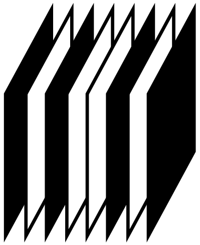
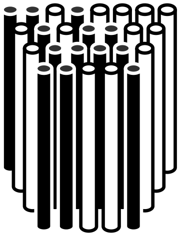
# 4. Advanced features
# DP and structural disorder I

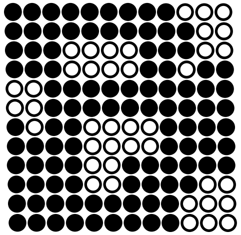
**Low dimensional order and prominent diffuse scattering**

- 2D order: layered compounds (cf. polytypes: SiC)
- 1D order: structures with filled channels (zeolites)
- Structures with local order: (finite domains, correlated environments)
- Statistical disorder (e. g. random distribution of vacancies)

**Real space**

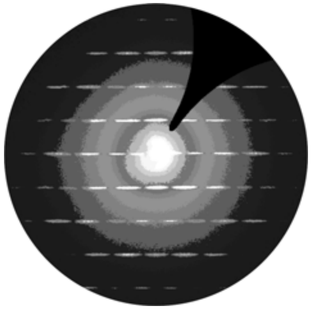




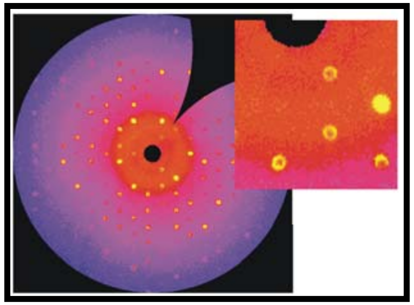


**Rec. space**

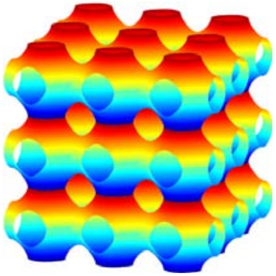
**diffuse rods**



**planes with diffuse scattering**



**3D diffuse scattering**



# 4. Advanced features
# DP and structural disorder II

**Crystal data**

| | |
|---|---|
| Formula sum | $Cu_{0.8} In_{2.4} Se_4$ |
| Crystal system | tetragonal |
| Space group | *I* -4 2 m (no. 121) |
| Unit cell dimensions | *a* = 5.7539(3) Å  *c* = 11.519(1) Å |
| Z | 2 |

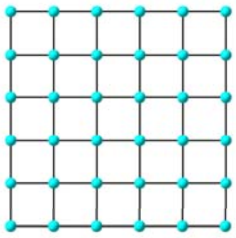
**Atomic coordinates**

| **Atom** | **Ox.** | **Wyck.** | **Occ.** | **x** | **y** | **z** |
|---|---|---|---|---|---|---|
| Cu1 | +1 | 2*a* | 0.8 | 0 | 0 | 0 |
| In1 | +3 | 4*d* | 1.0 | 0 | 1/2 | 1/4 |
| In2 | +3 | 2*b* | 0.4 | 0 | 0 | 1/2 |
| Se1 | -2 | 8*i* | 1.0 | 1/4 | 1/4 | 1/8 |

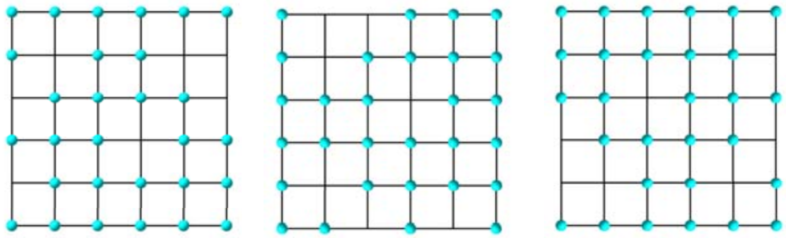
- **Average structure**
- **Random arrangement of vacancies: no prominent diffuse scattering**

# 4. Advanced features
# Average vs. real structure

Structure determination = X-ray diffraction = average of all different sections of a crystal



**typical section ordered crystal**
**all sites fully occupied**



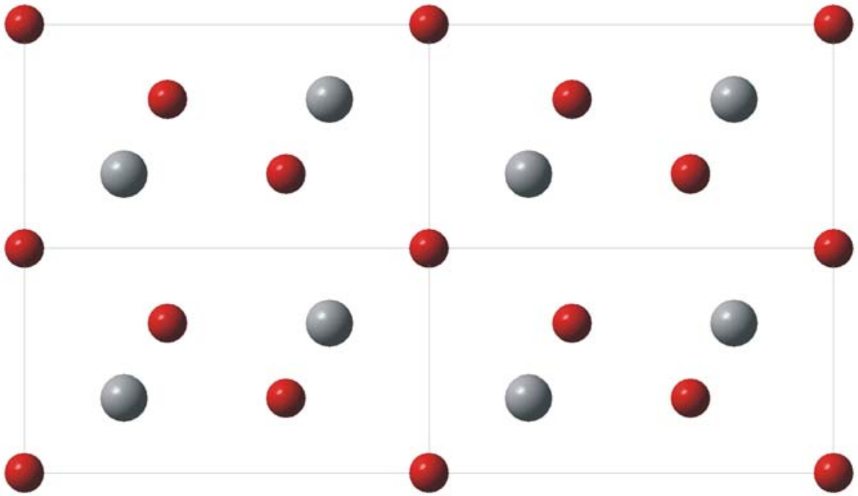
**typical sections disordered crystal**
**atoms and vacancies on one site**

Disordered crystal
billions of different sections

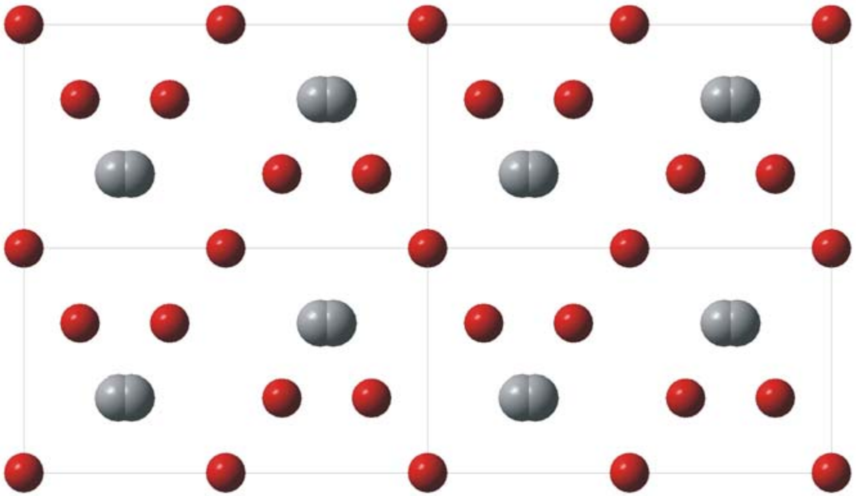
- **X-ray diffraction (standard procedure): average of the structure**
- **Consequence 1: a fraction of vacancies is on every site of the unit cell**
- **Consequence 2: reduced occupancy factor**
- **Consequence 3: average structures are not unambiguous**

