Course content

The course introduces the student to synthesis of inorganic and hybrid materials using a number of techniques: both traditional inorganic methods as well as the use of metalorganic precursors. The following methods are treated: ceram methods, flux methods, hydrothermal methods, chemical vapor transport, CVD, sol-gel, precursor methods, intercalation, soft chemistry, electrochemical methods. Materials are made in different forms from amorphous materials and single crystals to nanomaterials and thin films.
Objectives:

The student should be familiar with the different methods that can be used to synthesize inorganic materials. They will be able to judge the relative strengths and weaknesses of the different methods for synthesis of new materials.

Aim of the laboratory part:
Use different types of synthesis equipment
Work with dangerous chemicals
Learn why things went seriously wrong
Work with different synthesis methods.

Wednesday 10:15 -12:00, Room V172
(Week 43 and 44: Wednesday 12:15 – 14:00)
Friday 10:15 -12:00, Room V172

Laboratory course, Ø161
Responsible: Reidar Haugsrud
According to schedule:
Monday 12:00 -17:00,
Tuesday 13:15 -18:00,
Wednesday 12:00 -17:00

Reidar will schedule the lab after talking to you.
Pensum for KJM5100, H2008:
Synthesis of Inorganic Materials
Second revised and updated edition
Ulrich Schubert and Nicola Hüsing
ISBN: 3527310371

Ch.2 Solid-state reactions
Ch.3 Formation of solids from the gas phase
Ch.4 Formation of solids from solutions and melts
Ch.6 Porous materials
Ch.7 Nanostructured materials

Topics

2 Solid-State Reactions
2.1 Reactions Between Solid Compounds
2.1.1 Ceramic Method
2.1.2 Carbothermal Reduction
2.1.3 Combustion Synthesis
2.1.4 Sintering
2.2 Solid–Gas Reactions
2.3 Decomposition and Dehydration Reactions
2.4 Intercalation Reactions
2.4.1 General Aspects
2.4.2 Preparative Methods
2.4.3 Pillaring of Layered Compounds
3 Formation of Solids from the Gas Phase

3.1 Chemical Vapor Transport

3.2 Chemical Vapor Deposition
3.2.1 General Aspects
3.2.2 Metal CVD
3.2.3 Diamond CVD
3.2.4 CVD of Metal Oxides
3.2.5 CVD of Metal Nitrides
3.2.6 CVD of Compound Semiconductors

3.3 Aerosol Processes

4 Formation of Solids from Solutions and Melts

4.1 Glass
4.1.1 The Structural Theory of Glass Formation
4.1.2 Crystallization versus Glass Formation
4.1.3 Glass Melting
4.1.4 Metallic Glasses

4.2 Precipitation

4.3 Biomaterials
4.3.1 Biogenic Materials and Biomineralization
4.3.2 Synthetic Biomaterials
4.3.3 Biomimetic Materials Chemistry

4.4 Solvothermal Processes
4.4.1 Hydrothermal Synthesis of Single Crystals
4.4.2 Hydrothermal Synthesis
4.4.3 Hydrothermal Leaching

4.5 Sol–Gel Processes
4.5.1 The Physics of Sols
4.5.2 Sol–Gel Processing of Silicate Materials
4.5.3 Sol–Gel Chemistry of Metal Oxides
4.5.4 Inorganic–Organic Hybrid Materials
Topics

6 Porous Materials
6.1 Introduction to Porosity
6.2 Metallic Foams and Porous Metals
   6.2.1 Casting Techniques
   6.2.2 Gas–Eutectic Transformation
   6.2.3 Powder Metallurgy
   6.2.4 Metal Deposition
6.3 Aerogels
   6.3.1 Drying Methods
   6.3.2 Properties and Applications
6.4 Porous Solids with an Ordered Porosity
   6.4.1 Microporous Crystalline Solids
   6.4.2 Mesoporous Solids with Ordered Porosity
   6.4.3 Macroporous Solids with Ordered Porosity
6.5 Incorporation of Functional Groups into Porous Materials

Topics

7 Nanostructured Materials
7.1 Nanoparticles and Nanocrystalline Materials
   7.1.1 Nanocrystalline Ceramics
   7.1.2 Semiconductor Nanoparticles
   7.1.3 Metal Nanoparticles
7.2 Nanotubes
7.3 Mono- and Multilayers
   7.3.1 Multilayers of Inorganic Materials
   7.3.2 Langmuir Monolayers
   7.3.3 Self-assembled Monolayers
Synthesis in the laboratory

Zone melting (ampoule)          InSb
Alloys                        AuAl₂
Sol-Gel ("citrate-method")    YBa₂Cu₃O₇
Flux                          YBa₂Cu₃O₇
Vapour phase transport        GeO₂
Thin film (ALCVD)             MnO₂
Precursor method              BaTiO₃
Synthesis of nano-materials   Fe₃O₄
(Hydrotermal syntese)         Co₃O₄

Inorganic materials synthesis

• Known or partially known recipe
• General chemistry, properties of the elements in the periodic table
• Structural chemistry
• Materials chemistry
• Thermodynamics (incl. phase diagrams)
• Kinetics
• “Extreme-synthesis” pressure, temperature, field, chemical environments etc.
Reactions

Main principle in classical inorganic synthesis: Reaction between materials/compounds in physical contact. Diffusion governs the reaction rate.

