Lecture 6: Solid state synthesis

- The products are typically **single crystals**, **polycrystalline powders** or **thin films**
  - Recipes? Journal papers!

- Solid state reaction
- Low-temperature methods
- High-pressure synthesis
  - Multi-anvil press
  - Diamond-anvil cell
- Thin films
  - Sputtering
  - Chemical vapor deposition
  - Atomic layer deposition

Figure: http://lulelaboratory.blogspot.fi/

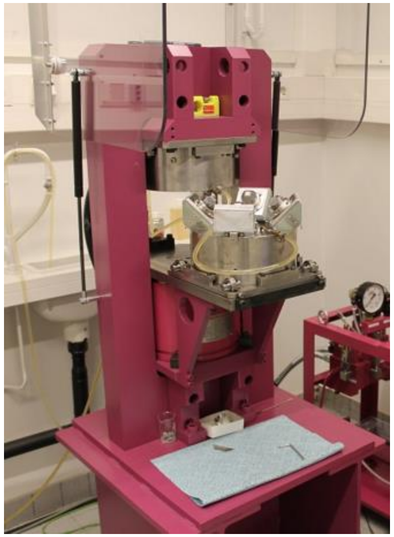


Figure: Aalto University

Figure: Aalto University

Solid state reaction

See [Solid State Chemistry Wiki]

- The oldest, simplest and still most widely used method to make inorganic solids
  - Mix together powdered reactants (and possibly press them into pellets)
  - Heat in a furnace for prolonged periods
- **Diffusion in solids is very slow**, thus high temperatures are needed
  - Although the reactants may be well mixed at the level of individual particles (e.g. µm scale), they are very inhomogeneous on the atomic level
- Solid state reactions are under **thermodynamical control**
  - The most stable phase or mixture at the reaction conditions will form
  - Reaction mechanisms and kinetics are usually not known well
  - Separating impurity phases from the product is usually impossible

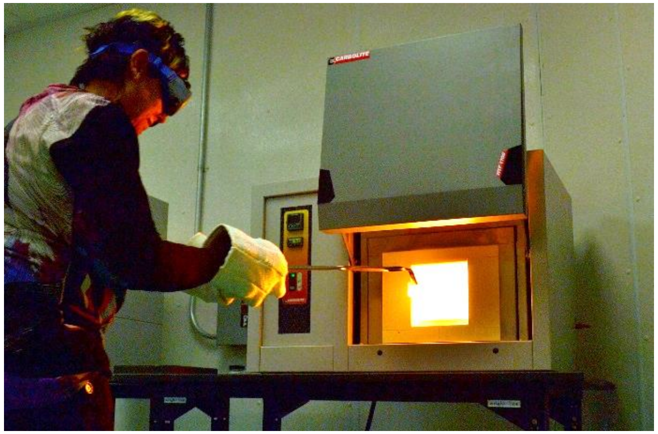
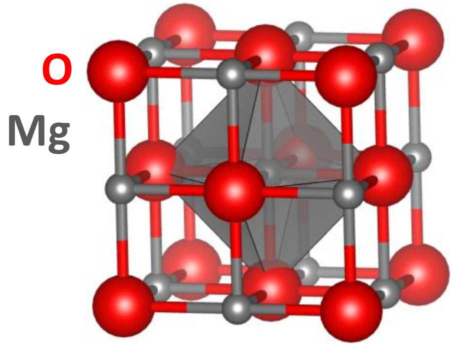


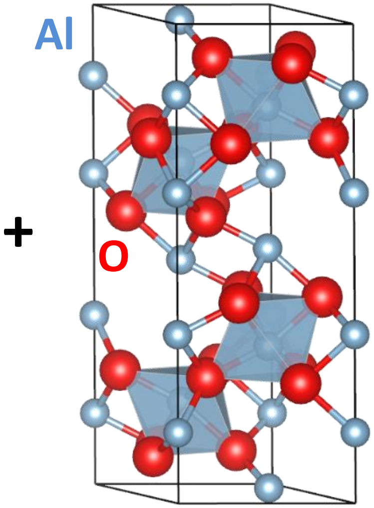
Figure: Aalto University

Example: $MgAl_2O_4$ spinel

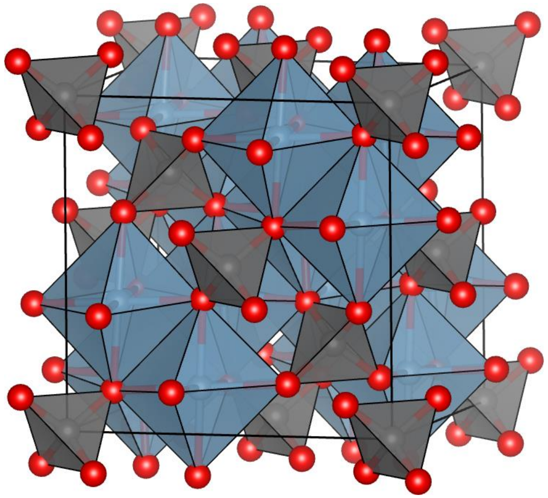
- Let’s consider a solid state reaction of MgO and Al_2O_3 powders to $MgAl_2O_4$ spinel
- Close-packed anions in all three compounds

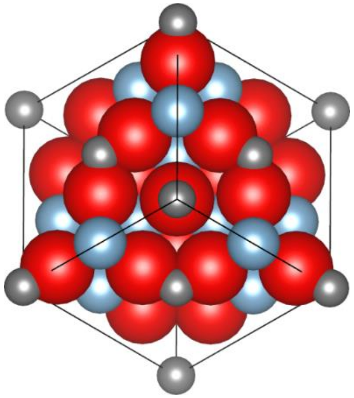


+



→





MgO (*Fm*-3*m*)
ccp anions
Octahedral Mg

Al_2O_3(*R*-3*c*)
hcp anions
Octahedral Al

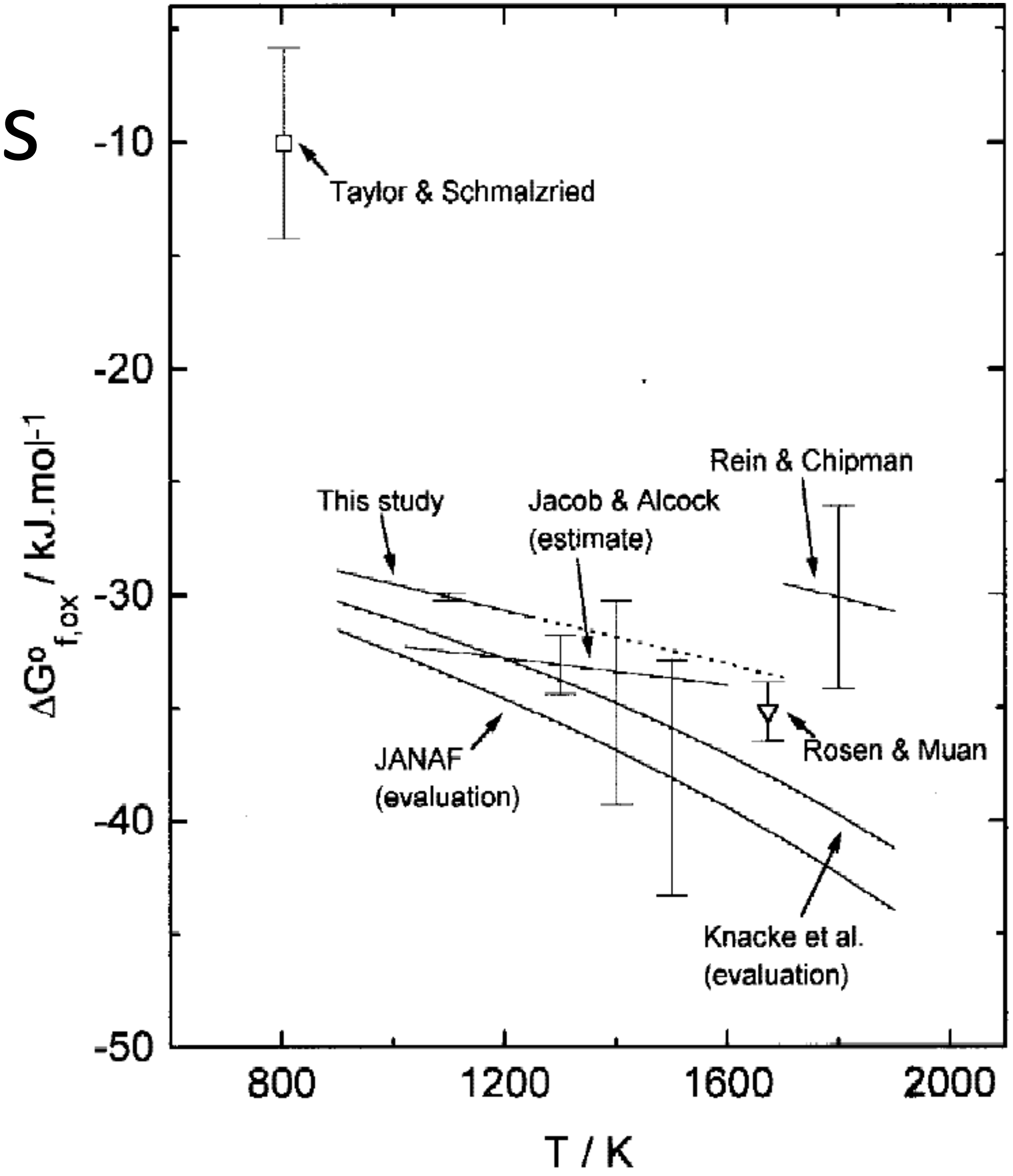
$MgAl_2O_4$ (*Fd*-3*m*)
ccp anions
Mg in tetrahedral interstitials (1/8 occupied)
Al in octahedral. interstitials (2/4 occupied)