# 4. Advanced features
## Example for an average structure I

**Example: $La_2O_3$ (A-Form)**



**Pauling, 1929; Schiller, 1985**

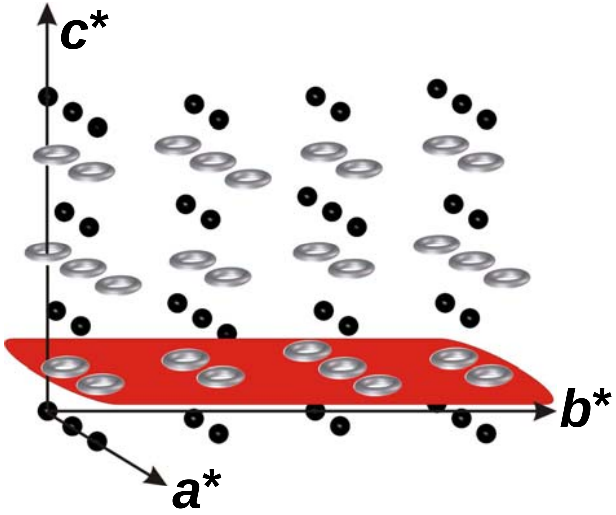


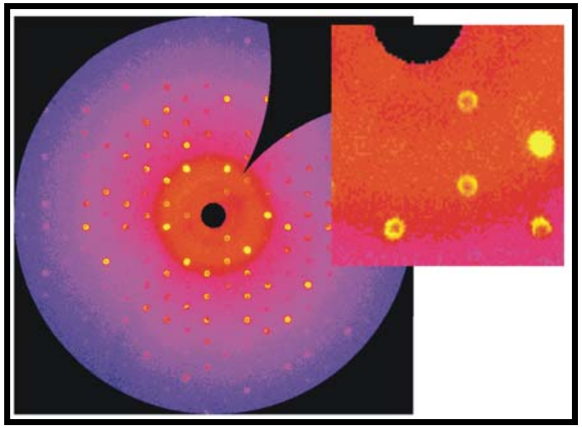
**Müller-Buschbaum, 1965**

● **La**
● **O**

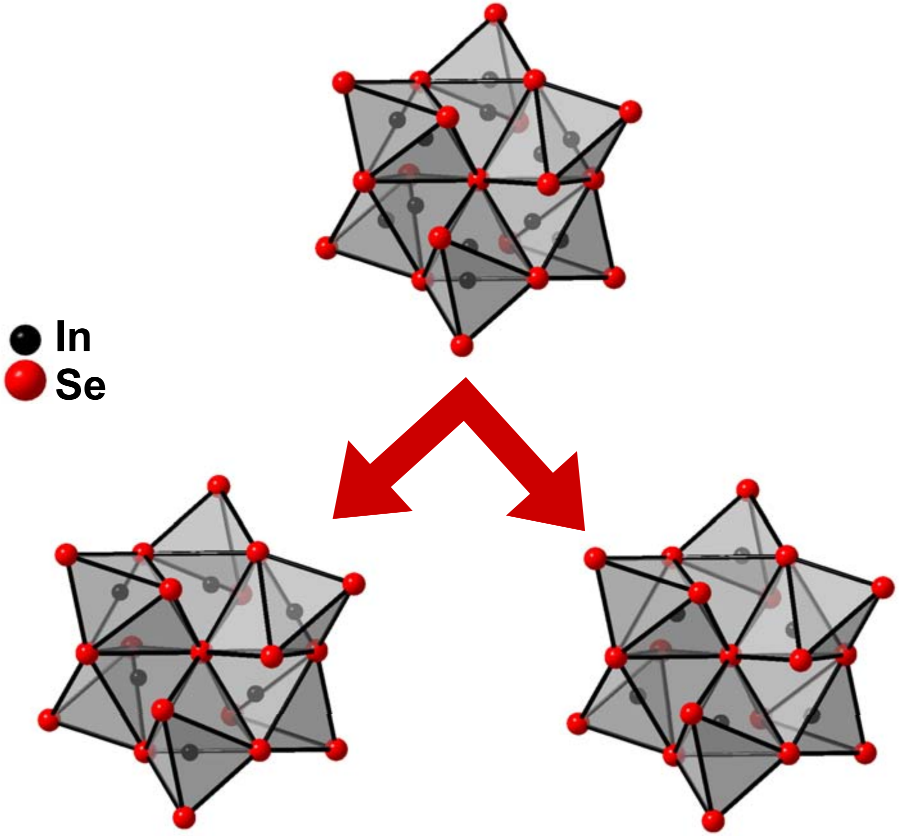
# 4. Advanced features
# Example for an average structure II

**1D order:**
**planes of diffuse intensity**





**Average structure:**
**split position of In, occ(In) = 0.5**



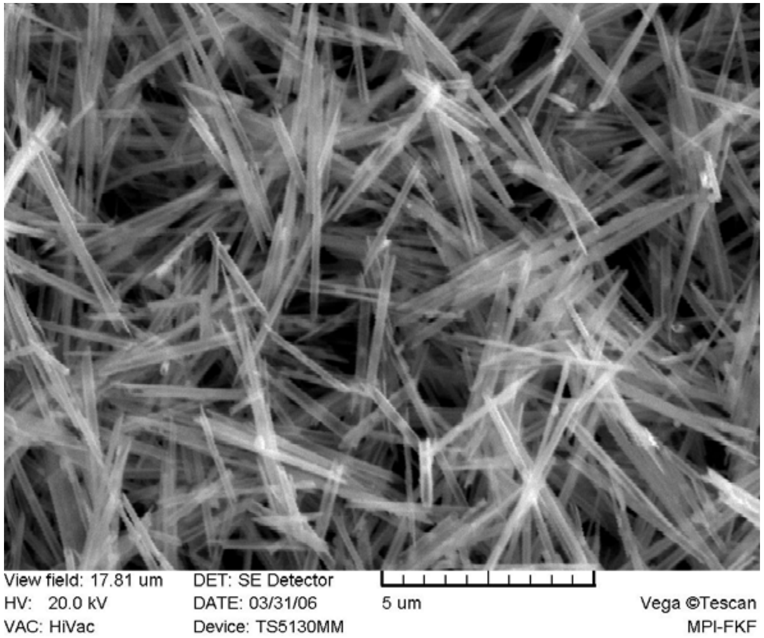
**Real structure:**
**superposition of two components, occ(In) = 1**

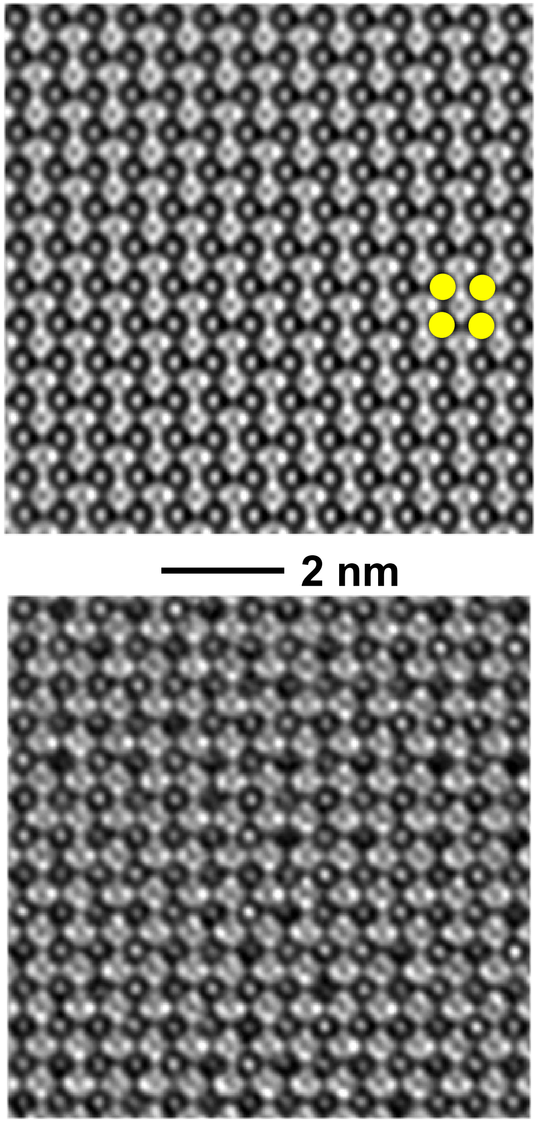
# Synthesis of solids

1. High temperature synthesis
2. Chemical vapour transport
3. Soft chemistry
4. Nanomaterials

# Introduction
# Goals of synthesis / preparation

- **Synthesis of new compounds**
- **Synthesis of highly pure, but known compounds**
- **Synthesis of highly pure single crystals (Iceberg-principle)**
- **Structural modification of known compounds bulk-structures and nanostructures**





