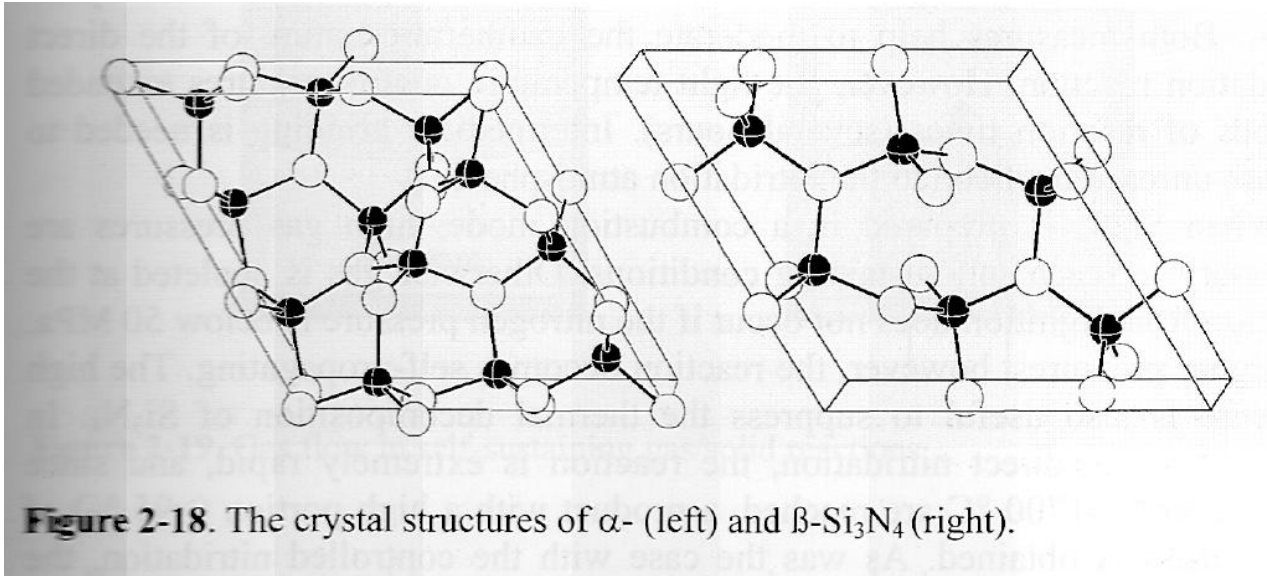# Solid-gas reactions

Overcoming the problems related to poor contact in solid-solid reactions
Excess gas is often used in order to shift reaction towards products.
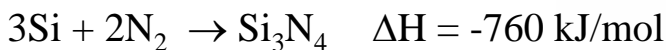
Example: Si_3N_4
α- and β-phase. (α-Si_3N_4 low temperature modification (< 1650°C) has
the best sintering behaviour)

Figure 2-18. The crystal structures of α- (left) and ß-Si_3N_4 (right).

1

|Direct reaction of between the elements

The reaction:

$$3Si + 2N_2 \rightarrow Si_3N_4 \quad \Delta H = -760 \text{ kJ/mol}$$

Is very exothermic, but kinetics is slow
below 1100°C.

The reaction rate depends on the particle
size and purity os the starting material.
Semiconductor grade Si may be used. The
process is catalyzed by iron.

Due to the exothermic nature of the reaction,
the reaction rate must be carefully controlled
to keep the temperature low enough (1250-
1350°C) to avoid sintering, melting and
formation of the β-phase.

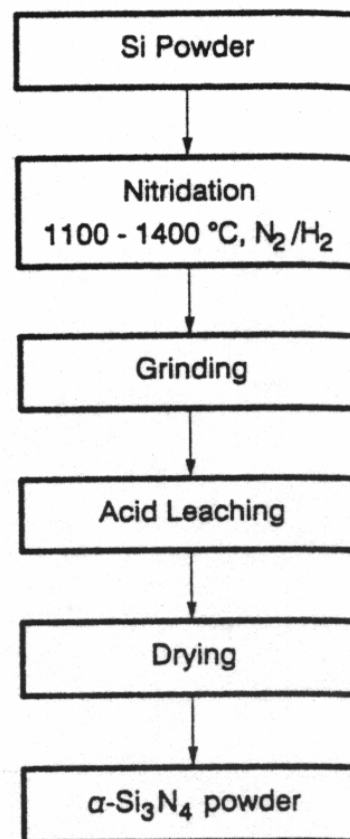Limit N_2 access (e.g. diluting with 20-
40% H_2) or dilute Si with Si_3N_4.


Fig. 4. Process for Si_3N_4 synthesis by direct nitridation.

Combustion mode, and self sustaining solid-gas reactions

Si_3N_4 may be prepared in a combustion mode, but high gas pressures must be used to obtain self-sustaining reactions. (avoid depletion of gas at the reaction front.) At high pressures the reaction is self propagating, and temperatures above 1700˚C are reached resulting in >95% β-Si_3N_4.

Oxides, hydrides, nitrides, oxynitrides may be formed by heating in air (oxygen), hydrogen, nitrogen or ammonia.

Co-current **Counter-current**

Figure 2-19. Gas flow in self-sustaining gas/solid reactions.
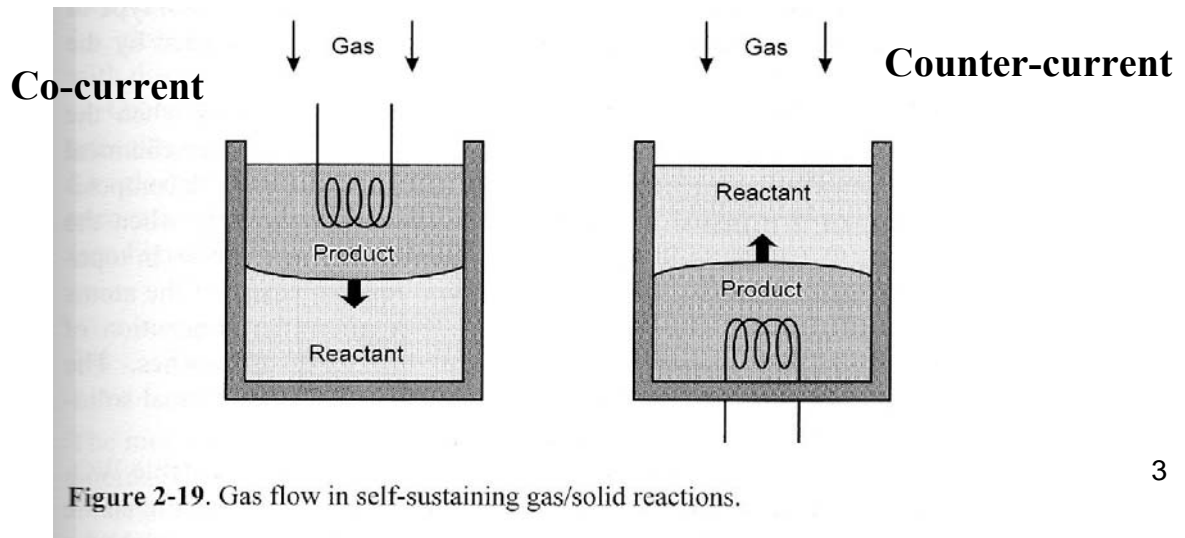
3

