Synthesis of materials

General synthetic approaches of inorganic materials

Liquid phase

Solid phase

Gas phase

Solid state material

PART 1:
Solid-state reactions

Reaction between two solids (sintering, ceramic method)

$$A + B \longrightarrow C$$
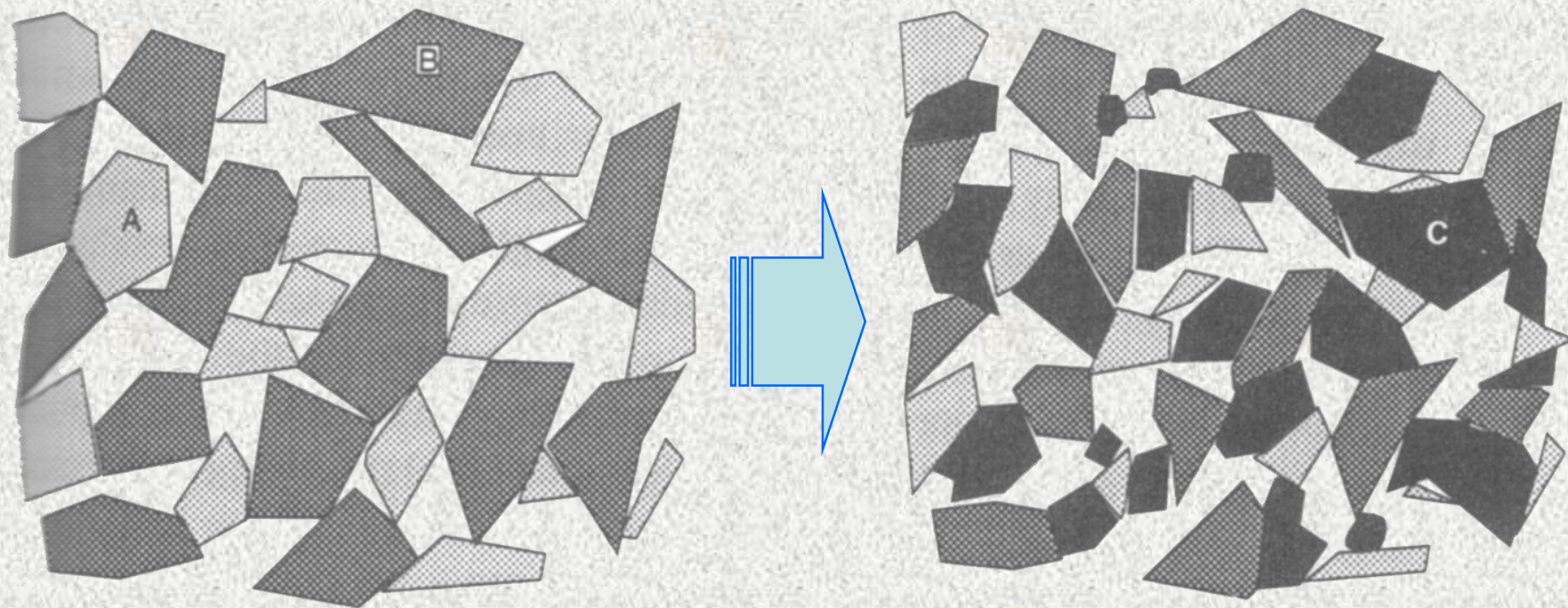
The growth of product (C) occurs on the contact of reagents' crystallites (A and B). After some time of the reaction there are no more contacts between A and B. Reaction almost stops, because the diffusion of ions in solid is very slow.

The completeness of the solid-state reactions could be ensured by

1) fine grinding of starting materials and pressing the mixture into a pellet
2) longer time (days, weeks) and higher temperatures (500-2000 °C) of the process
3) regrinding the raw product several times (ultimately, mechanochemical synthesis)

Acceleration of solid-state reactions

The time of the solid-state reactions depends on the diffusion rate (DR) of ions and diffusion distance (which is the particle size, PS): *reaction speed ~ DR / PS*

Therefore, in order to bring the solid-state reactions to a reasonable time scale, one should minimize the PS and maximize the DR.

■ Ions with small charge/radius ratio (*e.g.* alkali metals) have weaker interactions with lattice and, therefore, higher rate of diffusion:

$$Na_2O_2 + 2CuO \longrightarrow 2NaCuO_2$$ (relatively rapid reaction at 400 °C)

■ Small and strongly charged ions have lower diffusion rate:

$$MgO + Al_2O_3 \longrightarrow MgAl_2O_4$$ (heating for several days at 1400 °C)
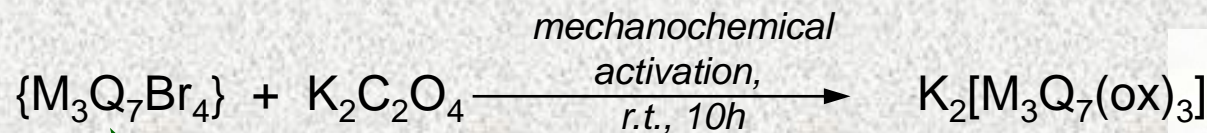
■ Higher temperature always accelerates the reaction, but there is an upper limit, such as the stability of the material

■ Defects greatly increase the ion migration rate

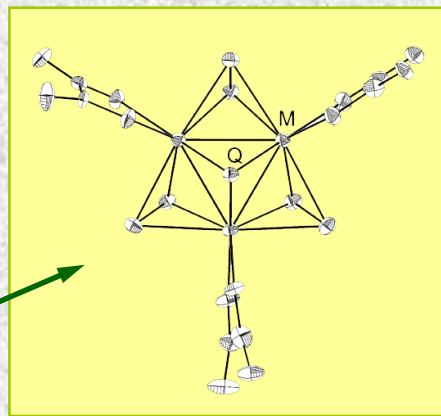■ The use of nonreactive ionic liquid as flux agent (флюс) for the reacting oxides:

$$BaCO_3 + TiO_2 \xrightarrow{KF} BaTiO_3 + CO_2$$ (1160 °C, 12h)

Mechanochemical synthesis

$$\{M_3Q_7Br_4\} + K_2C_2O_4 \xrightarrow{\text{mechanochemical activation, r.t., 10h}} K_2[M_3Q_7(ox)_3]$$
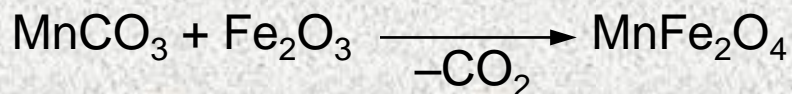
polymeric cluster
(insoluble and inert)

Structure of $[M_3Q_7(ox)_3]$
cluster complex

Pulverizing mill for
mechanochemical synthesis

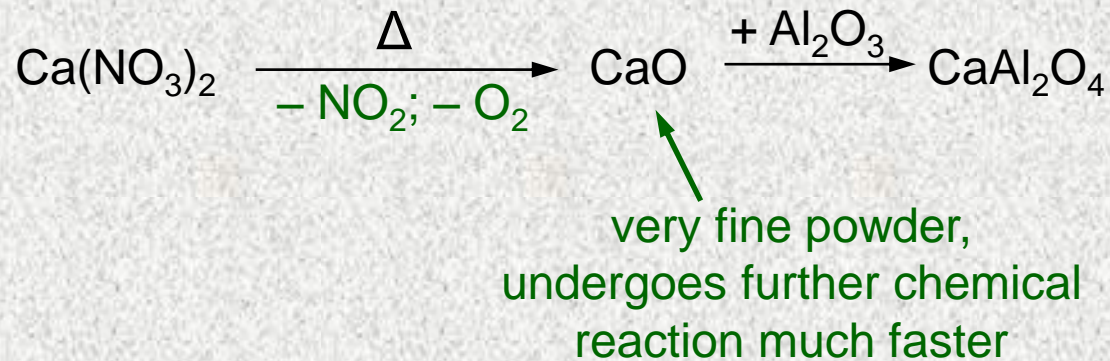$$MnCO_3 + Fe_2O_3 \xrightarrow{-CO_2} MnFe_2O_4$$

After 20 h the reflections of starting
materials disappear

(average $MnFe_2O_4$
particle size ~ 30 nm)

