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.

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.

Onsdag kl. 10:15 -12:00, Rom V 114

Fredag kl. 12:30 -14:15, Rom V 114

Laboratoriekurs:

Mandag kl. 12:00 -17:00,

Tirsdag kl. 13:15 -18:00,

Onsdag kl. 12:00 -17:00,

Laboratorium ØK24

Pensum for KJM5100, H2006:

Synthesis of Inorganic Materials

Second revised and updated edition

Ulrich Schubert and Nicola Hüsing

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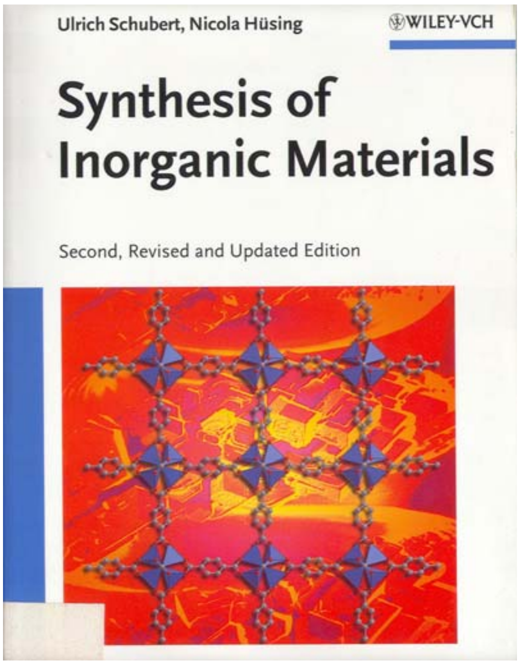


Ulrich Schubert, Nicola Hüsing

WILEY-VCH

Synthesis of Inorganic Materials

Second, Revised and Updated Edition

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

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

Topics

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

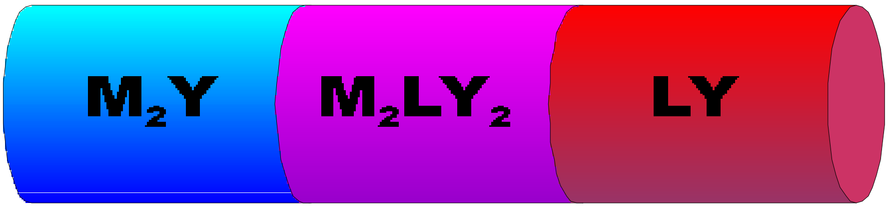
Sol-Gel (”citrate-method”)	**Li_xCoO_2**
Ceramic	**Li_xCoO_2**
Flux	**$YBa_2Cu_3O_7$**
Vapour phase transport	**GeO_2**
Zone melting (ampoule)	**InSb**
Alloys	**$AuAl_2$**
Thin film (ALCVD)	**MnO_2**
Precursormethod	**$BaTiO_3$**
Syntesis of nano-materials	**Fe_3O_4**
Hydrotermal syntese	**Co_3O_4**

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



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**

$A(s) \rightarrow B(s) + C(g)$

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

$M_mO_n(s) \rightarrow M_mO_{n-\delta}(s) + \delta/2O_2(g)$

M = Metal

(2) **Combination**

$A(s) + B(g) \rightarrow C(s)$

$2YBa_2Cu_3O_6(s) + O_2(g) \rightarrow$ 2YBa2Cu3O7(s)

(3) **Metathesis** (combination of (1) og (2))

$A(s) + B(g) \rightarrow C(s) + D(g)$

$Pr_6O_{11}(s) + 2H_2(g) \rightarrow 3Pr_2O_3(s) + 2H_2O(g)$

$MnO_2(s) + CO(g) \rightarrow MnO(s) + CO_2(g)$

$Al_2O_3(s) + 3C(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s) + 3CO(g)$

(4) **Addition**

a) $A(s) + B(s) \rightarrow C(s)$ — $ZnO(s) + Fe_2O_3(s) \rightarrow ZnFe_2O_4(s)$

b) $A(s) + B(l) \rightarrow C(s)$ — $BaO(s) + TiO_2(s) \rightarrow BaTiO_3(s)$

c) $A(s) + B(g) \rightarrow C(s)$ — $2NdCl_3(l) + Nd(s) \rightarrow 3\ NdCl_2(s)$

$3SiCl_4(g) + 4NH_3(g) \rightarrow Si_3N_4(s) + 12\ HCl(g)$

$A(l,s) + B(l,s) \rightarrow(\text{solvent})\rightarrow C(s)$ — $GaMe_3(g) + 4NH_3(g) \rightarrow GaAs(s) + CH_4(g)$

(5) **Exchange**

$AX(s) + BY(s) \rightarrow AY(s) + BX(s)$ — $ZnS(s) + CdO(s) \rightarrow CdS(s) + ZnO(s)$

$AX(s) + BY(g) \rightarrow AY(s) + BX(g)$ — $MnCl_2(s) + 2HBr \rightarrow MnBr_2(s) + 2HCl$

(6) **Gas phase transport and reactions**

$A(s) + X(g) \leftrightarrow AX(g)$ fulgt av — $MgO(s) + Cr_2O_3(s) \rightarrow O_2 \rightarrow MgCr_2O_4(s)$ via $CrO_3(g)$

$AX(g) + B(s) \rightarrow C(s) + X(g)$ — $Cr_2O_3(s) + 3/2O_2 \rightarrow 2\ CrO_3(g)$

$MgO(s) + 2CrO_3(g) \rightarrow MgCr_2O_4(s) + 3/2O_2$

Types of reactions

Most reactions are combinations of several reaction types

Examples:

Single step reaction:

$2Ca_{0.5}Mn_{0.5}CO_3(s) + ½O_2(g) \rightarrow CaMnO_3\ (s) + 2CO_2(g)$

Transport reaction:

$MgO(s) + Cr_2O_3(s) \rightarrow(O_2)\rightarrow MgCr_2O_4(s)$

Other transport reaktions:

$ZnS(s) + I_2 \leftrightarrow ZnI_2 + ½S_2$

$TaOCl_2(s) + TaCl_5 \leftrightarrow TaOCl_3 + TaCl_4$

$Nb_2O_5(s) + 3NbCl_5 \leftrightarrow 5NbOCl_3$

$GaAs(s) + HCl \leftrightarrow GaCl + ½H_2 + As$

Types of reactions

Reduction reactions: H_2, H_2-N_2, CO, CO-CO_2 etc.