Decomposition and dehydration reactions

Reactions involving transport of gases away from the reaction.
Carbonates, oxalates, nitrates, hydroxides… Used for formation of metal oxides.
Boehmite (2AlOOH $\rightarrow$ γ-Al_2O_3 + H_2O)
Thermal decomposition is also controlled by nucleation and growth, e.g. surfaces, grain boundaries, dislocations…

Topochemically controlled reactions: The reactivity id controlled by crystal structure rather than by chemistry.
Reactions my occur within the material without separation of a new phase.

Topochemical solid state reactions occur with only small structural rearrangements.
Allow preparation of e.g. metastable phases. Mild conditions, soft chemistry routes.

4

Formation of metastable WO$_3$.

Termodynamically stable phase WO$_3$ with a ReO$_3$ type structure. (monoclinic)
(corner sharing octahedra, perovskite type arrangement without the large A-cations)

Metastable hexagonal WO$_3$ may be obtained from WO$_3$ 1/3H$_2$O by heating at 300C
Structural elements in the hydrate: planes built from 6-rings of WO6 octahedra stacked with a shift of ½ ring diameter.
In the metastable WO$_3$ the rings are stacked on top of each other.
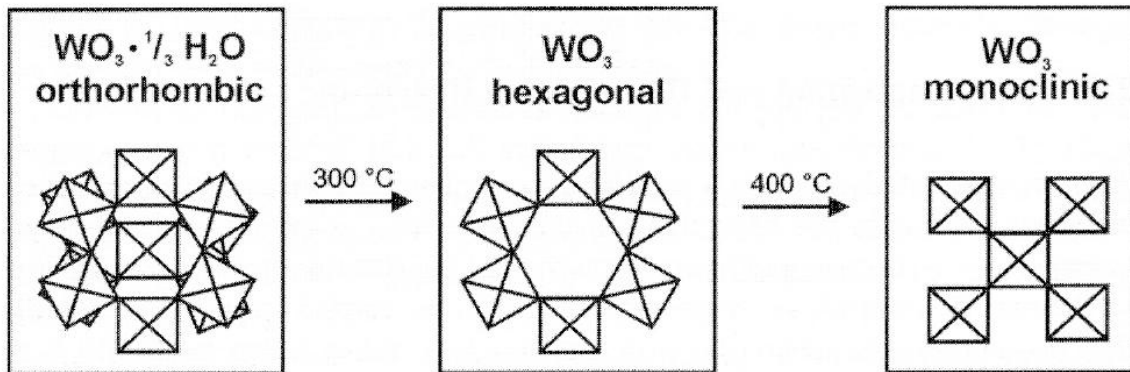
Figure 2-20. Structural relations in the dehydration of WO$_3$ · $^1/_3$ H$_2$O and in the phase transformations of WO$_3$. Each crossed square represents an octahedron viewed from above.

5

Phase transitions and dehydroxylation of τ-Zr(HPO$_4$)$_2$

Formation of a new polymorph of Zirconium pyrophosphate, Zr(P$_2$O$_7$), by Structurally Constrained Soft Chemistry

τ-Zr(HPO$_4$)$_2$ <-> ρ-Zr(HPO$_4$)$_2$ -> β-ZrP$_2$O$_7$ -> ZrP$_2$O$_7$

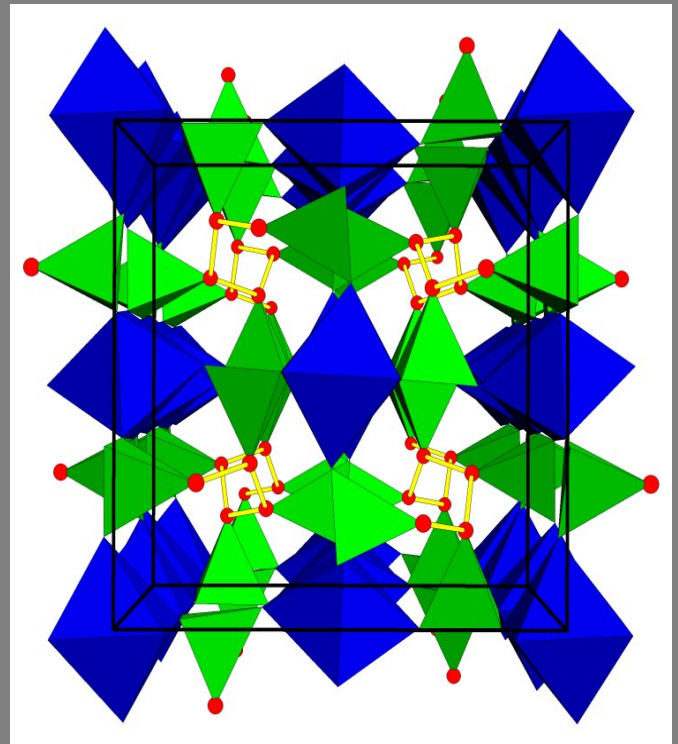## Anne Marie Krogh Andersen
Poul Norby

6

A 3-dimensional zirconium hydrogen phosphate, τ-Zr(HPO$_4$)$_2$

Tetragonal, I4$_1$cd
a=11.259, c=10.764 Å

Framework structure: Alternating ZrO$_6$ and HPO$_4$ polyhedra
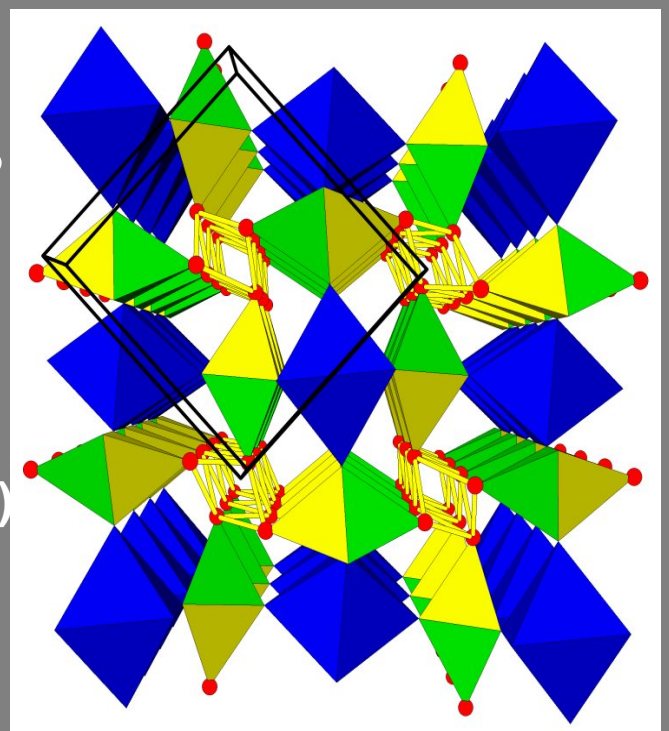
Hydrogen bonded spiral along the 4$_1$ axis

