Inorganic Solid State Chemistry –

a brief overview or „a fast ride“

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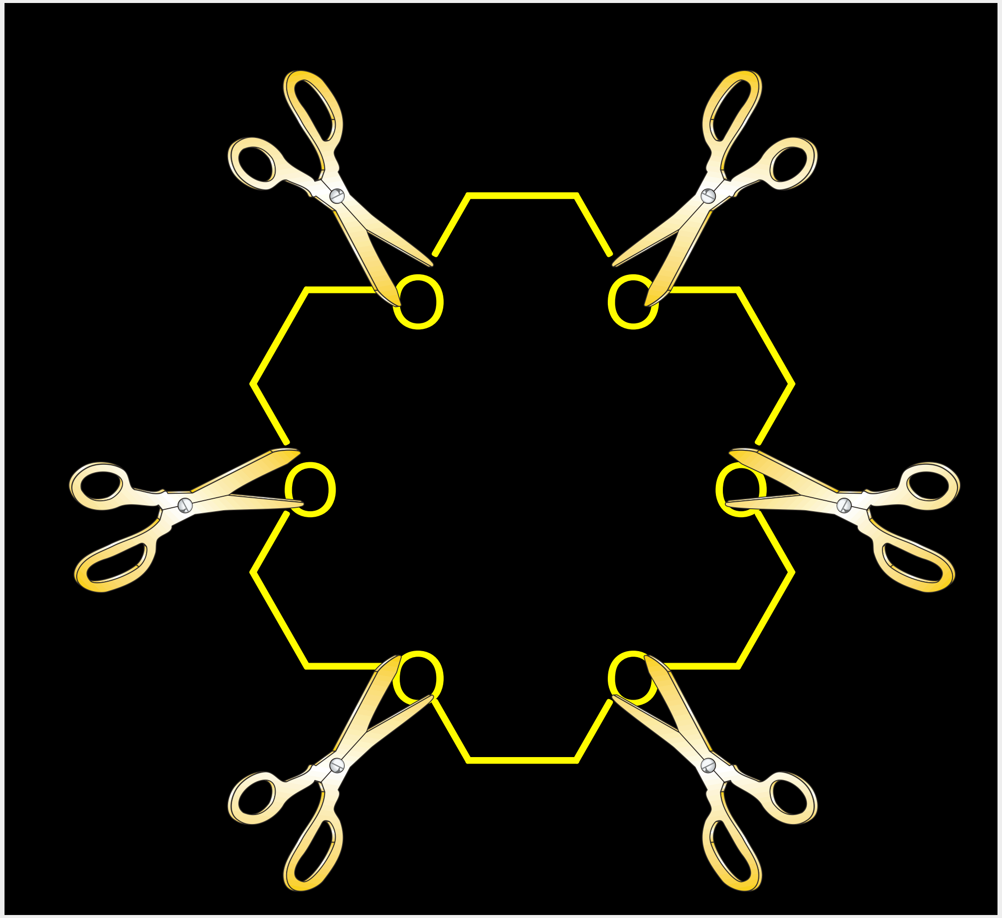
Berlin, Fritz-Haber Institut, 11.11.2011

Inorganic Solid State Chemistry

- High Temperature synthesis (ceramic methods)
- Reaction of thin films
- Co-Precipitation
- Precursor methods – thermal decomposition reactions
- Reactions under high pressure and high temperature
- High energy ball milling
- Intercalation reactions
- Chemical vapor deposition (CVD)
- Reactions in melts
- Chemical transport reactions
- Solvo-/hydrothermal reactions
- Sol-gel processes
- Microwave assisted reactions
- Sonochemical reactions
- Electrochemical reactions
- Reactions in confined spaces

Inorganic vs. organic synthesis

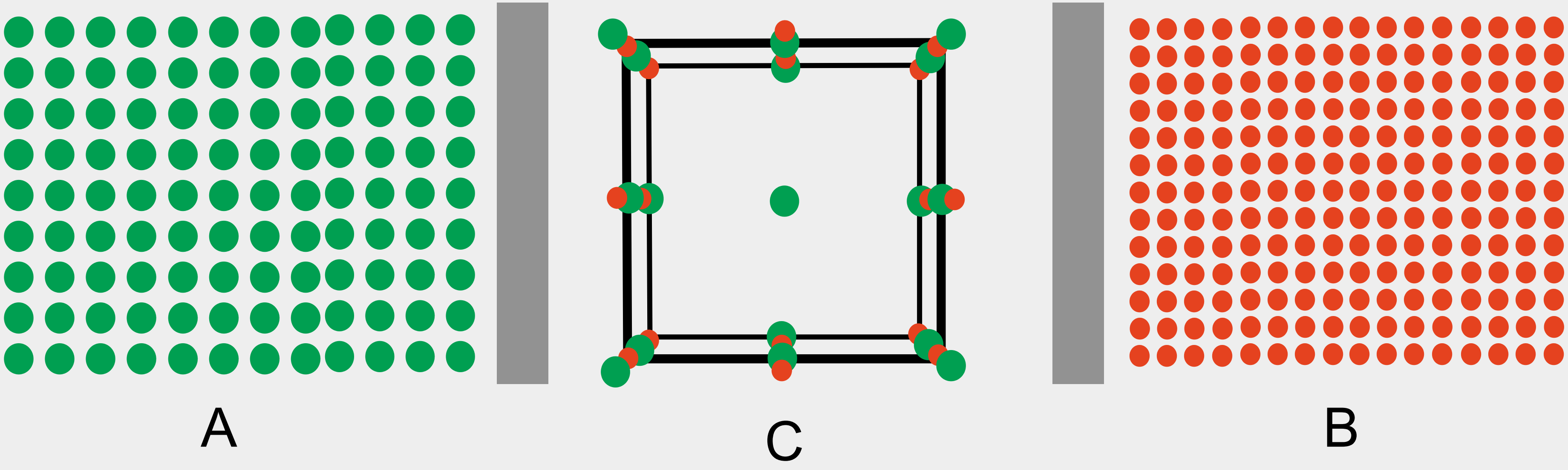


- rational: synthesis steps by analysing final product – retro synthesis
- very good control of product composition
- very good control of structure and topology

High Temperature Synthesis

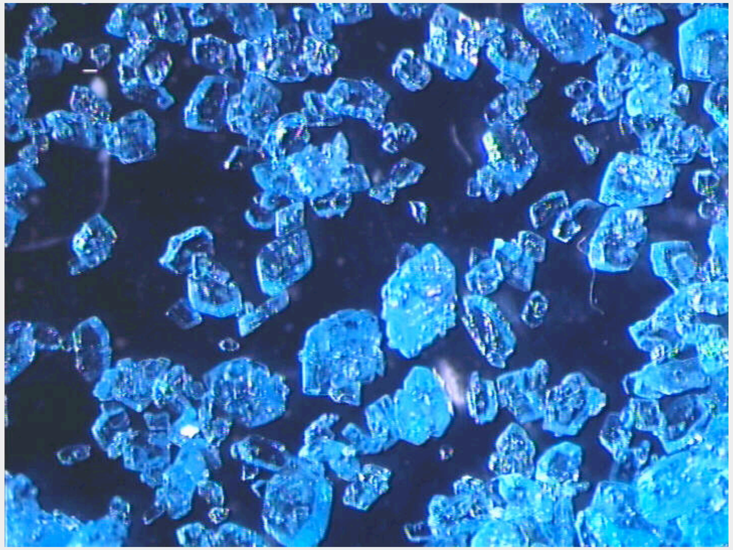
High temperature synthesis

$$A + B \longrightarrow C$$

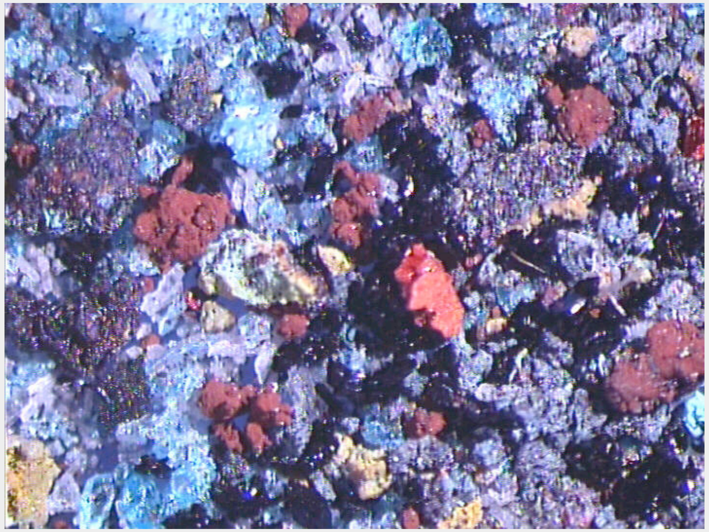


- Formation of thermodynamic stable phases → low product diversity
- More or less no control of composition of final product
- No control of final structure
- Mainly dense phases

Problem: Homogeneity of products



Optical homogeneous



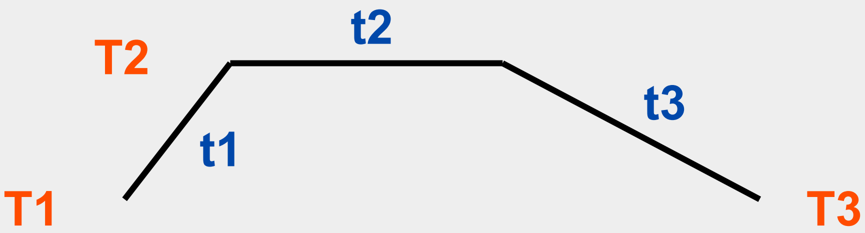
optical inhomogeneous (mixture)

Seperation often problematic

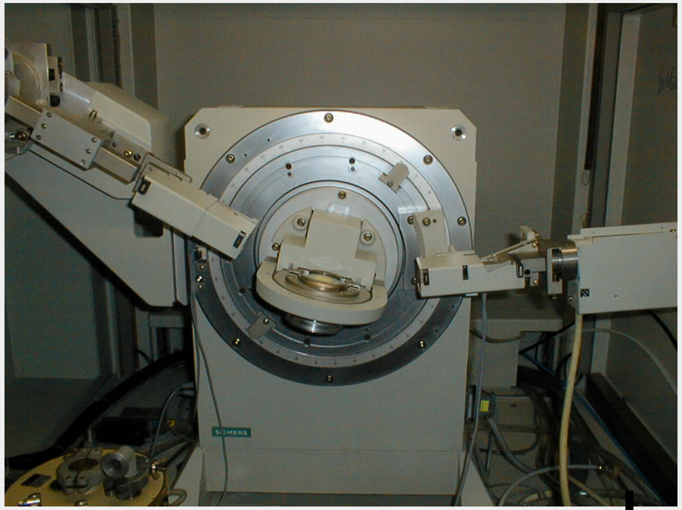
→ control of synthesis to obtain only one product

variation of educts/educt ratio, reaction time, reaction temperature,

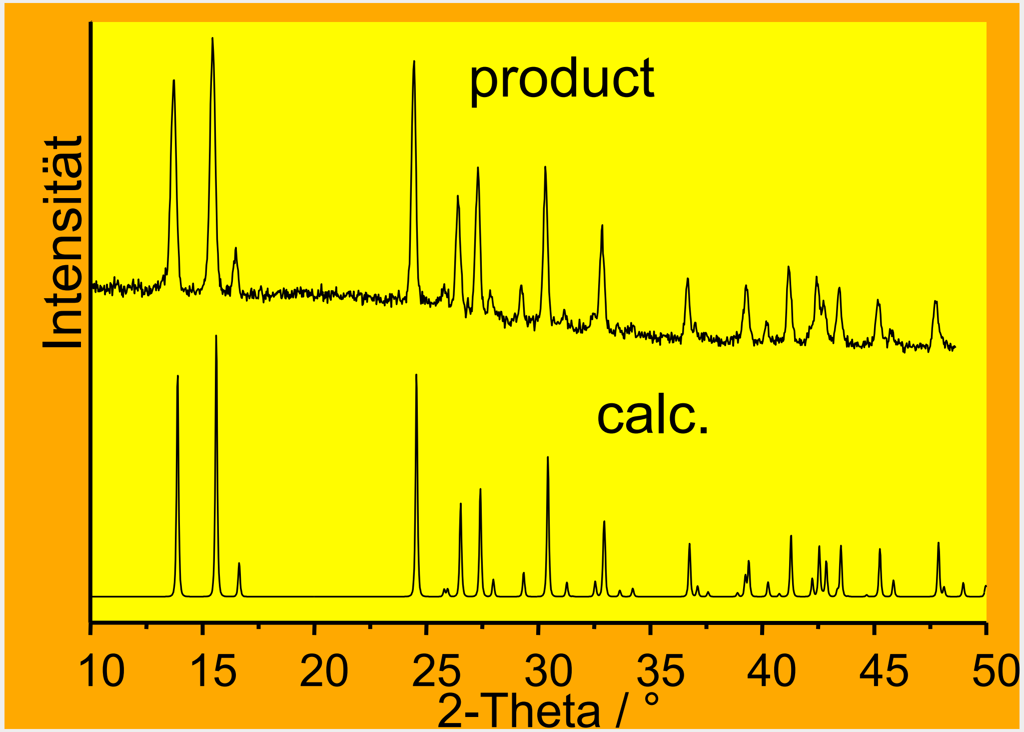
heating and cooling rates



Homogeneity



Powder pattern



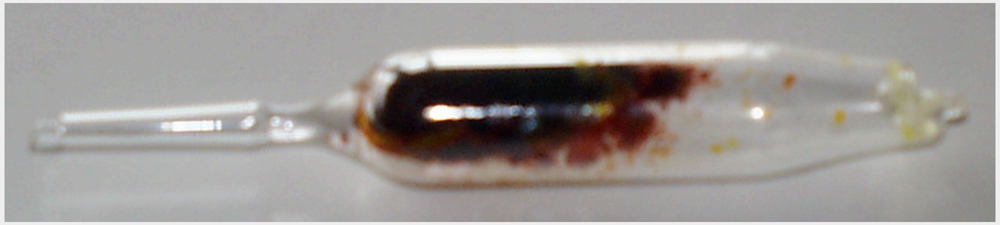
Charakteristics:

- position
- intensity
- broadness
- shape

Techniques

1. Ampoules (glass, quartz), vacuum, normal pressure, inert gases

2. Evacuation and fusing



High temperature syntheses - techniques

requirements:

- no reaction with educts
- no impurities
- dry and clean

Glass or Quartz:

- reactions observable
- but: not always inert, formation of silicides, oxides, silicates

examples:

Educt	Products	containers and reaction temperature
Li_2O, SiO_2	$Li_2Si_2O_5$	Pt crucible (air), 1100°C
Y_2O_3, $BaCO_3$, CuO	$YBa_2Cu_3O_7$	Al_2O_3 crucible (air), 1000°C
Na_2MoO_4, MoO_3, Mo	$NaMo_4O_6$	Mo ampoule, 1100°C
Ca, $CaCl_2$, C (Graphit)	$Ca_3Cl_2C_3$	Nb or Ta ampoule, 900°C
Y, YCl_3	Y_2Cl_3	Nb or Ta ampoule, 800°C
Y, N_2	YN	Mo boat, N_2 flow, 900°C
KHF_2, NiF_2	K_2NiF_4	Pt crucible, inert gas or vacuum, 700°C
La, LaI_3	LaI	Nb or Ta ampoule, 750°C
Mo, Pb, MoS_2	$PbMo_6S_8$	evacuated quartz ampoule, 900°C

High temperature synthesis (ceramic method)

- Reaction at elevated temperartures in suitable containers
- Why not at RT? Kinetically inhibited!
- From thermodynamics: reaction Fe_3O_4 + Al is favored
- Elevated temperatures: acceptable reaction rates

Reaction rate depend on:

1. Temperature:

Activation energy for diffusion decreases.

Empirical rule: $T_{\text{Reaction}} > 2/3\ T_{\text{melting point}}$ (T[K])

2. Energy

reactions are exothermic and controlled by thermodynamics!

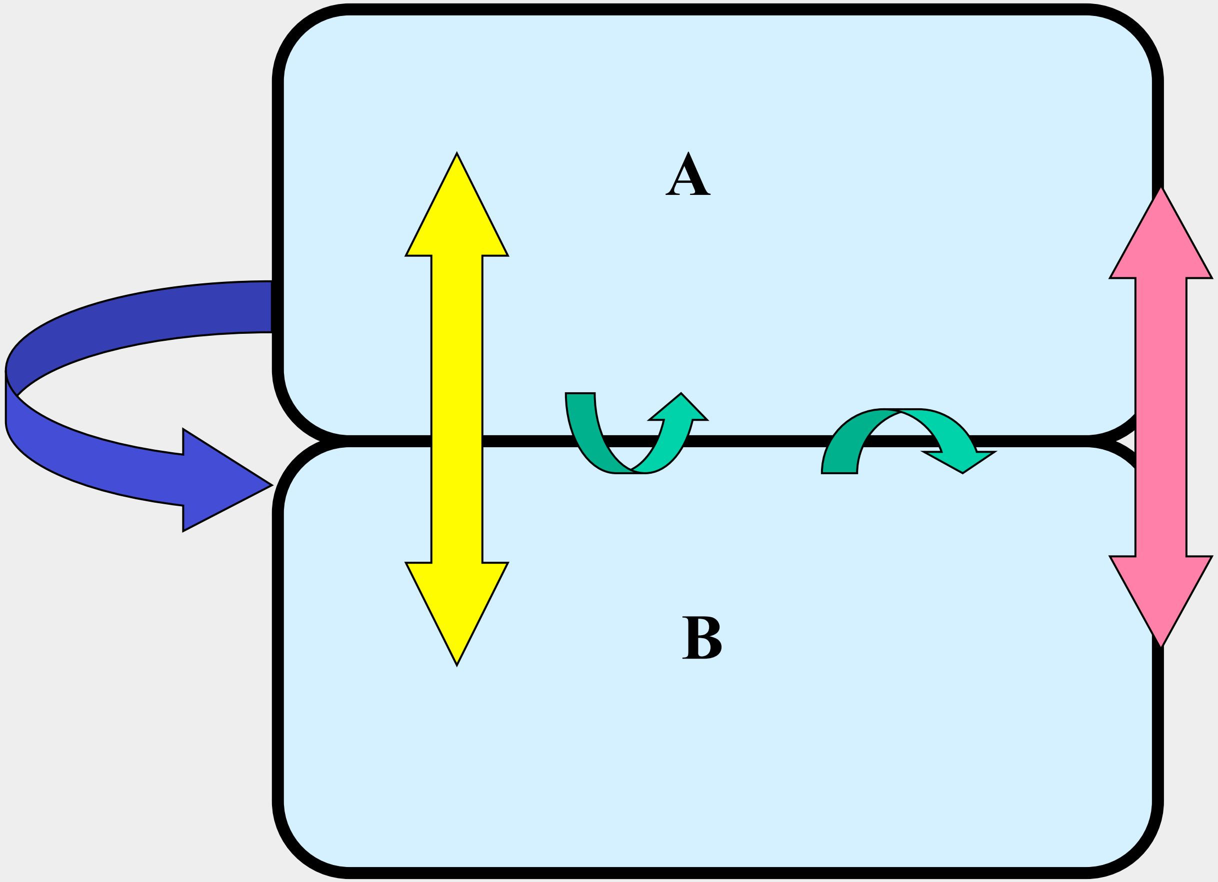
3. Grain sizes

porosity, sizes of grains, contact of reacting interfaces are important for reaction progress

$T_{\text{Reaction}} > 2/3\ T_{\text{melting point}}$

					T_{min}
2 Si	+	Ti	$\longrightarrow$	$TiSi_2$	1000°C
1410°C		1670°C			
V	+	C	$\longrightarrow$	VC	1400°C
1910°C		3730°C			
LaF_3	+	La_2O_3	$\longrightarrow$	3 LaOF	900°C
1200°C		2307°C			

Reaction pathways



🟦 Gasphase diffusion

🟩 Interface grain diffusion

🟨 Volume diffusion

🟥 Surface diffusion

Diffusion in solids

Typical diffusion coefficents D for ion in solids at 300 K: 10^{-13} cm^2 s^{-1}.

Solid ionic conductors like Ag^+ ions in α-AgI: $\approx 10^{-6}$ cm^2 s^{-1}

Diffusion coefficients depend exponentially from T:

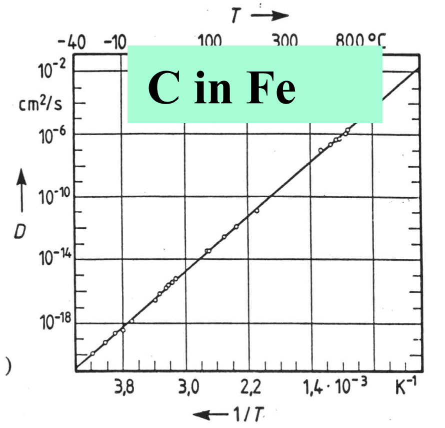
$$D = D_\infty \exp(-Q/kT)$$

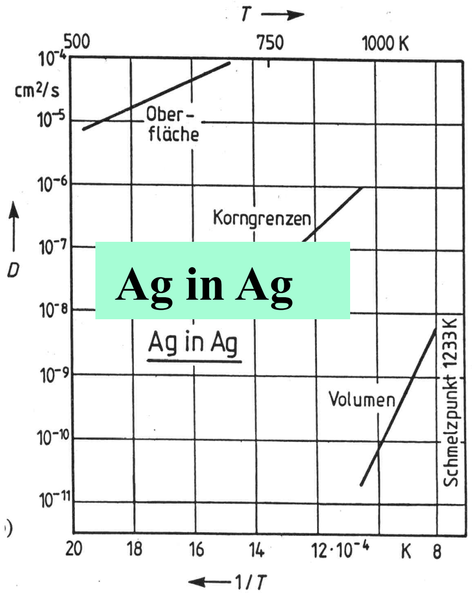
(D_∞: D for T→ ∞, pre-exponential factor; Q: activation energy for Diffusion, k: Boltzmann factor)

Plot log(D) vs. 1/T yields a straight line

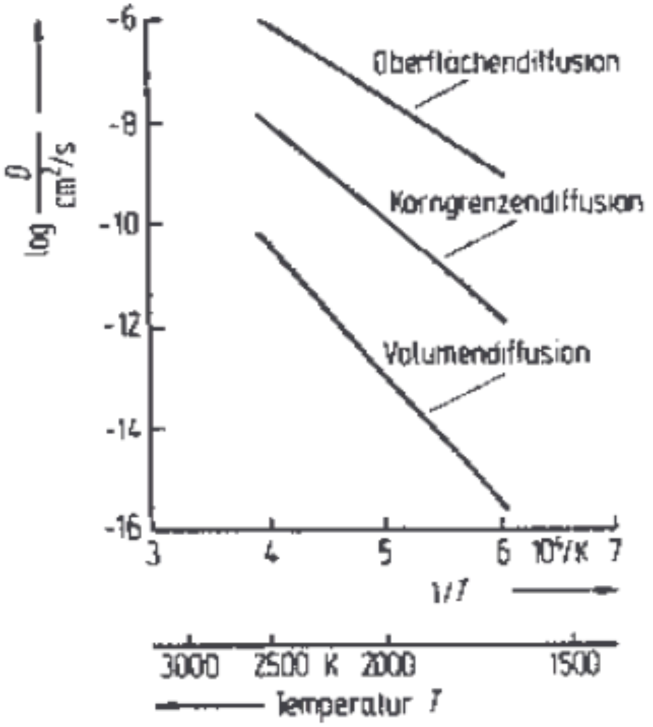
$$\boxed{\log(D) = \log(D_\propto) - Q/(RT)}$$