+-MnCO₃
o-Fe₂O₃
*-MnFe₂O₄
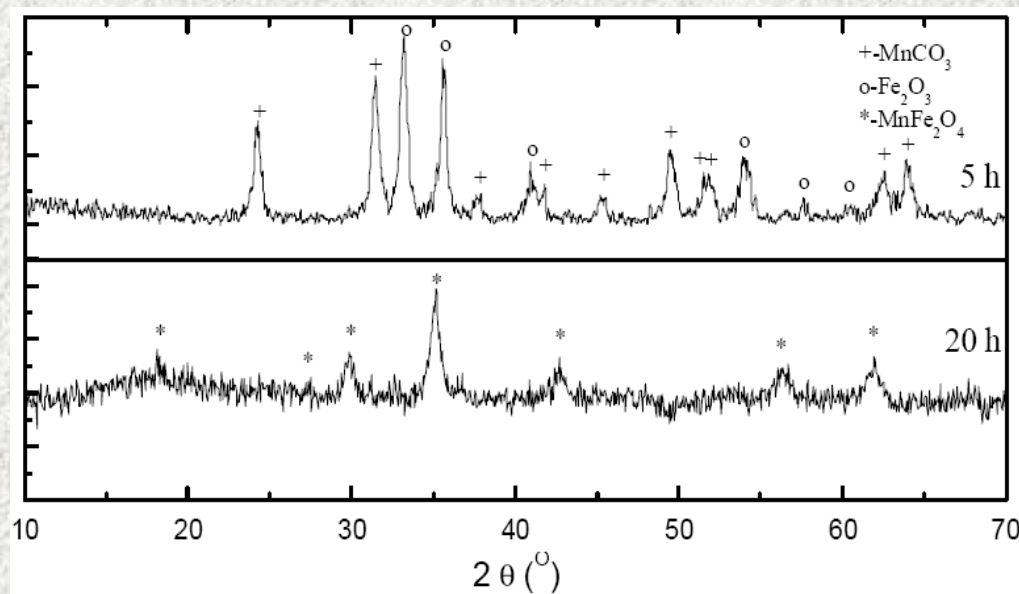
Precursor method for small particle size

There is a limit for the particle size, which could be obtained by grinding of starting materials (0.1 μm at best). Powders of oxide particles with even finer size could be obtained by chemical (non-mechanical) approach by decomposition of certain precursors (carbonates, nitrates, hydroxides) at moderate temperatures:

$$Ca(NO_3)_2 \xrightarrow[-NO_2;\ -O_2]{\Delta} CaO \xrightarrow{+Al_2O_3} CaAl_2O_4$$

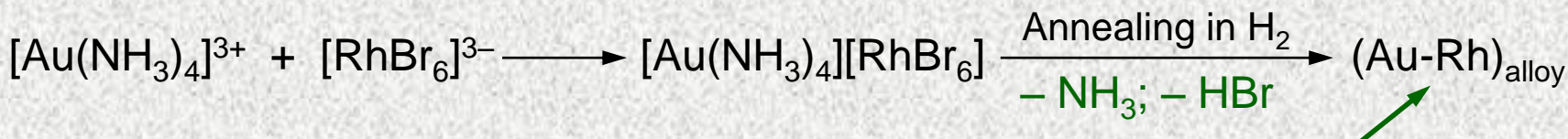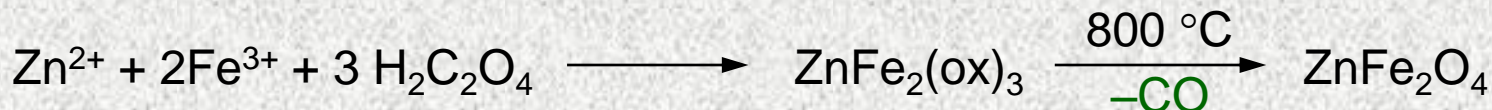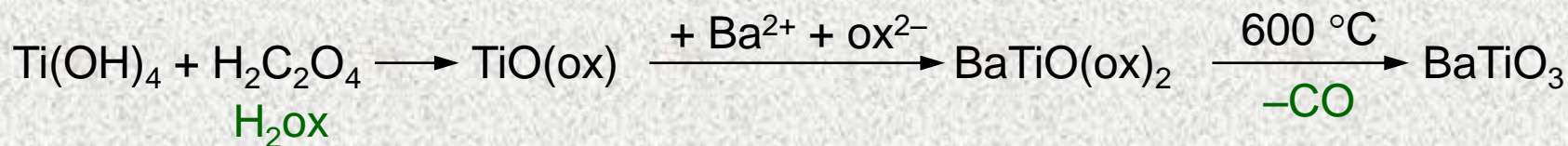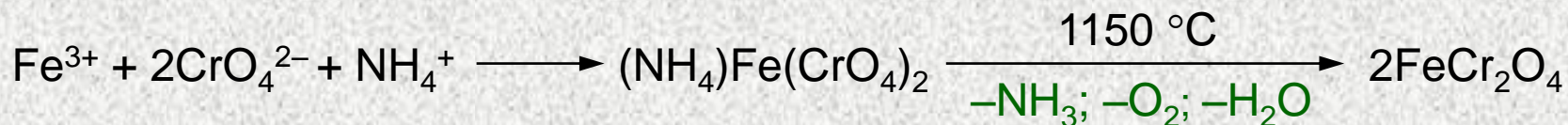very fine powder, undergoes further chemical reaction much faster

Ultimately, the starting materials could be **mixed at atomic level** for the highest reaction speed. There are several such approaches:

■ Single-source precursor method

■ Crystallization from the liquid melt

■ Sol-gel method

to be discussed later

Single-source precursor methods

In single-source precursor method the materials are prepared by decomposition of solid precursors, which have desired stoichiometry of elements. In these structures the starting materials (ions) are mixed on atomic level:

$$Fe^{3+} + 2CrO_4^{2-} + NH_4^+ \longrightarrow (NH_4)Fe(CrO_4)_2 \xrightarrow[-NH_3; -O_2; -H_2O]{1150\ °C} 2FeCr_2O_4$$

$$Ti(OH)_4 + H_2C_2O_4 \xrightarrow{\quad} TiO(ox) \xrightarrow{+ Ba^{2+} + ox^{2-}} BaTiO(ox)_2 \xrightarrow[-CO]{600\ °C} BaTiO_3$$
$$H_2ox$$

$$Zn^{2+} + 2Fe^{3+} + 3\ H_2C_2O_4 \longrightarrow ZnFe_2(ox)_3 \xrightarrow[-CO]{800\ °C} ZnFe_2O_4$$

$$[Au(NH_3)_4]^{3+} + [RhBr_6]^{3-} \longrightarrow [Au(NH_3)_4][RhBr_6] \xrightarrow[-NH_3; -HBr]{Annealing\ in\ H_2} (Au\text{-}Rh)_{alloy}$$

normally, Au and Rh are immiscible

Limitation: for some solids (especially of non-stochiometric compositions) finding a suitable precursor may be problematic ☹
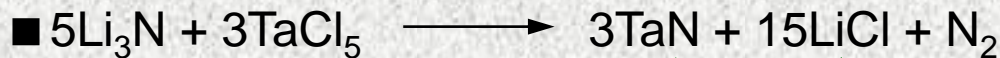
Combustion synthesis

In certain cases the solid-state reactions have strong driving force and are highly exothermic. After the initiation (ignition) the generated heat speeds-up the process. Such processes are known as combustion synthesis, solid-state metathesis (SSM), self-propagating high temperature synthesis (SHS) :

■ $Fe_2O_3 + Al \longrightarrow Al_2O_3 + Fe$ "thermite reaction"
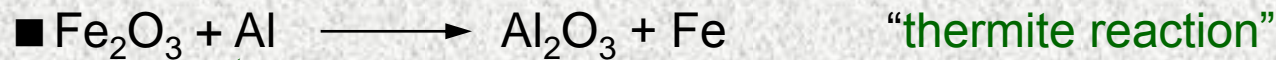
Highly active metal   Energetically very favorable product

■ $5Li_3N + 3TaCl_5 \longrightarrow 3TaN + 15LiCl + N_2$

Highly reactive   High lattice energy

■ $MgO + ZnO + 2\,Fe + Fe_2O_3 + NaClO_4 \longrightarrow 2Mg_{0.5}Zn_{0.5}Fe_2O_4 + NaCl$
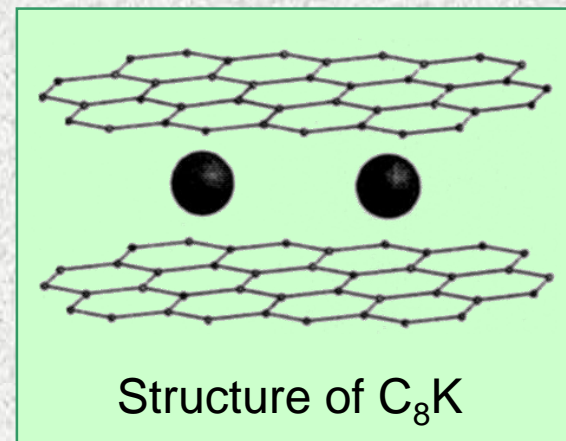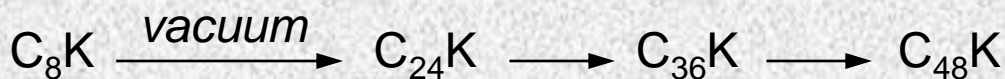
Very strong oxidizer

Limitation: such reactions tend to be quite violent (poor control, explosions risks)

