

KJM5100

Uorganisk materialsyntese

Synthesis of Inorganic Materials

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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.

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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 Haugrud

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.

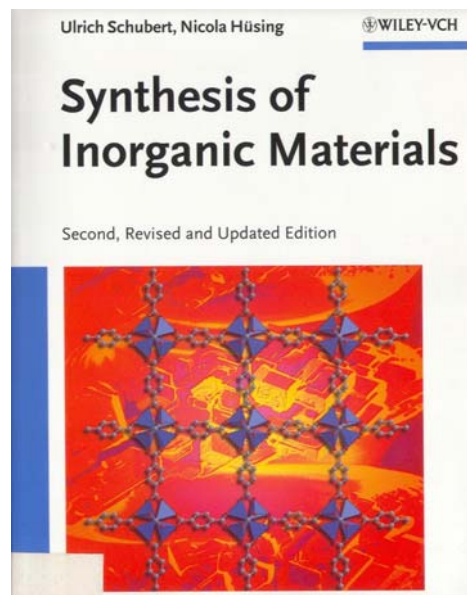
Pensum for KJM5100, H2008:

Synthesis of Inorganic Materials

Second revised and updated edition

Ulrich Schubert and Nicola Hüsing

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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

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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

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Topics

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

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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

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Topics

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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

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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

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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
(Hydrothermal 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.

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Types of reactions

- | | |
|---|--|
| <p>(1) Decompose
 $A(s) \rightarrow B(s) + C(g)$</p> | <p>$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
 $M_m O_n(s) \rightarrow M_m O_{n-\delta}(s) + \delta/2 O_2(g)$, (M = Metal)</p> |
| <p>(2) Combination
 $A(s) + B(g) \rightarrow C(s)$</p> | <p>$2YBa_2Cu_3O_6(s) + O_2(g) \rightarrow 2YBa_2Cu_3O_7(s)$</p> |
| <p>(3) Metathesis (combination of (1) og (2))
 $A(s) + B(g) \rightarrow C(s) + D(g)$</p> | <p>$Pr_6O_{11}(s) + 2H_2(g) \rightarrow 3Pr_2O_3(s) + 2H_2O(g)$
 $MnO_2(s) + CO(g) \rightarrow MnO(s) + CO_2(g)$
 $Al_2O_3(s) + 3C(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s) + 3CO(g)$</p> |
| <p>(4) Addition
 a) $A(s) + B(s) \rightarrow C(s)$
 b) $A(s) + B(l) \rightarrow C(s)$
 c) $A(s) + B(g) \rightarrow C(s)$

 $A(l,s) + B(l,s) \xrightarrow{\text{solvent}} C(s)$</p> | <p>$ZnO(s) + Fe_2O_3(s) \rightarrow ZnFe_2O_4(s)$
 $BaO(s) + TiO_2(s) \rightarrow BaTiO_3(s)$
 $2NdCl_3(l) + Nd(s) \rightarrow 3 NdCl_2(s)$
 $3SiCl_4(g) + 4NH_3(g) \rightarrow Si_3N_4(s) + 12 HCl(g)$
 $GaMe_3(g) + 4NH_3(g) \rightarrow GaAs(s) + CH_4(g)$</p> |
| <p>(5) Exchange
 $AX(s) + BY(s) \rightarrow AY(s) + BX(s)$
 $AX(s) + BY(g) \rightarrow AY(s) + BX(g)$</p> | <p>$ZnS(s) + CdO(s) \rightarrow CdS(s) + ZnO(s)$
 $MnCl_2(s) + 2HBr \rightarrow MnBr_2(s) + 2HCl$</p> |
| <p>(6) Gas phase transport and reactions
 $A(s) + X(g) \leftrightarrow AX(g)$ fulgt av
 $AX(g) + B(s) \rightarrow C(s) + X(g)$</p> | <p>$MgO(s) + Cr_2O_3(s) \xrightarrow{O_2} MgCr_2O_4(s)$ via $CrO_3(g)$
 $Cr_2O_3(s) + 3/2O_2 \rightarrow 2 CrO_3(g)$
 $MgO(s) + 2CrO_3(g) \rightarrow MgCr_2O_4(s) + 3/2O_2$</p> |

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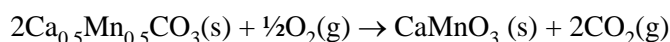
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Types of reactions

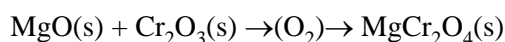
Most reactions are combinations of several reaction types

Examples:

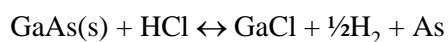
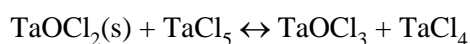
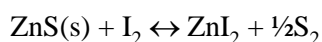
Single step reaction:



Transport reaction:

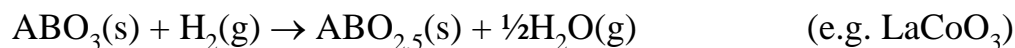
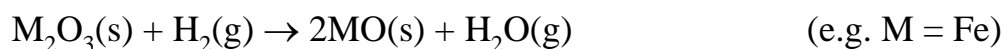


Other transport reactions:

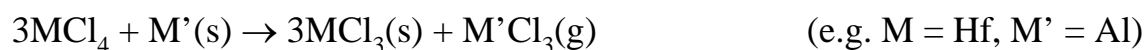


Types of reactions

Reduction reactions: H_2 , $\text{H}_2\text{-N}_2$, CO , CO-CO_2 etc.