Figures: AJK

$MgAl_2O_4$ thermodynamics

Literature data for Gibbs free energy of formation of $MgAl_2O_4$ from simple oxides MgO and Al_2O_3 ($\Delta G^0_{f,ox}$)

J. Am. Ceram. Soc., **1998**, 81, 209–212.



$MgAl_2O_4$ spinel from MgO and Al_2O_3

Ref: West p. 190

- The first few atomic layers of product nuclei may form easily, but subsequent growth or thickening of the product is more difficult
  - The two reactants, MgO and Al_2O_3, are separated by a spinel layer.
- A complex counter-diffusion process of Mg^{2+} and Al^{3+} ions is required
- As the reaction proceeds, the spinel layer thickens, the diffusion path length increases, and the reaction slows down (Mg^{2+} and Al^{3+} diffuse very slowly)
- Heating for **1 week at 1500°C** would be required to form a fairly pure spinel product

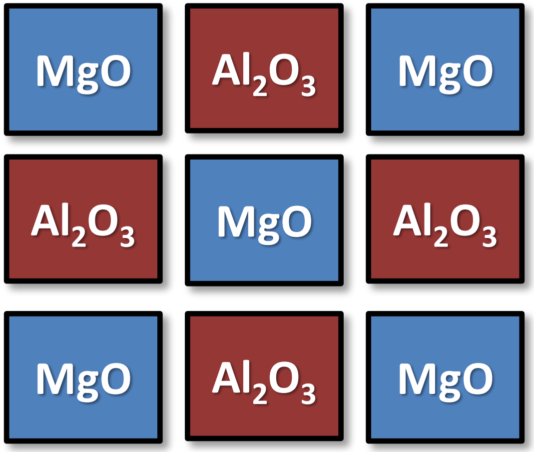
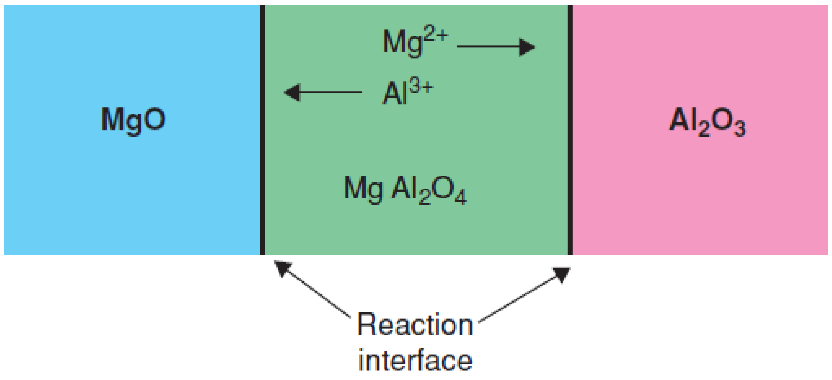


Figure: AJK

Idealized reaction mixture composed of grains of MgO and Al_2O_3. In practice, the grains will be irregular and not so arranged. Spinel formation occurs at the interfaces



Spinel product layer separating MgO and Al_2O_3 reactant grains

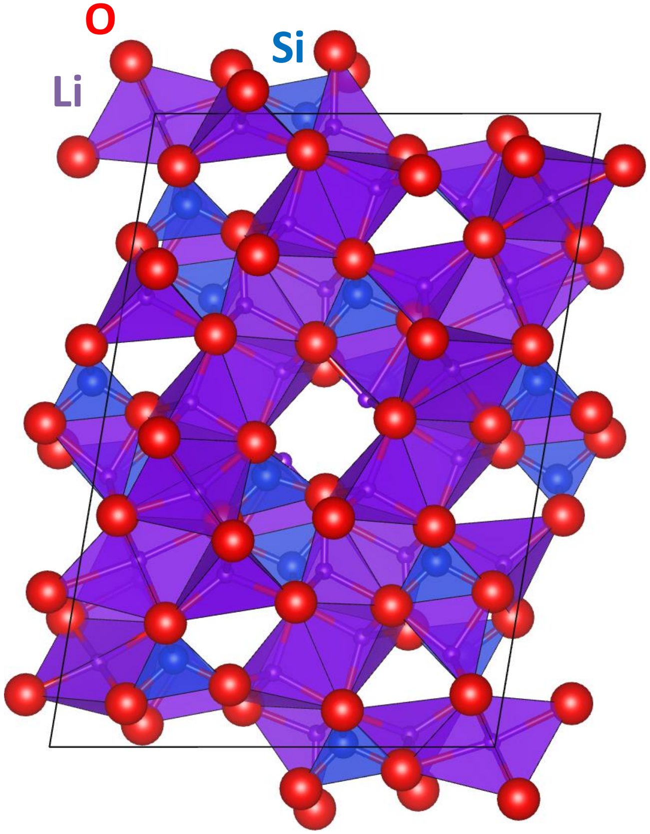
Some practical considerations for solid state reactions

- The $MgAl_2O_4$ spinel synthesis is difficult since both reagents, MgO and Al_2O_3, are very stable, inert, non-reactive solids
  - Solid state reactions may be easier if one or more of the starting materials is chemically reactive and/or contains ions that can diffuse easily
- Other possible problems:
  - Loss of reactants by evaporation (e.g. alkali metal oxides, PbO, Bi_2O_3, HgO)
  - Reactivity towards the container (e.g. transition metal-containing materials).
- Issues to consider when planning a solid state reaction:
  - Choice of starting materials (purity, reactivity, how finely they are ground)
  - Container (Pt / Ta / Au / Al_2O_3 / SiO_2 / graphite)
  - Heat treatment conditions (temperature program)
  - Atmosphere, especially O_2 partial pressure (pO_2) for oxides
    - Oxidizing (Air, O_2)
    - Inert or slightly reducing (vacuum, N_2, Ar)
    - Strongly reducing (H_2/Ar mix, H_2)

Solid state reaction of Li_4SiO_4

- Lithium orthosilicate Li_4SiO_4 is the parent phase for a family of Li^+ ion conductors that can be prepared by the following reaction (24 h at **~800 °C**):

  $2Li_2CO_3 + SiO_2 \rightarrow Li_4SiO_4 + 2CO_2$
- Problems:
  - Li_2CO_3 melts and decomposes above **~720 °C**.
  - It also is reactive towards most container materials, including Pt and silica glass.
- Solution:
  - Use gold containers
  - Carry out decomposition and pre-reaction of Li_2CO_3 at **~650 °C** for a few hours before final firing at 800–900 °C overnight.



Li_4SiO_4 (P 1 21/m 1)

Ref: West p. 193

Use of homogeneous, single-source precursors

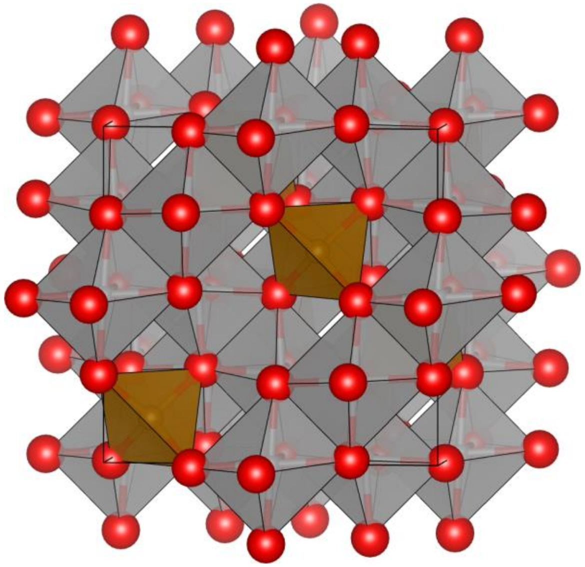
- Prepare a crystalline, homogeneous, single-phase precursor material that contains all the required cations in the correct ratio.
- Precursor should decompose to the desired product on heating.

- As an example, let’s see how $NH_4Fe(CrO_4)_2$ can be used as a precursor to $FeCr_2O_4$.
- The precursor is synthetized by precipitation from aqueous solution:

  Fe^{3+} (aq) + $2CrO_4^{2-}$ (aq) + NH_4^+ (aq) → $NH_4Fe(CrO_4)_2$

- The precursor decomposes on heating (at 1150 °C):

  $NH_4Fe(CrO_4)_2 \rightarrow 2FeCr_2O_4 + 2NH_3 + H_2O + 7/2\ O_2$



$FeCr_2O_4$ (*Fd*-3*m*)
ccp anions
(spinel, like $MgAl_2O_4$)

Ref: West p. 201

Low temperature methods

- Low temperature methods can be used to achieve atomic scale mixing of reactants, in gas, liquid, or even solid phases
  - Final heating at high *T* may be needed, especially for ceramic products
- May enable higher purity products than high temperature solid-state reaction, especially if prolonged heating at high temperature can be avoided
  - No contamination from container materials and furnace atmosphere
- Products with high chemical homogeneity are usually obtained

- Disadvantages:
  - Reagents are often costly and difficult to handle on a large scale
  - Considerable research may be required to optimize the synthesis of a particular material
  - Once suitable conditions have been found, they may not be readily applicable to the synthesis of related materials

Sol–gel method

See Solid State Chemistry Wiki

- The first stage is to prepare a homogeneous solution containing all the cationic ingredients in the desired ratio
- The solution is gradually dried and should transform
  - First to a viscous **sol** (particles of colloidal dimensions, ~1-1000 nm)
  - Finally to a transparent, homogeneous, amorphous solid known as a **gel**
  - Without precipitation of any crystalline phases
- The gel is then heated at high temperatures to remove volatile components trapped in the pores of the gel or chemically bonded hydroxyl and organic side-groups and to crystallize the final product.