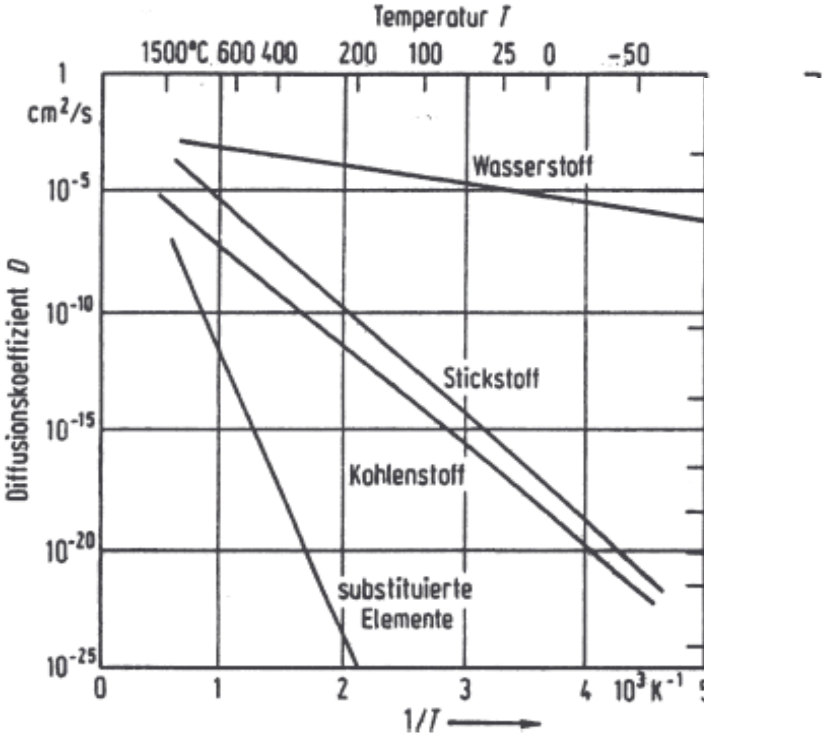
Slope: activation energy, intercept D_∞





Different types of diffusion



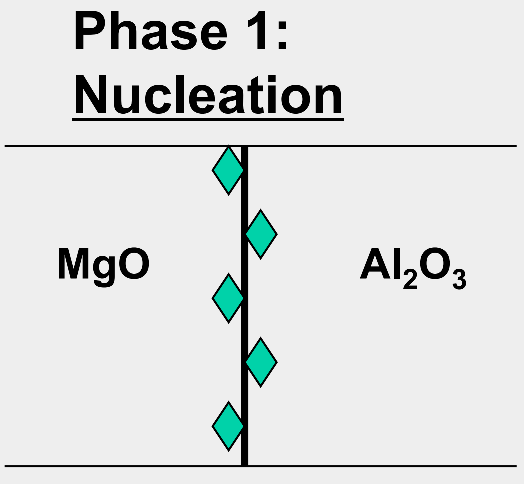


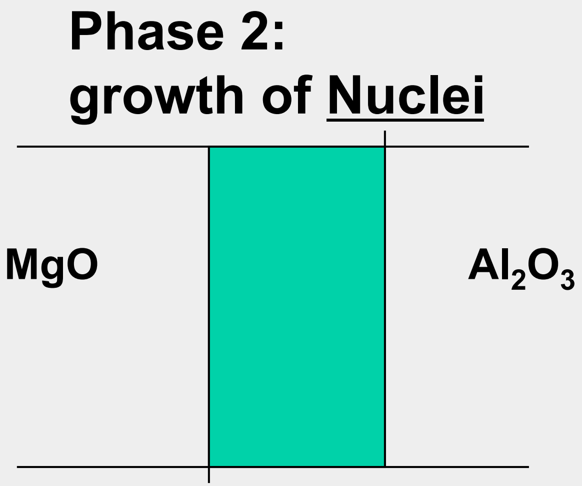
surface, interface, grain and volume diffusion

Model of solid-solid reaction

Planar interfaces between crystallites

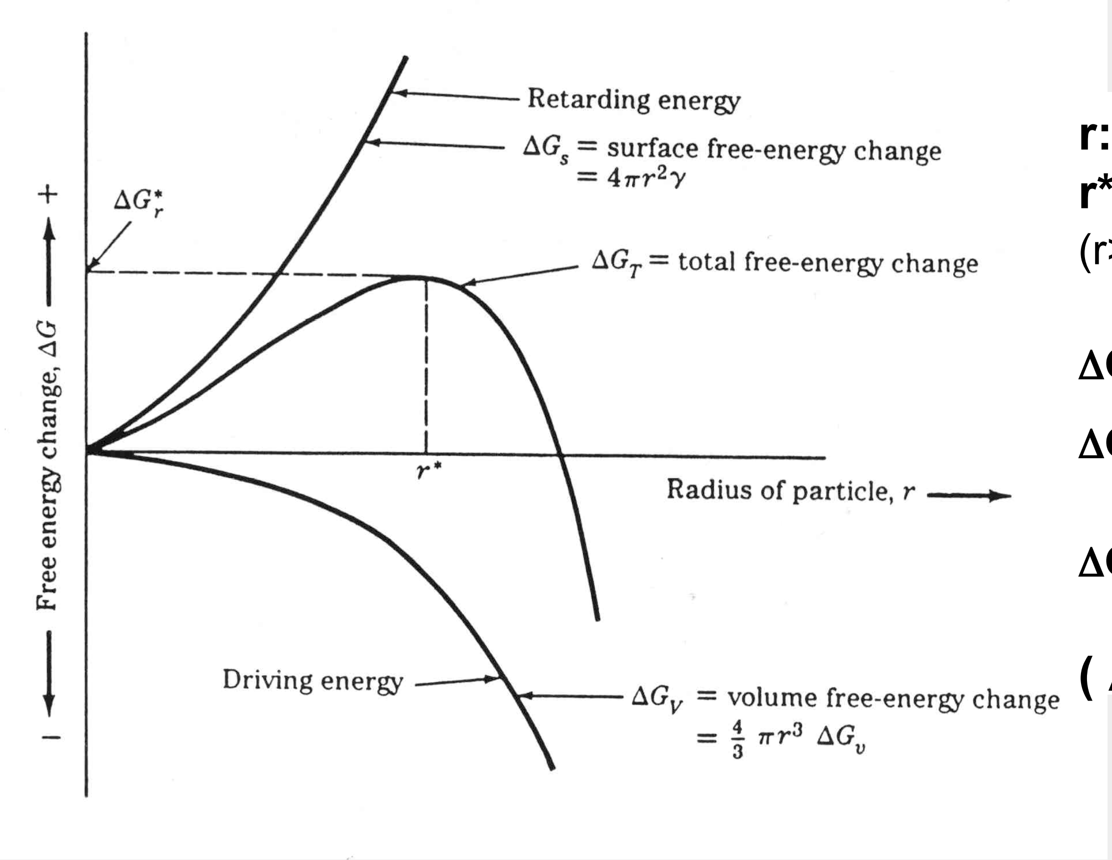
$MgO + Al_2O_3 \rightarrow MgAl_2O_4$ (Spinell)


Phase 1:
<u>Nucleation</u>


Phase 2:
growth of Nuclei

- Reaction starts at interface A-B
- First small nuclei are formed
- growth of nuclei

Nucleation



r: radius of spherical nuclei

r*: critical radius

(r>r* nuclei grow)

ΔG: total change of free energy

ΔG_s: change of free surface energy

ΔG_v: change of free volume energy

($\Delta G = \Delta G_s 4\pi r^2 + \Delta G_v 4/3\pi r^3$)

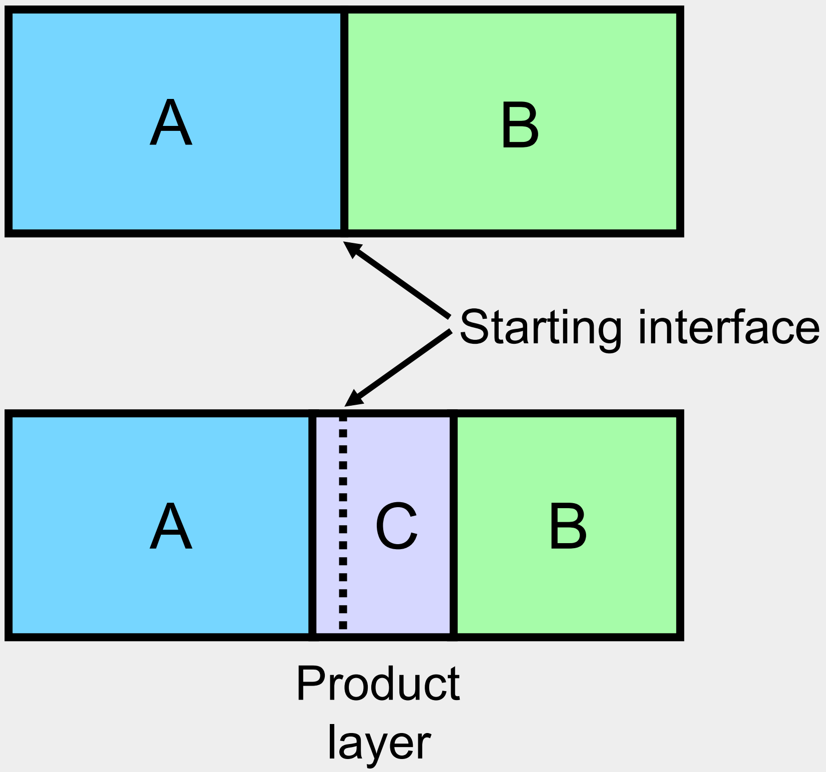
$\gamma = \Delta G_S$ = specific interface energy

$\gamma \Delta G_V$ = free enthalpy per volume

Diffusion and crystal growth

$A + B \longrightarrow C$

$MgO + Al_2O_3 \rightarrow MgAl_2O_4$



Starting interface

Product layer

- ➢ supply of A and B through diffusion
- ➢ formation of two interfaces A|C and C|B: A and B must diffuse through these layers
- ➢ product layer becomes thicker → diffusion of A and B slows down

Consequently: only at high temperatures diffusion is fast enough

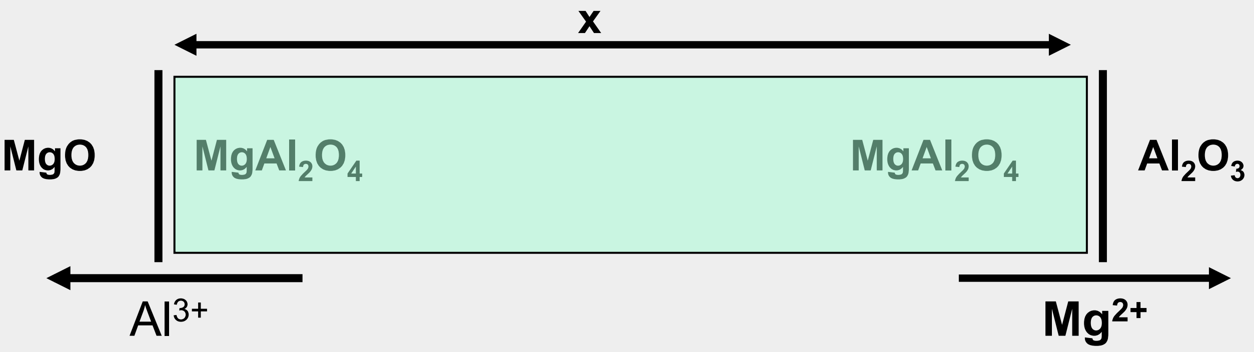
Investigation of growth? → Tracer experiments

Growth

Growth velocity determined by:

- → **Diffusion of Mg^{2+} and Al^{3+} ions**
- → **O^{2-} is fixed on the sites (!)**
- → **principal of charge neutrality!**

Reaction at the interface:

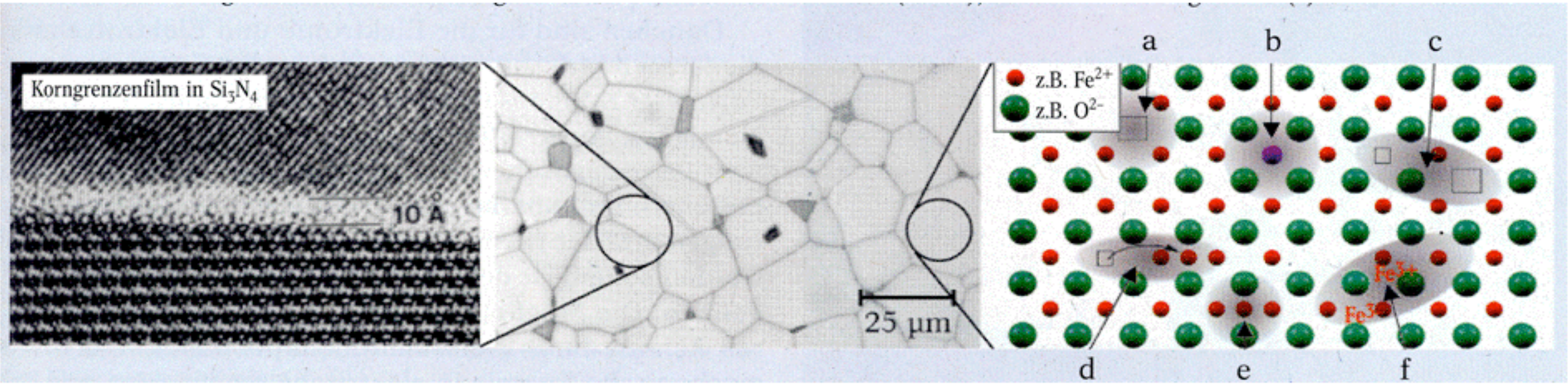


$2Al^{3+} - 3Mg^{2+} + 4\ MgO \rightarrow MgAl_2O_4$ $-2Al^{3+} + 3Mg^{2+} + 4\ Al_2O_3 \rightarrow 3\ MgAl_2O_4$

$dx/dt \sim 1/x$ (growth rate as function of time t), x = reaction rate

3 equivalents Mg^{2+} generate 3 equivalents $MgAl_2O_4$
2 equivalent Al^{3+} generate only 1 equivalent $MgAl_2O_4$
Product layer grows three times faster on Al_2O_3 side!

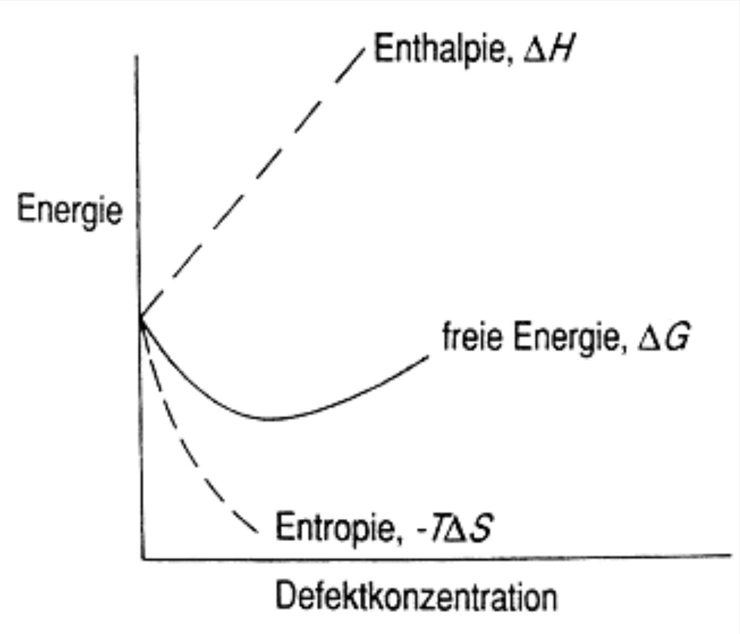
Parameters determining diffusion: 0D defects



a) Vacancy
b) Substitutional atoms
c) Interstitial atoms
d) Schottky defects
e) Frenkel defects
f) Charge defects

Reasons for defect formation

- not perfect crystals
- surface
- lattice vibrations T > 0 K
- structural defects



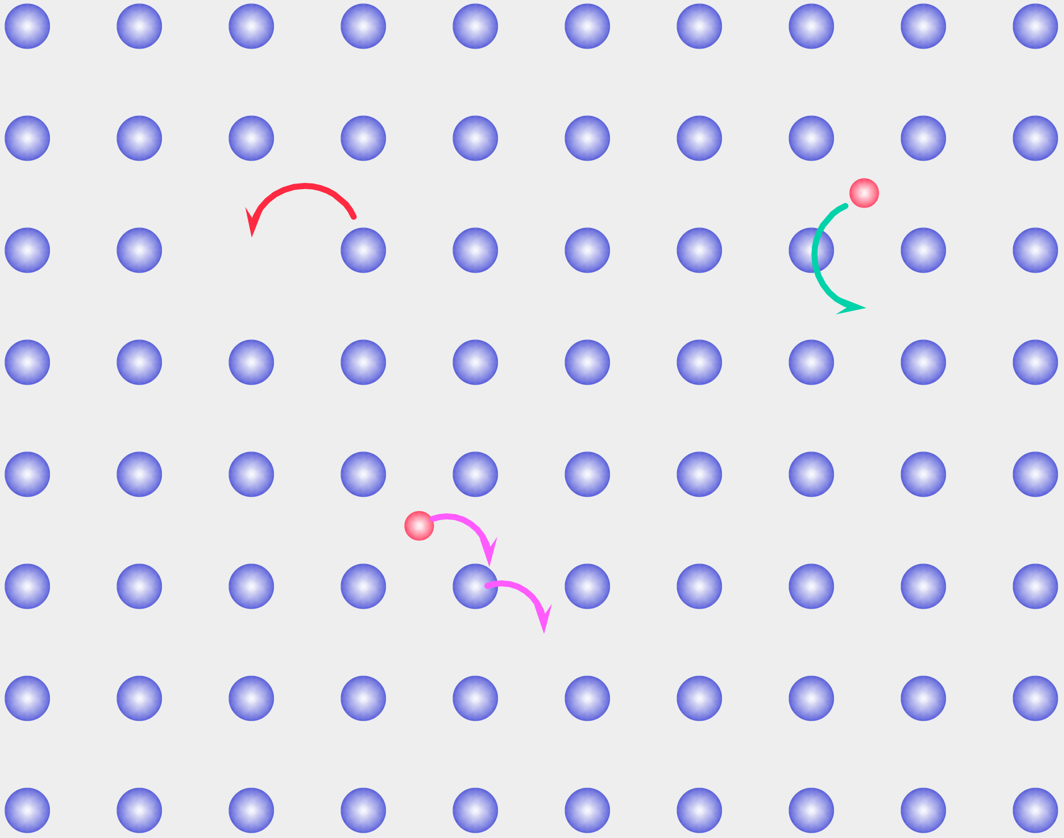
$\Delta H > 0$

$\Delta G = \Delta H - T\Delta S$

ΔS = configurational entropy

The free energy is reduced up to a distinct defect concentration

Important diffusion mechanisms



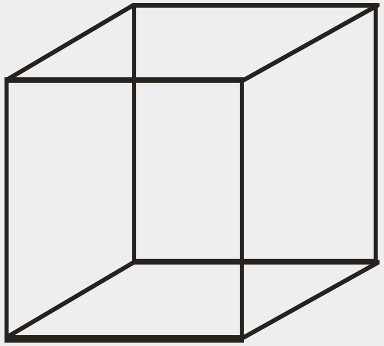
Vacancy mechanism

Interstitial mechanism

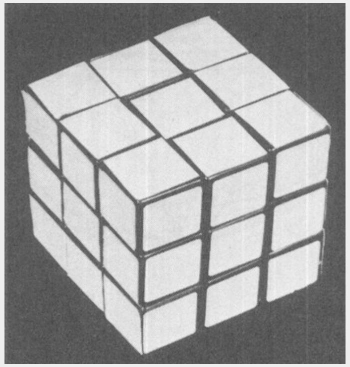
Displacement mechanism

Enhancement of reaction rates by reduction of particle size

cubic crystal:
$V = 1\ cm^3$
$F = 6 \cdot 1 = 6\ cm^2$



Reduction of each
face by factor 10



10^3 particles, $V =$
$0.1 \cdot 0.1 \cdot 0.1 = 0.001\ cm^3$
Drastic increase of surface

Educt – ball milling!

Educts – press pellets, increase of reacting surface

Particles of metals

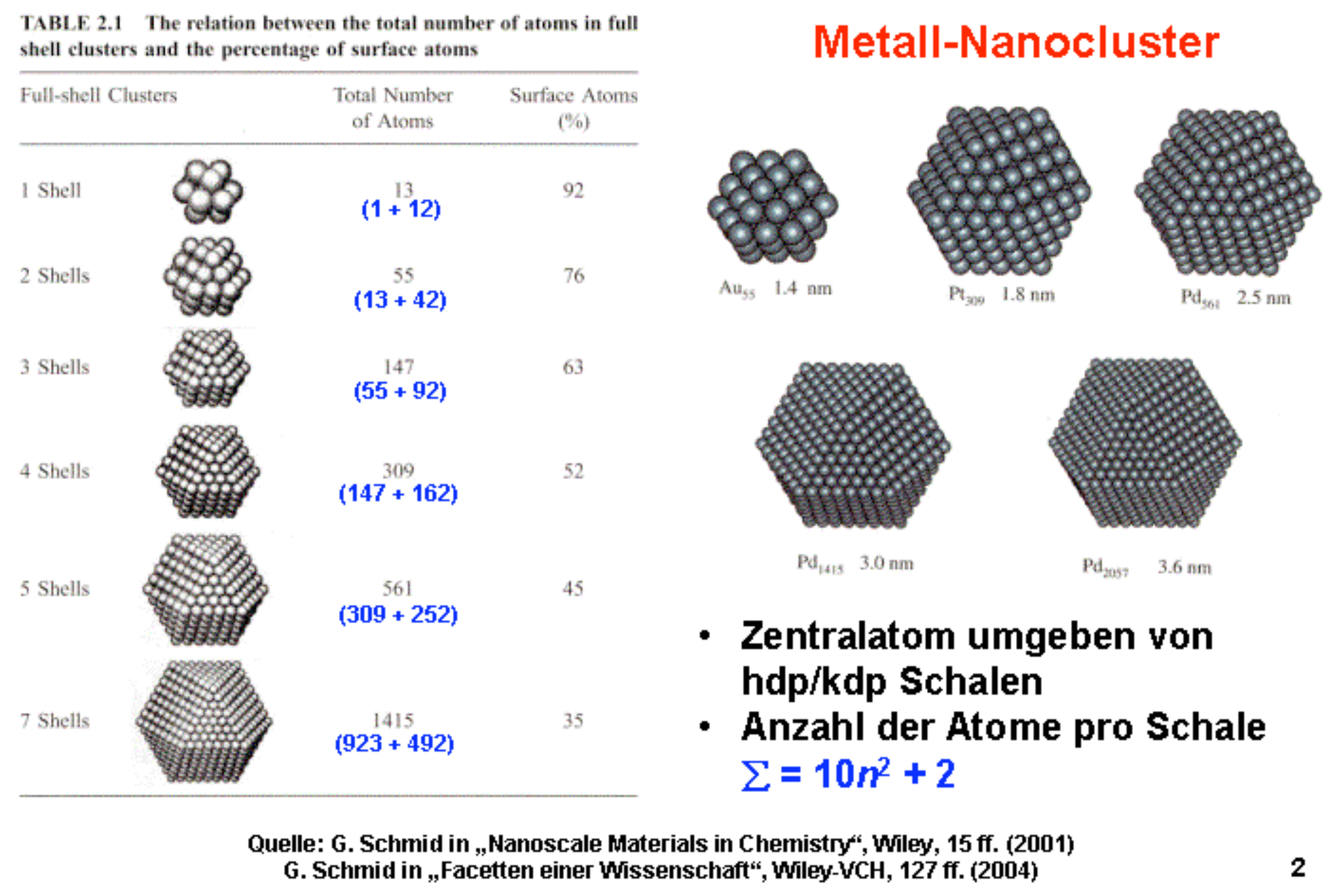


TABLE 2.1 The relation between the total number of atoms in full shell clusters and the percentage of surface atoms

Full-shell Clusters	Total Number of Atoms	Surface Atoms (%)
1 Shell	13 (1 + 12)	92
2 Shells	55 (13 + 42)	76
3 Shells	147 (55 + 92)	63
4 Shells	309 (147 + 162)	52
5 Shells	561 (309 + 252)	45
7 Shells	1415 (923 + 492)	35

Metall-Nanocluster

Au_{55} 1.4 nm

Pt_{309} 1.8 nm

Pd_{561} 2.5 nm

Pd_{1415} 3.0 nm

Pd_{2057} 3.6 nm

- **Zentralatom umgeben von hdp/kdp Schalen**
- **Anzahl der Atome pro Schale**
  $\Sigma = 10n^2 + 2$

Quelle: G. Schmid in „Nanoscale Materials in Chemistry“, Wiley, 15 ff. (2001)
G. Schmid in „Facetten einer Wissenschaft“, Wiley-VCH, 127 ff. (2004)