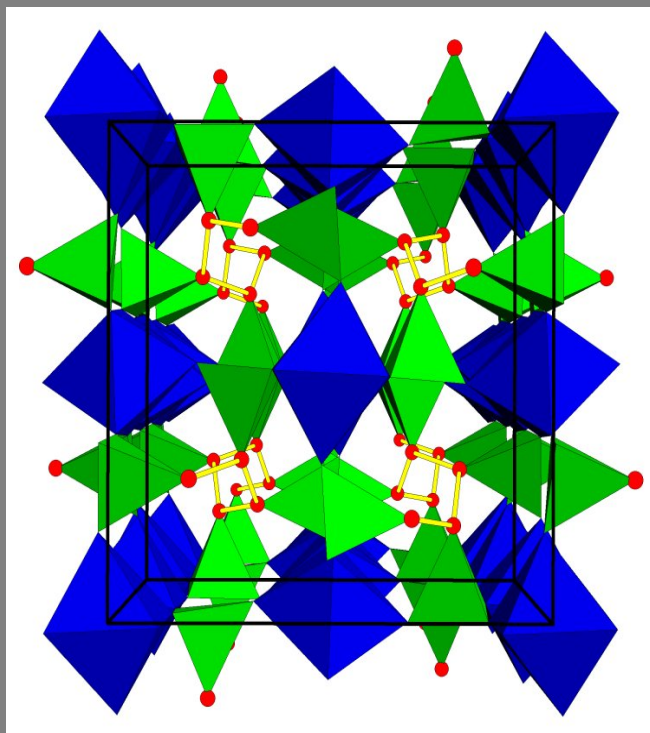**Reversible phase transition to**
ρ-Zr(HPO$_4$)$_2$ at ~325°C

Orthorhombic, Pnnm
a= 8.187, b=7.698, c=5.403

Disordered hydrogen phosphate groups
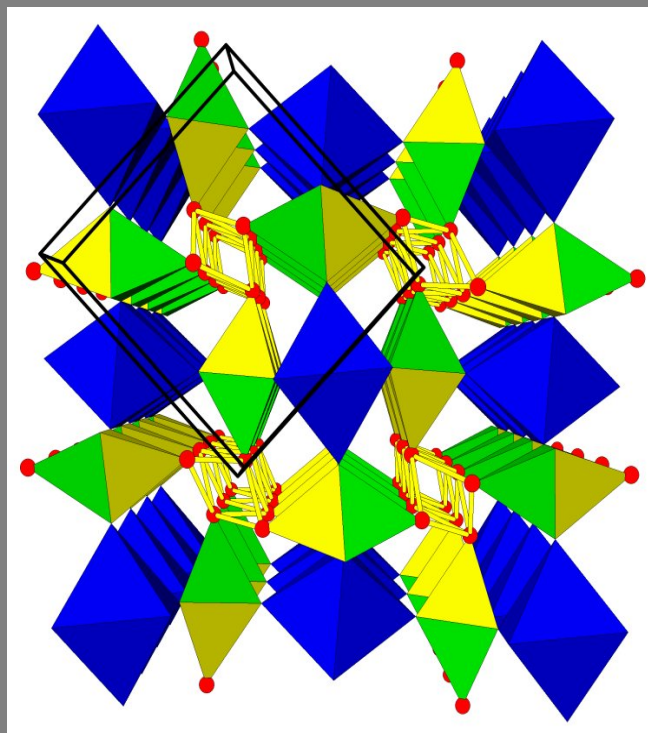(Yellow and green tetrahedra represent the two orientations)

Comparing τ and ρ-Zr(HPO₄)₂

τ-Zr(HPO₄)₂

ρ-Zr(HPO₄)₂

Dehydroxylation/condensation; formation of a new polymorph of ZrP₂O₇

$$2HPO_4^{2-} \longrightarrow P_2O_7^{4-} + H_2O$$

β-ZrP₂O₇ :
Orthorhombic, Pnnm
a = 8.289, b = 6.623, c = 5.329 Å

Cubic ZrP₂O₇ :
High temp.: Pa-3, a = 8.297 Å
Low temp.: Pa-3, a' = 3a

10

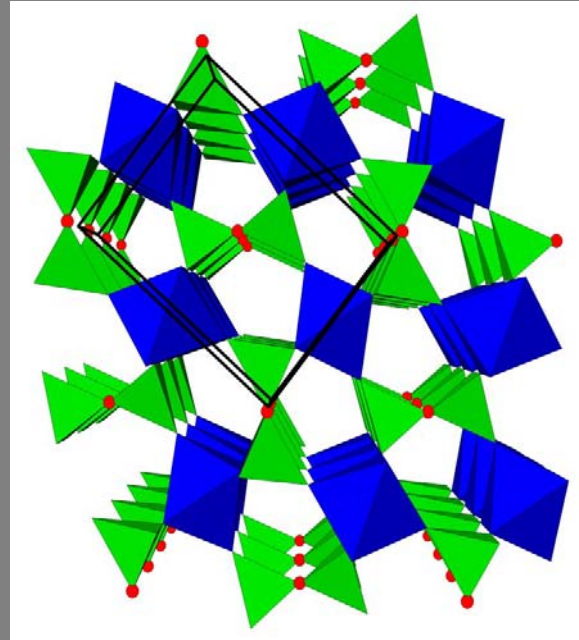# Comparing ρ-Zr(HPO$_4$)$_2$ and β-ZrP$_2$O$_7$

ρ-Zr(HPO$_4$)$_2$
(only one of the tetrahedra positions are shown)