Intercalation reactions

Intercalation – insertion of guest species into a layered structure with weak interlayer interactions

$$C_{graphite} + K_{liquid\ or\ vapor} \longrightarrow C_8K$$

$$C_8K \xrightarrow{vacuum} C_{24}K \longrightarrow C_{36}K \longrightarrow C_{48}K$$

Structure of C_8K

Guest molecule	Intercalate composition
Br_2	C_8Br, $C_{28}Br$
K	C_8K, $C_{24}K$; $C_{36}K$; $C_{48}K$
H_2SO_4	$C_{96}HSO_4$; $C_{48}HSO_4$; $C_{24}HSO_4$
$FeCl_3$	$C_{12}FeCl_3$; C_7FeCl_3
OsF_6	C_8OsF_6

Insertion reactions

■ Small ions (Li^+; H^+) can be smoothly inserted into open structures (like some oxides), without changing the host matrix

$$ReO_3 + LiI \longrightarrow Li_{0.3}ReO_3 + I_2$$

Reaction occurs even by grinding in mortar
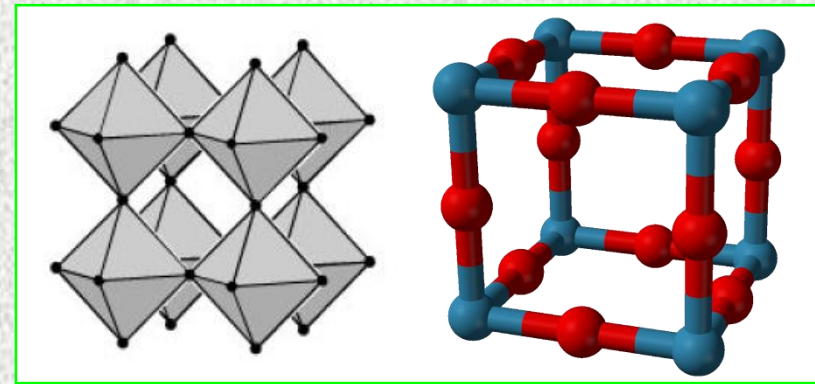
Structure of ReO_3

■ In some cases host structure undergoes phase transitions:

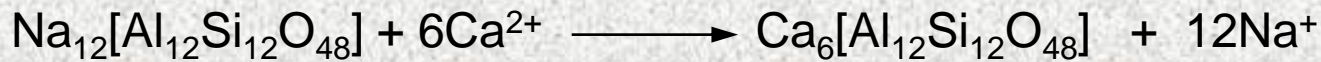$$TiO_{2\ (anatase)} + xBuLi \longrightarrow Li_xTiO_2 \text{ (lithiated anatase)}$$

$$Li_xTiO_2 \xrightarrow{500\ °C} Li_xTiO_2 \text{ (spinel structure)}$$

Insulator   Superconductor (T_c = 17K)
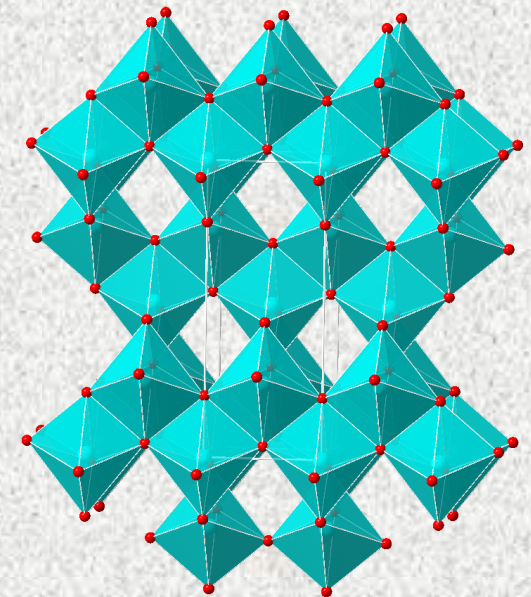
Structure of TiO_2 (anatase)

Ion exchange

■ Ion exchange in 3D ionic frameworks

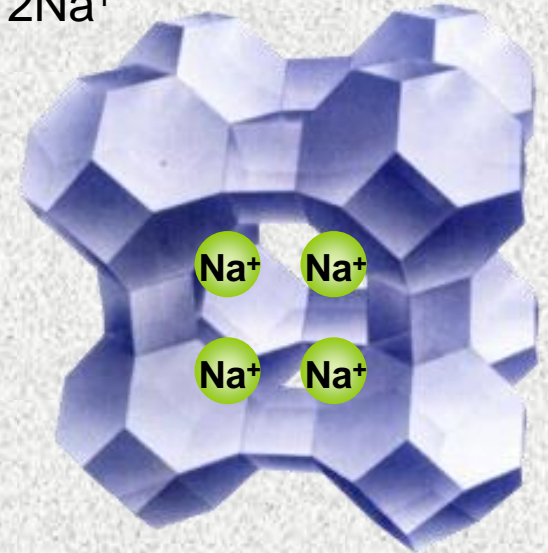$$Na_{12}[Al_{12}Si_{12}O_{48}] + 6Ca^{2+} \longrightarrow Ca_6[Al_{12}Si_{12}O_{48}] + 12Na^+$$

(the reaction is widely used for softening the water)

Structure of Zeolite 4A (NaA)

$$Na_{12}[Al_{12}Si_{12}O_{48}]$$
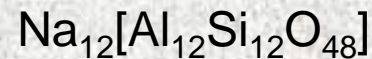
(channel dimension ~ 5 Å)

■ Ion exchange in layered compounds

$$Li + CoO_2 \underset{charge}{\overset{discharge}{\rightleftarrows}} Li_xCoO_2$$
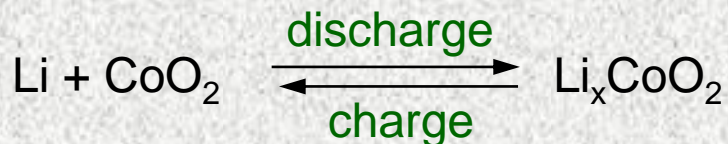
Li cations

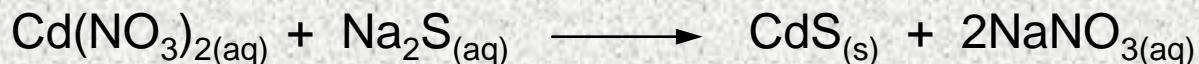Structure of LiCoO$_2$

J.B. Goodenough, 1980
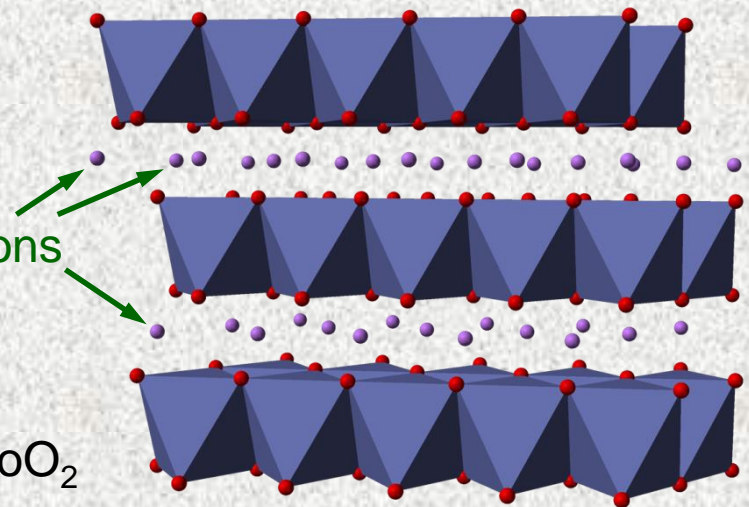
PART 2:
Liquid-phase techniques