→ The smaller the particles, the larger amount of surface atoms

Particle size and melting point

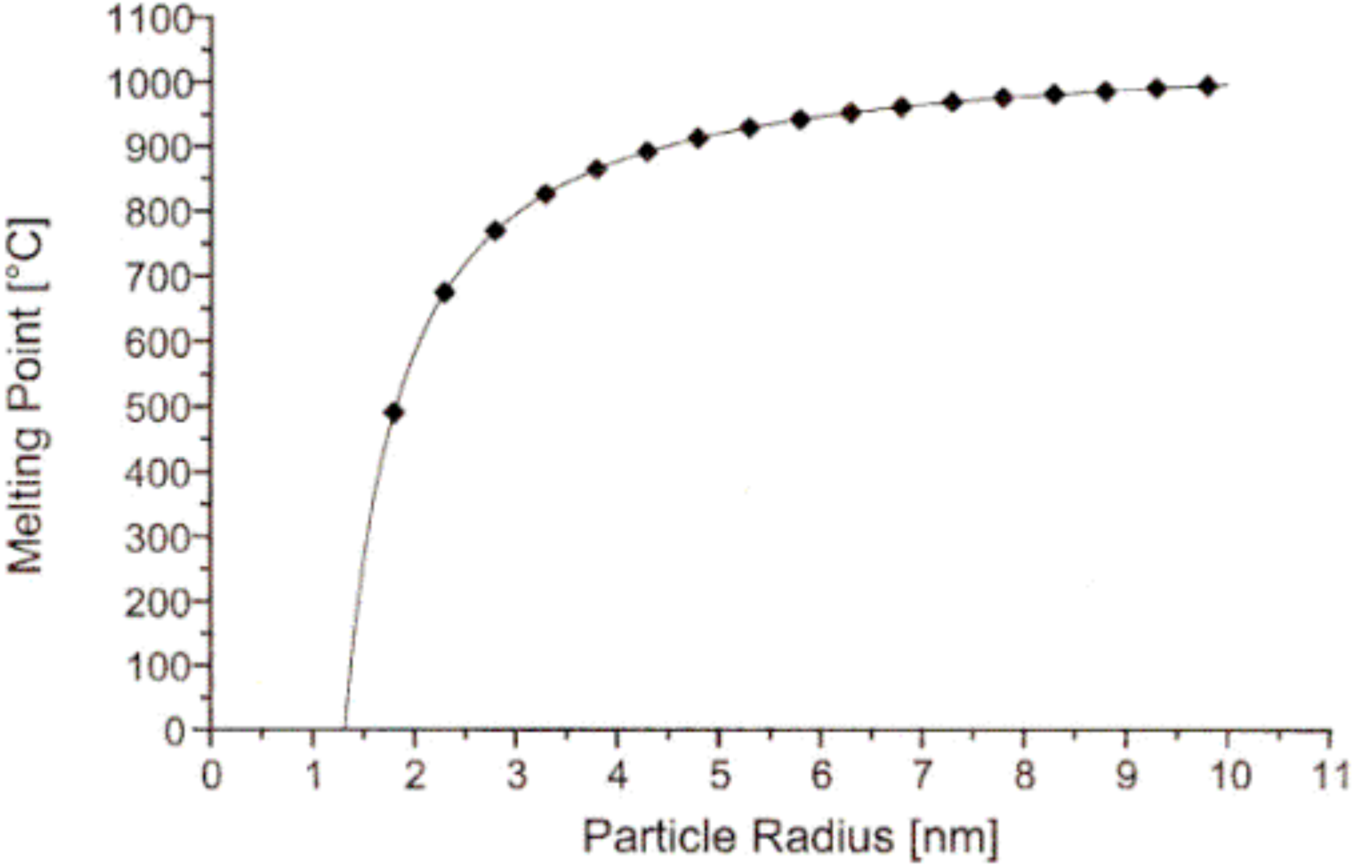


FIGURE 2.6 Relation between the size of gold particles and their melting point.

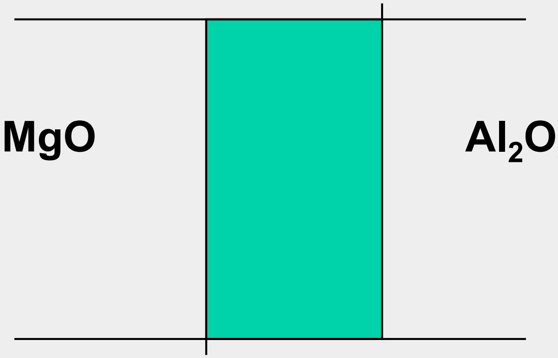
Quelle: G. Schmid in „Nanoscale Materials in Chemistry“, Wiley, 15 ff. (2001)

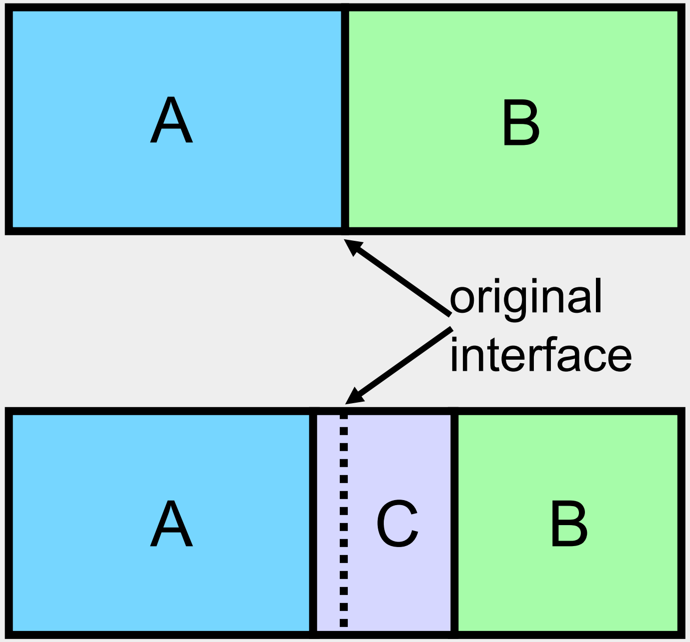
Thin Film Reaction

Model of a solid-solid reaction

Phase 1:
Nucleation

Phase 2:
growth of nuclei





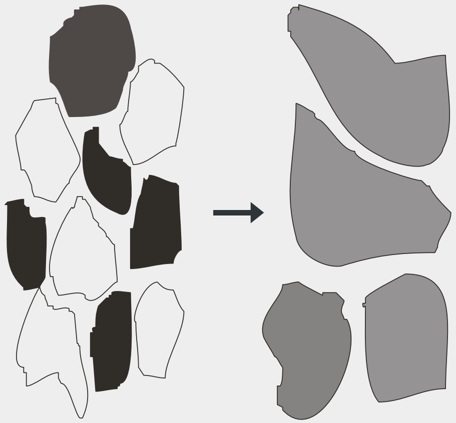
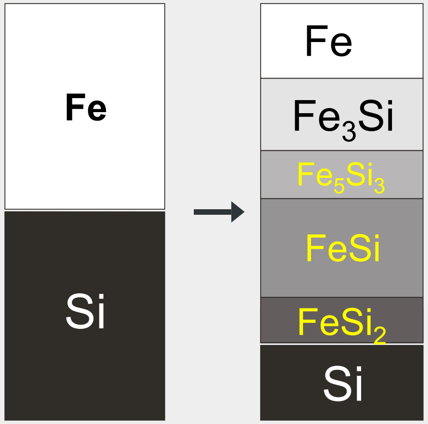
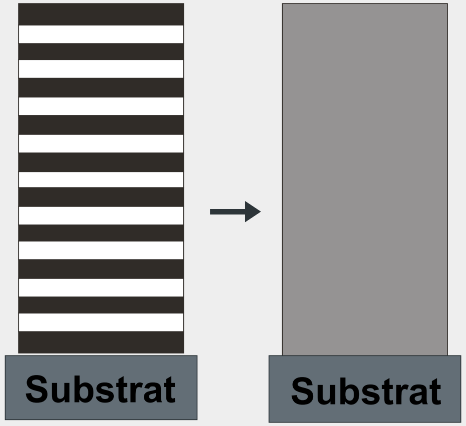
Product layer

Generally hold for solid-solid reactions?

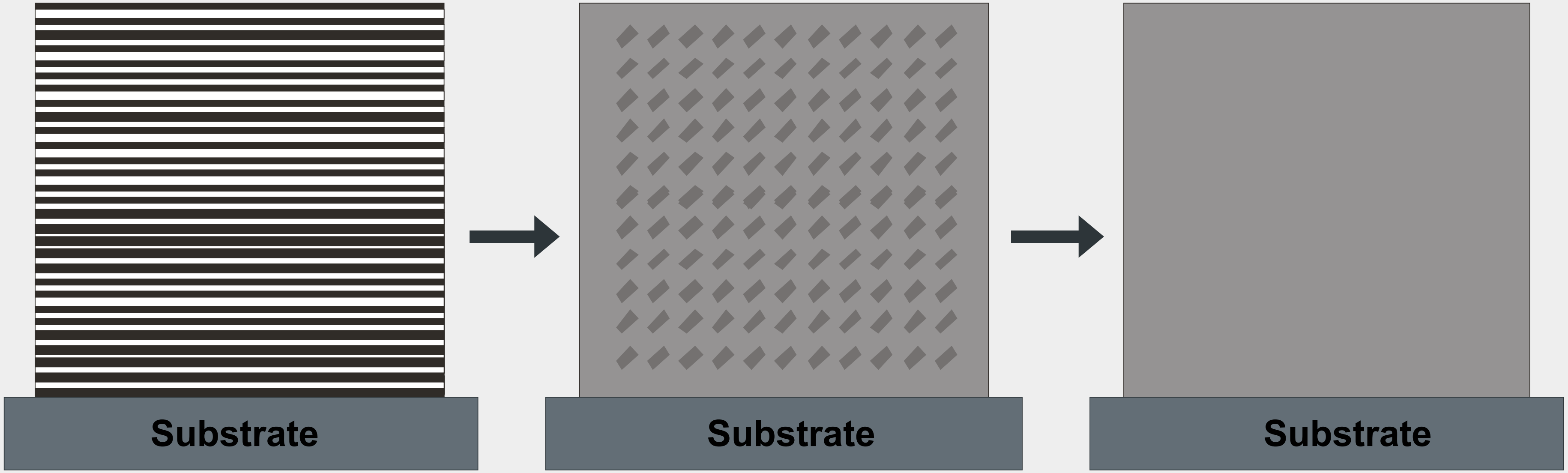
What is the exact mechanism?

Investigations of bulk materials very difficult

Syntheses using thin films

<table>
<tr><th>Bulk</th><th>Bulk diffusion pair</th><th>Thin films</th></tr>
<tr><td></td><td> </td><td> </td></tr>
<tr><td colspan="3">Lengths of diffusion paths</td></tr>
<tr><td>~10-1 μm</td><td>~10-1 μm</td><td>~100 - <1 nm</td></tr>
<tr><td colspan="3">Rate determining step</td></tr>
<tr><td>Diffusion</td><td>Diffusion</td><td>Nucleation</td></tr>
</table>

Syntheses using thin films

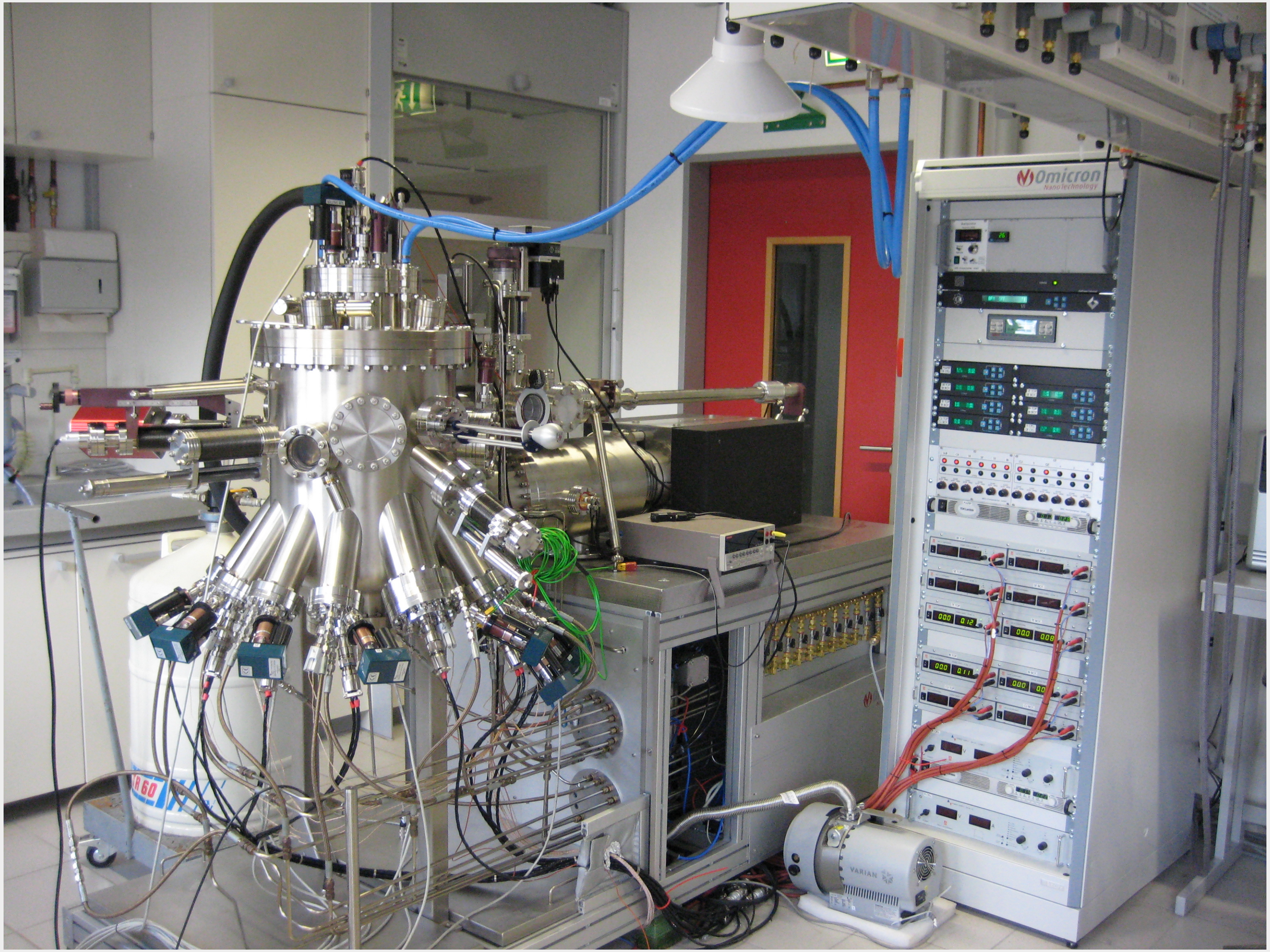


Very thin layers

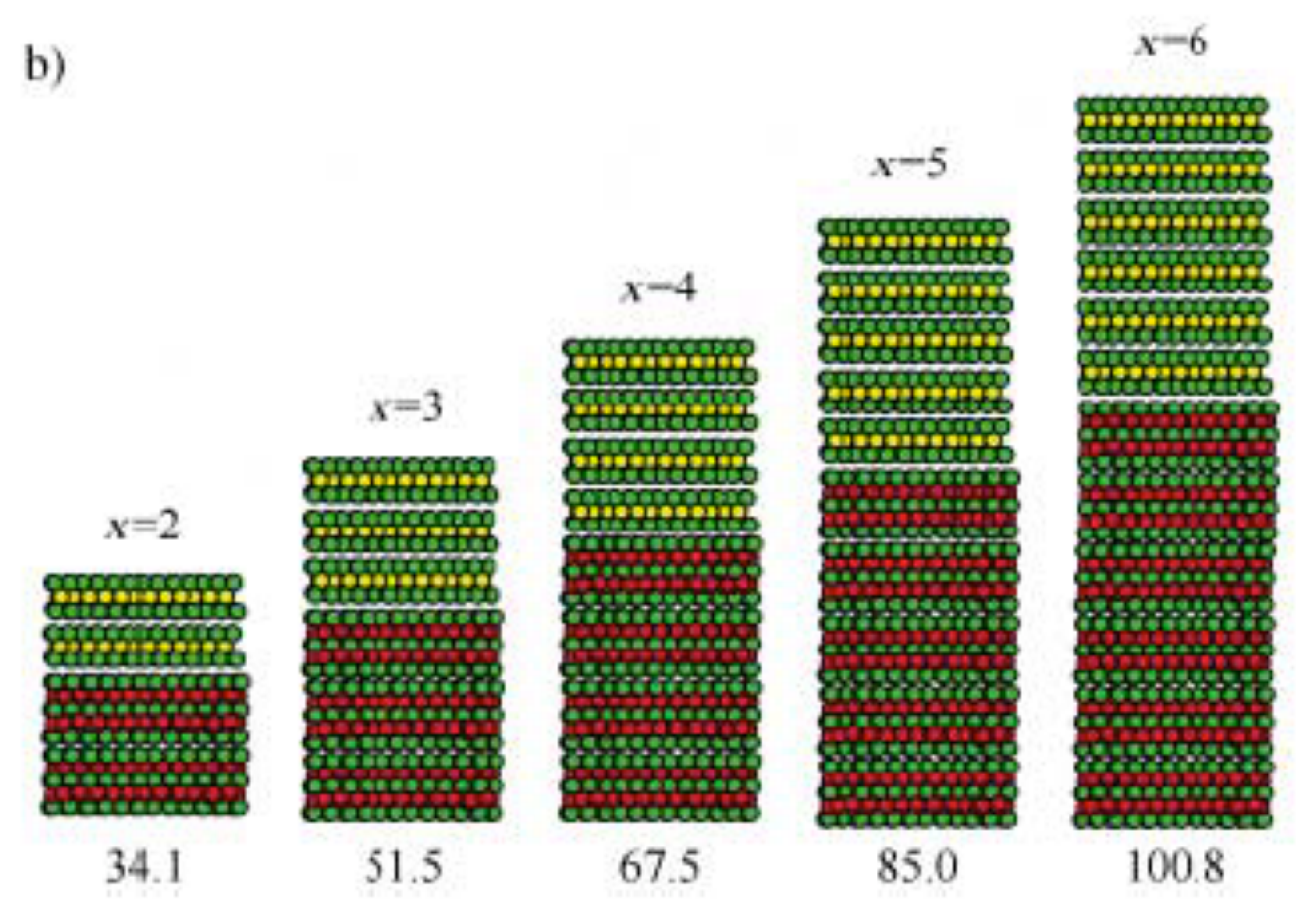
Amorphous intermediate

Crystalline product

Synthesis of thin films – MBE in Kiel

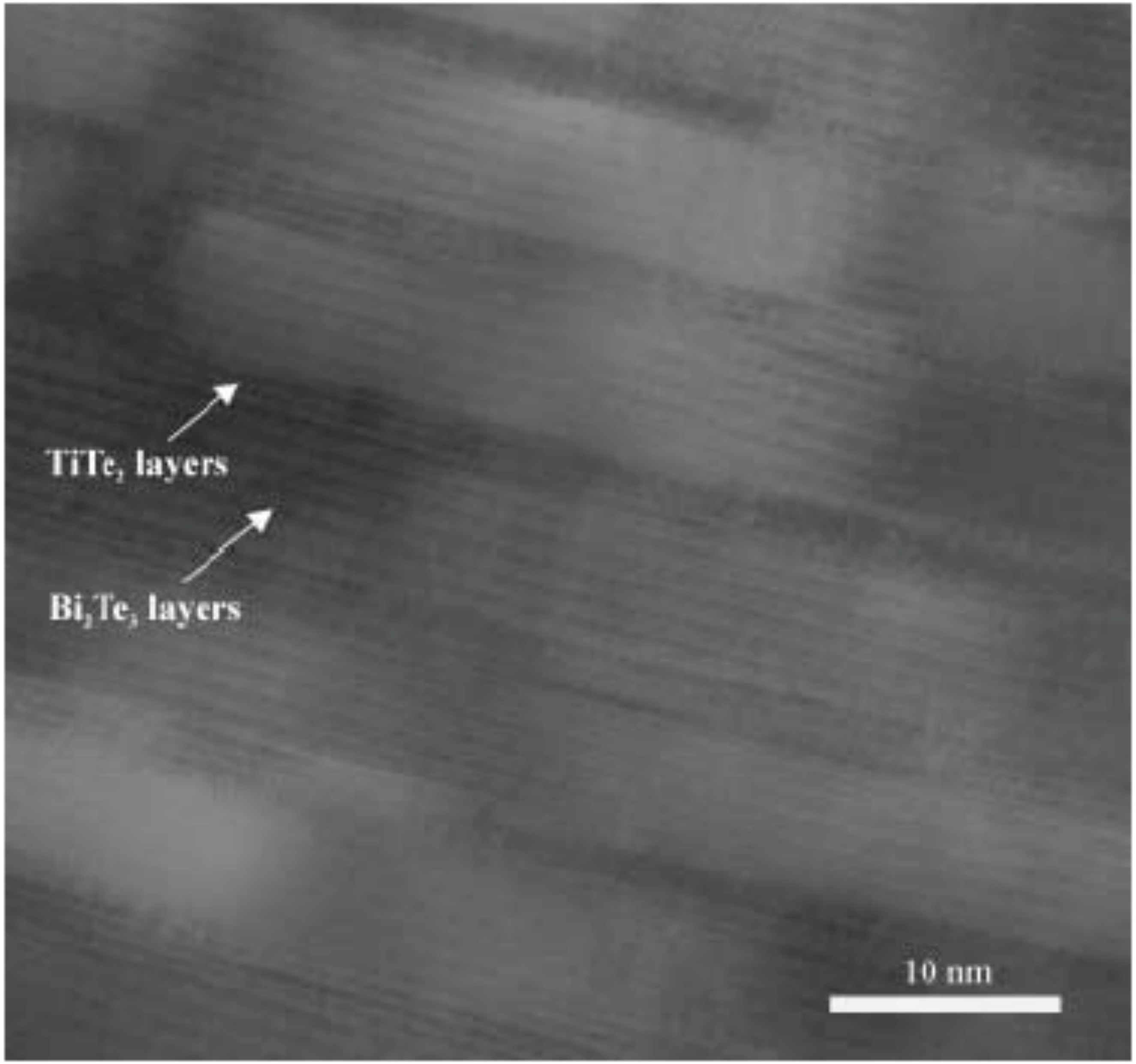


Synthesis of complex superlattices

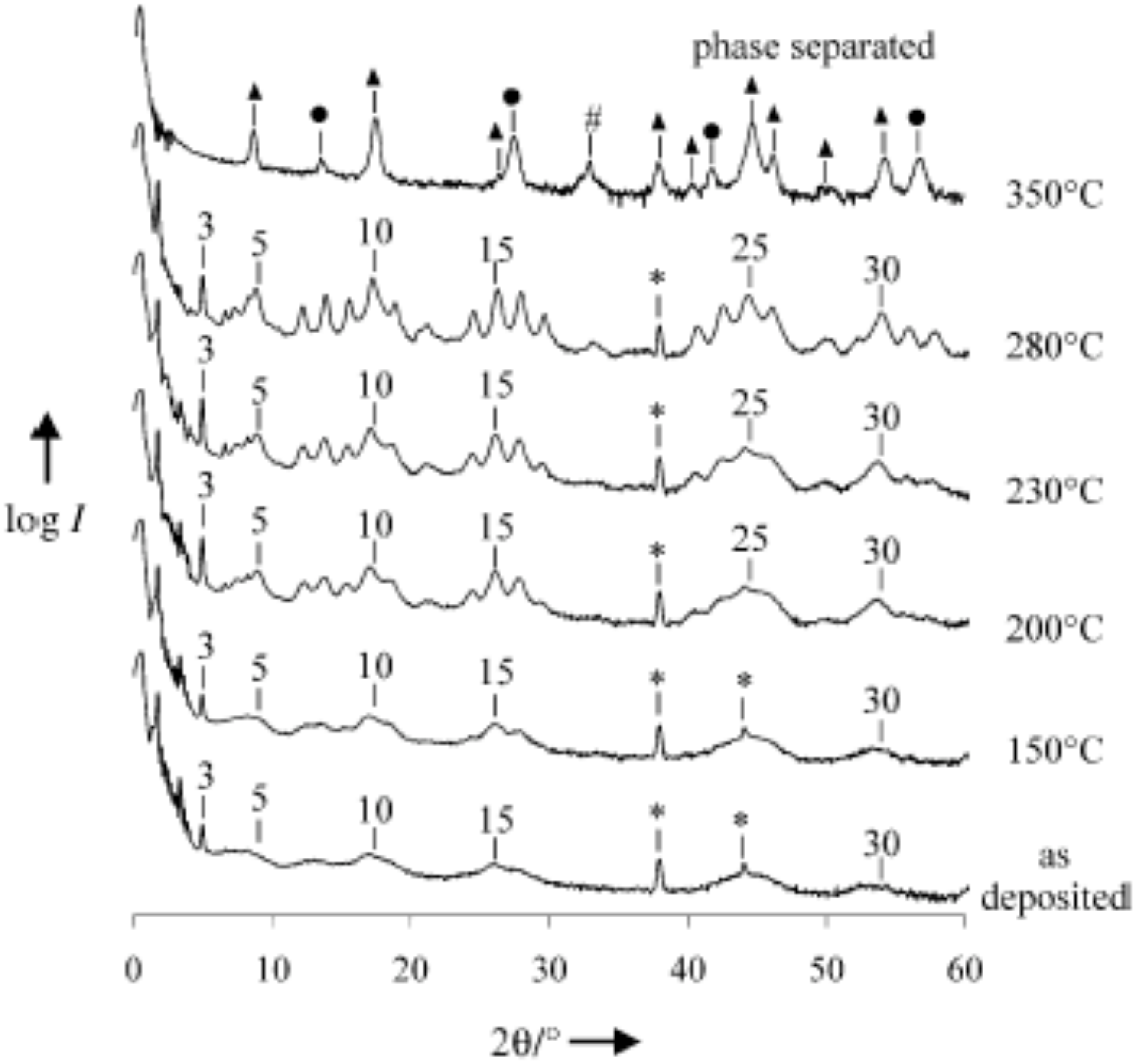


Scheme of a $[(Bi_2Te_3)_x(TiTe_2)_x]$ superlattice

TEM image of the superlattice



Formation of superlattice



Advantages and disadvantages

Advantages:

- More or less all element combinations possible
- control of product: composition of amorphous intermediate
- trap of new and metastable compounds: Na_3N, LiBr (Wurtzite), Mo_3Se, CrSb (Wurtzite)

Disadvantages:

- Special apparatus required (UHV)
- Sample throughput and amount of sample are low
- Characterization: time-consuming, special techniques required

Co-Precipitation Synthesis

Co-precipitation

- Dissolve salts in Wasser
- Co-precipitation by evaporation of solvent
- Hydroxides, carbonates, oxalates, formiates, citrates as sources
- Heating the precipitate at appropriate temperature in defined atmosphere

Example: synthesis of $ZnFe_2O_4$ (Spinel):

$$Fe_2(C_2O_4)_3 + Zn(C_2O_4) \xrightarrow{\Delta T} ZnFe_2O_4 + 4\ CO + 4\ CO_2$$

1. Dissolve 1 equivalent Fe oxalate and Zn oxalate in water
2. Partial evaporatation of water ---> powder and some remaining water
3. filtration
4. Annealing of precipitate

Thermal Decomposition Reaction

Precursor methods/thermal decomposition reaction

Thermal decomposition of suitable precursors containing the desired atoms in correct stoichiometric proportions

Special case: Redox compounds

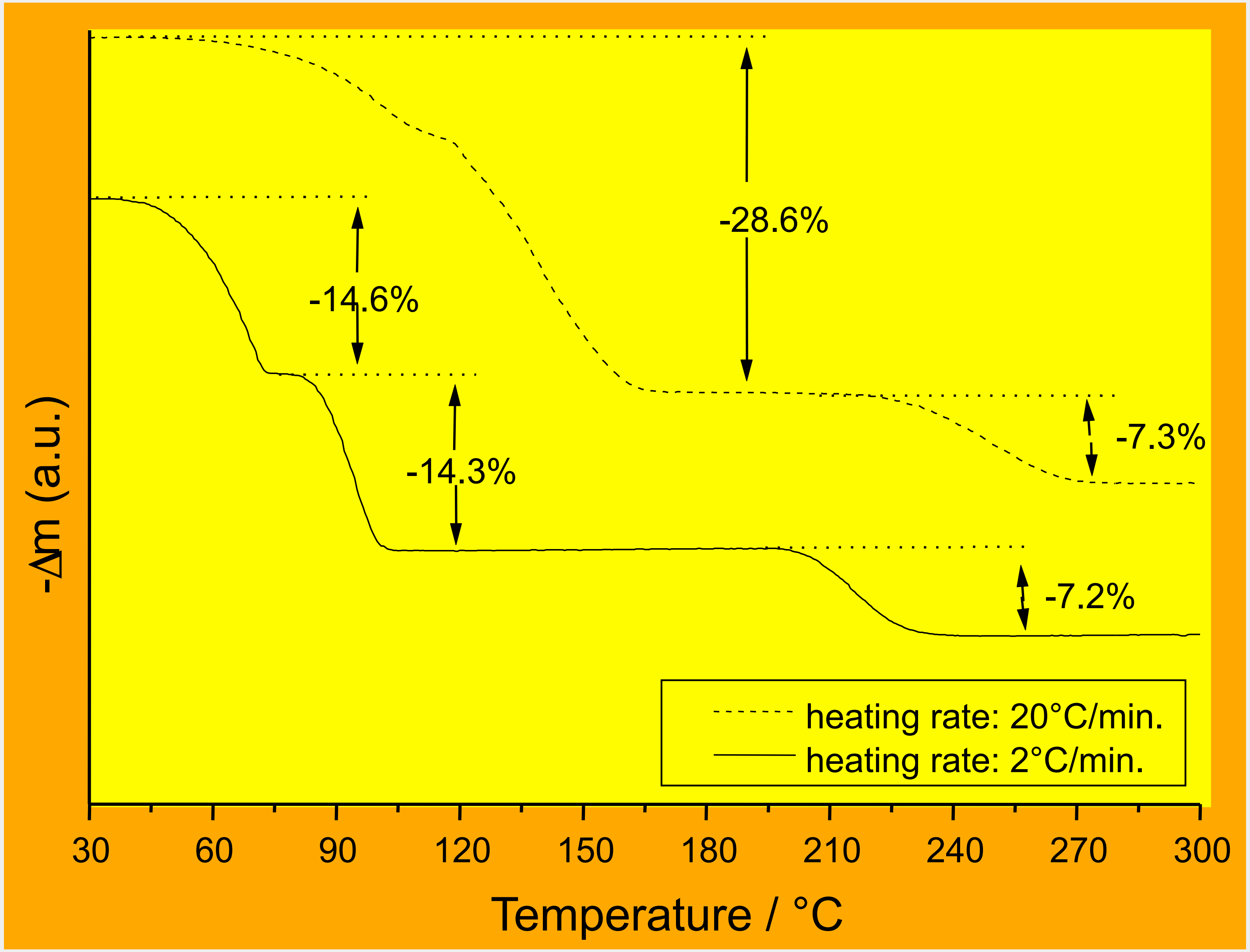
$$(NH_4)_2Mg(CrO_4)_2 \cdot 6\ H_2O \longrightarrow MnCr_2O_4 + N_2 + 10\ H_2O$$

Cr^{6+} ---> Cr^{3+}; N^{3-} ---> N^0

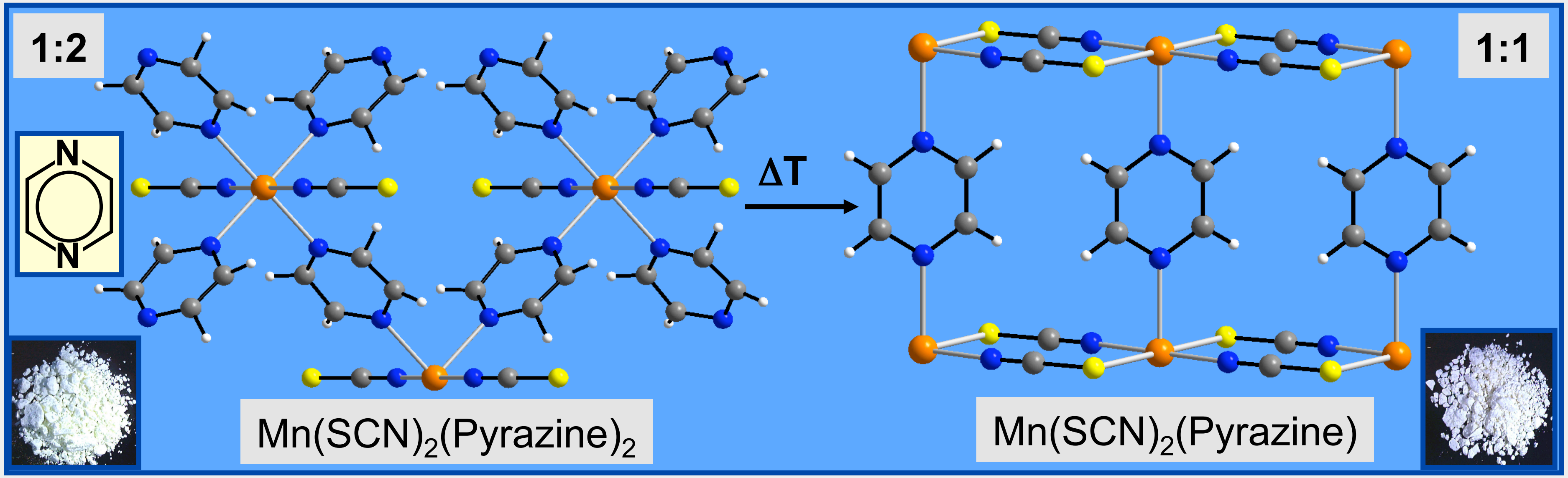
Precursor	**Product**
$La[Co(CN)_6] \cdot 5\ H_2O$	$LaCoO_3$
$Ba[TiO(C_2O_4)_2]$	$BaTiO_3$ (Perowskit ($CaTiO_3$))
$M_3Fe_6O_3(OH)(OAc)_{17} \cdot 12$ Pyridin	MFe_2O_4 (M = Mg, Mn, Co, Ni) (Spinell)
$(NH_4)_2M(CrO_4)_2 \cdot 6\ H_2O$	MCr_2O_4 (M = Mg, Ni) (Chromite)
$(NH_4)_2M(CrO_4)_2 \cdot 2\ NH_3$	MCr_2O_4 (M = Cu, Zn) (Chromite)
$MCr_2O_7 \cdot 4$ Pyridin	MCr_2O_4 (M = Mn, Co) (Chromite)
$MFe_2(C_2O_4)_3 \cdot x\ N_2H_4$	MFe_2O_4 (M = Mg, Ni, Co, Ni, Zn) (Ferrite)

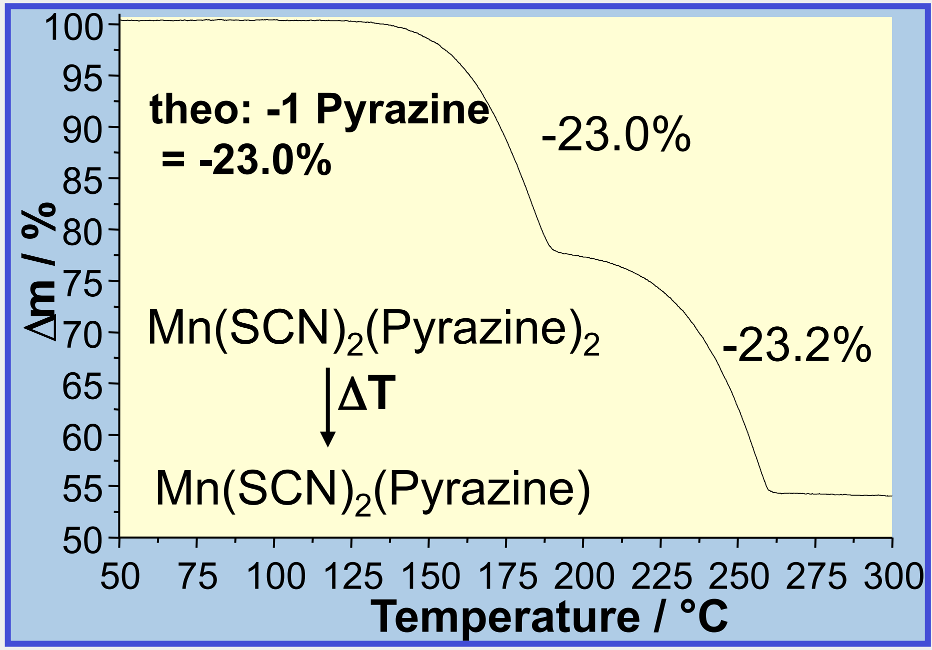
Thermal decomposition reactions

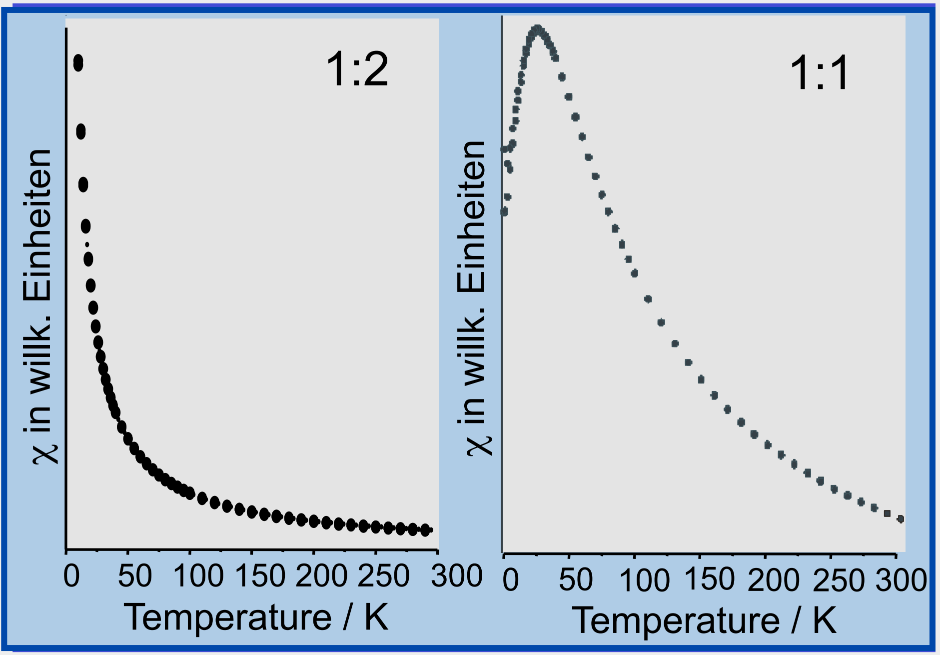
$$CuSO_4 \cdot 5\,H_2O \xrightarrow{\Delta T} CuSO_4 \cdot 3\,H_2O \xrightarrow{\Delta T} CuSO_4 \cdot H_2O \xrightarrow{\Delta T} CuSO_4$$



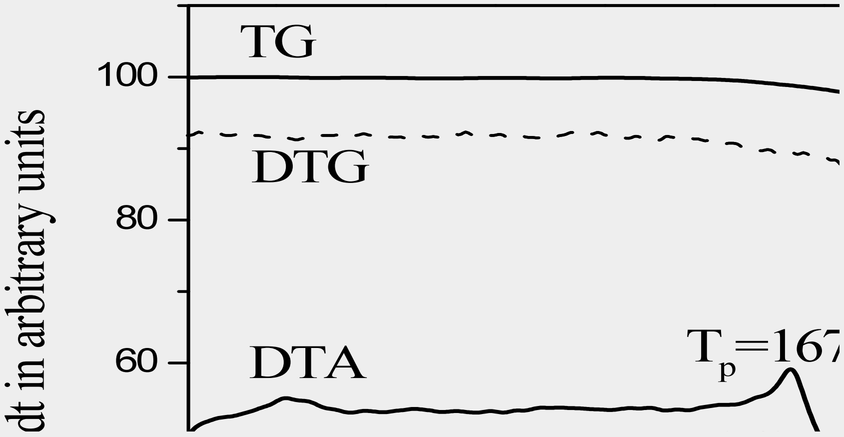
Thermal decomposition of $\mathrm{Mn(SCN)_2(Pyrazine)_2}$



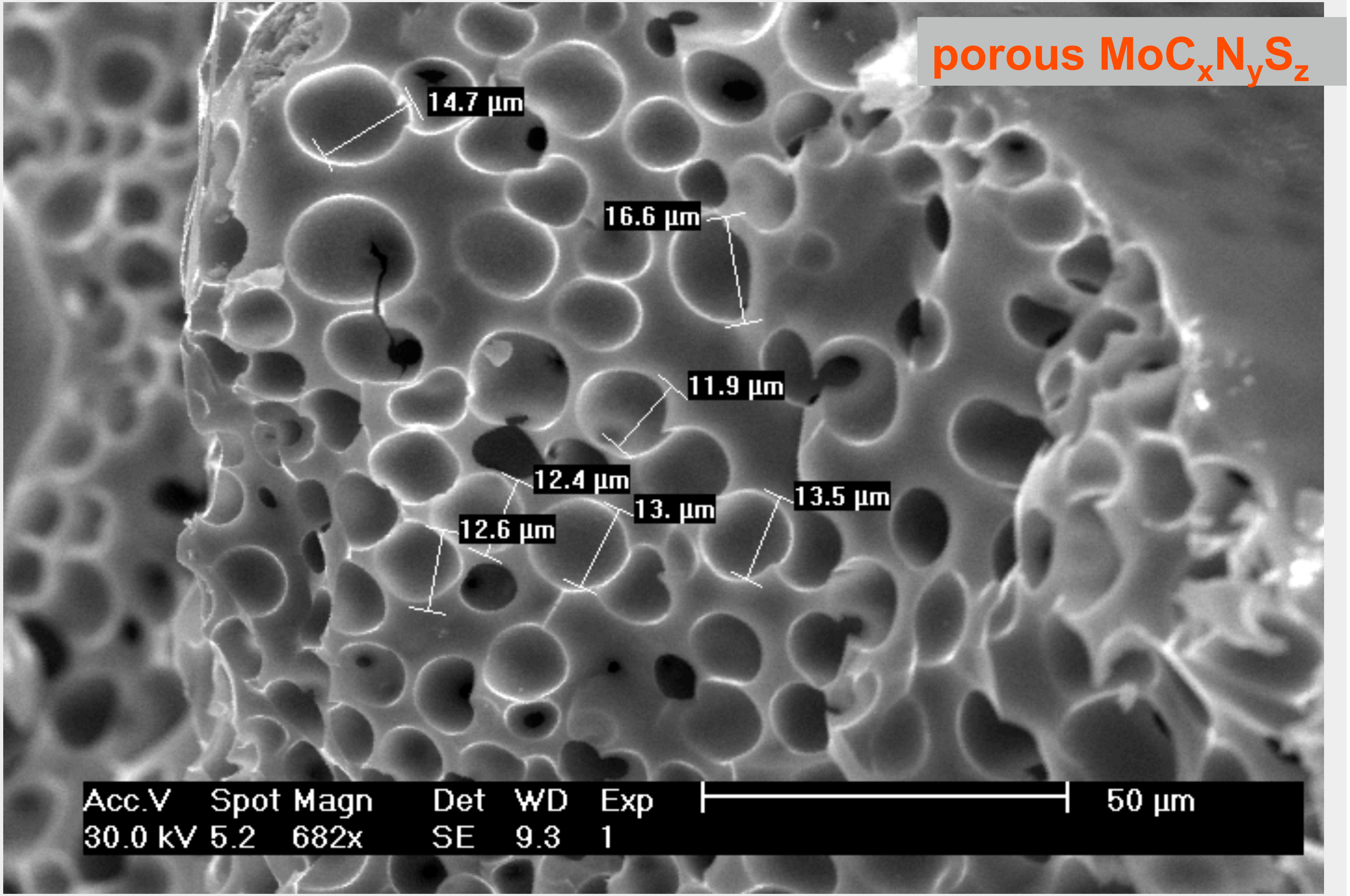




Thermal decomposition reaction $[(hexyl)_4N]_2[MoS_4]$

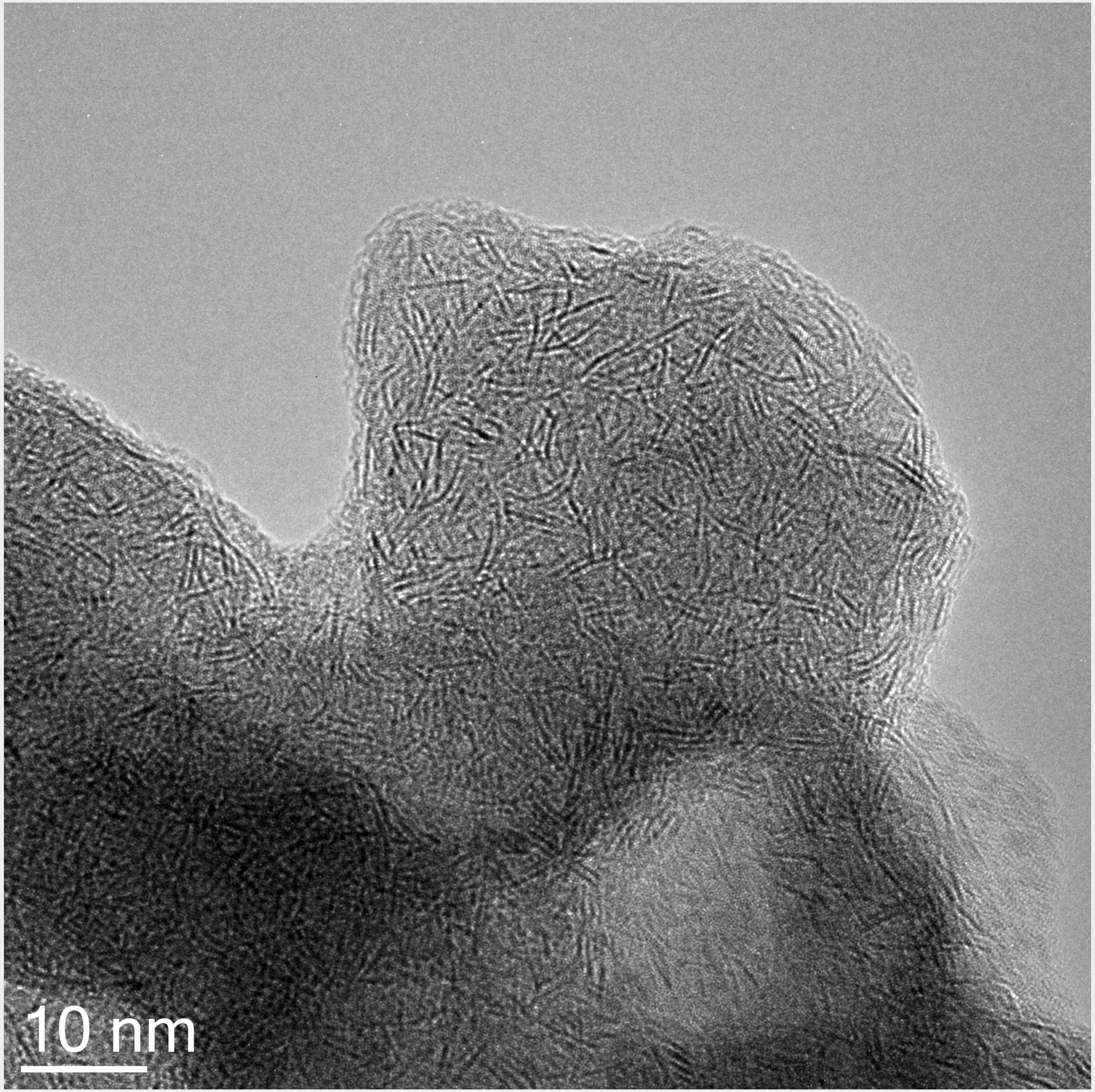


Thermal decomposition of $[(hexyl)_4N]_2[MoS_4]$



porous $MoC_xN_yS_z$

Thermal decomposition of $[(hexyl)_4N]_2[MoS_4]$



Intercalation and Deintercalation Reaction

Intercalation- and deintercalation reactions

Intercalation: reversible uptake of atoms, ions, charged or neutral molecules (guests) without significant changes of the host lattice structure.