Reduction also with metals, carbon etc



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

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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.

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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 (Cl_2 , NH_3 , O_2 , O_3 ...)
- High pressure (press, autoclave)

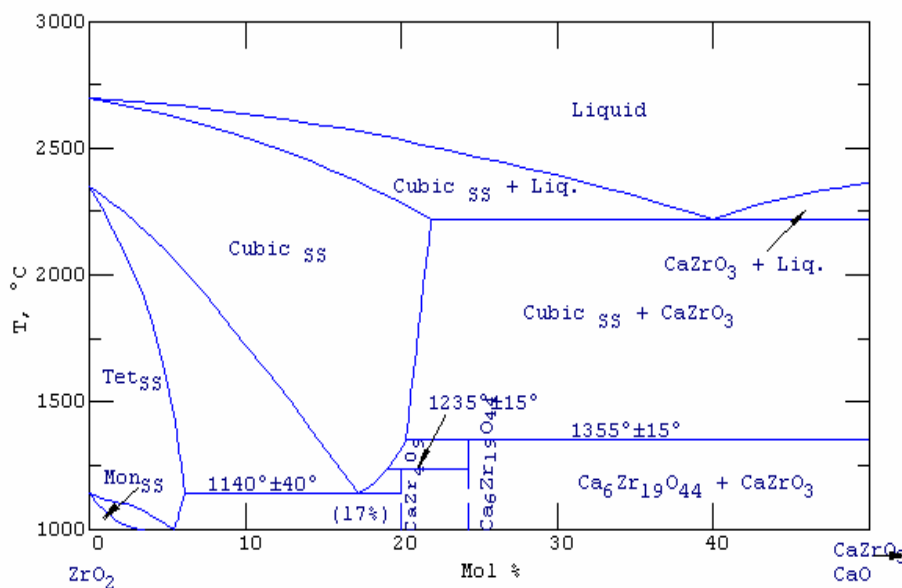
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Stable or metastable

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.



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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

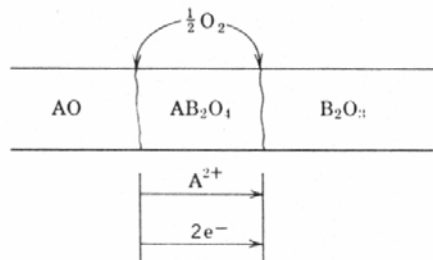
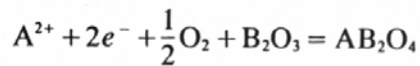
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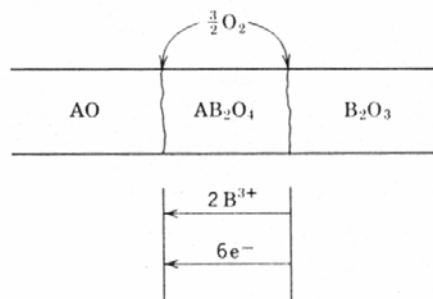
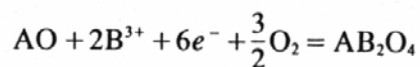
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Reactions

Reaction occurs at AB_2O_4 - B_2O_3 interface:
oxygen gas phase transport with A^{2+} ion and
electron transport through AB_2O_4 :



Reaction occurs at AO - AB_2O_4 interface:
oxygen gas phase transport with B^{3+} ion and
electron transport through AB_2O_4 :



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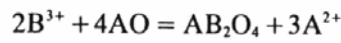
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Oxygen and cation transport through AB_2O_4 :

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

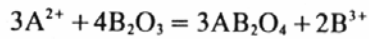
Reactions occur at

AO- AB_2O_4 interface



and at

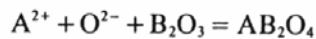
AB_2O_4 - B_2O_3 interface



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

Reaction at

AB_2O_4 - B_2O_3 interface



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

Reaction at

AO- AB_2O_4 interface

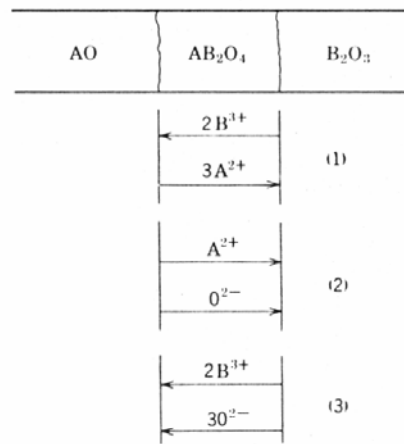
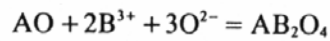


Fig. 9.6. Schematic representation of several mechanisms which may control the rate of AB_2O_4 (e.g., spinel) formation. From Ref. 1.