$M_2O_3(s) + H_2(g) \rightarrow 2MO(s) + H_2O(g)$	(e.g. M = Fe)
$ABO_3(s) + H_2(g) \rightarrow ABO_{2.5}(s) + ½H_2O(g)$	(e.g. $LaCoO_3$)
$MCl_3(s) + H_2(g) \rightarrow MCl_2(s) + HCl(g)$	(e.g. M = Fe)

Reduction also with metals, carbon etc

$MX_3 \rightarrow heat \rightarrow MX_2 + ½X_2$	(e.g. M = Cr)
$2MCl_3 + M \rightarrow 3MCl_2$	(e.g. M = Nd,Fe)
$3MCl_4 + M'(s) \rightarrow 3MCl_3(s) + M'Cl_3(g)$	(e.g. M = Hf, M’ = Al)
$M_2O_5 + 3M \rightarrow 5MO$	(e.g. M = Nb)

Characterization

Qualitalive/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)
Qrystallinity

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 recipies 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)

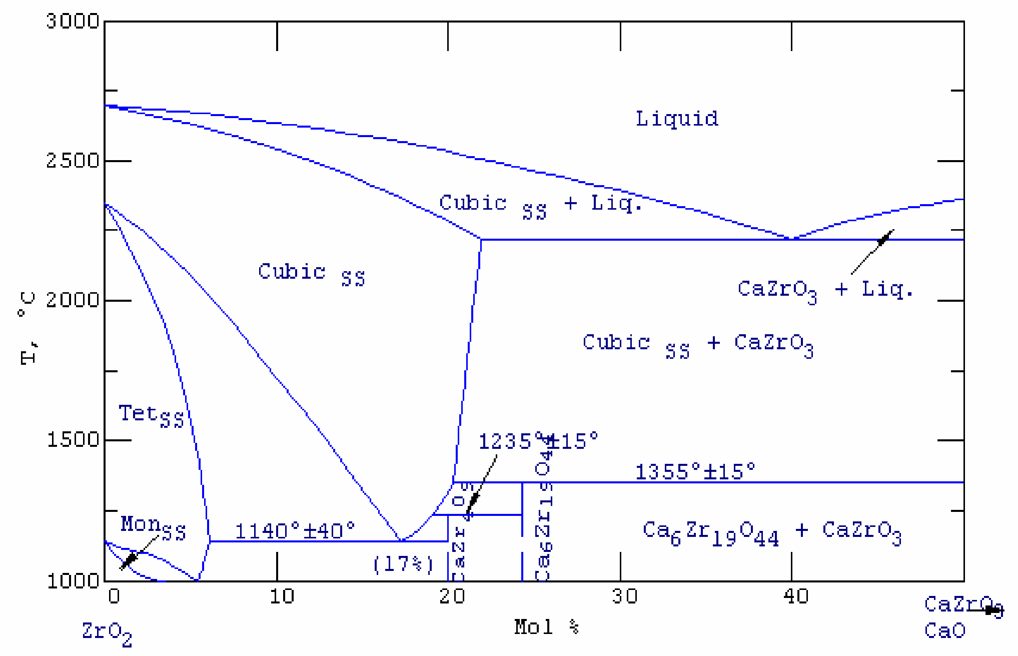
- Reactive gasses (Cl_2, NH_3, O_2, O_3...)

- 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.