Reversible process: deintercalation

Characteristics of intercalation reactions

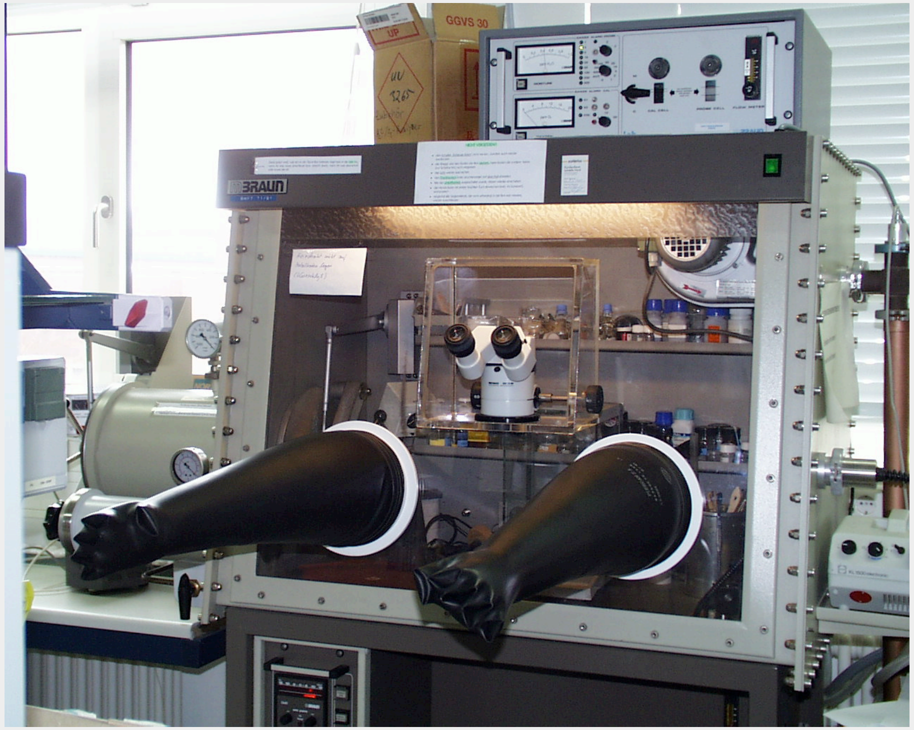
- Stable host lattice with empty sites for guests
- Empty sites must be interconnected, E_{act} for diffusion must be small
- Intercalation/deintercalation must be reversible
- Only small changes of host lattice structure

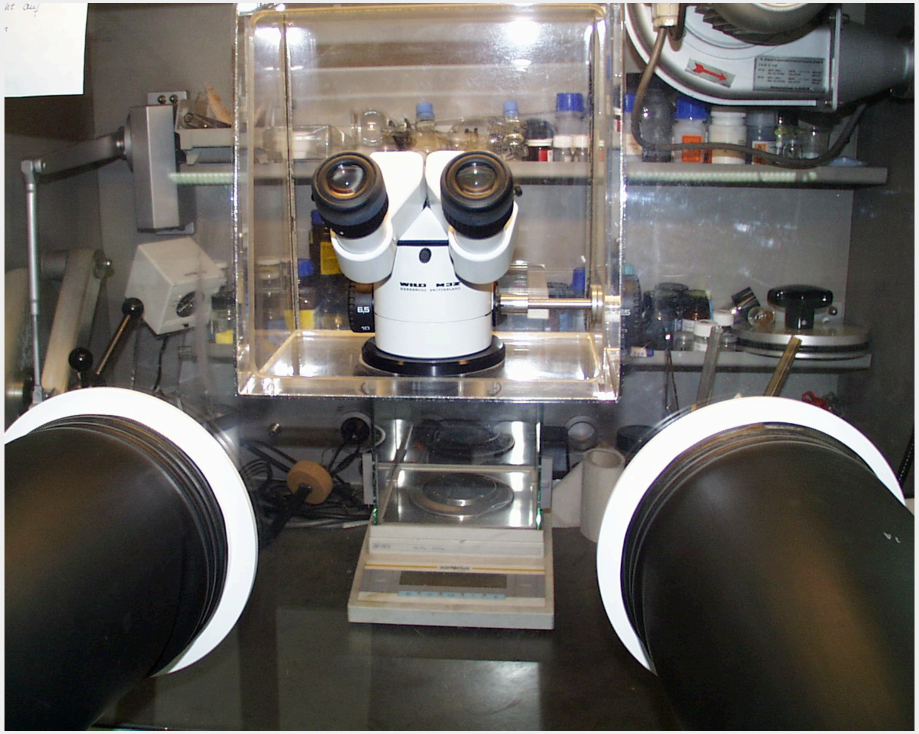
  topotactic reactions: defined relationship between structure before and after intercalation reaction, at least in one crystallographic direction
- Reactions at low temperatures leads bonds in host intact
- Kinetics dominates, metastable products
- Concentration of guests can be directed, control of chemical and physical properties
- Depending on electronic structure of host: intercalatio is accompanied by electron-ion transfer

Synthetic aspects of intercalation reactions

- Reaction types: solid-solid, solid-liquid, solid-gas
- Intercalation chemically or electrochemical
- Often: guest supllied in excess
- Control of guest concentration: time-temperature profiles, kinetics can be monitored
- Reaction conditions: host lattice should not be destroyed
- Reaction containers/vessels: depend on conditions
- Choice of host lattices and guests: „rational synthesis“

Synthesis of air and moisture sensitive solids – expensive solution

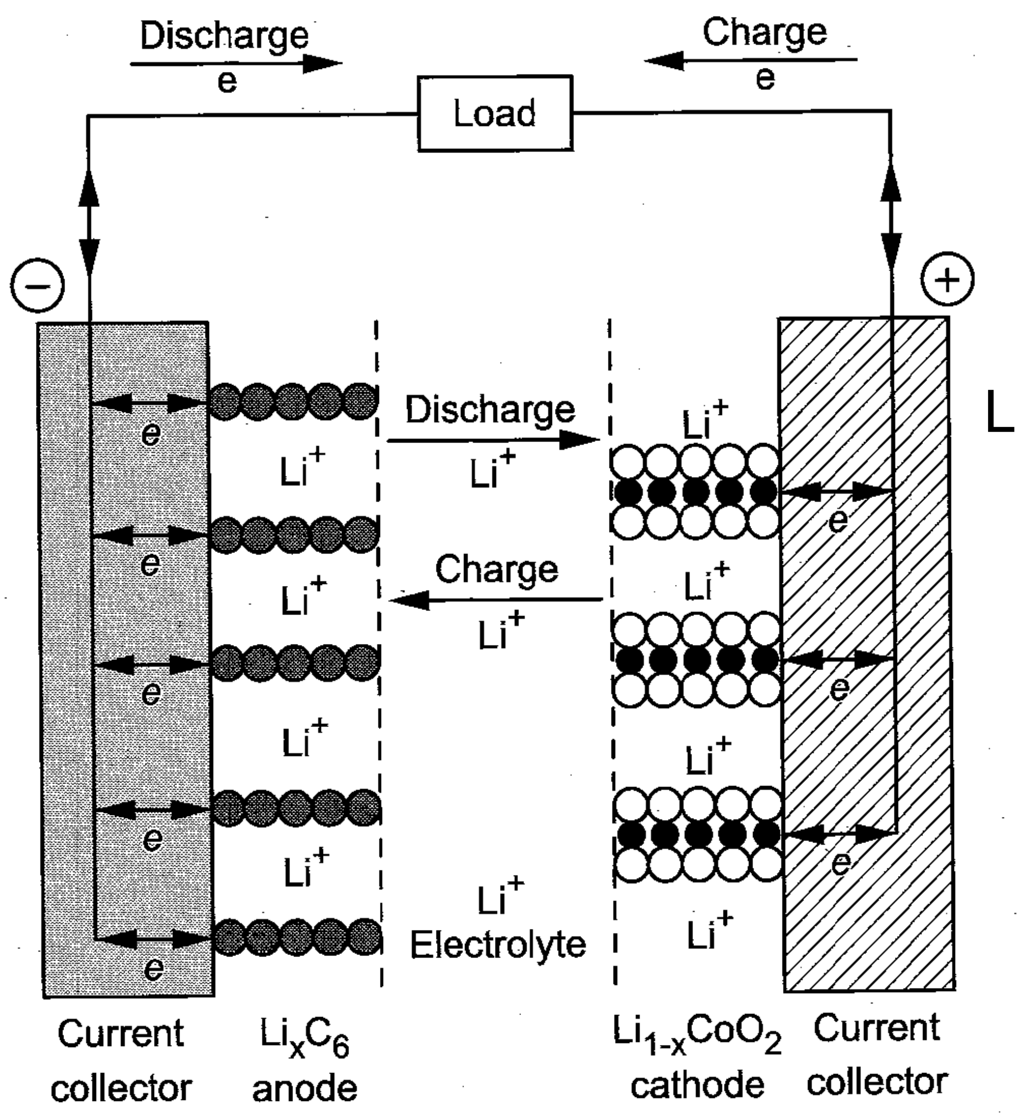




- **Charakteristics of glove boxes:**
- Very low level of O_2 and H_2O
- Different atmospheres possible (Ar / N_2)
- Special boxes for handling of solvents
- Microscope to manipulate small crystals
- Atmosphere is cleaned by catalysts and molecular sieves

Less expensive solution – Schlenk line

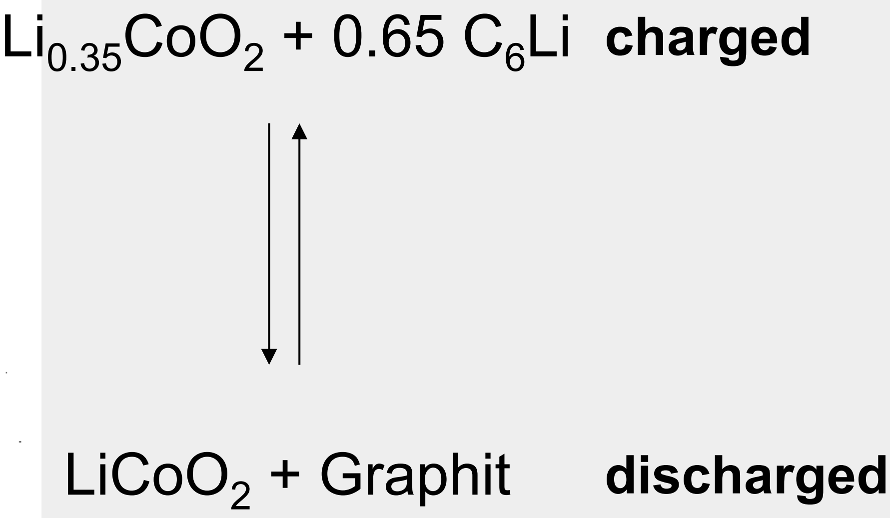
Intercalation reaction: battery



Polymer electrolyte

Li-ion battery

$LiCoO_2$: layer structure



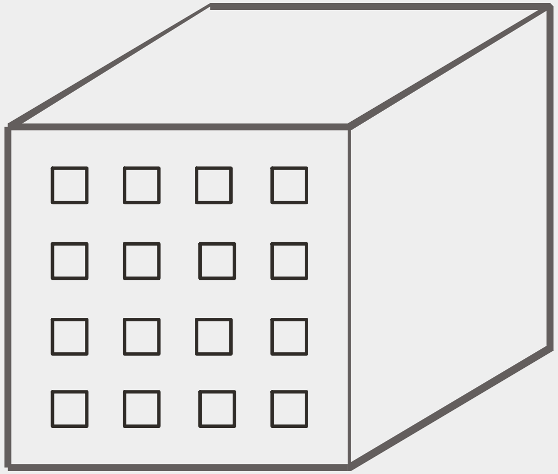
$Li_{0.35}CoO_2 + 0.65\ C_6Li$ **charged**

$\downarrow\uparrow$

$LiCoO_2$ + Graphit **discharged**

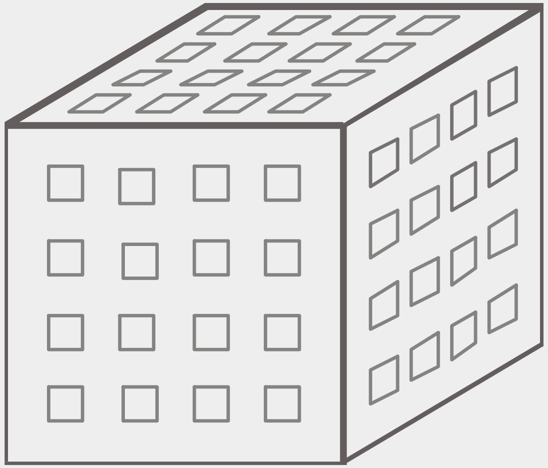
Schubert, Hüsing, Synthesis of Inorganic Materials

Host lattices



1D channel structure

Host lattice rigid
Size of guest restricted
Dimension in nm range



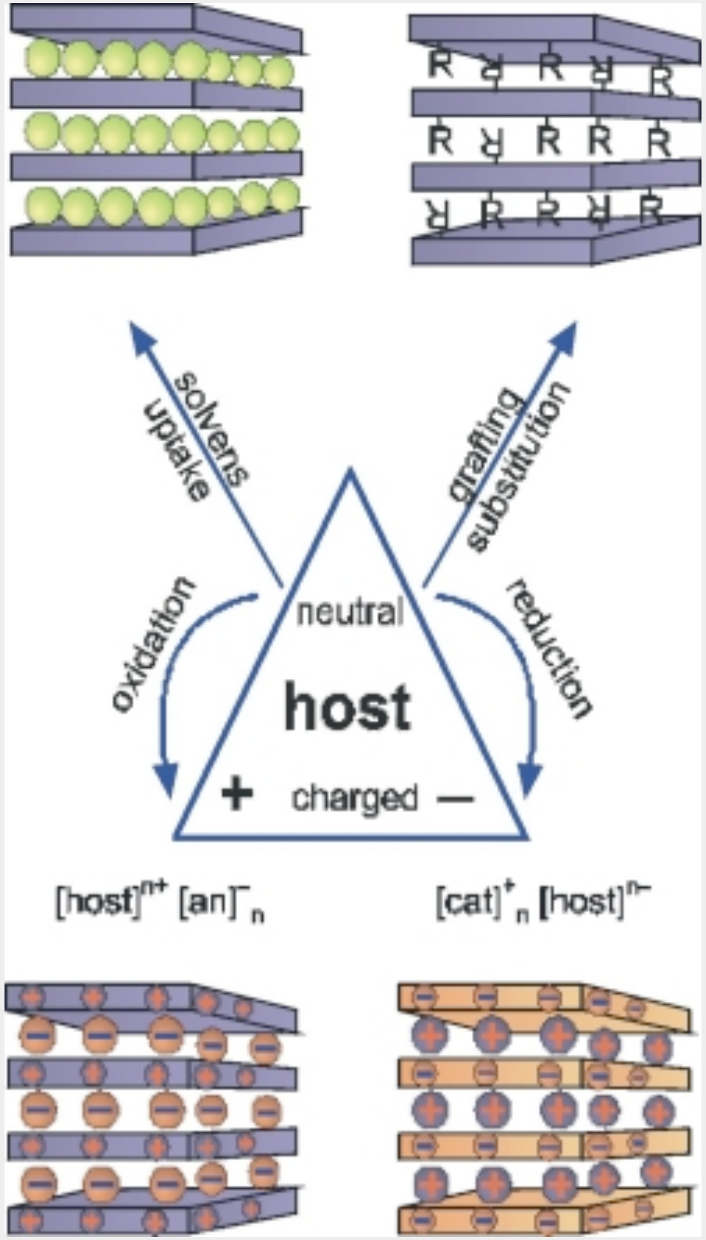
3D channel structure

1D chains

Host lattices flexible
Size of guest more or less not restricted

2D layers

Intercalation reaction types



Insulators:

nearly no change of physical properties due to intercalation, see e.g. Zeolites, Alumosilicates, Metallophosphates

→ Mainly ion exchange, catalysis, gas sorption

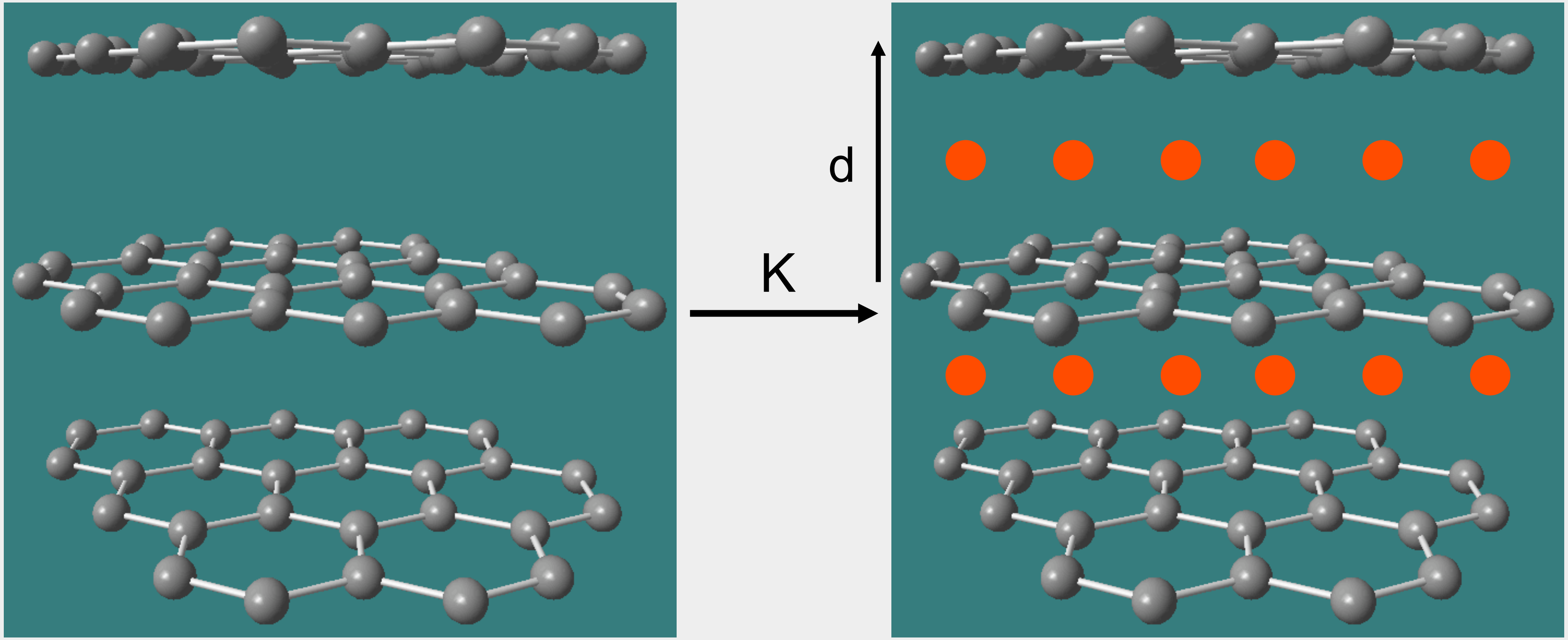
Conducting hosts:

Drastic changes of physical properties, see e.g. gpahite, TMC, V_2O_5, MoO_3, ZrNCl etc.