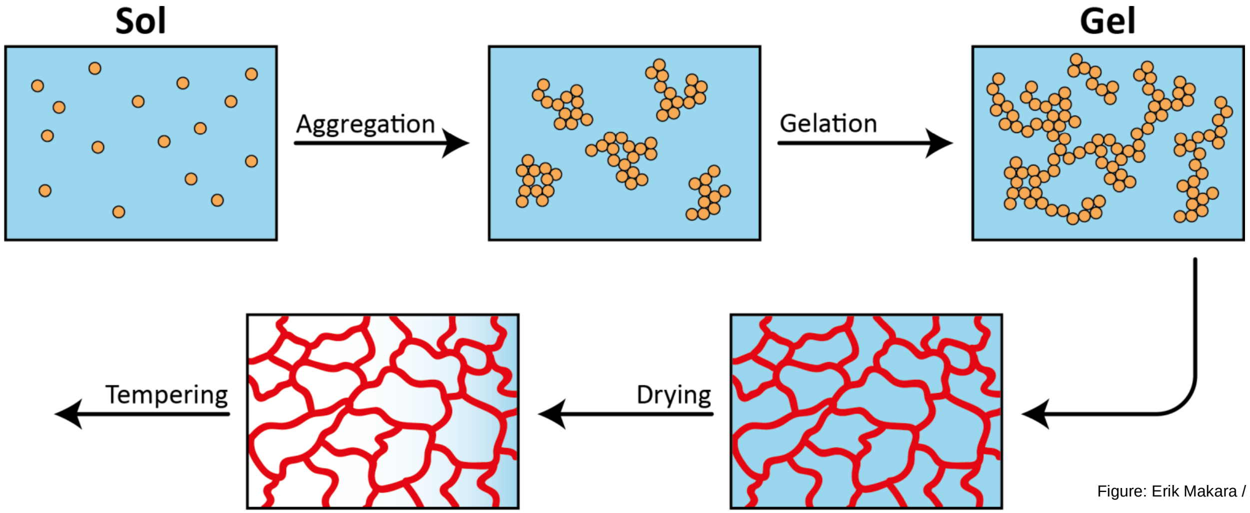
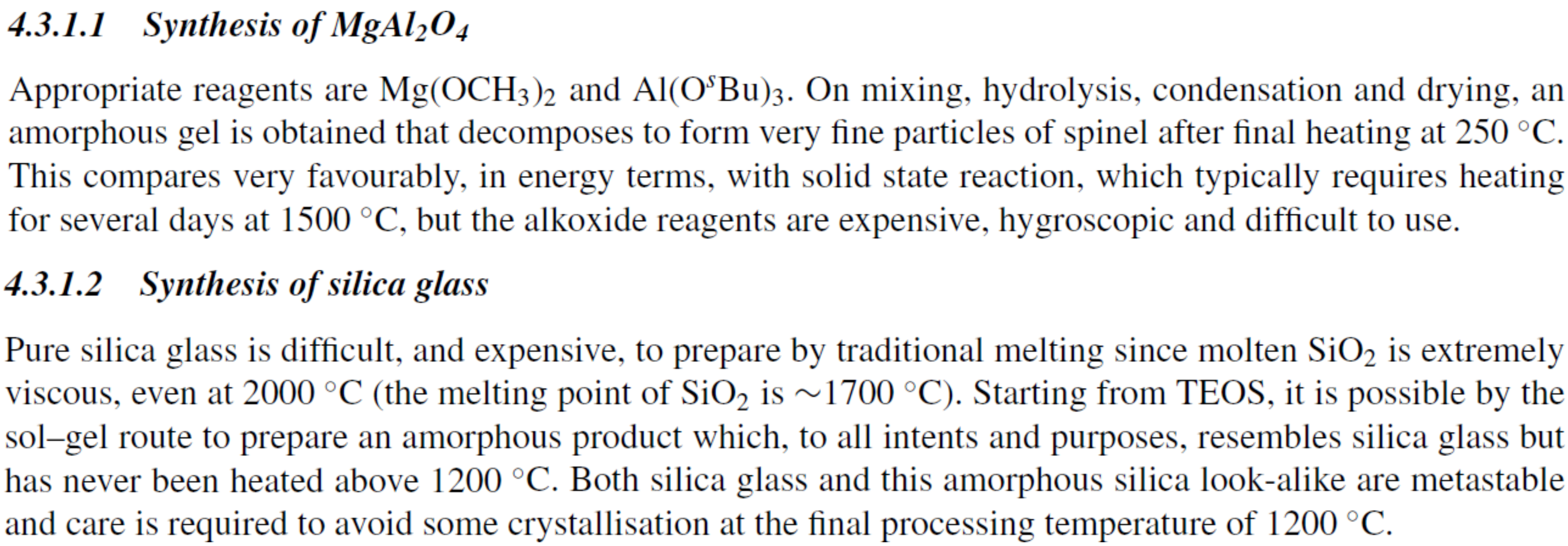


Figure: Erik Makara / Aalto

Ref: West p. 196

Alkoxide sol–gel method

- Organometallic precursors, particularly alkoxides, are widely used for the small-scale synthesis of known or new materials
  - Alkoxide: R-O$^-$-M$^+$ (for example, CH_3-O$^-$Na$^+$)
- The alkoxide-based sol–gel method is extremely versatile and can incorporate most elements of the periodic table

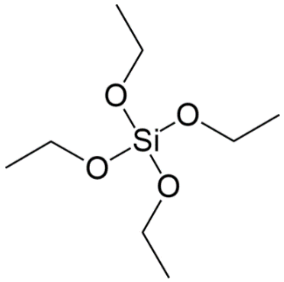


4.3.1.1 Synthesis of $MgAl_2O_4$

Appropriate reagents are $Mg(OCH_3)_2$ and $Al(O^sBu)_3$. On mixing, hydrolysis, condensation and drying, an amorphous gel is obtained that decomposes to form very fine particles of spinel after final heating at 250 °C. This compares very favourably, in energy terms, with solid state reaction, which typically requires heating for several days at 1500 °C, but the alkoxide reagents are expensive, hygroscopic and difficult to use.

4.3.1.2 Synthesis of silica glass

Pure silica glass is difficult, and expensive, to prepare by traditional melting since molten SiO_2 is extremely viscous, even at 2000 °C (the melting point of SiO_2 is ~1700 °C). Starting from TEOS, it is possible by the sol–gel route to prepare an amorphous product which, to all intents and purposes, resembles silica glass but has never been heated above 1200 °C. Both silica glass and this amorphous silica look-alike are metastable and care is required to avoid some crystallisation at the final processing temperature of 1200 °C.



TEOS = Tetraethyl orthosilicate

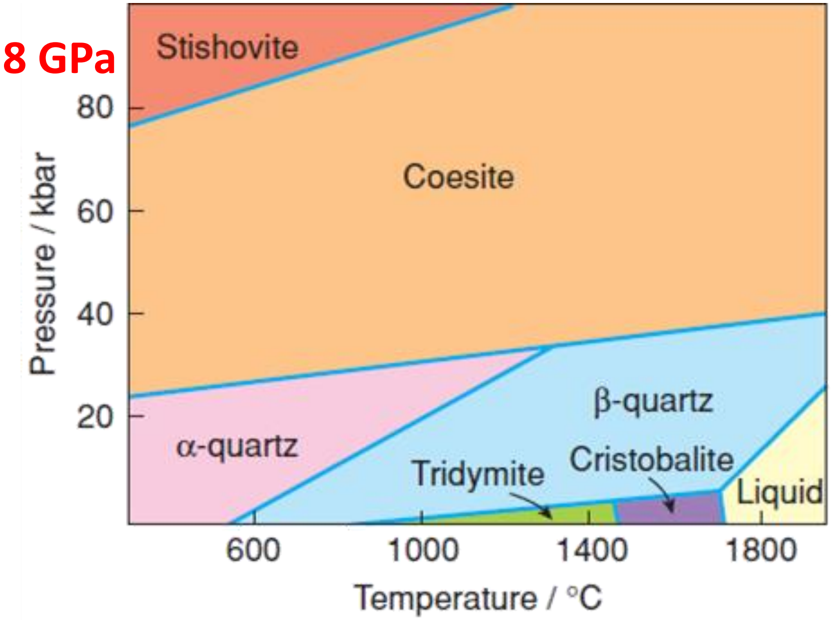
Ref: West p. 196

High-pressure chemistry

High-pressure chemistry (1)

