

Lecture 6: Synthesis

- The products are typically **single crystals**, **polycrystalline powders** or **thin films**
 - Recipes? Journal papers!
- Solid state reaction
- High-pressure synthesis
 - Multi-anvil press
 - Diamond-anvil cell
- Thin films
 - Sputtering
 - Chemical vapor deposition
 - Atomic layer deposition
- Low-temperature methods



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



Figure: Aalto University



Figure: Aalto University

Solid state reaction

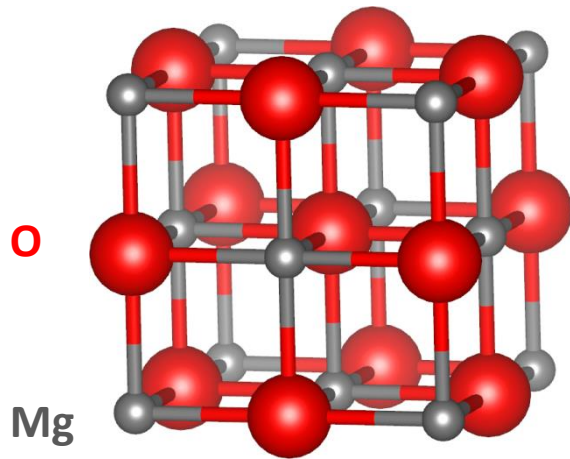
See [Solid State Chemistry Wiki](#)

- 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



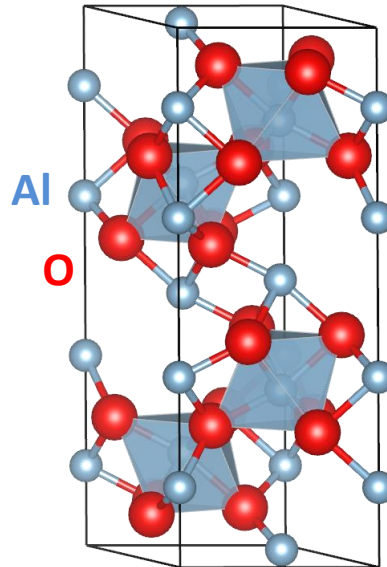
Example: MgAl_2O_4 spinel

- 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



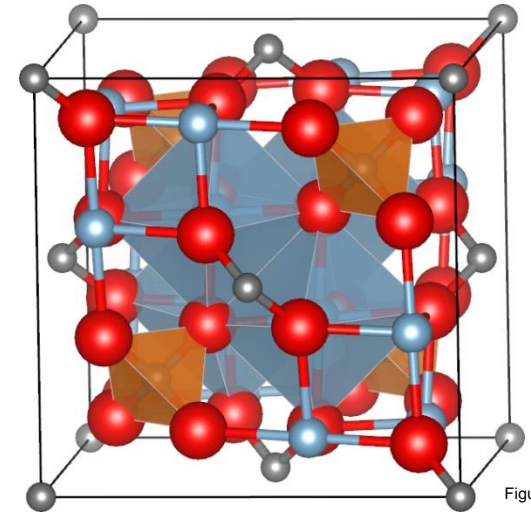
MgO ($Fm\text{-}3m$)

ccp anions



Al_2O_3 ($R\text{-}3c$)

hcp anions

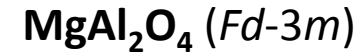
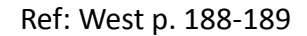


MgAl_2O_4 ($Fd\text{-}3m$)

ccp anions

Figures: AJK

MgAl₂O₄ spinel from MgO and Al₂O₃ (1)



fcc anion lattice.

Mg in tetrahedral interstitials
(1/8 occupied)

Al in octahedral interstitials (2/4 occupied)