→ batteries

Example: KC_8

→ 2D layer



Color: gold

Interlayer separation d: depends on concentration and guest type

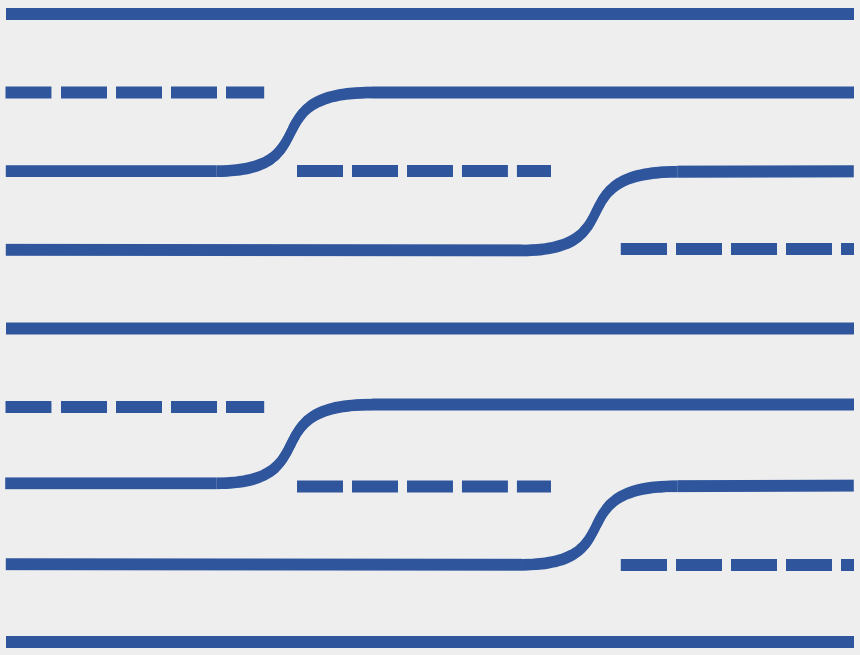
Mechanistic aspects: “Staging“

“Staging”: phenomenon of alternating empty and occupied layers

Rüdorff → Problem: change from stage 1 to stage 2 etc., cooperative mechanism

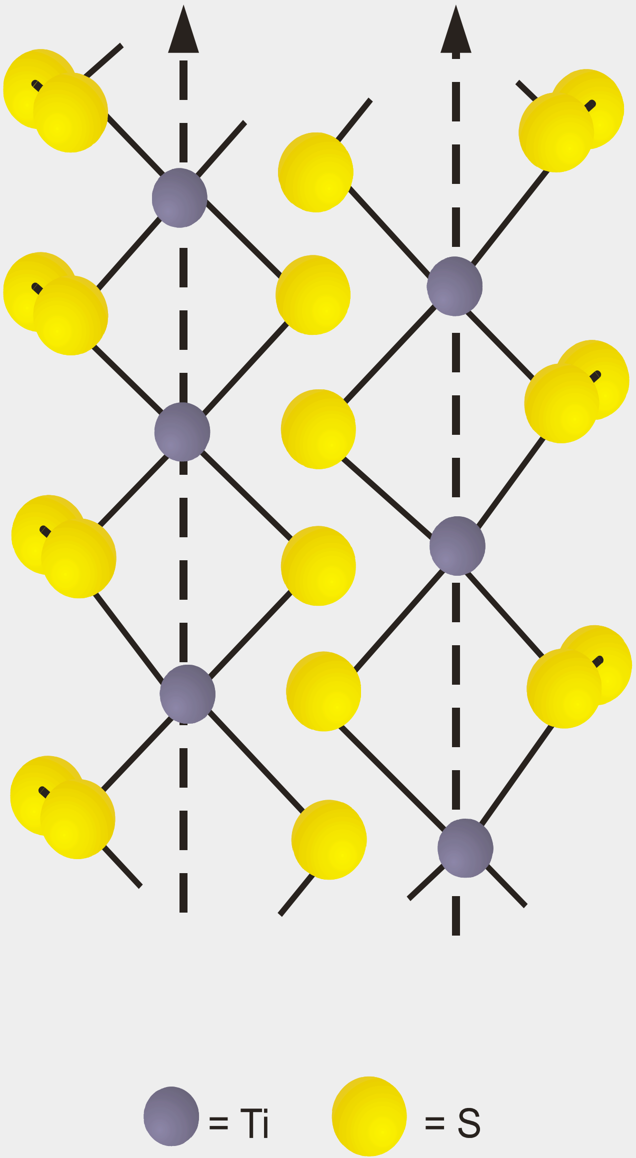
Real “Staging“

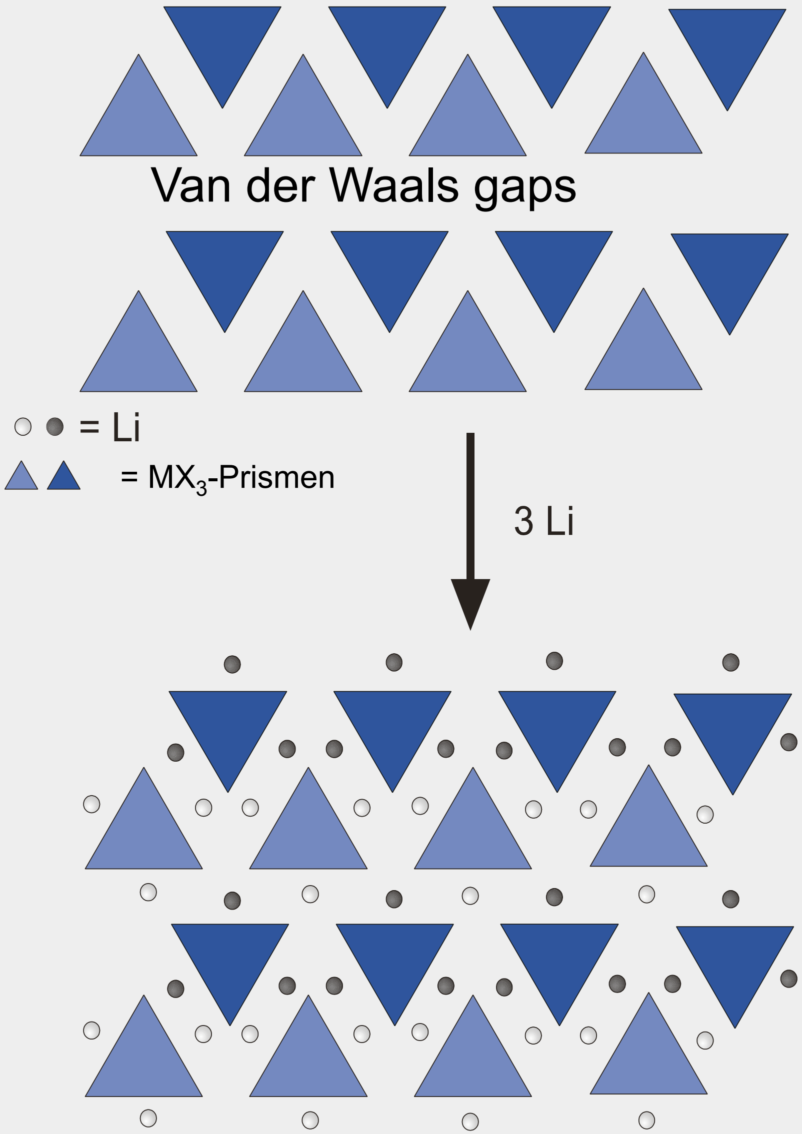
Model of Daumas-Herold



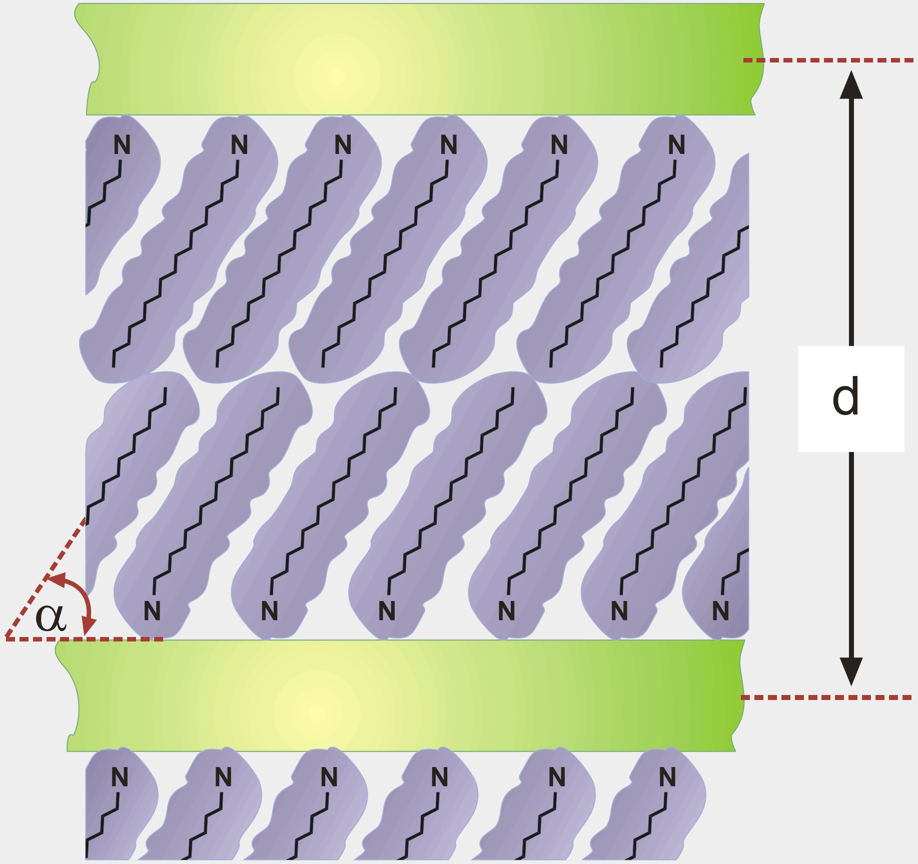
- ➢ All layers are involved
- ➢ Different local concentrations, islands smaller than crystal dimensions
- ➢ Domain structure with regularly stacked islands
- ➢ Thermodynamic properties of guests determine domains
- ➢ Regular stacking in equilibrium

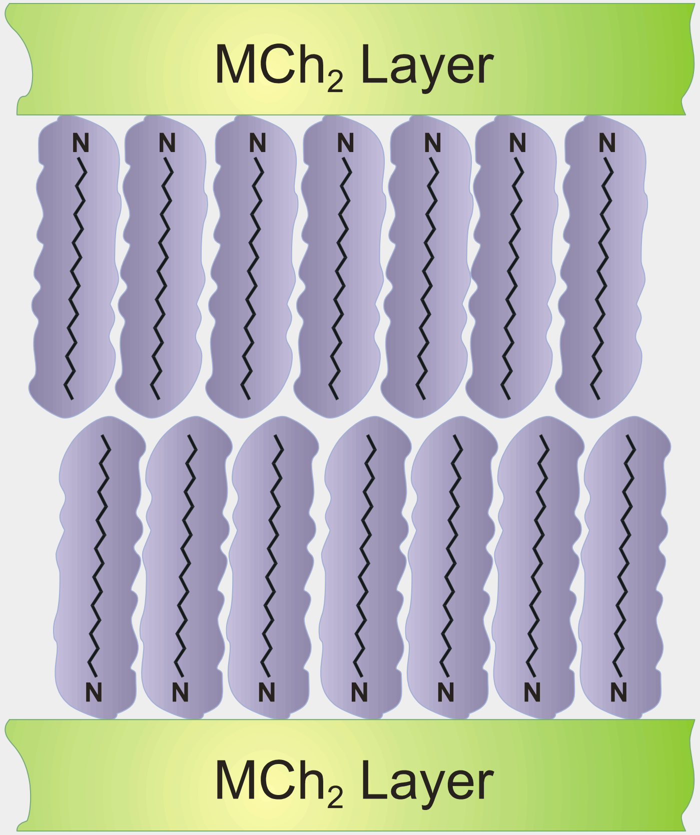
TiS$_3$: change of structure during intercalation

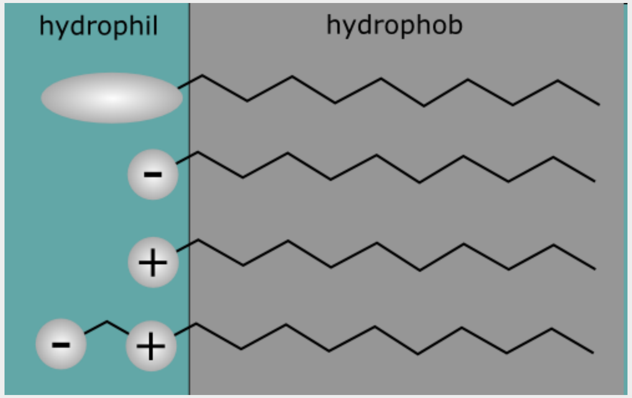




Arrangement of amphiphilic molecules

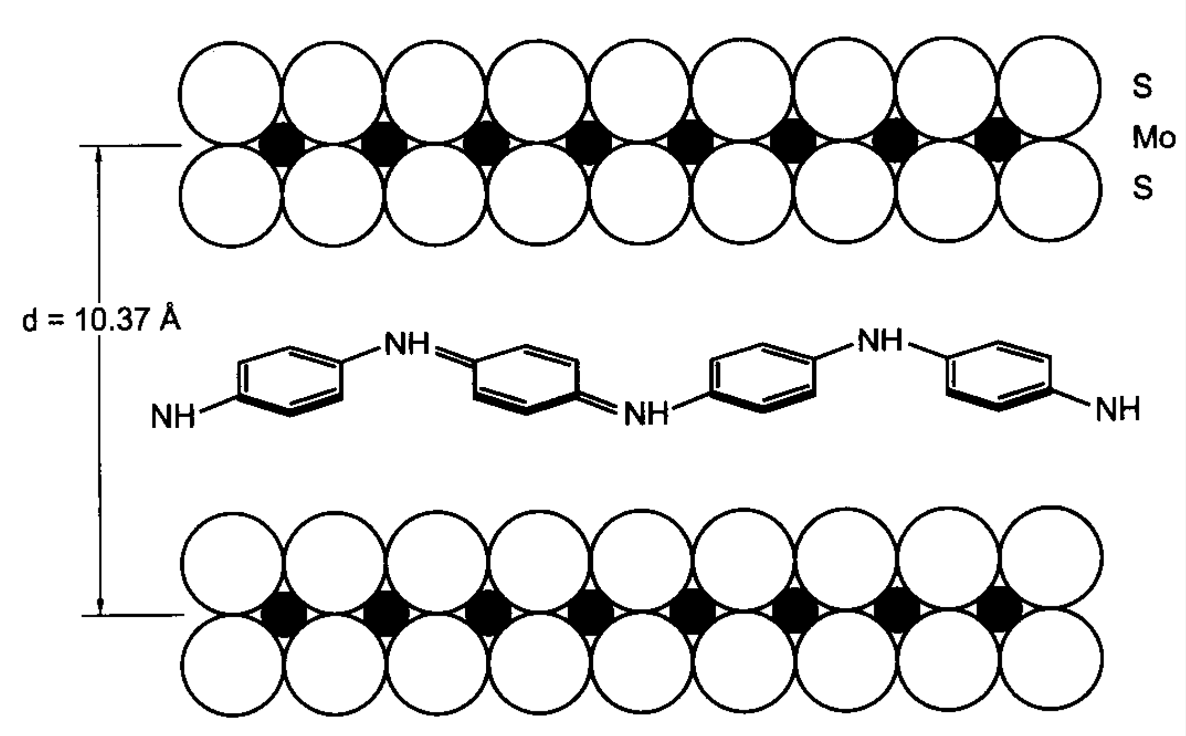






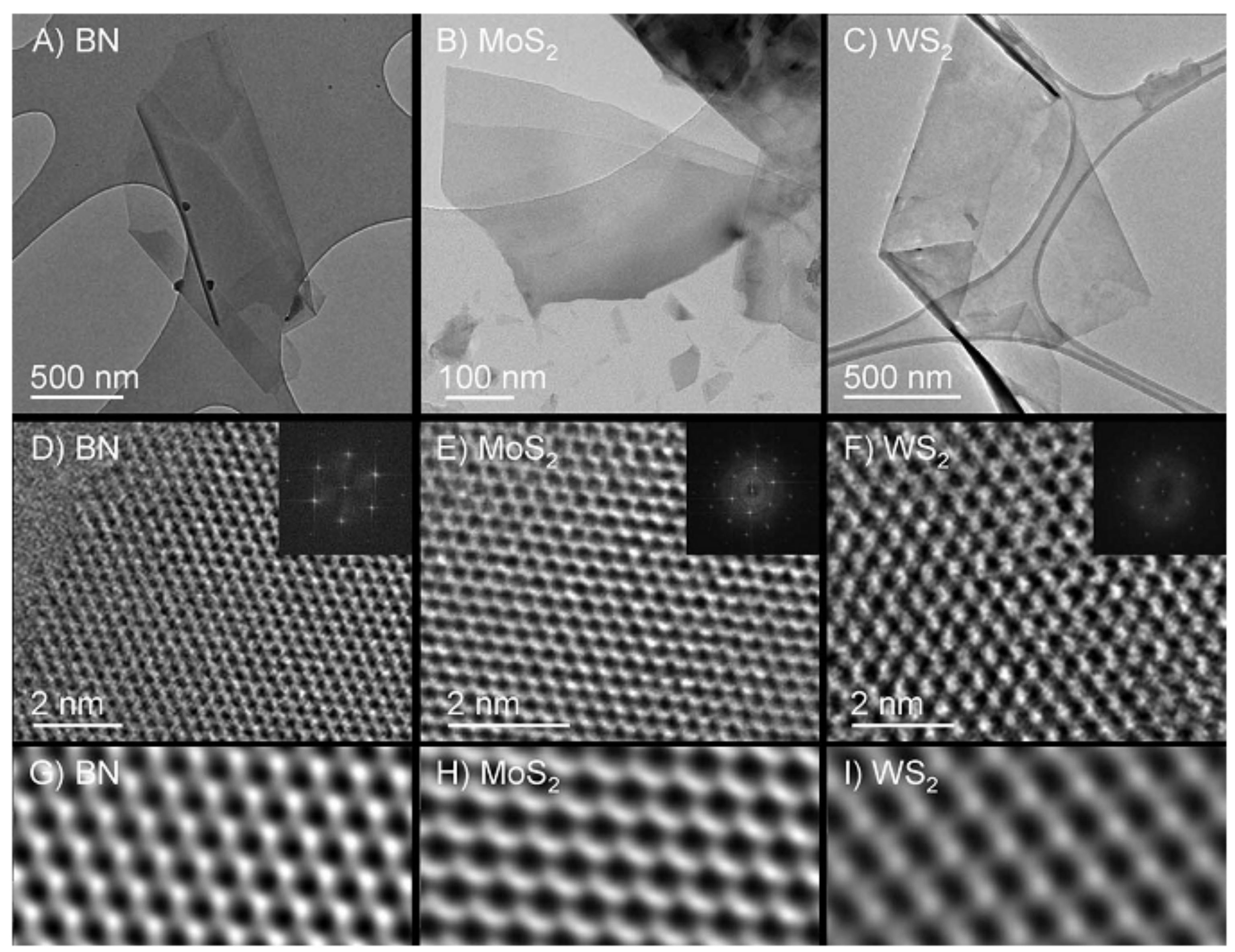
Intercalation of polymers: synthesis strategy

- 1. Synthesis of MoS_2 via HT-route
- 2. Intercalation with n-BuLi
- 3. Exfoliation (Delamination) by treating with H_2O/sonication, colloidal dispersion
- 4. Reaction with polymers leads to restacking
- 5. Precipitation by adding electrolytes or by evaporation of solvent (flocculation = Aggregation)



Polyaniline

Graphene analogues of layered materials: exfoliation by sonication



Coleman et al., Science 331, 568, 2011

Hydro-/Solvothermal Syntheses

Solvo- and hydrothermal syntheses

Characteristics:

- heterogeneous reactions in solvents above boiling point of solvent – autogeneous pressure
- very often: isothermal
- Solvothermal: general term
- Hydrothermal – water as solvent
- Ammonothermal – reactions in ammonia

Applications:

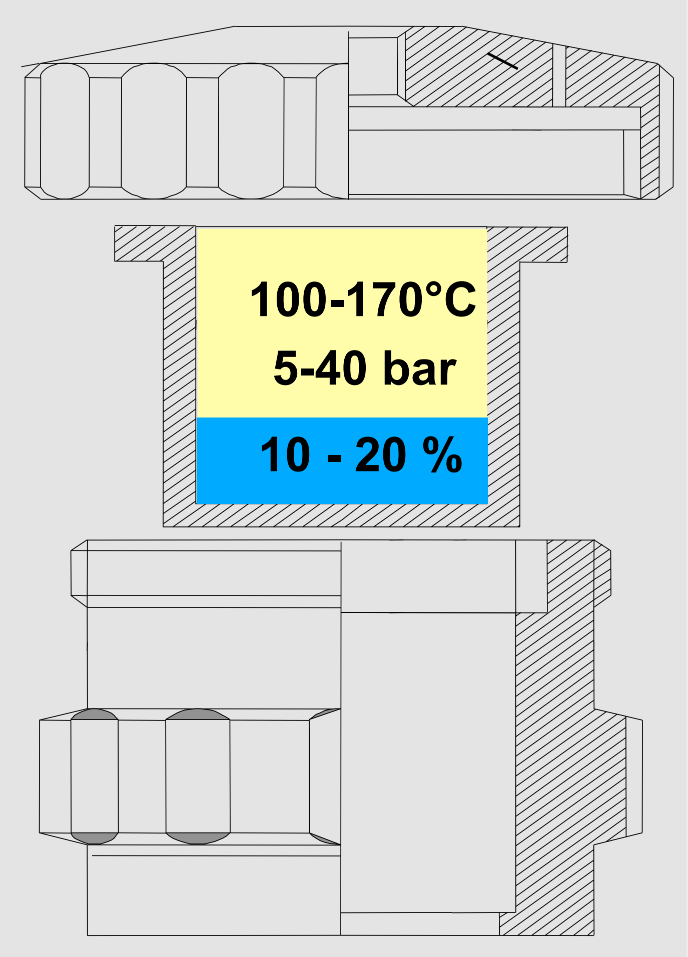
- Synthesis of new compounds
- Preparation of single crystals, recrystallization
- Preparation of zeolites, porous materials, gem stones
- Industrial processes like Bayer process

Advantages:

- relatively low T leaves molecular building groups intact
- high solubility of not easily dissoluble compounds
- short diffusion paths, fast reactions, high yield, open structures

Reactions in autoclaves

Often: Teflon due to inertness



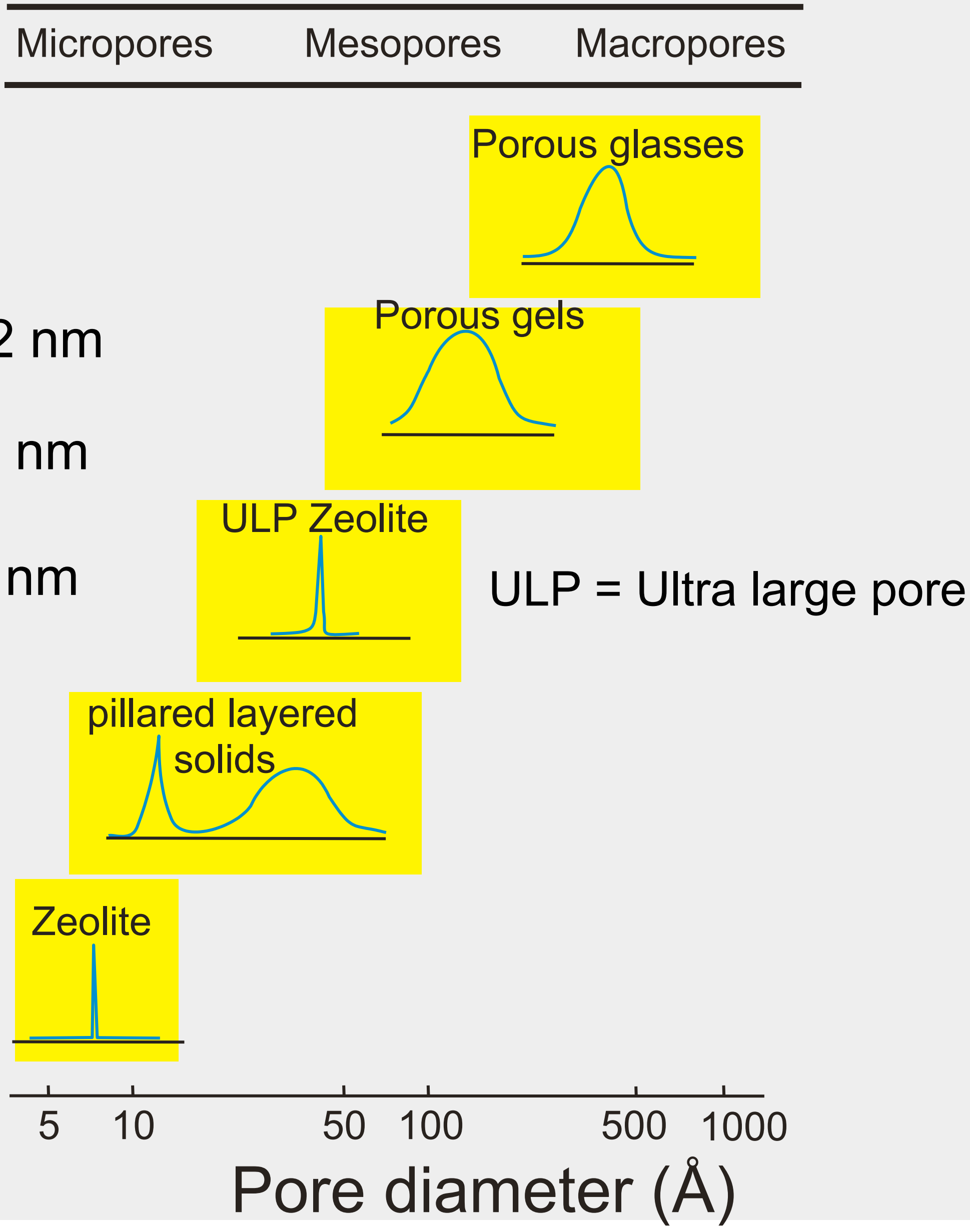
Porous materials

IUPAC

microporous: 0.7 - 2 nm

mesoporous: 2 - 50 nm

macroporous: > 50 nm



ULP = Ultra large pore

Important:
Pore-size distribution

Selected parameters influencing reaction paths and products

Mineralisator
acid
Base

Structure directing molecules

ageing

Reaction temperature

Temperature profile

[redacted]

Reaction time

Ostwald regime

Static or dynamic reaction

Educt sources

further influences:
Weekday,
researcher
Stellar constellation
etc.

