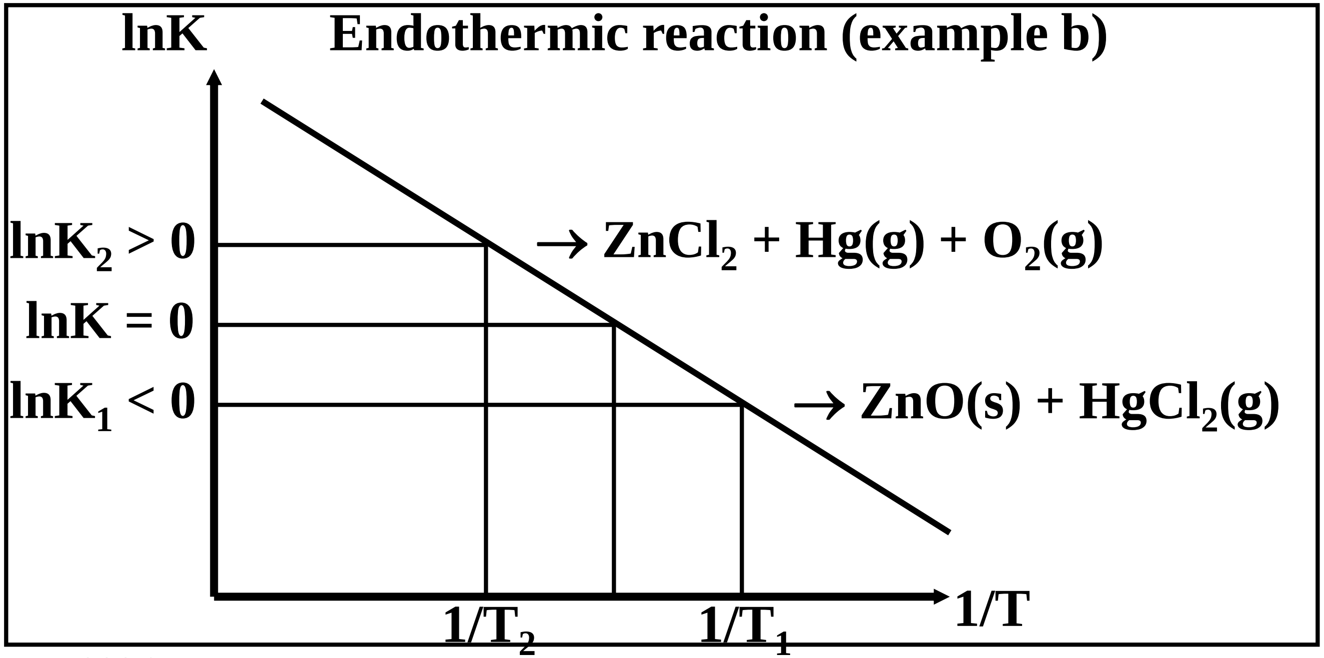
Thermodynamics

Temperature dependence of the equilibrium constant (van‘t Hoff equation):

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2}$$

Integration results in

$$\ln K = -\frac{\Delta H}{RT} + \text{const.}$$



Example

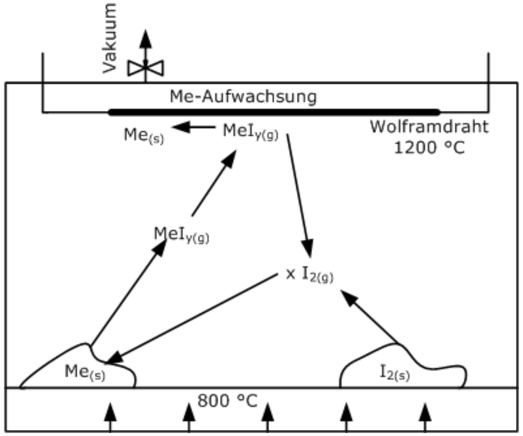
a) $3\ Fe_2O_3(s) + 6\ HCl(g) \underset{800\ °C}{\overset{1000\ °C}{\rightleftarrows}} 6\ FeCl_3(g) + 3\ H_2O(g)$ ⇒ in volcanos

b) $2\ ZnO(s) + 2\ HgCl_2(g) \underset{800\ °C}{\overset{900\ °C}{\rightleftarrows}} 2\ ZnCl_2(s) + 2\ Hg(g) + O_2(g)$ ⇒ crystal growth

c) $Ni(s) + 4\ CO(g) \underset{230\ °C}{\overset{50\ °C}{\rightleftarrows}} Ni(CO)_4(g)$ ⇒ „Mond method’’ for the purification of nickel

2.2.1 Chemical Transport Reactions

Application in purification and preparation



Source: Roland Mattern

Purification of metals (Arkel de Boer process)

$Ti + 2\ I_2 \rightleftharpoons TiI_4(g)$

$Cr + I_2 \rightleftharpoons CrI_2(g)$

also used for Zr, Hf, V, Ta, Th, Rh, Pa

Preparation by coupling transport reaction with a subsequent reaction

a) Synthesis of calcium stannate

$SnO_2 + CO \rightleftharpoons SnO + CO_2$ „transport reaction“

$SnO + 2\ CaO + CO_2 \rightarrow Ca_2SnO_4 + CO$ „subsequent reaction“

b) Synthesis of niobium silicide

$SiO_2 + H_2 \rightleftharpoons SiO + H_2O$ „transport reaction“

$3\ SiO + 8\ Nb \rightarrow Nb_5Si_3 + 3\ NbO$ „subsequent reaction“

2.2.1 Chemical Transport Reactions

Excursion: Chemical transport in light bulbs

Construction of a light bulb

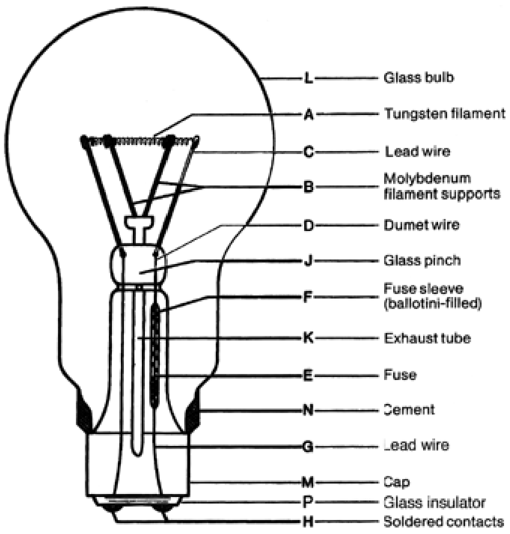
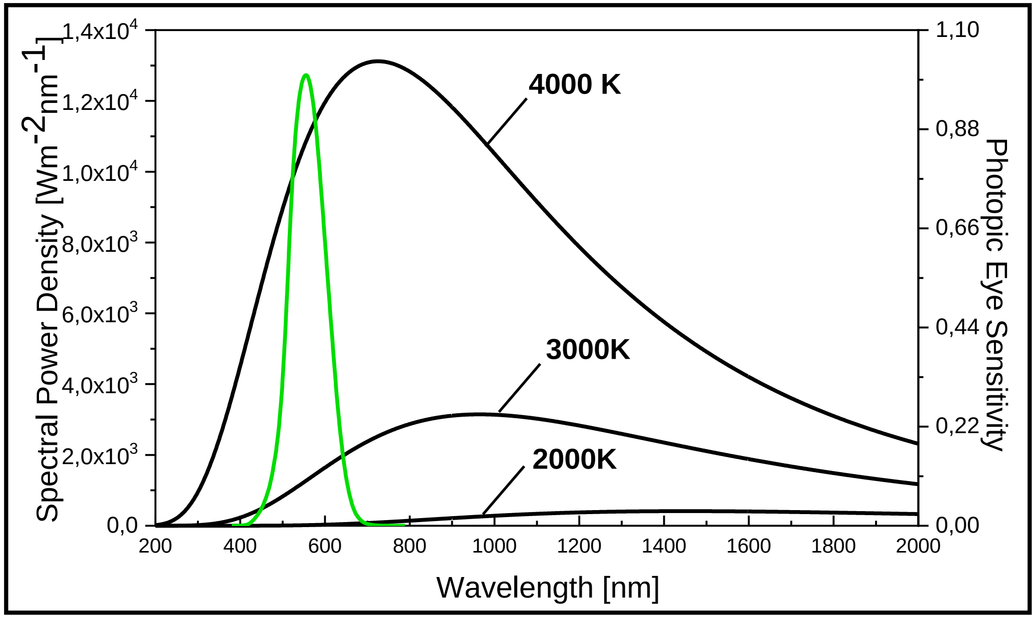


Fig. 8.1 Construction of a GLS Lamp.

Spectrum of incand. lamps ~ black body emitter



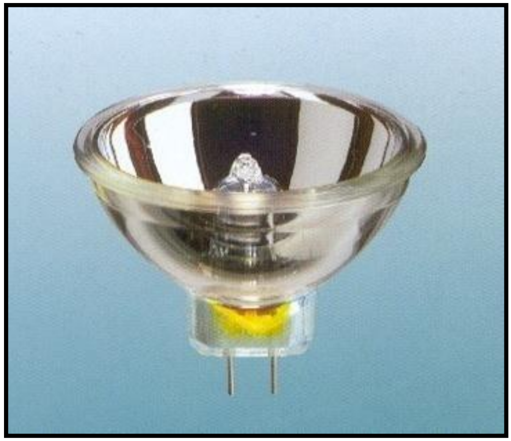
Filling of light bulbs: Ar, Kr, N_2

W-transport from the filament to the glass bulb (blackening)

Filament temperature T	visible light	rated lifetime
2600 K	7%	1000 h
3400 K	18%	10 h

2.2.1 Chemical Transport Reactions

Excursion: Chemical transport in halogen lamps



Filling:

- Inert gas: Ar, N_2
- Halide compounds: I_2, CH_3Br or HBr

Wall reaction:

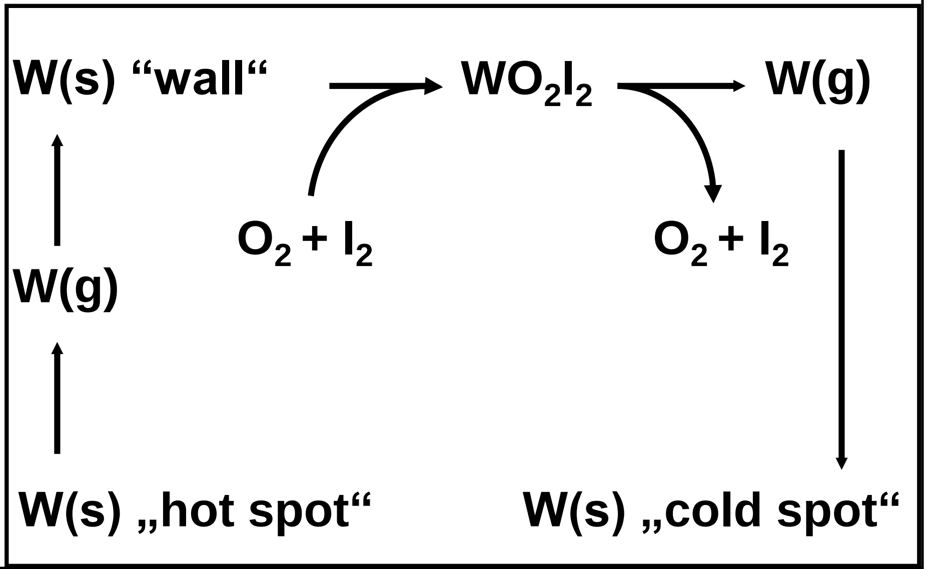
$$W + O_2 + I_2 \xrightarrow{600\ °C} WO_2I_2$$

Reaction at the W-filament (3000 °C):

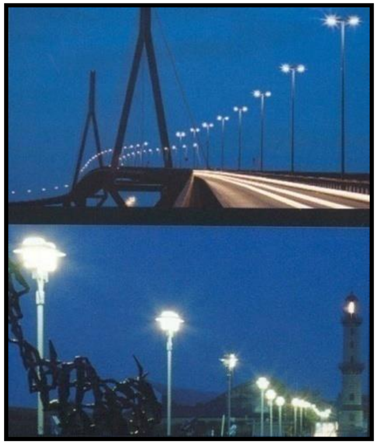
$$WO_2I_2 \rightarrow WO_2 \rightarrow WO \rightarrow W$$

Tungsten condenses at the coldest point of the W-filament (cold spot), but it evaporates from the hottest spot (hot spot)

Tungsten-halide cycle



2.2.1 Chemical Transport Reactions



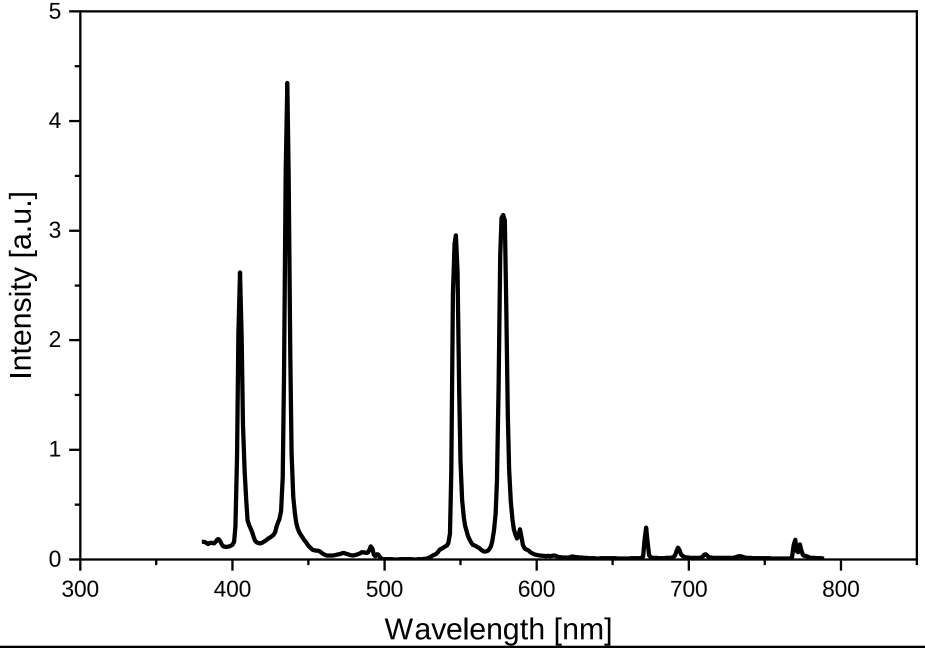
Excursion: Chemical transport in high-pressure mercury lamps

Burner: Polycrystalline Al_2O_3 or quartz (SiO_2)

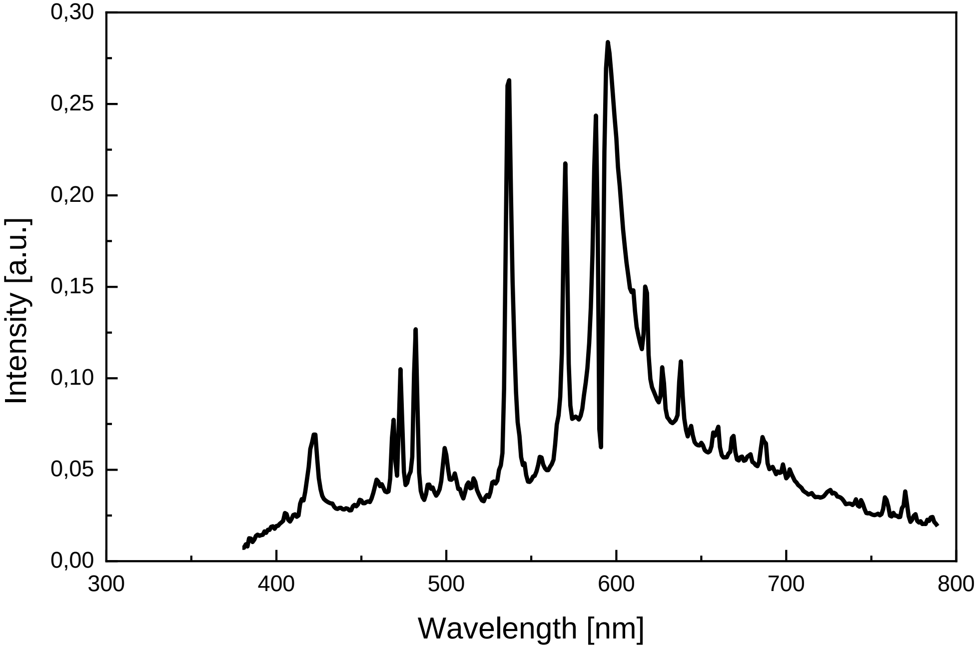
Filling:

- **Hg and Ar $\Rightarrow$ bluish-white spectrum (Hg lines)**
- **Iodide: NaI, DyI_3, TmI_3, HoI_3 $\Rightarrow$ white spectrum (Ln^{3+} lines)**

Pure Hg discharge

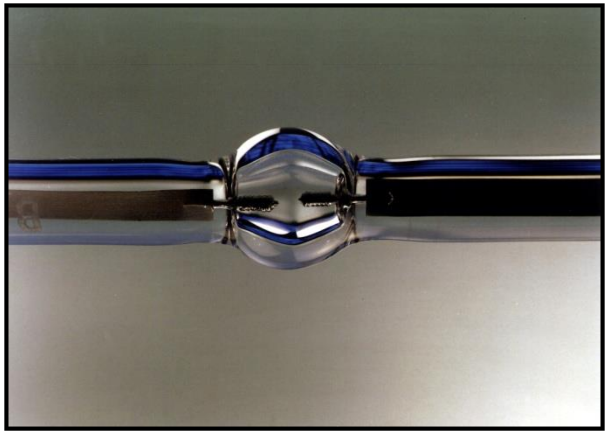


Hg + metal halides



2.2.1 Chemical Transport Reactions

Excursion: Chemical transport in high-pressure mercury lamps



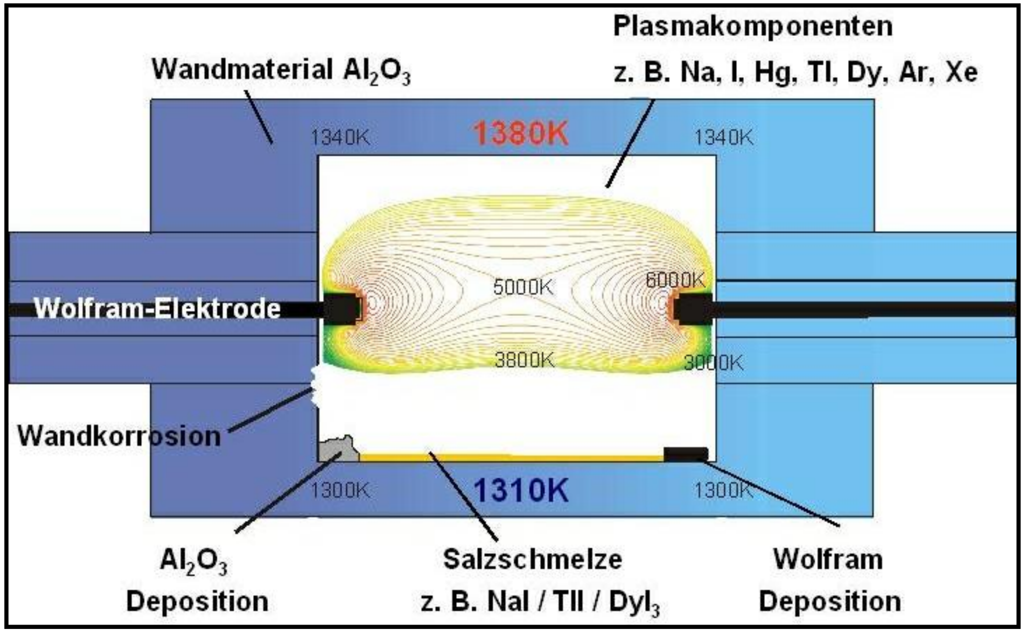
Ln^{3+} ions emit a variety of lines in the visible spectral range

$NaI + DyI_3 \rightarrow NaDyI_4$

$NaDyI_4 \rightarrow Na^+ + 4\ I^- + Dy^{3+*}$

$Dy^{3+*} \rightarrow Dy^{3+} + h\nu$ (480, 570 nm)

$Dy^{3+} + Na^+ + 4\ I^- \rightarrow NaDyI_4$



<u>Secondary reaction</u>

Formation of tungsten (oxy) halides

⇒ transport of W $\rightleftharpoons$ electrodes

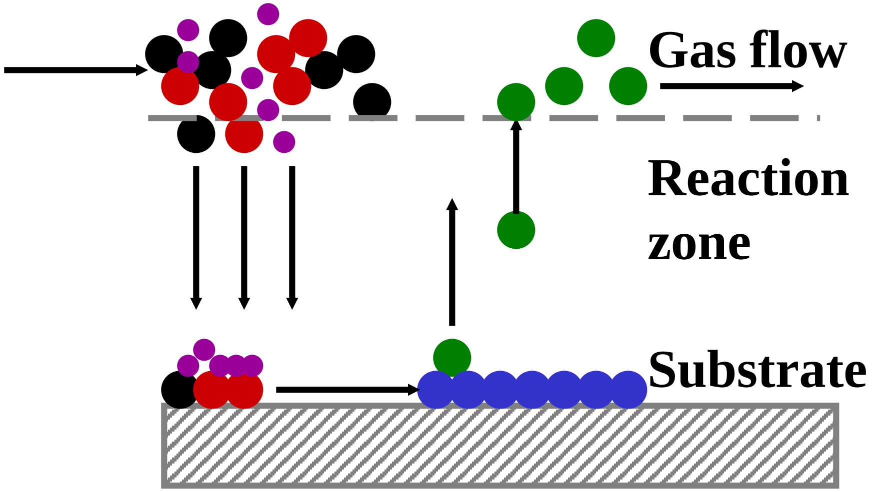
⇒ change of the electrode structure

2.2.2 Chemical Vapor Deposition

General aspects (Chemical Vapour Deposition CVD, also called MO-CVD)

Definition:

CVD is a chemical process in which one or more gaseous reactants are led into a reaction chamber, where they decompose and deposit on a heated substrate.



Applications:

- **Synthesis of high melting or inaccessible compounds, e.g. diamond or TiB_2**
- **Preparation of thin films on substrates, e.g. coating of glass with SnO_2**

Example:

$$TiCl_4(g) + 2\,BCl_3(g) + 5\,H_2(g) \rightarrow TiB_2(s) + 10\,HCl(g)$$

2.2.2 Chemical Vapor Deposition

Precursor materials

Requisite: high volatility, i.e. sufficiently high vapor pressure at temperatures below the decomposition temperature

Metal hydrides:

$SiH_4(g) \xrightarrow{h\nu} Si(s) + 2\ H_2(g)$

$GeH_4(g) \rightarrow Ge(s) + 2\ H_2(g)$

Metal halides:

$SiCl_4(g) + 2\ H_2(g) \rightarrow Si(s) + 4\ HCl(g)$

$ZnCl_2(g) + H_2S(g) \rightarrow ZnS(s) + 2\ HCl(g)$

$WF_6(g) + 3\ H_2(g) \rightarrow W(s) + 6\ HF(g)$ ⇒ **Formation of corrosive by-products**

Organometallic compounds (MOCVD):

$Si(C_2H_5)_4(g) + 14\ O_2(g) \rightarrow SiO_2(s) + 8\ CO_2(g) + 10\ H_2O(g)$

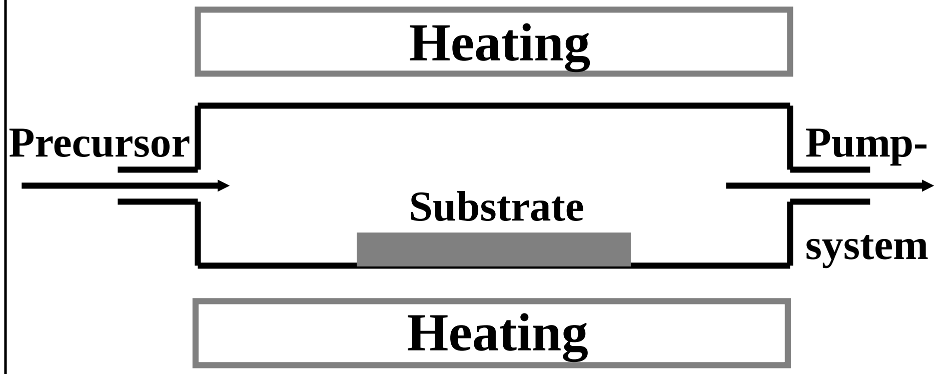
$Ga(CH_3)_3(g) + NH_3(g) \rightarrow GaN(s) + 3\ CH_4(g)$

2.2.2 Chemical Vapor Deposition

CVD eqipment

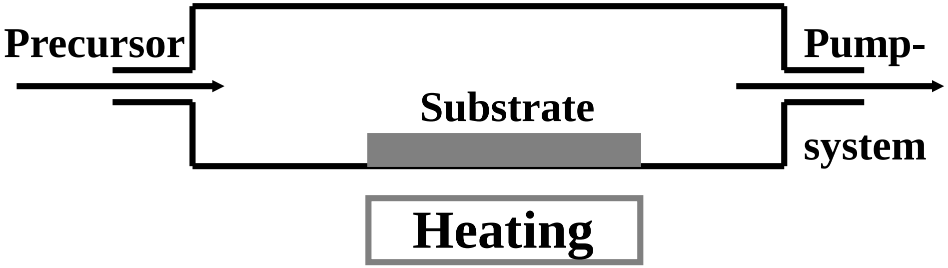
Components: precursor injection system + reactor + pumping system

„Hot-wall“ Reactor



Homogeneous substrate temperature

„Cold wall“ Reactor



Higher deposition rate, since the deposition takes place solely onto the substrate

2.2.2 Chemical Vapor Deposition

Fluidised Bed Chemical Vapour Deposition (FB-CVD)

Deposition of oxides on a powder substrate in a fluidized state (fluidized bed reactor)

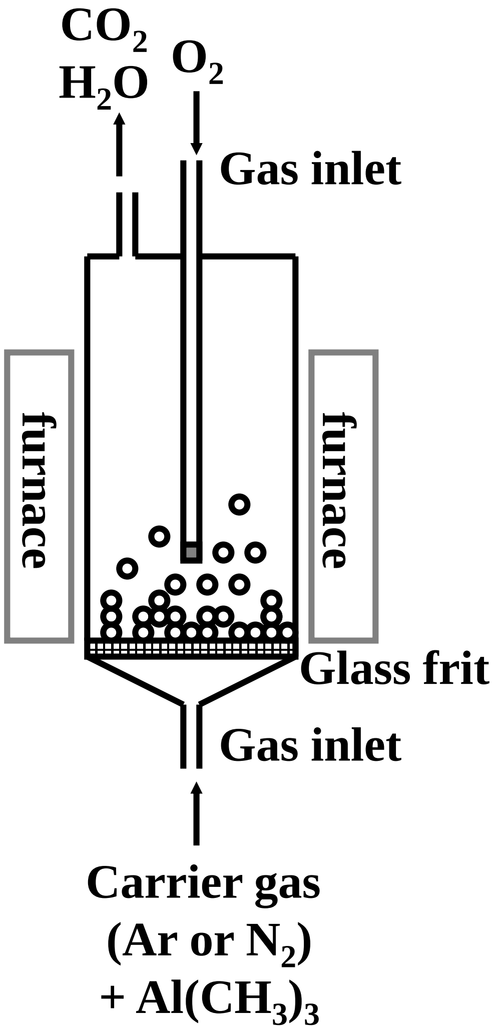
Example:

Deposition of (alpha-)Al_2O_3 on phosphor powders as a protective coating

$$2\ Al(CH_3)_3(g) + 12\ O_2(g) \rightarrow Al_2O_3(s) + 6\ CO_2(g) + 9\ H_2O(g)$$

Homogeneous coating of microparticles to increase the mechanical and chemical stability of pigments:

-	QDots	Cd(S,Se), Ga(P,As)
-	Oxides	$(Ca,Sr,Ba)_2SiO_4$:Eu, $BaMgAl_{10}O_{17}$:Eu
-	Nitrides	$Ba_2Si_5N_8$:Eu, $CaAlSiN_3$:Eu



2.2.2 Chemical Vapor Deposition

Excursion: Fluidised Bed Chemical Vapour Deposition (FB-CVD)

Coating with $Al(CH_3)_3$ or AlR_3

→ Oxidation

→ Pyrolysis

Polymerization by pyrolysis leads to brew (polymeric) by-products during the process

- **Blockage of the fritted material**
- **Graying of the (phosphor) pigment**

Reaction		Relative Rate
$2\ R_3Al + O_2$	$\rightarrow 2\ R_2AlOR$	100
$2\ R_2AlOR + O_2$	$\rightarrow 2\ RAl(OR)_2$	25
$2\ RAl(OR)_2 + O_2$	$\rightarrow 2\ Al(OR)_3$	1

Heating

$$Al(OR)_3 \rightarrow Al_2O_3 + CO_2 + H_2O$$

Heating

Secondary reaction: $R_xAl(OR)_y \xrightarrow{\Delta T} \text{Crosslinking} \xrightarrow{\Delta T} Al_4C_3$