See Solid State Chemistry Wiki

- High pressures (> 1 GPa = 10 000 atm) enable the synthesis of huge number of new materials that are unattainable in the atmospheric pressure
- In ultra-high pressures (Mbar range, > 100 GPa), the compression energy rivals or even exceeds the energy of the chemical bond!
  - New materials that are completely unintuitive from the ”normal” point of view



Phase diagram of SiO_2

High-pressure chemistry (2)

Paul F. McMillan, *Chem. Soc. Rev.*, **2006**, *35*, 855 (DOI)

- By the time a typical solid or liquid is compressed to above a few hundred thousand atmospheres, its molar volume is reduced by approximately 50%
- Once the megabar range is reached, average interatomic distances can be decreased by up to a factor of two.
- Major changes will occur in the outer electron shells, leading to substantial modifications of the chemical and physical properties
- Even the arrangement of the Periodic Table has to be reconsidered for high pressure conditions.
- As a simple example, we can consider the typical alkaline earth metals such as Ca and Sr that possess a fully close-packed ***fcc*** structure at ambient conditions
- However, pressurising Ca to P > 200 kbar (20 GPa) causes it to transform to a ***less efficiently*** packed ***bcc*** structure with a lower coordination of the metal atoms
  - Pressure-induced mixing occurring between 3d and 4s electronic shells, giving Ca the character of a transition metal rather than an alkaline earth element

High-pressure chemistry (3)

- Ultimately, most substances should become metallic at the most extreme pressures, as the close approach of atoms results in electronic overlap
- In moderate pressures (< 10 GPa), the pressure effects are not as extreme as in ultra-high pressures and typical phenomena are for example the increase of coordination number and structure type
  - In moderate pressures, a huge number of new materials that are only metastable in atmospheric pressure can be realized
  - Often the new materials remain intact in atmospheric pressure (e.g. diamond!)

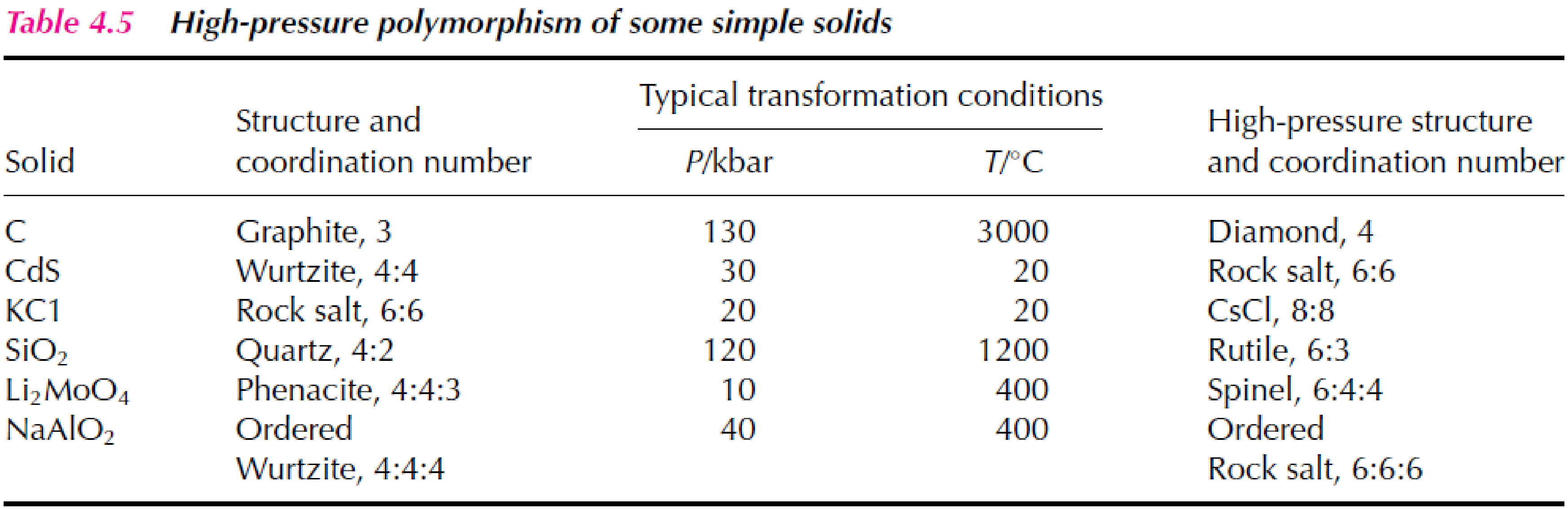


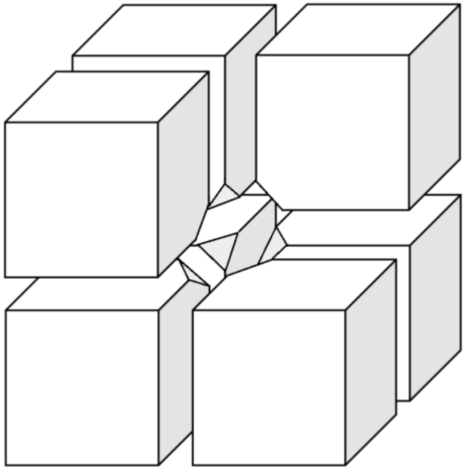
Table 4.5 ***High-pressure polymorphism of some simple solids***

Solid	Structure and coordination number	Typical transformation conditions		High-pressure structure and coordination number
		P/kbar	*T*/°C	
C	Graphite, 3	130	3000	Diamond, 4
CdS	Wurtzite, 4:4	30	20	Rock salt, 6:6
KC1	Rock salt, 6:6	20	20	CsCl, 8:8
SiO_2	Quartz, 4:2	120	1200	Rutile, 6:3
Li_2MoO_4	Phenacite, 4:4:3	10	400	Spinel, 6:4:4
$NaAlO_2$	Ordered Wurtzite, 4:4:4	40	400	Ordered Rock salt, 6:6:6

Ref: West p. 226

Multi-anvil press

- Sample is compressed between anvils, either cubic or octahedral
- Heating by running a current through graphite
- Pressures of up to 20 GPa (200 000 atm)
- Used mainly for materials synthesis
- Characterization done mainly *ex-situ* (outside the press)

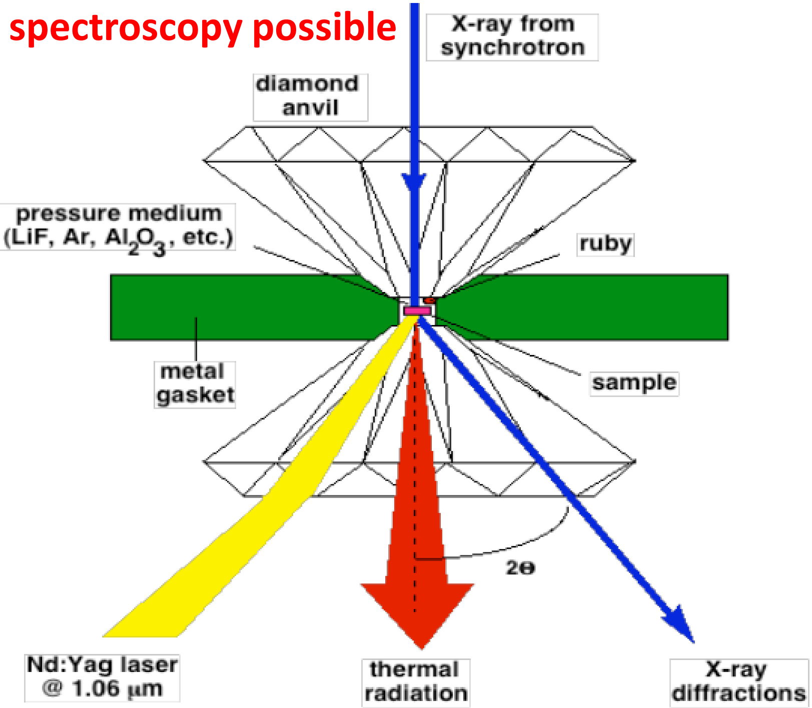


Octahedral 8-anvil with eight corner-cut cubes enclosing an octahedral sample space (Kawai cell)