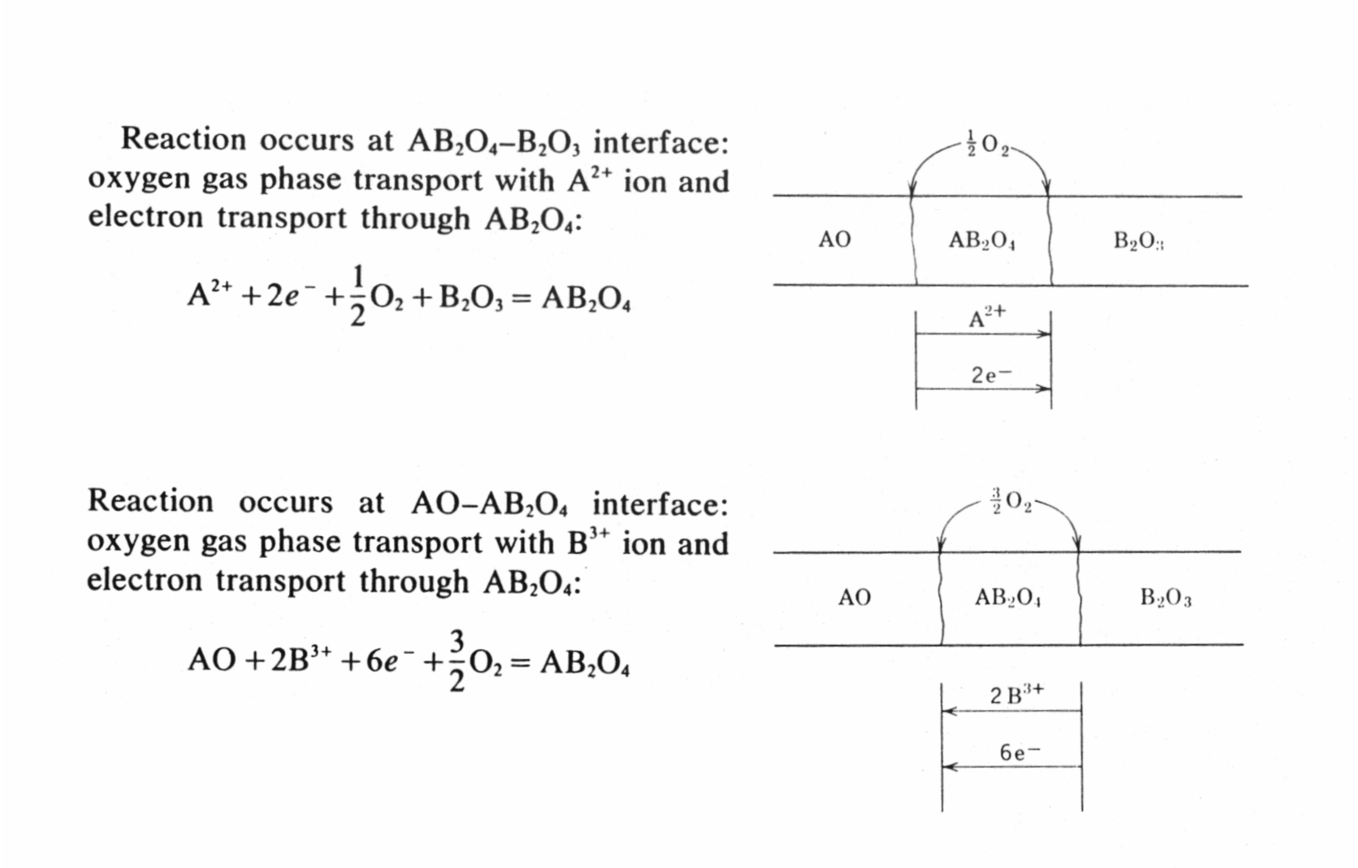
The desired product

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 AB_2O_4–B_2O_3 interface: oxygen gas phase transport with A^{2+} ion and electron transport through AB_2O_4:

$$A^{2+} + 2e^- + \frac{1}{2}O_2 + B_2O_3 = AB_2O_4$$

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

$$AO + 2B^{3+} + 6e^- + \frac{3}{2}O_2 = AB_2O_4$$

Oxygen and cation transport through AB_2O_4:

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

Reactions occur at

AO–AB_2O_4 interface

$$2B^{3+} + 4AO = AB_2O_4 + 3A^{2+}$$

and at

AB_2O_4–B_2O_3 interface

$$3A^{2+} + 4B_2O_3 = 3AB_2O_4 + 2B^{3+}$$

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

AB_2O_4–B_2O_3 interface

$$A^{2+} + O^{2-} + B_2O_3 = AB_2O_4$$

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

AO–AB_2O_4 interface

$$AO + 2B^{3+} + 3O^{2-} = AB_2O_4$$

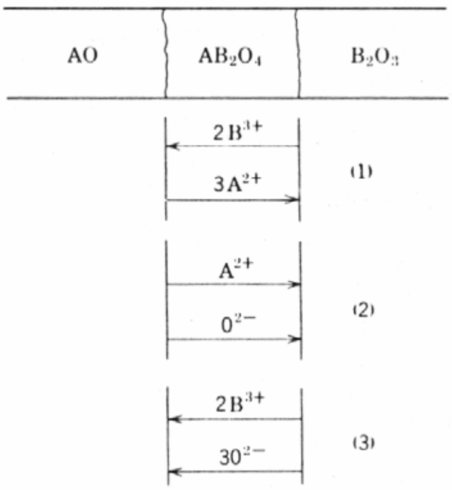


Fig. 9.6. Schematic representation of several mechanisms which may control the rate of AB_2O_4 (e.g., spinel) formation. From Ref. 1.

Mobility

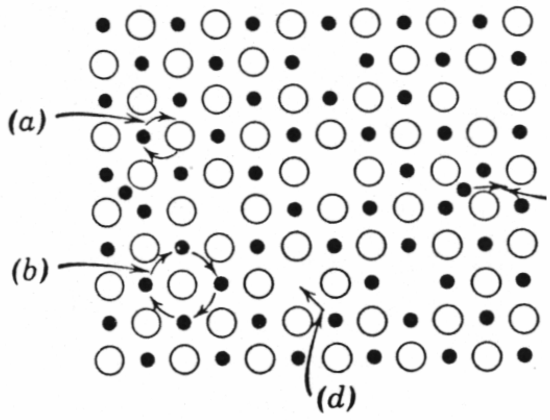


Fig. 6.1. Atomic diffusion mechanisms. (*a*) Exchange; (*b*) ring rotation; (*c*) interstitial; (*d*) vacancy.

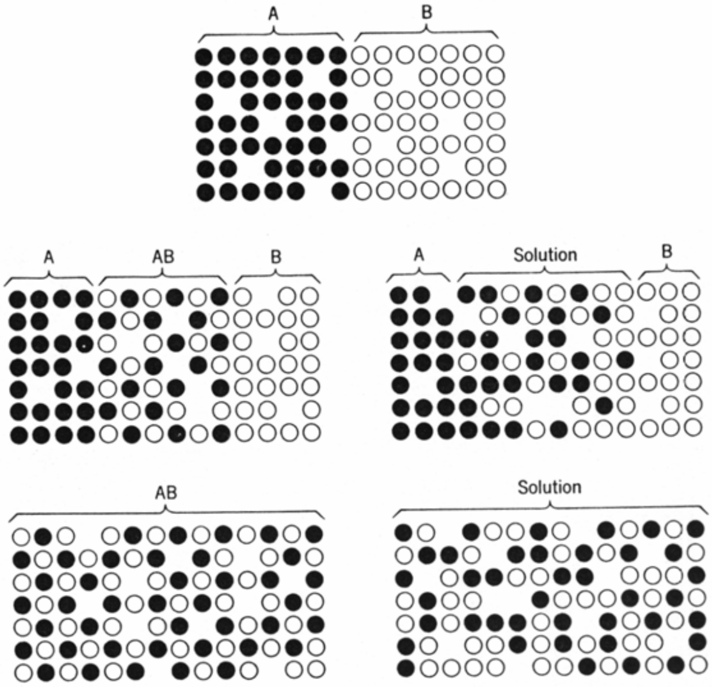


Fig. 6.2. Diffusion processes to form a new compound AB or a random solid solution from pure starting materials A and B.