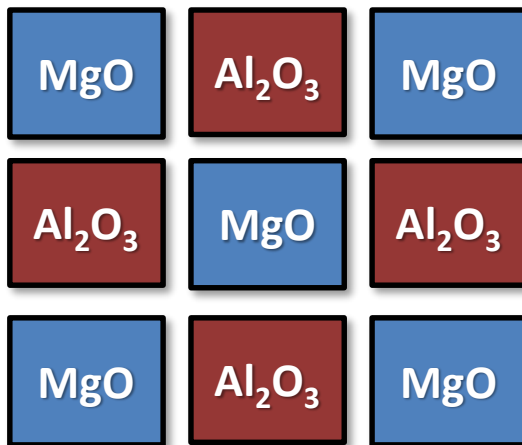
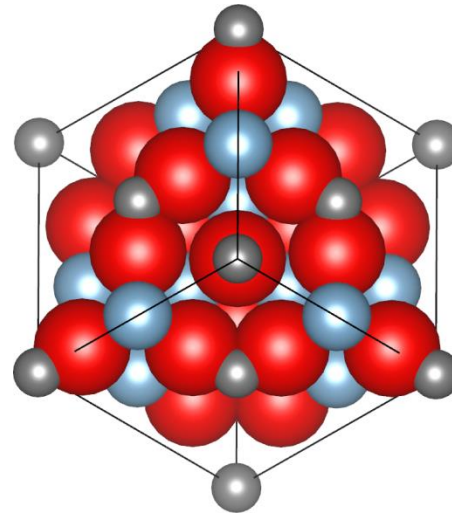
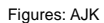
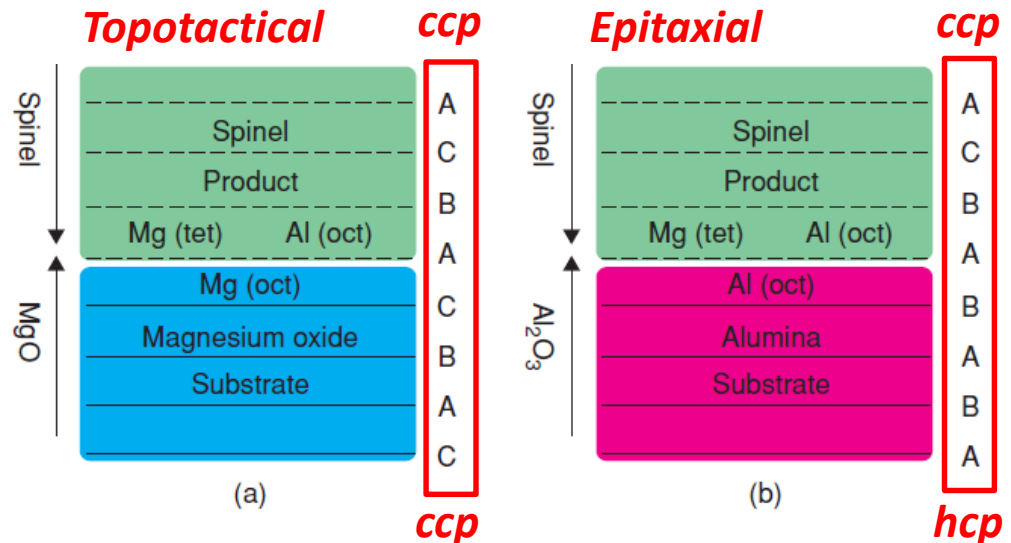


Figure: AJK

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

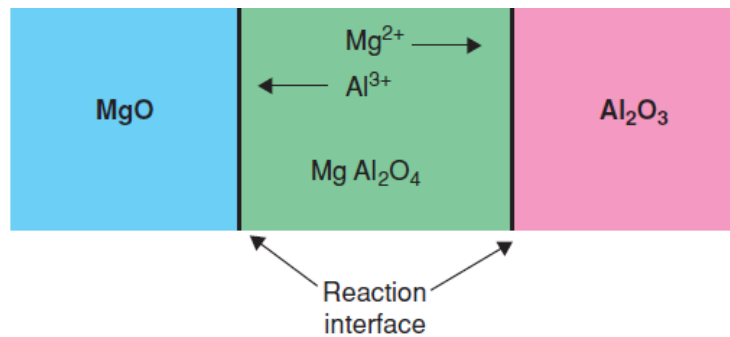


Nucleation of MgAl_2O_4 spinel on (a) MgO and (b) Al_2O_3 . Letters A, B, C refer to close-packed layers of O^{2-} ions.

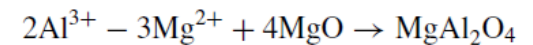
MgAl₂O₄ spinel from MgO and Al₂O₃ (2)

Ref: West p. 190

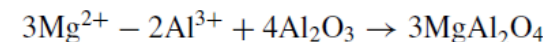
- The first few atomic layers of product nuclei may form easily, but subsequent growth or thickening of the product is more difficult
 - The two reactants, MgO and Al₂O₃, are separated by a spinel layer.
- A complex counter-diffusion process is then required
 - Mg²⁺ ions diffuse away from the MgO/MgAl₂O₄ interface
 - Al³⁺ ions diffuse towards the MgO/MgAl₂O₄ interface
 - Vice versa for the MgAl₂O₄/Al₂O₃ interface
- As the reaction proceeds, the spinel layer thickens, the diffusion pathlength increases, and the reaction slows down (Mg²⁺ and Al³⁺ diffuse very slowly)
- Heating for **1 week at 1500°C** would be required to form a fairly pure spinel product