Mobility

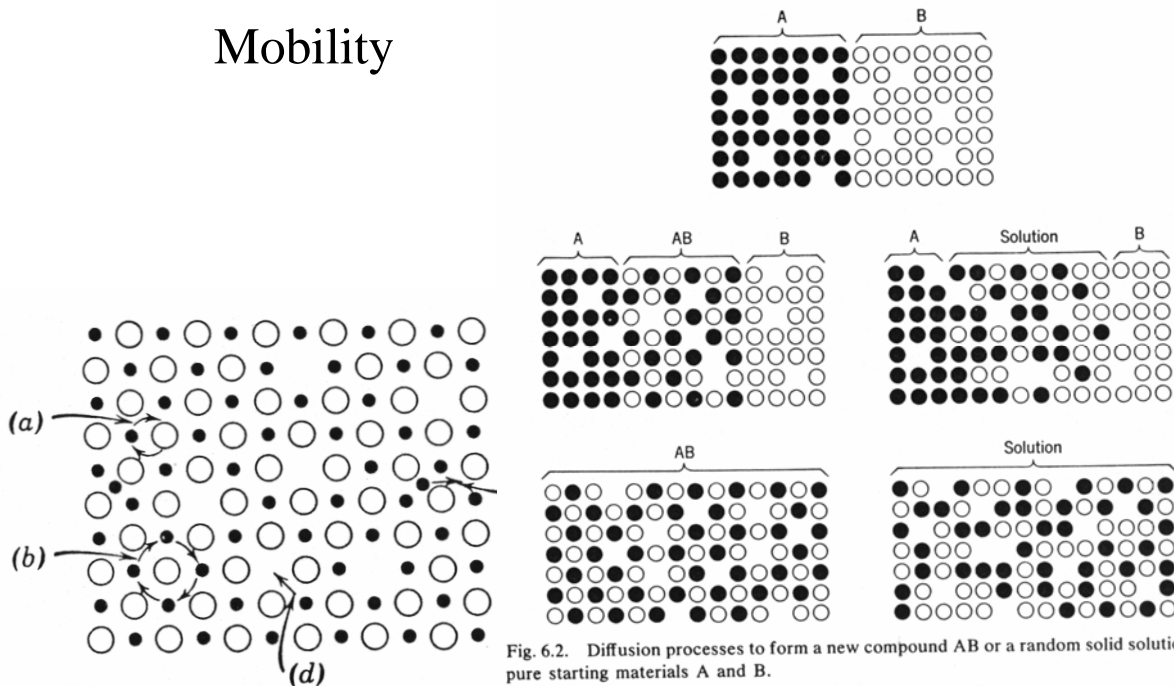


Fig. 6.2. Diffusion processes to form a new compound AB or a random solid solution from pure starting materials A and B.

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

Reactivity

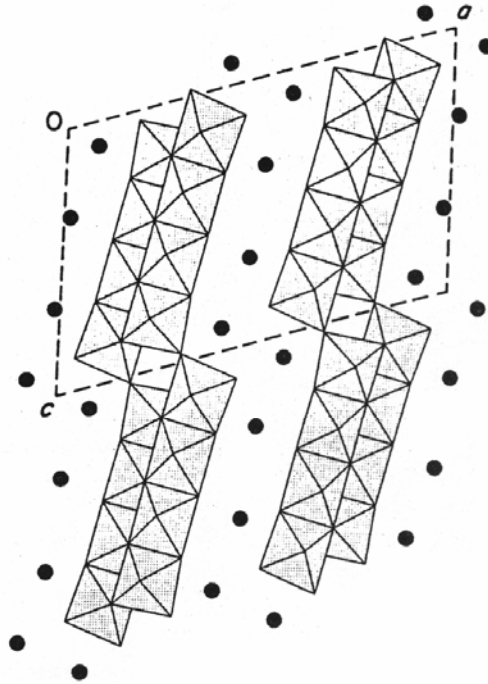


Figure 3. Projection of the crystal structure of $K_2Ti_4O_9$ along the $[010]$ direction. The Ti-O substructure is represented with shaded octahedra, and the K atoms are given as black circles. The K atoms lie in $y/b = 0$ (center) and in $y/b = 1/2$ (left and right). The edges of the unit cell are emphasized with broken lines.