β-ZrP$_2$O$_7$

11
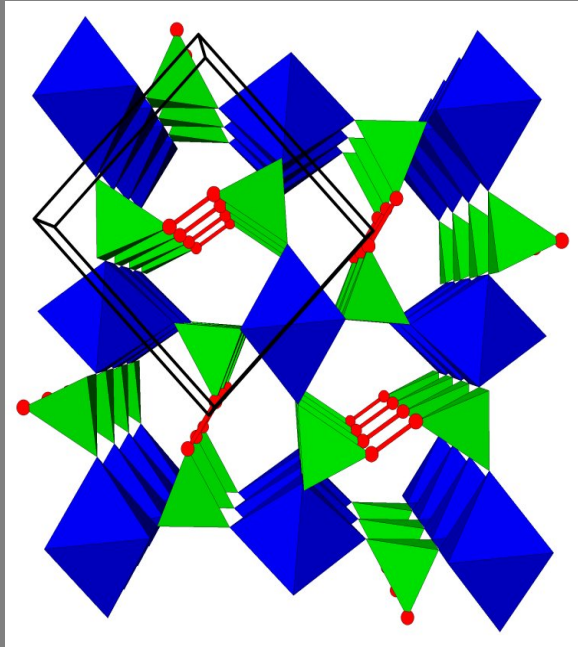
β-ZrP$_2$O$_7$ and ZrP$_2$O$_7$, 5_5 layers

β-ZrP$_2$O$_7$

Cubic ZrP$_2$O$_7$

12
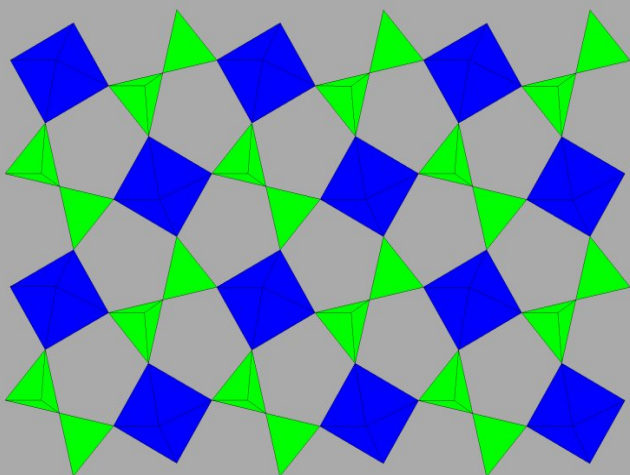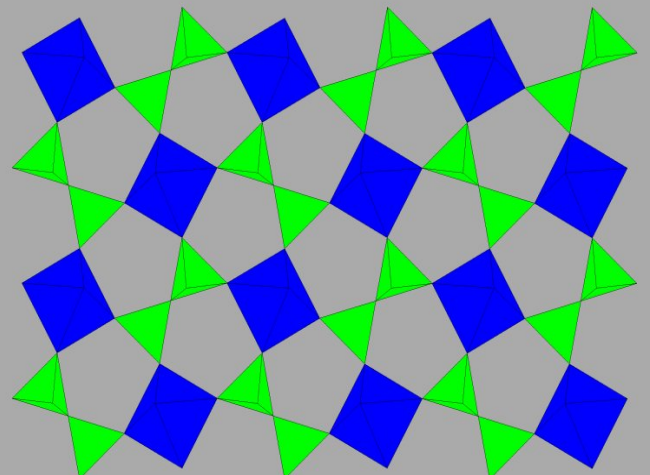
β-ZrP₂O₇; 4-6-layer