# 1. High temperature synthesis
# Classical solid state reaction from the elements

**Standard procedure:**

**“Shake and bake”, “heat and beat”, “trial and error”**

**“The starting materials are finely grinded, pressed to a pellet and heated to a temperature „near“ the melting temperature.”**

**Parameters influencing the reaction:**

- **Purity of educts (sublimation)**
- **Handling of educts (glove box, Schlenck technique)**
- **Temperature: T(reaction) > 2/3 T(melting point), rule of Tamann. Effects on real structure (more defects at elevated T) and diffusion (increase with T)**
- **Solid state reactions are exothermic, “thermodynamically controlled“: Consequence: No metastable products (see e.g. Zeolites)**
- **Porosity, grain size distribution and contact planes: High reactivity of nanoparticles / colloides (low CN)**

# 1. High temperature synthesis
# Classical solid state reaction from the elements

**Experimental consequences:**

(1) large contact areas
(2) small path lengths
(3) small pore volume

} *Reactive sintering: pellets of fine powders*

**Problems / Pitfalls:**

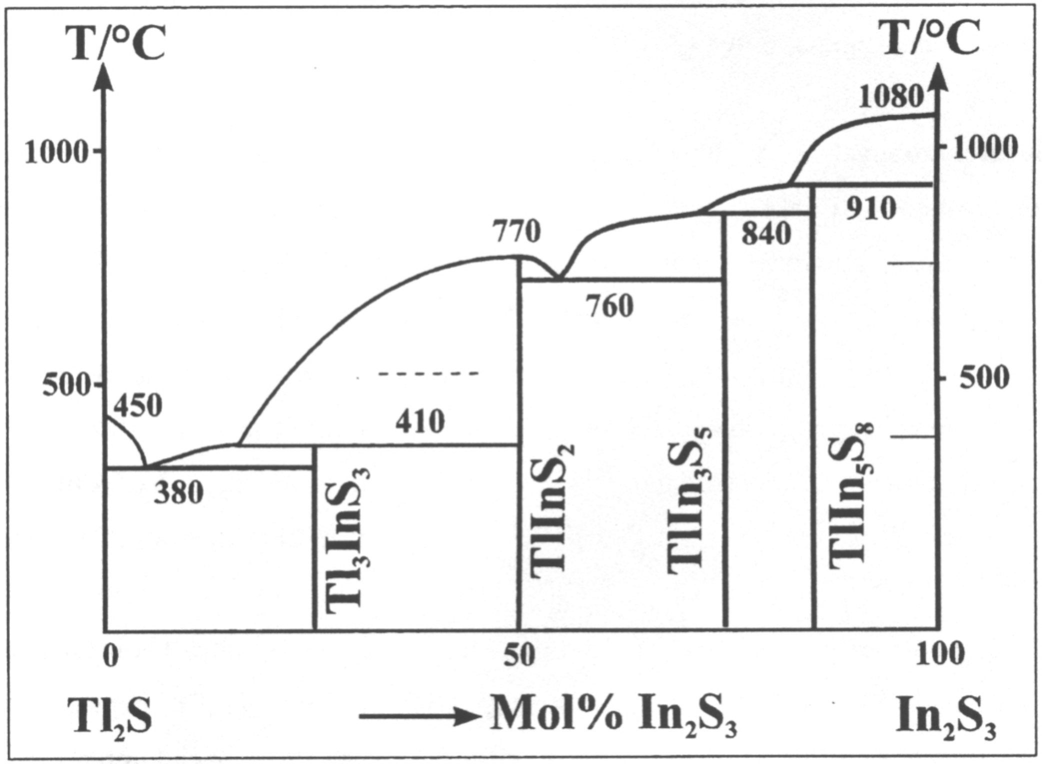
- "Chemical problems" of containers materials: use of reactive materials remedy: double / coated containers
- "Physical problems" of containers: compatible expansion/compression coefficients, sufficiently stable to withstand pressure
- Separation of educts, remedy: special furnaces, reduced free volume, tricks
- No intrinsic purification processes

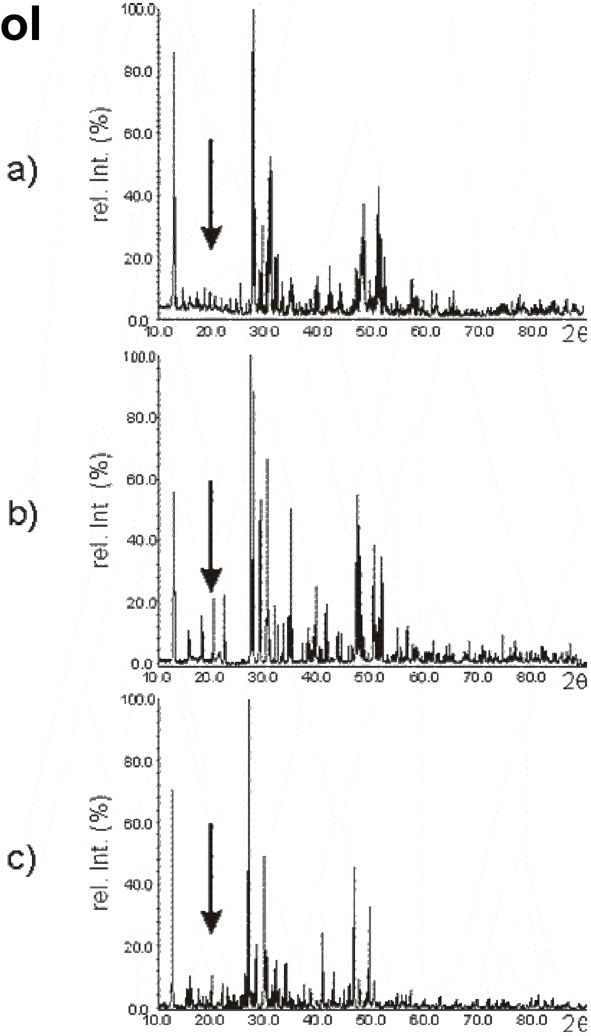
**Ex.: $2\ Li_2CO_3 + SiO_2 \rightarrow Li_4SiO_4 + 2CO_2$ (800 °C, 24 h)**

- Li-compounds are highly reactive against containers (use of Au)
- Production of a gas, consequence: cracking of containers

# 1. High temperature synthesis
# From “Trial and Error” to systematic procedure

- Examining pseudobinary sections under DTA control
- Systematic observations on mixed crystal series control by powder diffraction





# 1. High temperature synthesis
## Tricks

- **Application of a “gaseous solvent” *chemical* or *vapor phase transport***
  **Ex.:** $Cr_2O_3(s) + 3/2\ O_2(g) \rightarrow 2\ CrO_3(g)$
  $MgO(s) + 2\ CrO_3(g) \rightarrow MgCr_2O_4(s) + 3/2\ O_2(g)$

- **Separation of educts in a temperature gradient (to avoid explosions)**
  **Ex.:** $2\ Ga(l) + 3\ S(g) \rightarrow Ga_2S_3(g)$