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Ceramics by solid state reactions "Shake'n bake"

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

The method in short:

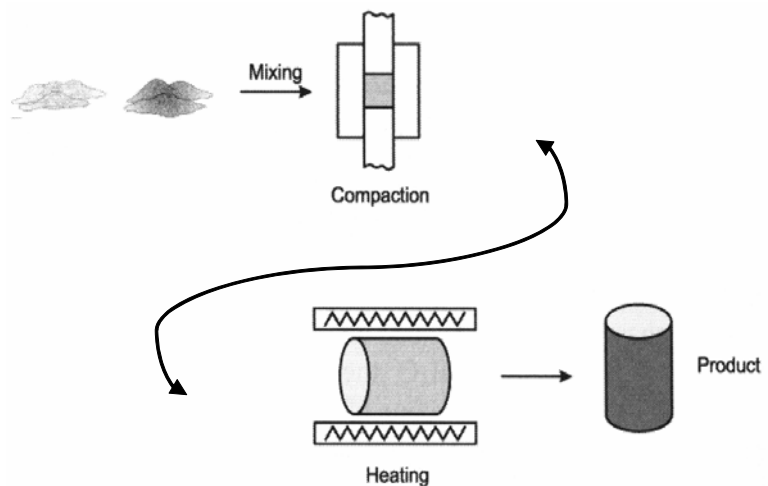
-Crush and mix the starting materials

-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.



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How high is high?



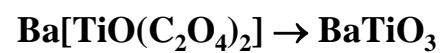
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Precursor methods

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

- Carbonate precursors
- Alkoxide precursors



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Carbonate precursors

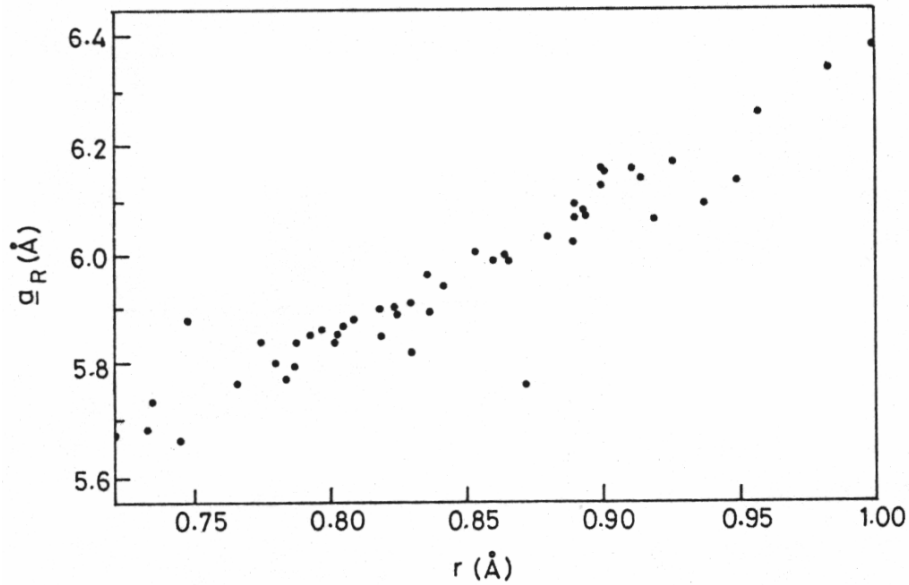


Fig. 1. Plot of the rhombohedral lattice parameters a_R of a variety of binary and ternary carbonates of calcite structure (e.g. Ca-M, Ca-M-M, Mg-M, M-M where M,M \equiv Mn, Fe, Co, Cd, etc.) against the mean cation radius.

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Carbonate precursors

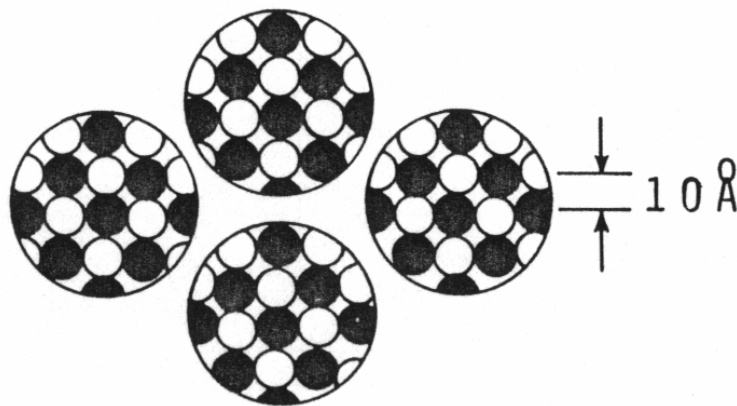


Figure 2. Solid solution precursor techniques give fast reaction kinetics

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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 need for final reaction