β-ZrP_2O_7; 4-6-layer
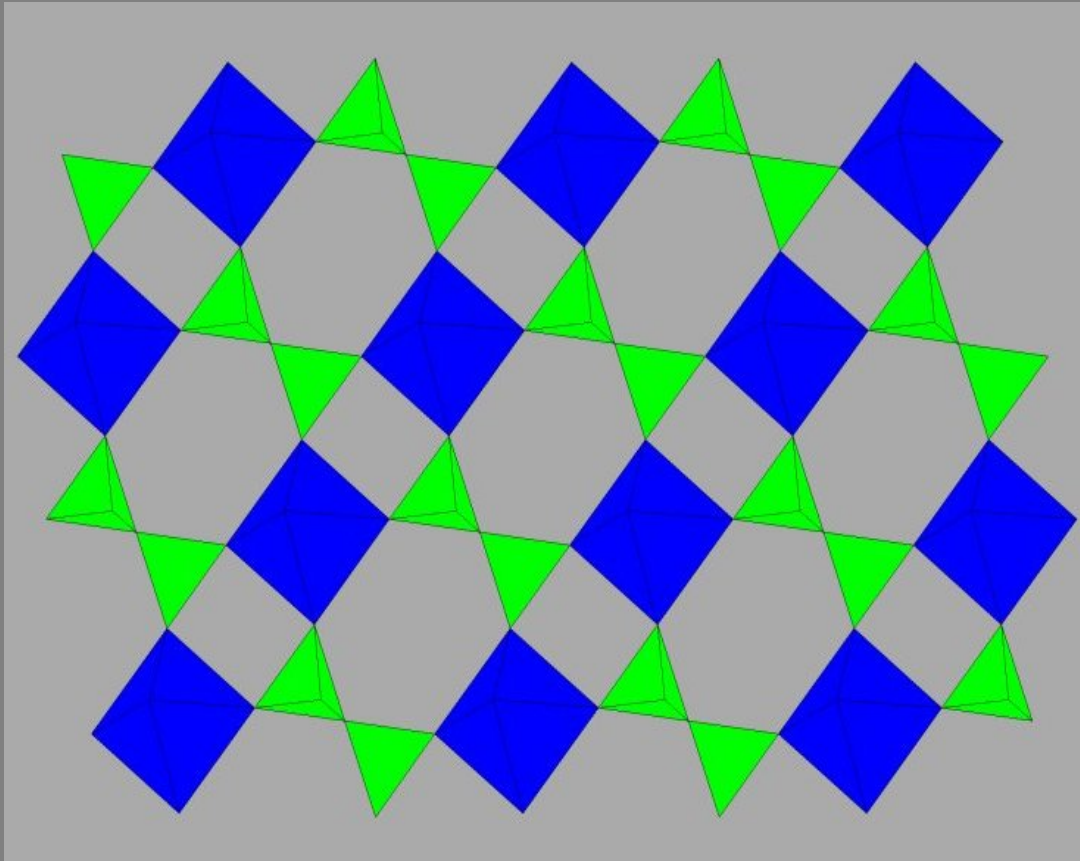
13

Thermal expansion

Thermal expansion coefficients

t-$Zr(HPO_4)_2$ ~0 K^{-1}

r-$Zr(HPO_4)_2$ $- 0.3 \cdot 10^{-6} \ K^{-1}$

b-ZrP_2O_7 $7.9 \cdot 10^{-6} \ K^{-1}$

Cubic ZrP_2O_7 $1.6 \cdot 10^{-6} \ K^{-1}$

Legend:
- ● τ-$Zr(HPO_4)_2$
- ■ τ'-$Zr(HPO_4)_2$
- ▲ β-ZrP_2O_7
- ▼ ZrP_2O_7

y-axis: unit cell volume pr. Zr (Å³)
x-axis: Temperature (°C)
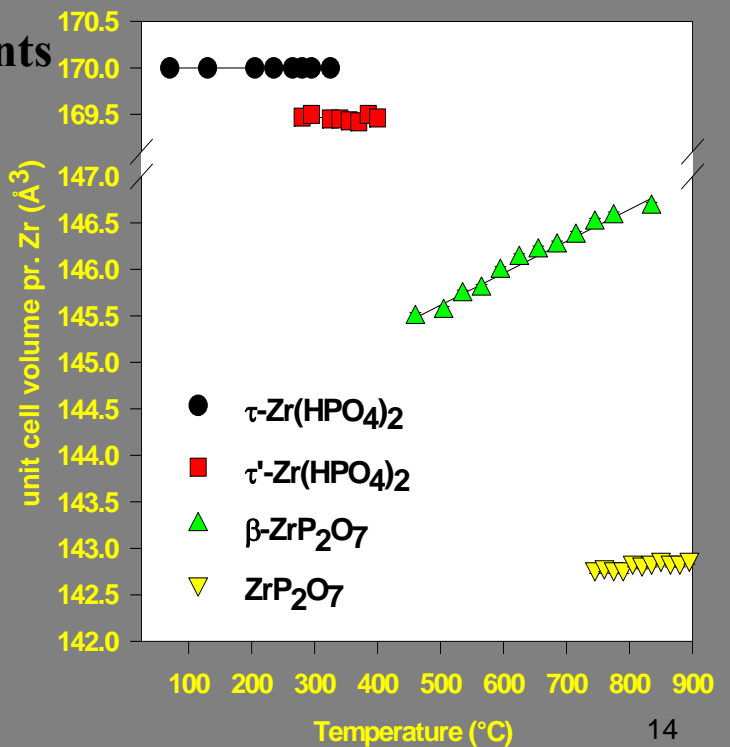
14

Intercalation/deintercalation

Intercalation: insertion of species (atoms, molecules, ions) into a crystalline host material.
The host material (and guest) may undergo perturbations in their geometrical, chemical or electronic environment.

Two general systems.
Three dimensional lattices with parallel channels or interconnected channels (e.g. zeolites) Uptake is restricted by channel size.
Low dimensional host lattices. Layered materials or materials built from chain structures. Spacing between layers or chains may change to accommodate guest species.

Layered materials: Strong intralayer bonds, weak interlayer bonds.

Neutral layers: Van der Waals interactions, e.g. graphite, oxychlorides (FeOCl) and metal disulfides
Negatively charged layers separated by mobile (exchangeable) cations. e.g. clays, transition metal phosphates…
Positively charged layers separated by anions, e.g. layered double hydroxides, $M^{II}_{1-x}M^{III}_x(OH)_2\ A^{-n}_{x/n}\ m\ H_2O$

15

Intercalation in graphite

Single-atom thick graphite layers. Interlayer distance 3.35Å (0.335nm)

Intercalation of:
lithium: 3.71Å
potassium: 5.35Å
AsF5: 8.15Å
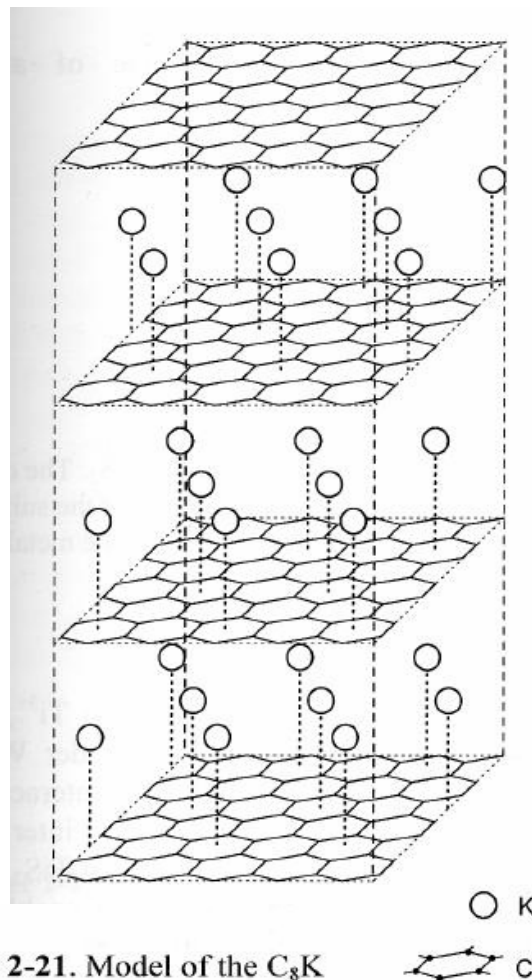KHg: 10.22 Å (three layers of K and Hg)

Figure 2-21. Model of the C_8K structure.

○ K
⬡ C

Electronic properties

- **Insulator host lattices:** (e.g. zeolites, layered aluminosilicates, metal phosphates): The basic physical properties (of the host lattice) are not changes by intercalation. Catalysts, catalyst supports, adsorbants, ion exchangers…

- **Host lattices with redox properties**. May reversibly uptake electrons from or donate electrons (less often) to the guest. E.g. graphite, metal dichalcogenides, metal oxyhalides…) Strong changes in the physical properties, e.g. electric conductivity. Interesting as electrode materials for lithium batteries, electrochromic systems, sensor materials…

Many metal dichalcogenides, MX_2, have layered structures,
M = Zr, Ti, Hf, V, Mo, Nb, Ta, W, Sn
X = S, Se

Two layers of closed packed chalcogenide ions with metal ions between (octahedral or trigonal prismatic coordination) Sequence: X-M-X . .X-M-X . .

Classic example. TiS_2: $Li + TiS_2 \leftrightarrow Li^+[TiS_2]^-$
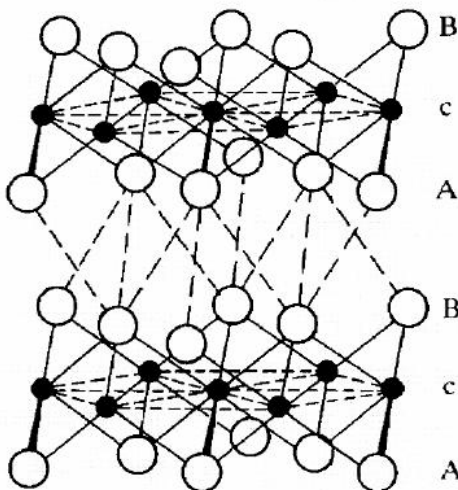
Figure 2-22. The structure of TiS_2. The open circles (A and B layers) represent the sulfur atoms, the full circles (c layers) the metal atoms.