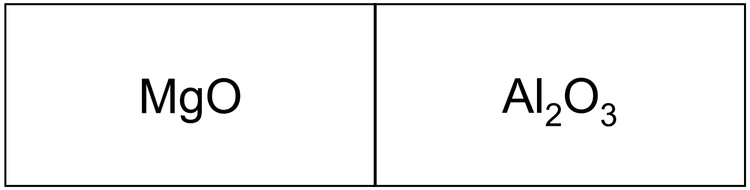
- **Use of precursors for reactive educts**
  **Ex.:** **Thermal decomposition of $MN_3$ (M = Na, K, Rb, Cs)**
  **Thermal release of reactive gases: ($O_2$: $MnO_2$, $CO_2$: $BaCO_3$, $H_2$: $LnH_2$)**
  **Coprecipitation and thermal decomposition (e.g. oxolates to oxides)**

- **Use of fluxes**
  **Ex.:** $Li_2CO_3 + 5\ Fe_2O_3 \rightarrow 2\ LiFe_5O_8 + CO_2(g)$ **(incompl. :grind-fire-regrind, etc.)**
  **Or: Flux of $Li_2SO_4/Na_2SO_4$ (dissolves $Li_2CO_3$, remove flux with water)**

- **Metathesis reaction**
  **Ex.:** $2GaCl_3 + 3Na_2Te \rightarrow Ga_2Te_3 + 6NaCl$**, very exothermic!**

# 1. High temperature synthesis
# Orientation and transport during synthesis

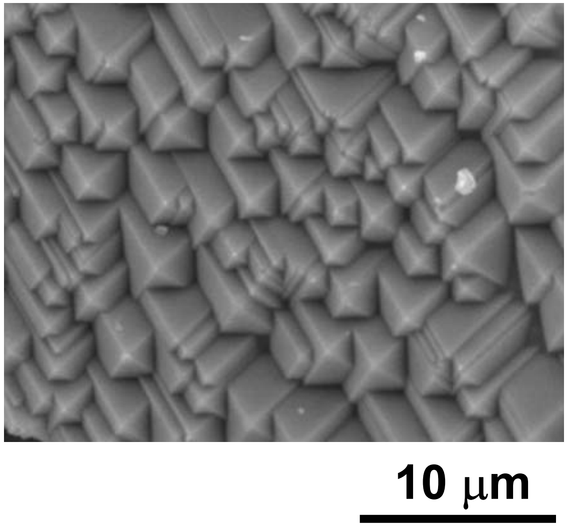
**Ex.: spinel: no electron transport, counter diffusion of ions**



**Initially**

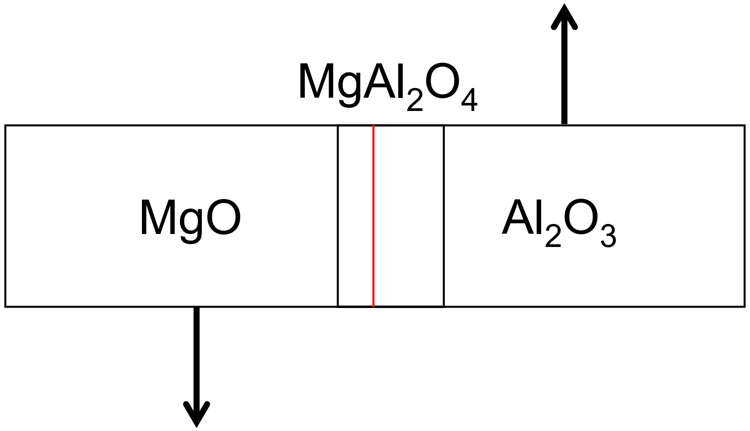
**What happens at the boundary?**

- **Nucleation: facilitated by O-arrangement**
- **$Al_2O_3$: Epitaxy (2D), MgO: Topotaxy (3D)**



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

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



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

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

# 2. Chemical vapour transport
## Principles

A solid is dissolved in the gas phase at one place (T=T1) by reaction with a transporting agent (e.g. $I_2$). At another place (T=T2) the solid is condensed again. Use of a temperature gradient.

$$ZnS(s) + I_2(g) = ZnI_2(s) + S(g)$$

- Used for purification and synthesis of single crystals (fundamental research)
- Reactions with large absolute value of ΔH° gives no measurable transport
- The sign of ΔH° determines the direction of transport:
  - *exothermic reactions: transport from cold to hot*
  - *endothermic reactions: transport from hot to cold.*

# 2. Chemical vapour transport Examples

- Mond-process: $Ni(s) + 4\ CO(g) = Ni(CO)_4(g)$
  ΔH° = -300 kJ/mol, transport from 80° to 200°C

- Van Arkel / De Boer: $Zr(s) + 2\ I_2(g) = ZrI_4(g)$; (280 to 1450 °C)

- $Si(s) + SiX_4(g) = 2\ SiX_2(g)$; (1100° to 900°)

- Mixtures of Cu and $Cu_2O$:
  $3\ Cu(s) + 3\ HCl(g) = Cu_3Cl_3(g) + (3/2)\ H_2(g)$; (High T to Low T)
  3/2 Cu2O(s) + 3 HCl(g) = $Cu_3Cl_3(g) + 3/2\ H_2O(g)$; (Low T to High T)

- Transport of $Cu_2O(s)$:
  $3/2\ Cu_2O(s) + 3\ HCl(g) = Cu_3Cl_3(g) + 3/2\ H_2O(g)$; (Low T to High T)
  $Cu_2O(s) + 2\ HCl(g) = 2\ CuCl(g) + H_2O(g)$; (High T to Low T)

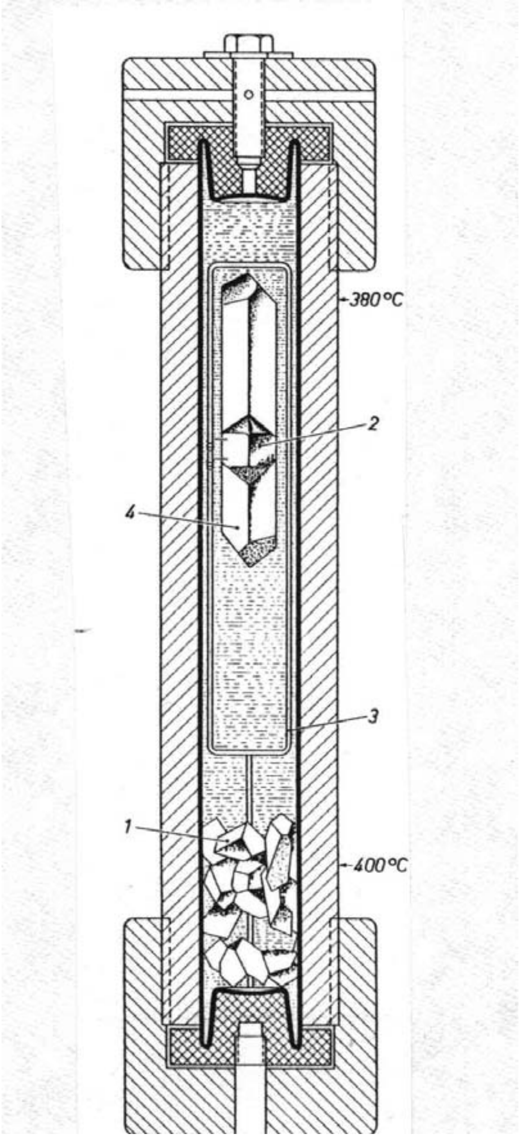
# 3. Soft chemistry
# Hydrothermal synthesis