Reactions are:
Determined by the intermediate or final products
Diffusion controlled
Intermediate phases may hinder diffusion
The reaction rate is increased by increased temperature (or melting!)
Usually high temperature phases are obtained

By using indirect methods, other products may be obtained.

Types of reactions

(1) Decompose
A(s) → B(s) + C(g)
CaCO₃(s) → CaO(s) + CO₂(g)
MₙOₙ(s) → MₙOₙ₋δ(s) + δ/2O₂(g), (M = Metal)

(2) Combination
A(s) + B(g) → C(s)
2YBa₂Cu₃O₆(s) + O₂(g) → 2YBa₂Cu₃O₇(s)

(3) Metathesis (combination of (1) og (2))
A(s) + B(g) → C(s) + D(g)
Pr₃O₁₁(s) + 2H₂(g) → 3Pr₂O₃(s) + 2H₂O(g)
MnO₂(s) + CO(g) → MnO(s) + CO₂(g)
Al₂O₃(s) + 3C(s) + 3Cl₂(g) → 2AlCl₃(s) + 3CO(g)

(4) Addition
a) A(s) + B(s) → C(s)
ZnO(s) + Fe₂O₃(s) → ZnFe₂O₄(s)
b) A(s) + B(l) → C(s)
BaO(s) + TiO₂(s) → BaTiO₃(s)
c) A(s) + B(g) → C(s)
2NdCl₃(l) + Nd(s) → 3 NdCl₂(s)
3SiCl₄(g) + 4NH₃(g) → Si₃N₄(s) + 12 HCl(g)
A(l,s) + B(l,s) →(solvent)→ C(s)
GaMe₃(g) + 4NH₃(g) → GaAs(s) + CH₄(g)

(5) Exchange
AX(s) + BY(s) → AY(s) + BX(s)
ZnS(s) + CdO(s) → CdS(s) + ZnO(s)
AX(s) + BY(g) → AY(s) + BX(g)
MnCl₂(s) + 2HBr → MnBr₂(s) + 2HCl

(6) Gas phase transport and reactions
A(s) + X(g) ↔ AX(g) fulgt av
AX(g) + B(s) → C(s) + X(g)
MgO(s) + Cr₂O₃(s) →O₂ → MgCr₂O₄(s) via CrO₃(g)
Cr₂O₃(s) + 3/2O₂ → 2 CrO₃(g)
MgO(s) + 2CrO₃(g) → MgCr₂O₄(s) + 3/2O₂
Most reactions are combinations of several reaction types

**Examples:**

**Single step reaction:**

\[ 2\text{Ca}_{0.5}\text{Mn}_{0.5}\text{CO}_3(s) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CaMnO}_3(s) + 2\text{CO}_2(g) \]

**Transport reaction:**

\[ \text{MgO}(s) + \text{Cr}_2\text{O}_3(s) \rightarrow (\text{O}_2) \rightarrow \text{MgCr}_2\text{O}_4(s) \]

Other transport reactions:

\[ \text{ZnS}(s) + \text{I}_2 \leftrightarrow \text{ZnI}_2 + \frac{1}{2}\text{S}_2 \]
\[ \text{TaOCl}_2(s) + \text{TaCl}_5 \leftrightarrow \text{TaOCl}_3 + \text{TaCl}_4 \]
\[ \text{Nb}_2\text{O}_5(s) + 3\text{NbCl}_5 \leftrightarrow 5\text{NbOCl}_3 \]
\[ \text{GaAs}(s) + \text{HCl} \leftrightarrow \text{GaCl} + \frac{1}{2}\text{H}_2 + \text{As} \]

**Types of reactions**

**Reduction reactions:** \( \text{H}_2, \text{H}_2\text{-N}_2, \text{CO}, \text{CO-CO}_2 \) etc.

\[ \text{M}_2\text{O}_3(s) + \text{H}_2(g) \rightarrow 2\text{MO}(s) + \text{H}_2\text{O}(g) \quad \text{ (e.g. M = Fe)} \]
\[ \text{ABO}_3(s) + \text{H}_2(g) \rightarrow \text{ABO}_2.5(s) + \frac{1}{2}\text{H}_2\text{O}(g) \quad \text{ (e.g. LaCoO}_3 \text{)} \]
\[ \text{MCl}_3(s) + \text{H}_2(g) \rightarrow \text{MCl}_2(s) + \text{HCl}(g) \quad \text{ (e.g. M = Fe)} \]