2.2.2 Chemical Vapor Deposition

Embodiments of the CVD process

a) **Thermal CVD (see above)**

⇒ **Coating of powder particles or surfaces**

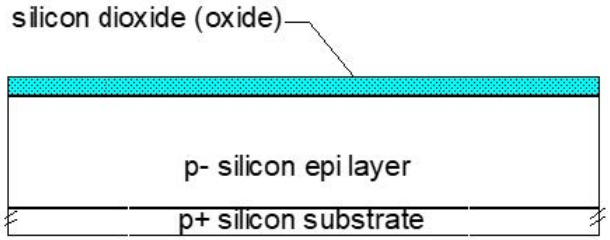
b) **Molecular Beam CVD (MBCVD)**

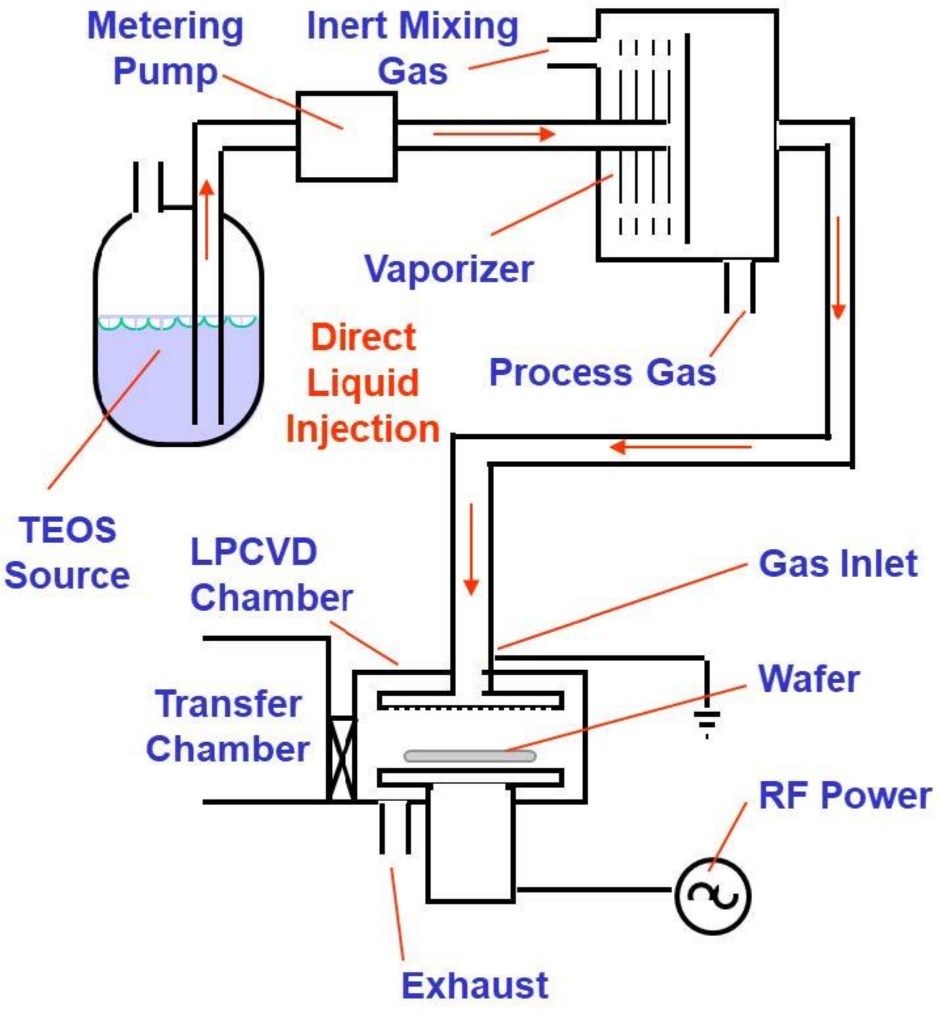
c) **Laser Assisted CVD (LACVD)**

d) **Plasma Assisted CVD (PACVD)**

⇒ **Production of diamond films**

Epitaxy ⇒ Deposition of single crystalline films





* High proportion of the total product use

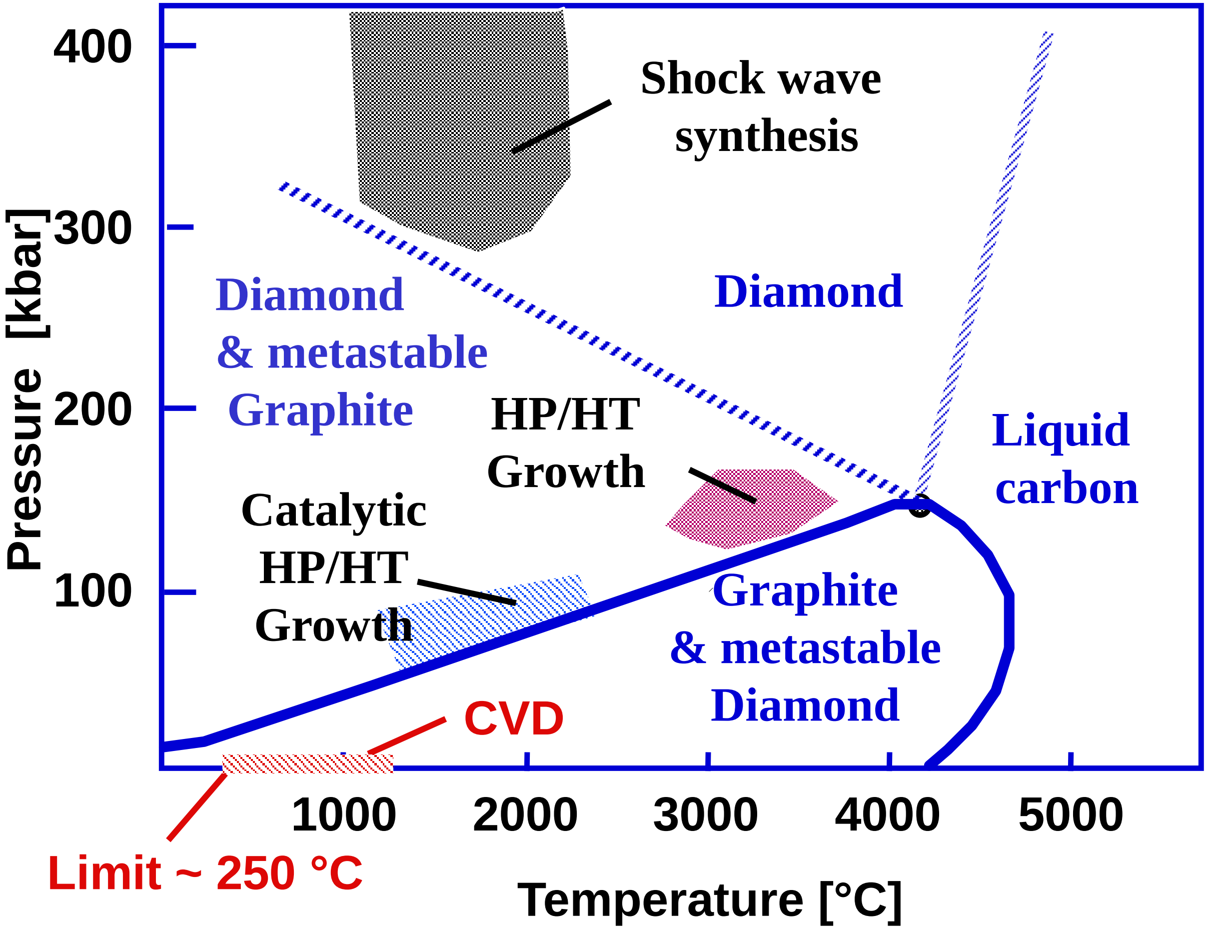
2.2.2 Chemical Vapor Deposition

Plasma Assisted CVD of diamond layers

Properties of diamond:

- sp^3-hybridized C-atoms
- C-C distance = 155 pm
- ν(C-C) = 1332 cm^{-1}
- Large optical band gap E_g = 5.4 eV
- Extreme hardness
- Low compressiblitiy $8.3 \cdot 10^{-13}$ m^2N^{-1}
- High speed of sound 18.2 kms^{-1}
- High thermal conductivity $2 \cdot 10^3$ $Wm^{-1}K^{-1}$

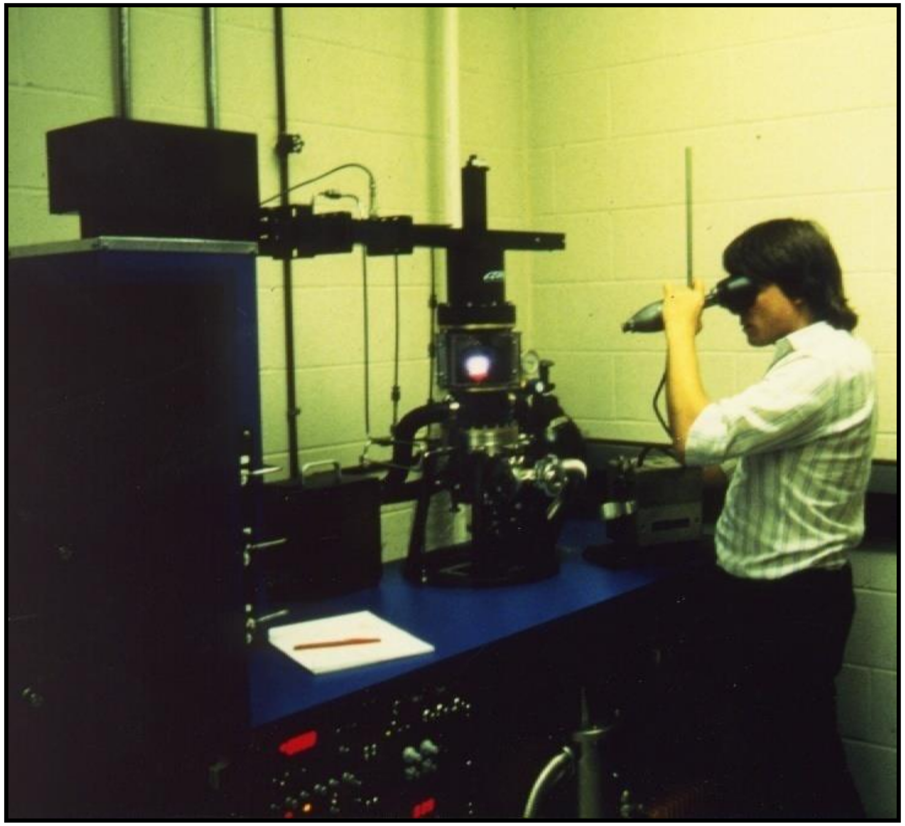
T-p phase diagram of elemental carbon

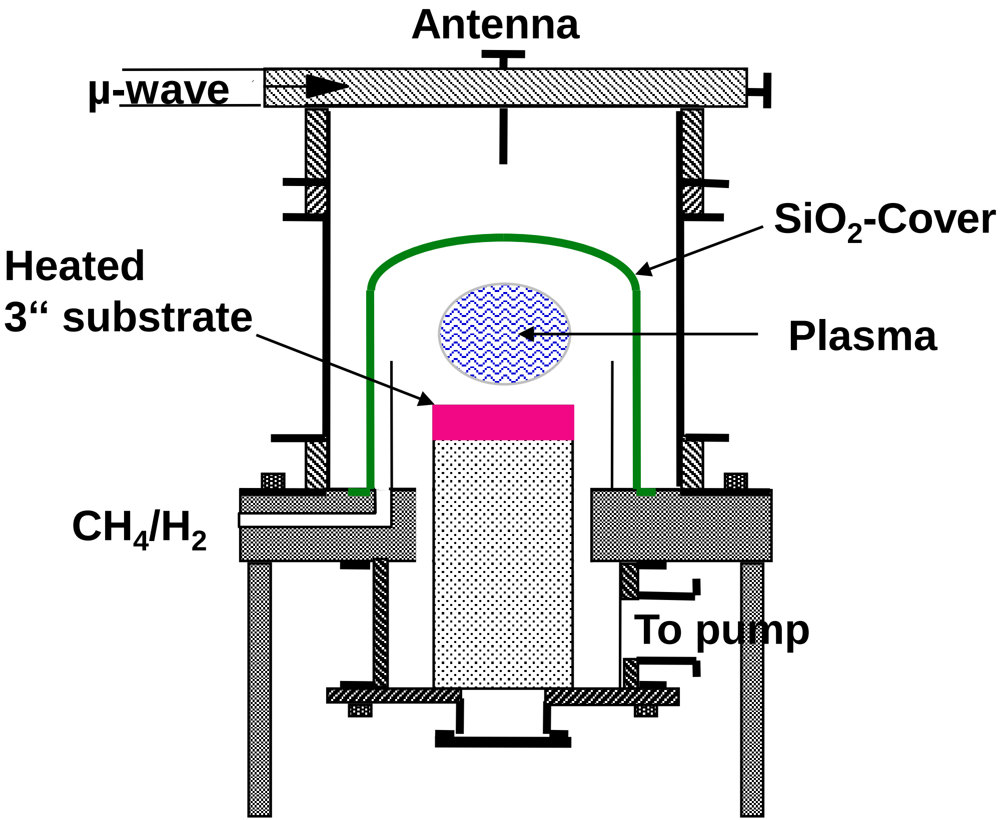


2.2.2 Chemical Vapor Deposition

Plasma Assisted CVD of diamond layers

a) Energy source: Microwaves



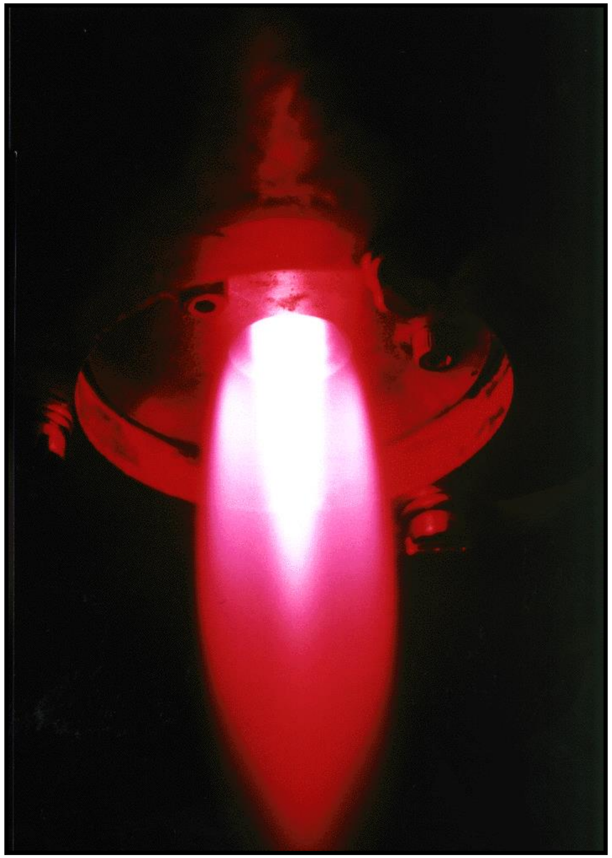


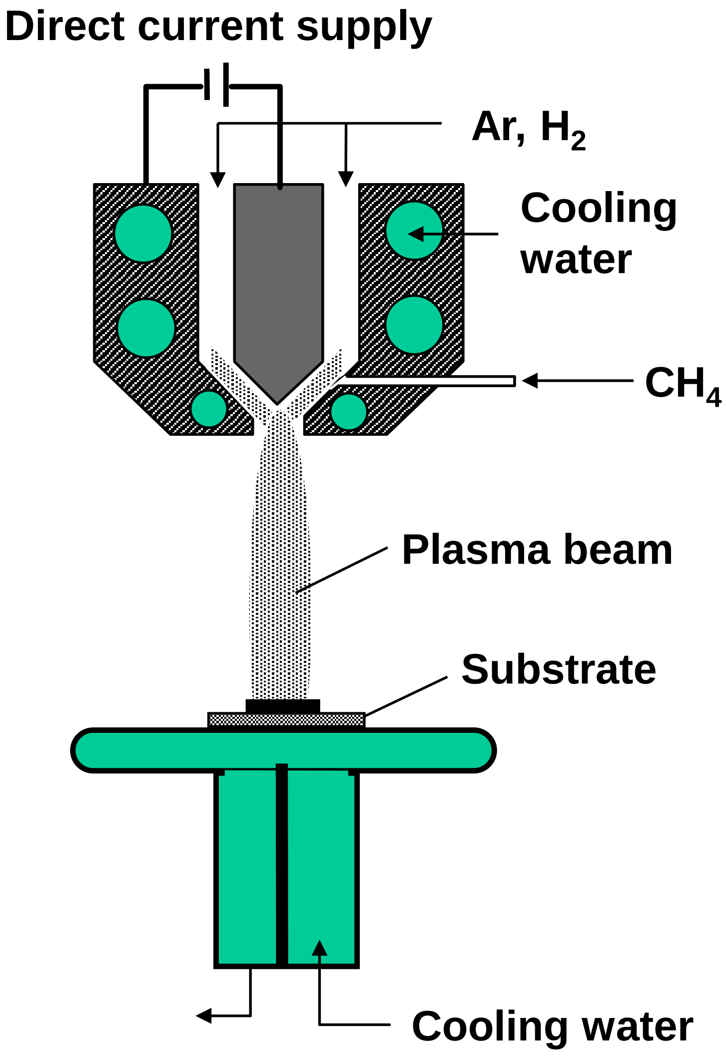
Peter K. Bachmann at Philips Research Aachen

2.2.2 Chemical Vapor Deposition

Plasma Assisted CVD of diamond layers

b) Energy source: Direct-current arc discharge

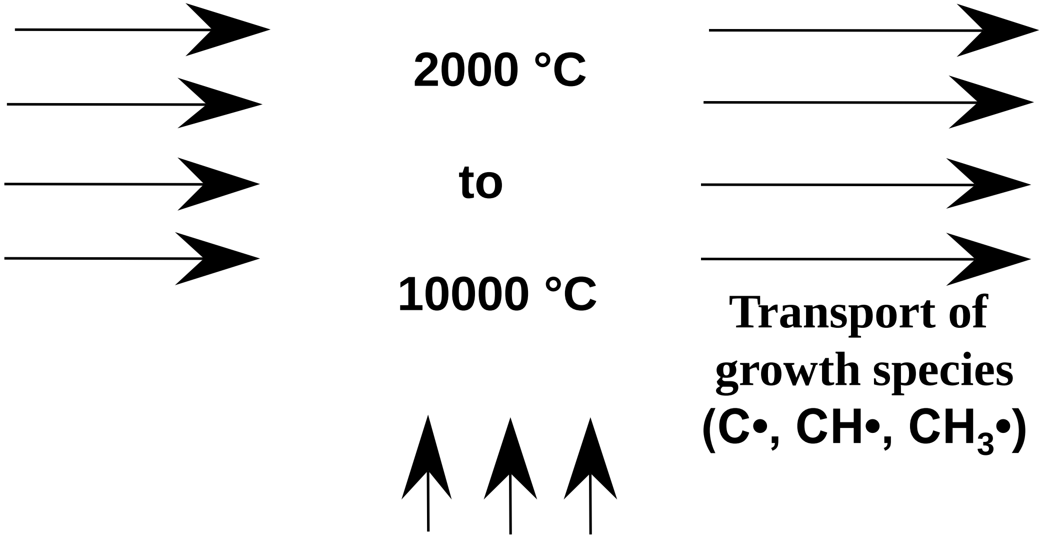




Lit.: P.K. Bachmann, U. Linz, Spektrum der Wissenschaft 9 (1992) 30

2.2.2 Chemical Vapor Deposition

Plasma Assisted CVD of diamond layers - Fundamental principle



Gas supply

Precursor
CH_4, H_2, C_2H_2
Carrier gas
Ar
Doping gas
NH_3, BH_3

Excitation area

2000 °C
to
10000 °C

Transport of growth species
(C•, CH•, CH_3•)

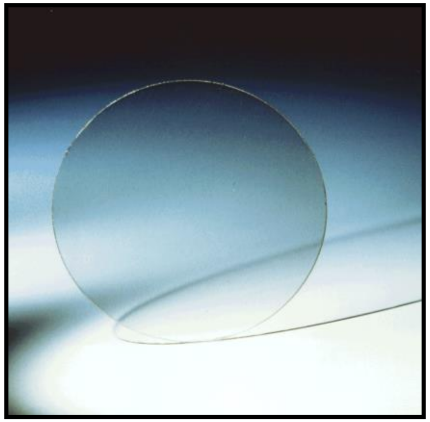
Deposition area

500 °C
to
1200 °C

Metals, glass, semiconductor

Energy source

Microwave
Radio waves
Arc discharges
Flames

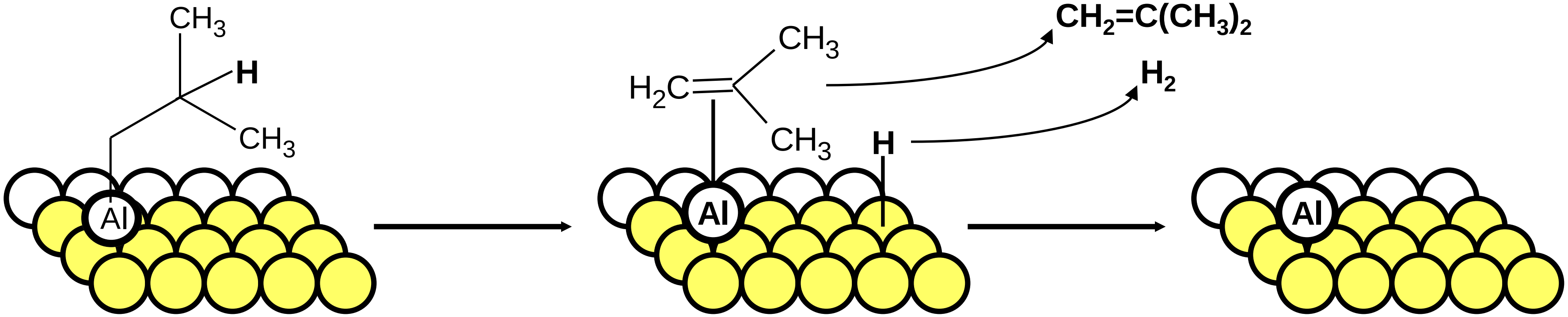


2.2.2 Chemical Vapor Deposition

Deposition of metals

Example: Aluminum for metallization of polymers (PET, PP, packages), metal cont.

$Al(iso\text{-}butyl)_3 \rightarrow Al + 3\ CH_2{=}C(CH_3)_2 + 3/2\ H_2$ **ß-Hydrogen elimination**



$Al_2(CH_3)_6 \rightarrow$ ß-Hydrogen elimination is not possible

In $N_2 \Rightarrow 2\ Al_2(CH_3)_6 \rightarrow Al_4C_3 + 9\ CH_4$ **Al_4C_3 is thermodynamically more stable**

In $H_2 \Rightarrow Al_2(CH_3)_6 + 3\ H_2 \rightarrow Al + 6\ CH_4$

2.2.2 Chemical Vapor Deposition

Deposition of metals

Tungsten: Coating of cutting and grinding tools
Metal contacts on silicon (ICs)

$2\ WF_6(g) + 3\ Si(s) \rightarrow 2\ W(s) + 3\ SiF_4(g)$ < 400 °C

$WF_6(g) + 3\ Si(s) \rightarrow W(s) + 3\ SiF_4(g)$ > 400 °C

Copper: Metal contacts on silicon (ICs)

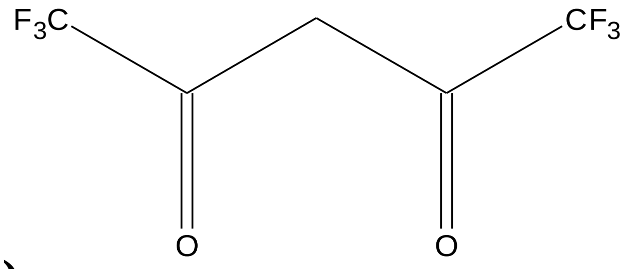
Cu^{2+} precursor (ß- Diketone complex)

$Cu(hfac)_2(g) + H_2(g) \rightarrow Cu(s) + 2\ H\text{-}hfac(g)$

Cu^{+} precursor (complexes with ß-Diketonat + co-ligand)

$2\ Cu(hfac)(PMe_3)(g) \rightarrow Cu(s) + Cu(hfac)_2(g) + 2\ PMe_3(g)$

2 H-hfac



2.2.2 Chemical Vapor Deposition

Deposition of metal oxides

SiO_2: Insulating layers, surface passivation

Based on gaseous silane

$SiH_4 + O_2 \rightarrow SiO_2 + 2\,H_2$

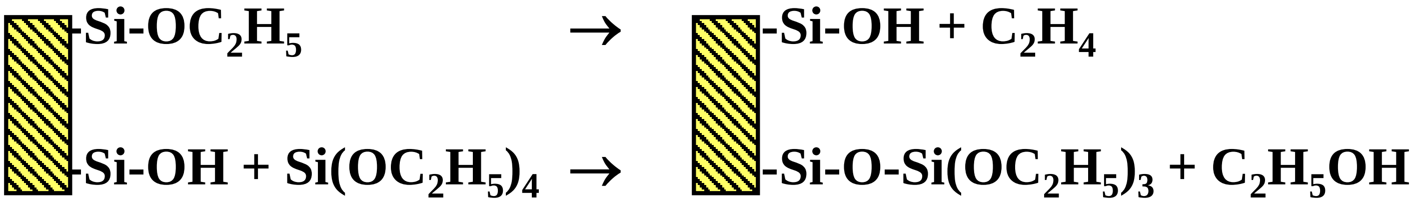
$SiH_4 + 2\,O_2 \rightarrow SiO_2 + 2\,H_2O$ Oxygen excess is necessary

$SiH_4 + 2\,N_2O \rightarrow SiO_2 + 2\,N_2 + 2\,H_2$ No formation of water

Based on tetra alkoxy silicate, e. g. tetraethyl orthosilicate (TEOS)

$Si(OC_2H_5)_4 \rightarrow SiO_2 + 2\,H_2O + 2\,C_2H_4 + 2\,C_2H_5OH$

Reaction mechanism



$-Si-OC_2H_5 \rightarrow -Si-OH + C_2H_4$

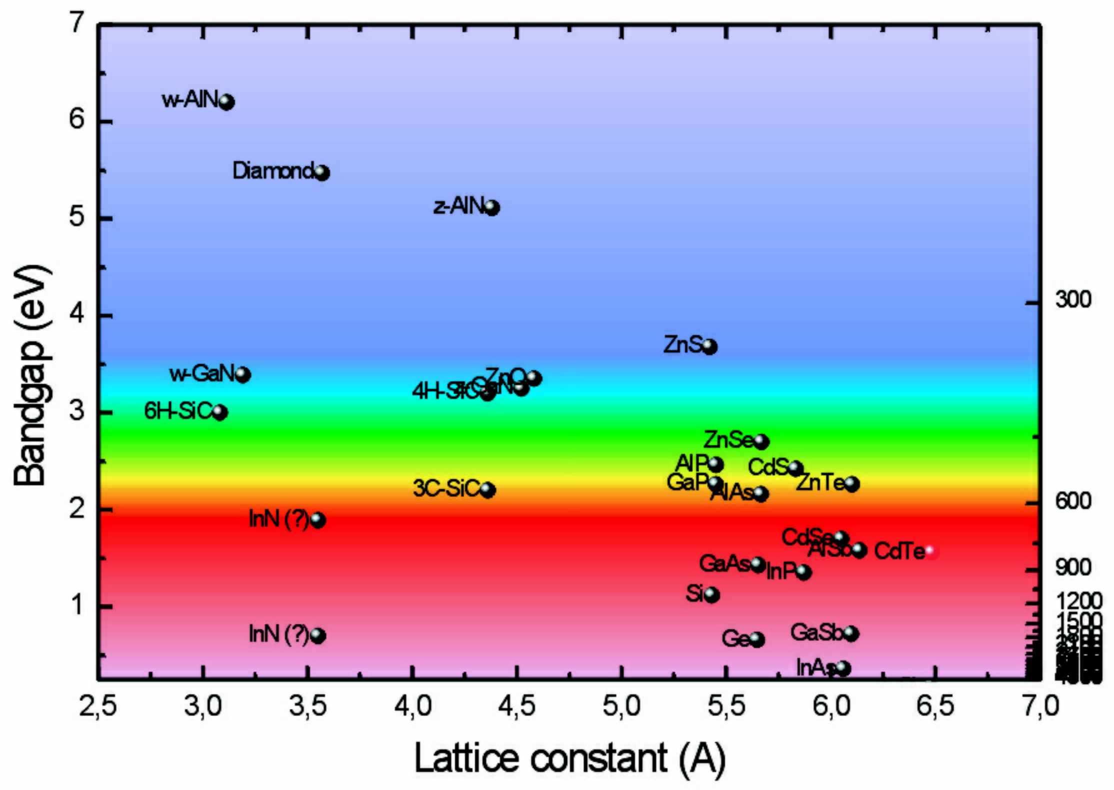
$-Si-OH + Si(OC_2H_5)_4 \rightarrow -Si-O-Si(OC_2H_5)_3 + C_2H_5OH$

2.2.2 Chemical Vapor Deposition

Deposition of semiconductor materials

Optical band gap of III-V semiconductors

AlN	**6.2 eV (200 nm)**
AlP	**2.5 eV (500 nm)**
AlAs	**2.2 eV (570 nm)**
GaN	**3.5 eV (370 nm)**
GaP	**2.3 eV (520 nm)**
GaAs	**1.5 eV (830 nm)**
InN	**0.8 eV (1.55 µm)**
InP	**1.3 eV (0.96 µm)**
InAs	**0.35 eV (3.5 µm)**



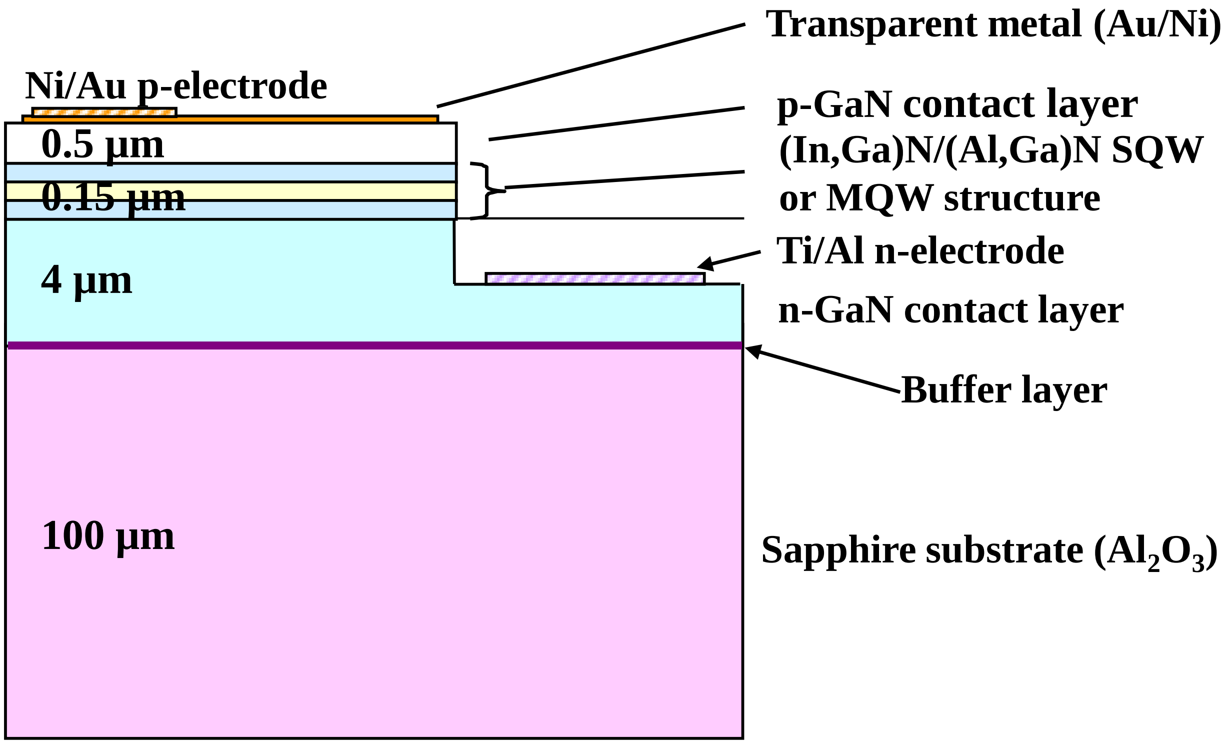
2.2.2 Chemical Vapor Deposition

Deposition of semiconductor materials

Production of

- Solar cells
  Si, GaAs
- LEDs
  (Al,Ga,In)As
  (Al,Ga,In)P
  (Al,Ga,In)N
- Solid-state laser
  (Al,Ga,In)(N,P,As,Sb)
  (Laser pointer, 4K, Blue-ray-, DVD-, CD-Player)
- High-speed ICs
  GaAs

Chip construction (Al,In,Ga)N/Al_2O_3-LED



Lit.: S. Nakamura and G. Fasol, The Blue Laser Diode: GaN Based Light Emitters and Lasers, Springer, Berlin, 1997)

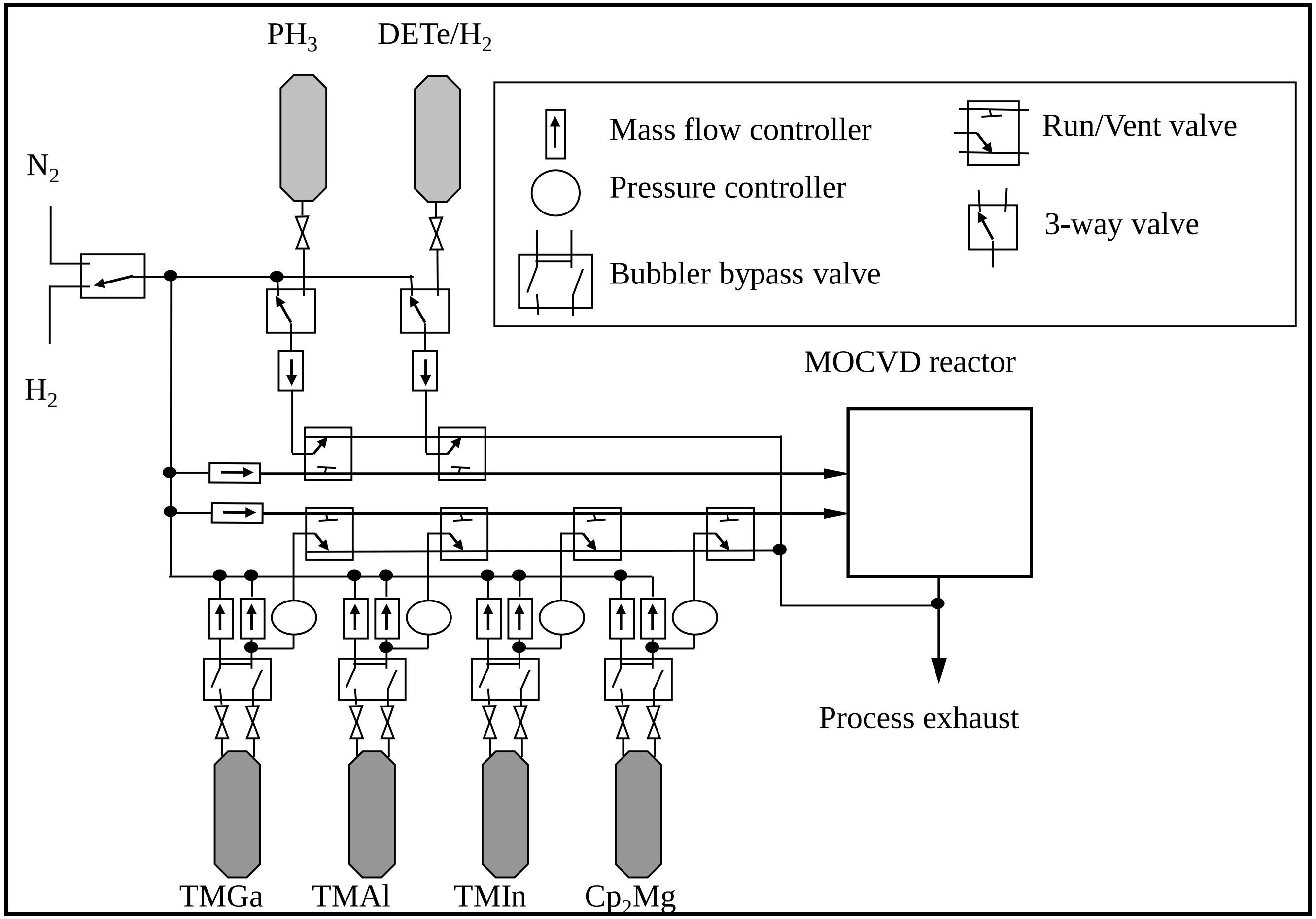
2.2.2 Chemical Vapor Deposition

Deposition of semiconductors by Metal Organic CVD (MOCVD)