**Chemical transport in supercritical aqueous solution ($H_2O$: $T_k$= 374 °C, $p_k$= 217,7 atm)**

**Autoclave for the growth of <u>$SiO_2$ single crystals (→ quartz)</u>**

**1500 bar, T- gradient 400 →380 °C**

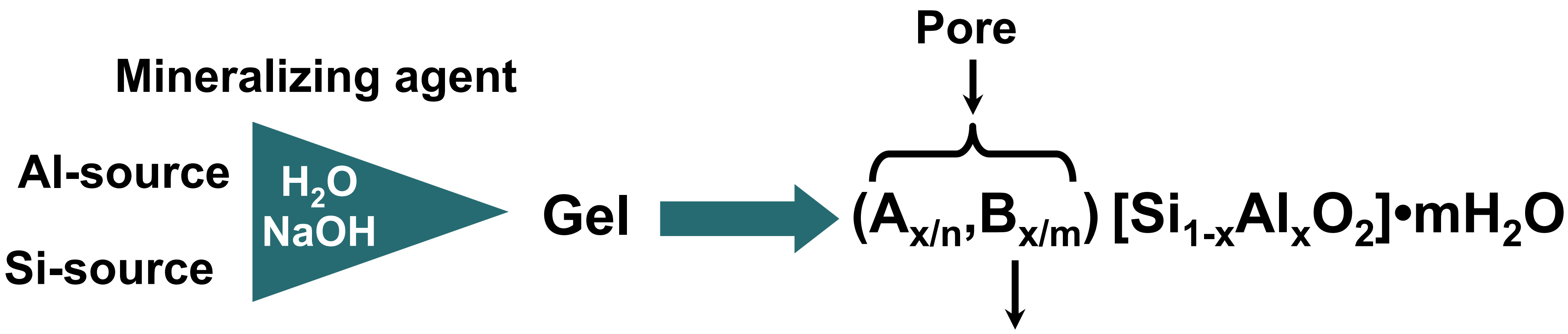
**1: nutrient (powder), 2: seed crystal,**
**3: mechanical fixing of crystal**
**4: product crystal**



**Lit.: Die Rolle der Hydrothermalsynthese in der präparativen Chemie, A. Rabenau, Angew. Chem. *97* (1985) 1017**

# 3. Soft chemistry
# Synthetic Zeolites

## Templated Hydrothermal Synthesis



Mineralizing agent

Al-source

Si-source

$H_2O$
NaOH

Gel

$$\overbrace{(A_{x/n},B_{x/m})}^{\text{Pore}}\ [Si_{1-x}Al_xO_2]\bullet mH_2O$$

Template (B)

$B^{m+}$ = org. Cation
(quart. Alkylammoniumion)

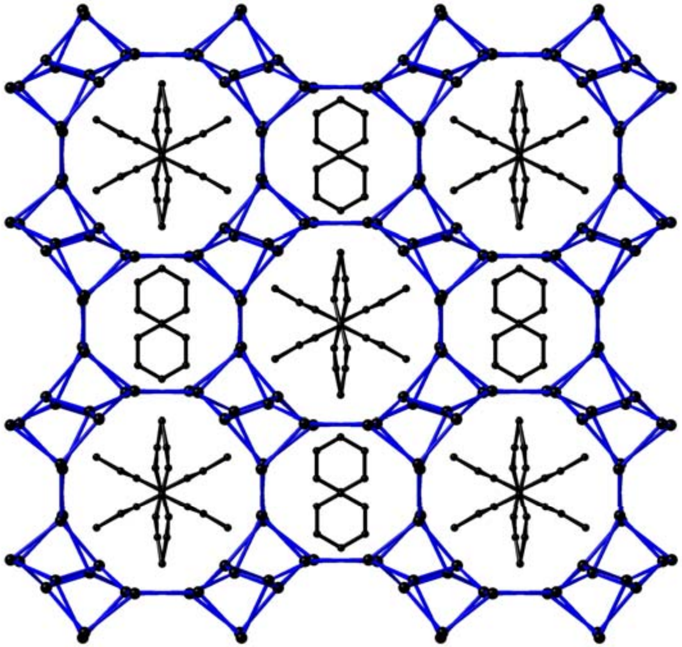
Charge compensation

Template for pore size and geometry

*„... vielfach ist aber die Funktion des Templats wenig oder überhaupt nicht verstanden“*
*(F. Schüth, 2003)*

# 3. Soft chemistry
# Zeolites – comments on function of the template

**TREN-GaPO**



- **Only rare examples/indications for a clear correlation between pore size and shape of the template molecules**

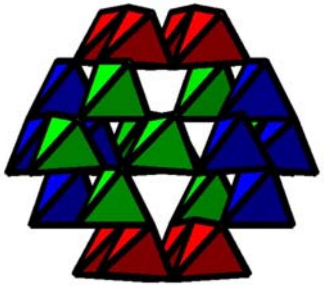
- **Zeolites occurring as minerals don’t need any template for their formation**

- **Zeolites can be synthesized without any template**

# Repetition
# X-ray analysis

- Space groups
- Content of IT A
- Diffraction: Fourier transformation (FT) of $\rho(r)$
- Atomic scattering factor
- FT of periodic objects: Amplitude and phase of the scattered wave is approximated by the structure factor, $F_{hkl} = \Sigma f_i \exp(2\pi i(hx + ky + lz))$
- Structure factor calculations: Intensity and extinctions
- Systematic of extinctions: Translations
- Bragg's law: position of the peaks (lattice parameters)

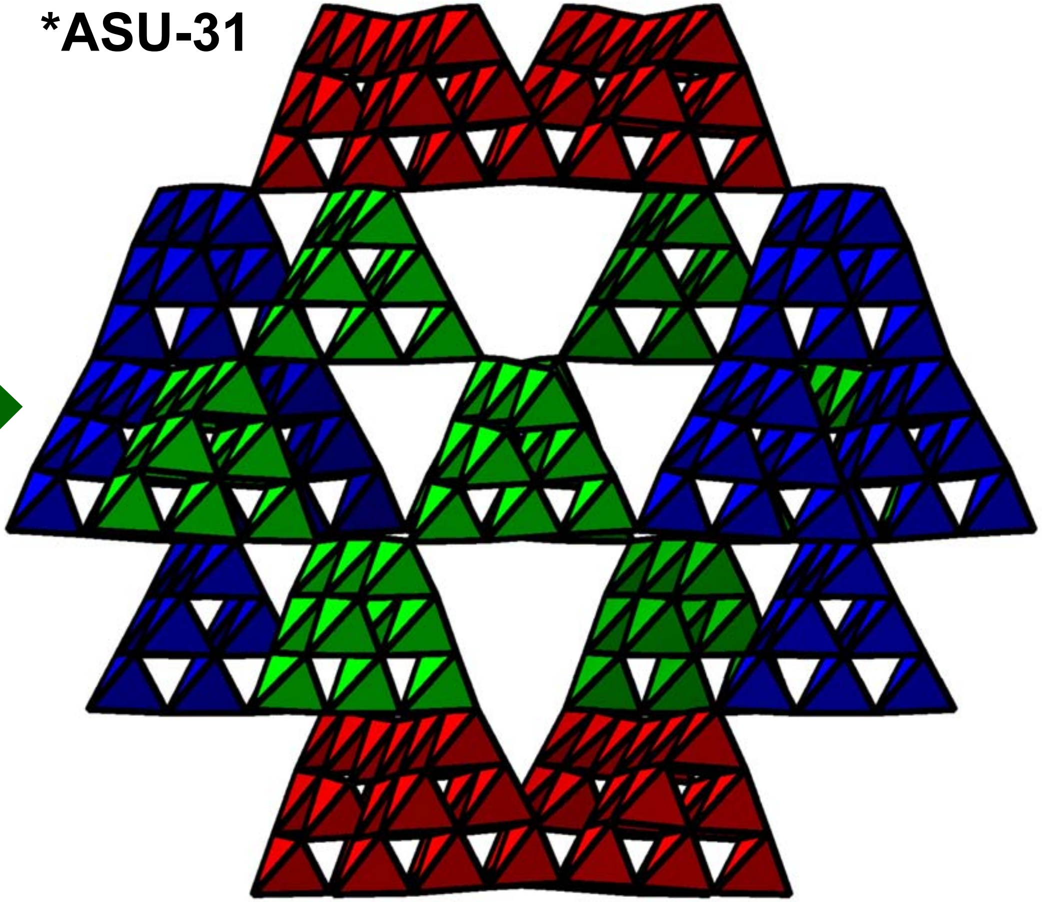
# 3. Soft chemistry
## Solvothermal synthesis