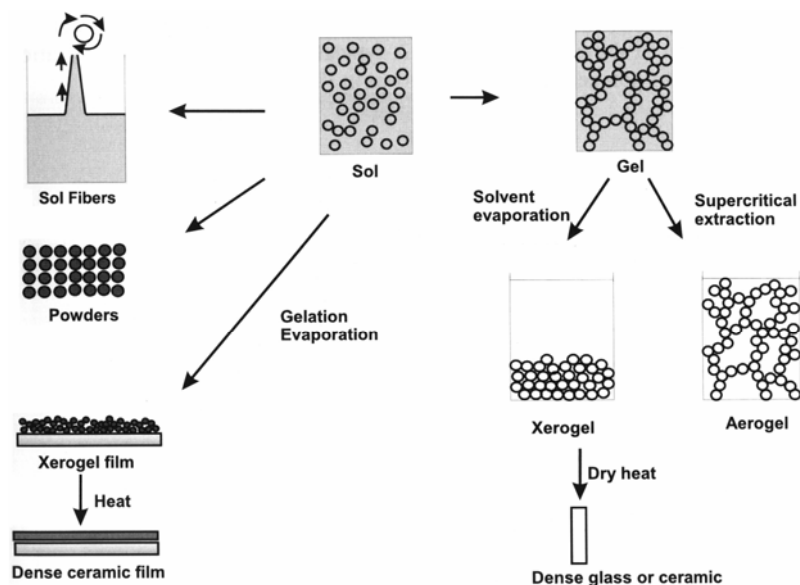


Figure 4-42. Sol-gel processing options.

Intercalation methods

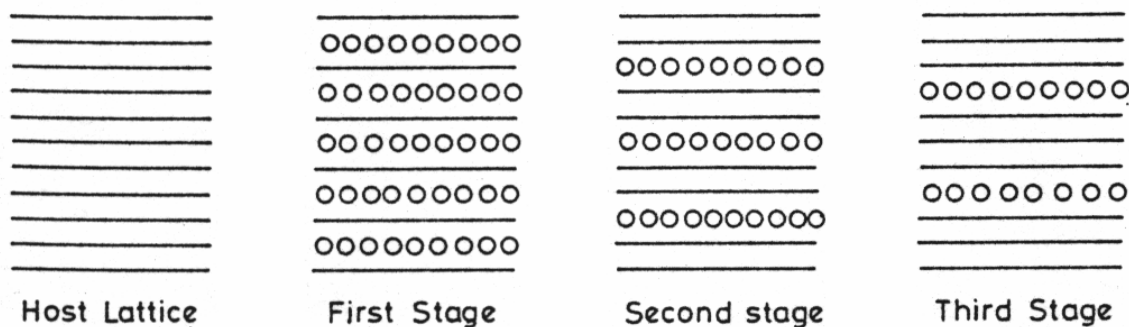


Fig. 8. Schematic diagram of staging in intercalation compounds. Guest molecules are represented by circles in between the layers (shown by lines).

Topochemical and topotactical methods

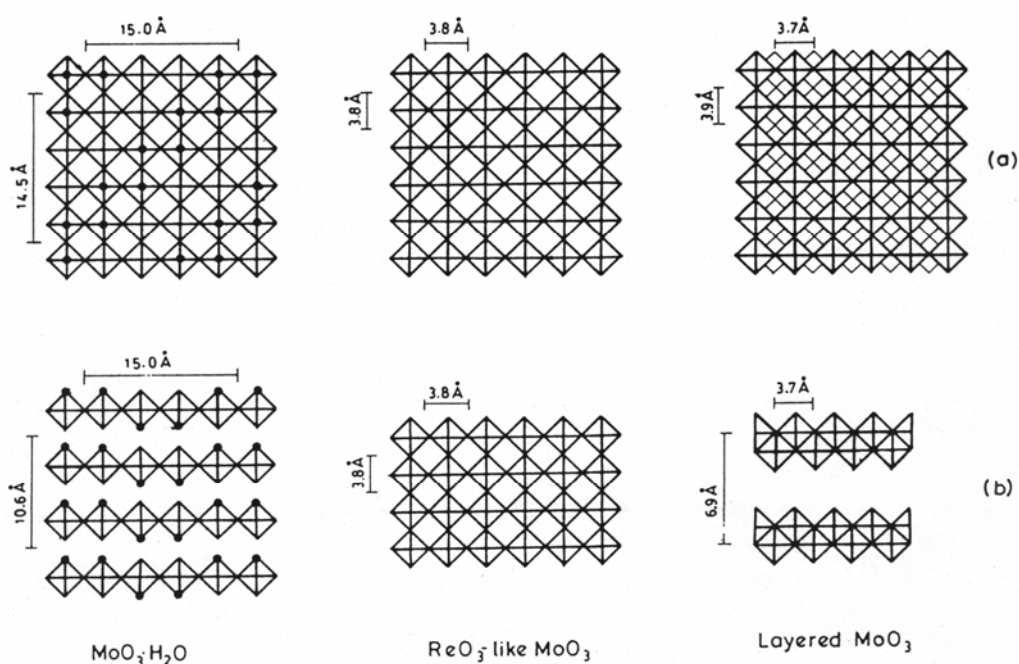


Fig. 6. Schematic representation of MoO₃·H₂O (or WO₃·H₂O), ReO₃-like MoO₃ (or WO₃) and the layered structure of MoO₃.