Production of semiconductor chips for inorganic LEDs

Precursor materials

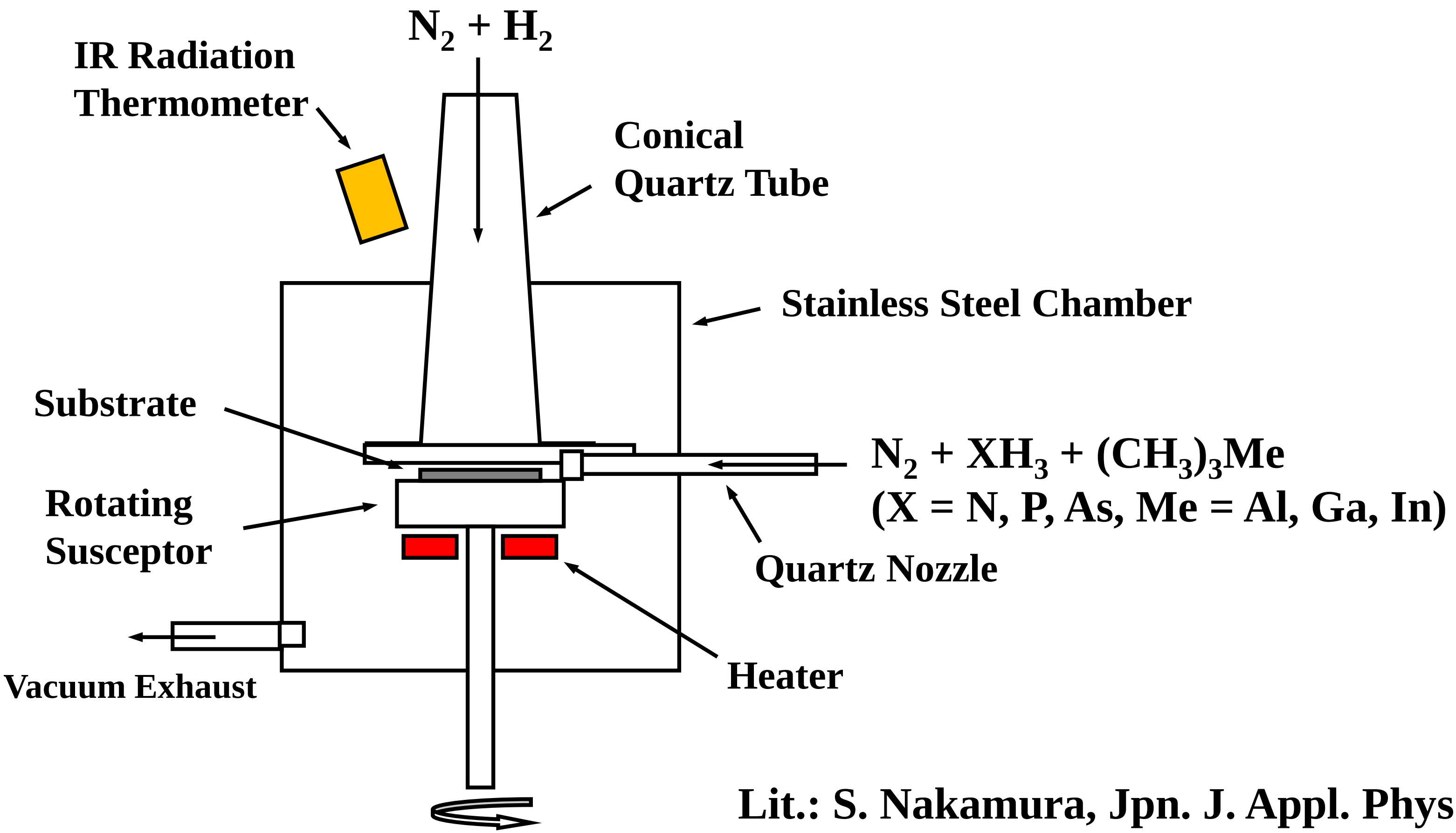
NH_3	
PH_3	
AsH_3	
$(CH_3)_3Al$	(TMAl)
$(CH_3)_3Ga$	(TMGa)
$(CH_3)_3In$	(TMIn)
$(C_5H_5)_2Mg$	(Cp_2Mg)
$(C_2H_5)_2Te$	(DETe)
$(CH_3)_2Zn$	(DMZn)
SiH_4	(Silan)
Si_2H_6	(Disilan)



2.2.2 Chemical Vapor Deposition

Deposition of semiconductors by MOCVD

Schematic construction of a typical MOCVD reactor



$N_2 + H_2$

IR Radiation Thermometer

Conical Quartz Tube

Stainless Steel Chamber

Substrate

$N_2 + XH_3 + (CH_3)_3Me$

(X = N, P, As, Me = Al, Ga, In)

Rotating Susceptor

Quartz Nozzle

Vacuum Exhaust

Heater

Lit.: S. Nakamura, Jpn. J. Appl. Phys. 30, L1705, 1991

2.2.2 Chemical Vapor Deposition

Deposition of semiconductors by MOCVD

$$x\,(CH_3)_3Al + y\,(CH_3)_3Ga + z\,(CH_3)_3In + PH_3 \rightarrow Al_xGa_yIn_zP + 3\,CH_4\ (x + y + z = 1)$$

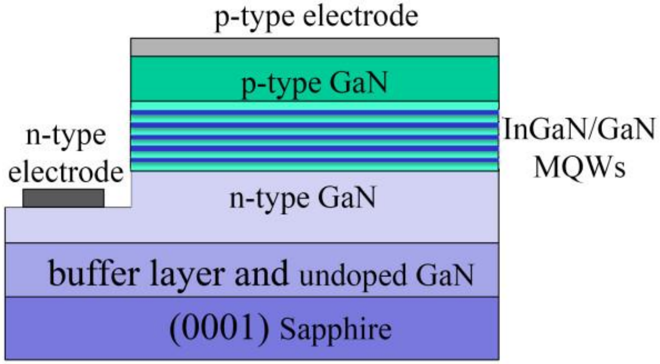
$$x\,(CH_3)_3Al + y\,(CH_3)_3Ga + z\,(CH_3)_3In + NH_3 \rightarrow Al_xGa_yIn_zN + 3\,CH_4\ (x + y + z = 1)$$

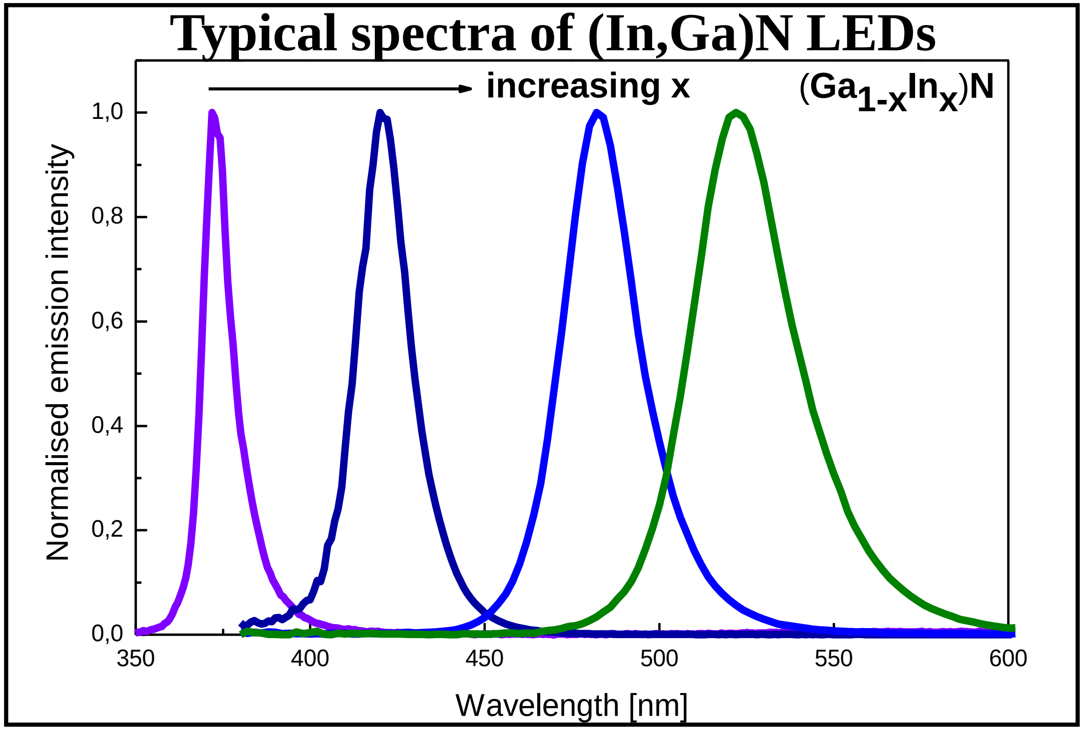
p-type doped layers

MeN:Mg or MeP:Mg

n-type doped layers

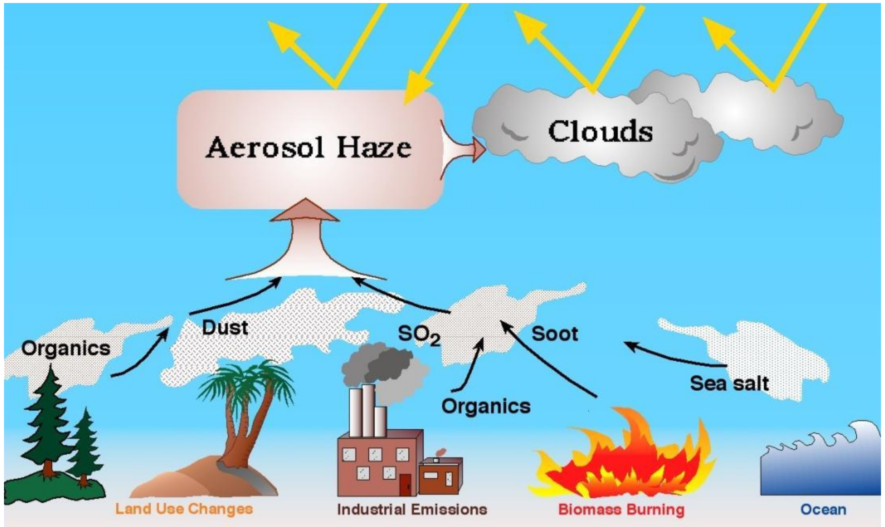
MeN:Si or MeP:Si





2.2.3 Aerosol Processes

Definitions and advantages



Aerosol

Suspension of droplets or nanoscale particles in a gaseous medium

Aerosol process (gas phase powder synthesis)

Synthesis technique, in which powder particles are produced by the physical or chemical processes in the gas phase

Advantages (in comparison with liquid phase syntheses)

- Solvent-free
- High reaction conversion is possible
- Products with high purity are possible
- Simple synthesis of nanoparticles

2.2.3 Aerosol Processes

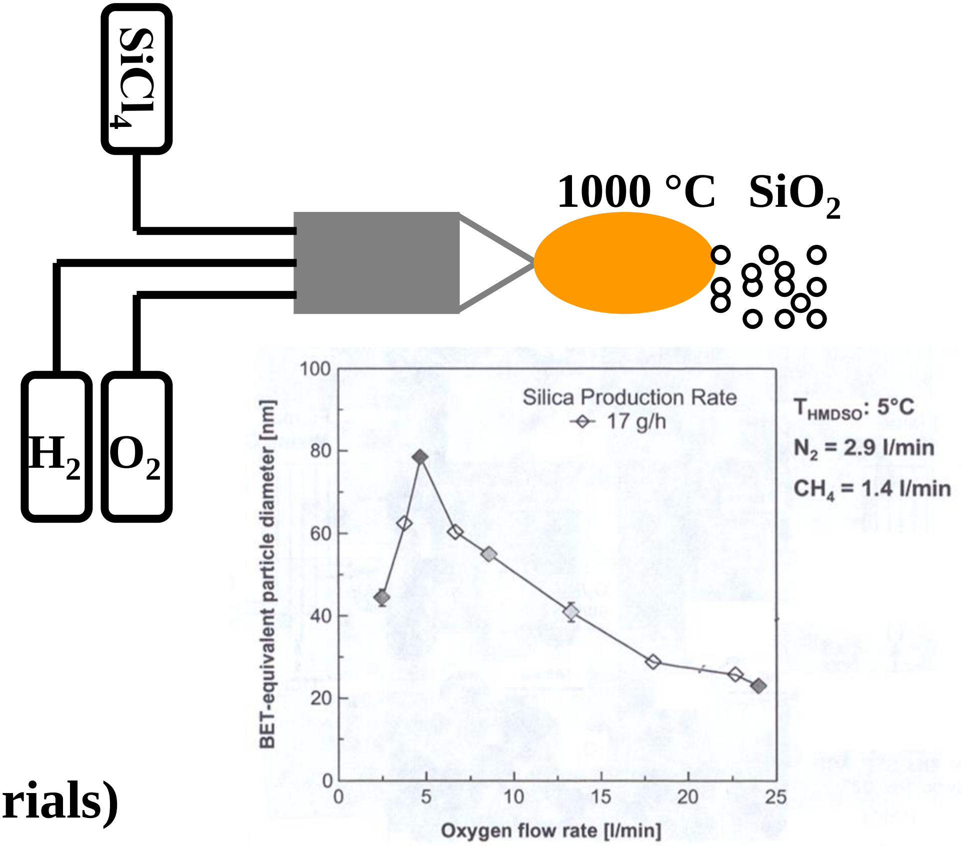
Synthesis of Aerosil®

By a pyrolytic process, in which e.g. SiO_2 nanoscale powder is produced

$2\ H_2 + O_2 \rightarrow 2\ H_2O$

$SiCl_4 + 2\ H_2O \rightarrow SiO_2 + 4\ HCl$

$SiCl_4 + 2\ H_2 + O_2 \rightarrow SiO_2 + 4\ HCl$



Product with high specific surface area

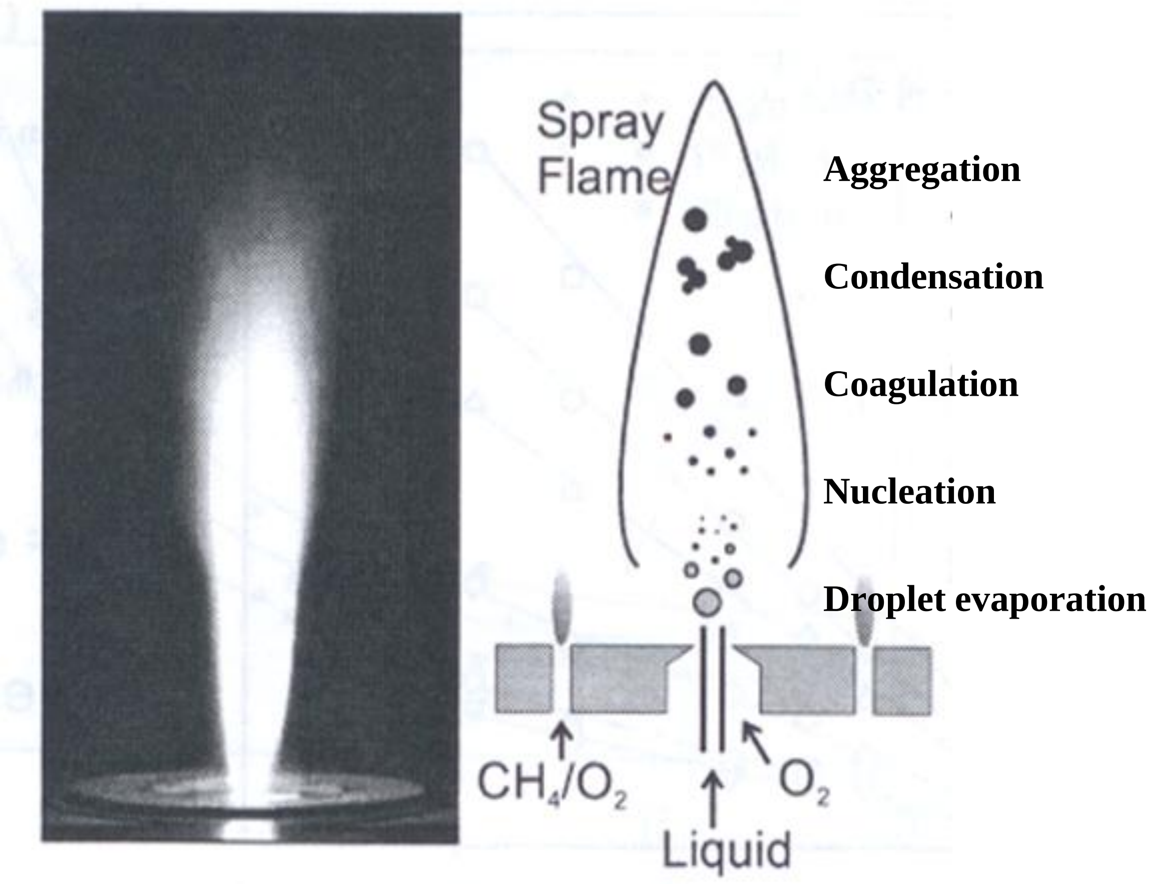
Aerosil® 130	130 ± 25 m^2/g
Aerosil® OX50	50 ± 15 m^2/g

Applications: Thermal insulation (materials)
Starting material for the synthesis of silicates

2.2.3 Aerosol Processes

Synthesis of carbon black

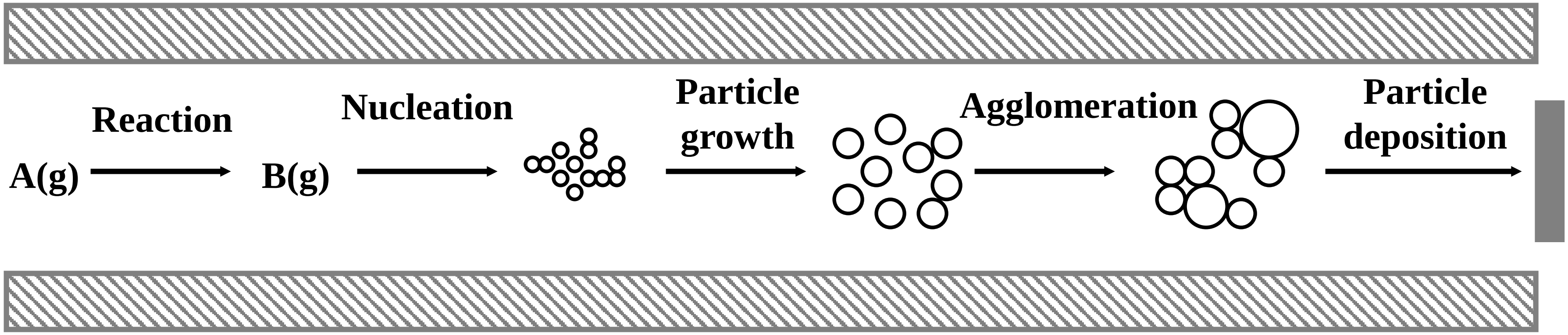
- **Versatile**
- **Large variety of gaseous precursors**
- **Controllable**
- **Scalable**



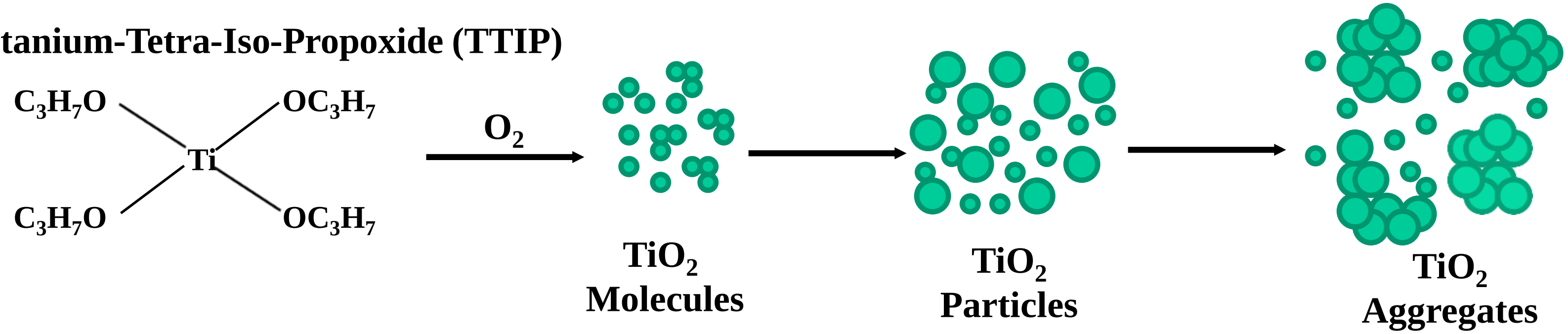
2.2.3 Aerosol Processes

Gas particle conversion

Reaction of gaseous precursor, like e.g. $SiCl_4$, $AlCl_3$, or $TiCl_4$ at high temperatures



Titanium-Tetra-Iso-Propoxide (TTIP)



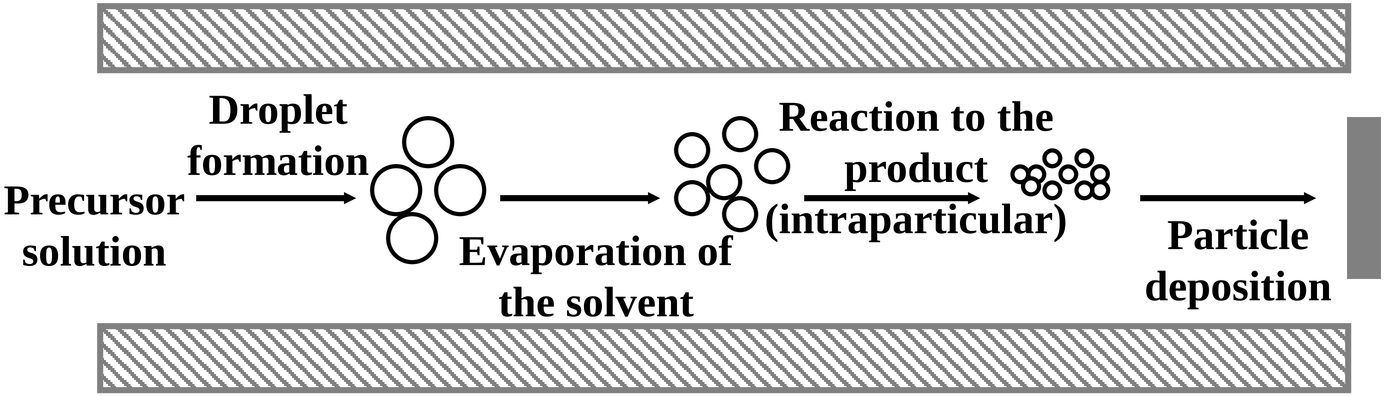
Usually the product is a dense, non-porous, and nanoscale powder

→ SiO_2, Al_2O_3, TiO_2, ZrO_2 and other oxides

2.2.3 Aerosol Processes

Spray pyrolysis

Spraying a precursor solution in the carrier gas stream, whereas the resulting aerosol is passed through a tube furnace



Precursor solution

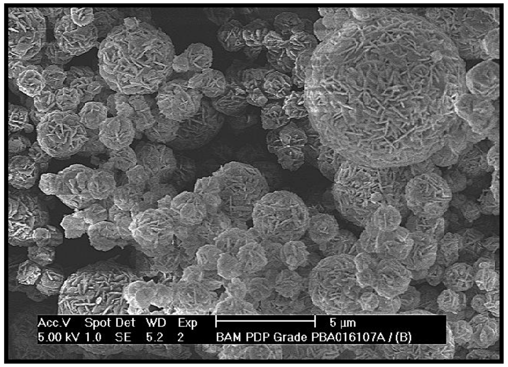
Droplet formation

Evaporation of the solvent

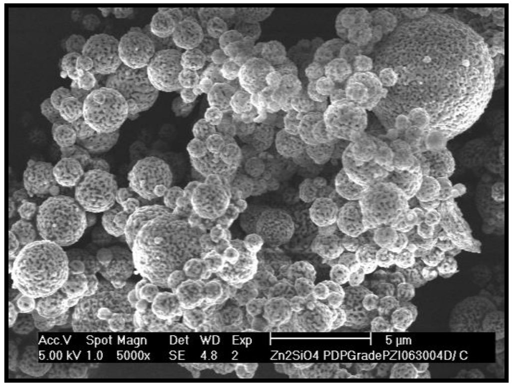
Reaction to the product (intraparticular)

Particle deposition

- **The particle size of obtained product is proportional to the droplets sizes**
- **Product is often porous**
- **Spherical particles, which can be hollow**



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



Zn_2SiO_4:Mn

2. Synthesis Techniques of Material Technology

2.3. Syntheses in Solution

2.3.1 Solvothermal syntheses

Definition and Application

General Aspects

Hydrothermal Single Crystal Growth

Hydrothermal Synthesis

Hydrothermal Leaching Out

Non-Aqueous Solvents

2.3.2 Sol-Gel Syntheses

Definition of Sol and Gel

The Sol-Gel Process

Excursion: PZC of oxides

Physics of the Sol

PZT Ceramics

Sol-Gel Chemistry of Silicates

Sol-Gel Chemistry of Metal Oxides

2.3.1 Solvothermal Syntheses

Definition and application

Definition

Generally solvothermal synthesis is a preparation technique, which leads to a crystallization of the products from highly heated solutions

(solvothermal = temperature > T_b(solvent) and pressure > 1 bar)

Important solvent

H_2O (hydrothermal)

NH_3 (ammonothermal)

Application of hydrothermal processes

- Crystallization (geological processes) → Gemstones
- Synthesis of oxides → Zeolites
- Leaching out from ores → Bauxite

Natural quartz crystals

2.3.1 Solvothermal Syntheses

General aspects

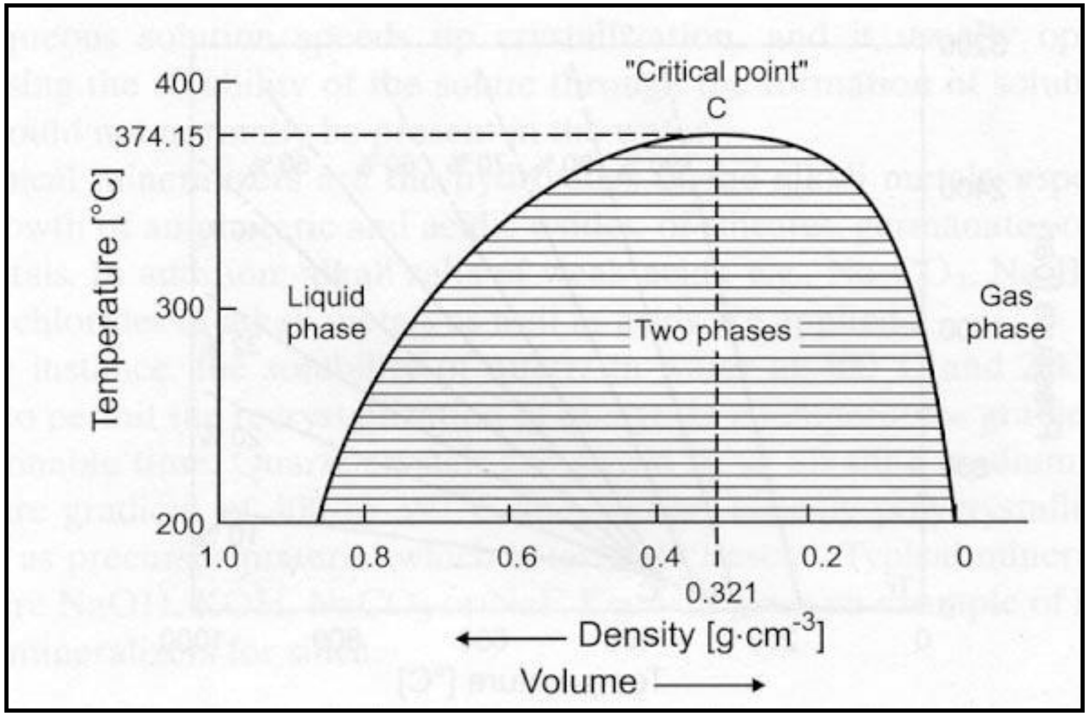
Advantages of solvothermal processes

- **Increase of the solubility of the reactants**
- **Increase of the ionic product of the solvent**
- **Reduce the viscosity of the solvent**

Implementation

- **In a closed quartz or Teflon container, in pressurized reservoirs (steel autoclave)**
- **Filling degree of the solvent approx. 10 - 60%**
- **Reaction time: a few days**

Temperature-density diagram of water



2.3.1 Solvothermal Syntheses

General aspects

The resulting pressure in the pressure vessel depends on the filling degree and on the temperature of the reaction container, whereby above the critical temperature solvent changes into its supercritical state.