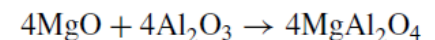
interface MgO/MgAl₂O₄:



interface MgAl₂O₄/Al₂O₃:



overall reaction:



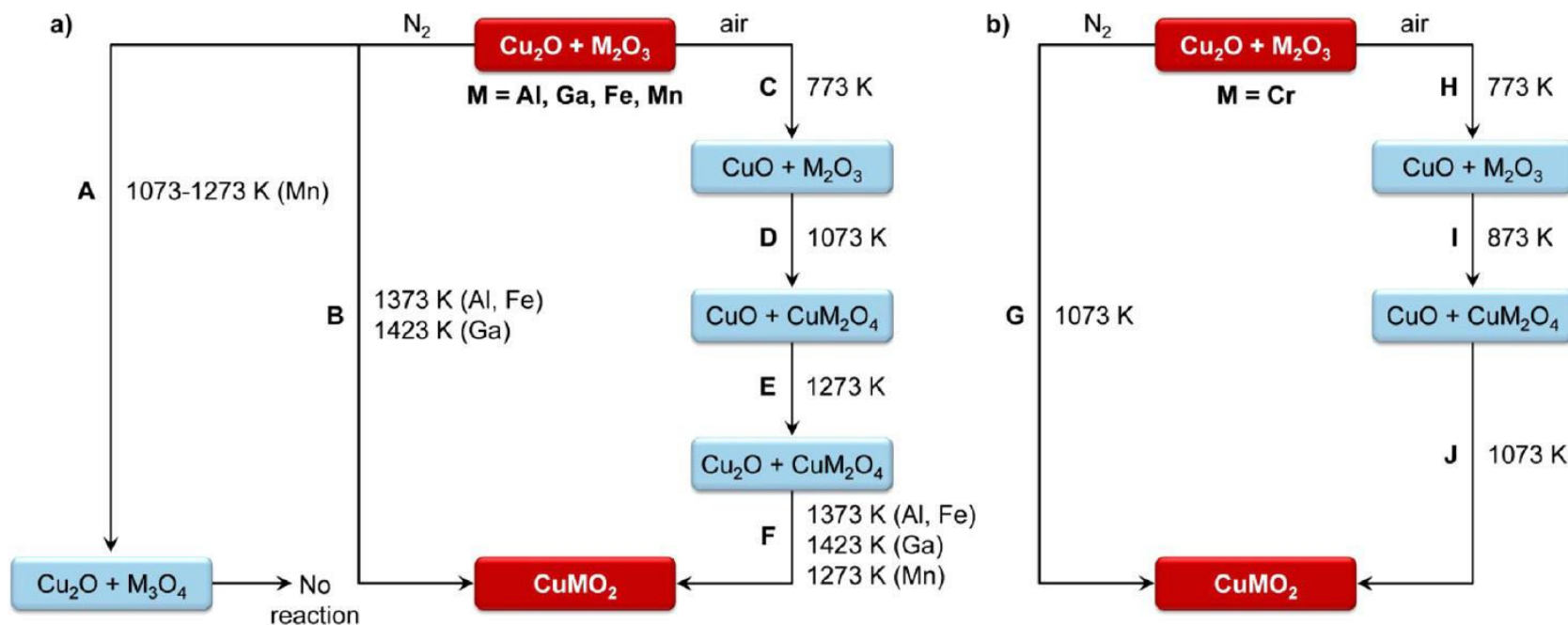
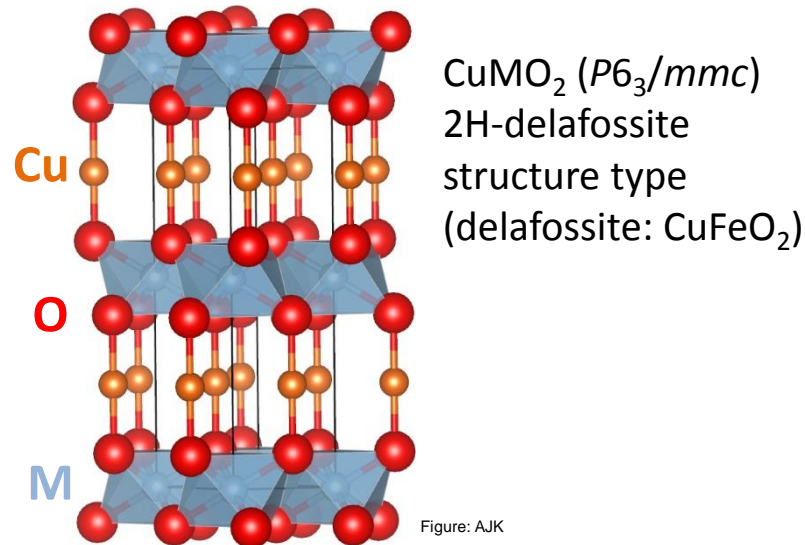
Spinel product layer separating MgO and Al₂O₃ reactant grains