Figures: Linda Sederholm / Aalto

Diamond anvil cell

In-situ X-ray or Raman spectroscopy possible



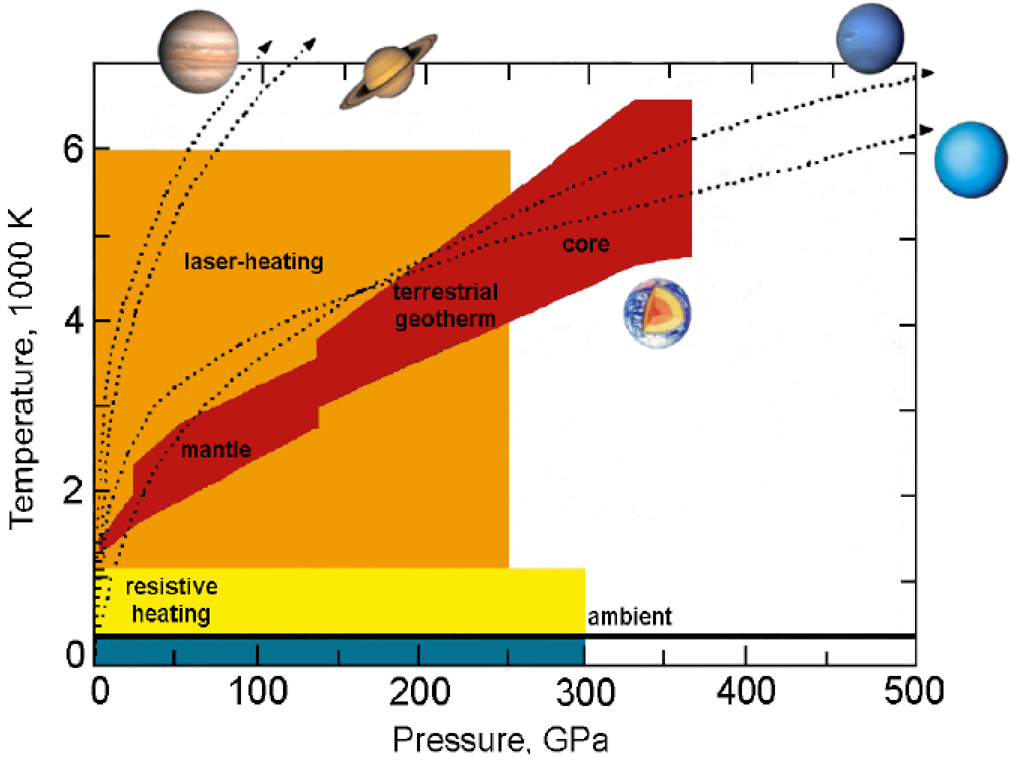


Figure: Choong-Shik Yoo, Washington State University

The most incompressible metal osmium at static pressures above 750 gigapascals

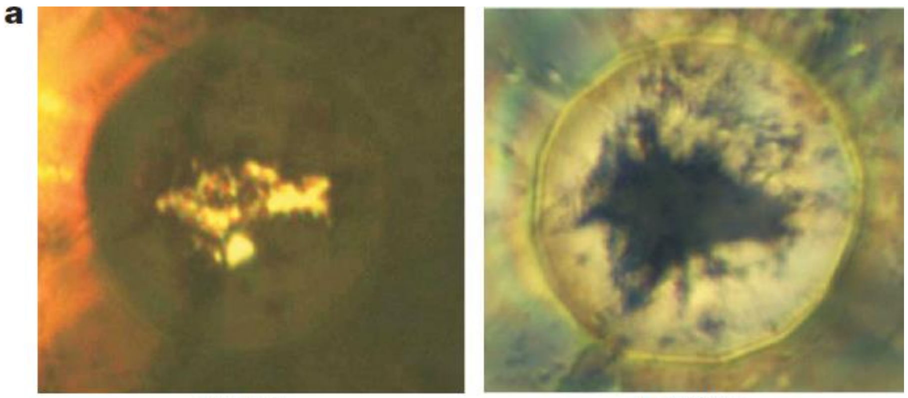
L. Dubrovinsky[1]*, N. Dubrovinskaia[2]*, E. Bykova[1,2], M. Bykov[2], V. Prakapenka[3], C. Prescher[3], K. Glazyrin[4], H.-P. Liermann[4], M. Hanfland[5], M. Ekholm[6,7], Q. Feng[6,7], L. V. Pourovskii[6,8], M. I. Katsnelson[9,10], J. M. Wills[11] & I. A. Abrikosov[7,12]

10 SEPTEMBER 2015 | VOL 525 | NATURE | 227

Transparent dense sodium

NATURE|Vol 458|12 March 2009 **LETTERS**

Yanming Ma[1,2], Mikhail Eremets[3], Artem R. Oganov[2,4]†, Yu Xie[1], Ivan Trojan[3], Sergey Medvedev[3], Andriy O. Lyakhov[2]†, Mario Valle[5] & Vitali Prakapenka[6]

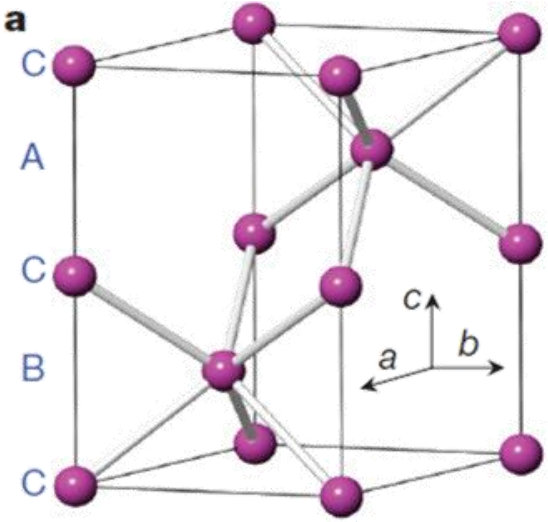


199 GPa 156 GPa

Na-Na distance decreases from
3.72 Å to **1.89 Å**

Na 3s valence electrons are pushed to the interstitial space

Na metal transforms to optically transparent ”self-salt” (Na^+ / interstitial e^-)



Structure of Na-*hP4* (*$P6_3/mmc$*) predicted by USPEX

Thin-film techniques

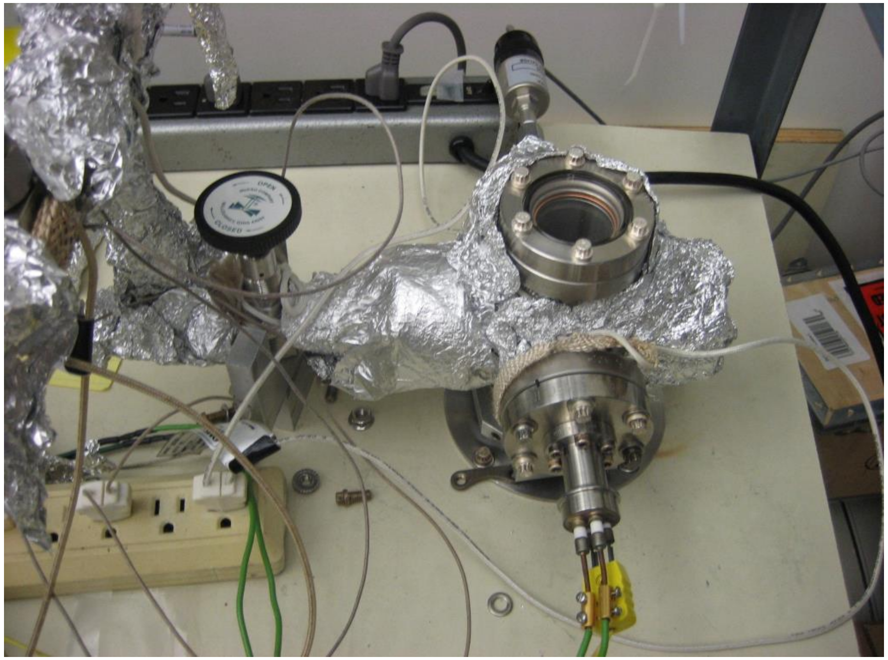
Thin film techniques

- Physical Vapor Deposition
  - Sputtering and evaporation
- Chemical Vapor Deposition (CVD)
- Atomic Layer Deposition (ALD)

Figure: MPA industrie

CVD reactor for TiC, TiCN, Al_2O_3, TiN deposition on hard metals and steels

Figure: Zaera Group at UC Riverside



A homemade ALD reactor. A small stainless steel chamber houses a nickel-made sample holder, where the substrate can be heated to up to 500 ^oC. A gas feeding line is used to introduce the precursor into the reaction chamber. A homemade bubbler is used to carry the vapor of liquid precursors into the reactor. The whole ALD reactor can be heated to up to 150 ^oC to avoid the water contamination. A separate pumping line is set to purify the precursor in order to avoid contaminating the sample in the reaction chamber. An Alcatel 2008A vacuum pump is used to pump the system down to a base pressure few mtorr.

Sputtering and evaporation

See [Solid State Chemistry Wiki]

Physical Vapor Deposition (PVD)

Pressure 10^{-1} .. 10^{-2} Torr of inert gas (e.g. Ar, Xe)
Sputtering involves the transfer of momentum from the gaseous ions to the cathode in such a way that atoms or ions are ejected (sputtered) from the cathode to the substrate