Reduction also with metals, carbon etc

\[ \text{MX}_3 \rightarrow \text{heat} \rightarrow \text{MX}_2 + \frac{1}{2}\text{X}_2 \quad \text{ (e.g. M = Cr)} \]
\[ 2\text{MCl}_3 + \text{M} \rightarrow 3\text{MCl}_2 \quad \text{ (e.g. M = Nd, Fe)} \]
\[ 3\text{MCl}_4 + \text{M}'(s) \rightarrow 3\text{MCl}_3(s) + \text{M}'\text{Cl}_3(g) \quad \text{ (e.g. M = Hf, M' = Al)} \]
\[ \text{M}_2\text{O}_5 + 3\text{M} \rightarrow 5\text{MO} \quad \text{ (e.g. M = Nb)} \]
Characterization

**Qualitative/Quantitative**
Which phases are present? And in what amounts? (Main product, additional phases, contaminants)

**Quality**
What is the quality of the products? (Crystalline/amorphous…)
(Compared with the desired state)

**Crystallinity**

**Methods**
Sensitivity, reliability, reproducibility
Which kind of information is obtained?
General methods – Specific methods.

Diffraction (X-ray, neutron, electrons)(Powder, single crystal)
Spectroscopy (MAS-NMR, IR, Raman, UV/VIS, ESR/EPR…)
Thermal analysis (TG, TGA/DSC…)
Chemical analysis, XRF …
Magnetic, electrical/electronic properties
SEM, TEM, AFM, STM ….

Decisions, decisions

• Reaction type
• Starting materials
• Reaction path (direct/indirect)
• Reaction conditions (temperature, pressure, solvent, Static/dynamic conditions, gradients, reaction time, variation of conditions, closed vs. open system)
• Storage conditions
• Characterization
• Purification (if possible)
• Container (for reaction)

Knowledge of inorganic chemistry combined with practical experience in synthesis is important for a successful result.

Materials synthesis is an art and a craft, and needs experience, practice and a lot of "fingerspitzengefühl"

Do not always trust the recipes to give you the correct product. There are lots of essential tricks which are not mentioned.
Equipment

- Crushing and grinding (mortar, planetary mill, ball mill...)
- Furnaces (Laboratory oven, tube furnace, muffle furnace, induction furnace, special heating equipment)
- Containers (crucibles) (glass, quartz glass, alumina, glassy carbon, nickel, platinum, iridium...)
- Gass equipment (Burners, regulators, reduction valves)
- Vacuum equipment (pumps, vacuum line)
- Inert atmosphere (glove box, glove bag, vacuum line)
- Reactive gasses (Cl₂, NH₃, O₂, O₃...)
- High pressure (press, autoclave)

Stable or metastable

Inorganic syntheses are often performed at high temperature, and often the thermodynamic stable phase is produced.

When the synthesis is performed at mild conditions or indirect methods, it is possible to prepare metastable compounds, or phases stable at lower temperatures.
The desired product

Not only the composition and phase is important in materials synthesis. Often a specific shape, state, size and morphology of the end product is desired, and this will influence or determine the synthesis route.

- Amorphous
- Nano/microcrystalline
- Porous
- Crystal shape/morphology
- Powder
- Polycrystalline pellet (dense, porous?)
- Single crystal
- Thin film
- Thick film
- Self supporting sheets (membranes)
- Sponge-like materials with open or closed pore architecture

Reactions

Reaction occurs at $\text{AB}_2\text{O}_4$--$\text{B}_2\text{O}_3$ interface: oxygen gas phase transport with $A^{2+}$ ion and electron transport through $\text{AB}_2\text{O}_4$:

$$A^{2+} + 2e^- + \frac{1}{2}O_2 + B_2O_3 = \text{AB}_2\text{O}_4$$

Reaction occurs at $\text{AO}$--$\text{AB}_2\text{O}_4$ interface: oxygen gas phase transport with $B^{3+}$ ion and electron transport through $\text{AB}_2\text{O}_4$:

$$\text{AO} + 2B^{3+} + 6e^- + \frac{3}{2}O_2 = \text{AB}_2\text{O}_4$$
Oxygen and cation transport through AB$_2$O$_4$:

(1) Both cations diffuse ($J_{A^{2+}} = \frac{2}{3} J_{A^{3+}}$).

Reactions occur at:
- AO–AB$_2$O$_4$ interface
  \[ 2B^{3+} + 4AO = AB_2O_4 + 3A^{2+} \]
- and at
  \[ 3A^{2+} + 4B_2O_3 = 3AB_2O_4 + 2B^{3+} \]

(2) A$^{2+}$ and O$^{2-}$ diffuse.