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Chemical transport methods

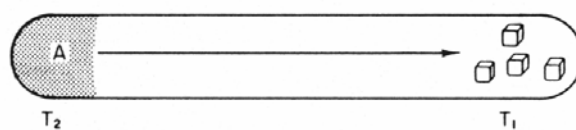
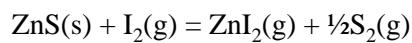
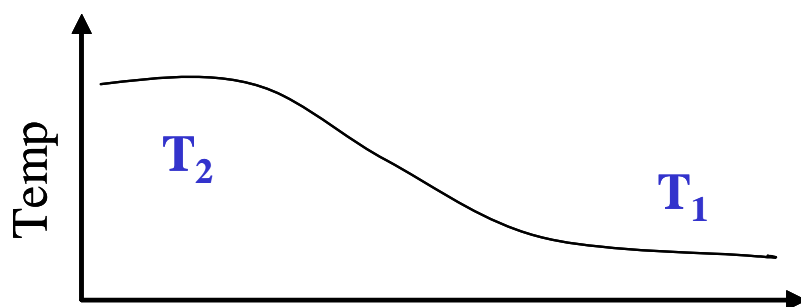


FIG. 1. Chemical transport in a cylindrical tube. Transport is from temperature T_2 to T_1 .



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Thin films (CVD)

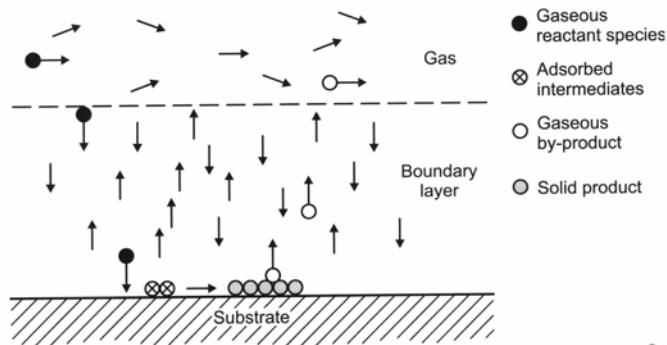


Figure 3-5. Schematic representation of the steps in CVD process:

- Gaseous reactant species
- ⊗ Adsorbed intermediates
- Gaseous by-product
- Solid product

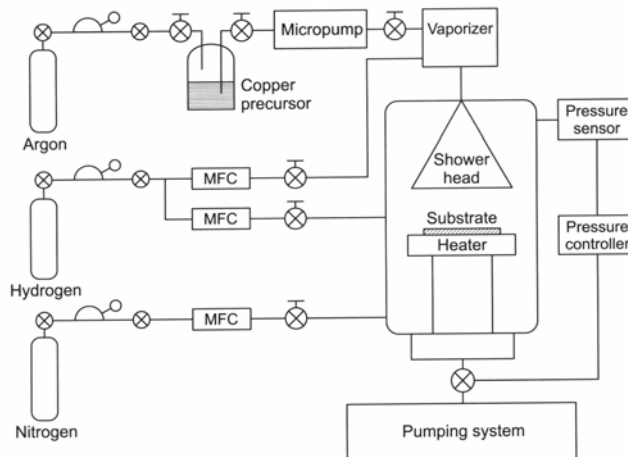


Figure 3-6. Schematic of a thermal CVD reactor for copper CVD from a Cu(II) precursor (see Eq. 3-19) (MFC = mass flow controller).

Electrochemical methods

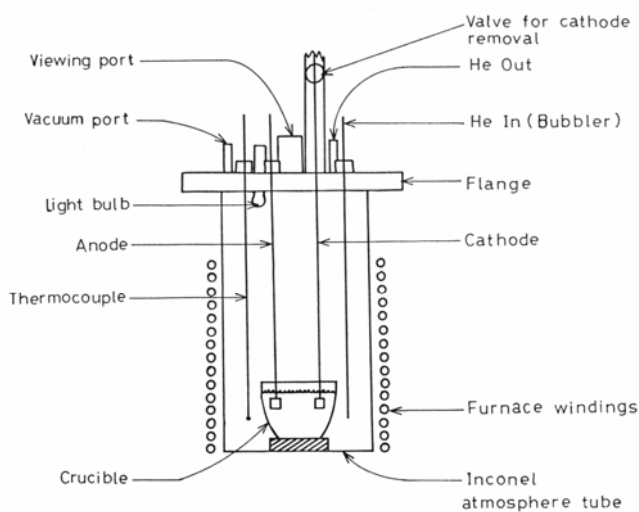
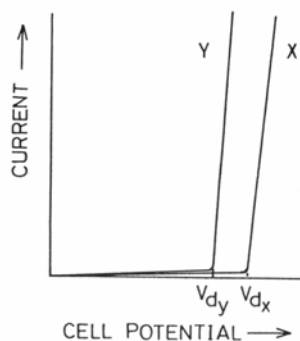


Figure 3. Molten salt electrolysis system (7)