Ti^{4+} reduced to Ti^{3+} and Li oxidized to Li^+

The layers become charged (negative) and the Van der Waals forces are replaced by Coulomb interactions. The interlayer spacing is expanded in $LiTiS_2$ compared to TiS_2.
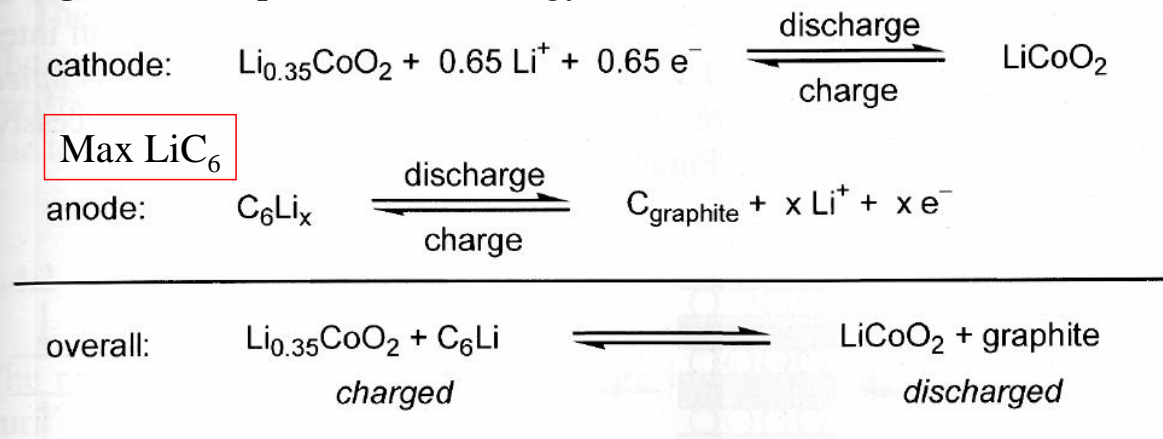
Rechargeable (secondary) lithium batteries

Reversible lithium intercalation/deintercalation is the heart of lithium battery electrode technology. In order to operate at ambient temperatures, a highly mobile ion is needed which is able to penetrate into solids. Apart from protons, lithium is the obvious choice. Lithium also have suitable redox properties.
Both electrodes in lithium batteries use reversible lithium insertion. Both are usually layered intercalation materials. (e.g. graphite and $LiCoO_2$)

Discharge: The difference in chemical potential for Li at the two electrodes results in a flow of Li^+ cations through the electrolyte from the cathode to the anode. Discharge delivers energy
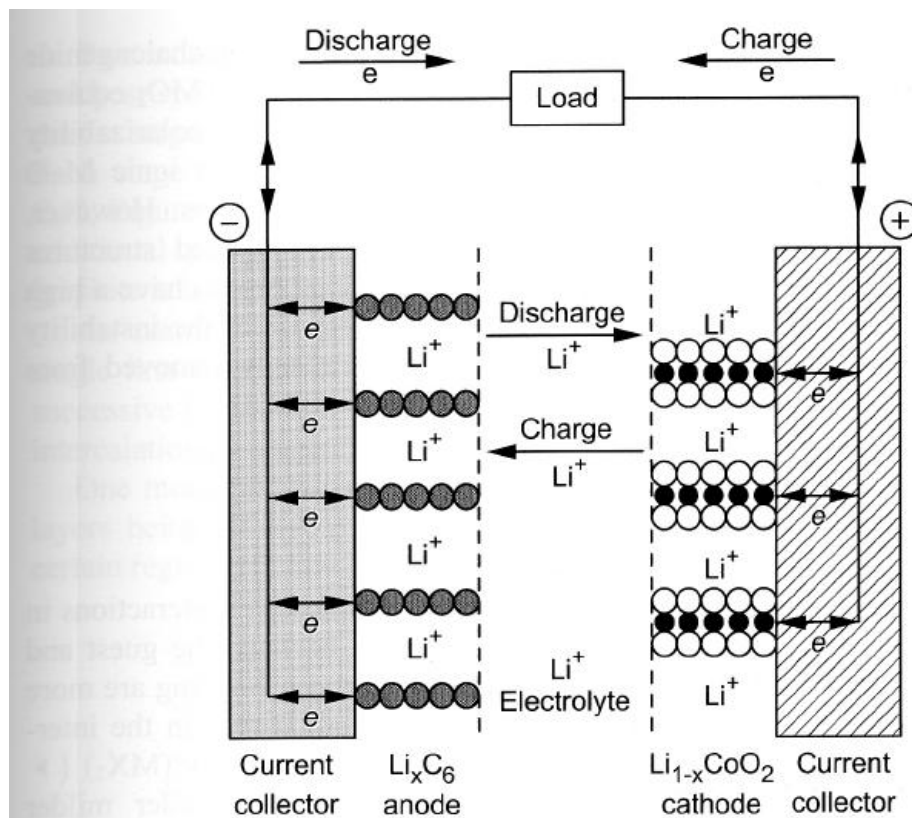**Charge**: Reverse process, cost energy.

cathode: $\quad Li_{0.35}CoO_2 + 0.65\,Li^+ + 0.65\,e^- \xrightleftharpoons[\text{charge}]{\text{discharge}} LiCoO_2$

Max LiC_6

anode: $\quad C_6Li_x \xrightleftharpoons[\text{charge}]{\text{discharge}} C_{graphite} + x\,Li^+ + x\,e^-$

overall: $\quad Li_{0.35}CoO_2 + C_6Li \rightleftharpoons LiCoO_2 + graphite$

charged $\qquad\qquad\qquad\qquad$ *discharged*

9

Figure 2-23. Schematic illustration of the charge/discharge process in a rechargeable lithium ion battery.

20

Mechanistic aspects

Staging in intercalation.

During intercalation, interactions between layers are broken, and are replaced by interactions between layers and guests.

Illustrated by the easy of intercalation in MX_2: Disulfides easily intercalated at milder conditions than the diselenides, while the ditellurides have not been reported to intercalate.

Staging has the effect of decreasing the difficulty of breaking interlayer interactions. Some layers are partly or completely filled, while others are empty. This is often obtained in an ordered fashion.

The order of the staging is given as the number of layers between successive filled or partially filled layers.
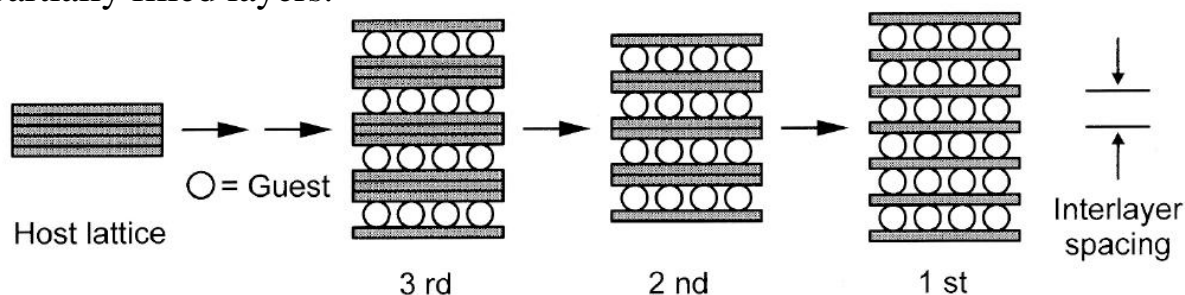

Figure 2-24. Representation of nth stage intercalates (n = 1–3).