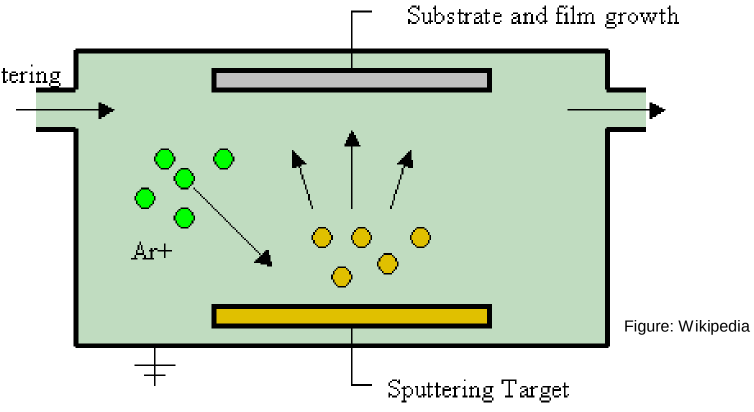
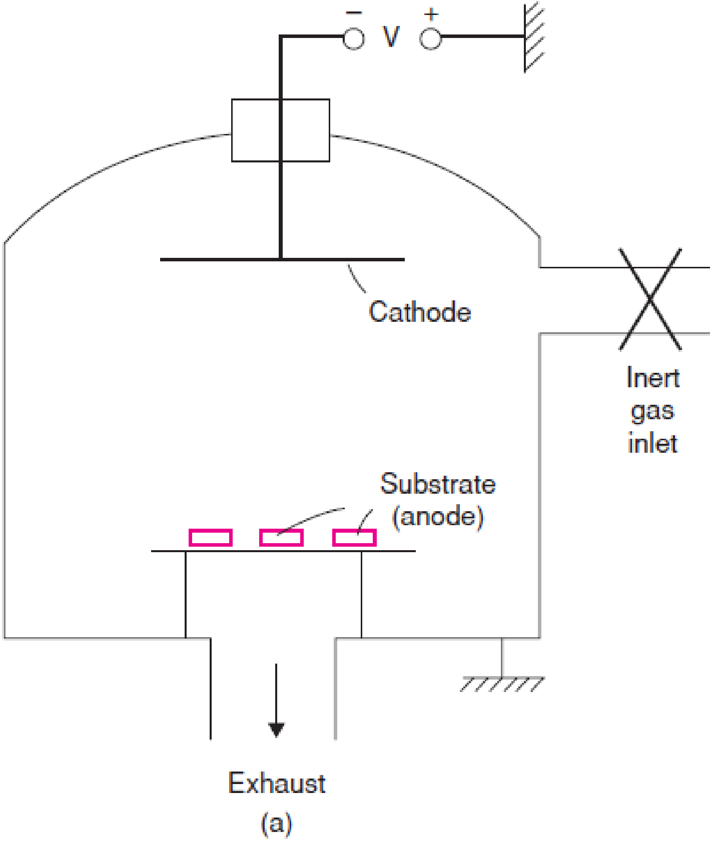
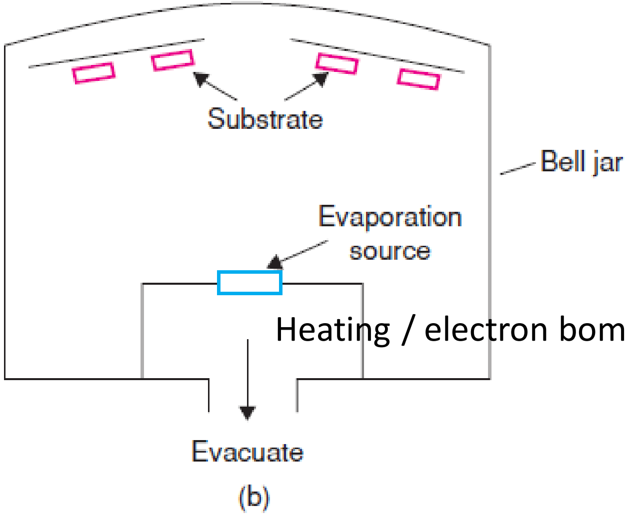


Figure: Wikipedia



Vacuum evaporation method: High vacuum of 10^{-6} Torr or better



Heating / electron bombardment

Ref: West p. 222

Figure 4.17 (a) Cathode sputtering equipment and (b) vacuum evaporation equipment for thin-film deposition.

Chemical Vapor Deposition (1)

See Solid State Chemistry Wiki

- Extremely important technique of making high-purity thin films and coatings for
  - Industrial applications, especially in electronics,
  - Fundamental scientific research
- Precursor molecules containing the elements of interest are decomposed in the gas phase and the products deposit as thin films.
- Example of a simple, volatile precursor molecule:
  - SiH_4 -> Si (polycrystalline) + $2H_2$
- To deposit compounds such as GaAs, a mixture of precursors is needed
  - An alternative is to use (organometallic) **single-source precursors** which contain all the elements of interest and in the correct ratio

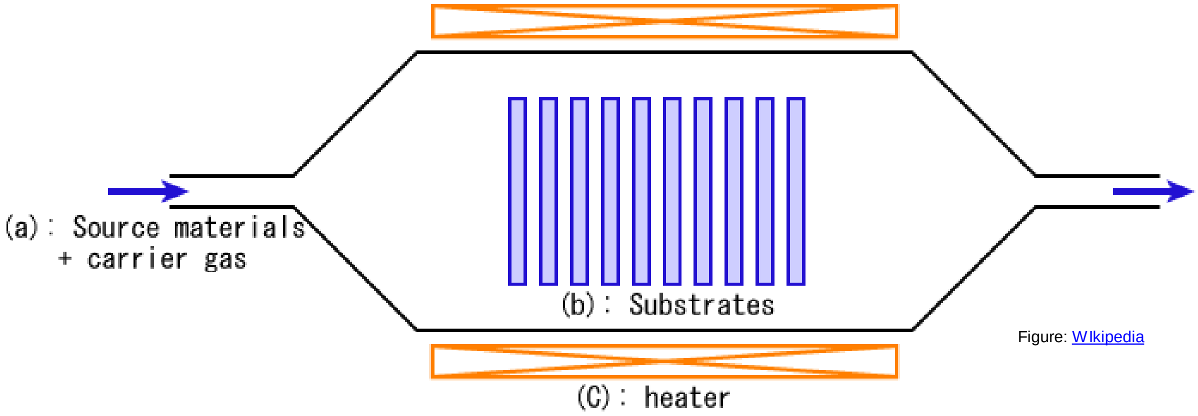


Figure: WIkipedia

Chemical Vapor Deposition (2)

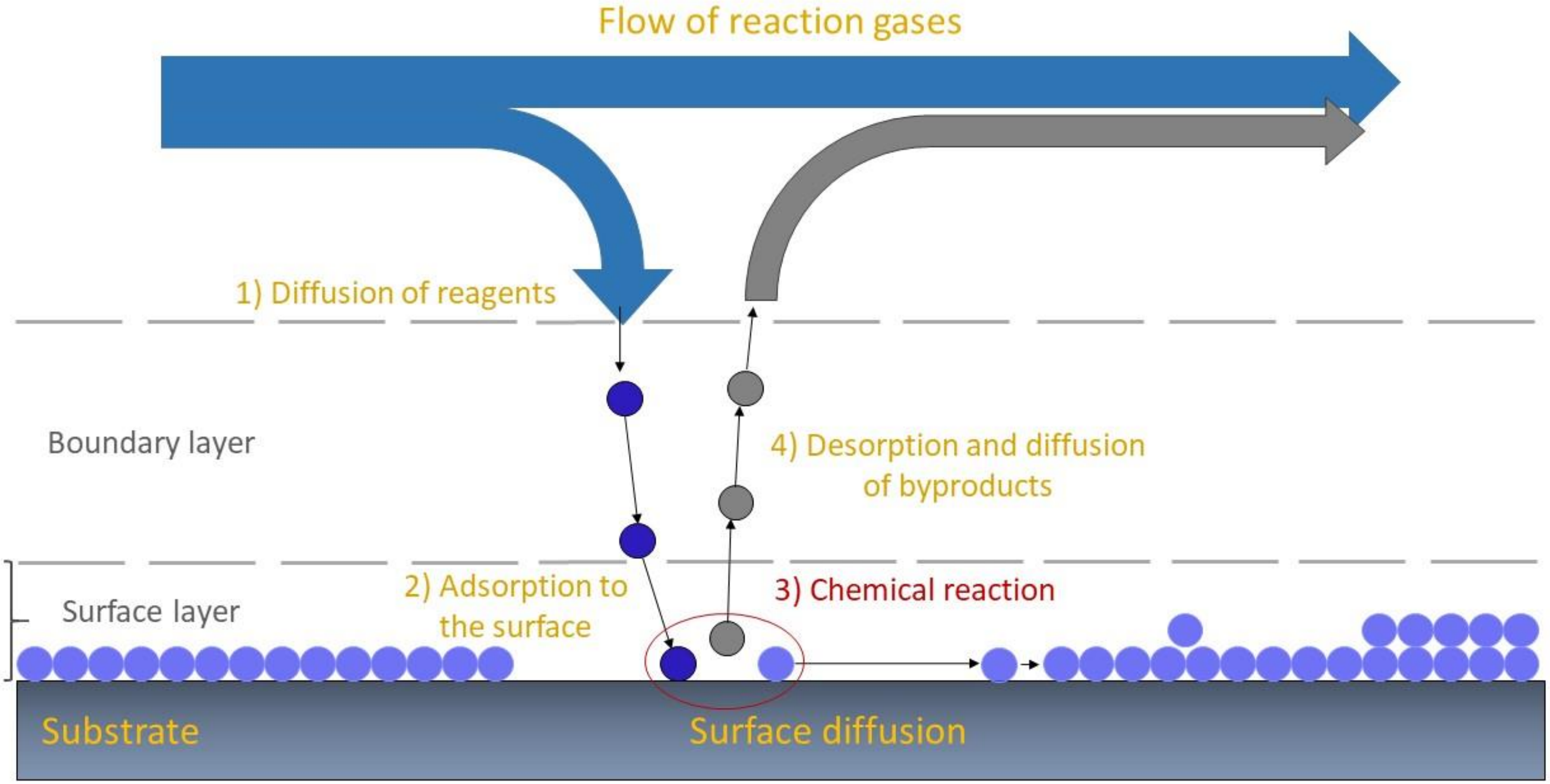


Figure: Samuel Rantataro / Aalto

Chemical Vapor Deposition (3)