Precipitation from solution

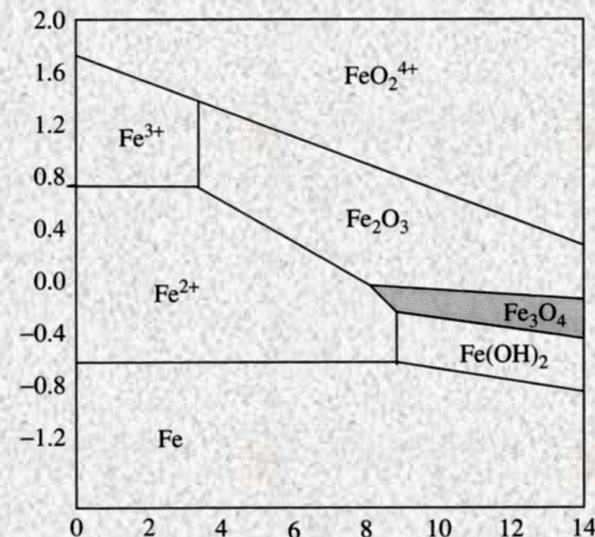■ Ion metathesis, one of the simplest and oldest methods to obtain solid materials

$$AB + CD \longrightarrow AC + DB$$

$$Cd(NO_3)_{2(aq)} + Na_2S_{(aq)} \longrightarrow CdS_{(s)} + 2NaNO_{3(aq)} \qquad K_L(CdS) = 3.6 \cdot 10^{-29}$$

$$KF_{(aq)} + MnCl_{2(aq)} \longrightarrow KMnF_{3(s)} + 2KCl_{(aq)}$$

■ Precipitation reactions are often used to generate precursors

$$Fe^{2+} + Fe^{3+} + HO^- \longrightarrow \text{``}Fe_2(OH)_5\text{''} \xrightarrow[-H_2O]{200\ °C} Fe_3O_4$$

$$Fe^{3+} + HO^- \longrightarrow Fe(OH)_3 \xrightarrow{200\ °C} Fe_2O_3 + H_2O$$
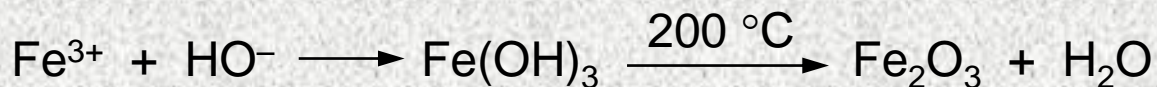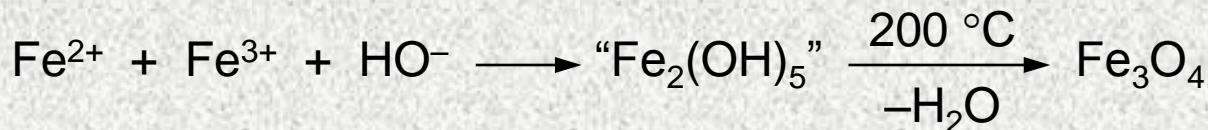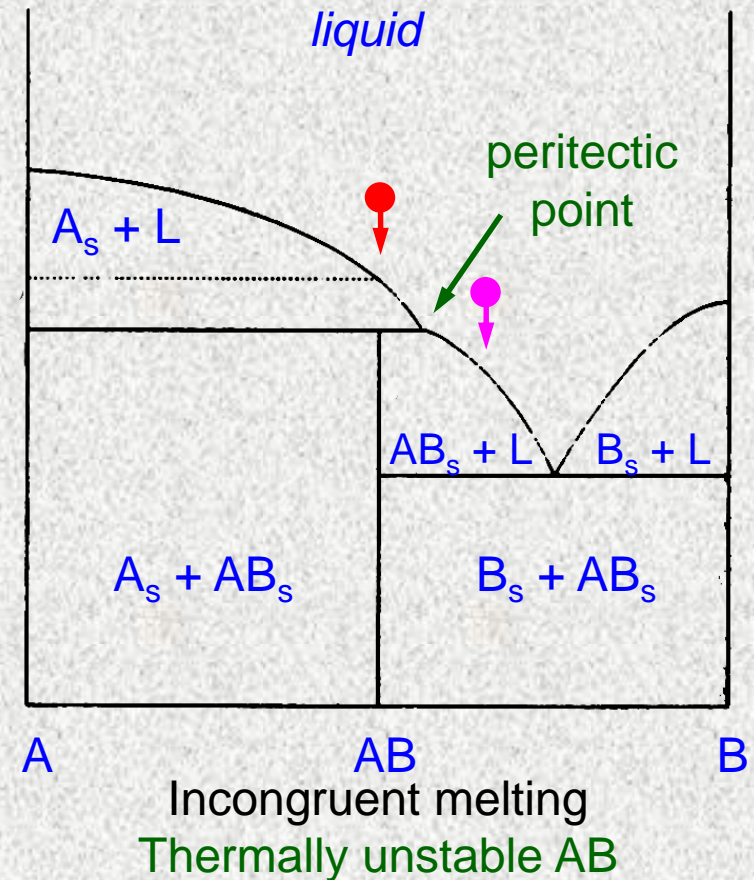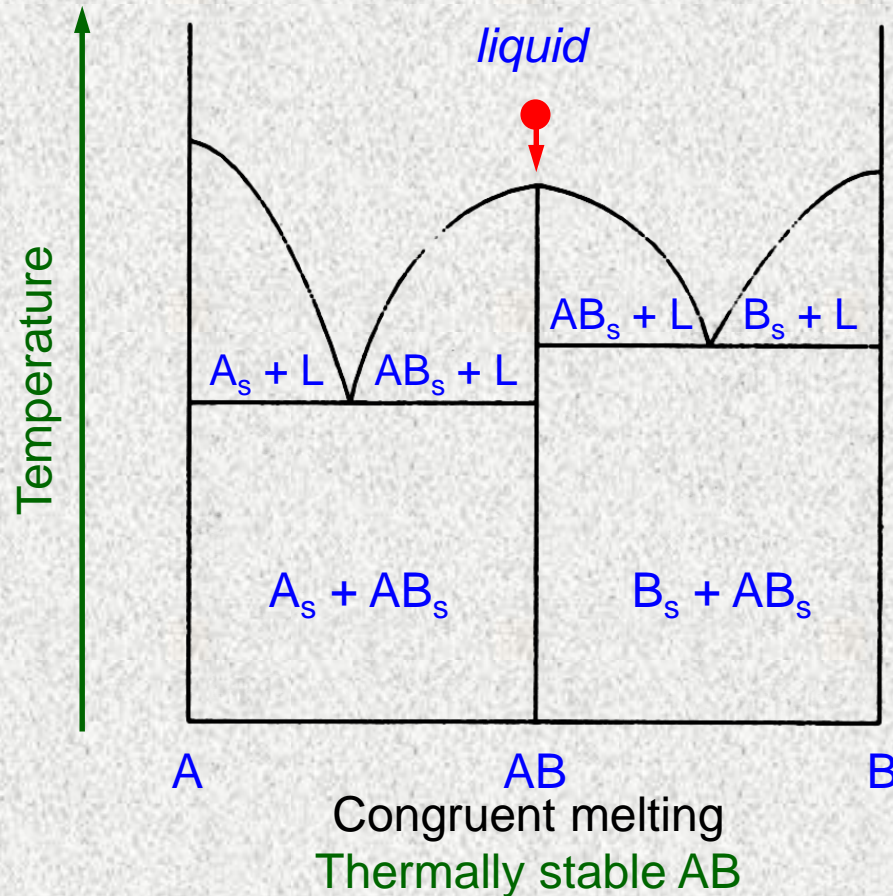

Pourbaix diagram
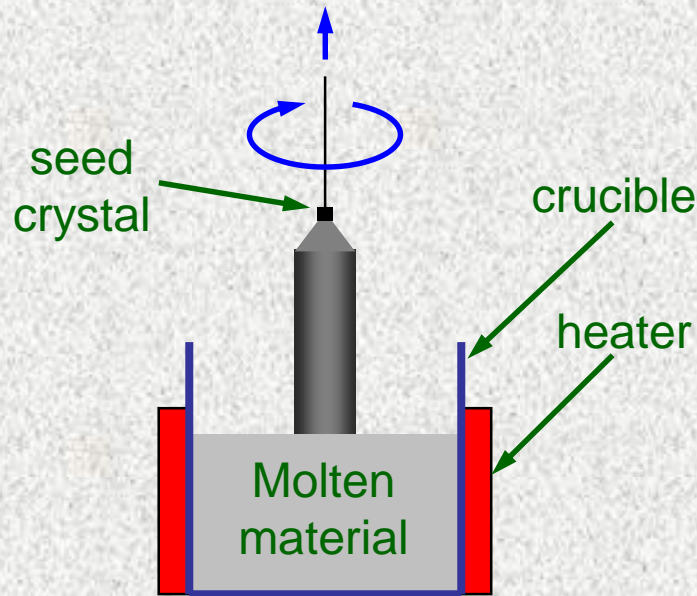(predominance diagram)
Ox/Red *vs.* pH

Crystallization from melts

Crystallization works well for single-component materials. In case of multicomponent mixtures the crystallization from liquid melts does not always give desired result.