Reactivity

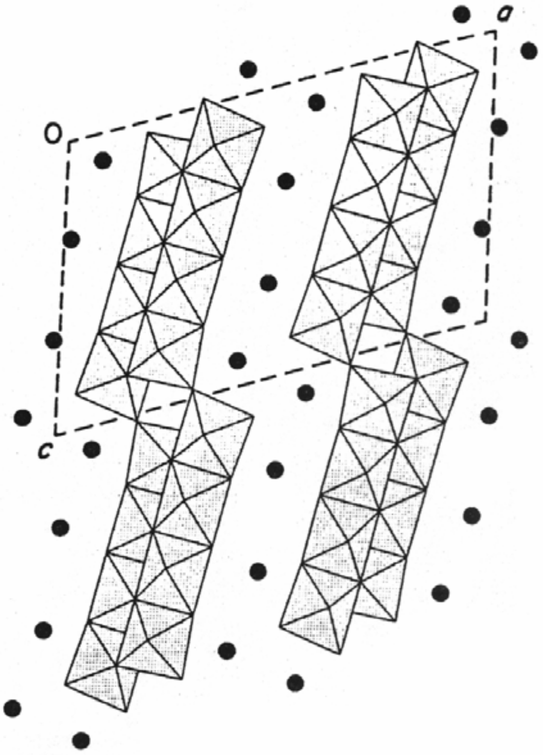


Figure 3. Projection of the crystal structure of $K_2Ti_4O_9$ along the [010] direction. The Ti–O substructure is represented with shaded octahedra, and the K atoms are given as black circles. The K atoms lie in y/b = 0 (center) and in $y/b = {}^1/_2$ (left and right). The edges of the unit cell are emphasized with broken lines.

Ceramics by solid state reactions
”Shake’n bake”

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

The method in short:

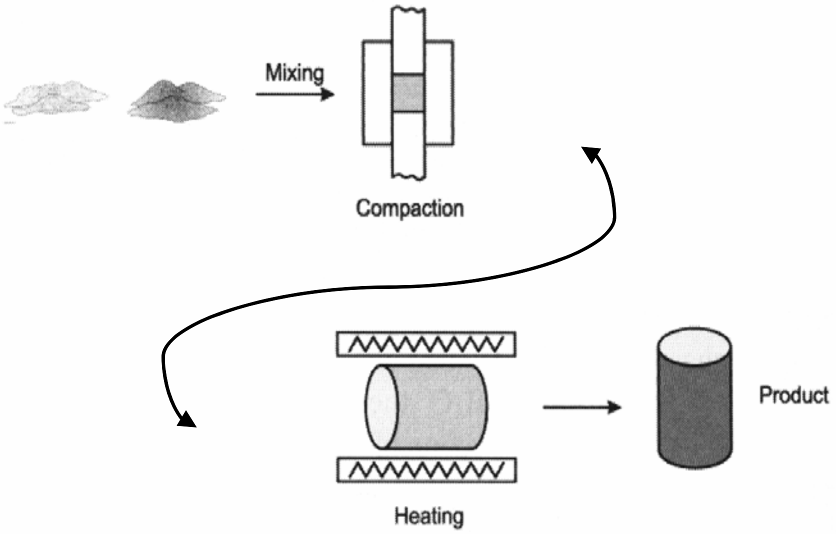
-Crush and mix the starting materials

-Press in order to achieve large contact area

-Heat the mixture so that the species diffuse an dreacts 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**

$\mathbf{LaCo(CN)_6 \bullet 5H_2O \rightarrow LaCoO_3}$

$\mathbf{LaFe(CN)_6 \bullet 5H_2O \rightarrow LaFeO_3}$

$\mathbf{Ba[TiO(C_2O_4)_2] \rightarrow BaTiO_3}$

$\mathbf{Li[Cr(C_2O_4)_2(H_2O)_2] \rightarrow LiCrO_2}$

Carbonate precursors

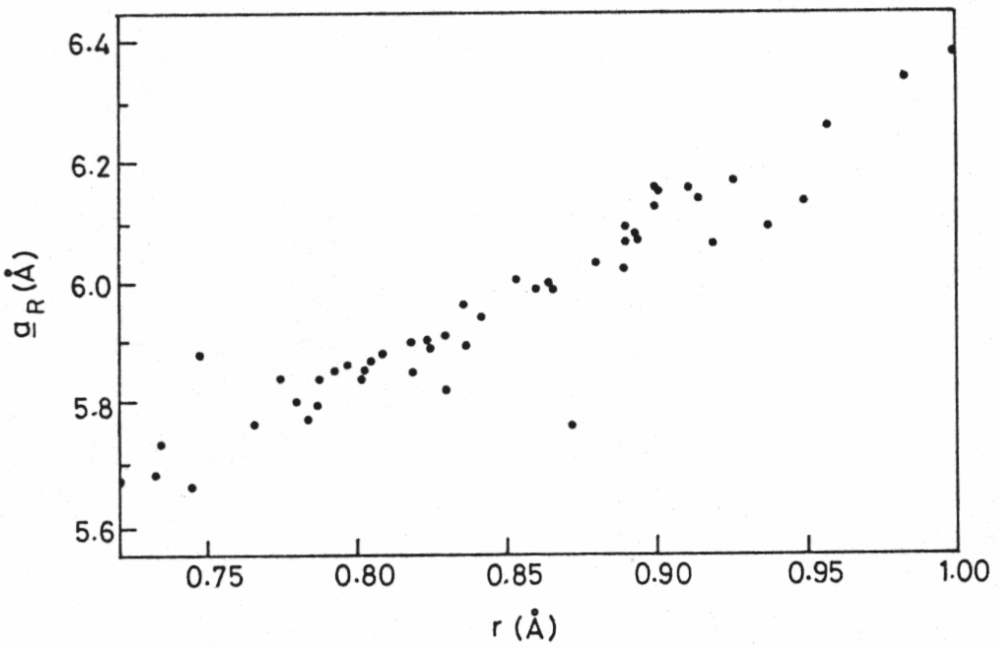


Fig. 1. Plot of the rhombohedral lattice parameters a_R of a variety of binary and ternary carbonates of calcite structure (e.g. Ca–M, Ca–M–M, Mg–M, M–M where M,M ≡ Mn, Fe, Co, Cd, etc.) against the mean cation radius.