**Sodalite cage**

**Scaling**

***ASU-31**

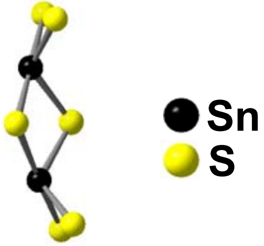


**Expanded Sodalite cage with T3**

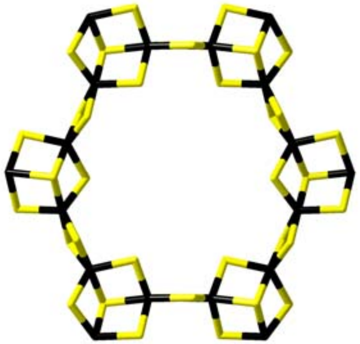
***Arizona State University**

# 3. Soft chemistry
# Precipitation at low temperature

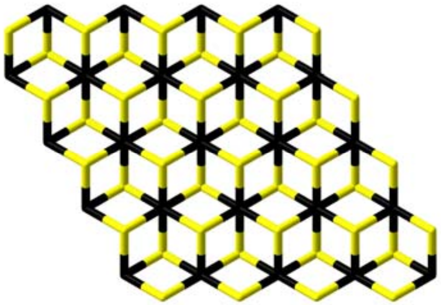
- Starting point: aqueous solution of $R_4Sn_2S_6$ (pH~13)
- Condensation products by decreasing pH

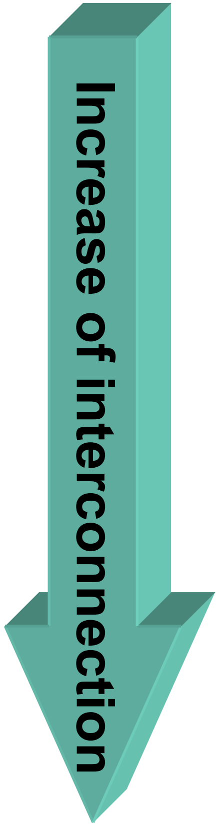


- pH > 11: layers



- pH ~ 9 ($CO_2$-flow): Polymerization to R-SnS-1
- pH < 9 ($HCl_{aq}$): Formation of Berndite



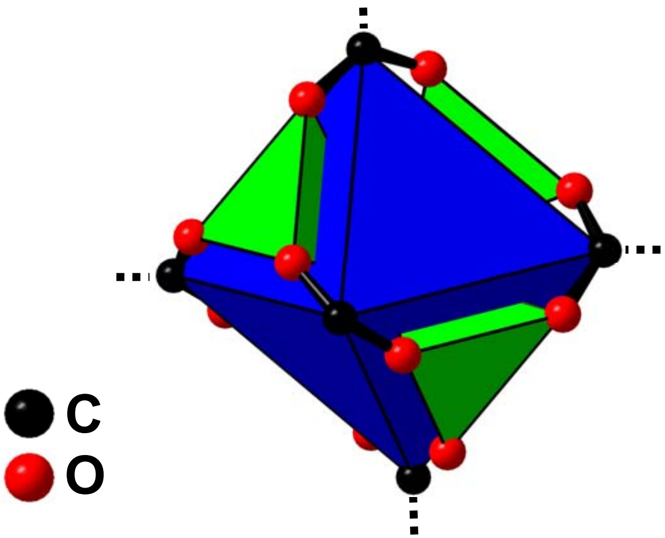

Increase of interconnection

# 3. Soft chemistry
# Precipitation at low temperature

**MOF = Metal organic framework**

**Synthesis: Diffusion of Zn(II)salt-solutions in organic bifunctional acids**
**simple chemistry (precipitation) – remarkable results**