Congruent melting
Thermally stable AB
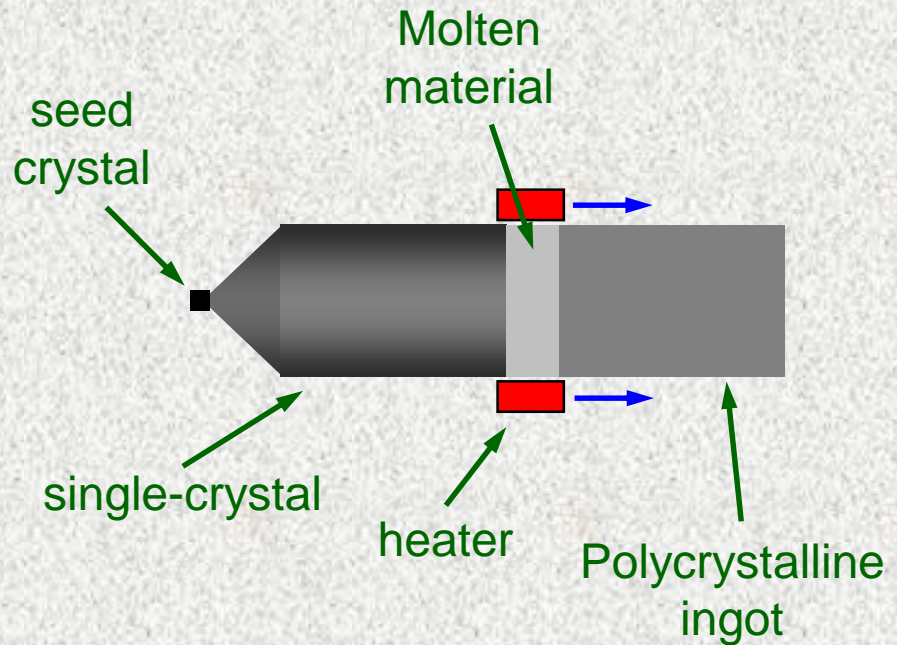
Incongruent melting
Thermally unstable AB

In case of incongruent melting, the target compound AB will be contaminated by other solid precipitate (A or B), even if the melt composition is the same as solid AB

Production of single crystals from melts

seed crystal

crucible

heater

Molten material

Czochralski method

seed crystal

Molten material

single-crystal

heater

Polycrystalline ingot

Zone melting of float-zone method

■ The ingot diameter in Czochralski method could be controlled by adjusting the pulling and rotation speeds.

■ The float-zone method is more commonly employed for **purification** of material through multiple melting-crystallization steps. Middle part of the ingot is the purest one, while both ends contain impurities better soluble in melt/solid state, respectively.
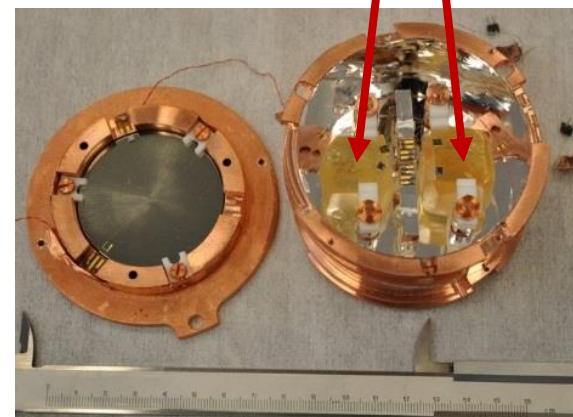
Crystal production at NIIC SB RAS
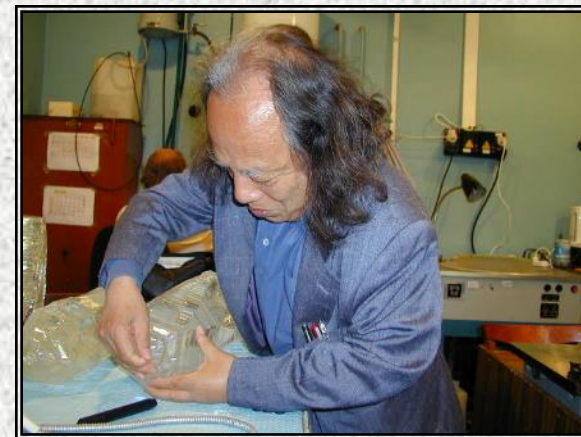
Элементы из BGO цилиндрической формы.

A zinc molybdate (Zn^{100}MoO$_4$) crystal boule

enriched in ^{100}Mo to 99.5 % with a mass of 171 g

was grown for the first time

by the low-thermalgradient Czochralski technique.

Two crystals of 59 and 63 g, obtained from the boule, show a good detection performance

The response of the device

meets the requirements

of a high-sensitivity double beta decay search

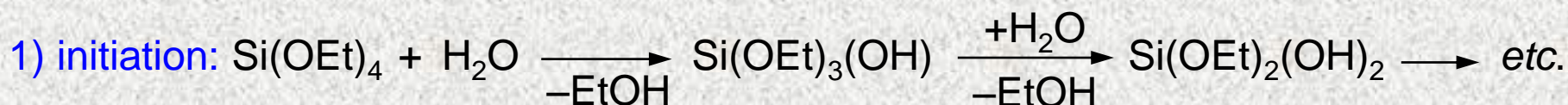**Assembled Zn^{100}MoO$_4$ bolometer**

Sol-gel method

This method is used for solid materials **fabrication** from small molecules. It involves the controlled hydrolysis of organometallic compounds (usually alkoxides) and their mixtures to obtain homogeneous gel without precipitation of any separate crystalline phases. The gel is then aged, dried and calcined at high temperatures to remove organics.

Example: hydrolysis of silicon alcoxides to a binary oxide SiO_2.

1) initiation: $Si(OEt)_4 + H_2O \xrightarrow[-EtOH]{} Si(OEt)_3(OH) \xrightarrow[-EtOH]{+H_2O} Si(OEt)_2(OH)_2 \longrightarrow$ *etc.*

Base-catalyzed hydrolysis: $Si(OR)_4 + OH^- \longrightarrow Si(OR)_3(OH) + RO^-$

Acid-catalyzed hydrolysis: $Si(OR)_4 + H^+ + Cl^- \longrightarrow Si(OR)_3(OH) + R\text{-}Cl$

2) condensation: $Si(OEt)_3(OH) + Si(OEt)_4 \longrightarrow (EtO)_3Si\text{–}O\text{–}Si(OEt)_3 + EtOH$
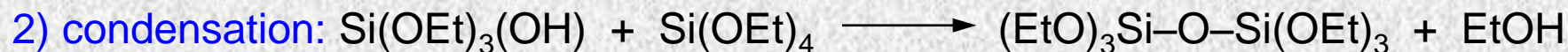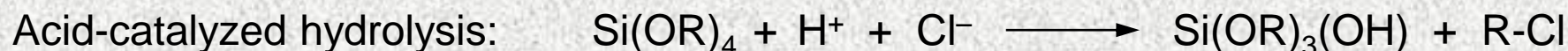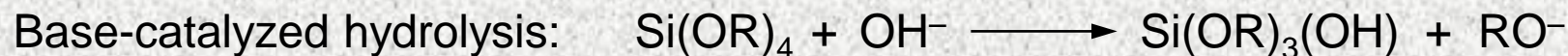
For the synthesis of complex oxides cross-condensation is required: A–O–B

Structure of sol-gel colloids of silica (SiO$_2$)
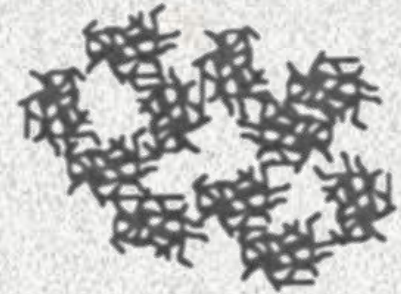
Sol-gel synthesis progress

Sol with low concentration.

The number of sol particles gradually increases.

When the particle concentration is high enough, gel structure with cross-links is formed.