Carbonate precursors

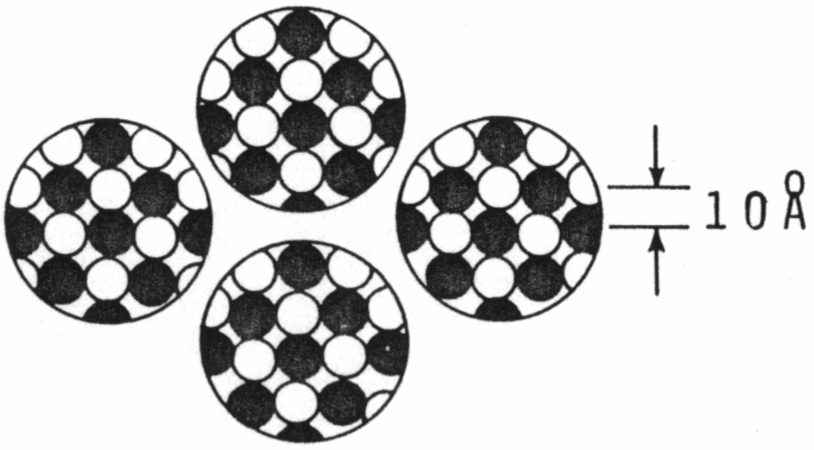


Figure 2. Solid solution precursor techniques give fast reaction kinetics

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

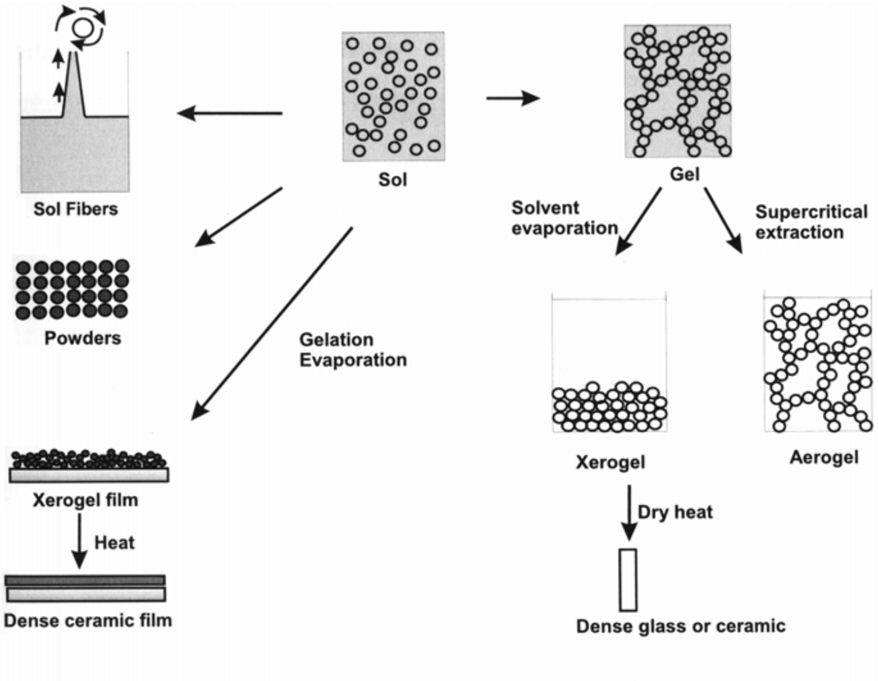


Figure 4-42. Sol–gel processing options.

Intercalation methods

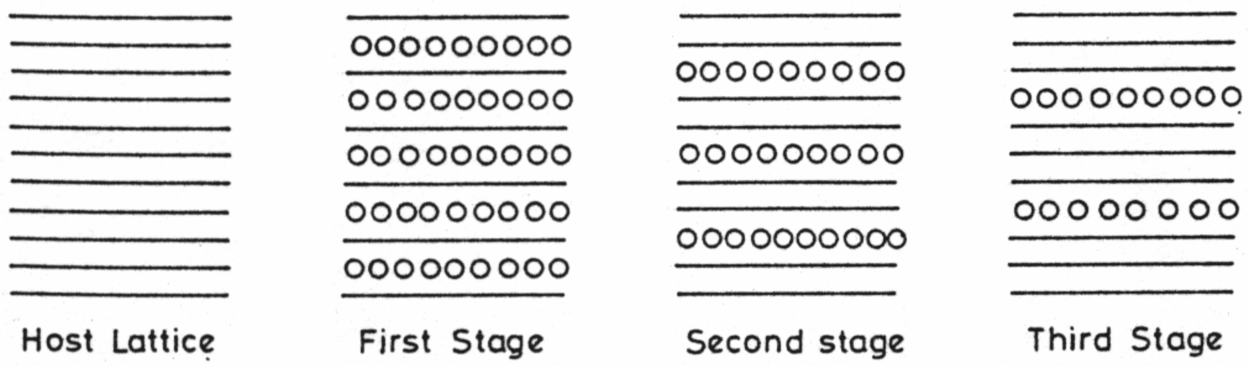


Fig. 8. Schematic diagram of staging in intercalation compounds. Guest molecules are represented by circles in between the layers (shown by lines).