Example

Solvent: H_2O

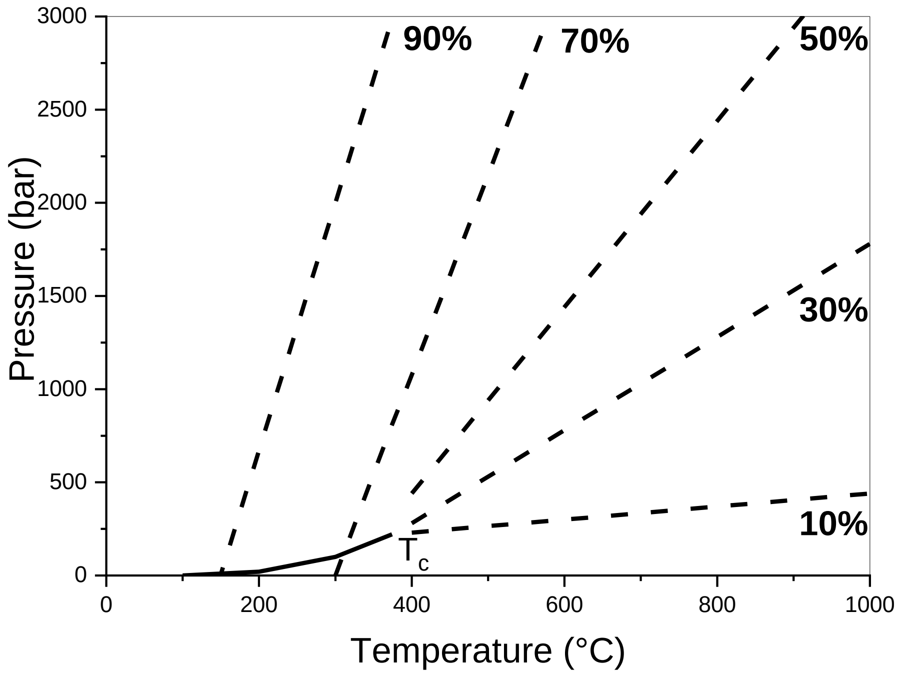
T_c = 374.15 °C

Filling degree = 30%

Temperatur = 600 °C

⇒ Pressure = 800 bar

p-T-Diagram of water



2.3.1 Solvothermal Syntheses

Hydrothermal single crystal growth

Example: Growth of α-quartz single crystals

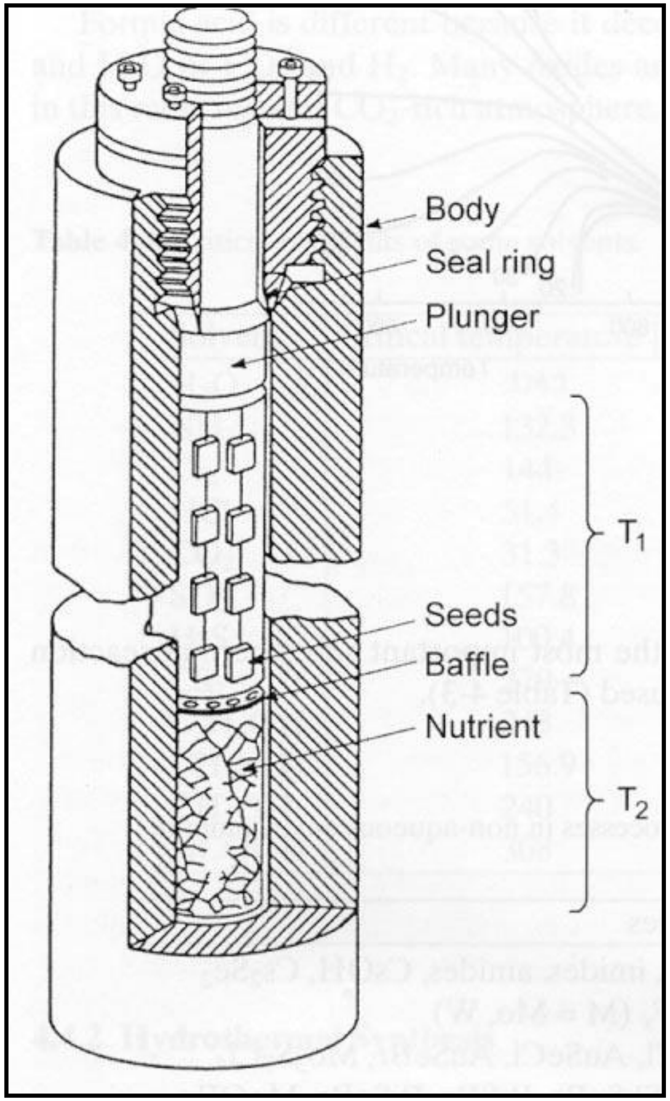
Hot zone (T_2)
$SiO_2(s) \rightarrow SiO_2(aq)$ solubility at 600 °C ~ 0.1 wt-%

Cold zone (T_1)
$SiO_2(aq) \rightarrow SiO_2(s)$

World annual production in 1985: 1500 t
World annual market in 2021: 8535 Mill. USD

Application of quartz single crystals:
- **Piezo crystals (quartz clocks, electronic devices)**
- **Optical crystals (prisms, window materials)**

⇒ $E_g = 8.4$ eV(148 nm), n(200 nm) = 1.55, $n_D = 1.46$



2.3.1 Solvothermal Syntheses

Hydrothermal single crystal growth

In many cases the solving power in the supercritical state is not sufficient to achieve a sufficiently high reaction rate

⇒ **Addition of mineralizer**

Hydroxides of alkali metals (NaOH, KOH)

Alkaline salt of weak acids, such as Na_2CO_3

For SiO_2: NaOH, KOH, NaF

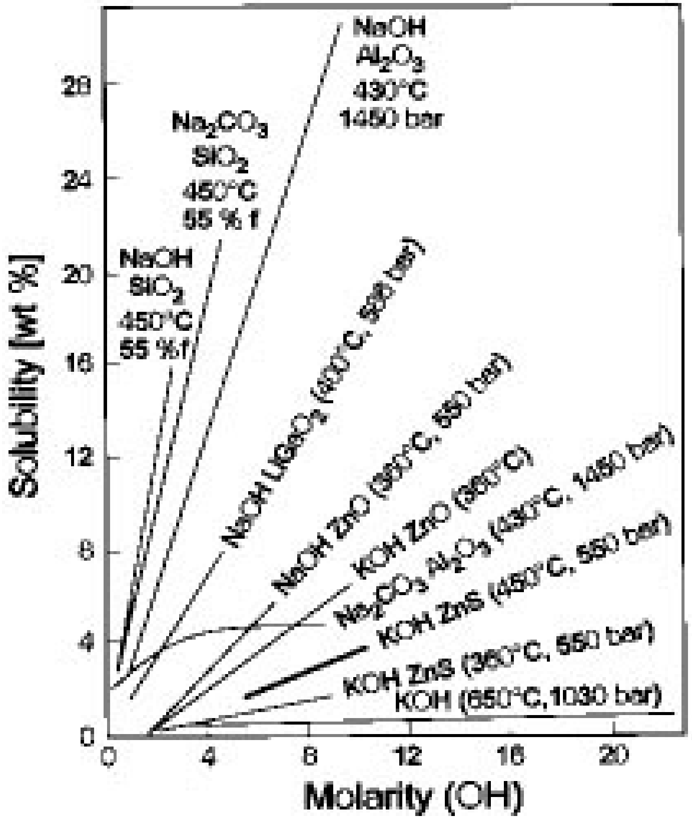
$$SiO_2(s) + 2\,OH^- \rightleftharpoons SiO_3^{2-}(aq) + H_2O$$

For Al_2O_3: NaOH, KOH

$$Al_2O_3(s) + 3\,H_2O + 2\,OH^- \rightleftharpoons 2\,Al(OH)_4^-(aq$$

(Doping with Cr^{3+} results in ruby-crystal Al_2O_3:Cr(0.1-0.3%))

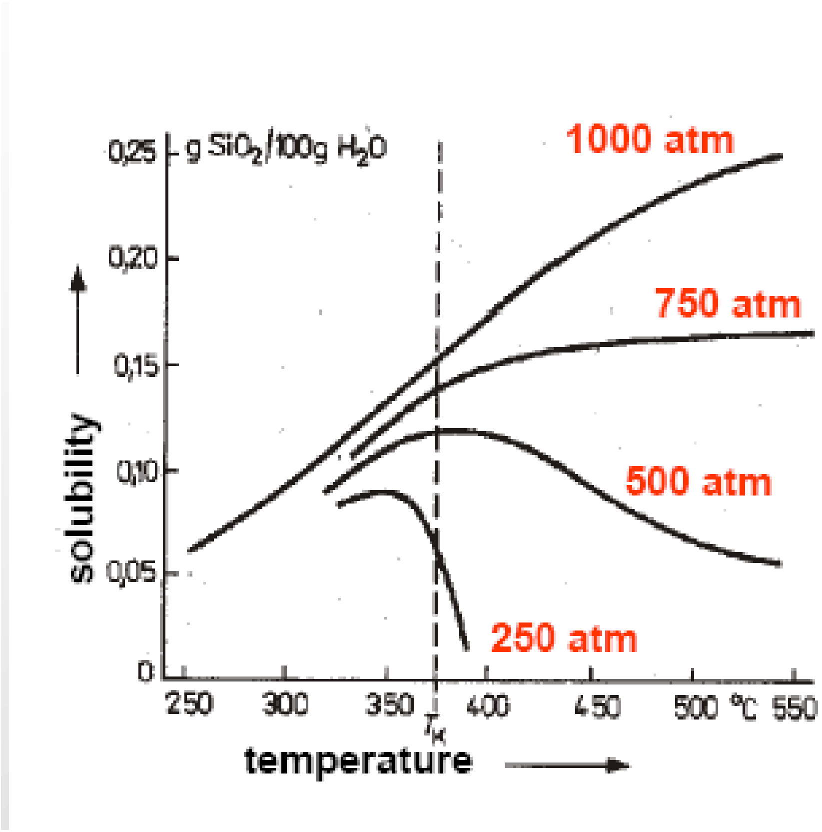
Solubility of some hydrothermal systems

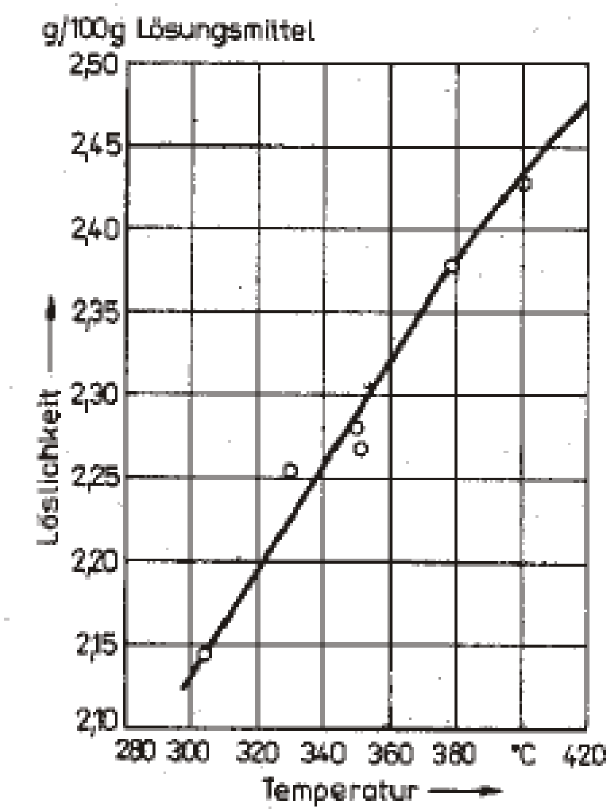


2.3.1 Solvothermal Syntheses

Hydrothermal single crystal growth

Solubility of SiO_2 in H_2O (left) and in 0.5 M NaOH-solution (right)



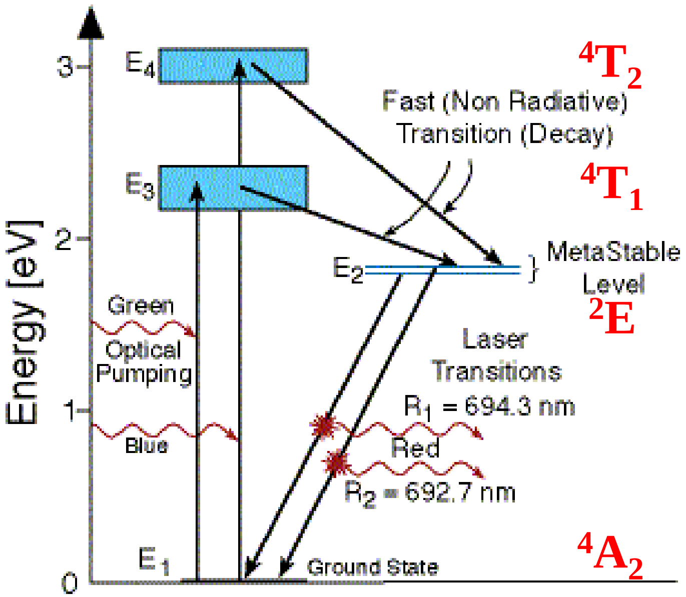


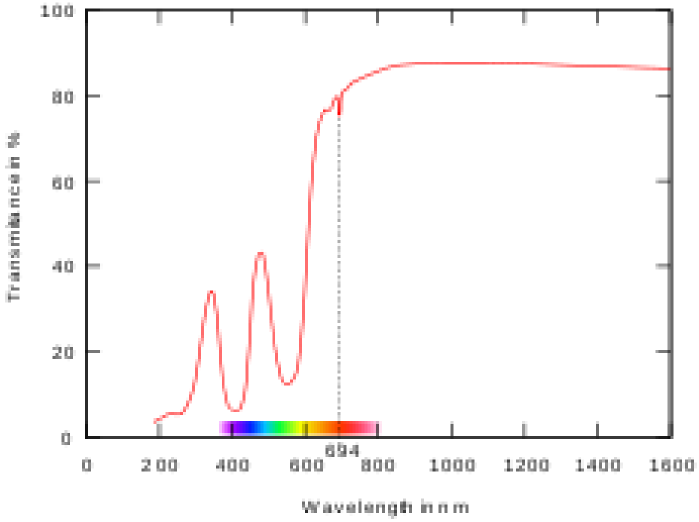
0.5 M NaOH
(80% filling)

Source: A.R. West, Solid State Chemistry and its Applications, Wiley & Sons, 1984

Excursion: Ruby-Laser

Ruby $Al_2O_3:Cr^{3+}$





Pumping by (flash) excitation in the blue and green spectral region, i.e. excitation of Cr^{3+} [Ar]$3d^3$ (RS ground term: ^4F_J → Crystal field terms: ^2E, $^4T_1$, $^4T_2$)

The lifetime of the ^4F_J states is very short, While relaxation into the metastable E-level takes place

On the E-level electrons accumulate themselves, whereby a population inversion occurs

Further irradiation leads to the stimulated emission and to the complete depletion of the E-states

2.3.1 Solvothermal Syntheses

Hydrothermal synthesis - Examples

1. Synthesis of $BaTiO_3$ (high dielectric constant: capacitors, piezo crystals)

$$Ba(OH)_2(aq) + TiO_2(s) \rightarrow BaTiO_3(s) + H_2O$$

2. Synthesis of zeolites (high specific surface area: ion exchanger, catalysts)

$$\begin{tikzcd}
NaAl(OH)_4(aq) + Na_2SiO_3(aq) + NaOH(aq) \arrow[d, "25\ °C"] \\
Na_a(AlO_2)_b(SiO_2)_c \cdot NaOH \cdot H_2O(gel) \arrow[d, "125 – 200\ °C,\ 1 – 100\ bar"] \\
Na_{5b+4c}(AlO_2)_b(SiO_2)_c) \cdot mH_2O(s)
\end{tikzcd}$$

2.3.1 Solvothermal Syntheses

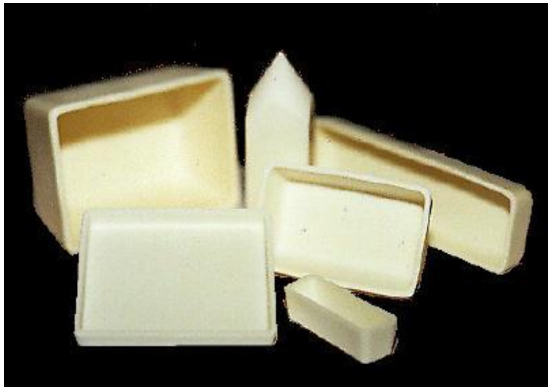
Hydrothermal leaching out

Extraction of aluminum hydroxide and alumina from bauxite ($AlOOH + Al(OH)_3$) by the Bayer process

1. $Al(OH)_3 + NaOH \xrightarrow{120 - 250\ °C} NaAl(OH)_4(aq)$
   $AlOOH + 2\ NaOH + H_2O \rightarrow NaAl(OH)_4(aq)$

2. **Filtration for the separation of SiO_2 and Fe_2O_3**

3. **Cooling and addition of $Al(OH)_3$ seeds**
   $Al(OH)_4^- \rightarrow Al(OH)_3 + OH^-$



4. **Sintering**
   $2\ Al(OH)_3 \rightarrow \alpha\text{-}Al_2O_3\ (corundum) + 3\ H_2O$
   ⇒ **Al-production, glass, ceramics, fibers.......**

2.3.1 Solvothermal Syntheses

Non-aqueous solvents

Solvent	Crit. Temp. [°C]	Crit. Pressure [bar]	Examples
H_2O	374.1	221.2	SiO_2, Al_2O_3, fluorides
NH_3	132.3	111	nitrides, amides, imides
Cl_2	144	77.1	
HCl	51.4	83.2	$AuTe_2Cl$, $Mo_3S_7Cl_4$
CO_2	31.3	73	
SO_2	157.8	79	
H_2S	100.4	90.1	ß-Ag_2S
CS_2	279	79	monoclinic Se
C_2H_5OH	243	64	SbI_3, BiI_3
CH_3NH_2	156.9	40.7	CH_3NHLi
CH_3OH	240	81	
HCOOH	308	decomposes	

Lit.: Angew. Chem. Int. Ed. 24 (1985) 1026

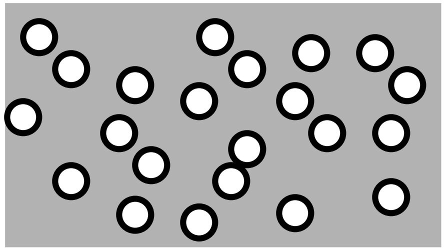
2.3.2 Sol-Gel Syntheses

Definition of Sol and Gel

Sol

A **Sol** is a stable suspension of solid colloidal particles in a dispersing agent:

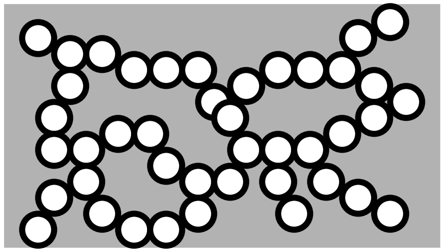
Matrix	*Type*
Glass, polymer	Vitreosol (gold ruby glass)
Water	Lyosol (colloidal Au-solution)
Air	Aerosol (fog)



Gel

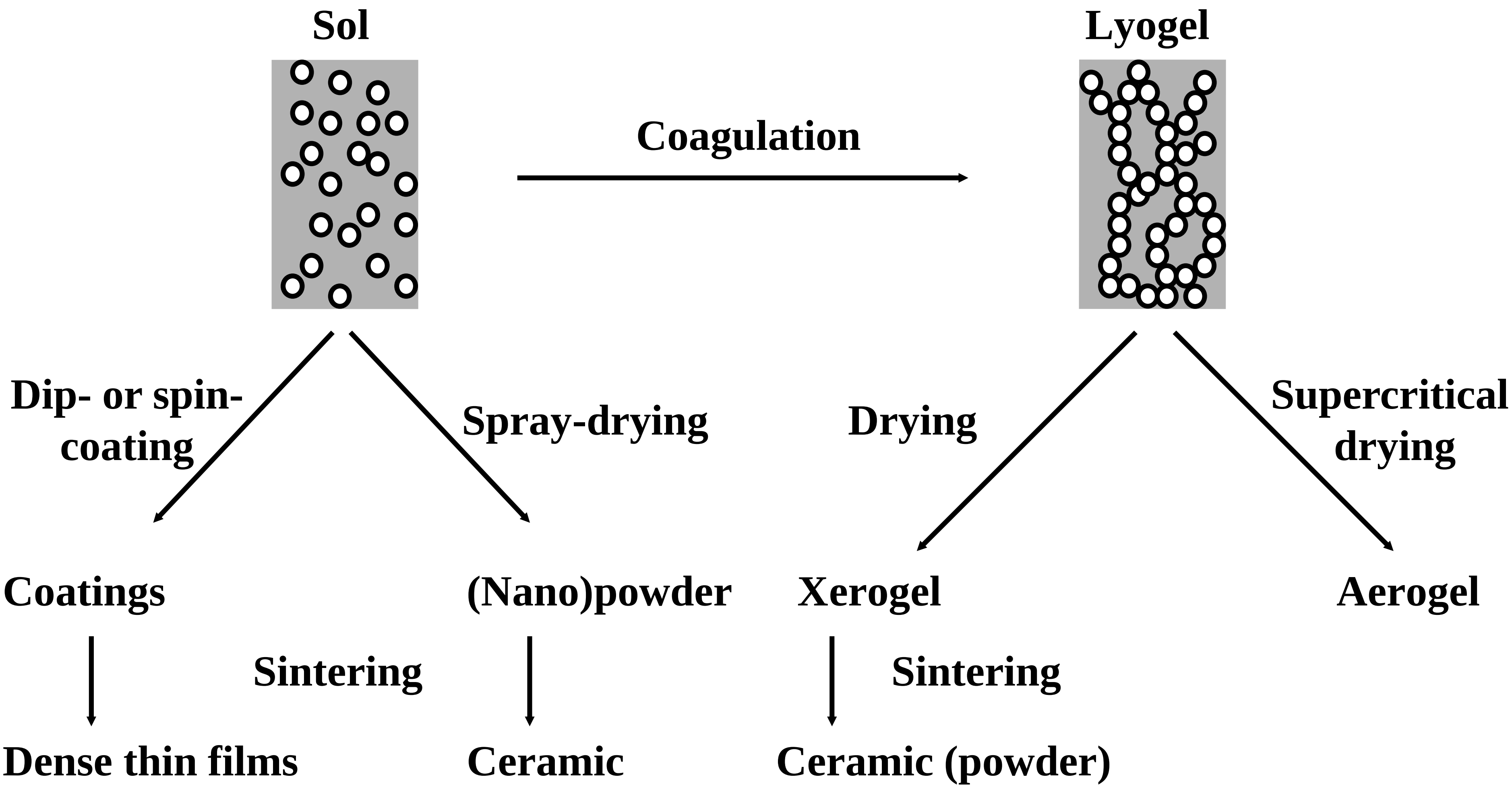
A **Gel** consists of a three-dimensional (3D) network of solid colloidal particles, which is formed by coagulation of a colloidal system

$$\text{Colloidal system} \underset{\text{Peptisation}}{\overset{\text{Coagulation}}{\rightleftharpoons}} \text{Gel}$$



2.3.2 Sol-Gel Syntheses

The Sol-Gel process



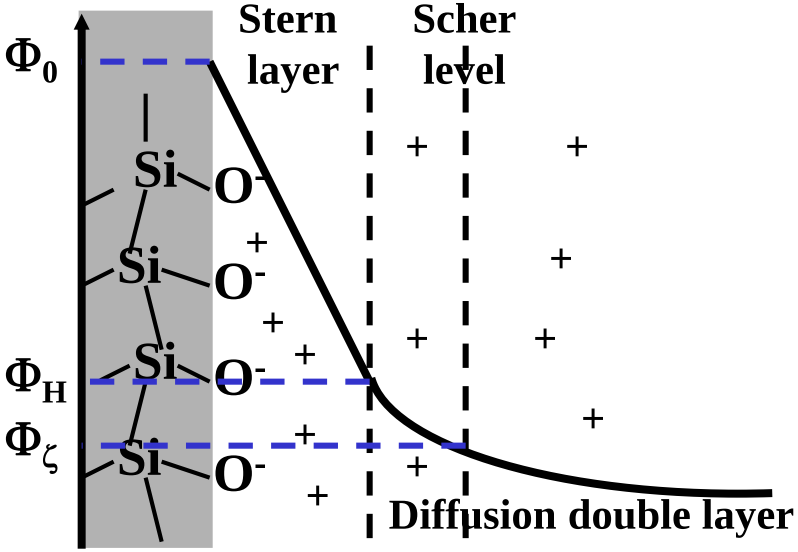
2.3.2 Sol-Gel Syntheses

Physics of the Sol

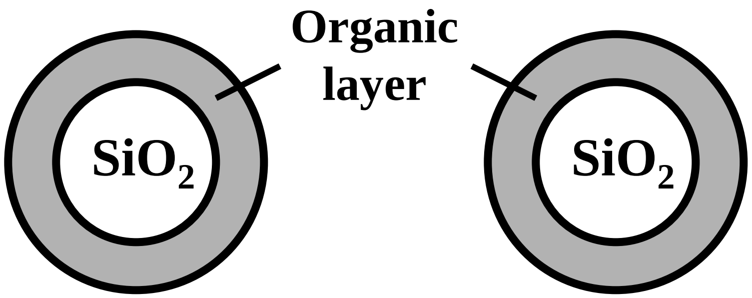
Coagulation of colloids is initiated by van der Waals forces (Dipole-Dipole-interaction). These are weak and short range interaction (a few nm)

Stabilization of colloidal suspensions

1. **Electrostatic repulsion:**
   Stability is proportional to the size of the ζ-potential



2. **Steric hindrance:**
   Adsorption of an organic layer
   Surfactants: Na-stearate, Na- dodecyl sulfate
   Polymers: Gelatin, polyvinyl alcohol



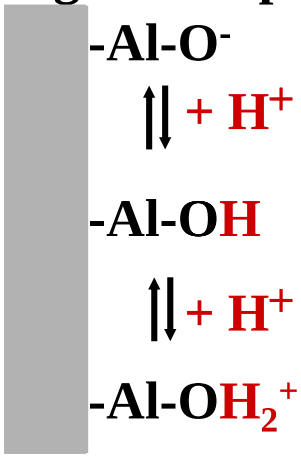
2.3.2 Sol-Gel Syntheses

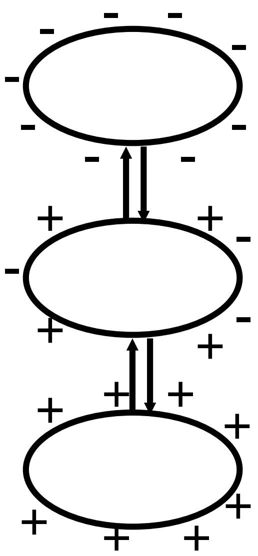
Physics of the Sol

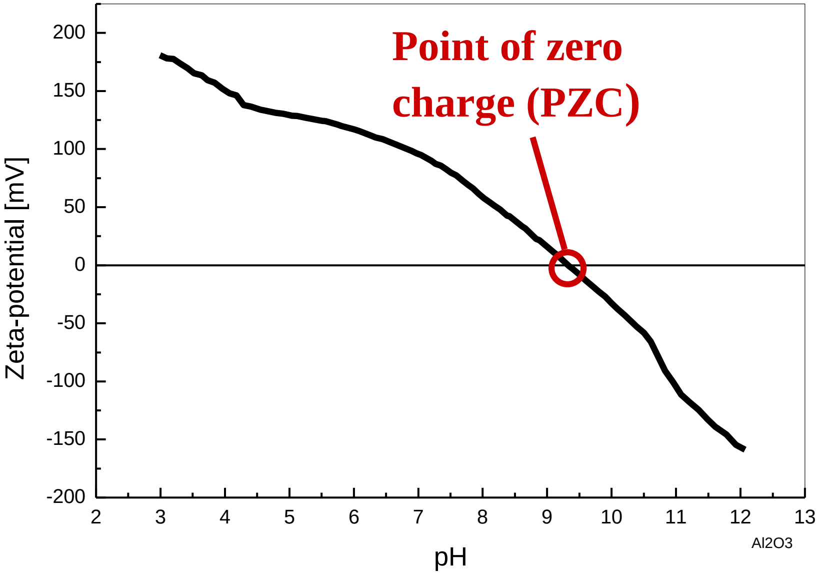
Coagulation takes place, when the electrostatic repulsion forces existing between the particles become smaller than the Van der Waals interaction, i.e. the ζ-potential approaches zero value at so called Point of Zero Charge (PZC)

Possibilities for the reduction of the ζ-potential:

1. **Change of the pH value**





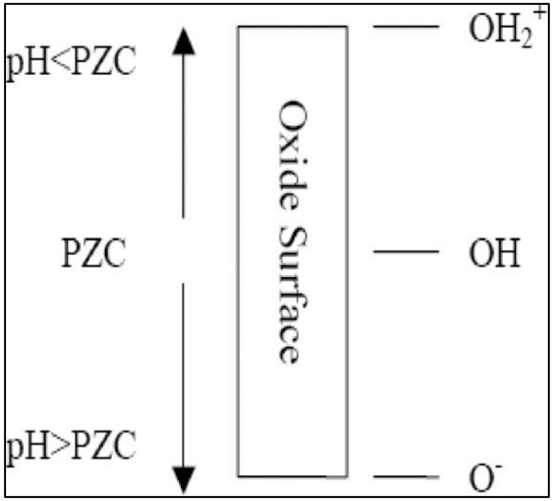


2. **Change of the pH value ⇒ Reduction of the diffusion double layer’s thickness**

2.3.2 Sol-Gel Syntheses

PZC of oxides

The electric charge of a solid surface in suspension depends on pH value and on the nature of the chemical compounds.



Material	PZC [pH]
WO_3	0.2-0.5
SiO_2	1.7-3.5
SnO_2	4.5
TiO_2	6.0
ZrO_2	6.5
YPO_4	7.0
Al_2O_3	9.0
Y_2O_3	9.1
ZnO	8.7-9.7
MgO	12.1-12.7

Electron density on O^{2-} anions

~ alkaline character of the oxide

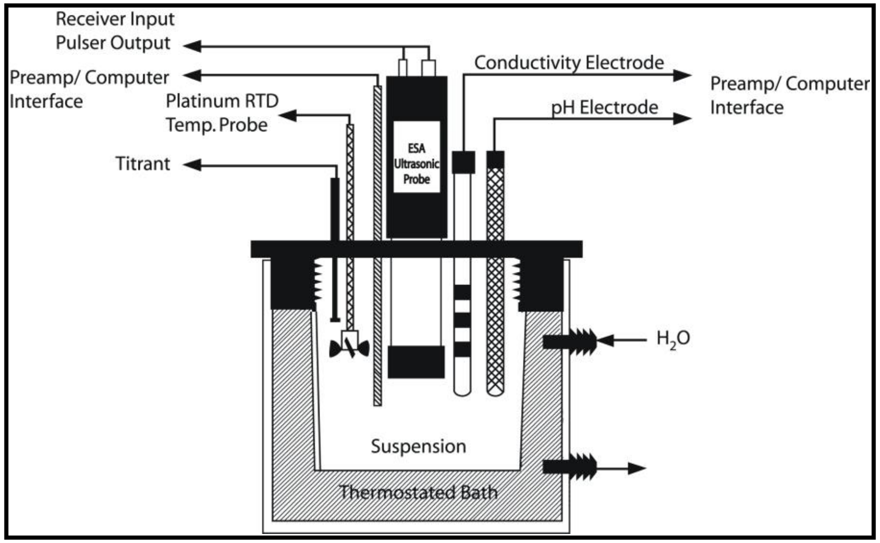
~ electronic polarisibility

The PZC therefore determines the agglomeration behavior and adhesion on surfaces and the adsorption of charged species

Example: Adsorption of Hg^+ (consumption) in Hg low-pressure discharge lamps

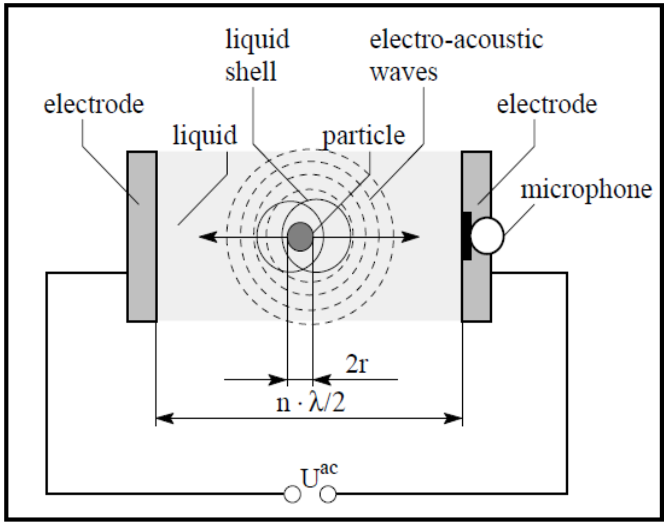
2.3.2 Sol-Gel Syntheses

Excursion: Determination of the PZC by an Electrokinetic Sonic Amplitude (ESA) measurement



Procedure

1. Suspension of the sample in a conducting liquid, e.g. H_2O/KNO_3
2. Application of high voltage AC pulses
3. Oscillation of the charged particles of the sample
4. Registration of emitted electro-acoustic waves amplitude ⇒ ESA signal ~ ζ-potential
5. Implementation of one or more acid-base titrations for recording ESA signal as function of the pH value



2.3.2 Sol-Gel Syntheses

PZT ceramics

Perovskites with the composition $Pb(Zr_{1-x}Ti_x)O_3$ (PZT, $x_{optimal}$ ~ 0.47) find global application as ferro- and piezoelectric ceramics in electronics

Ceramic synthesis

$PbO + x\ TiO_2 + (1-x)\ ZrO_2 \rightarrow PbZr_{1-x}Ti_xO_3$ at 1100 °C

Due to the high volatility of PbO the exact composition is difficult to control

Sol-Gel synthesis

1. $Pb(OAc)_2 \cdot 3H_2O + Ti(OPr)_4 + Zr(OPr)_4$ + acetylacetone ⇒ Reaction solution

2. Evaporation ⇒ PZT precursor

3. Assimilation in ethanol ⇒ PZT coating Sol

4. Substrate coating and sintering at T between 575 – 700 °C ⇒ Polycrystalline PZT film

2.3.2 Sol-Gel Syntheses

Sol-gel chemistry of silicates

General operation sequence

1. Hydrolysis and condensation
   molecular precursor ⇒ sol
2. Gel formation (sol-gel-conversion)
3. Aging
4. Drying

Typical precursor

Na_2SiO_3 „waterglass“
$Si(OCH_3)_4$
$Si(OC_2H_5)_4$
$Si(n\text{-}OC_3H_7)_4$
$Si(i\text{-}OC_3H_7)_4$