Examples of CVD processes:

$$Si(CH_2CH_3)_4 + 14O_2 \longrightarrow SiO_2 + 8CO_2 + 10H_2O$$

$$GeH_4 \xrightarrow{h\nu} Ge + 2H_2$$

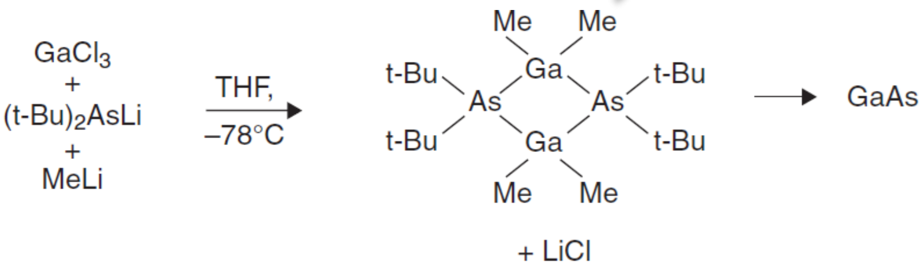
$$CrCl_2 + H_2 \xrightarrow{600\,^\circ C} Cr + 2HCl$$

$$W(CO)_6 \rightarrow W + 6CO$$

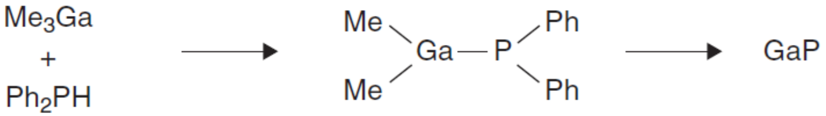
$$Fe(C_5H_5)_2 + 7/2O_2 \rightarrow Fe + 10CO + 5H_2O$$

$$Ga(CH_3)_3 + AsH_3 \xrightarrow[h\nu]{heat} GaAs + 3CH_4$$

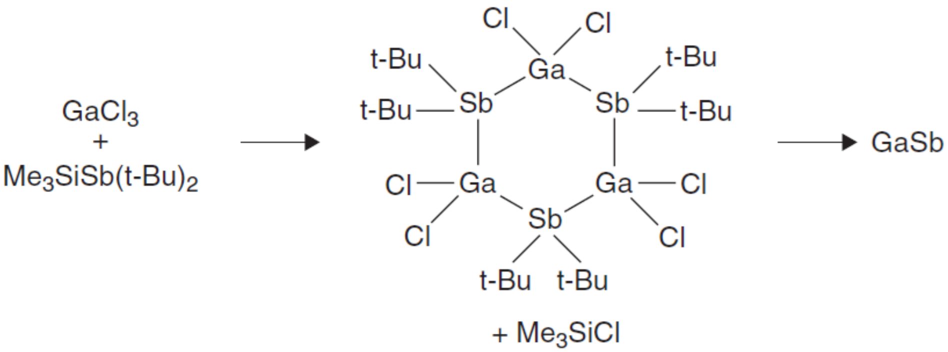
Single-source precursor molecules for **metal-organic CVD** (MOCVD)



(a)



(b)

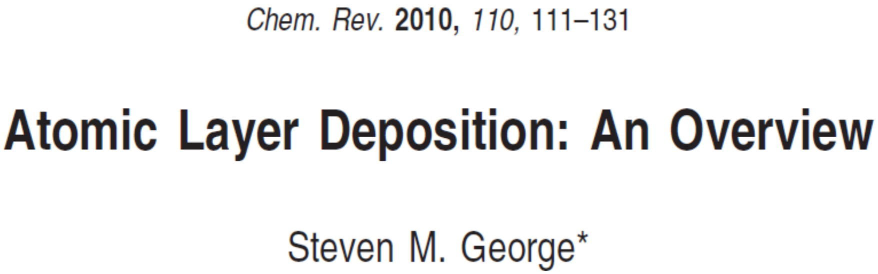


(c)

Ref: West p. 217

Atomic Layer Deposition (1)

See Solid State Chemistry Wiki



Chem. Rev. **2010,** *110,* 111–131

Atomic Layer Deposition: An Overview

Steven M. George*

Crystallinity of inorganic films grown by atomic layer deposition: Overview and general trends

Ville Miikkulainen,[1,a)] Markku Leskelä,[1,b)] Mikko Ritala,[1,c)] and Riikka L. Puurunen[2,d)]

JOURNAL OF APPLIED PHYSICS **113**, 021301 (2013)

A brief review of atomic layer deposition: from fundamentals to applications

Richard W. Johnson[1,3], **Adam Hultqvist**[2,3] **and Stacey F. Bent**[1,2,*]

Materials Today • Volume 17, Number 5 • June 2014

Atomic Layer Deposition (2)

For example: ZnO

Materials Today • Volume 17, Number 5 • June 2014

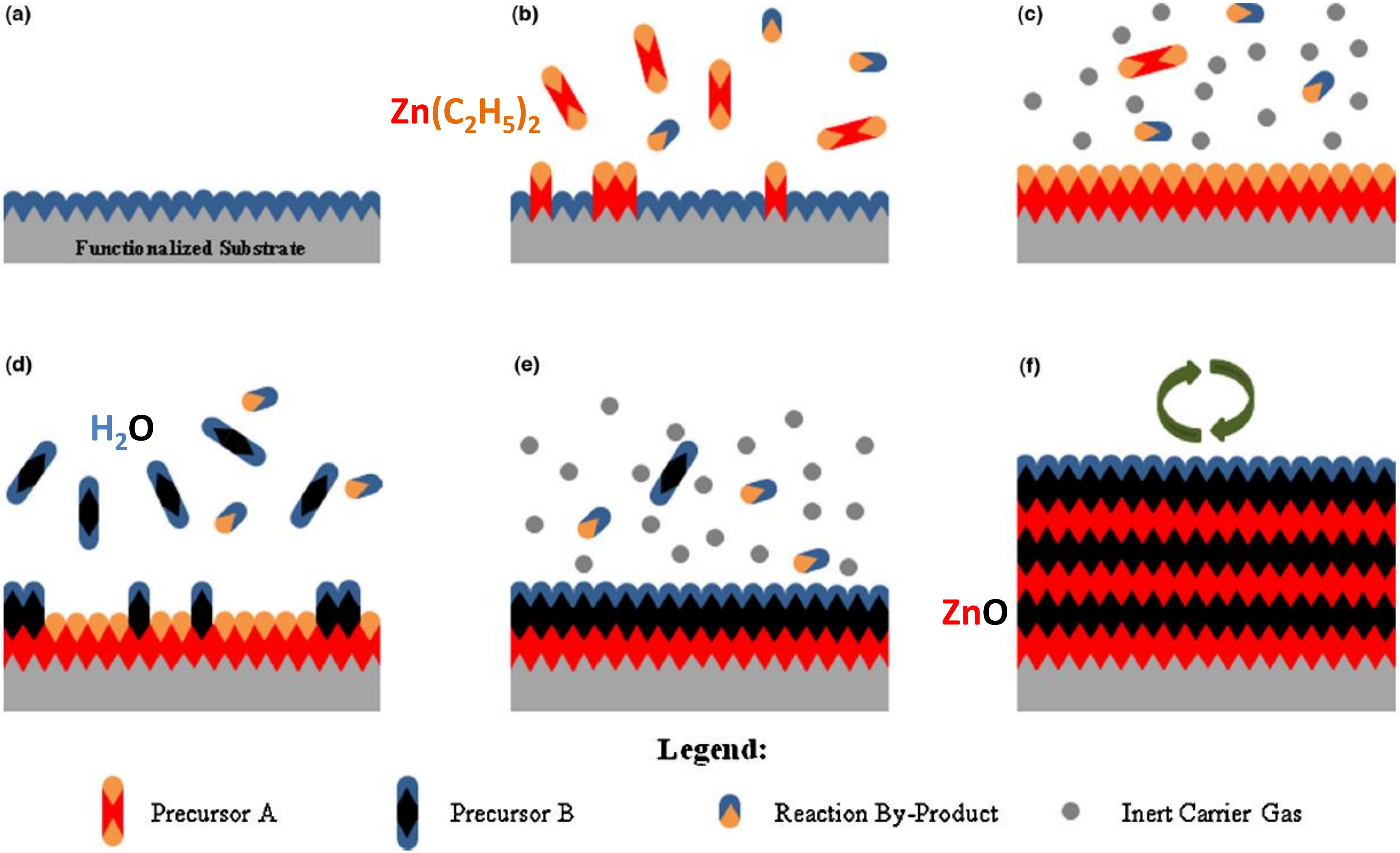


FIGURE 1

Schematic of ALD process. (a) Substrate surface has natural functionalization or is treated to functionalize the surface. (b) Precursor A is pulsed and reacts with surface. (c) Excess precursor and reaction by-products are purged with inert carrier gas. (d) Precursor B is pulsed and reacts with surface. (e) Excess precursor and reaction by-products are purged with inert carrier gas. (f) Steps 2–5 are repeated until the desired material thickness is achieved.