Staging examples

Example 1: Intercalation of K in graphite. A successive sequence of stages down to stage 1 are observed when potassium is reacted with graphite. Each stage correspond to a specific stoichiometry.

Example 2: Li_xTiS_2: A single first stage with partially filled layers is formed over the entire composition range.

One model for staging:

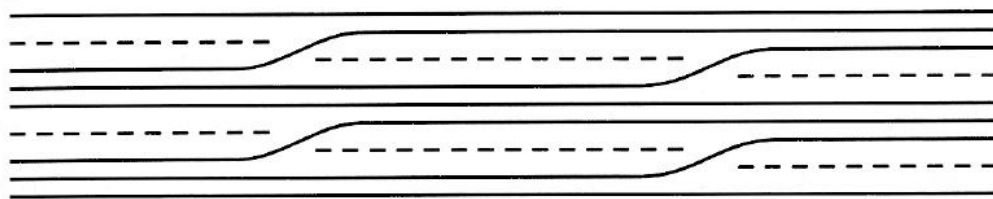**Figure 2-25.** Model of a stage 3 compound with the intercalated compound (---) between all layers.

TEM: Mixed staging in C- FeCl$_2$

TEM: Flexible layers in intercalation in graphite

Preparative methods.

Direct reaction:

Direct reaction between guest and host. E.g. reaction between dichalcogenides and metal vapour at 6-800C. Also reactions with alkali metals dissolved in liquid ammonia has been used. (cointercalation of ammonia)

Reaction with butyllithium is a good and simple way of intercalating lithium:

$$x\, LiBu + MX_n \rightarrow Li_xMX_n + x/2\, C_8H_{18}$$

Intercalation of liquid or low melting compounds may be performed using the pure compounds. Solid organic or organometallic guests are often dissolved.

Graphite may undergo reductive or oxidative intercalation:
C_8K or C_8Br, $C_{24}NO_3 \cdot 3HNO_3$

Table 2-4. Examples for the direct reaction.

Reactants (host/guest)	Products
TaS_2/pyridine	$TaS_2(C_5H_5N)_{0.5}$
VSe_2/Cp_2Co	$VSe_2(Cp_2Co)_{0.25}$
TiS_2/Na(naphthalide)	$NaTiS_2$
α-$Zr(HPO_4)_2 \cdot H_2O$/RNH_2	$Zr(HPO_4)_2(RNH_2)_2$
$V(O)PO_4$/EtOH	$V(O)PO_4(EtOH)_2$
graphite/K	C_8K
graphite/H_2SO_4	$C_{24}^{+}HSO_4^{-} \cdot 2\, H_2SO_4$
graphite/OsF_6	$C_8(OsF_6)$
graphite/$AlBr_3$/Br_2	$C_9(AlBr_3)(Br_2)$
FeOCl/pyrrole	$FeOCl(polypyrrole)_{0.34}$
FeOCl/Cp_2Fe	$FeOCl(Cp_2Fe)_{0.16}$
$NiPS_3$/LiBu	$Li_{4.4}NiPS_3$
MoO_3/H^{+}/reductant	$H_{1.7}MoO_3$
V_2O_5/LiI	$Li_xV_2O_5$

Cp

cyclopentadienyl

Ion exchange

Replacing an intercalated guest ion with another by ion exchange
Zeolites, clays…
Often intercalation in steps may be necessary. Changes ion exchange and
intercalation properties.
E.g. swelling of smectic clays

Table 2-5. Examples for ion-exchange reactions.

Reactants	Products	Solvent
$Na_xTiS_2/LiPF_6$	Li_xTiS_2	dioxolane
$K[Al_2(OH)_2(Si_3AlO_{10})]/Na^+$	$Na[Al_2(OH)_2(Si_3AlO_{10})]$	H_2O
$Na_{0.33}(H_2O)_{0.66}TaS_2/[Cp_2Co]I$	$TaS_2(Cp_2Co)_{0.2}$	MeOH
$MnPS_3/KCl$	$Mn_{0.8}PS_3(K)_{0.4}(H_2O)_{0.9}$	H_2O
$Mn_{0.8}PS_3(K)_{0.4}(H_2O)_{y}/[Ru(bipy)_3]^{2+}$	$Mn_{0.8}PS_3[Ru(bipy)_3]_{0.2}$ *	H_2O

* bipy = 2,2'-bipyridyl

Exfoliation and reflocculation/restacking

Under the correct conditions some layered materials may display "infinite
swelling". The layers are exfoliated or delaminated into a colloidal dispersion.
Classical: smectic clays at low ionic strength.

Hydrated alkali metal dichalcogenides (e.g. $Na_x(H_2O)_yTaS_2$)
Also layered titanates, manganates, layered perovskite related materials…
Also anionic clays as hydrotalcites.

Reconstruction of the layered material using guest species: e.g. ferrocenes,
polymers… Reflocculation by evaporation or changes in electrolyte
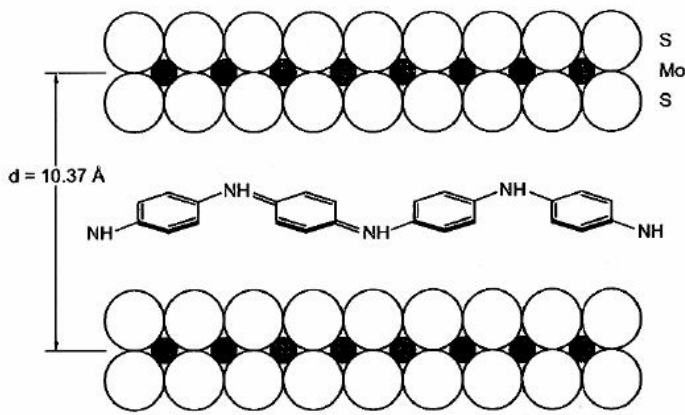concentration

Electrointercalation

Electrointercalation e.g. used in batteries
Oxidation/reduction of perovskite related materials

$$A_xB_yO_z + 2\delta OH^- \rightarrow A_xB_yO_{z-\delta} + \delta H_2O + 2\delta \, e^-$$