Fundamental reaction steps, typically S_N2 type (acid or base catalysis)

Hydrolysis: $Si(OR)_4 + H_2O \rightarrow Si(OR)_3(OH) + ROH$

Condensation: $\equiv Si\text{-}OH + \text{-}Si\text{-}OR \rightarrow \equiv Si\text{-}O\text{-}Si\text{-} + ROH$

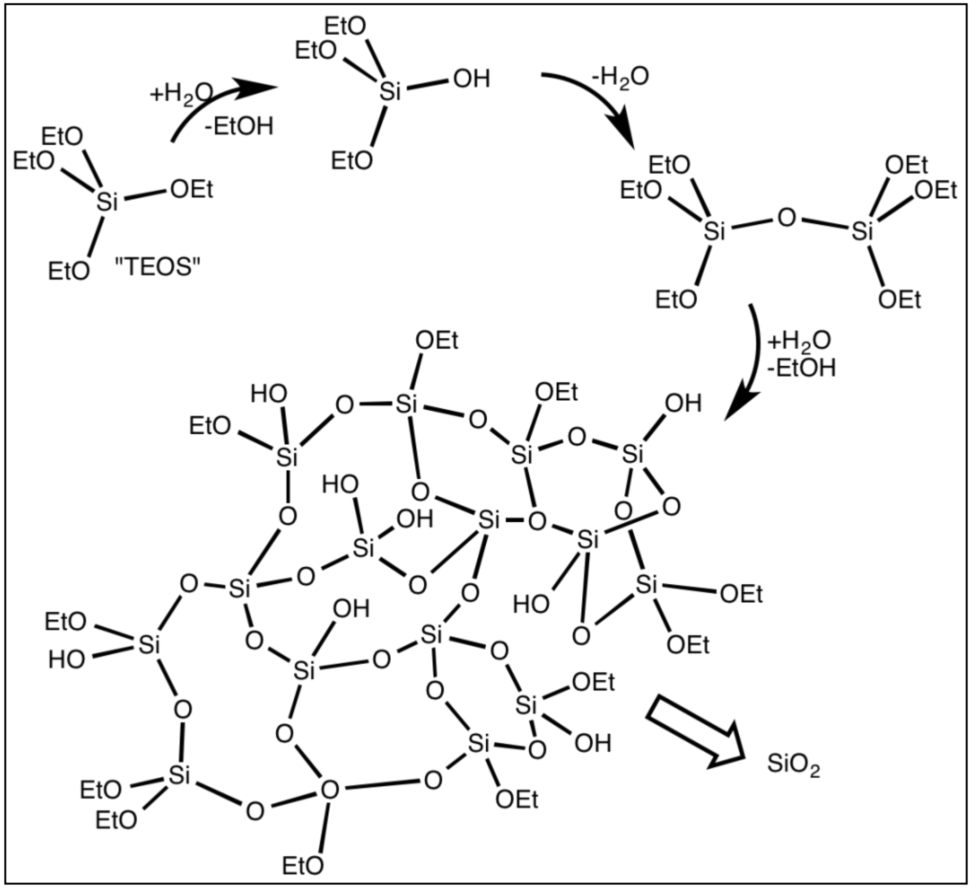
$\equiv Si\text{-}OH + HO\text{-}Si\equiv \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O$

2.3.2 Sol-Gel Syntheses

Sol-gel chemistry of silicates

Dependence on reaction process and reaction speed

- Type and concentration of the precursor
- Alkoxy groups/H_2O-ratio (R_w)
- Type of the catalyst
- Type of the solvent
- pH value
- Temperature
- Complexing agent (ligand)
- Ion strength
- Speed of stirring



2.3.2 Sol-Gel Syntheses

Sol-gel chemistry of silicates

Type of the precursor

Steric demand of R:

$Si(OCH_3)_4$ > $Si(OC_2H_5)_4$ > $Si(n\text{-}OC_3H_7)_4$ > $Si(i\text{-}OC_3H_7)_4$

⇒ hydrolysis rate decreases with size and branching of R

Electron density on the Si atom:

$\equiv Si\text{-}R > \equiv Si\text{-}OR > \equiv Si\text{-}OH > \equiv Si\text{-}O\text{-}Si\equiv$

← Speed of the acid catalysis

→ Speed of the basic catalysis

⇒ acid catalysis provides chain-like networks

⇒ basic catalysis provides highly branched network

2.3.2 Sol-Gel Syntheses

Sol-gel chemistry of silicates

Alkoxy groups / H_2O-ratio (Rw)

Complete condensation (little H_2O) **$R_w = 2$**

$$Si(OR)_4 + H_2O \rightarrow [Si(OH)(OR)_3] + ROH$$

$$[Si(OH)(OR)_3] + H_2O \rightarrow [Si(OH)_2(OR)_2] + ROH \rightarrow \rightarrow \rightarrow SiO_2$$

No condensation, i.e. initially only hydrolysis (a lot of H_2O) **$R_w = 1$**

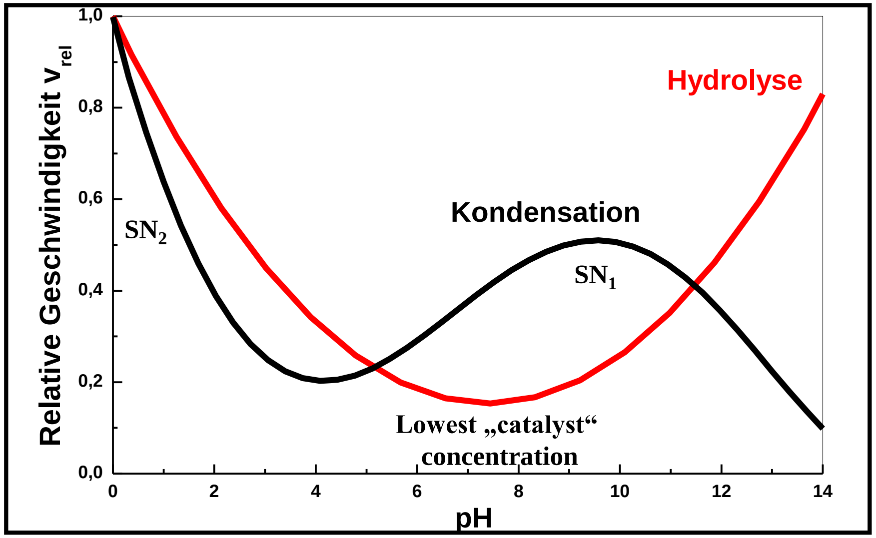
$$\begin{tikzcd}
Si(OR)_4 + 4\,H_2O \arrow[r] & Si(OH)_4 + 4\,ROH \arrow[d, shift right] \\
 & SiO_2 + 2\,H_2O \arrow[u, shift right]
\end{tikzcd}$$

Preference of the condensation reaction of $[SiO_x(OH)_y(OR)_z]_n$ **$R_w >> 2$**

The formation of silanol groups is favored, because the Condensation to SiO_2 is in principle reversible. **$R_w < 1$**

2.3.2 Sol-Gel Syntheses

Sol-gel chemistry of silicates



Type of the catalyst

The hydrolysis of the alkoxides is catalyzed by H^+ and OH^-, or is slow in the neutral pH range

pH < 2.5 „acid catalyzed“

Hydrolysis is favored and the condensation speed is the determining step

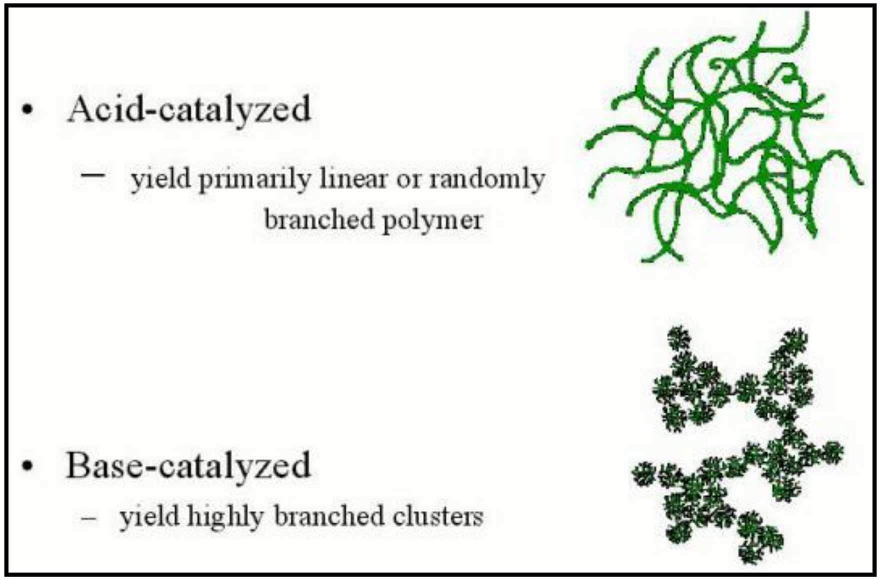
⇒ Simultaneous formation of many silanol groups, which then polymerize

pH > 7 „base catalyzed“

Condensation is favored and the hydrolysis speed is the determining step

⇒ Formation of many agglomerated clusters

⇒ Powders(nanoscale)



- Acid-catalyzed
  - yield primarily linear or randomly branched polymer
- Base-catalyzed
  - yield highly branched clusters

2.3.2 Sol-Gel Syntheses

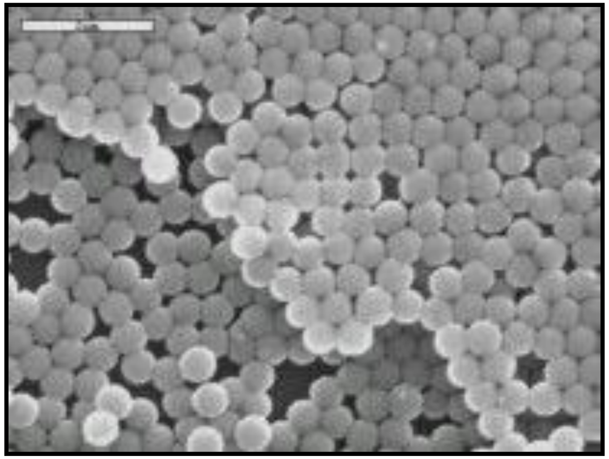
Sol-gel chemistry of silicates

Synthesis of monodisperse SiO_2-particles by the "Stöber" process

- Small colloidal particles have a higher solubility than larger particles
- Large particles grow at the expense of small particles, which dissolve until a uniform particle size is present
- Formation of a stable colloid

⇒ Ostwald ripening

500 nm Monosphere



Example

Hydrolysis of $Si(OC_2H_5)_4$ at high pH value with NH_3 as catalyst and low R_w (~ 0.5 – 0.05)

⇒ Very monodisperse SiO_2 particle with 0.1 - 1 µm particle diameter

2.3.2 Sol-Gel Syntheses

Sol-gel chemistry of metal oxides

In principle, the sol-gel chemistry can be applied to all metal oxides, whereby the reactivity or reaction rate depends strongly on the electronegativity and the preferred coordination number of the metal cation.

Cation	EN (Allred-Rochow)	r [Å]	preferred CN	
Si^{4+}	1.74	0.40	4	↓
Sn^{4+}	1.72	0.69	6	
Ti^{4+}	1.32	0.56	6	Reactivity
Zr^{4+}	1.22	0.73	7	
Ce^{4+}	1.08	1.02	8	
Fe^{2+}	1.83	0.92	6	Hydrolysis at about pH 6
Fe^{3+}	1.96	0.69	6	Hydrolysis at about pH 3

2.3.2 Sol-Gel Syntheses

Sol-gel chemistry of metal oxides

Hydrolysis of Al^{3+} salts in aqueous solution

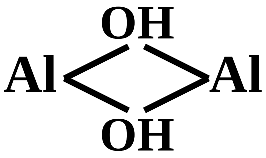
pH < 3: $Al^{3+} + 6\ H_2O \rightarrow [Al(H_2O)_6]^{3+}$ „Hexaquoaluminum cation“

pH > 3: $[Al(H_2O)_6]^{3+} + \rightarrow [Al(OH)_x(H_2O)_{6-x}]^{(3-x)+} + x\ H^+$

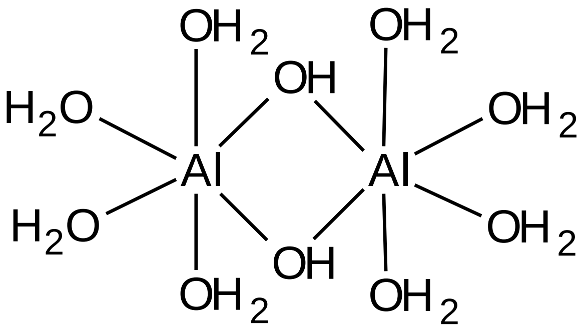
Condensation reactions of $[Al(OH)_x(H_2O)_{6-x}]^{(3-x)+}$ in concentrated solution:

1. **Olation: Formation of μ_2-hydroxo bridges**

Al-OH + HO-Al →



$$\mathrm{Al{-}OH + HO{-}Al} \rightarrow \mathrm{Al}\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{<\!>}}\mathrm{Al}$$



2. **Oxolation: Formation of μ_2-oxo bridges**

$Al\text{-}OH + HO\text{-}Al \rightarrow Al\text{-}O\text{-}Al + H_2O$

2.3.2 Sol-Gel Syntheses

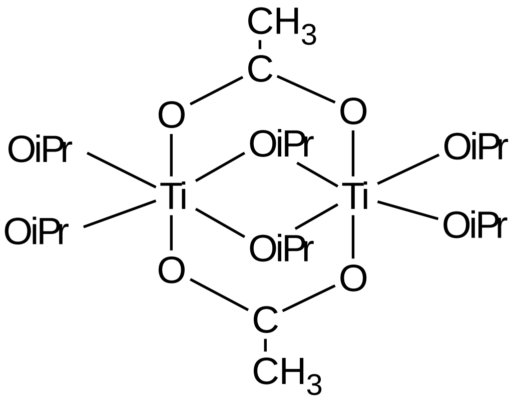
Sol-gel chemistry of metal oxides

Reactivity of alkoxide precursors:

- **$Si(O^i\text{-}Pr)_4$ <<< $Sn(O^i\text{-}Pr)_4$, $Ti(O^i\text{-}Pr)_4$ < $Zr(O^i\text{-}Pr)_4$ < $Ce(O^i\text{-}Pr)_4$**
- **Generally, metal alkoxides are stronger Lewis acids than silicon alkoxides and thus are more reactive (easier attack by nucleophile)**

Moderation of the high reactivity through complexing agents, like e.g. carboxylates

$$2\ Ti(O^i\text{-}Pr)_4 + 2\ CH_3COOH \rightarrow 2\ Pr^iOH +$$



or acetylacetone (H-acac)

$$Ti(O^i\text{-}Pr)_4 + CH_3\text{-}CO\text{-}CH_2\text{-}CO\text{-}CH_3 \rightarrow Ti(O^i\text{-}Pr)_3(acac) + Pr^iOH$$

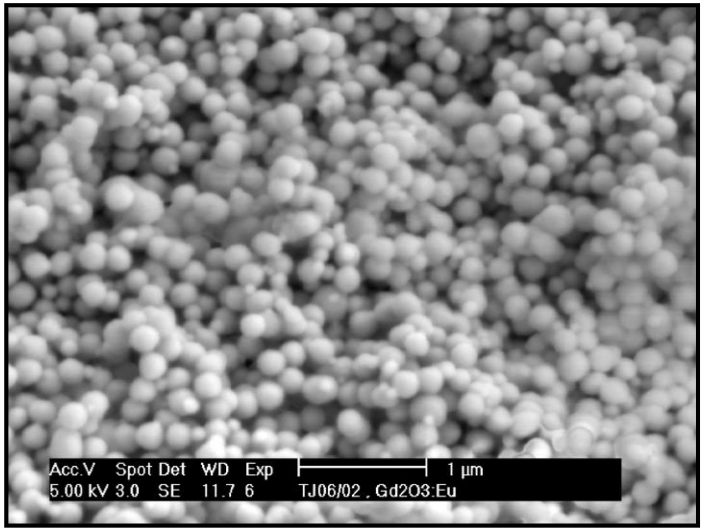
The new precursor has lower reactivity with respect to hydrolysis and condensation

2. Synthesis Techniques of Material Technology

2.4. Nanoparticles

- 2.4.1 Classification of nanoparticles
- 2.4.2 Physical and Chemical Properties
  - Optical Properties
  - Electrical Properties
  - Thermodynamic Properties
  - Surface Chemistry
- 2.4.3 Synthesis of Nanoparticles
  - Deposition from the Gas Phase
  - Reduction of Metal Salts
  - Polyol Method
  - Sol-gel Chemical Synthesis
  - Microemulsion Method
  - Excursion: Nanotubes
- 2.4.4 Applications of Nanoparticles

Y_2O_3:Eu^{3+} phosphor (~200 nm)



2.4.1 Classification of Nanoparticles

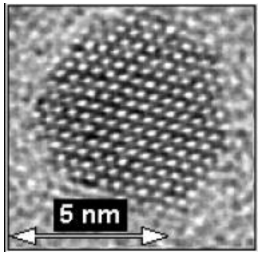
By nanoparticles one understands particles with a medium size from 1 to 100 nm

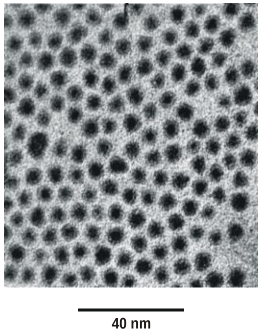
0.1 nm 1 nm 10 nm 100 nm 1 µm 10 µm 100 µm 1 mm 10 mm 100 mm

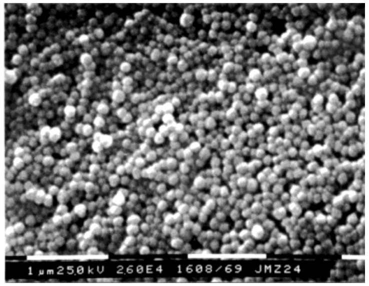
Atoms ***Nanoparticles*** ***Microparticles*** ***Single crystals***

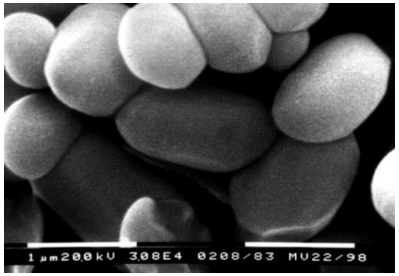
1 ~100 ~100000 $6*10^6$ ~$\propto$ Atoms/molecules → ceramics/crystals

Quantum chemistry ↔ **Quantum size effect** ↔ **Photonics/Solid-state physics Optics** ↔

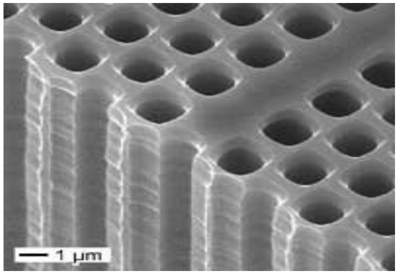








0-dim.	**Quantum dots**	**Luminescent marker**
1-dim.	**Quantum wires**	**Field emitter**
2-dim.	**Quantum wells**	**Active zone in LEDs**
3-dim.	**Bulk**	**Photonic crystals** ⟶

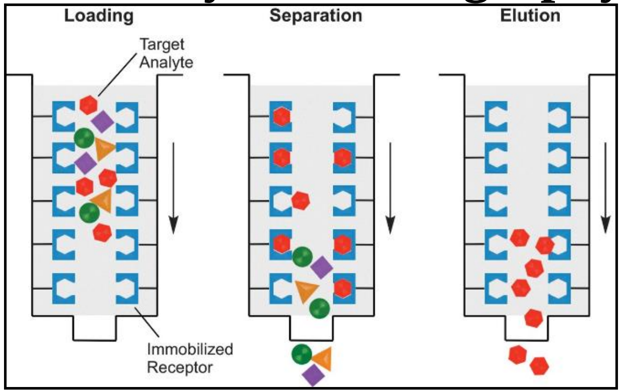


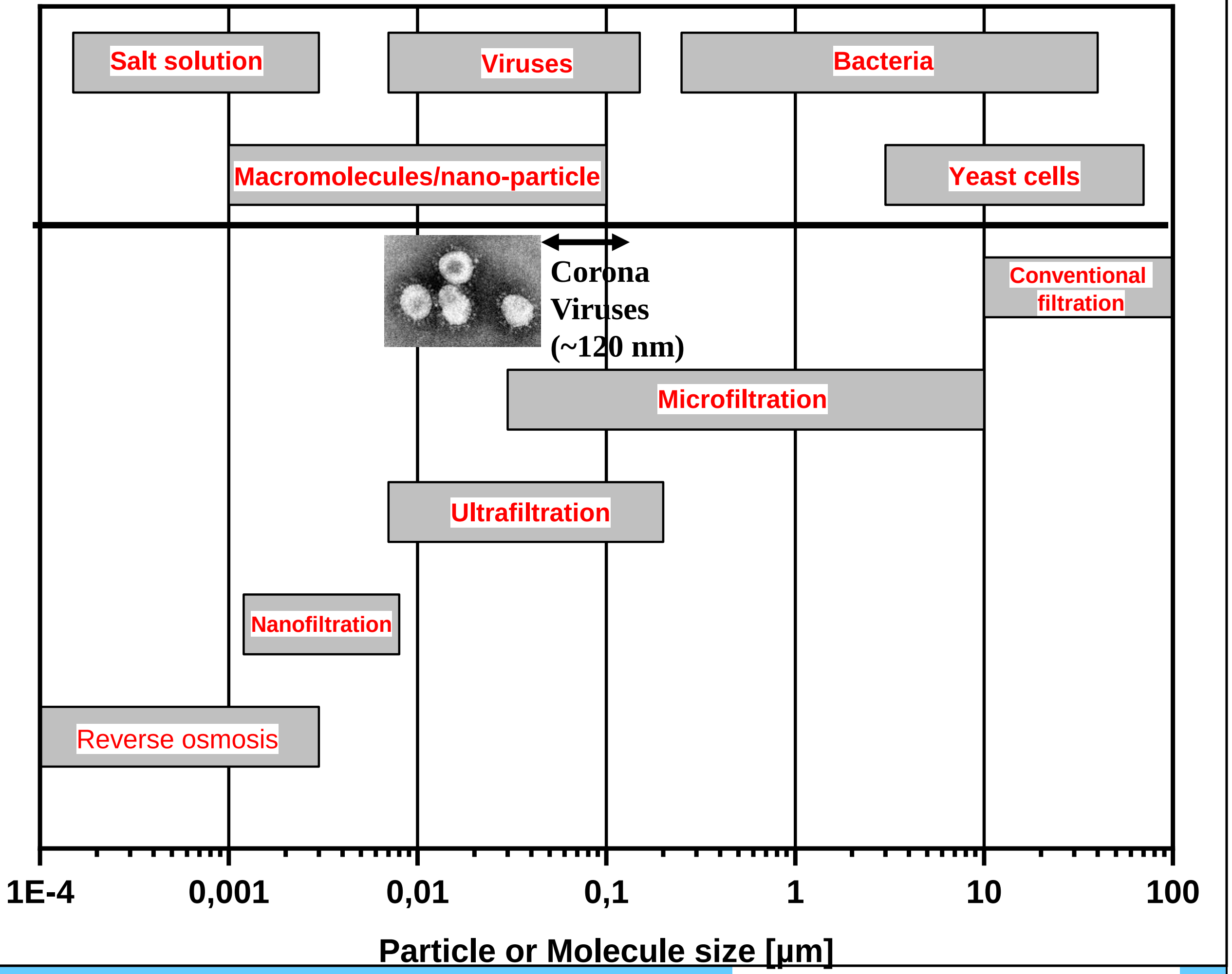
2.4.1 Classification of Nanoparticles

Also viruses and organic macromolecules can be concerned as nanoparticles, which behave in suspension similarly to inorganic nanoparticles

Isolation and separation of nanoparticles:

1. Filtration
2. (Ultra) centrifugation
3. Electrophoresis
4. Affinity chromatography

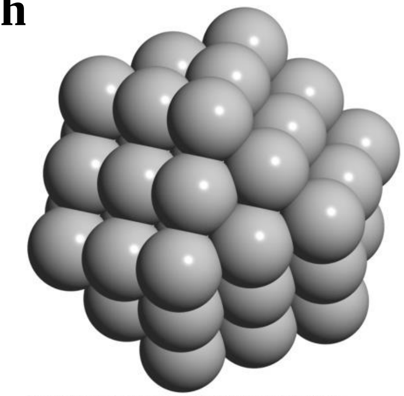




2.4.1 Classification of Nanoparticles

Nanoparticles can be regarded as surface material in macroscopic quantity

Au-cluster with 55 atoms



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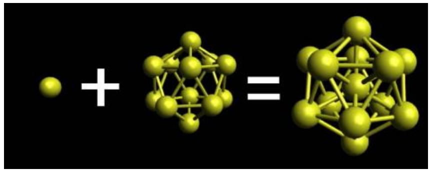
Example

Au-particles with ccp, i.e. cubic-close packing (CN = 12)

Crystal system: cubic with a = 4.08 Å and d(Au-Au) = 2.88 Å

Number of atoms per shell = $10*n^2 + 2$ with n = shell number

n	Atoms in the cluster	Surface atoms	Cluster size
0	1	100 %	-
1	13	92 %	0.58 nm
2	55	76 %	1.4 nm
3	147	63 %	2.1 nm
4	309	52 %	2.8 nm
5	561	45 %	3.5 nm
7	1415	35 %	5 nm
9	2869	28 %	6.5 nm



Formation of Au_{13} cluster

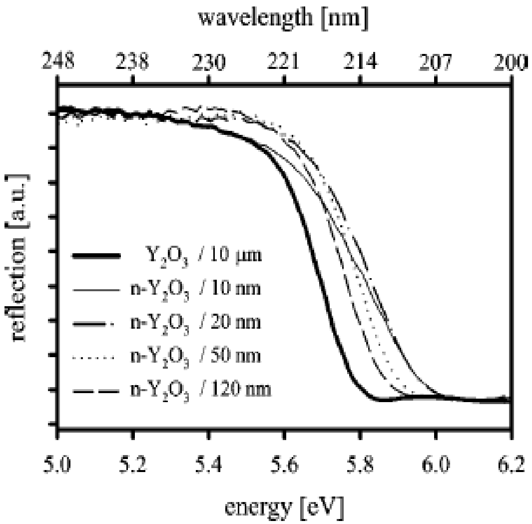
Lycurgus cup (4th century)

2.4.2 Physical and Chemical Properties

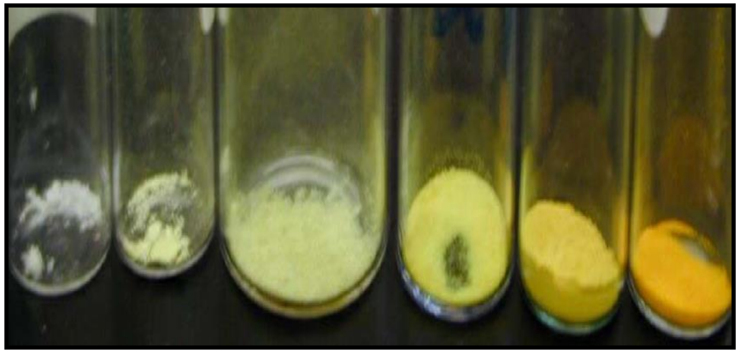
Optical properties

With decreasing particle size the absorption edge of a solid shows a blue shift
(ΔE_g: Oxides < sulphides < selenides < tellurides)

Y_2O_3 (10 nm → 10 µm)



CdS (1 nm → 1 µm)



Increasing particle size

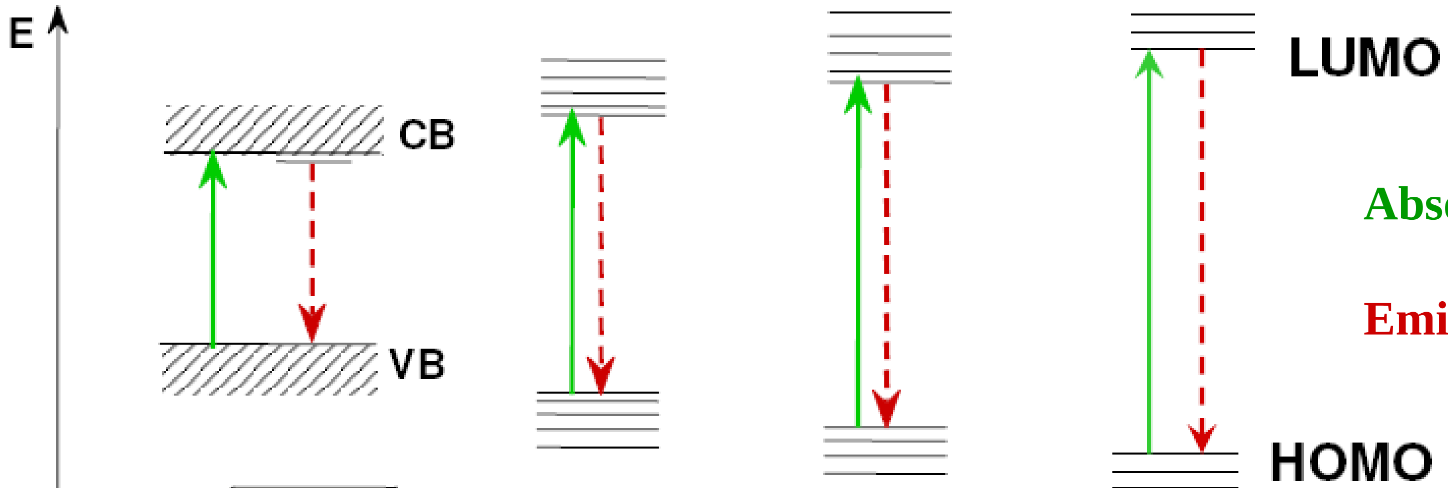
HgS (1 nm → 1 µm)

Further examples

- Colour of precipitated HgS particles: red (freshly produced) or black (aged)
- Colour of Au colloids in glass („Gold Ruby Glass“): yellow to red

2.4.2 Physical and Chemical Properties

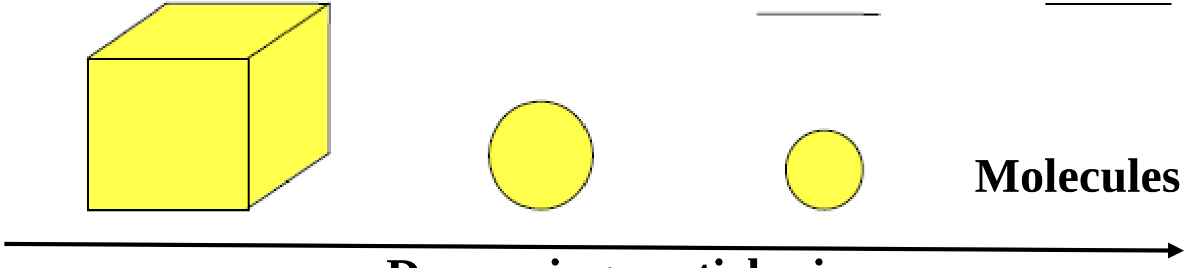
Optical properties



Absorption

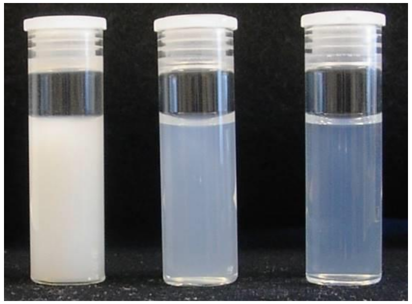
Emission

Solid state compounds



Molecules

Decreasing particle size



100 nm 40 nm 20 nm

particle size

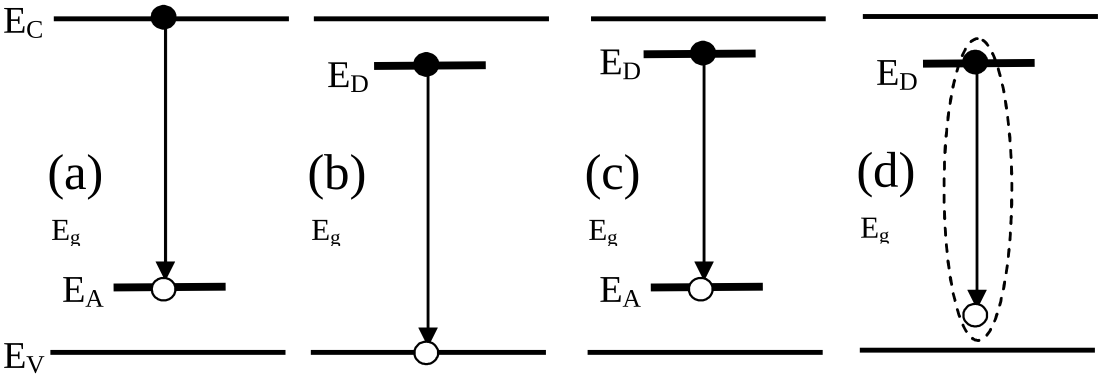
→ enhanced band gap by quantum size effects