Syntheses of zeolits and porous materials

General composition of zeolites:

$$M_{x/n}[Al_xSi_yO_{2(x+y)}] \cdot z\ H_2O$$

- M = group 1 or 2 metal, organic caions also possible
- any Si/Al ratio

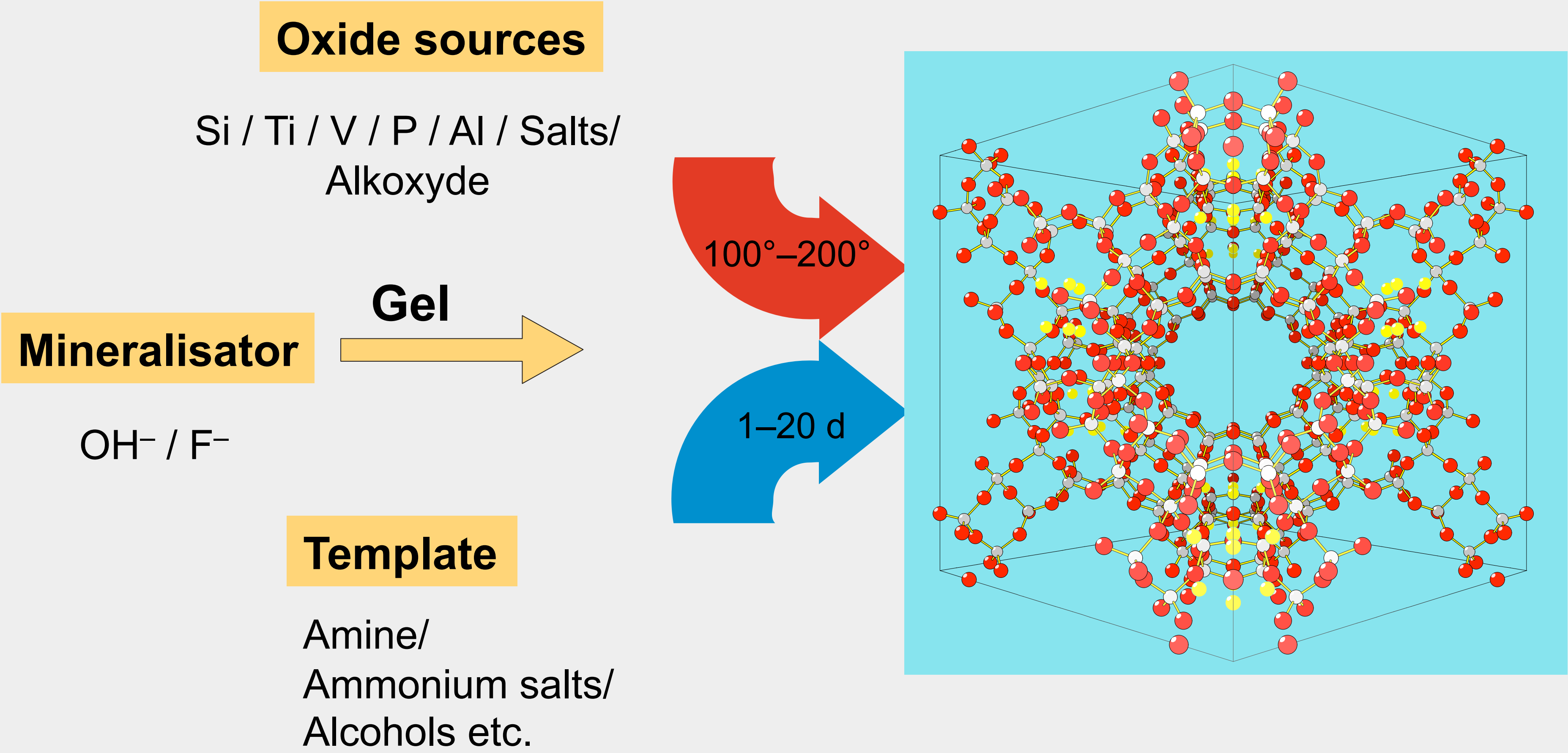
Discovery:

1756, Cronstedt (boiling stones)

Selected applications:

- ion exchange
- catalysts
- molecular sieves
- Gas sorption
- non-linear optical materials (NLO)

The classical zeolite synthesis



Oxide sources

Si / Ti / V / P / Al / Salts/
Alkoxyde

Mineralisator

OH⁻ / F⁻

Gel

Template

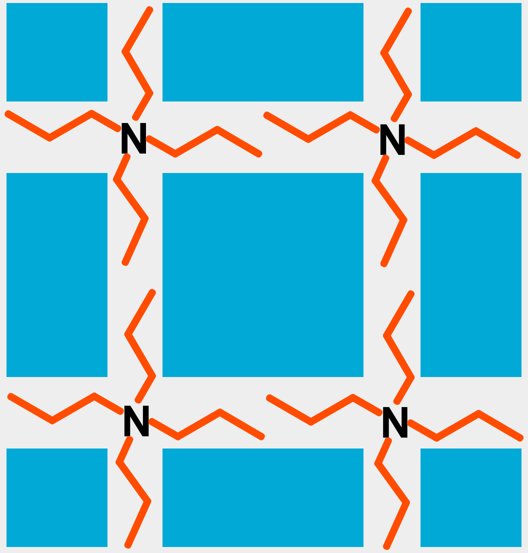
Amine/
Ammonium salts/
Alcohols etc.

100°–200°

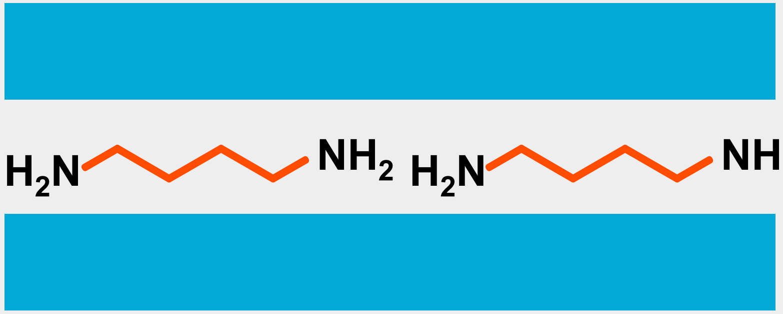
1–20 d

The template effect

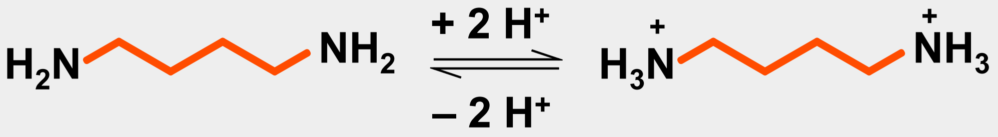
- template



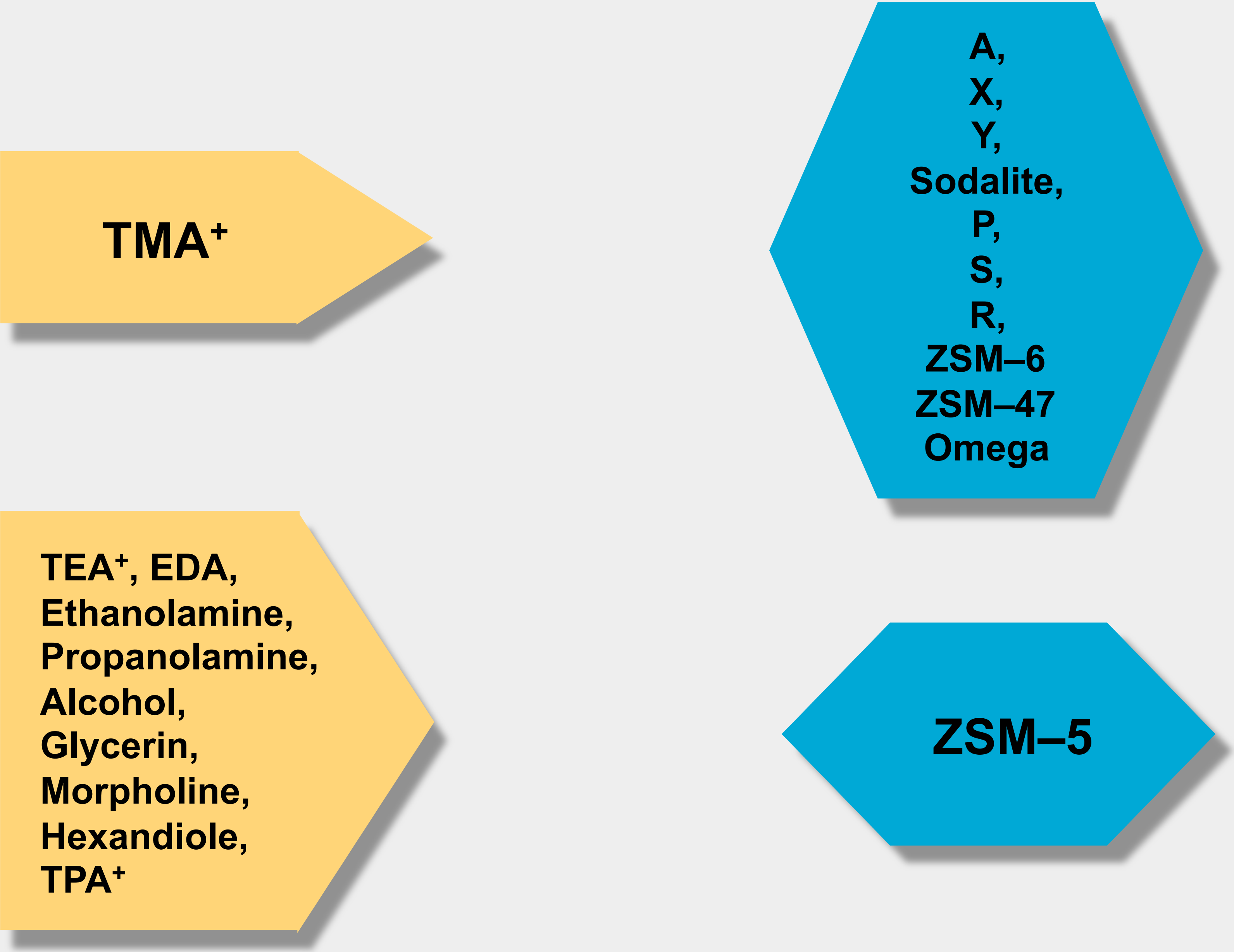
- Pore filler



- pH stabilisation (buffer)



The template effect ??????



TMA$^+$

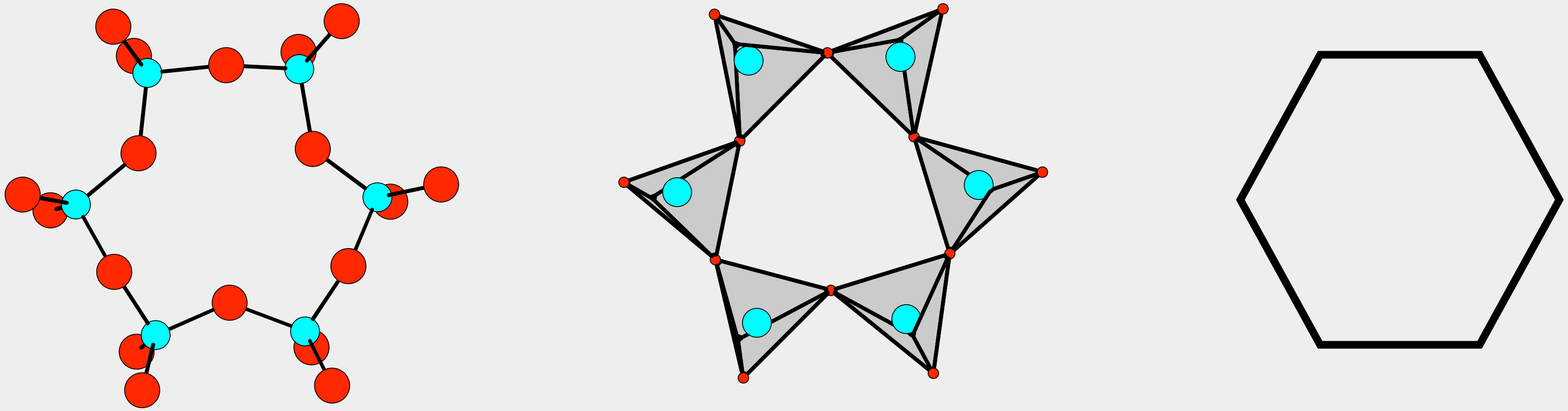
A,
X,
Y,
Sodalite,
P,
S,
R,
ZSM–6
ZSM–47
Omega

TEA$^+$, EDA,
Ethanolamine,
Propanolamine,
Alcohol,
Glycerin,
Morpholine,
Hexandiole,
TPA$^+$

ZSM–5

Structures of zeolites

- primary units: tetrahedra T
- tetrahedra share common corners
- only Si-O-Al and Si-O-Si-interconnection
- no Al-O-Al-joints (Loewenstein rule)
- extremly flexible T-O-T-angles: 100 - 180° - large structural diversity
- formation of secondary building units (SBU)

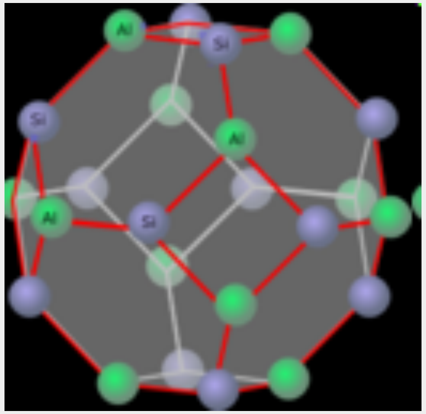


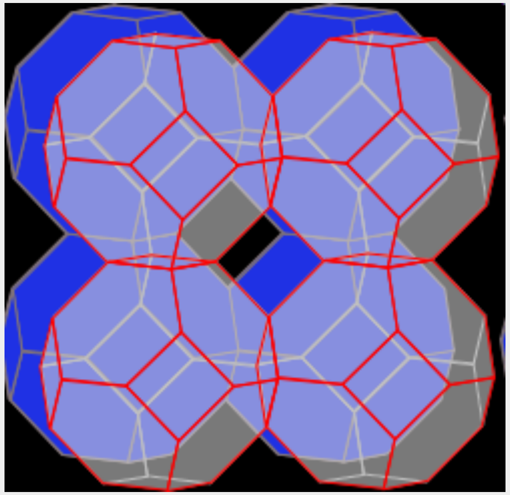
- 6-Rings: six corner-linked T

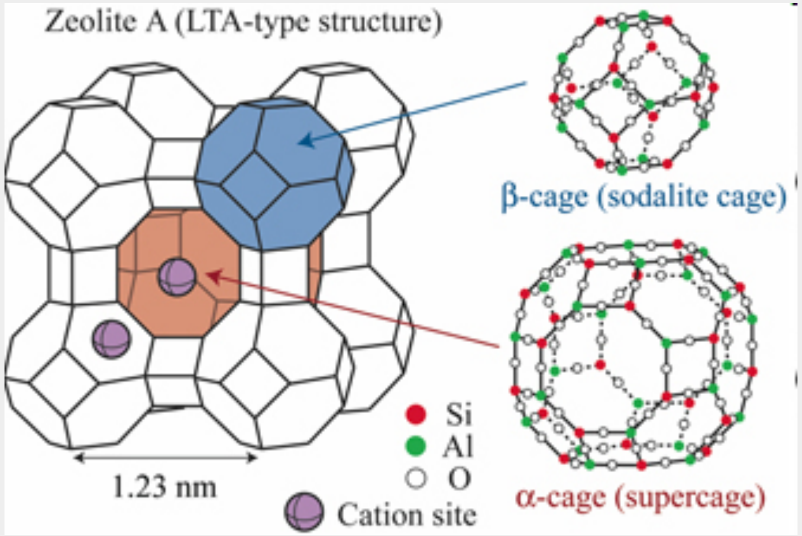
Structure of hosts - zeolites

Zeolites composed of β-cages (Sodalit cages)

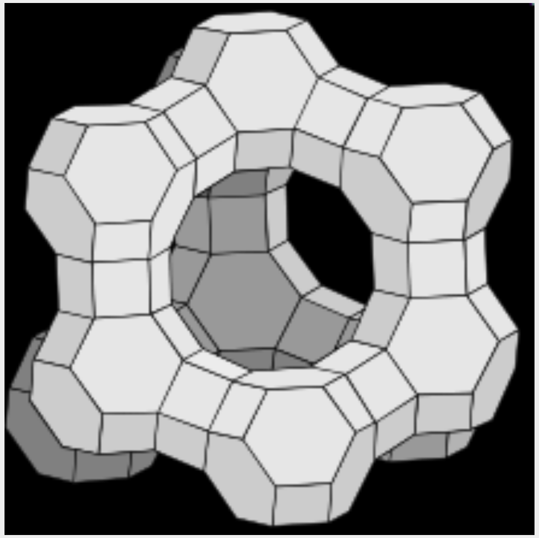
Sodalith (SOD)



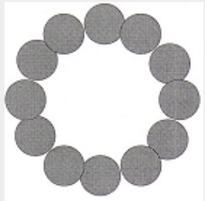




Faujasite



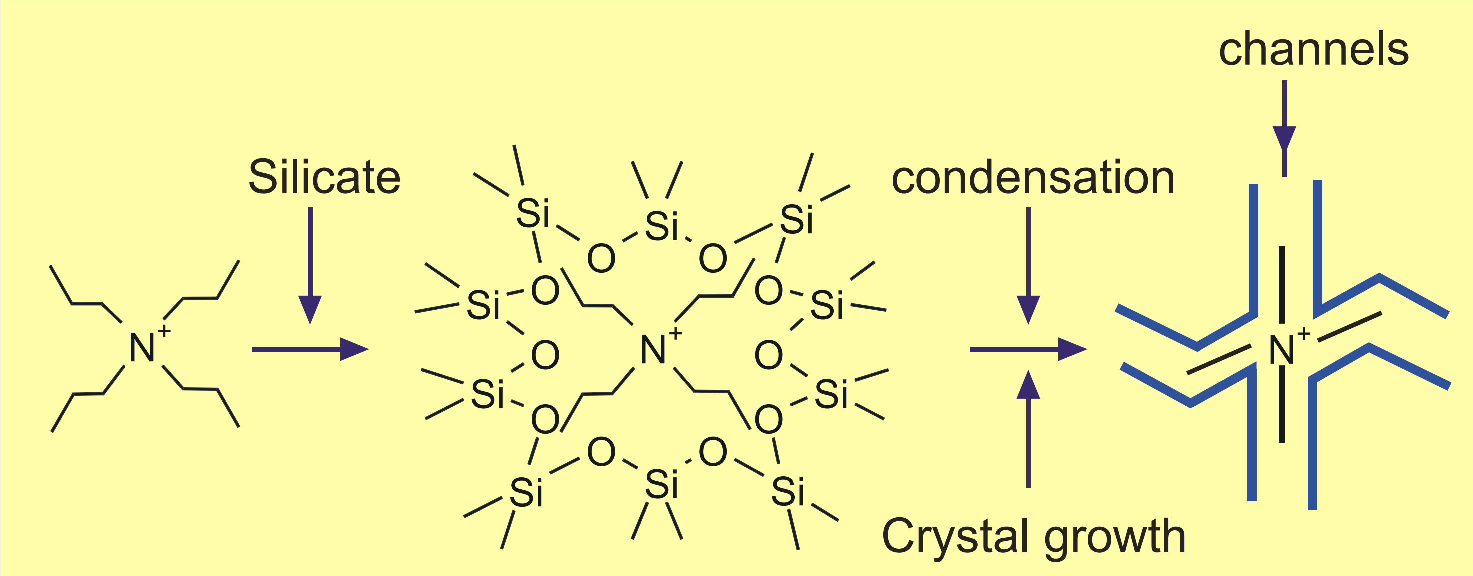
0.35-0.45 nm

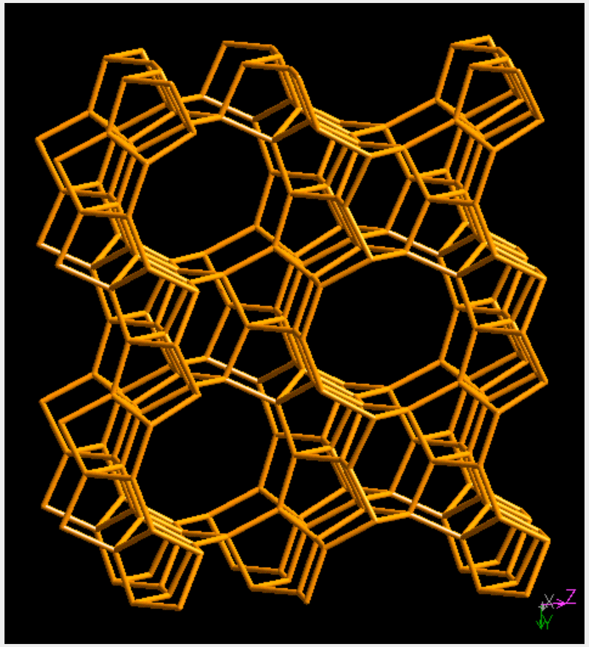


0.6-0.8 nm

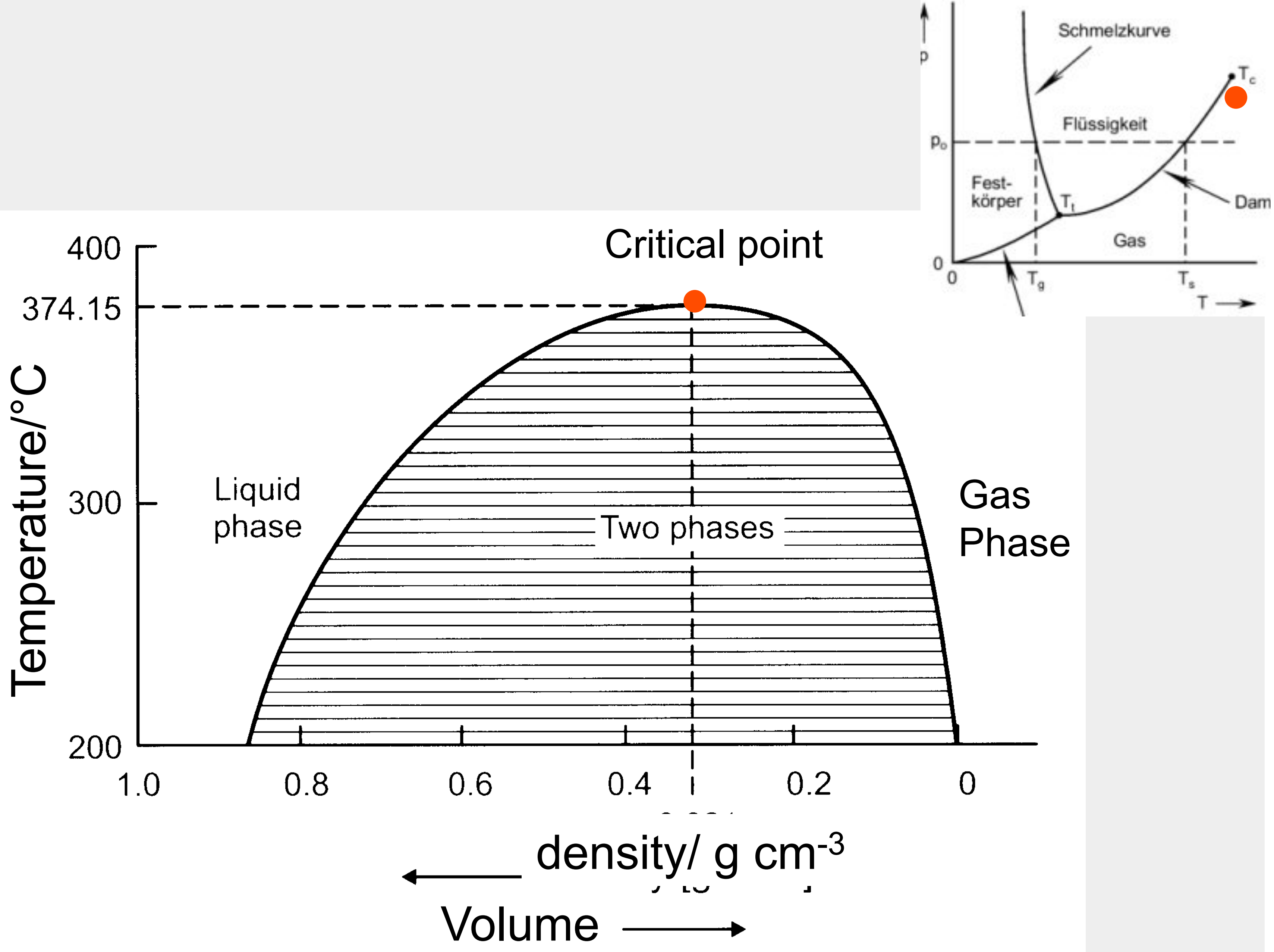
→ Ion exchange, catalysis

Formation of ZSM-5

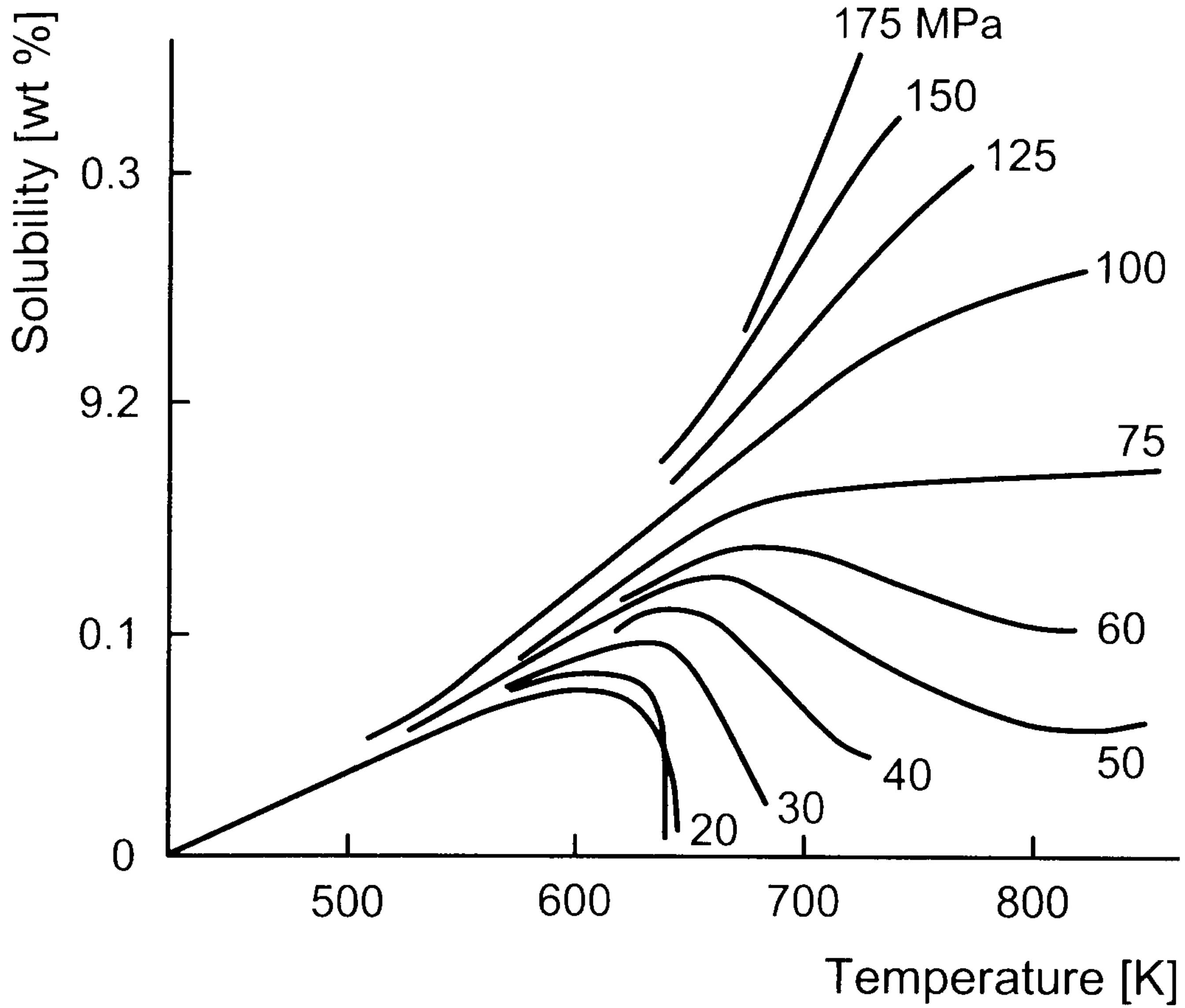




V/p diagramm of water



Solubility of SiO_2 in water



Solubility of SiO_2 in water

Increase of solubility:

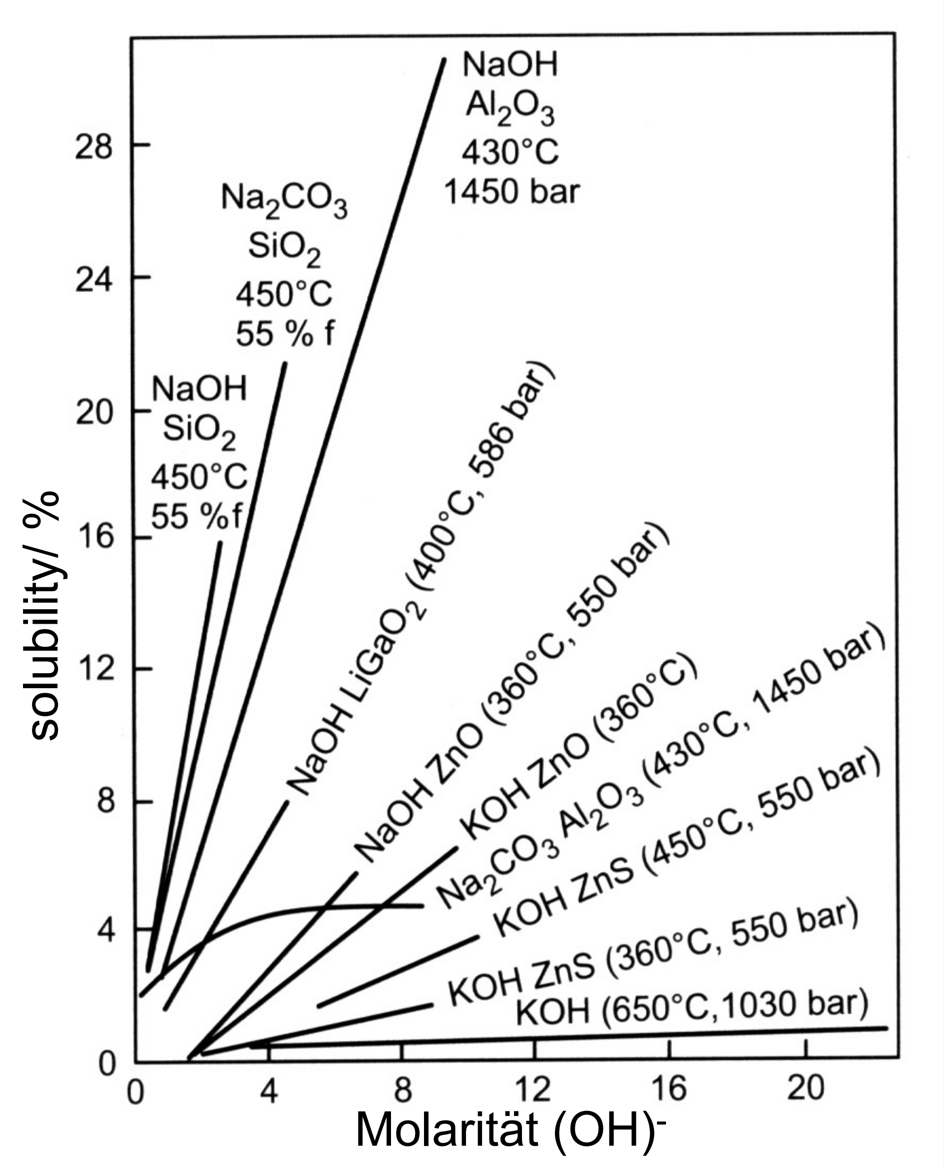
Add mineralisator

Formation of dissolved species

Example:

Crystallization of Quartz

$$SiO_2 + 2\,OH^- \rightleftharpoons SiO_3^{2-} + H_2O$$



Hydrothermal synthesis

Stabilisation of unusual oxidation states

→ ferromagnetic CrO_2 (Rutil structure): Cr_2O_3 and CrO_3 at 350°C

high pressure of O_2 suppresses decomposition of CrO_2

$$CrO_3 \rightarrow CrO_2 + \frac{1}{2} O_2$$

$$Cr_2O_3 + CrO_3 \rightarrow 3\, CrO_2$$

→ pressure: 440 bar

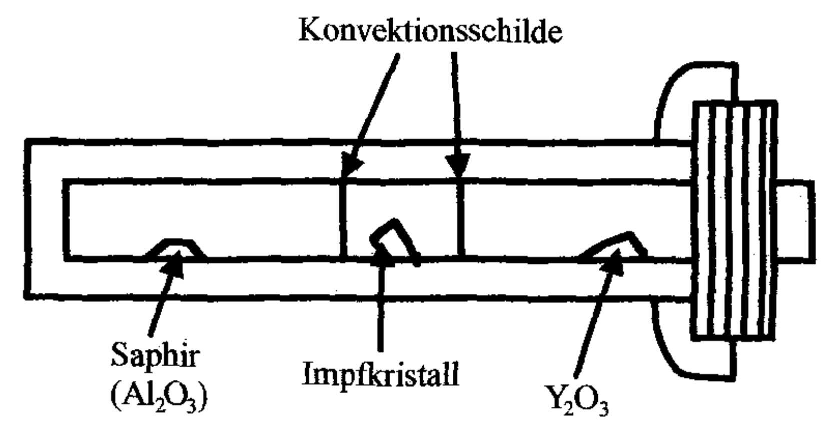
Y-Al-Garnet: (YAG = $Y_3Al_5O_{12}$) → IR-Laser (1064 nm)

Solubility of educts is different: Y_2O_3 und Al_2O_3

→ Autoklav with temperature gradient

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

Hot zone

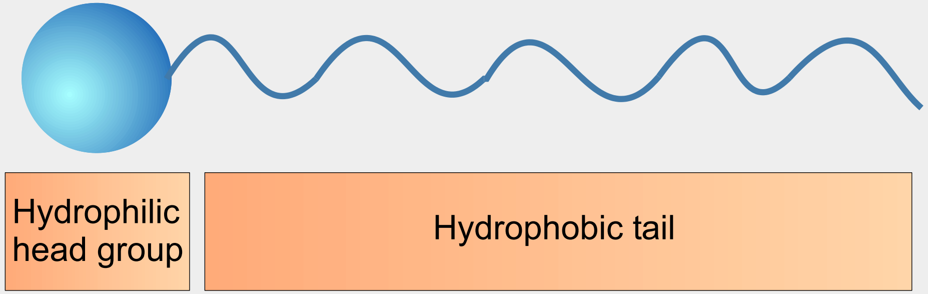


Cold zone

MCM-Materials

Very large pores/channels

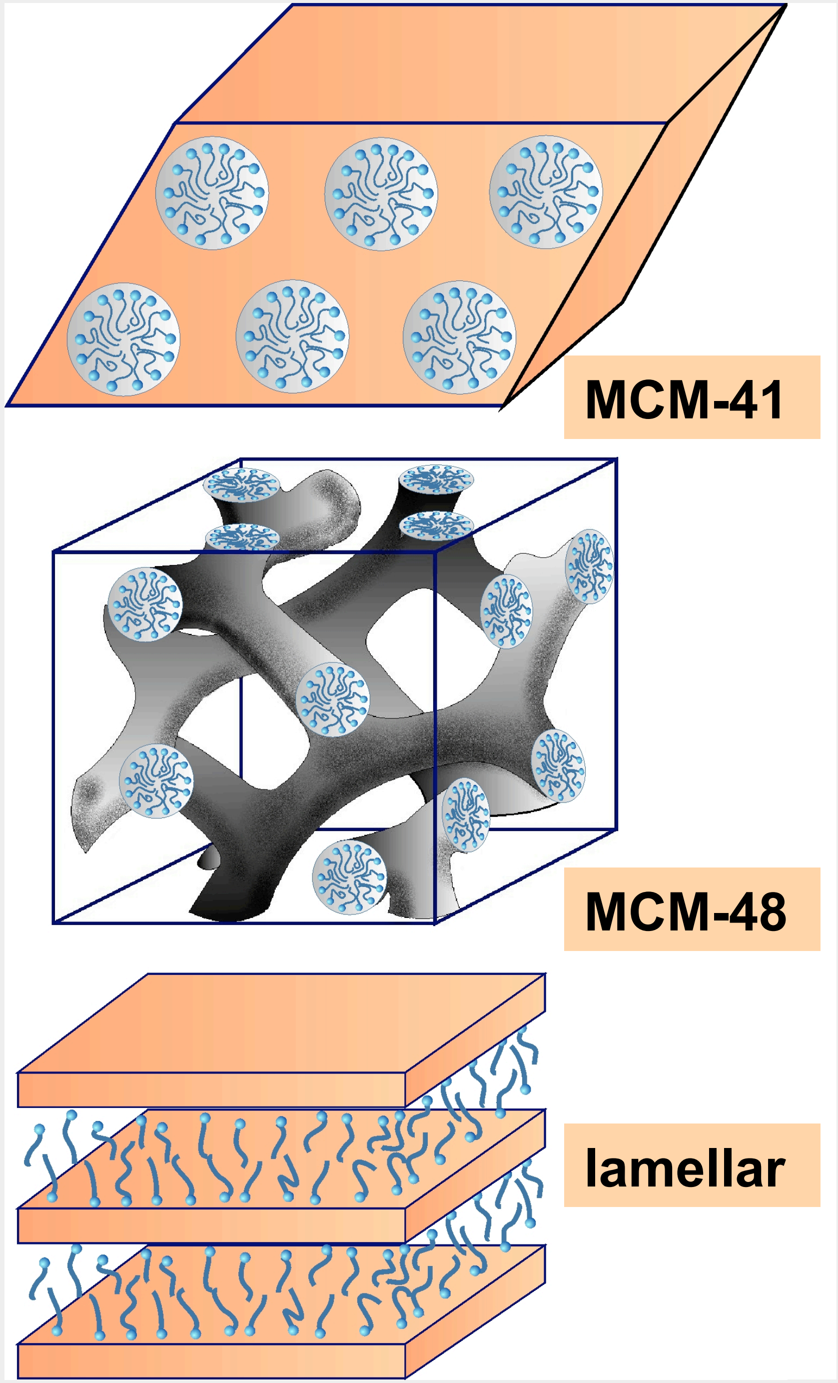
Liquid crystals as templates



Hydrophilic head group

Hydrophobic tail

- ➢ mesoporous: 2 - 50 nm
- ➢ small pore size distribution

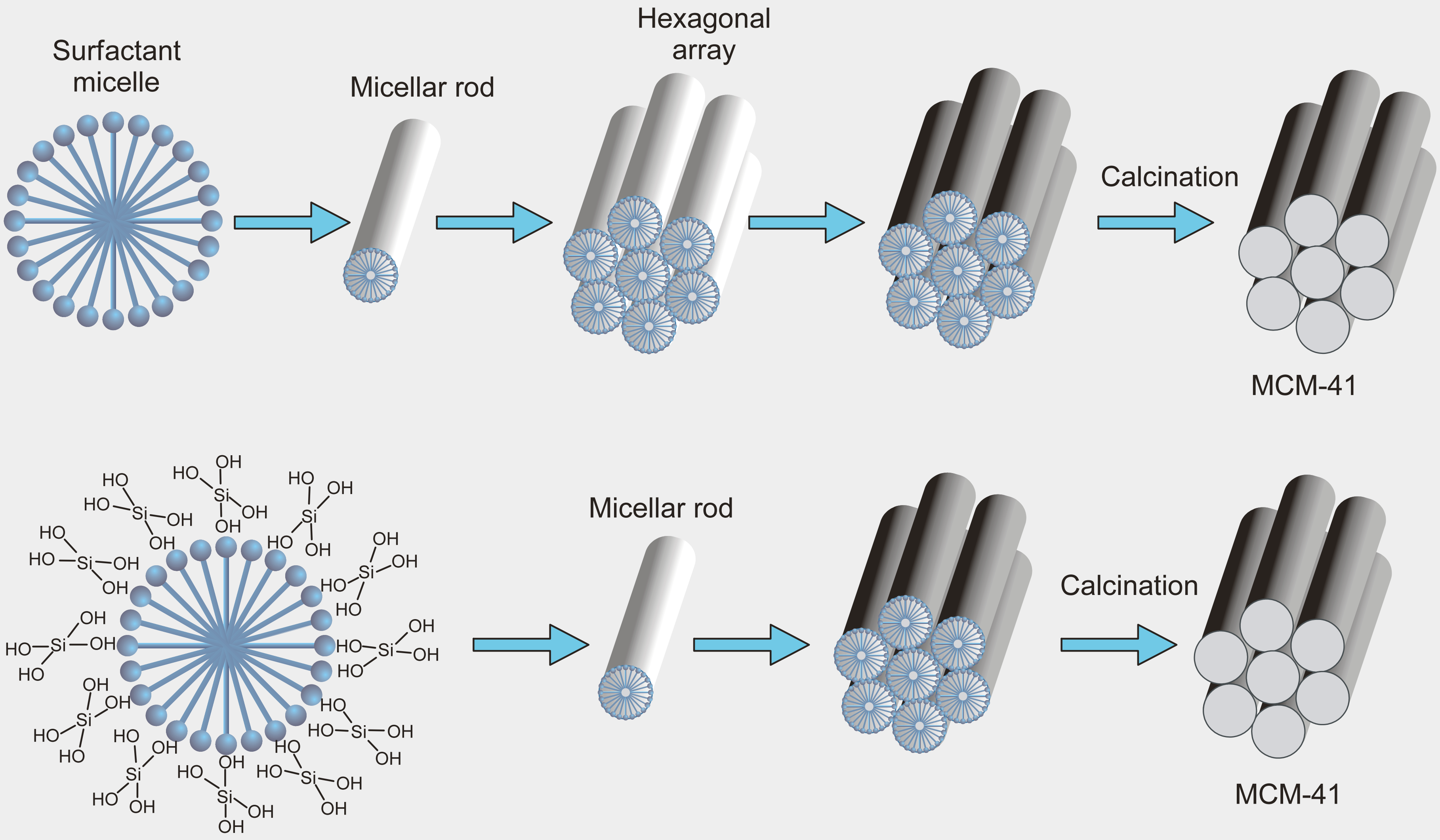


MCM-41

MCM-48

lamellar

Formation mechanism



Surfactant micelle

Micellar rod

Hexagonal array

Calcination

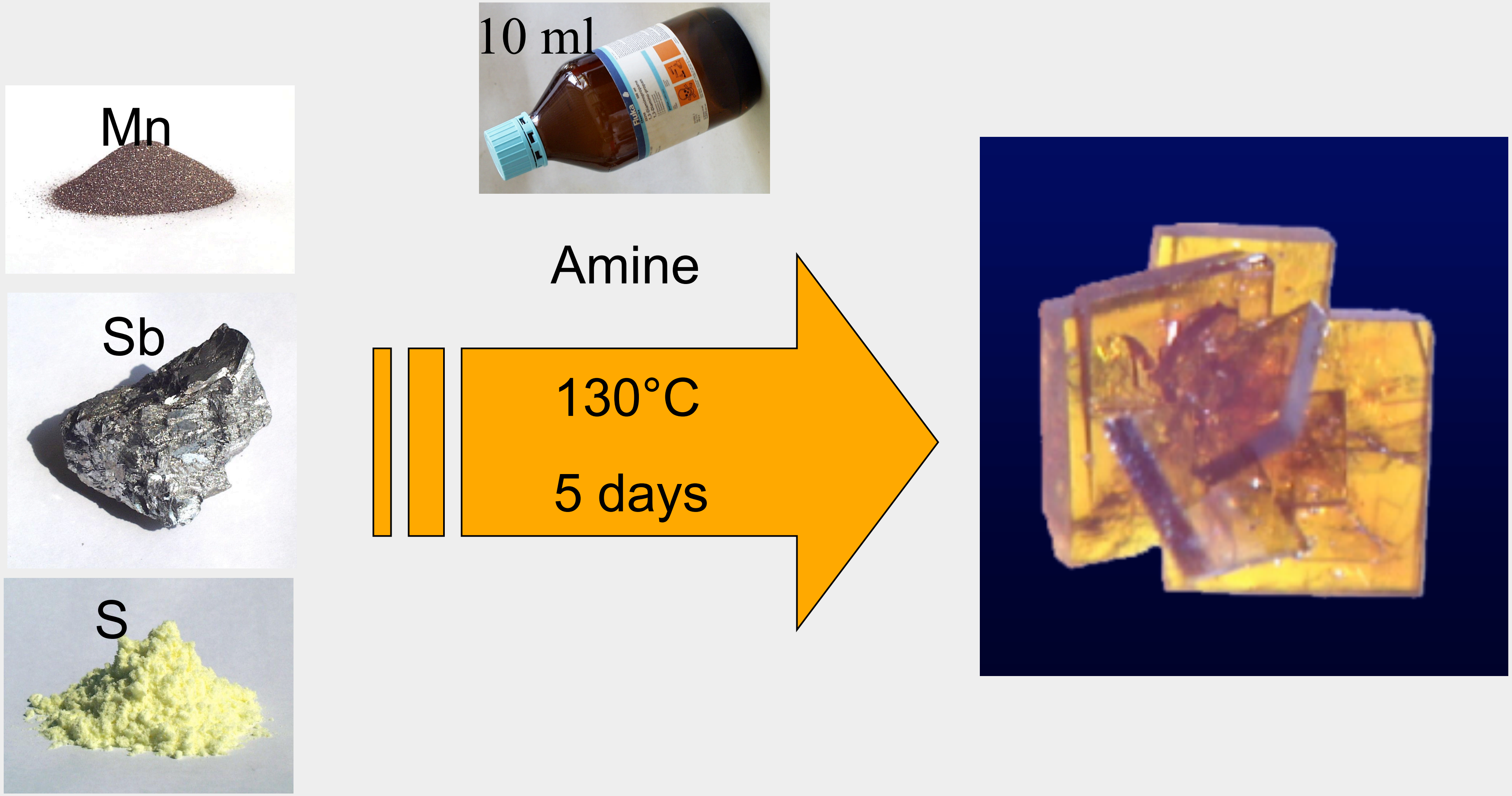
MCM-41

Micellar rod

Calcination

MCM-41

Synthesis of thiometallates



Mn

Sb

S

10 ml

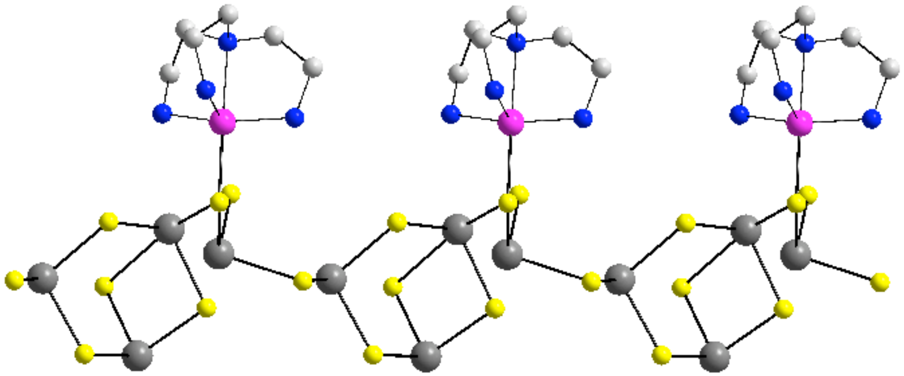
Amine

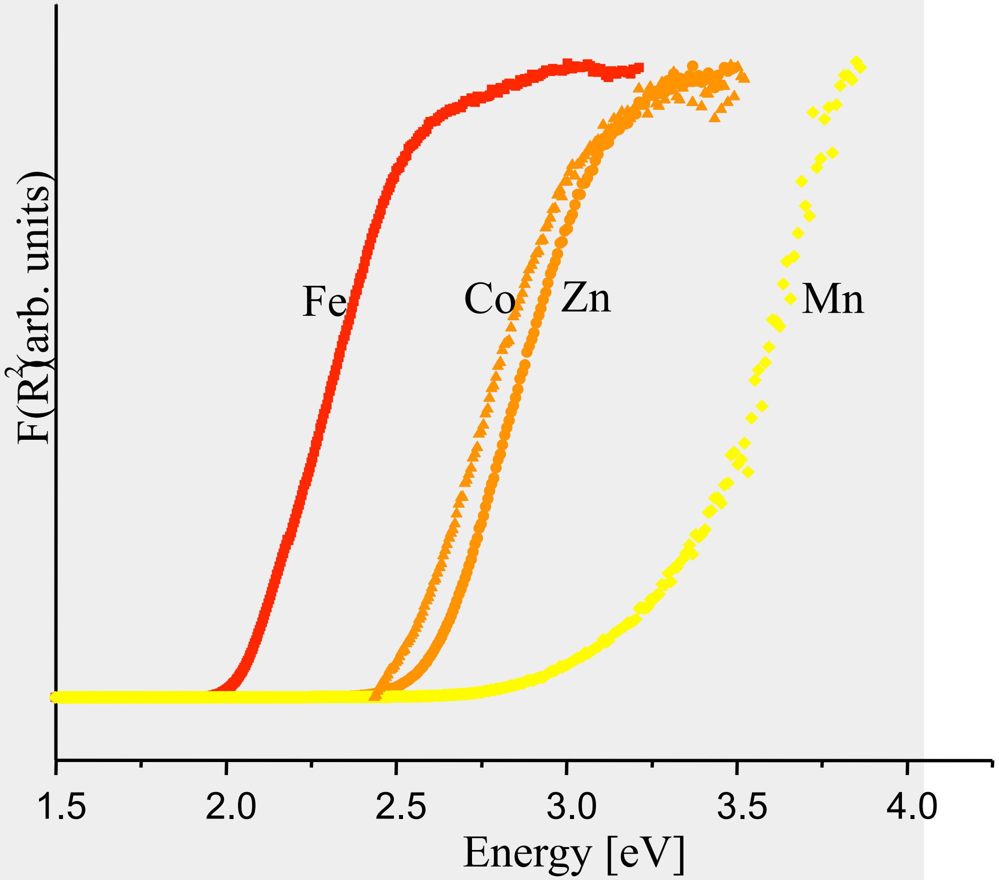
130°C

5 days

Thiometallates with defined optical bandgap

[M(tren)]Sb_4S_7





Synthesis: M : Sb : S = 1 : 1 : 2.5 mmol; 20% tren solution, 140 °C, 7 d

Many more methods are established

technical, chemical and physical backgrounds –

much more time required