Topochemical and topotactical methods

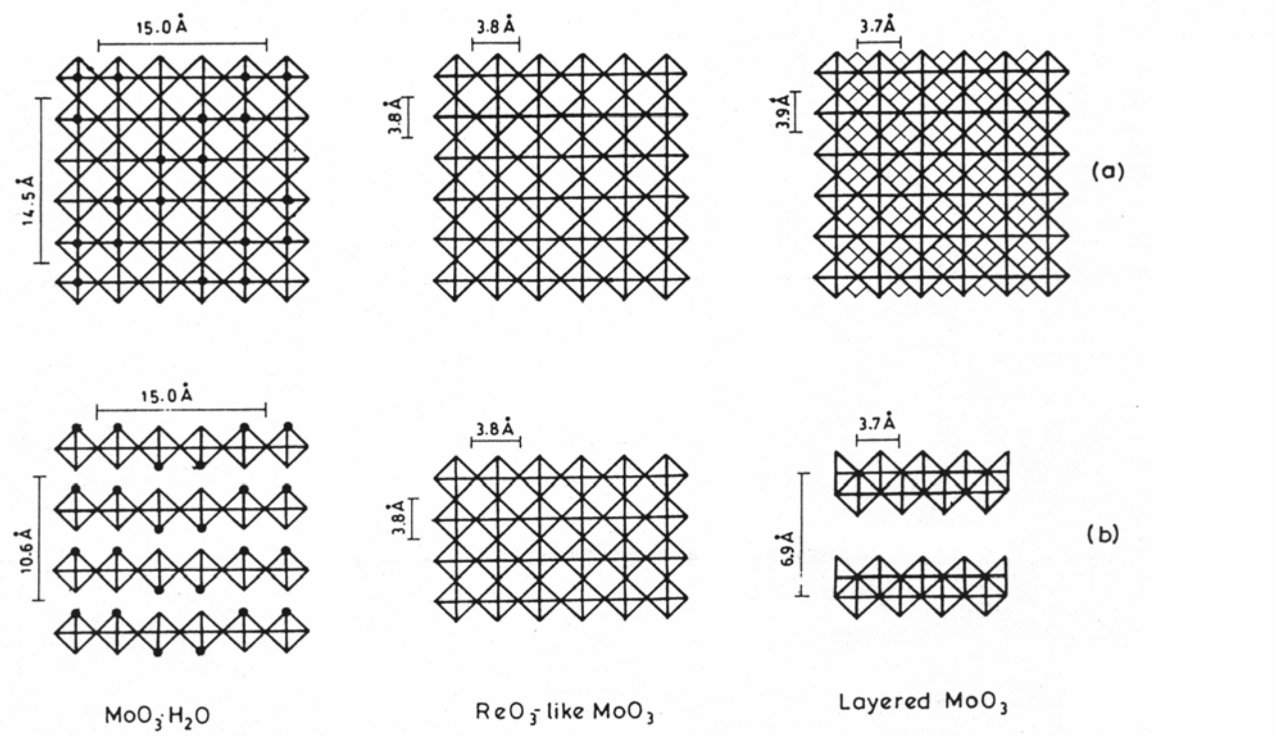


Fig. 6. Schematic representation of $MoO_3 \cdot H_2O$ (or $WO_3 \cdot H_2O$), ReO_3-like MoO_3 (or WO_3) and the layered structure of MoO_3.

Chemical transport methods

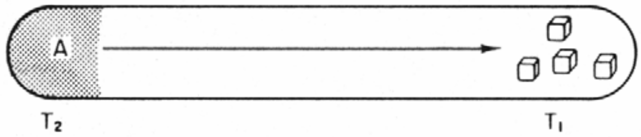
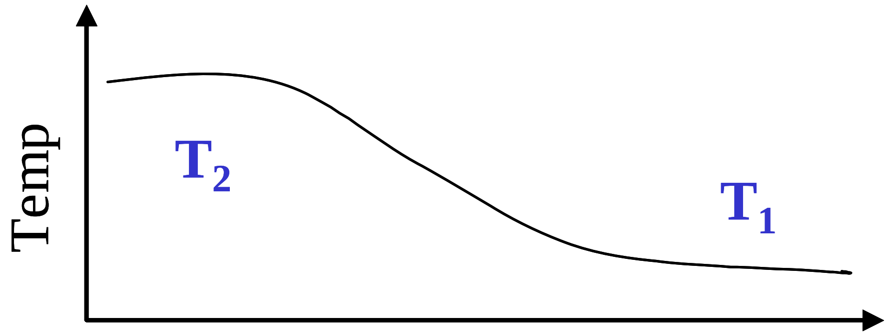


FIG. 1. Chemical transport in a cylindrical tube. Transport is from temperature T_2 to T_1.



$ZnS(s) + I_2(g) = ZnI_2(g) + ½S_2(g)$

Thin films (CVD)