Acid-catalyzed
linear entangled chains

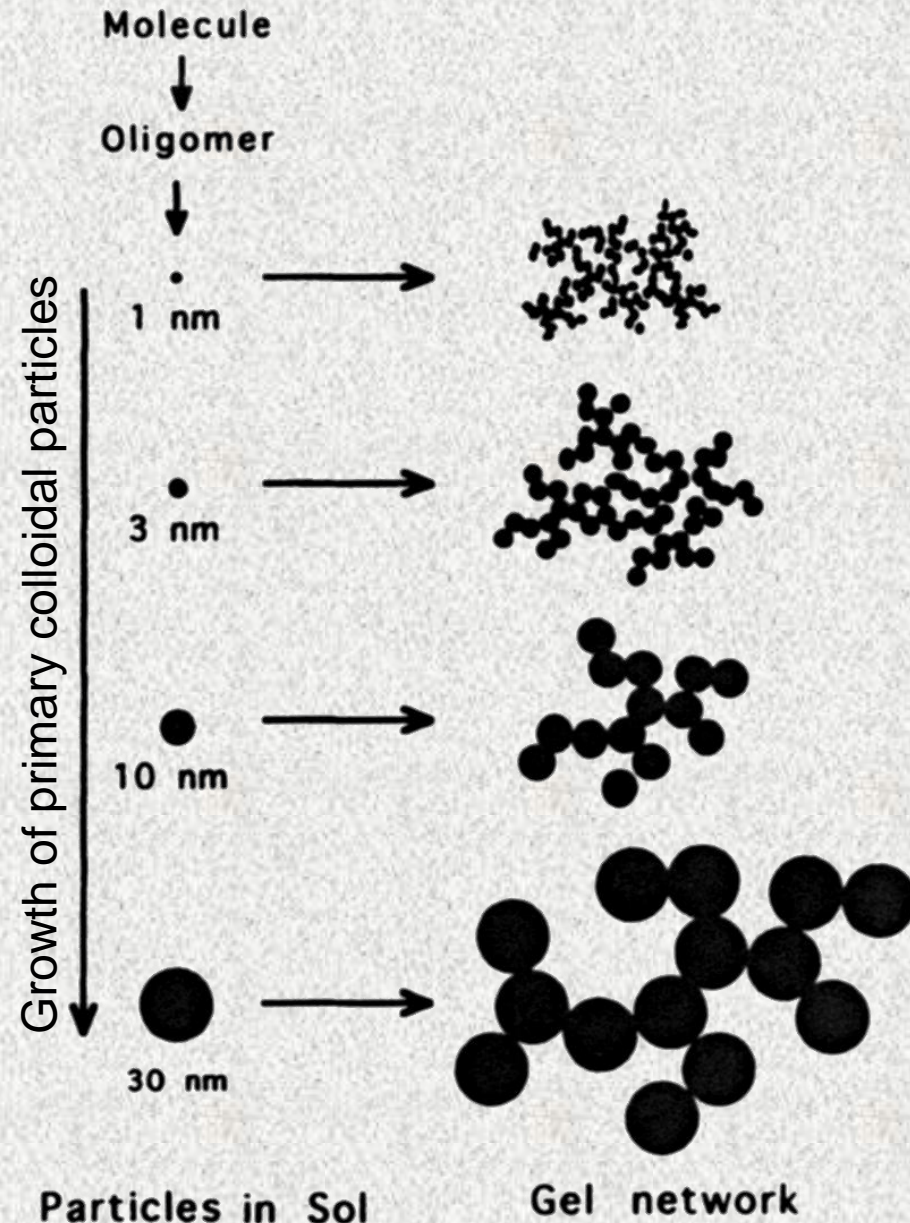Base-catalyzed
strongly branched chains

Growth of sol colloids and formation of gel

Sol particles grows as long as reactant molecules are present
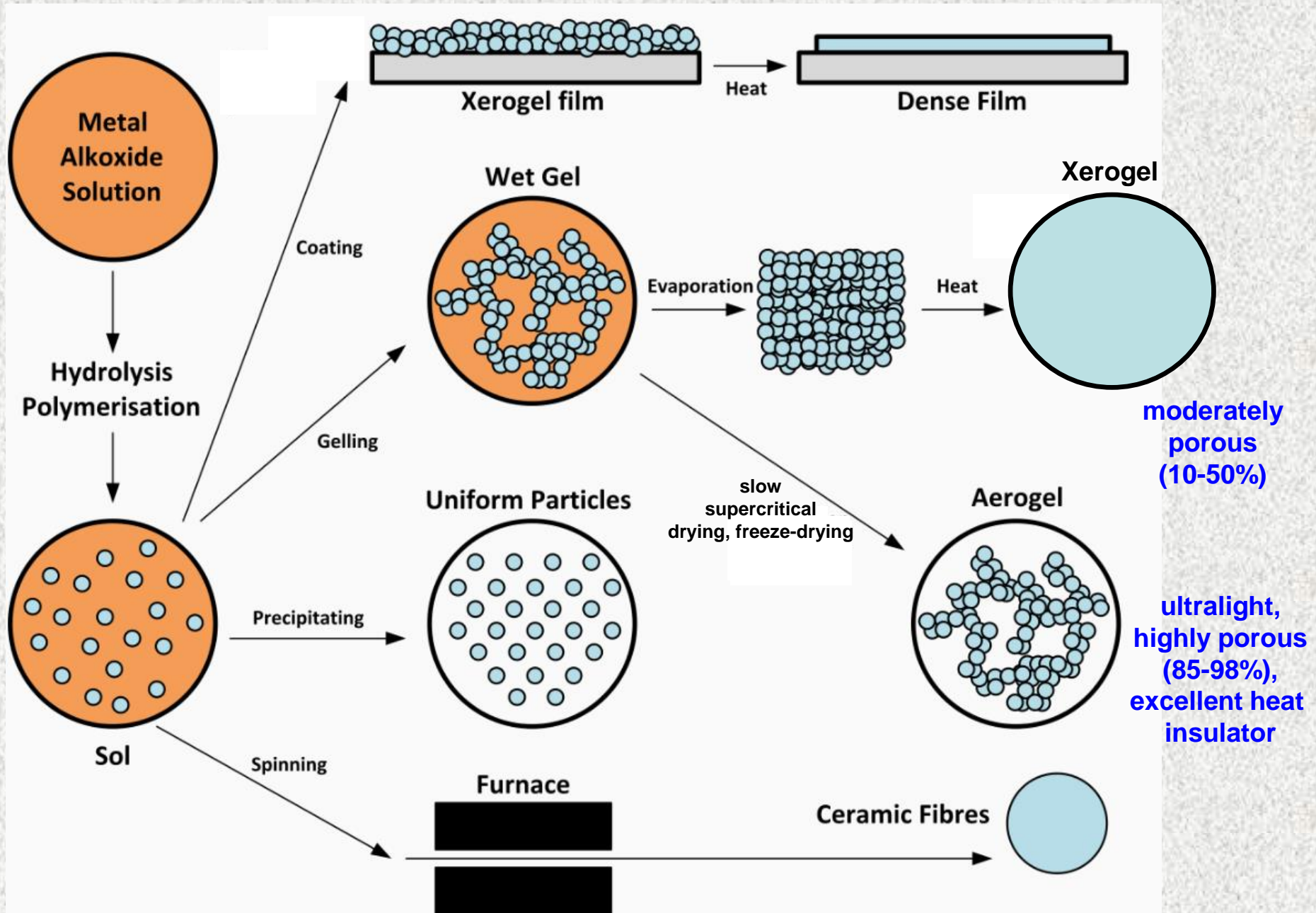
Gel is formed when particle concentration is high enough

■ A number of the sol-gel synthetic conditions could be adjusted (concentrations, pH, viscosity, templates, surfactants, *etc.*) to control the structure and porosity of gel network (zeolyte synthesis) or to fabricate fibers, film coatings and other forms, rather than microcrystalline powder in conventional precipitation reaction.

■ The chemical composition of oxide made by sol-gel method depends on the composition of starting mixture in solution. Therefore, the method could be used to prepare non-stochiometric phases or metastable ("nonexistent") complex oxides, such as $CaO \cdot 4SiO_2$, $LiAl_5O_8$, *etc.*

Molecule
↓
Oligomer
↓

Growth of primary colloidal particles

1 nm

3 nm

10 nm

30 nm

Particles in Sol   Gel network

Various routes of the sol-gel technology (examples)

# Aerogel: extremely light and heat-resistant material

Gel method

This is very versatile method, combining solid-state reaction, precursor method and sol-gel method. Gel serves as matrix for mixed dissolved ions, preventing them from formation of bulk solids of the starting materials, after drying the solution.
On the final calcination step the organic gel network is destroyed.

Example: synthesis of $YBa_2Cu_3O_7$ superconducting ceramic:

1) Prepare the aqueous solution of nitrate salts in stoichiometric amounts

2) Addition of citric acid and ethyleneglycole as jellifying agents

3) Heating the solution produces wet solid gel

4) Aging and evaporation of water gives rise a dry gel with trapped metal ions, thoroughly mixed on atomic level inside the gel network structure

5) Heating at 700 °C for a few hours destroys the gel and produces $YBa_2Cu_3O_7$

Note: direct solid-state reaction between the corresponding oxides requires heating at 950 °C for several days

mixture of starting salts → jellified solution → aged gel → dried gel → oxide ceramic
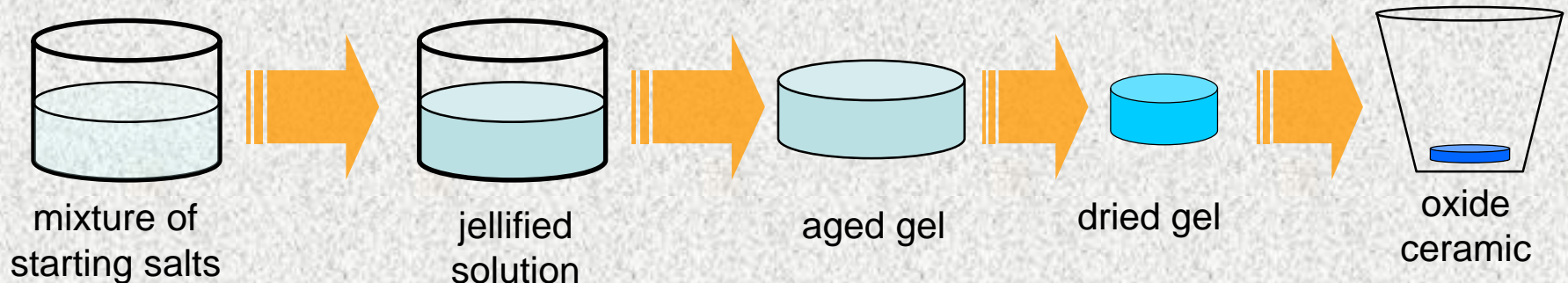
Hydrothermal (solvotermal) synthesis

Hydrothermal synthesis – reactions in aqueous media above boiling point (100 °C) in a sealed steel autoclave ("bomb") which sustains high pressure. Method is often employed for the growth of single crystals.