Idealized current vs. voltage curves for deposition of two species

Hydrothermal methods

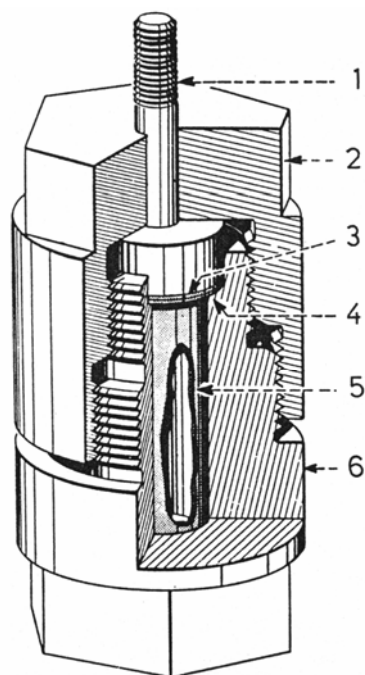


FIG. 9

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Zeolites

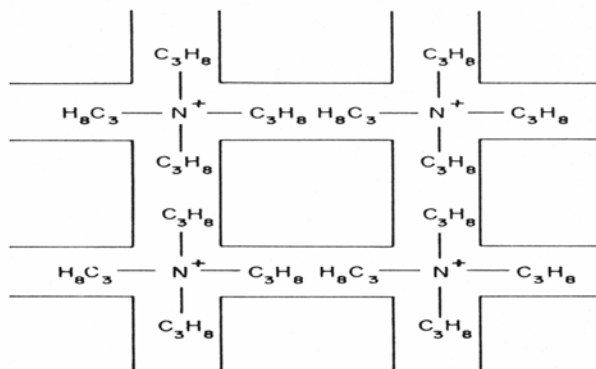
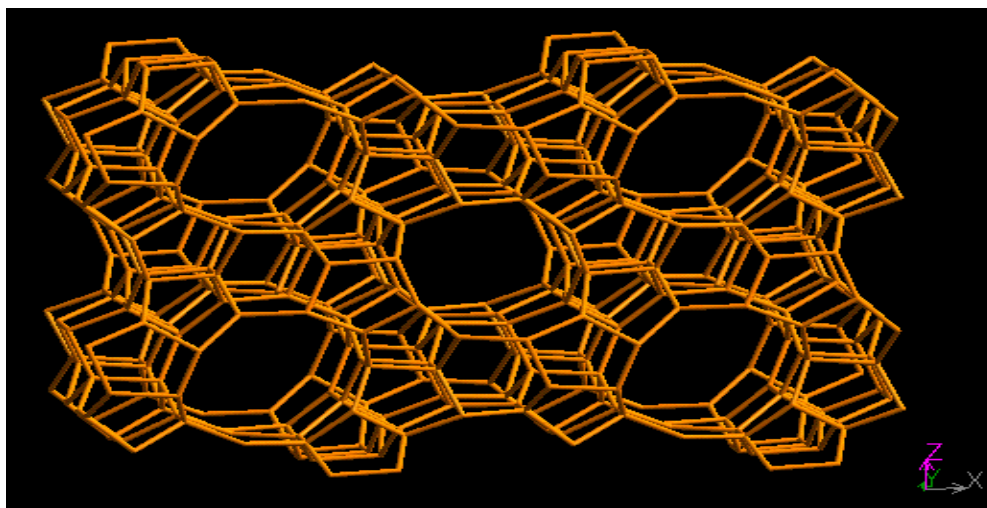


Fig. 51. The orientation of TPA in the channels of ZSM-5 (as synthesized)



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High pressure

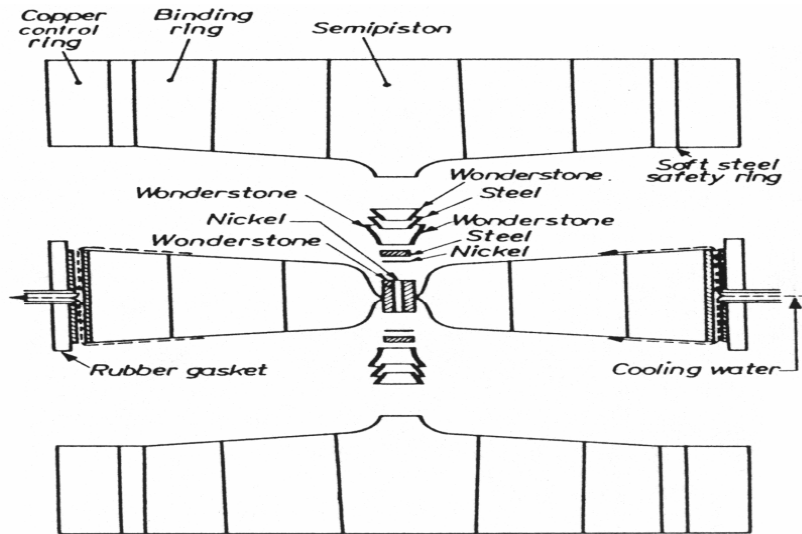


FIG. 25. The "belt," a high-temperature, high-pressure apparatus; "exploded" assembly. After Hall (1960).