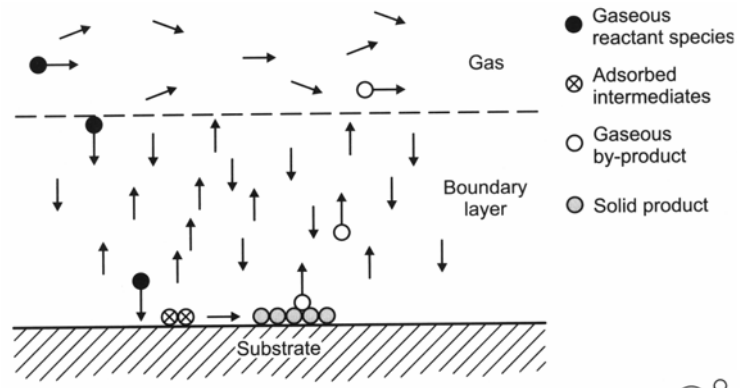


Figure 3-5. Schematic representation of the steps in CVD process

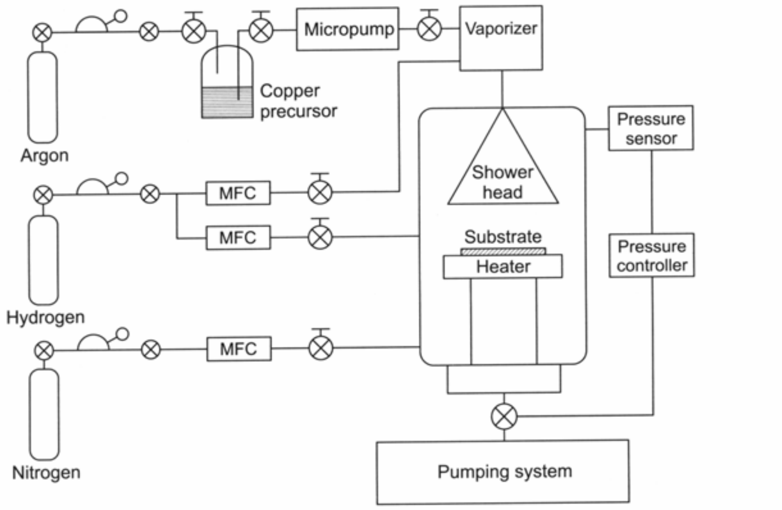
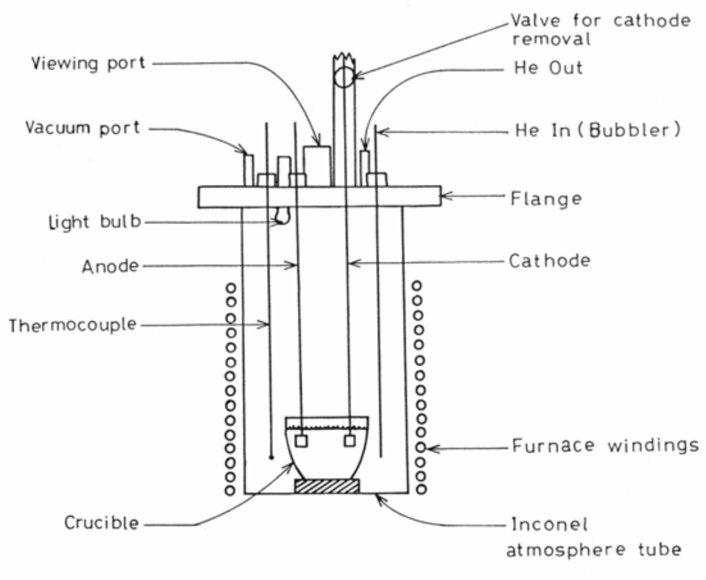


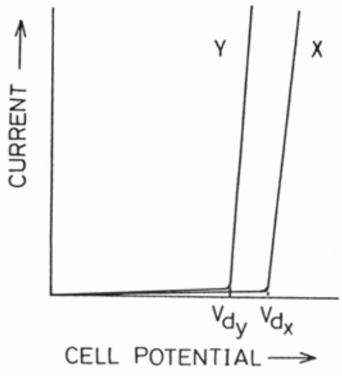
Figure 3-6. Schematic of a thermal CVD reactor for copper CVD from a Cu(II) precursor (see Eq. 3-19) (MFC = mass flow controller).

Electrochemical methods



Journal of Crystal Growth

Figure 3. Molten salt electrolysis system (7)



Idealized current vs. voltage curves for deposition of two species

Hydrothermal methods

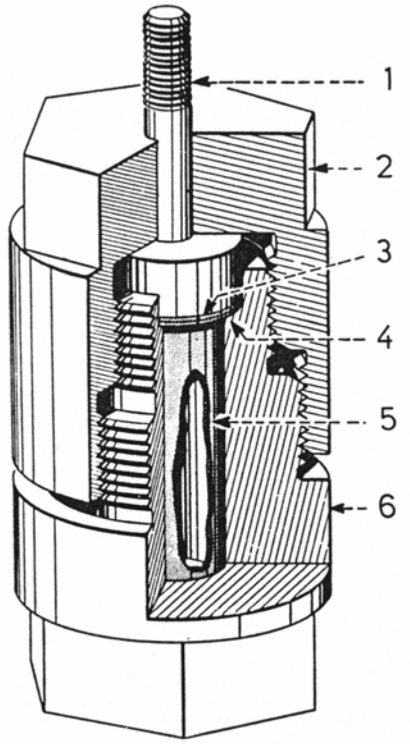
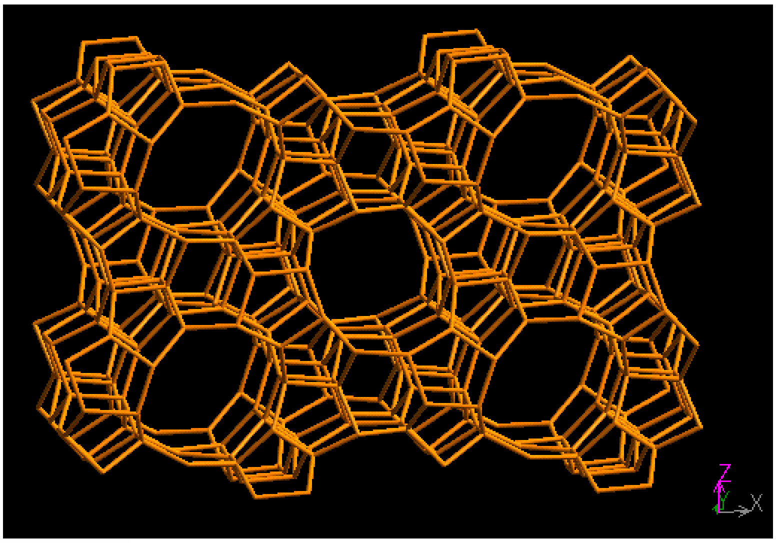


FIG. 9

Zeolites



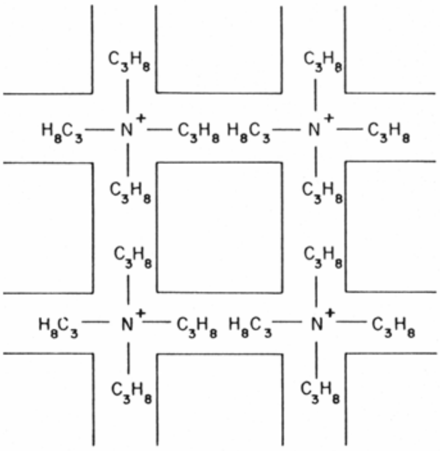


Fig. 51. The orientation of TPA in the channels of ZSM-5 (as synthesized)