Atomic Layer Deposition (3)

- Based on sequential, self-limiting reactions
  - Offers exceptional conformality on high aspect ratio structures
  - Thickness control at the Ångstrom level (usually ~10-100 nm thickness; max ~1 µm)
  - Tunable film composition
- Powerful tool for many industrial and research applications

Chem. Rev. **2010**, *110*, 111–131

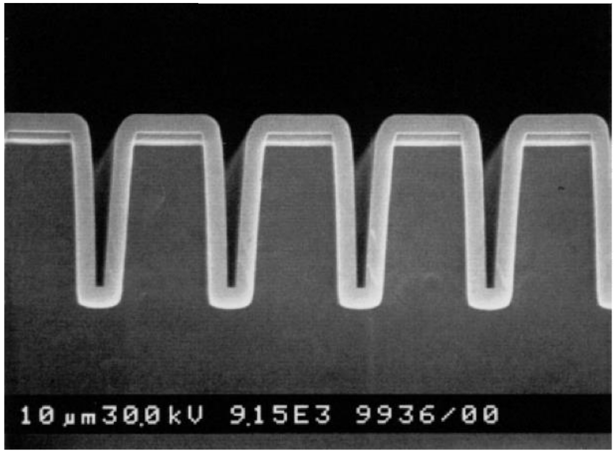


Figure 3. Cross-sectional SEM image of an Al_2O_3 ALD film with a thickness of 300 nm on a Si wafer with a trench structure.

TABLE 1 Materials Today • Volume 17, Number 5 • June 2014

List of materials grown by ALD [5,25–30].

Elemental	Oxides	Nitrides	Sulfides	Other compounds
C, Al, Si, Ti, Fe, Co, Ni, Cu, Zn, Ga, Ge, Mo, Ru, Rh, Pd, Ag, Ta, W, Os, Ir, Pt	Li, Be, B, Mg, Al, Si, P, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Sr, Y, Zr, Nb, Ru, Rh, Pd, In, Sn, Sb, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, W, Ir, Pt, Pb, Bi	B, Al, Si, Ti, Cu, Ga, Zr, Nb, Mo, In, Hf, Ta, W	Ca, Ti, Mn, Cu, Zn, Sr, Y, Cd, In, Sn, Sb, Ba, La, W	Li, B, Mg, Al, Si, P, Ca, Ti, Cr, Mn, Co, Cu, Zn, Ga, Ge, As, Sr, Y, Cd, In, Sb, Te, Ba, La, Pr, Nd, Lu, Hf, Ta, W, Bi

TABLE 2

Available reactant groups for specific elements [4,25–30].

Elemental	Halides	Alkyls	Cyclopentadienyls	β-diketonates	Other reactants
Mg, Mn, Zn, Ga, Cd, In, Sn	B, C, Ti, V, Cr, Mn, Cu, Zn, Ga, Ge, Zr, Nb, Mo, Cd, In, Sn, Sb, Hf, Ta, W, Pb	Be, Al, Si, Zn, Ga, Ge, Cd, In, Sn, Hg	Mg, Sc, Ni, Sr, Y, Zr, Ru, Lu, Os, Pt	Mg, Ca, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Ga, Sr, Y, Zr, Ru, Pd, In, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Ir, Pt, Pb	Li, P, Ti, Fe, Co, Ni, Cu, Zn, Ge, As, Zr, Rh, Ag, Sb, Te, La, Pr, Yb, Hf, Ta, W, Ir, Pt, Pb, Bi

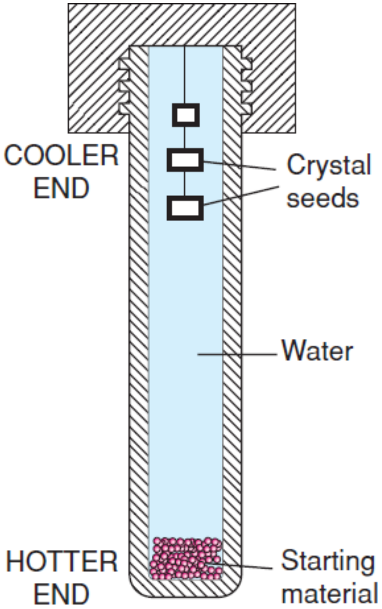
Extra slides

“Nice-to-know”-type material that is not needed for completing the exercises

Hydrothermal and solvothermal synthesis (1)

See [Solid State Chemistry Wiki]

- Hydrothermal synthesis involves heating reactants in water/steam at high pressures and temperatures
- The water has two functions pressure-transmitting medium and as a solvent, in which the solubility of the reactants is (*p*,*T*)-dependent
- The reactants and water are placed inside a PTFE-lined cylinder (autoclave / 'bomb') which is either sealed or connected to an external pressure control
- The bomb is placed in an oven, usually at T = 100–500°C
- A temperature gradient is maintained between the opposite ends of the growth chamber
- At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal
- Solvothermal synthesis is similar to hydrothermal synthesis but uses supercritical solvents or solvent mixtures
  - Supercritical fluid: Distinct liquid and gas phases do not exist
  - In water, the critical point occurs at around 374 °C and 22 MPa

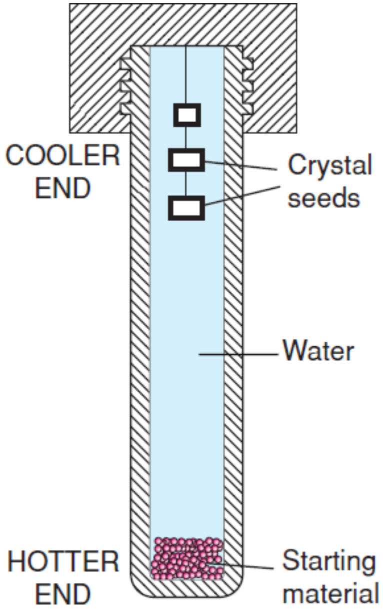


Ref: West p. 202

Hydrothermal and solvothermal synthesis (2)

2. Single crystals of quartz, SiO_2, which are used as piezoelectrics in a range of applications, are grown hydrothermally in a temperature gradient using the arrangement shown in Fig. 4.7(b). The solubility of SiO_2 in NaOH solution increases with increase in temperature; effectively, therefore, SiO_2 dissolves at the hot end, is transported to the cooler end by convection and crystallises on the suspended seeds. In this reaction, NaOH acts as a *mineraliser*. SiO_2 is only sparingly soluble in water, but solubility increases greatly when NaOH is dissolved in the water and speeds up the growth of quartz crystals by hydrothermal treatment.
3. Many phases can be prepared hydrothermally at much lower temperatures than would be required for solid state reaction. For example, to produce the magnetoplumbite phase, $BaFe_{12}O_{19}$, would require heating of the oxide components, $BaCO_3$ and α-Fe_2O_3, at e.g. 1250 °C but hydrothermally can be carried out at a much lower temperature:

$$Ba(OH)_2 + \alpha\text{-}FeOOH \xrightarrow{325\,^\circ C} BaFe_{12}O_{19}$$



Microwave synthesis

See Solid State Chemistry Wiki

- The use of microwave heating is well established in organic chemistry and is increasingly used in the inorganic synthesis, especially at the nanolevel
- Reaction times are orders of magnitude less than required for solid state reaction and side reactions are less problematic
  - Improved yield and reproducibility
- The microwave region covers the range 0.3 GHz (1 m)–300 GHz (1 mm), but most ovens are restricted to the frequency 2.45 GHz
  - Absorption at the range of molecular rotations -> increase in temperature
- Microwaves are absorbed and the sample is heated, to a certain penetration depth
  - Conventional heating, by contrast, requires in-diffusion of heat

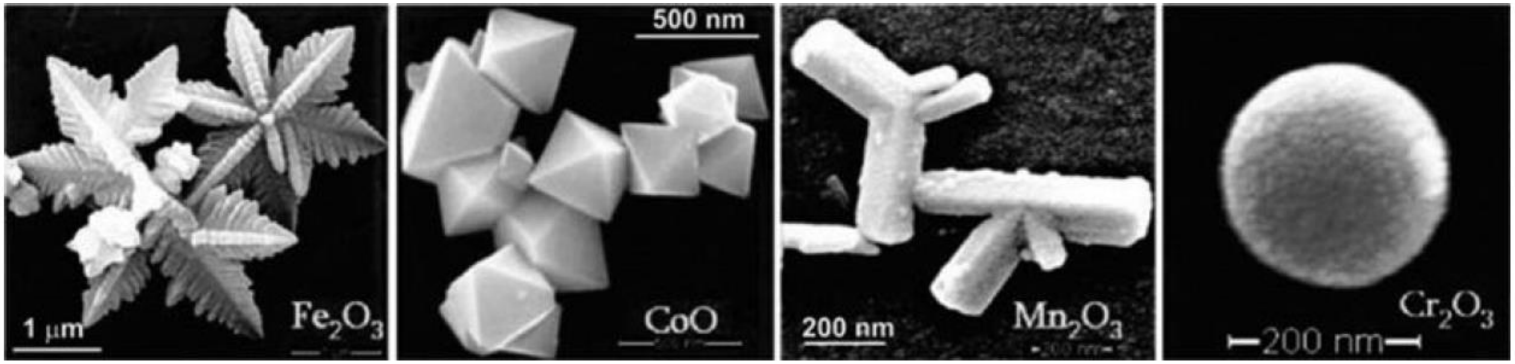


Figure 4.9 SEM images of various metal oxide nanostructures. Reproduced with permission from I. Bilecka and M. Niederberger, Nanoscale, 2, 1358, © 2010 Royal Society of Chemistry.

Ref: West p. 204