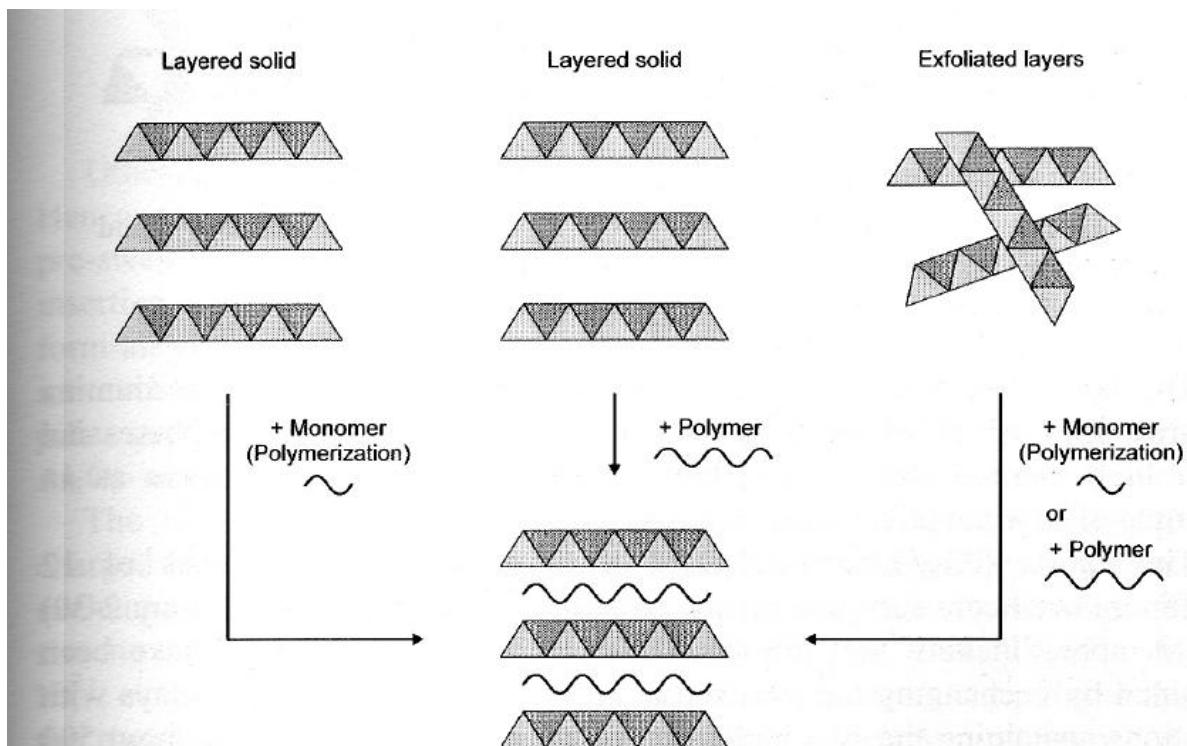# Intercalation of polymers

Figure 2-27. Schematic structure of polyaniline/MoS_2.

Intercalation of monomer molecules with subsequent in-situ polymerization
Direct intercalation of polymer chains into the host lattice (slow)
Delamination of the host lattice into a colloidal dispersion, adding the polymer followed by reprecipitation
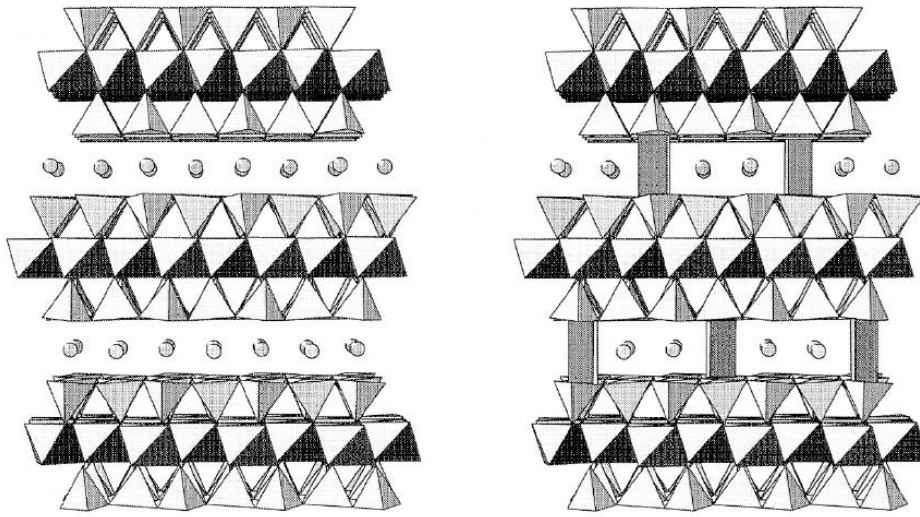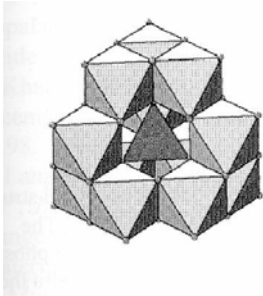
Figure 2-28. Strategies for the synthesis of inorganic-organic hybrid materials from layered solids.
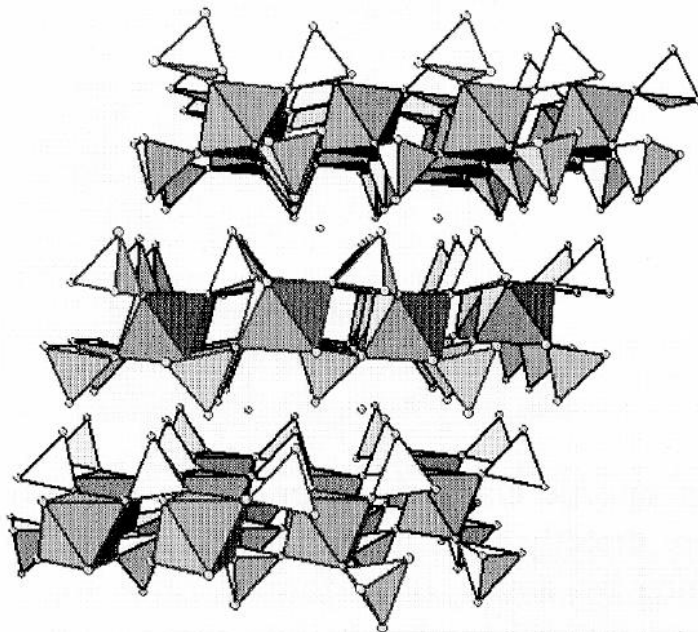
Pillared clays

Figure 2-29. The layer structure of muscovite (left) with 2:1 layers (see above) and schematic representation of the clay with pillars (right).

Figure 2-30. The structure of $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ("Al_{13}")

Figure 2-31. The crystal structure of α-$Zr(HPO_4)_2 \cdot H_2O$. The tetrahedra represent the phosphate groups, and the octahedra the coordination polyhedra of the zirconium atoms. The small circles in the interlayer space represent water molecules.