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Crystal growth Czochralski

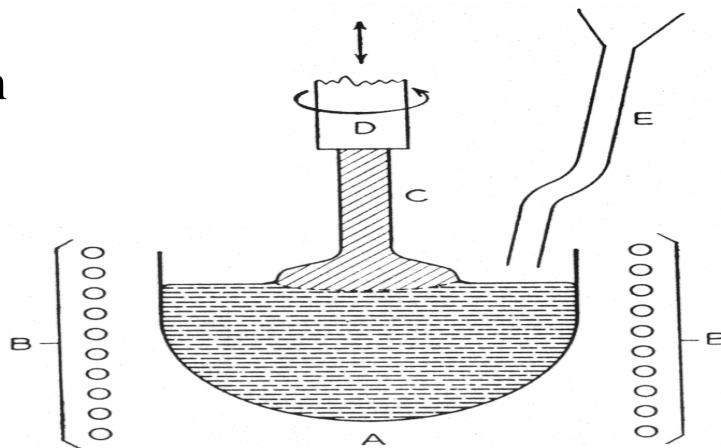


Figure 3.11. Diagram of the basic elements of a crystal puller.

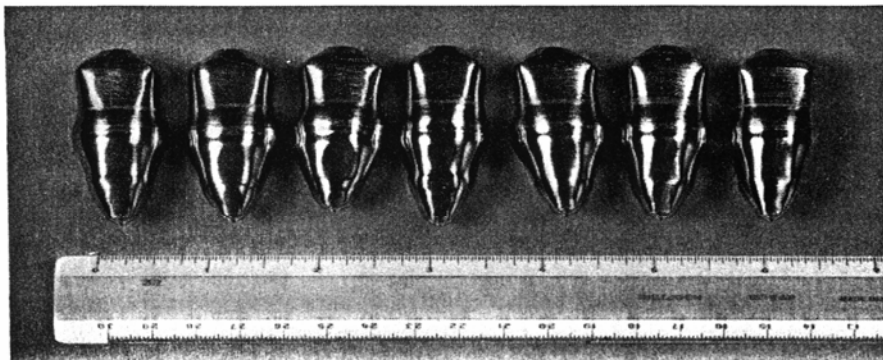
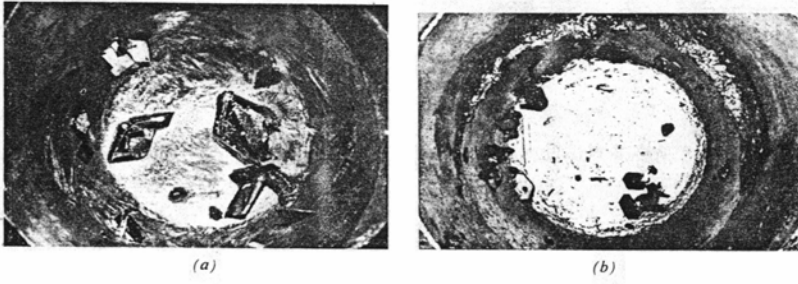


Figure 3.12. Pulled germanium single crystals grown with automatic programming to produce a uniform diameter over the first half of the crystals. The flat sides) are approximately (110) planes. Scale in inches and centimeters.

Flux



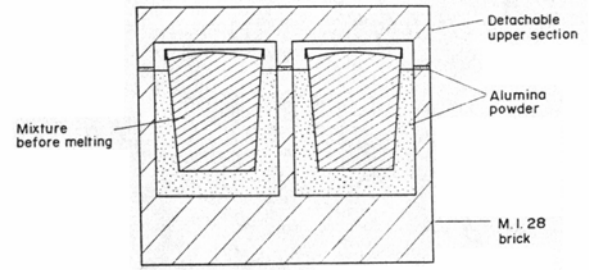
(a)

(b)

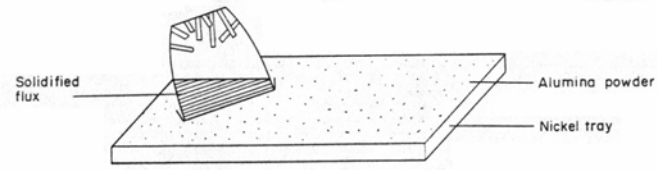


(c)

FIG. 7.3. Contents of crucibles after removal of flux (actual si
(a) $\alpha\text{Fe}_2\text{O}_3$ ex $\text{Pb}_2\text{V}_2\text{O}_7$. (b) Cr_2O_3 ex $\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$. (c) Fe_2TiO_4
 $\text{Pb}_2\text{V}_2\text{O}_7$.



(a)



(b)

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

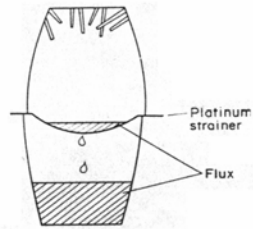


FIG. 7.4. Hot draining of flux.