High pressure

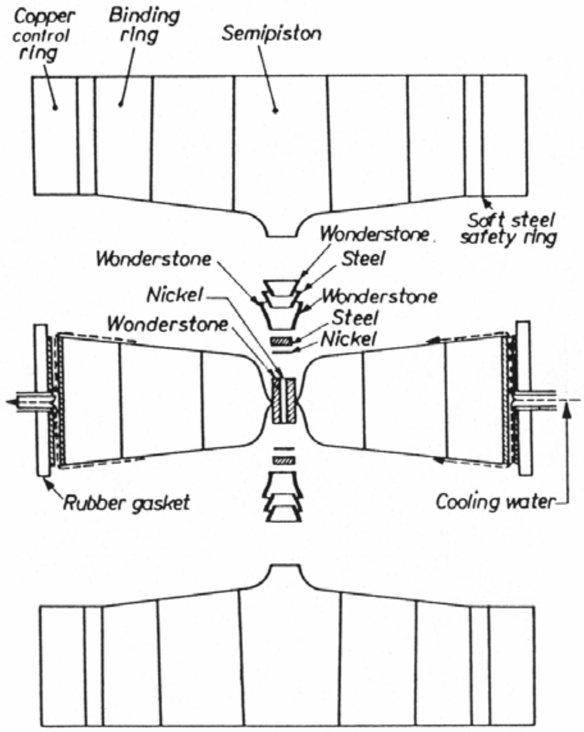


FIG. 25. The "belt," a high-temperature, high-pressure apparatus; "exploded" assembly. After Hall (1960).

Crystal growth
Czochralski

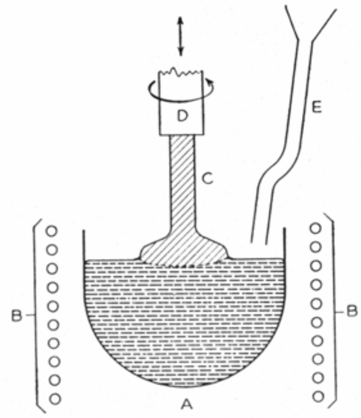


Figure 3.11. Diagram of the basic elements of a crystal puller.

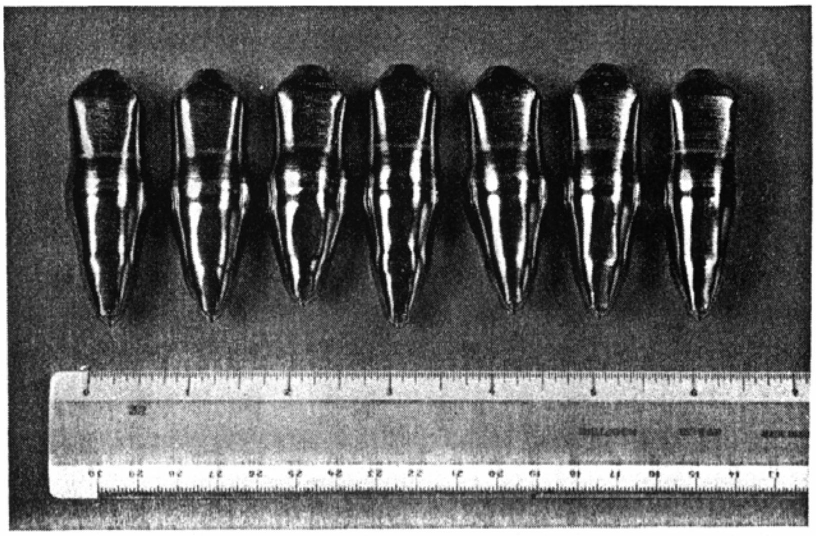
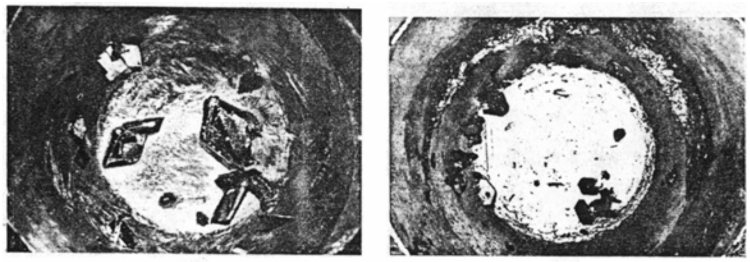


Figure 3.12. Pulled germanium single crystals grown with automatic progr
ing to produce a uniform diameter over the first half of the crystals. The flat si
e approximately (110) planes. Scale in inches and centimeters.

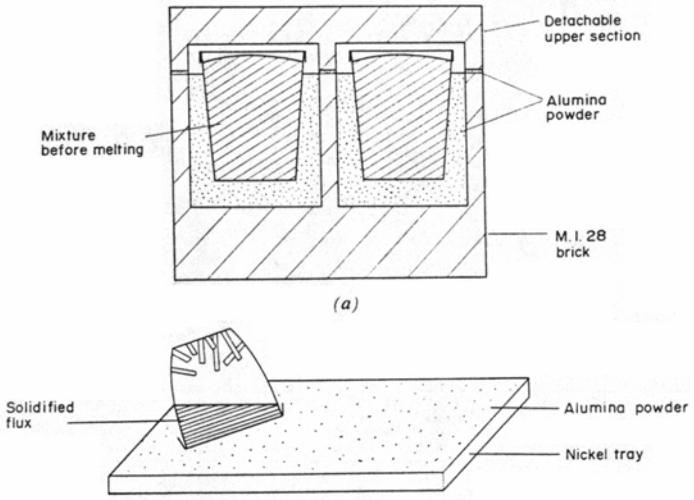
Flux growth



(a) (b)

(c)

Fig. 7.3. Contents of crucibles after removal of flux (actual size). (a) αFe_2O_3 ex $Pb_2V_2O_7$. (b) Cr_2O_3 ex Bi_2O_3–V_2O_5. (c) Fe_2TiO_5 ex $Pb_2V_2O_7$.



(a)

(b)

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

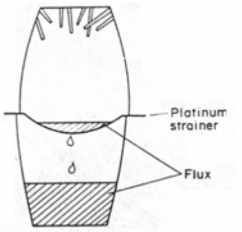


Fig. 7.4. Hot draining of flux.