→ reduced scattering („Tyndall effect“) → bluish shine

2.4.2 Physical and Chemical Properties

Optical properties – InP QDots

Intrinsic luminescence mechanisms and energy



Radiating recombination via defect states :

(a) Conduction band-acceptor state transition

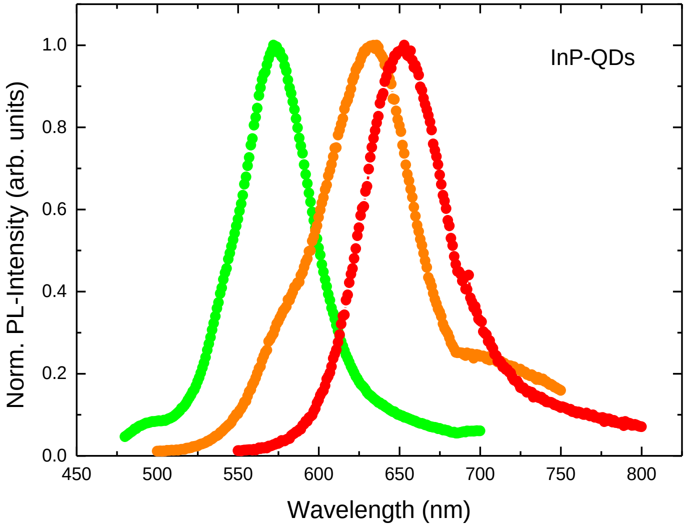
(b) Donor state-valence band transition

(c) Donor-acceptor recombination

(d) "Bound exciton" recombination

The energy of transition depends substantially on the band gap of the material

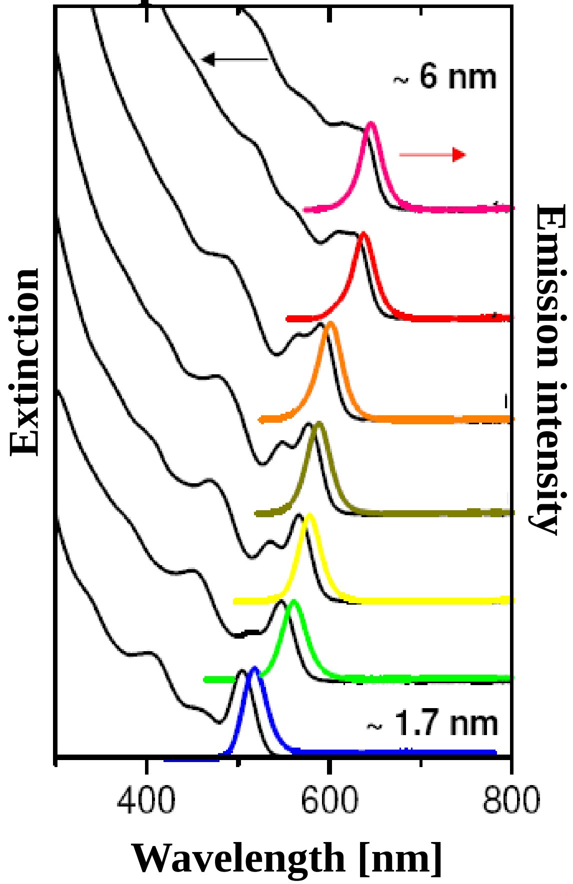
Emission color of InP QDots



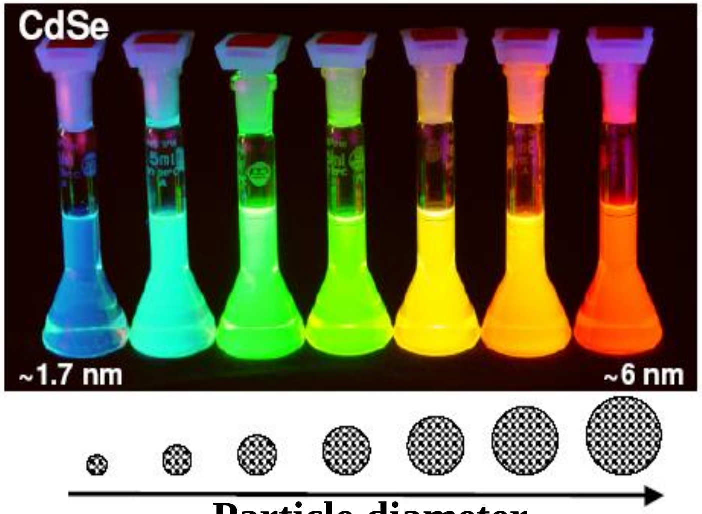
2.4.2 Physical and Chemical Properties

Optical properties – CdSe QDots

Absorption and emission spectra



Photoluminescence upon UV excitation



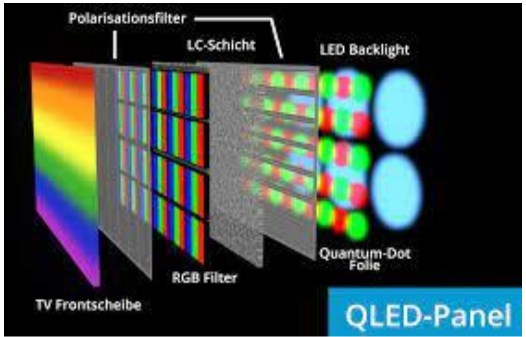
Particle diameter

~200 Atoms ~6200 Atoms

Application in TV sets:

Nano Crystal Technology

→ **QLED-Panels**

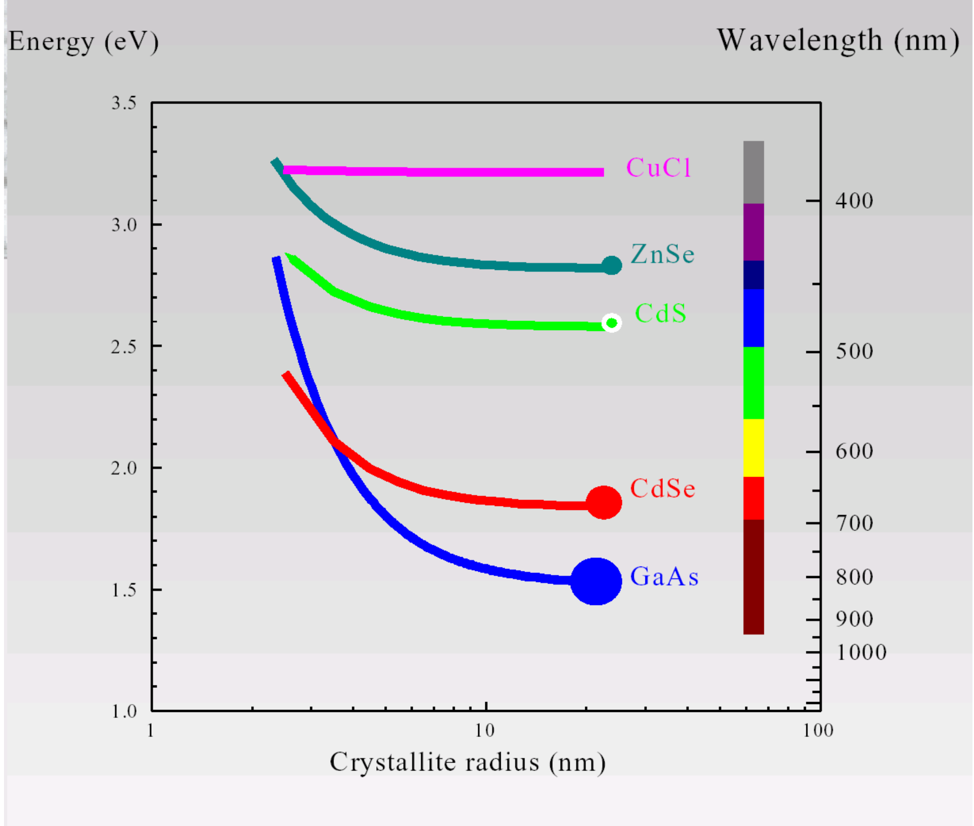


2.4.2 Physical and Chemical Properties

Optical properties – Luminescence as function of host and particle size

with $$r_B = \frac{4\pi\epsilon_0\epsilon_r\hbar^2}{m_e e^2}\left(\frac{m_e^*+m_h^*}{m_e^* m_h^*}\right)$$

Semiconductor	Bohr radius r_B	Band gap E_g
CuCl	1.3 nm	3.4 eV
ZnSe	8.4 nm	2.58 eV
CdS	5.6 nm	2.53 eV
CdSe	10.6 nm	1.74 eV
GaAs	28.0 nm	1.43 eV

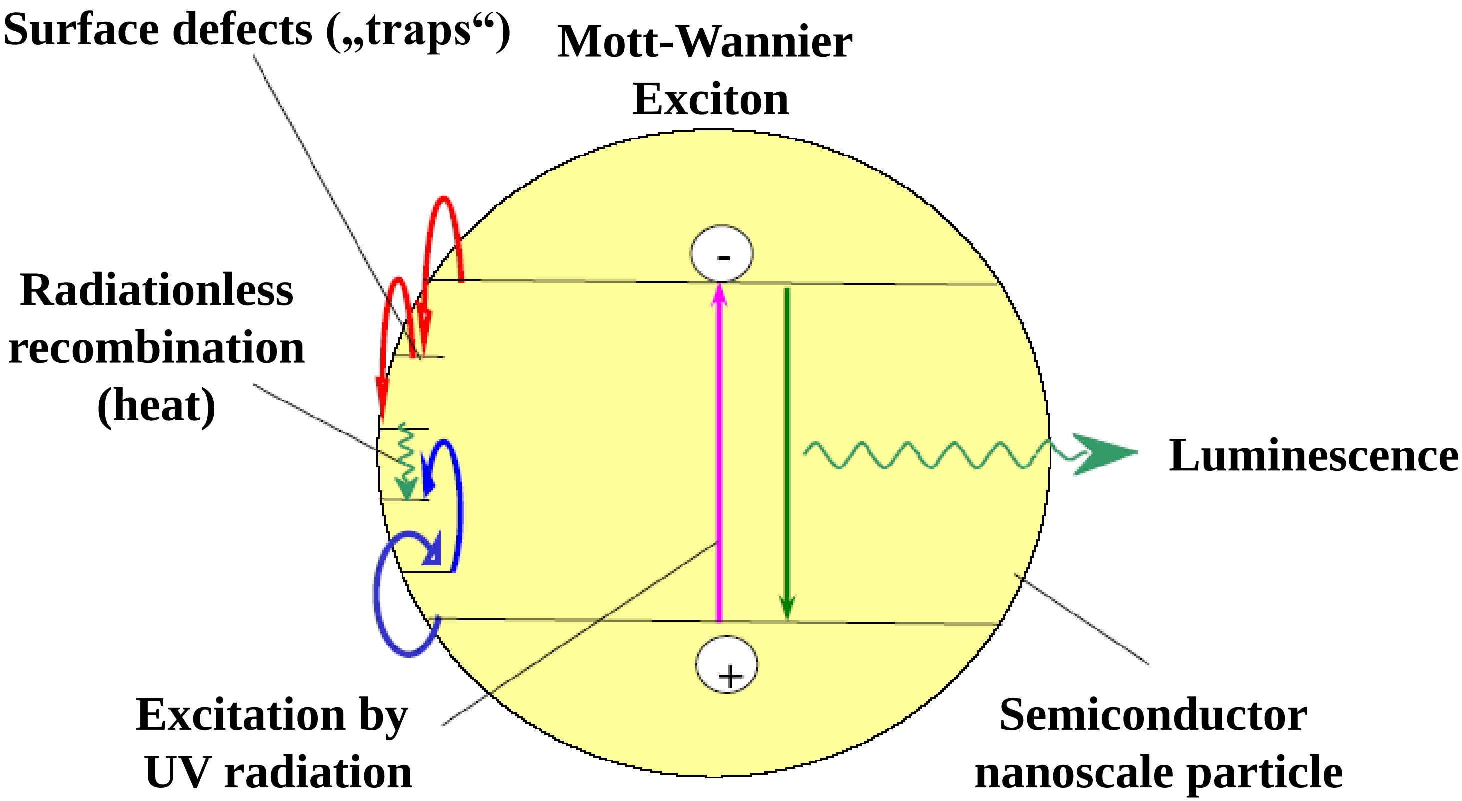


Dependence of optical properties on PSD

- **strong for chalcogenides and pnictides**
- **weak for oxides and fluorides**

2.4.2 Physical and Chemical Properties

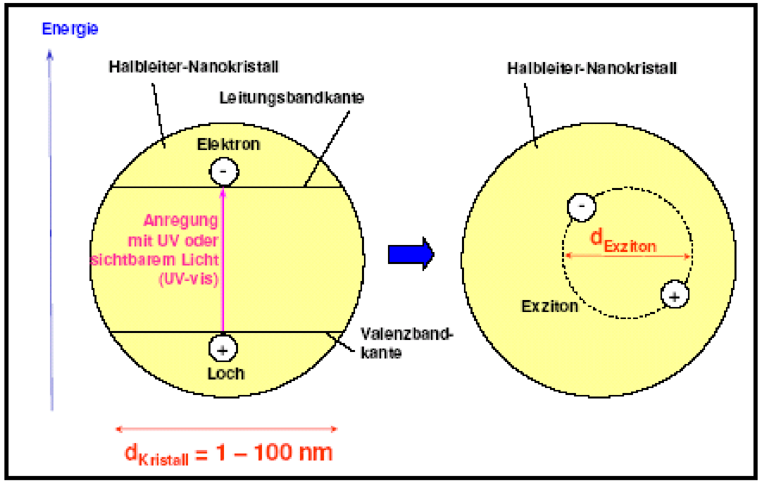
Optical properties – Quenching due to surface defects or surface phonons



Consequence: Internal PL quantum yield decreases with declining particle size IQY = τ/τ_r

2.4.2 Physical and Chemical Properties

Optical properties - Capped Quantum Dots (QDots)

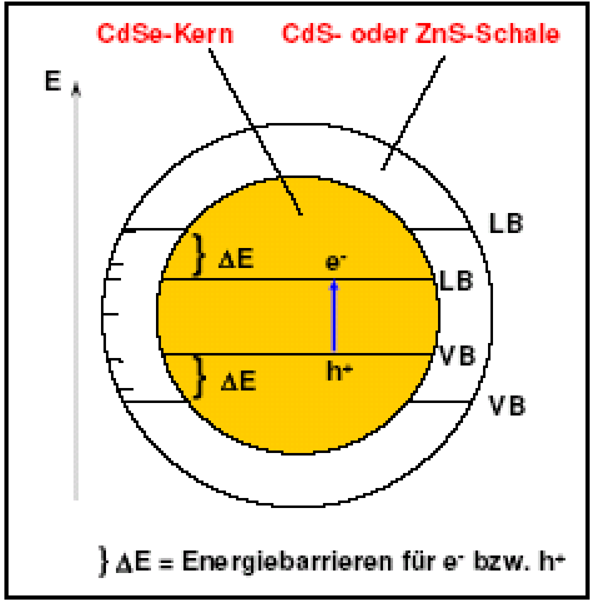


Main application problems of QDots

- **Stability (diffusion)**
- **Thermal quenching**
- **Surface quenching of excited states (excitons) due to their large exciton Bohr radius**

Material	r_B* [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

Exciton Bohr radius $r_B^* = \varepsilon_r \cdot (m/\mu) \cdot r_B$ and $r_B = 0.053$ nm



Epitactic exciton reflective coating → core-shell/core-shell-shell

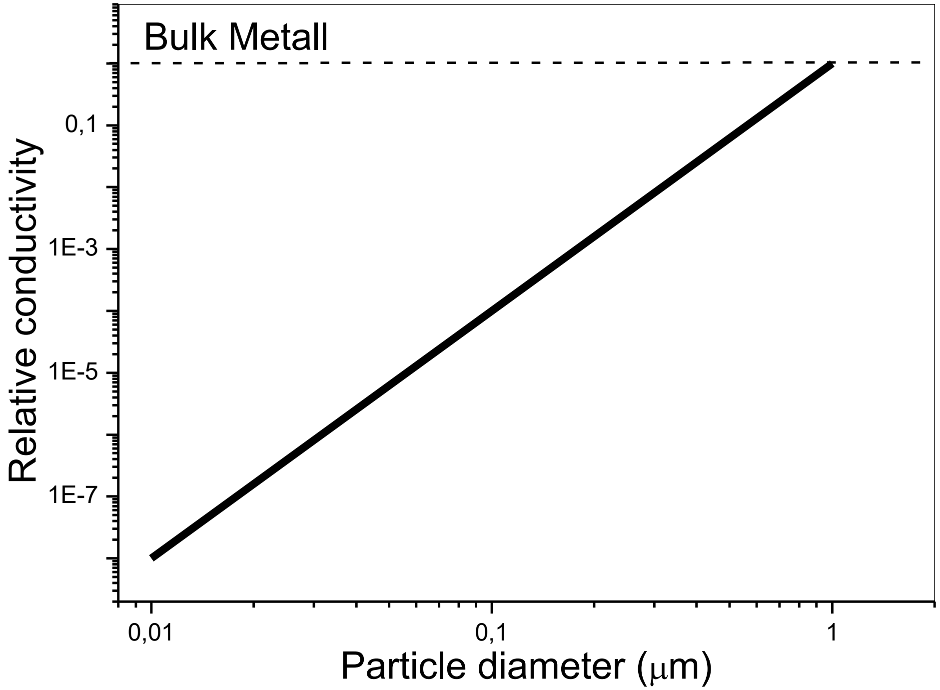
2.4.2 Physical and Chemical Properties

Electrical properties

Conductivity is a consequence of the band structure of solids and the resulting delocalization of the electrons

With decreasing particle size the electrical conductivity of metal particles decreases, since an increasing localization of the electrons occurs

⇒ Very small particles are virtually non conductive by the discretization of the energy levels



2.4.2 Physical and Chemical Properties

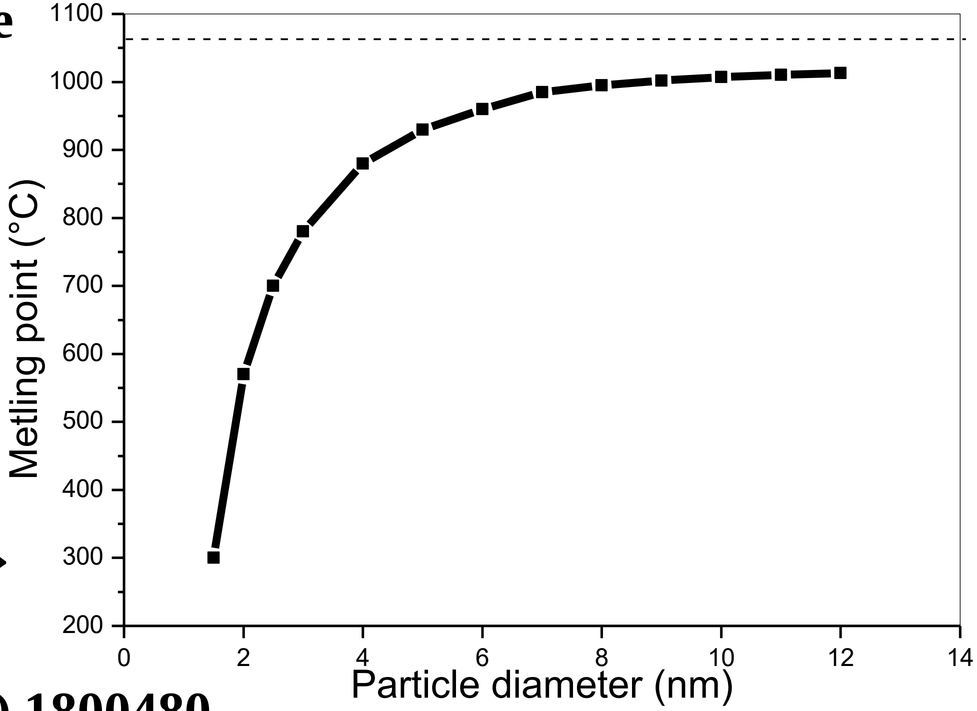
Thermodynamic properties

With decreasing particle size the melting point decreases, while the solubility increases ⇒ Lower coordination number of surface atoms

The particle size can thus also influence thermodynamic quantities

T_m(Au, bulk) = 1063 °C
T_m(Au, „nano“) < 1063 °C

„Hüttig“ temperature: ~ 319 °C
→ Au surface atoms become mobile →



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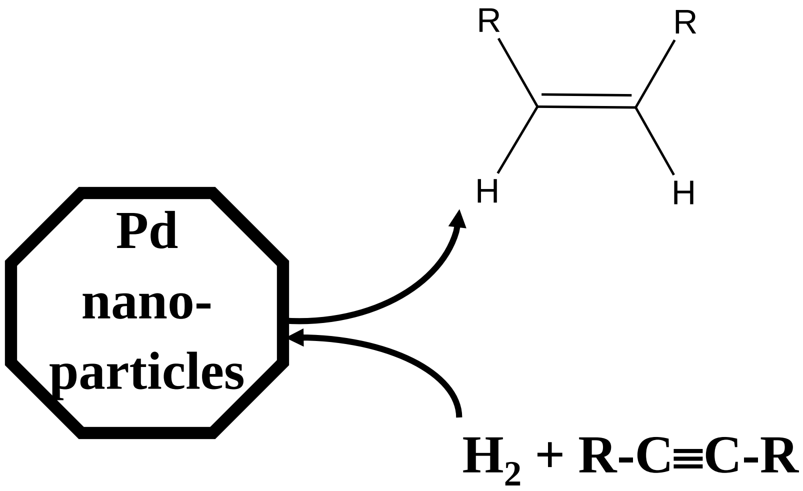
2.4.2 Physical and Chemical Properties

Surface chemistry

Nanoparticles find a multiplicity of applications in the heterogeneous catalysis due to their high specific surface area

⇒ e.g. as the Pd catalyst for stereoselective hydrogenations in the automotive catalyzer

$CH_3\text{-}C{\equiv}C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 + H_2 \rightarrow$ cis-2-hexene + trans-2-hexene



$H_2 + R\text{-}C{\equiv}C\text{-}R$

Automotive catalyzer

Pd/Pt on a ceramic substrate

$2\,CO + O_2 \rightarrow 2\,CO_2$

$C_xH_y + (x + y/4)\,O_2 \rightarrow x\,CO_2 + y/2\,H_2O$

$2\,NO + 2\,CO \rightarrow N_2 + 2\,CO_2$

$C_xH_y + (2x + y/2)\,NO \rightarrow$

$x\,CO_2 + (x + y/4)\,N_2 + y/2\,H_2O$

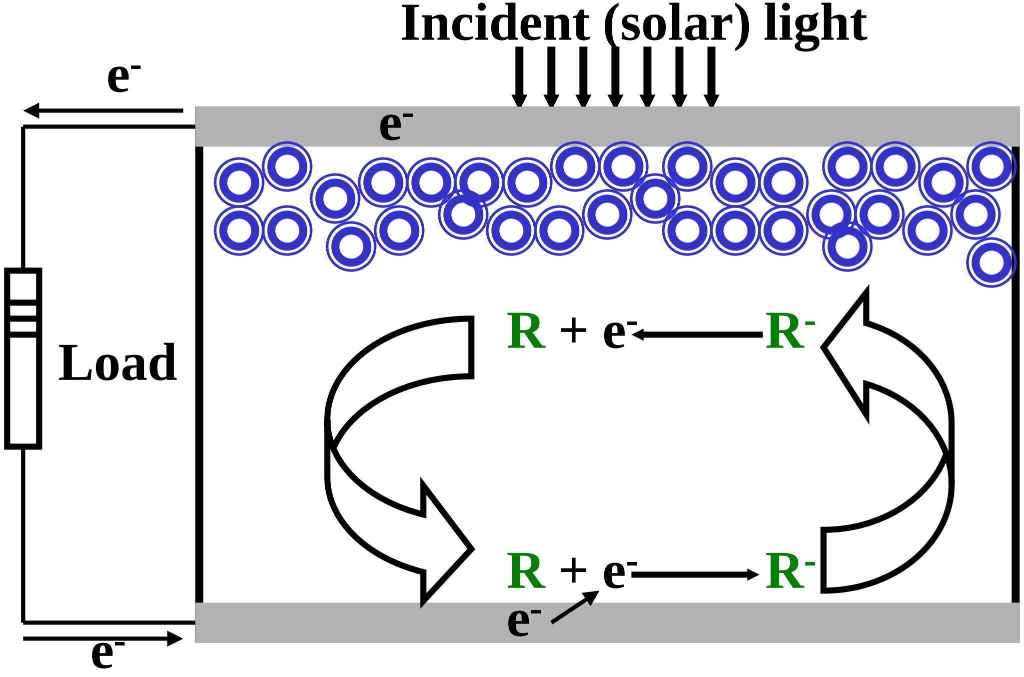
2.4.2 Physical and Chemical Properties

Surface chemistry

Nanoparticles can very easily absorb or emit electrons due to their high specific surface area

⇒ Applications in solar cells and cathodes (as thermionic emitters, e.g. (Ca,Sr,Ba)O onto W-electrodes)

Grätzel solar cell



Glass substrate with SnO_2:F (0.5 µm)

TiO_2 nanoparticle membrane (thickness: 5-10 µm)

Electrolyte solution comprising a redox mediator R

Glass substrate with SnO_2:F (0.5 µm) and Pt-coating (2 µm)

2.4.3 Synthesis of Nanoparticles

Driving force for particle growth $G = G_{surface} + G_{volume}$

Minimization of a particle energy by minimization the ratio of surface to volume:

Surface energy increases quadratically:

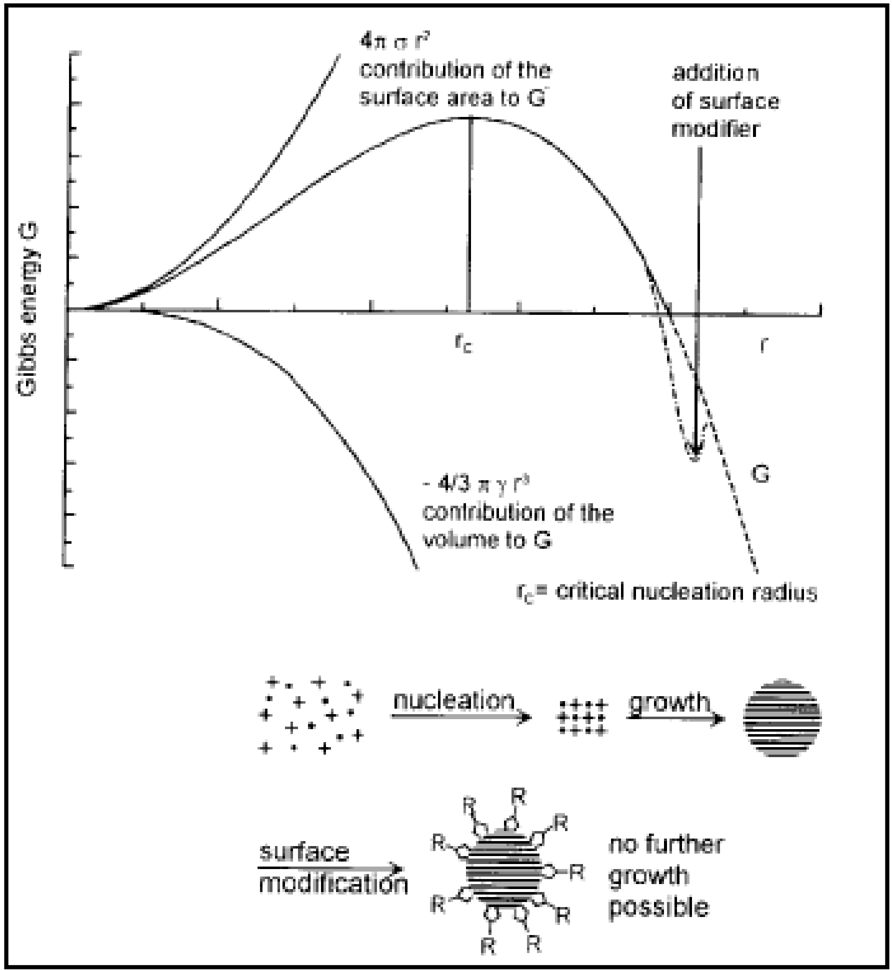
$G_{surface} \sim 4\pi r^2\sigma$ with σ = surface tension [N/m]

Volume energy increases cubically:

$G_{volume} \sim 4/3\pi r^3\gamma$ with γ = chemical potential

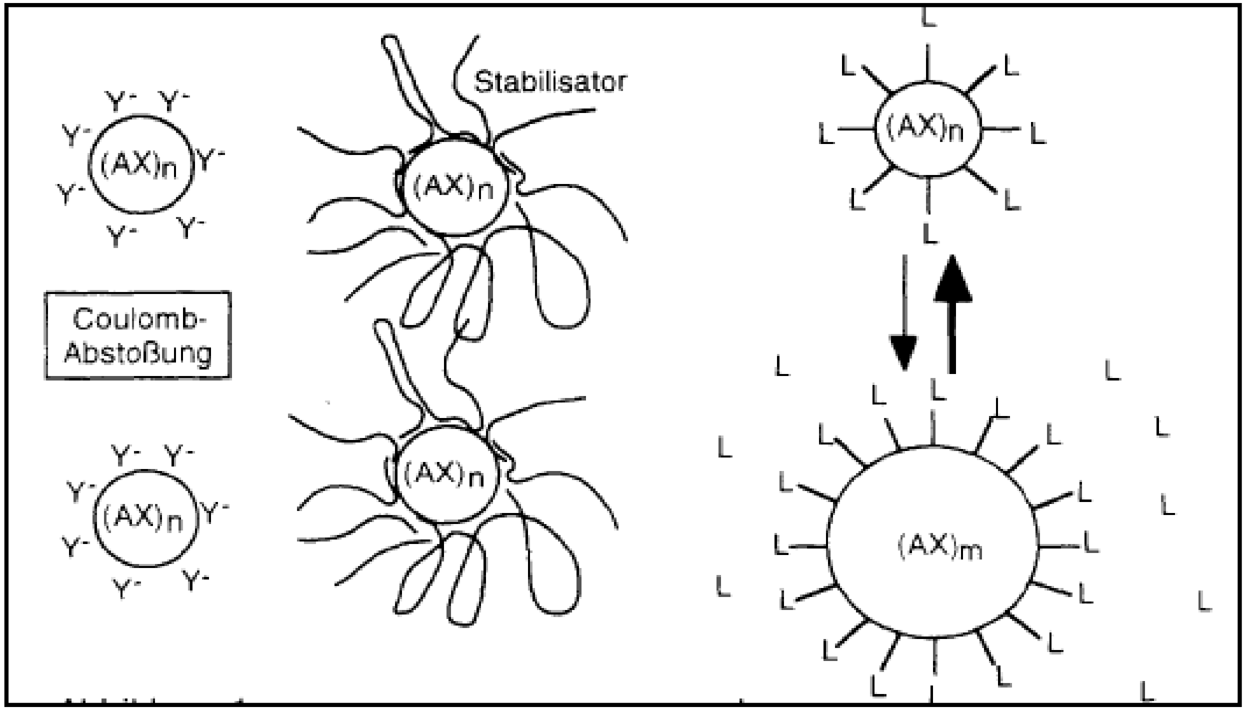
Overcompensation of the surface energy at a defined radius r_{min}

Very small particles ($\sim r_c$) are very reactive, since they possess a higher chemical potential than micrometer particles



2.4.3 Synthesis of Nanoparticles

Growth stop of NPs and the adjustment of particle size



Possibilities of stabilization

1. **Electrostatic:** **Adsorption of ions at the surface**
2. **Steric/entropic:** **Long-chain compounds/polymers onto the surface**
3. **Thermodynamic:** **Ligand molecules bound tightly to the surface and Energy balance by doubling of the particle radius:**