**Two components (SBU = secondary building unit)**
**of the microporous structure**

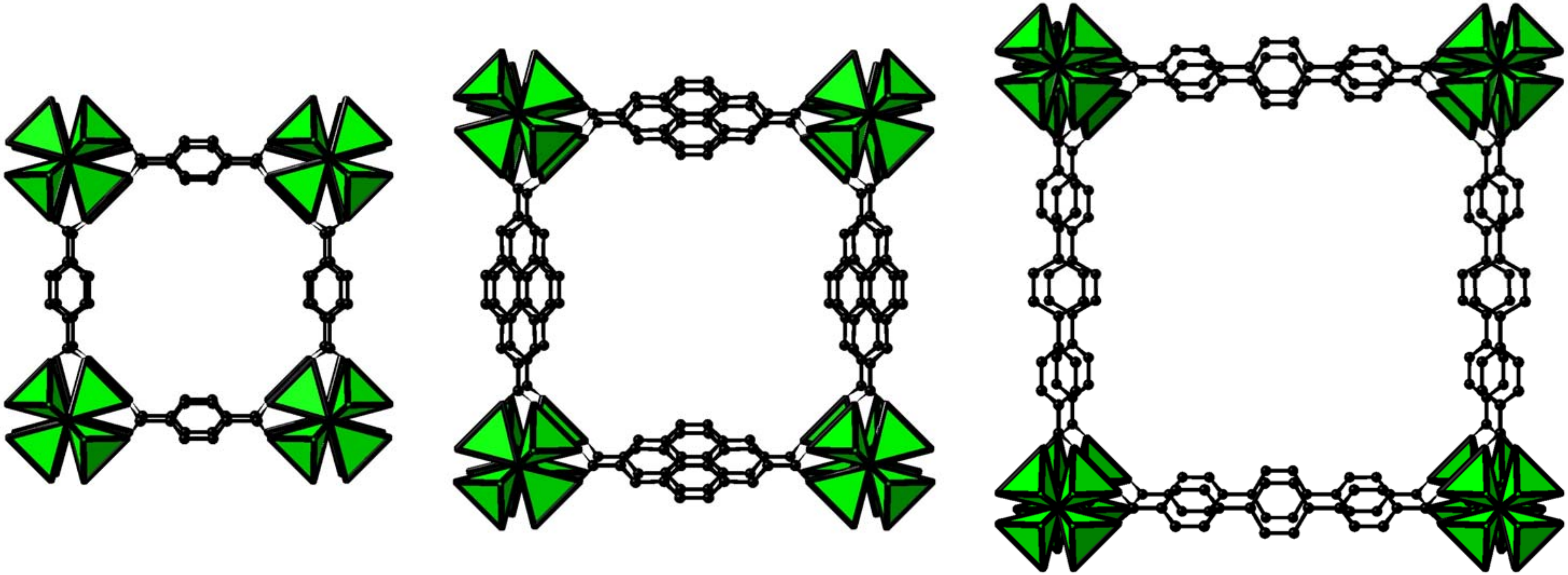


**SBU 1: inorganic component**
**cluster of $ZnO_4$ tetrahedra**
**with six junctures**

**Organic linker**

**SBU 2: organic component**
**CH-core of bifunctional acid**

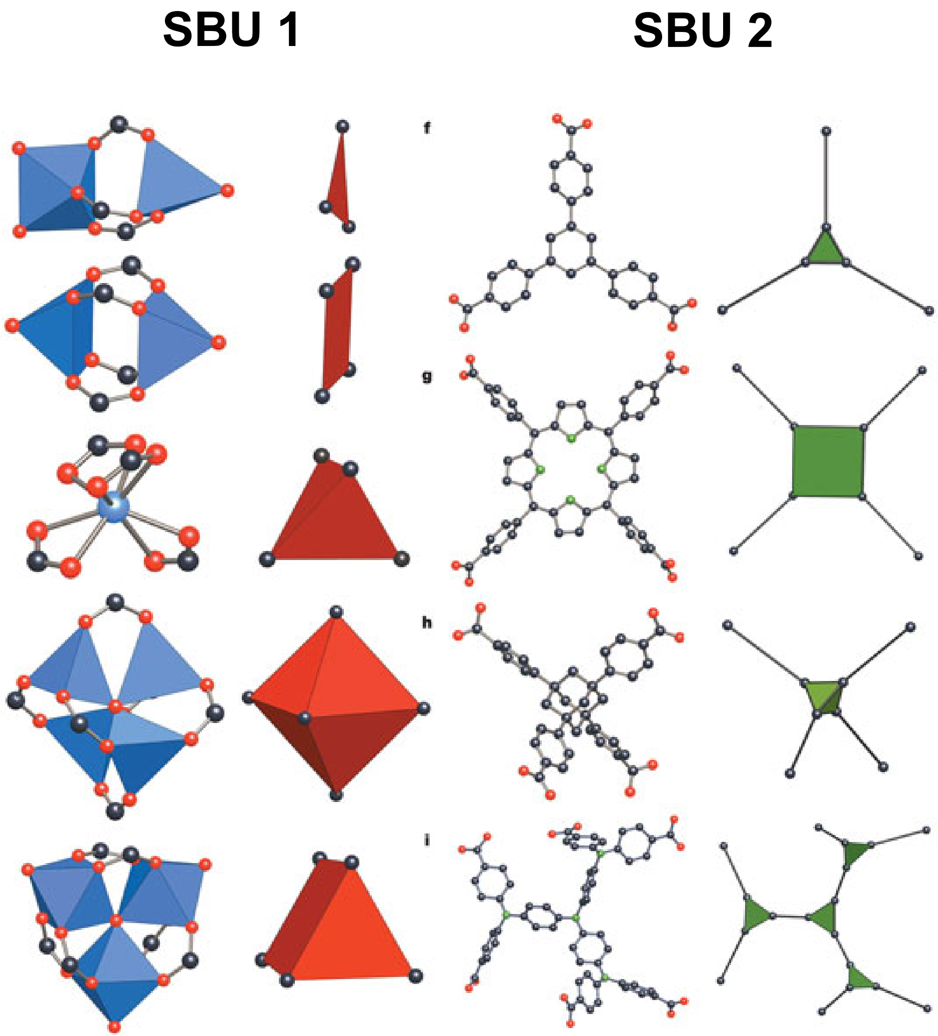
# 3. Soft chemistry
# Precipitation at low temperature



**Unique structural features**

- principle of scaling, ab initio design of materials
- highly crystalline materials
- lowest density of crystalline matter, up to 0.21 g/cm$^3$
- Future applications: adsorbent, container for in situ chemistry, sensor

# 3. Soft chemistry
Reticular syntheses of MOF



**Concept for ab initio design:**

1) Synthesis of SBU 1, 2 with defined topology

2) Prediction of framework topology, structure, pore sizes, chirality...

**Examples:**

**Octahedron-Octahedron: $\alpha$-Po**
**Octahedron-Trig. prism: NiAs**

**O. M. Yaghi et al. Nature 423, 705 (2003)**

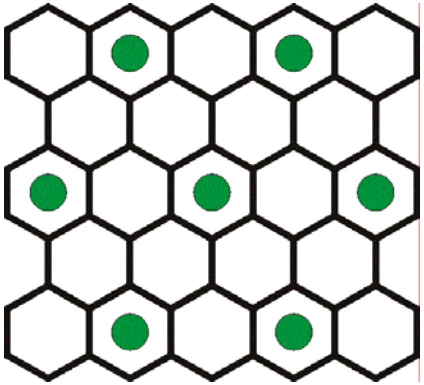
# 3. Soft chemistry
# Intercalation of layered compounds

**Intercalation:**

**continuous adsorption (desorption) of atoms in holes of structures**

**Example 1: Hydrides**

- **salt-like compounds: e. g. $MgH_2$ (hydrogen storage)**
- **semiconductors: e. g. $LaH_3$**



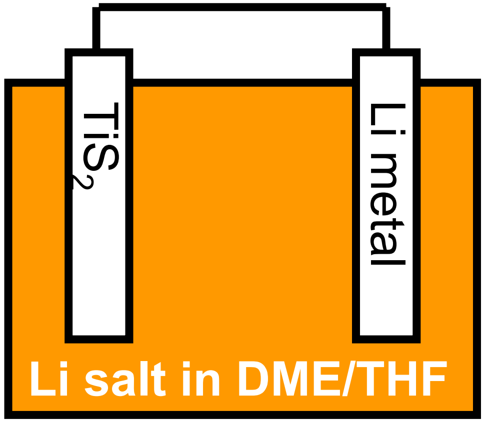
**Example 2: Graphite**

- **Electron donors (alkali metals, e. g. $KC_8$)**
- **Electron acceptors ($NO_3^-$, $Br_2$, $AsF_5$...)**
- **Properties: increase of interlayer spacing, color change, increase of conductivity, change of electronic structure**

**Example 3: $TiS_2$ ($CdI_2$-type)**

- **Electron donors (alkali metals, BuLi, organic amines)**
- **Application: Li-$TiS_2$-battery**

$$x\text{Li (metal)} \rightarrow x\text{Li}^+\text{(solv)} + xe^-$$
$$x\text{Li}^+\text{(solv)} + \text{TiS}_2 + xe^- \rightarrow \text{Li}_x\text{TiS}_2\text{(s)}$$