Cooler end

Crystal seeds

Water

Hotter end

Starting material
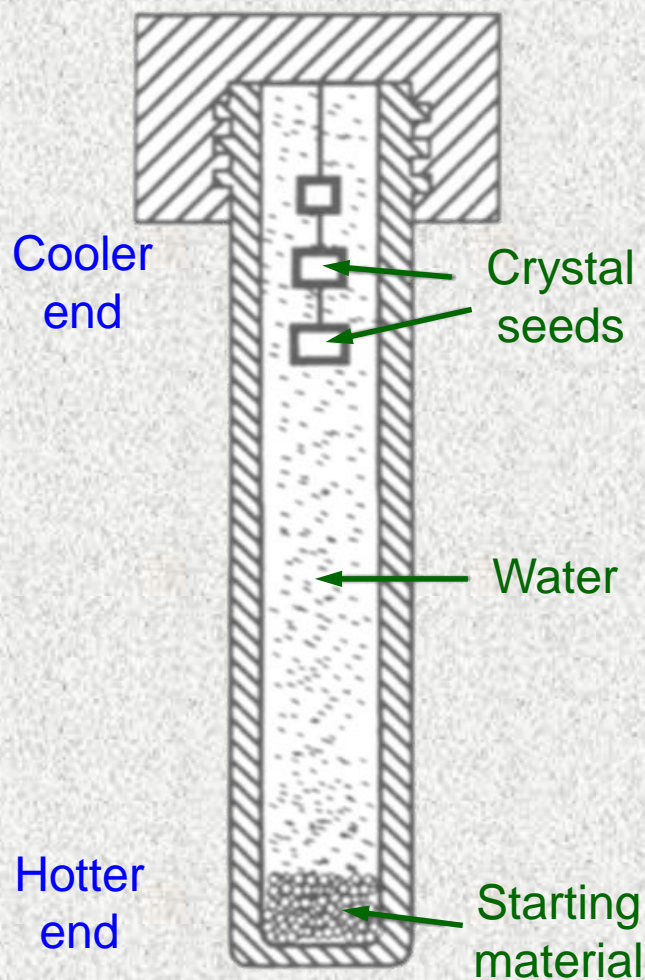
For many materials the solubility in water increases dramatically at high temperatures and in the presence of dissolving agent (e.g. NaOH).

Examples:

1) synthesis of single crystal of SiO_2 (see picture). NaOH is used as mineralizing (dissolving) agent.

2) Synthesis of zeolytes combines sol-gel and hydrothermal methods. Zeolyte ZSM-5 is synthesized by heating the mixture of silicic acid $SiO_2 \cdot nH_2O$, NaOH, aluminum sulphate $Al_2(SO_4)_3$, tetrapropylammonium bromide $(n\text{-Pr})_4NBr$, n-propylamine $Pr\text{-}NH_2$ in water at 160°C for several days. Organic template molecules could be removed later by calcination, leaving intact porous alumosilicate framework.

PART 3:
Gas-phase techniques

Physical vapor deposition (PVD)

In PVD some small amount of the material is transferred from the source to the substrate *via* gas phase. The method is used to fabricate films or protective coatings.

■ Vacuum evaporation: source is kept at higher temperature than the substrate. The material naturally sublimes off the source and condenses on the cooler substrate. Frequently used heating methods: oven, electron beam impact (EB-PVD), cathodic arc deposition, laser beam (laser ablation). In the latter case, evaporation is very fast and vapor composition <u>does not</u> depend on the equilibrium vapor pressure, so mixture of solids evaporates with the same composition as target source: useful for the deposition of complex solids.

■ Sputtering : small (atomic) particles of substrate are generated mechanically due to bombardment of the substrate surface by accelerated ions of inert gas.
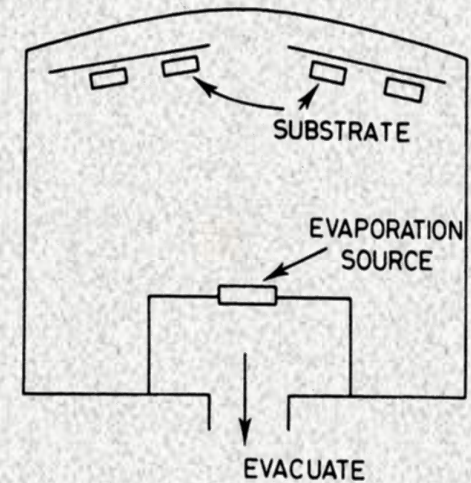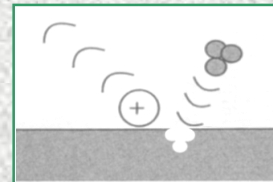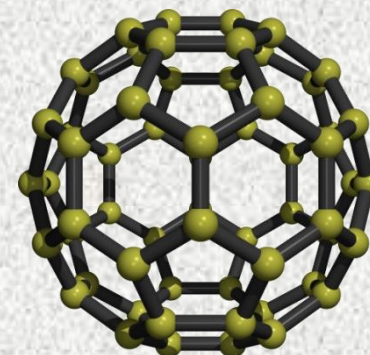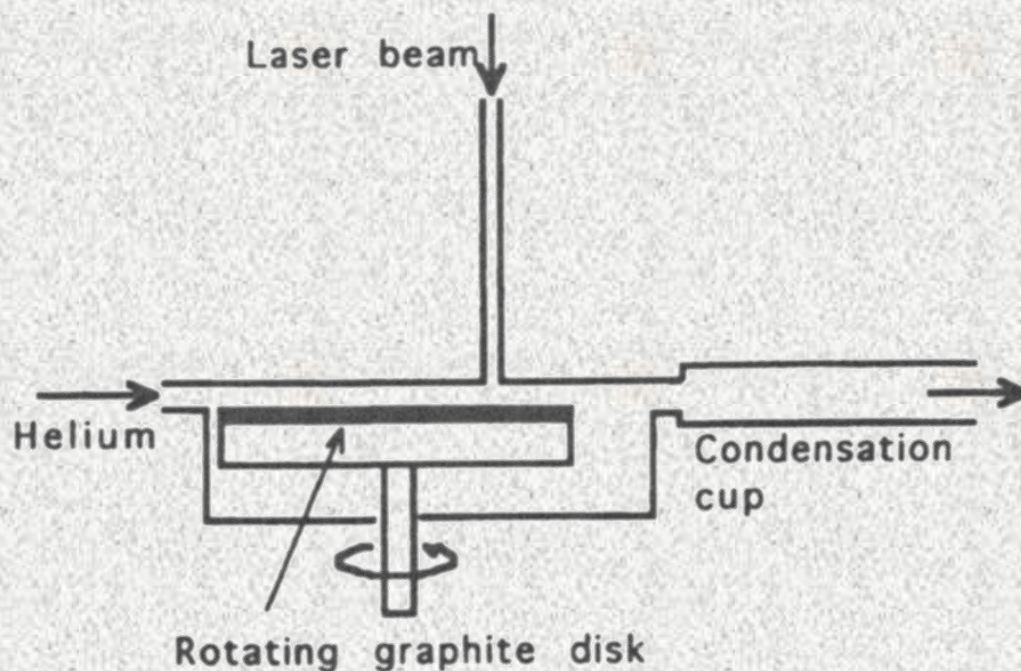

evaporation PVD
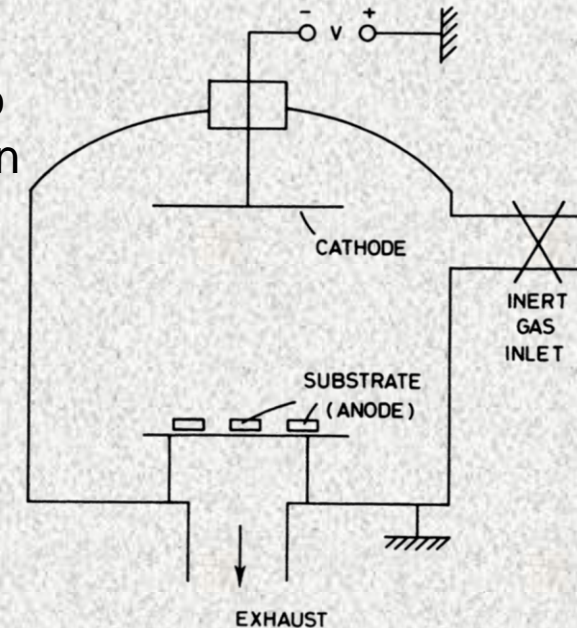
sputtering PVD

TiN coating

Example of PVD method

■ Fullerenes (C_{60}, C_{70}, C_{76}, C_{84}, etc) are prepared by PVD from graphite source. Carbon is evaporated by laser or in an arc discharge (T ~ 10000 °C). The spherical products are extracted by toluene.