$8\ (AX)_nL_k \rightarrow (AX)_{8n}L_{4k} + 4k\ L$ (free ligands) ⇒ Separation of ligands i.e. strong metal-ligand bonding are energetically more favorable than small clusters

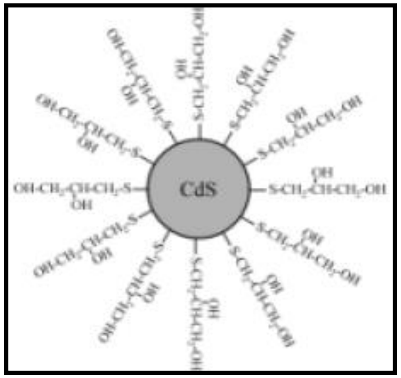
2.4.3 Synthesis of Nanoparticles

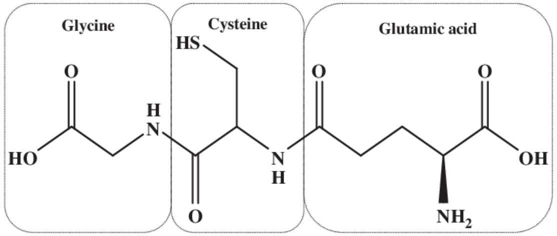
Growth stop: adjustment of the particle size

To 3: Thermodynamic Stabilization

The particle growth is stopped by complexation of surface atoms by ligands

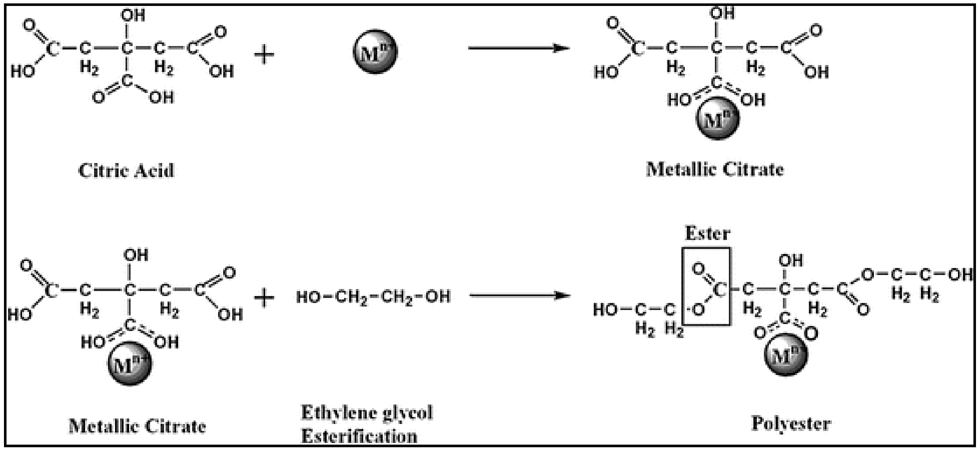
Class of materials	Example	Suitable ligands
Sulfides	CdS	Cystein, glutathione, thioglycerol
Oxides	$Y_3Al_5O_{12}$	Citrate, EDTA, oleate
Phosphide, arsenide	InP, GaAs	Trioctylphosphinoxide (TOPO)
Fluorides	$Na(Y,Yb)F_4$	CaF_2





2.4.3 Synthesis of Nanoparticles

Formation of nanoscale particles through the polymerization of metal complexes (Pechini method)



Requirement

- Chelating ligands, which can undergo polymerisation or polycondensation e.g. as polyesters
- Carboxylates: Citrate, tartrate, malonate, oxidation products of PVA

Reaction principle on the example of the formation of TiO_2 nanoparticles

1. $Ti(OPr^i)_4$ + propanol + H_2O + citric acid → $Ti_8O_{10}(C_6H_5O_7)_4(H_2O)_{12}\cdot 14H_2O\cdot 3HOPr^i$
2. Polycondensation of metal complexes by heating or by oxidation of alcoholate (oxidising agent: NO_3^- or CrO_4^{2-})
3. Decomposition of the polycondensate by strong heating leads to the TiO_2 nanopowders

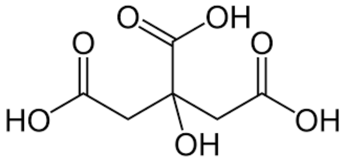
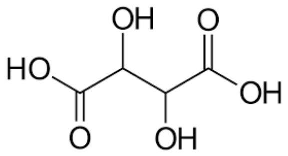
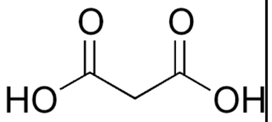
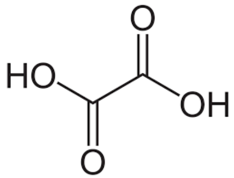
2.4.3 Synthesis of Nanoparticles

Modifications of Pechini method

Di- and polyols

ethanediol → propanediol → butanediol → PVA

Acid strength of the chelating agents (pKs values)

Citric acid	$C_6H_8O_7$	$H_3Cit \overset{(3.13)}{\rightleftharpoons} H_2Cit^- \overset{(4.76)}{\rightleftharpoons} HCit^{2-} \overset{(6.4)}{\rightleftharpoons} Cit^{3-}$	
Tartaric acid	$C_4H_6O_6$	$H_2Tar \overset{(3.03)}{\rightleftharpoons} HTar^- \overset{(4.37)}{\rightleftharpoons} Tar^{2-}$	
Malonic acid	$C_3H_4O_4$	$H_2Mal \overset{(2.85)}{\rightleftharpoons} HMal^- \overset{(5.7)}{\rightleftharpoons} Mal^{2-}$	
Oxalic acid	$C_2H_2O_4$	$H_2Ox \overset{(1.25)}{\rightleftharpoons} HOx^- \overset{(3.81)}{\rightleftharpoons} Ox^{2-}$	

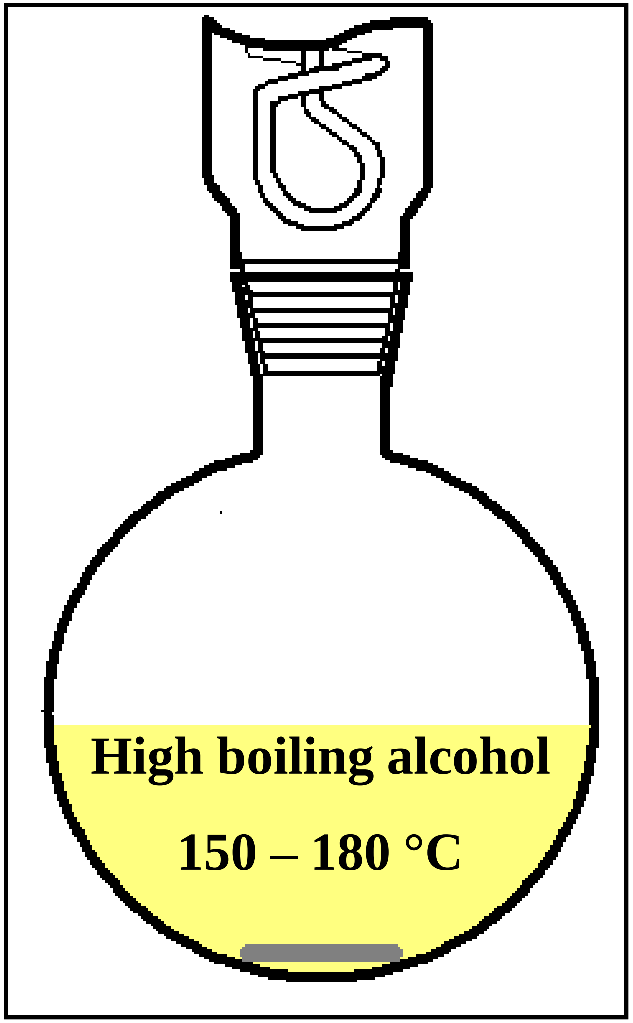
2.4.3 Synthesis of Nanoparticles

Summary of the nanomaterials produced so far by the Pechini method

Compound	Structural Type	Decomposition at [°C]	Cristallisation at [°C]
$BaTiO_3$	Perovskite	600	600
Al_2O_3	α-Corundum	800	1150
SiO_2	ß-Cristobalite	800	1100
$Al_6Si_2O_{13}$	Mullite	800	1300
$ZrSiO_4$	Zircon	800	1100
$CaSiO_3$	Wollastonite	650	900
ß-Ca_2SiO_4	Belite	700	800
$Y_3Al_5O_{12}$	Garnet	600	900
$Y_3Fe_5O_{12}$	Garnet	600	900
$Mg_2Al_4Si_5O_{18}$	Cordierit	800	1200
$BaAl_2Si_5O_{18}$	Hexacelsiane	800	1100
YPO_4	Xenotime	500	830
Y_2O_3	Bixbyite	650	650

2.4.3 Synthesis of Nanoparticles

Polyol method



Application for production of

1. **Metal nanoparticles**
2. **Oxide nanoparticles**

← **soluble salts**

a) Pure alcohol (reductive synthesis)

b) + H_2O

c) + H_2O + $NH_4H_2PO_4$

d) + Thioglycerol

Centrifugation

+ washing →

a) Ag, Pd, Fe, Co, Ni
b) ZnO, $CoAl_2O_4$, Fe_2O_3
c) $LaPO_4$, YPO_4
d) ZnS, CdS

2.4.3 Synthesis of Nanoparticles

Polyol method

Precursor: Acetates

$Co(CH_3COO)_2$
$AlOH(CH_3COO)_2$
$Fe(CH_3COO)_3$
$La(CH_3COO)_3$
$Zn(CH_3COO)_2$

Precipitants

$H_2O \rightarrow OH^- \rightarrow O^{2-}$
$NH_4H_2PO_4 \rightarrow PO_4^{3-}$
Thiourea $\rightarrow S^{2-}$

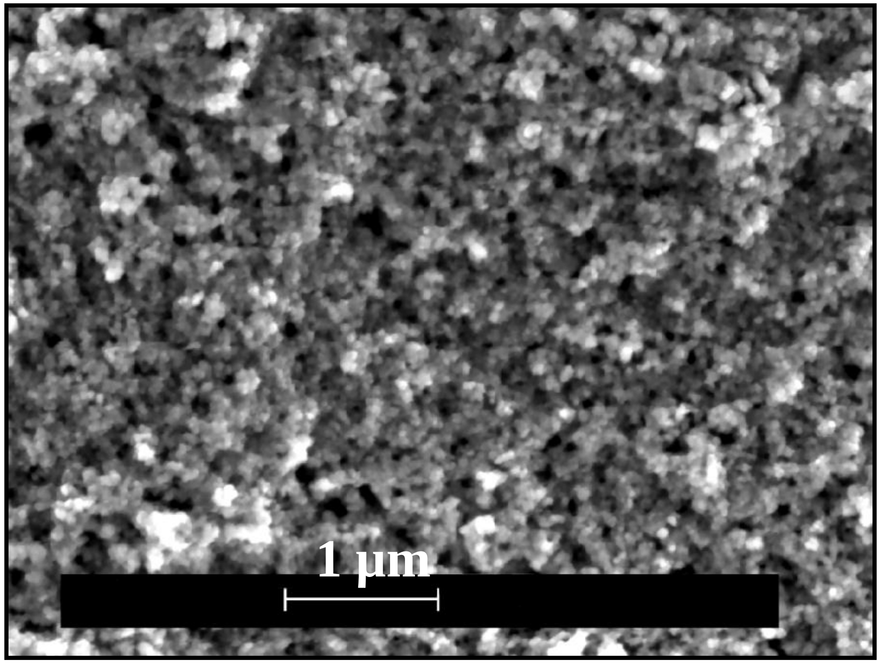
Solvents

Diethylene glykol
Ethylene glycol
Glycerol
Glycerin

Typical particle size:

20 – 200 nm

SEM image of $LaPO_4$ nanoparticles



2.4.3 Synthesis of Nanoparticles

Sol-gel chemical synthesis

Synthesis of a nanoparticle suspension → Layer preparation

$Ti(OCH(CH_3)_2)_4$ in i-Propanol

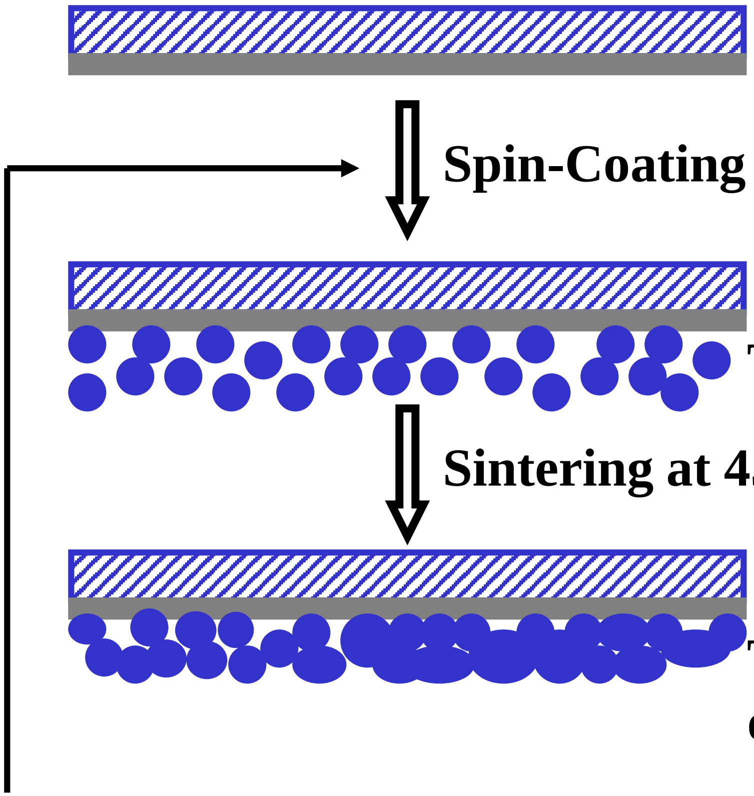
Hydrolysis ⇩ + H_2O

Amorphous TiO_2 in i-Propanol/H_2O

Condensation ⇩ + HNO_3

Cristallization ⇩ 8 h 80 °C

Colloidal TiO_2 (Anatas, 8 nm) in H_2O



Glass substrate

⇩ Spin-Coating

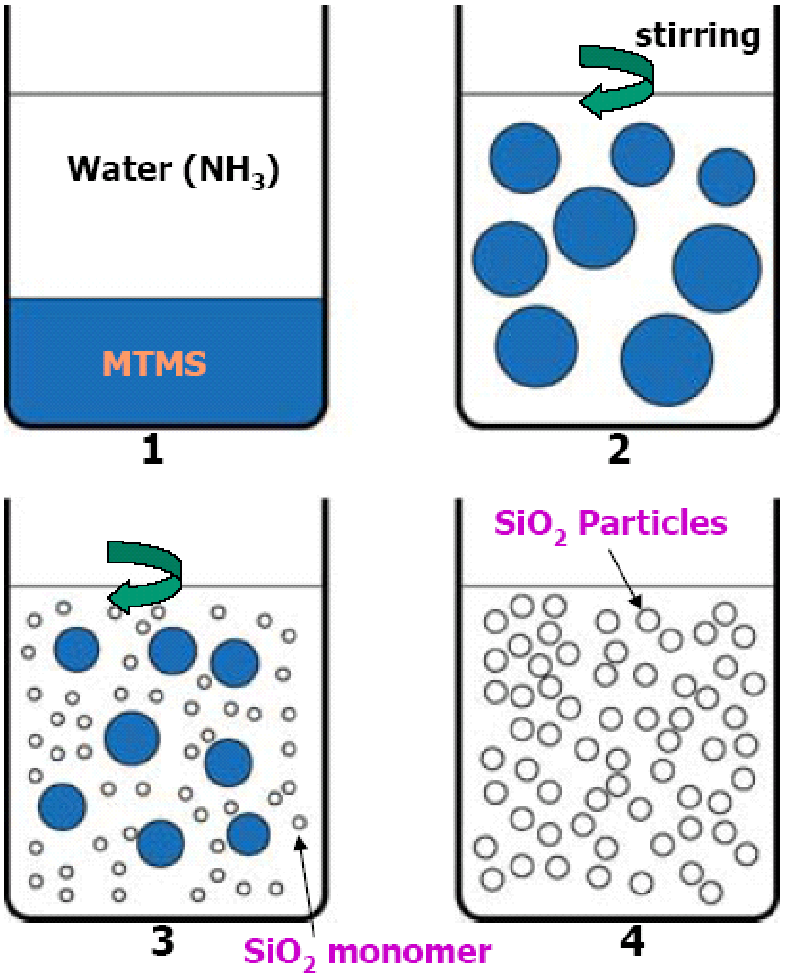
TiO_2-layer

⇩ Sintering at 450 °C

TiO_2-layer
d ~ 10 – 30 nm

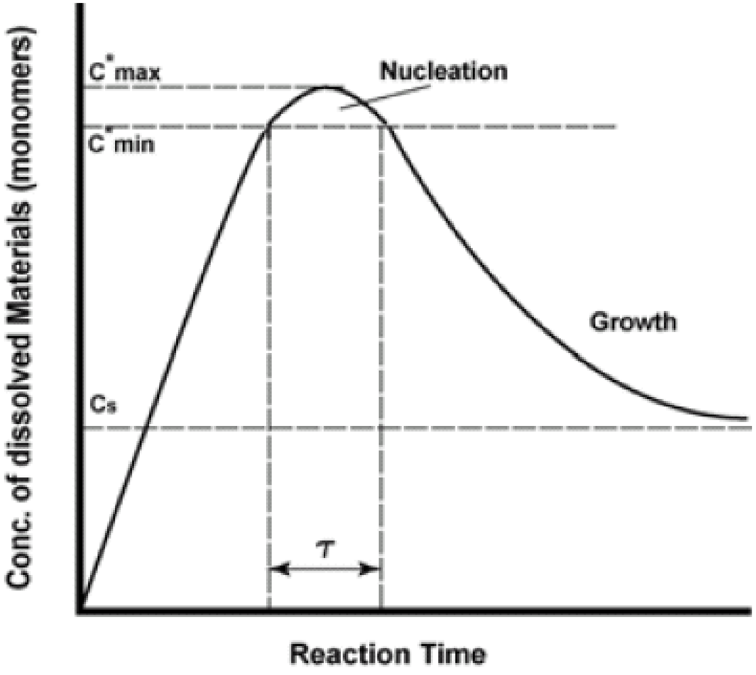
2.4.3 Synthesis of Nanoparticles

Sol-gel chemical synthesis



MTMS = Methyltrimethoxysilan

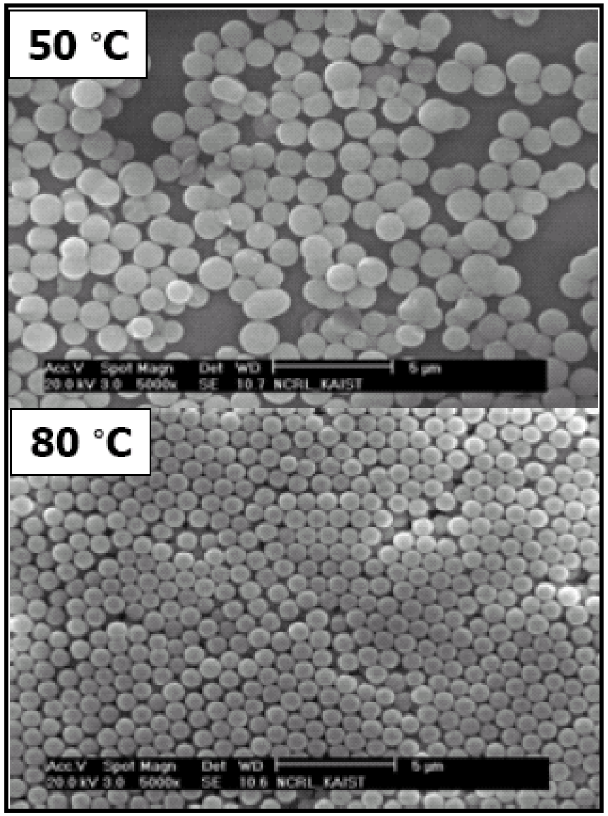
Lamer diagram



- To make monodispersed Particles, the time τ should be decreased.

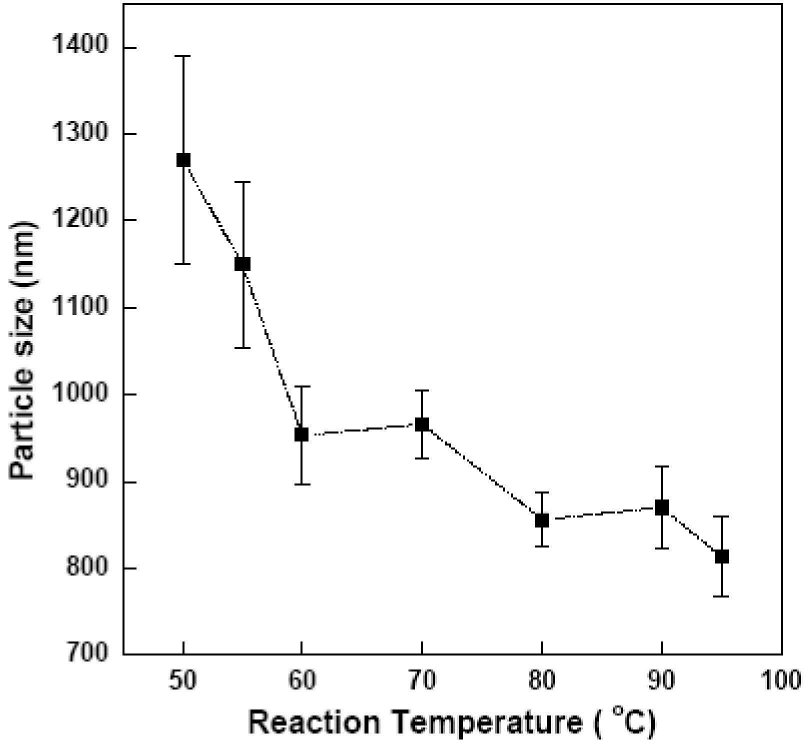
2.4.3 Synthesis of Nanoparticles

Sol-gel chemical synthesis



0.6 M MTMS, 1 M NH_3

Particle size as a function of temperature

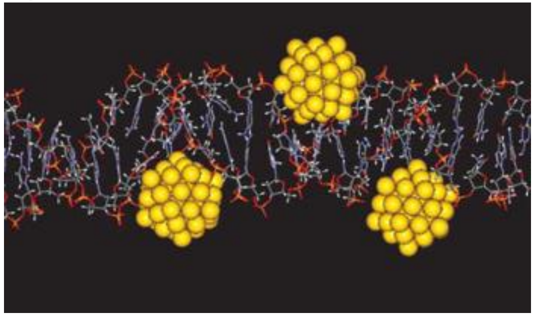


Temperature↑ ⇒ Reaction rate↑ ⇒ Nucleation time↓ ⇒ Particle size↓

2.4.3 Synthesis of Nanoparticles

Reduction of metal salts

For the synthesis of metal clusters
e.g. of citrate-stabilized Au clusters (Au_{55})



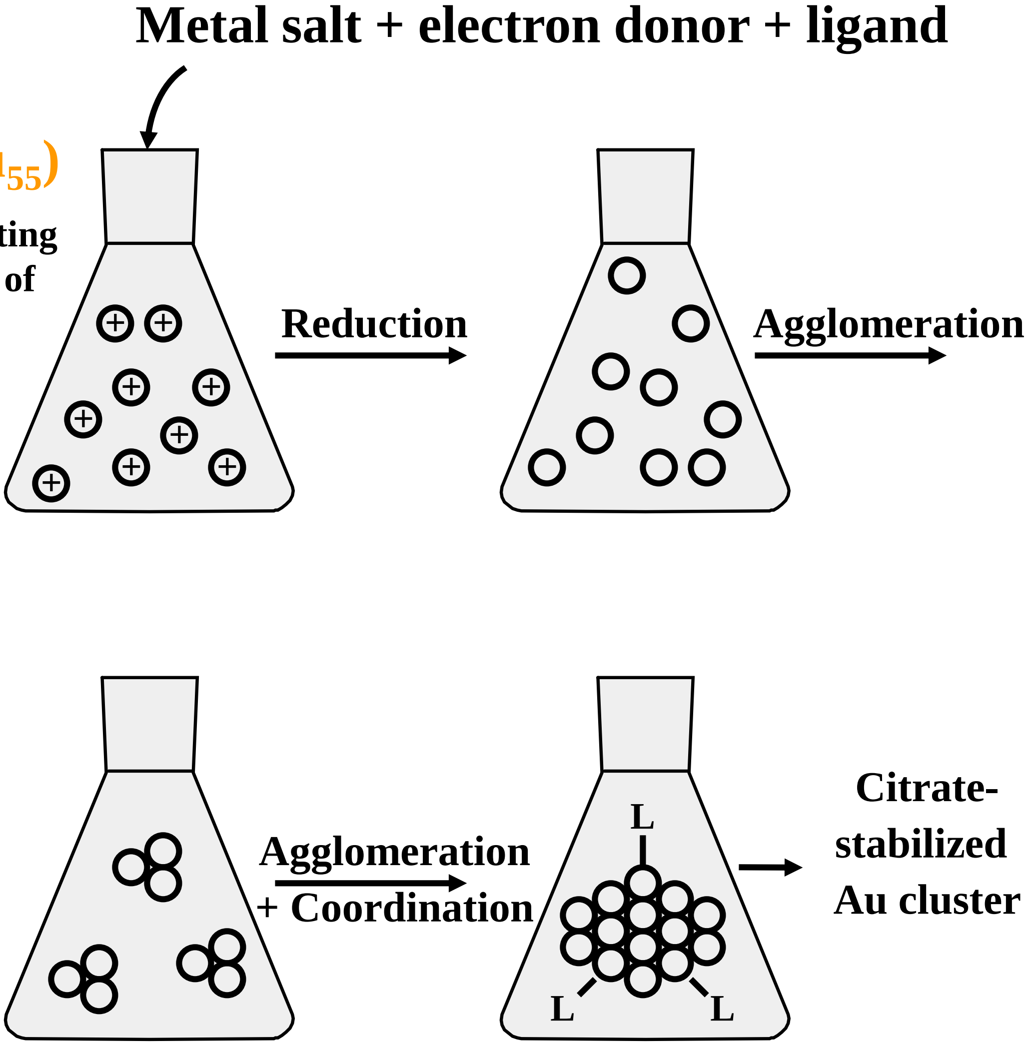
Au_{55} cluster interacting with major grooves of B-DNA, applied as radiosensitizer in cancer therapy

$HOC(COOH)(CH_2COOH)_2 + 10\ OH^-$
$\rightarrow\ 6\ CO_2 + 18\ e^- + 8\ H^+ + 5\ H_2O$

$n\ HAuCl_4 + 3n\ e^- \rightarrow$
$n\ Au + n\ HCl + 3n\ Cl^-$

$n\ Au + x$ citrate $\rightarrow$
$Au_n(\text{citrate})_x$-complex

Analogous with Rh, Ir, Pd, Pt, Cu, Ag



2.4.3 Synthesis of Nanoparticles

Reduction of metal salts

Synthesis of metal nanoparticles requires strong reducing agents

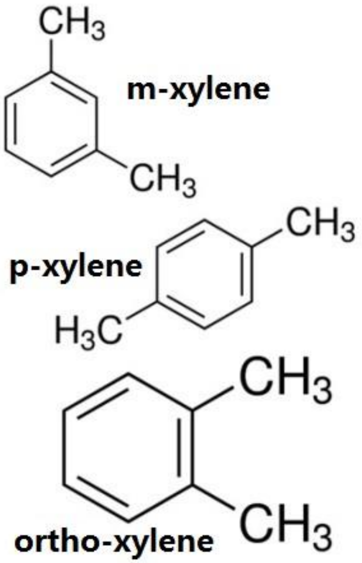
Reduction with $NaBH_4$:

a) In water

$4\ Co^{2+} + 8\ BH_4^- + 18\ H_2O \rightarrow Co_2B + 25\ H_2 + 6\ H_3BO_3$

b) In Diglyme

$Co^{2+} + 2\ BH_4^- \rightarrow Co(s) + H_2(g) + B_2H_6(g)$



Reduction with alkali metals in xylene (Rieke method)

$AlCl_3 + 3\ K \rightarrow Al + 3\ KCl$

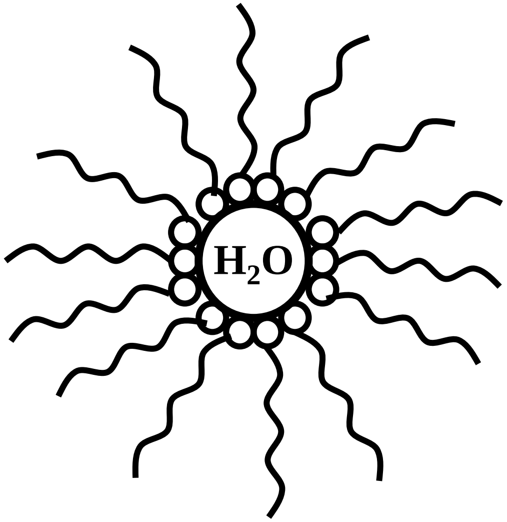
(Activation of the potassium by addition of naphthalene or anthracene)