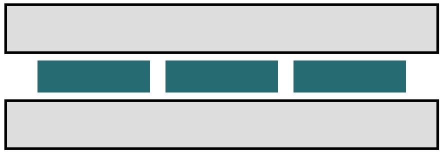


# 3. Soft chemistry
# Filling of zeolites zeolites

## Filled microporous materials

**Molecules (bulk):**
**random arrangement**

**Composite materials:**
**confinement → ordered arrangement**

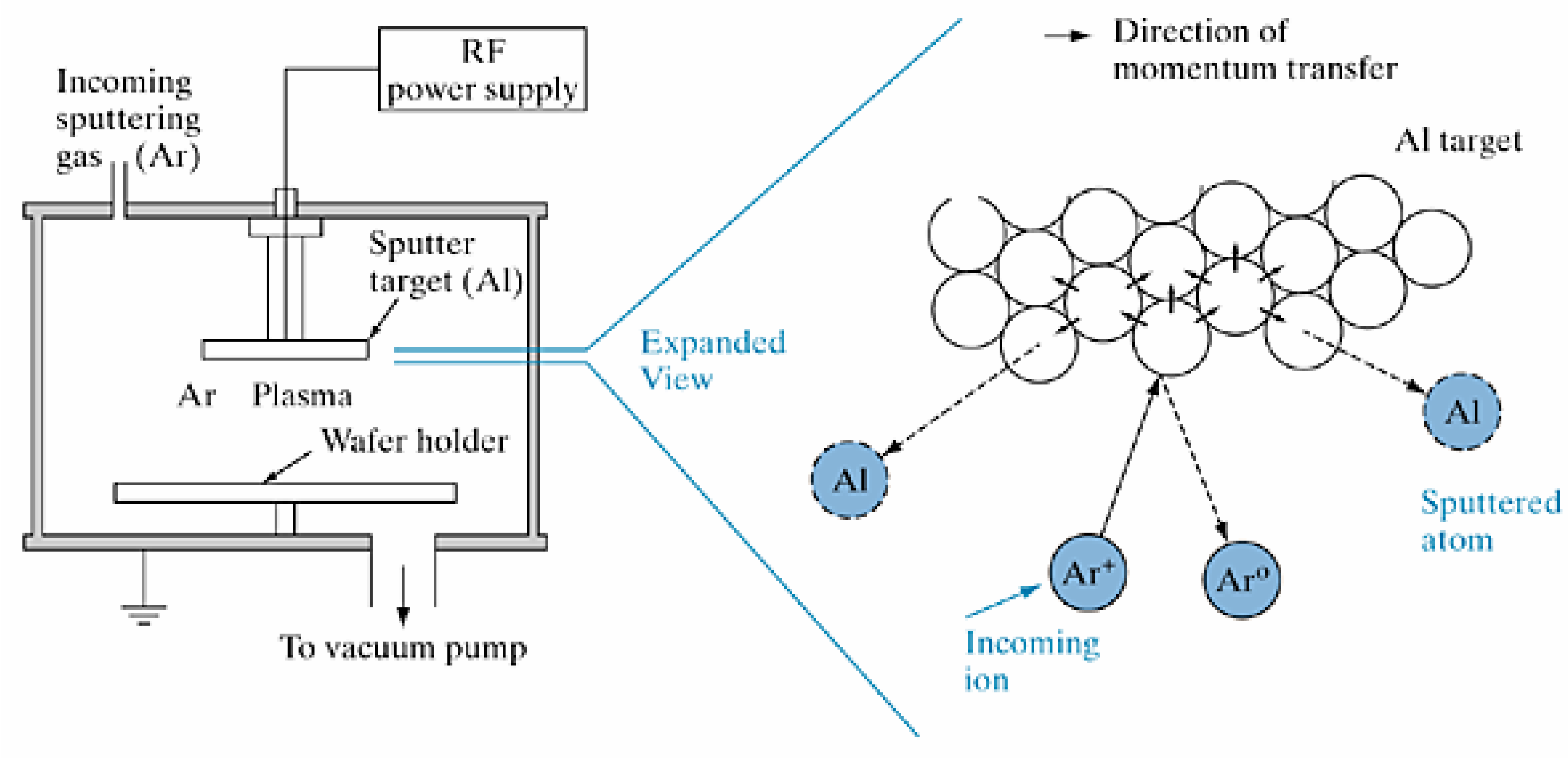


**Examples:**

- **Organic molecules + zeolites: highly anisotropic optical materials**
- **Dyes + zeolites: antenna materials, brilliant pigments (no bleaching)**
- **Metal clusters + zeolites: hydrochromy, barochromy**
- **Semiconductors + zeolites: tuning of optical properties**
- **Polymers + zeolites: formation of quantum wires**

# 4. Nanomaterials
# 2D nanomaterials – physical approaches

- **Sputtering**
  - **originally a method to clean surfaces**
  - **$Ar^+$-ions are accelerated in an electrical field and „hit“ the target**
  - **consequence: surface atoms are removed from the surface**
  - **application: SEM, getter-pump (ionization, UHV devices)**

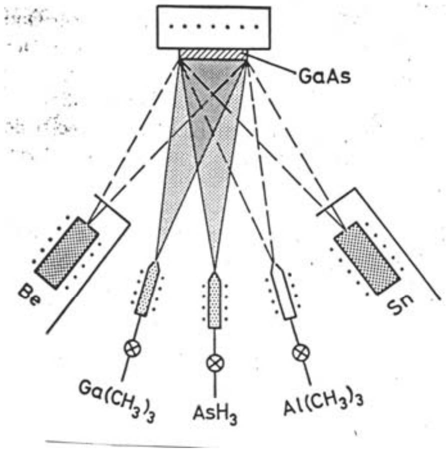


# 4. Nanomaterials
# 2D nanomaterials – chemical approaches

- **Epitaxy:**
  - **thin orientated layers of similar crystal structures**
  - **e.g. InAs: a=603,6 pm on GaAs: a=565,4 pm, both sphalerite structures**

- **CVD (Chemical Vapour Deposition)**
  - **decomposition of molecules in the gas phase by electron beam or laser**
  - **deposition on suitable substrates**
  - **e.g. fabrication of LEDs with GaP and $GaAs_{1-x}P_x$, epitaxial layers are produced by thermal decomposition of compounds like $AsH_3$, $AsCl_3$, $PH_3$, $PCl_3$, ...**

- **MBE**

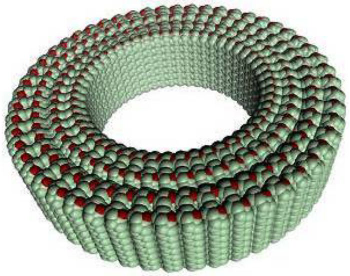


**Production of a $Ga_{1-x}Al_xAs$ on GaAs by the MBE process**

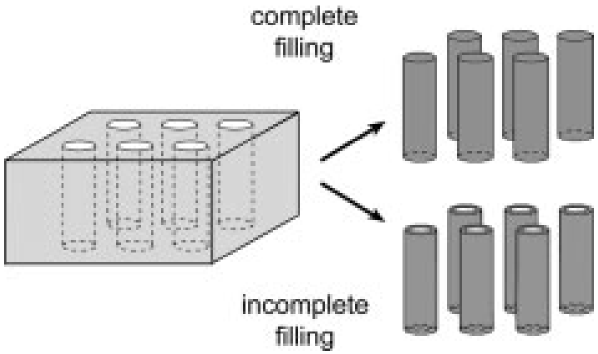
# 4. Nanomaterials
# Formation of 1D nanomaterials

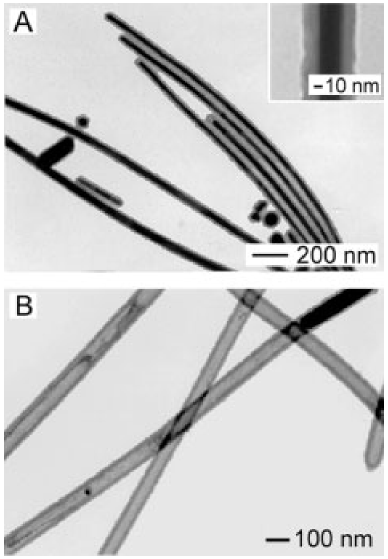
**Misfit in double layers → strain relaxation: bending of the layers nanorolls (asbestos etc.)**

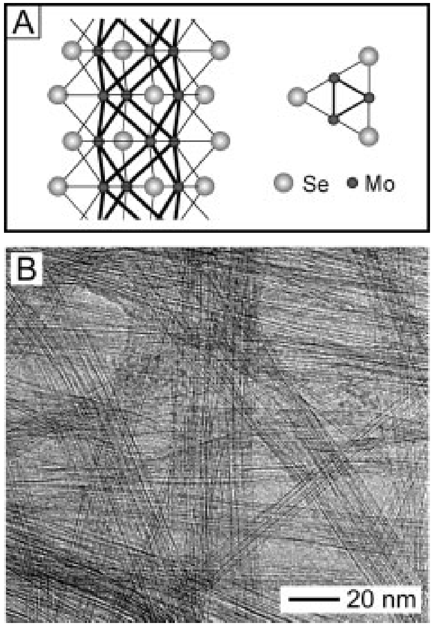
**section**



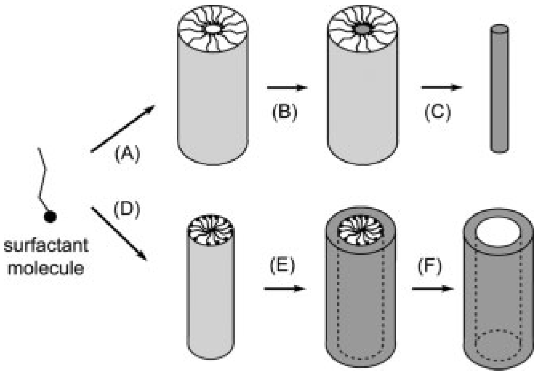
**Silica as hard templates nanorods, nanotubes**







**highly anisotropic crystal structures (Se, Te, $LiMo_3Se_3$)**



**Amphiphilic molecules as soft templates, self assembly nanorods, nanotubes**