■ $M^{n+}@C_{xx}$ could be prepared if metal cations M^{n+} are present in the gas phase and act as templates for the carbon shell C_x.   (M = Li^+, K^+, La^{3+}, Y^{3+}, etc...)
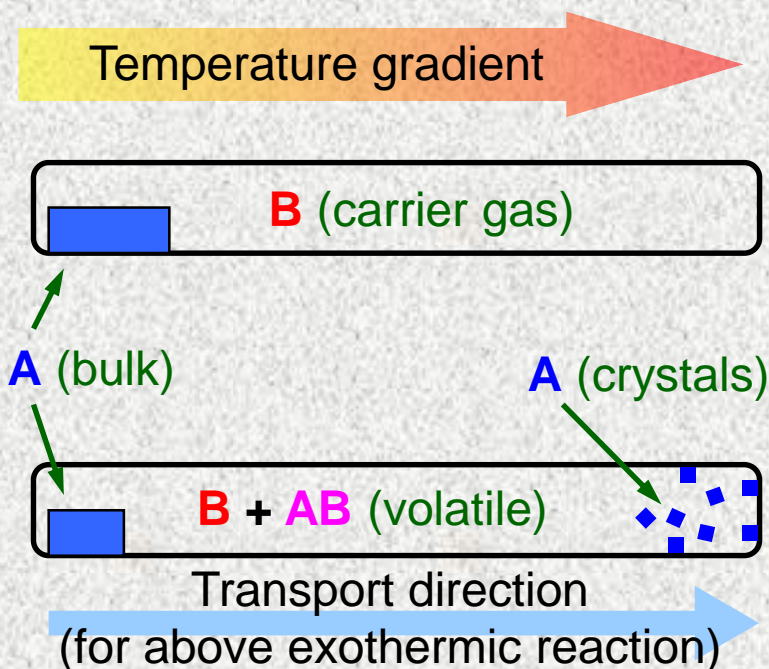
Laser beam

Helium

Condensation cup

Rotating graphite disk

Schematic of laser ablation PVD equipment
for the synthesis of fullerenes

Structure of C_{60}

Vapor transport

Vapor transport method utilizes unstable volatile intermediate, which contains at least one elements of the desired product.

The method could be used for: a) grow single crystals, b) purification of compounds, c) synthesis of new materials, d) device improvements.

The method requires sealed tube with temperature gradient, the reactant is placed on the one end. The tube is degassed or has some small amount of carrier agent.
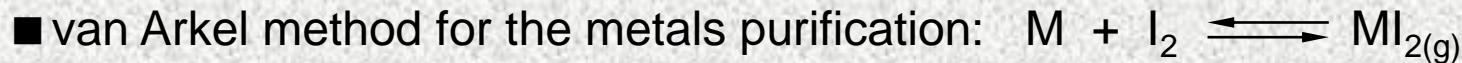
$$A_{(s)} + B_{(g)} \xrightleftharpoons{K} AB_{(g)}$$

Temperature gradient

B (carrier gas)

A (bulk)   **A** (crystals)

B + **AB** (volatile)

Transport direction
(for above exothermic reaction)

■ There must be a <u>reversible</u> equilibrium

■ K should not be very small (no AB formation, no transport)

■ K should not be very high (too stable AB, no A deposition on the other end of the tube)

■ The transport direction follows the principle of Le Châtelier for exo/endo-thermal reactions
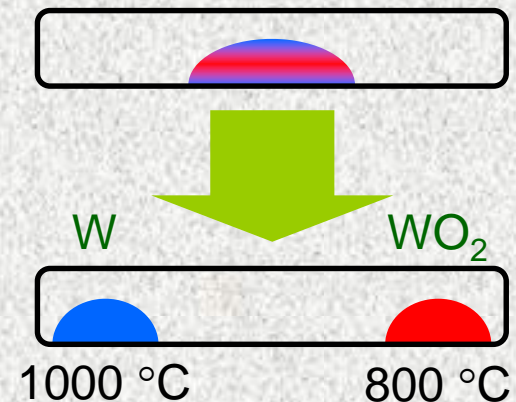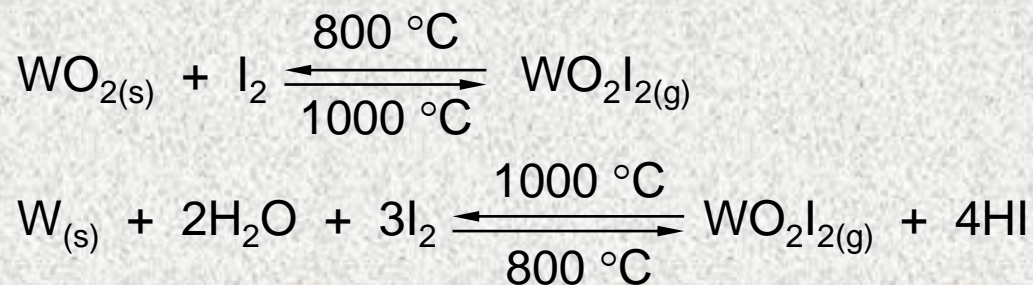
Examples of vapor transport reactions

■ $Pt_{(s)}$ + O_2 ⇌ $PtO_{2(g)}$ $T \sim 1200\ ^\circ C$
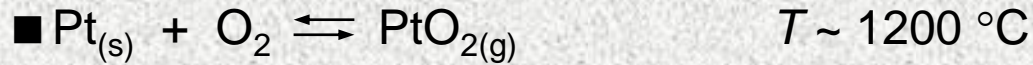
Platinum single crystals are deposited in the cooler end

■ van Arkel method for the metals purification: M + I_2 ⇌ $MI_{2(g)}$

M = Ti, V, Cr, Fe, Cu, Hf, Nb, Ta, Th.

The reaction is exothermic, therefore metal is deposited at higher temperatures

■ Separation of WO_2 and W. The process uses H_2O and I_2 as carrier gases

$$WO_{2(s)} + I_2 \underset{1000\ ^\circ C}{\overset{800\ ^\circ C}{\rightleftharpoons}} WO_2I_{2(g)}$$

$$W_{(s)} + 2H_2O + 3I_2 \underset{800\ ^\circ C}{\overset{1000\ ^\circ C}{\rightleftharpoons}} WO_2I_{2(g)} + 4HI$$
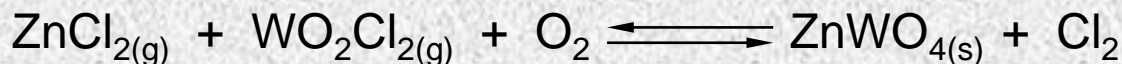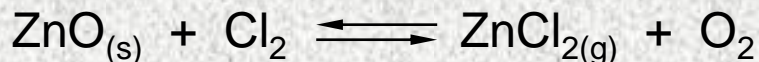
W WO_2

1000 °C   800 °C

Transport reactions involving volatile intermediates

■ Synthesis of the nickel chromite $NiCr_2O_4$ from NiO and Cr_2O_3 is very slow, but speeds up in a presence of oxygen:

$$Cr_2O_{3(s)} + 1.5O_2 \rightleftharpoons 2CrO_{3(g)}$$

$$2CrO_{3(g)} + NiO \rightleftharpoons NiCr_2O_4 + 1.5O_2$$
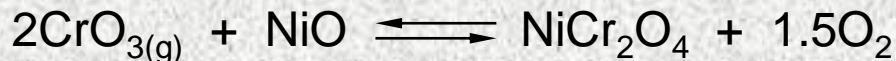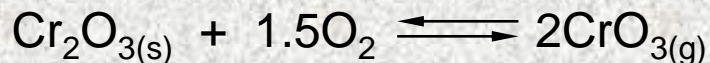
■ $ZnWO_4$ is synthesized from ZnO and WO_3 (heated at 1060 °C) in a presence of Cl_2. Crystals of $ZnWO_4$ grow at 980 °C due to formation of volatile chlorides:

$$ZnO_{(s)} + Cl_2 \rightleftharpoons ZnCl_{2(g)} + O_2$$

$$WO_{3(s)} + Cl_2 \rightleftharpoons WO_2Cl_{2(g)} + O_2$$

$$ZnCl_{2(g)} + WO_2Cl_{2(g)} + O_2 \rightleftharpoons ZnWO_{4(s)} + Cl_2$$

■ Addition of I_2 to halogen incandesced lamps increases the temperature and the lifetime of the tungsten filament:

$W_{(s)} \dashrightarrow W_{(s)}$ (tungsten precipitation on the bulb's wall)

$W + I_2 \rightleftharpoons WI_{2(g)}$ (tungsten recovery from bulb's wall)

$T \sim 300\ °C$

$T \sim 1500\ °C$