2.4.3 Synthesis of Nanoparticles

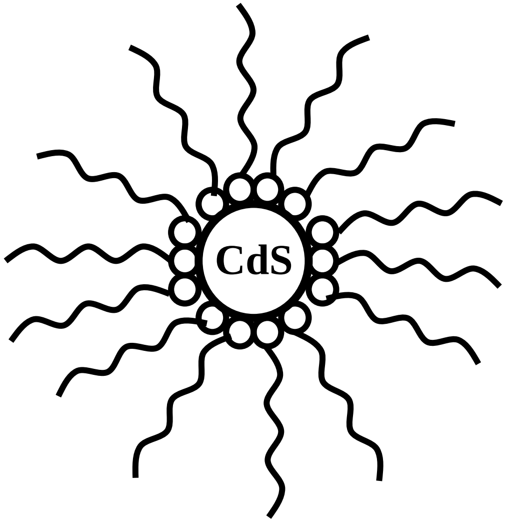
Microemulsion method

Water/oil microemulsion

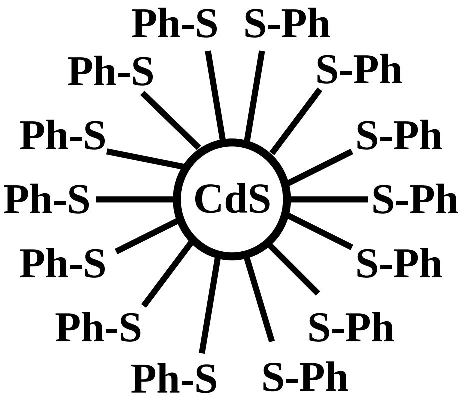
$$H_2O + \text{detergent} \xrightarrow{\text{Hydrocarbon}}$$



$$\xrightarrow[2)\ S^{2-}]{1)\ Cd^{2+}}$$



$$\xrightarrow{\text{Ph-SH}}$$



Detergent = alkyl sulfate, alkyl carboxylate

2.4.3 Synthesis of Nanoparticles

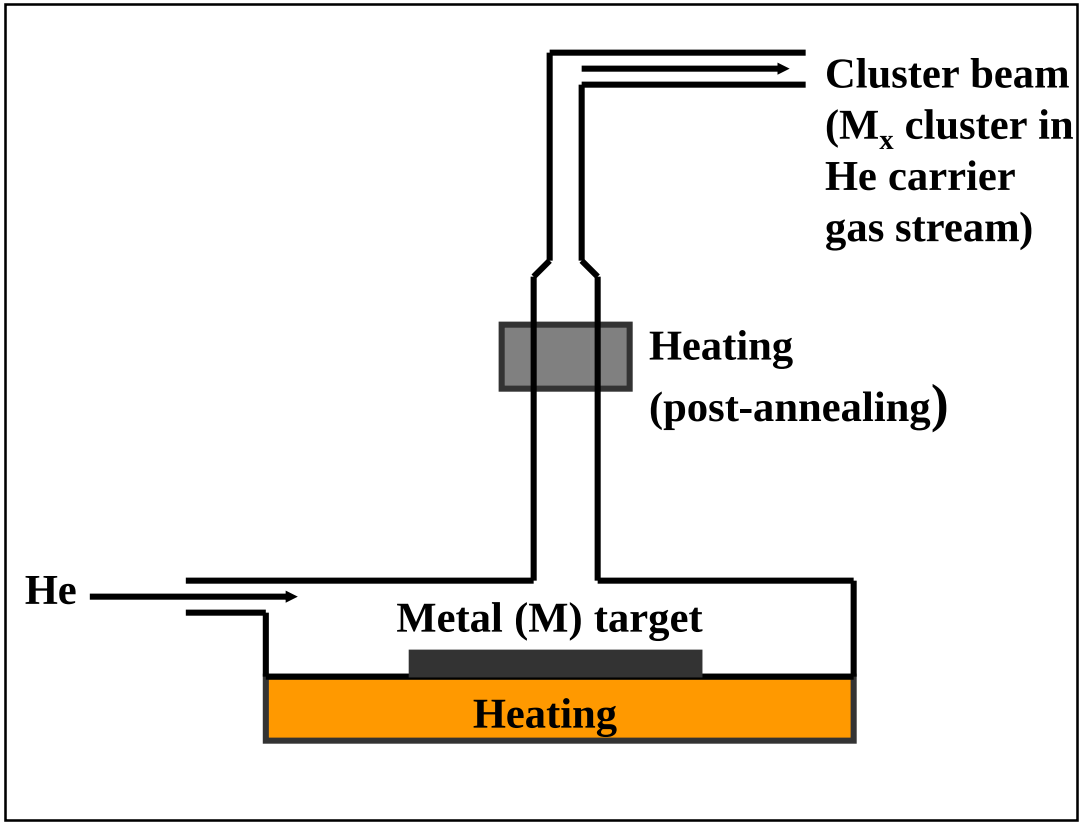
Deposition from the gas phase

1. Oxides (see chapter 2.2.3. Aerosol Processes)
2. Metals (Cluster-Beam Generator)

Metals as a target

Evaporation through

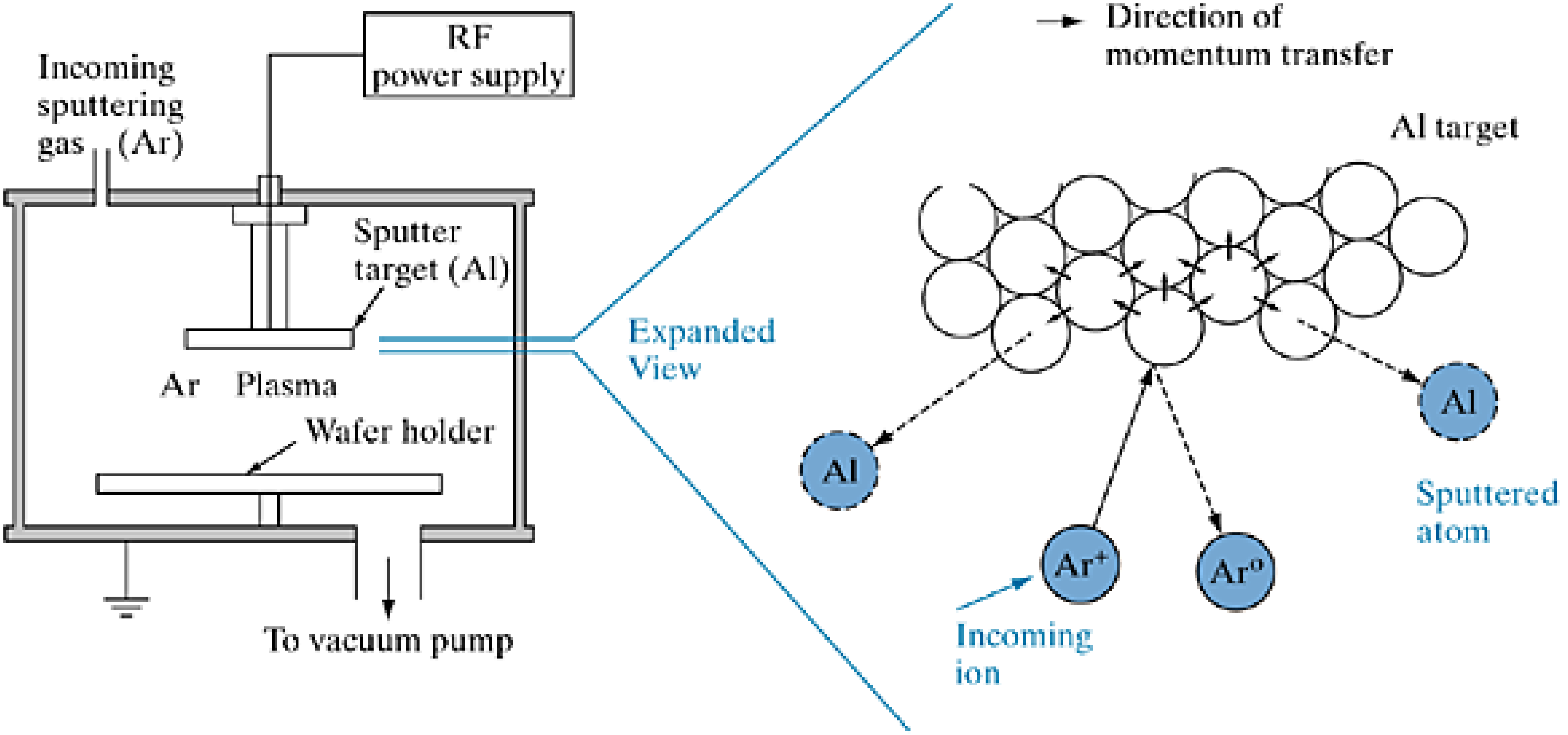
a) Heating
b) Laser irradiation
c) Ion bombardment, e.g. Ar^+ ion sputtering
d) Electron bombardment



2.4.3 Synthesis of Nanoparticles

Deposition from the gas phase

Example: Ar^+ ion sputtering

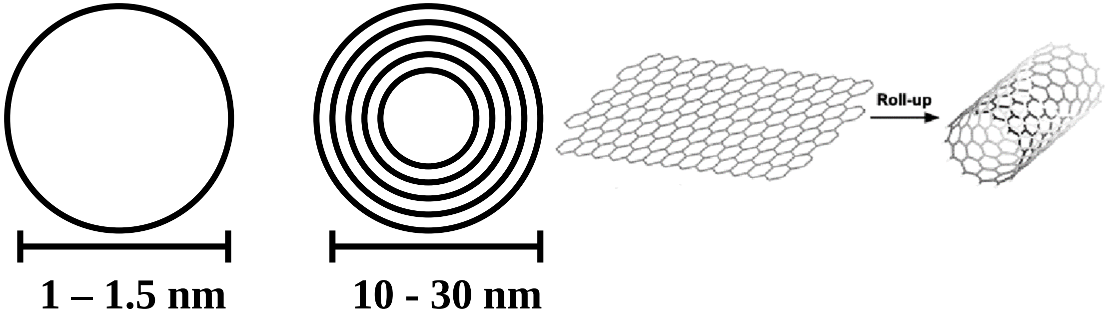


2.4.3 Synthesis of Nanoparticles

Excursion: Nanotubes

Nanotubes can be formed from substances with layered structure:

- **Carbon Nano Tubes (CNTs)** **single-walled multi-walled graphene & SW-CNT**
- **$B_xC_yN_z$, z.B. BN, BC_3, BC_2N**
- **SiO_2**
- **Metal oxides**
- **Metal sulfides, e.g. WS_2, MoS_2**



<u>Synthesis</u>

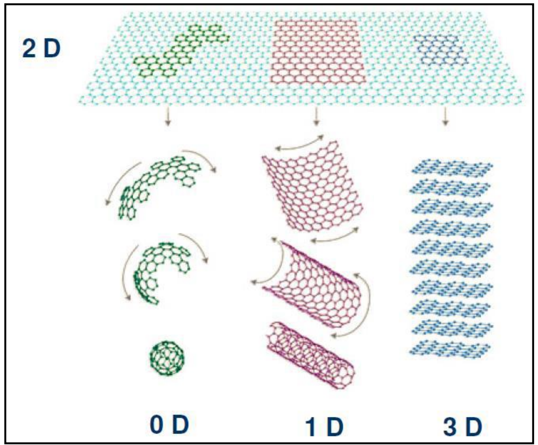
CNTs: Deposition of carbon from the gas phase or plasma

VO_x-NTs:

$VO(OR)_3 + H_2N\text{-}(CH_2)_n\text{-}NH_2 \rightarrow$ Hydrolysis, aging, hydrothermal synthesis

<u>Applications</u>

Gas sensors, field emitters in field emission displays (FEDs), molecular transistors, nanocontainers, hydrogen storage, etc.



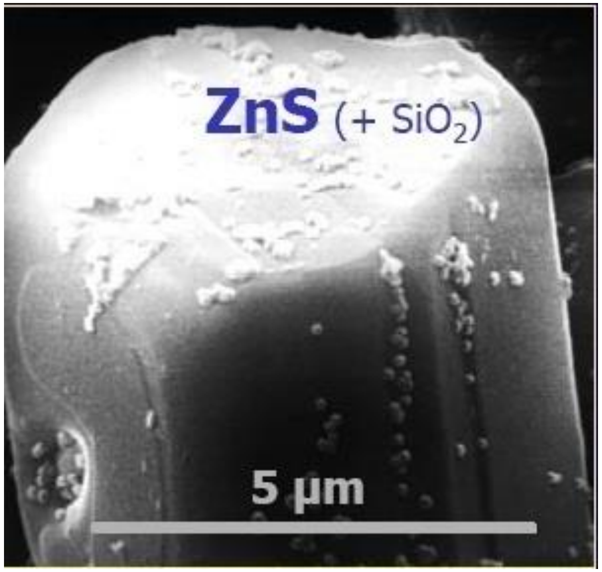
2.4.4 Applications of Nanoparticles

Nanoparticles find application in many technology fields, e.g. …..

Technology	Examples
- Energy production	Solar cells: Si, Grätzel cells
- Energy storage	Lithium batteries, Ni-metal hydride batteries
- Data processing	Field emission transistors with nanotubes
- Photonics	Photonic band materials
- Sensor technology	Bio and gas sensors
- Materials	Self-cleaning surfaces
- Catalysis	Organic synthesis with metal nanoparticles
- Optical markers	Markers for DNA, RNA, proteins Product anticounter feiting
- Pharmaceutics	Drugs with high solubility (drug delivery) radical scavenger, neutralizing agent
- Diagnostics	Magnetic nanoparticles for contrast enhancement for MR tomography Optical imaging (NIR up-converter)
- Dentistry	Ceramic teeth

2.4.4 Applications of Nanoparticles

Nanoparticles in the lighting and display technology



As functional layers (e.g for light modulation)

- Color filters in displays, such as CRTs, PDPs, LCDs, …
- Interference coatings
- Scattering layers for frequency-selective reflectors
- As luminescent materials, however, low quantum yield limits the possible applications

For the material optimization or synthesis

- Protective coating of µ-scale phosphors
- Functional coatings of µ-scale phosphors
- Precursors for µ-scale phosphors
- Precursors for transparent ceramics, e.g. as LASER ceramics
- Influence of electrochemical properties

2.4.4 Applications of Nanoparticles

Nanoparticle for the synthesis of photonic band gap materials (photonics)

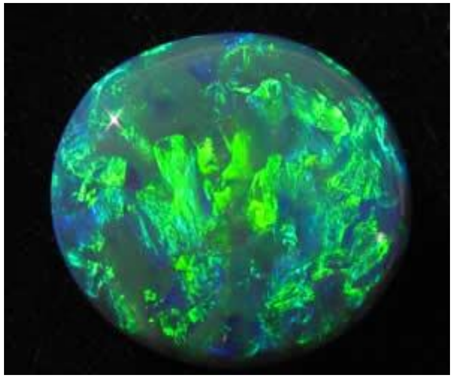
Example: Inverse opals (materials with photonic band gap)

Procedure

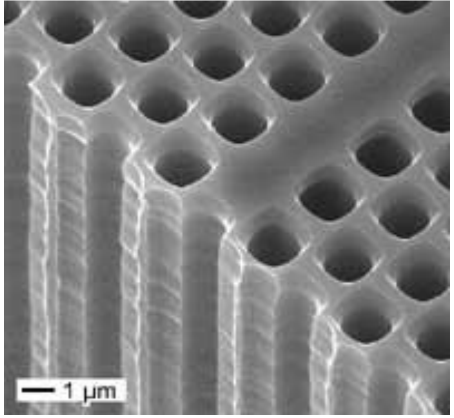
1. **Synthesis of monodispers colloidal particles, such as consisting of PMMA**
2. **Cristallisation "of the colloidal particles, i.e. formation of a 3D structure ⇒ Template crystal**
3. **Impregnation with „precursor"**
4. **Conversion of the Precursors to solid state and removal of the templates**

⇒ Crystal with photonic band gap

Gemstone Opal



Inverse Si-Opal



2. Synthesis Techniques of Material Technology

2.5. Single Crystal Growth Technique

2.5.1 Czochralski Method

2.5.2 Zone Melting

2.5.3 Bridgman-Stockbarger Method

2.5.4 Traveling Solvent Floating Zone Method

2.5.5 Chemical Vapour Deposition

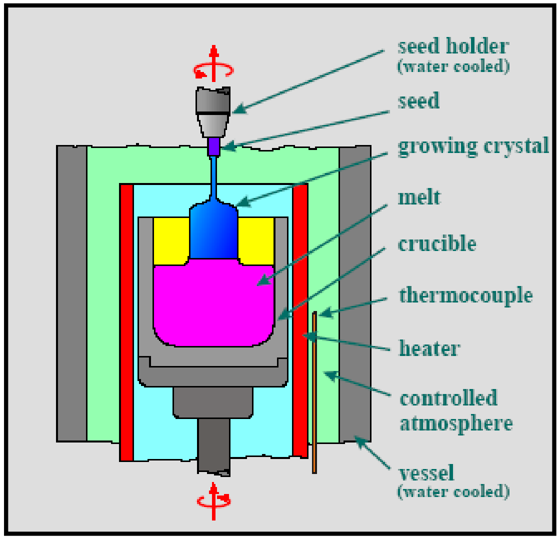
2.5.6 Single Crystal Growth from Solution

2.5.7 Application of Single Crystals

$KEuW_2O_8$ Crystal (FEE)
703 nm laser gain medium

2.5.1 Czochralski Method

Pulling crystals from a melt



<u>**Sequence**</u>

- Melting the starting materials
- Introduction of a seed crystal
- Shoulder formation
- Grow by pulling out under rotation

<u>**Examples of successful breeding of single crystals**</u>

Elements: Si, Ge, Sn, Bi, Au

Compounds: AlSb, InSb, GaSb, CsI, KBr, CaF_2, BaF_2, ...

<u>**Problems with doped crystals (semiconductor)**</u>

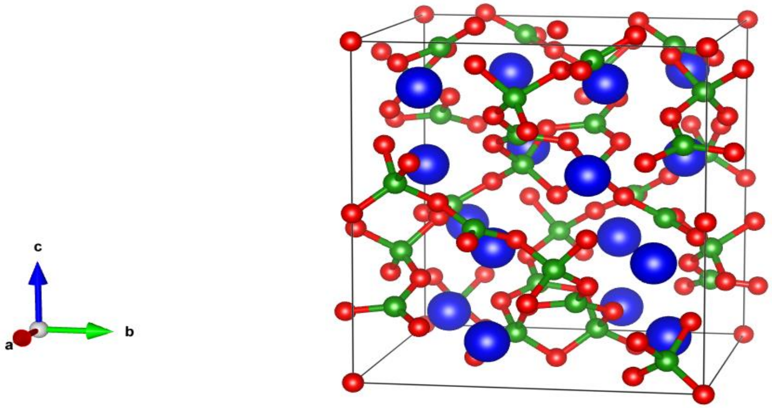
- Introduction of impurities
- Segregation of dopants, as $C_{solid}/C_{liquid} < 1$ and for each component it differs $\Rightarrow$ Enrichment of the liquid phase in impurities
- Dopant concentration gradient in the crystal

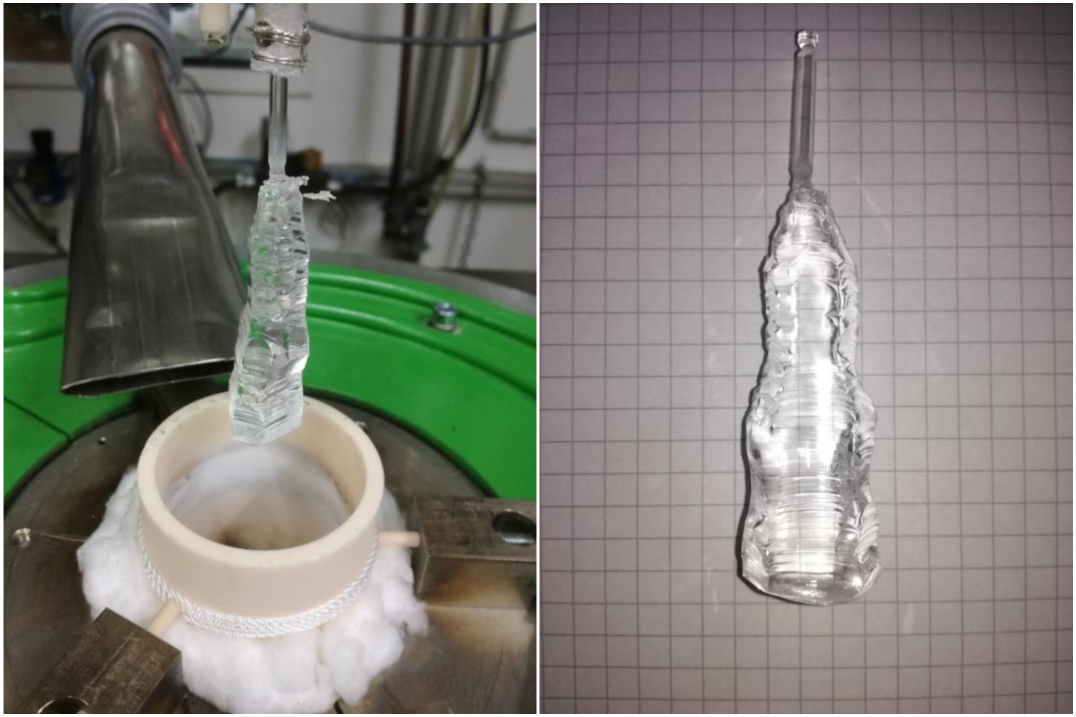
2.5.1 Czochralski Method

Growth of NLO material $Li_2B_4O_7$ at a temperatur of 980 °C (FEE Idar-Oberstein)

Tetragonal crystal system

- $a = b \neq c$
- $\alpha = \beta = y = 90°$





2.5.1 Czochralski Method

Single crystal growth of silicon

Starting materials: Polycrystalline silicon

Procedure

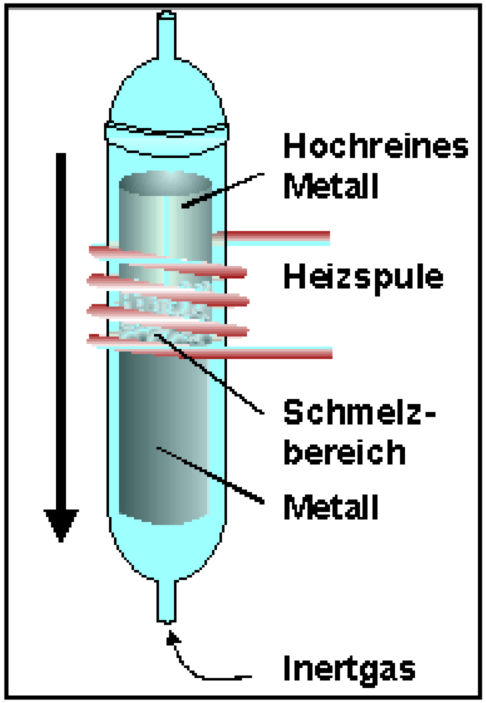
- **Melting polycrystalline Si in quartz crucibles**
  T_m(Si) = 1412 °C
- **Immersion of seed crystal**
- **Slowly pulling out the seed crystal**
  (duration ~ 3 days)
- **Obtained single crystal:**
  ~ 50 kg, max. diameter ~ 300 mm (12“)

Cutting into discs provides e.g. 12“ Wafers
⇒ Semiconductor production

2.5.2 Zone Melting

Example: Purification and growth of silicon

Zone melting in a high-frequency furnace (Pfann 1952)

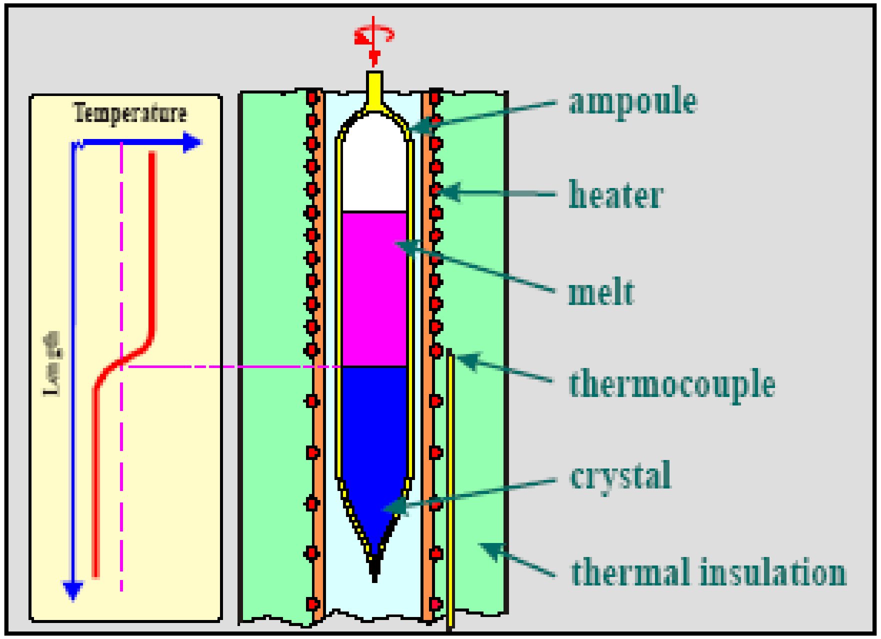


- **Silicon rod is inductively melted at one end**
- **The coil is moved along the rod**
- **The contamination collect themselves in the liquid phase and thus at the end of the single crystal, since they dissolve better in the liquid phase**
- **Segregation coefficient :** $k_0 = \frac{C_{solid}}{C_{liquid}} < 1$
- **n iterations:** $k_n = (k_0)^n = 0$ **für** $n \rightarrow \infty$

Element	k_0
Li	0.01
B	0.8
Al	0.002
P	0.35
As	0.3

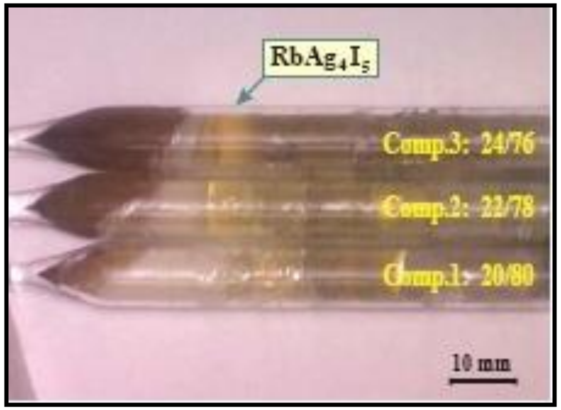
2.5.3 Bridgman-Stockbarger Method

In these methods, a spatial or time dependent temperature gradient is used for single crystal growth



Process

- Positioning the starting materials in a (quartz) ampule and melting the ampoule
- Heating up to melting
- The ampule is driven through the T gradient



Examples

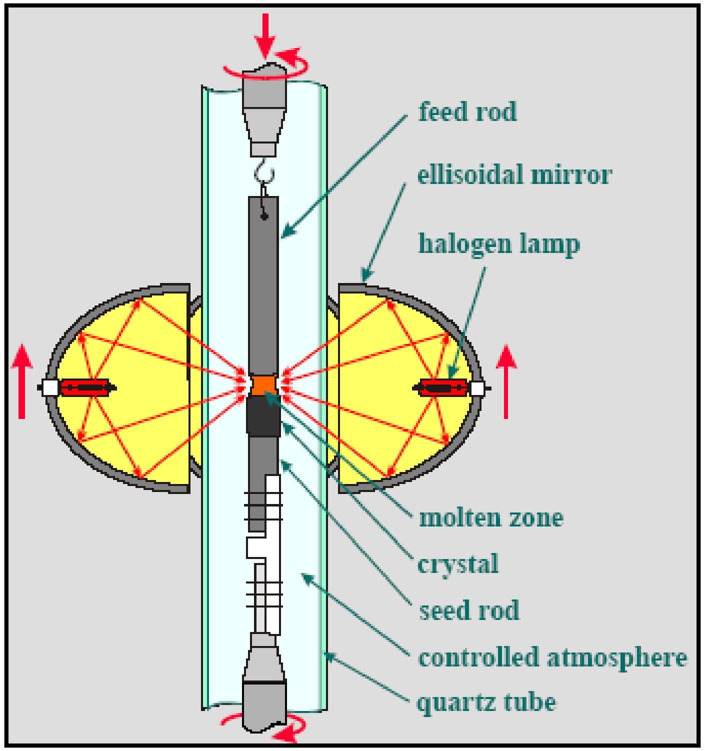
Binary halides: LiI, $LaCl_3$, $PrCl_3$, ...

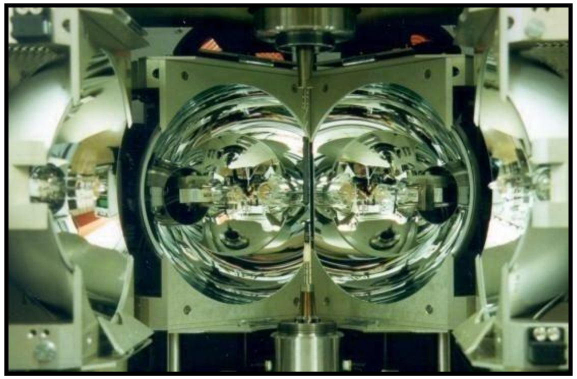
Ternary halides: RbI + 4 AgI → $RbAg_4I_5$

Alloys: $AuTe_2$, SnAs, SiAs, …

2.5.4 Travelling Solvent Floating Zone Methode

Crystallization by local melting of a green body





Sequence

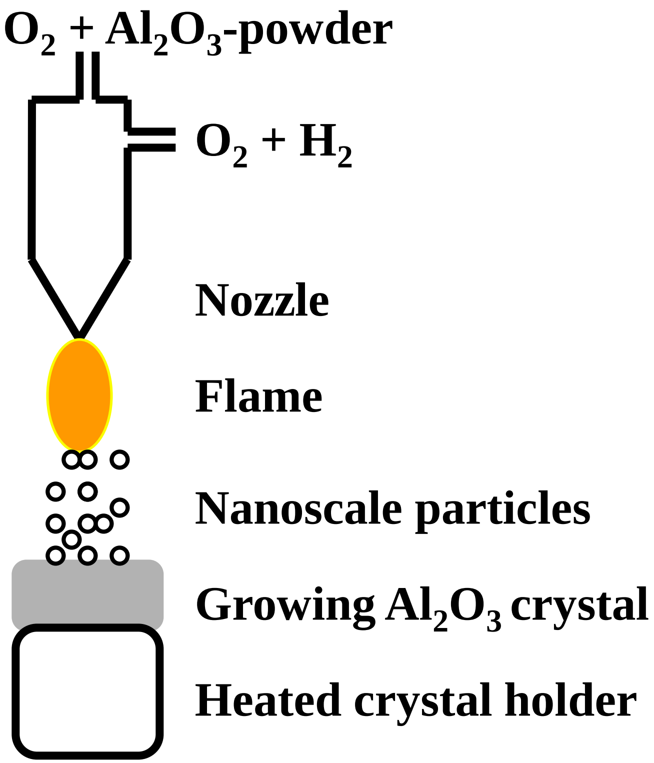
- Mixing and calcining the starting materials
- Isostatic pressing and sintering
- Presintering of the green body
- Formation of a molten zone by infrared heating (halogen lamps in ellipsoidal mirrors)
- Crystal growth by moving the focus of the mirrors

Examples of successful breed of single crystals

$Bi_2Sr_2CaCuO_{8+\delta}$, Ln_2CuO_4 (Ln = La, Nd)
$LaMnO_3$, $LnBa_2Cu_3O_{7-\delta}$ (Ln = Y, Pr, Nd)

2.5.5 Chemical Vapour Deposition

The growth of crystals of high-melting materials (Al_2O_3, diamond)



O_2 + Al_2O_3-powder

O_2 + H_2

Nozzle

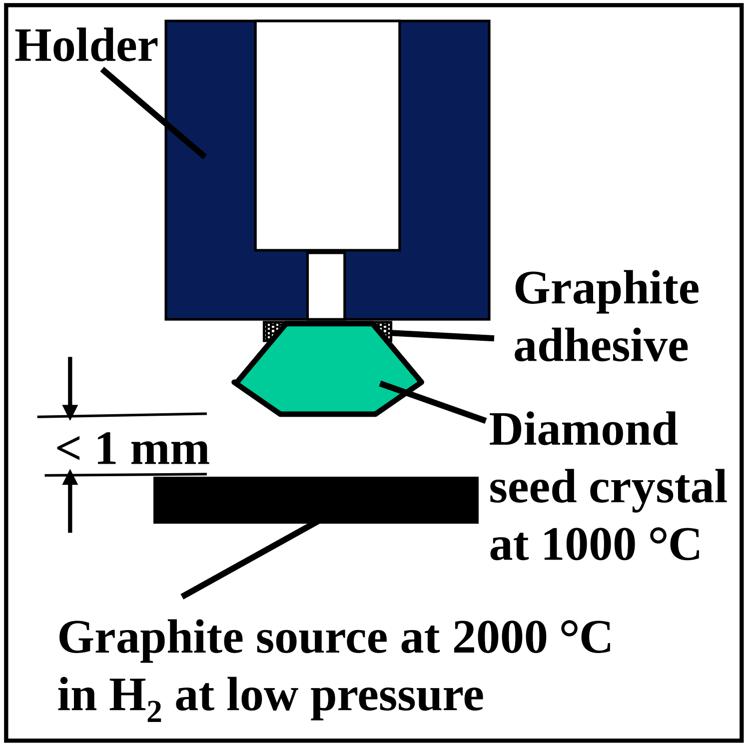
Flame

Nanoscale particles

Growing Al_2O_3 crystal

Heated crystal holder

Growth of diamond crystals



Holder

Graphite adhesive

Diamond seed crystal at 1000 °C

< 1 mm

Graphite source at 2000 °C in H_2 at low pressure

<u>Growing of artificial gemstones</u>

Al_2O_3:Cr	Ruby
Al_2O_3:Ti	Sapphire
C_{sp^3}	Diamond

High economic profit by exceeding certain critical weight, e.g. 1 carat

2.5.6 Single Crystal Growth from Solution

Breeding of single crystals based on soluble substances, and crystallization is achieved by exceeding the solubility

Precipitation condition for a AB salt

$c_{AB} > (K_L)^{1/2}$ $K_L = c_A \cdot c_B = c_{AB}^2$ [mol^2l^{-2}] = f(T, p, ion strength, solvent, etc.)

Example

Solubility product of HgS: $K_L = 1 \cdot 10^{-54}$ mol^2l^{-2}

Threshold concentration : $c_{Hg}{}^{2+} = 10^{-27}$ $moll^{-1}$

⇒ 1 Hg^{2+}-ion per m^3 water

⇒ 0.5 mg of HgS in the world ocean ($1.4 \cdot 10^{18}$ t H_2O)

⇒ Crystal breed of HgS from solution is not possible!

Exceed the threshold concentration

Fast ⇒ Precipitation (micro- or nanocrystallite)

Slow ⇒ Crystallization (single crystals:: mm ... cm)

2.5.6 Single Crystal Growth from Solution

Methods for exceeding the threshold concentration

1. Temperature decrease

Principle: The solubility decreases with falling temperature

Solubility of $KClO_4$ in H_2O:

1.3 $moll^{-1}$ at 100 °C

0.14 $moll^{-1}$ at 20 °C

2. Evaporation of the solvent

Principle: Slow increase in concentration of the dissolved components

Use of a seed crystal → Deposition on the seed crystal

3. Condensation of secondary solvents

Principle: Lowering the polarity of the solvent mixtures

Diethyl ether → CH_3CN, CH_3NO_2

Tetrahydrofuran (THF) → H_2O