Reaction at:
- AB$_2$O$_4$–B$_2$O$_3$ interface
  \[ A^{2+} + O^{2-} + B_2O_3 = AB_2O_4 \]

(3) B$^{3+}$ and O$^{2-}$ diffuse.

Reaction at:
- AO–AB$_2$O$_4$ interface
  \[ AO + 2B^{3+} + 3O^{2-} = AB_2O_4 \]

Fig. 9.6. Schematic representation of several mechanisms which may control the rate of AB$_2$O$_4$ (e.g., spinel) formation. From Ref. 1.

---

**Mobility**

![Diagram of atomic diffusion mechanisms](image)

Fig. 6.1. Atomic diffusion mechanisms. (a) Exchange; (b) ring rotation; (c) interstitial; (d) vacancy.

Fig. 6.2. Diffusion processes to form a new compound AB or a random solid solution from pure starting materials A and B.
Reactivity

Ceramics by solid state reactions
"Shake’n bake"

Solid state reaction; Solid materials react to form new solid phases.

The method in short:
- Crush and mix the starting materials
- Press in order to achieve large contact area
- Heat the mixture so that the species diffuse and react to the desired product, and sintering occur.
- If necessary, post treatment in controlled atmosphere

A quite universal method for producing thermodynamically stable compounds.
How high is high?

Precursor methods

Uses materials/compounds which may be changed into the desired product, e.g.:

- Carbonate precursors
- Alkoxide precursors

LaCo(CN)$_6$•5H$_2$O $\rightarrow$ LaCoO$_3$

LaFe(CN)$_6$•5H$_2$O $\rightarrow$ LaFeO$_3$

Ba[TiO(C$_2$O$_4$)$_2$] $\rightarrow$ BaTiO$_3$

Li[Cr(C$_2$O$_4$)$_2$(H$_2$O)$_2$] $\rightarrow$ LiCrO$_2$
Carbonate precursors

Fig. 1. Plot of the rhombohedral lattice parameters $a_R$ of a variety of binary and ternary carbonates of calcite structure (e.g. Ca–M, Ca–M–M, Mg–M, M–M where M,M = Mn, Fe, Co, Cd, etc.) against the mean cation radius.

Figure 2. Solid solution precursor techniques give fast reaction kinetics.
**Sol-Gel method**

Starting solution of the species to ensure homogeneous mixing at an atomic level. Often a sol is produced (i.e. the species are not dissolved)

The sol is gelified

The gel is dried and heated/calcined, so that all surplus species are removed (in a gaseous state)

Pressed, heated and sintered as in the ceram method

Advantages:

Efficient mixing of the elements

Low temperature neede for final reaction

**Intercalation methods**

Fig. 8. Schematic diagram of staging in intercalation compounds. Guest molecules are represented by circles in between the layers (shown by lines).
Topochemical and topotactical methods

![Monolayer and bilayer structures]

Fig. 6. Schematic representation of MoO$_3$H$_2$O (or WO$_3$H$_2$O), ReO$_3$-like MoO$_3$, and the layered structure of MoO$_3$.

Chemical transport methods

![Chemical transport in a cylindrical tube]

Fig. 1. Chemical transport in a cylindrical tube. Transport is from temperature $T_2$ to $T_1$.

ZnS(s) + I$_2$(g) = ZnI$_2$(g) + $\frac{1}{2}$S$_2$(g)
Thin films (CVD)

Figure 3-5. Schematic representation of the steps in CVD process

Figure 3-6. Schematic of a thermal CVD reactor for copper CVD from a Cu(II) precursor (see Eq. 3-19) (MFC = mass flow controller).

Electrochemical methods

Figure 3. Molten salt electrolysis system (7)
Hydrothermal methods

Fig. 9

Zeolites

Fig. 51. The orientation of TPA in the channels of ZSM-5 (as synthesized)
High pressure

Fig. 25. The “belt,” a high-temperature, high-pressure apparatus; “exploded” assembly. After Hall (1960).

Crystal growth
Czochralski

Figure 3.11. Diagram of the basic elements of a crystal puller.

Figure 3.12. Pulled germanium single crystals grown with automatic programming to produce a uniform diameter over the first half of the crystals. The flat sides are approximately (110) planes. Scale in inches and centimeters.
Fig. 7.3. Contents of crucibles after removal of flux (actual size)
(a) $\text{Ca}_4\text{O}_7$ ex $\text{Pb}_2\text{V}_2\text{O}_{9}$. (b) $\text{Ca}_4\text{O}_7$ ex $\text{Bi}_2\text{O}_3\text{V}_2\text{O}_7$. (c) $\text{Fe}_2\text{TiO}_5$.

Fig. 7.4. Hot draining of flux.

Fig. 7.2. (a) Cross-section of end of brick, showing two embedded crucibles. (b) Flux separation by crucible inversion.