Some practical considerations

- 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 ($p\text{O}_2$) for oxides
 - Oxidizing (Air, O_2)
 - Inert or slightly reducing (vacuum, N_2 , Ar)
 - Strongly reducing (H_2 /Ar mix, H_2)

Example: Cu delafossites CuMO_2

Chem. Mater. **2013**, 25, 4423–4435 ([DOI](#))



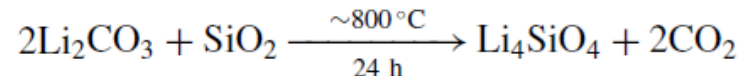
Steps involved in the formation of cuprous delafossites by the solid-state reaction of the single oxides.
(a) Four-step mechanism for the delafossites forming in air above 1273 K; (b) three-step route for CuCrO_2 , which forms below 1273 K.

Few solid state reaction examples

Ref: West p. 193

4.2.2.1 Li_4SiO_4

Li_4SiO_4 is the parent phase for a family of Li^+ ion conductors that can be prepared by the reaction:

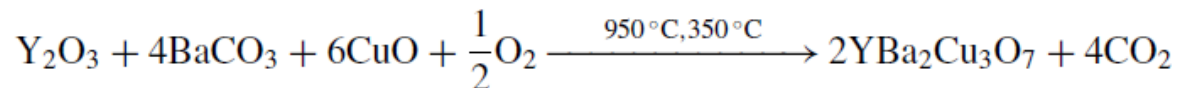


Problem: Li_2CO_3 melts and decomposes readily above $\sim 720^\circ\text{C}$; it is reactive towards most container materials, including Pt and silica glass.

Solution: Use Au containers; carry out decomposition and pre-reaction of Li_2CO_3 at $\sim 650^\circ\text{C}$ for a few hours before final firing at $800\text{--}900^\circ\text{C}$ overnight.

4.2.2.2 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

$\text{YBa}_2\text{Cu}_3\text{O}_7$, YBCO, is the classic 90 K superconductor. It can be prepared by the reaction



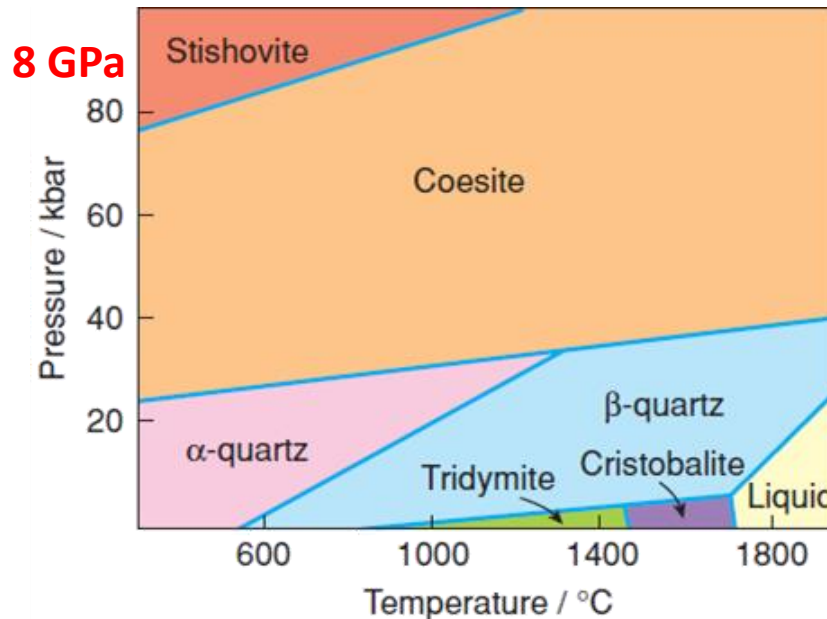
Problems: (i) BaCO_3 is particularly stable on heating and it can be difficult to remove the last traces of CO_2 during reaction. Also, many materials, such as YBCO, may react slowly with atmospheric CO_2 causing a partial reversal of the reaction used in the synthesis. (ii) CuO is reactive to most container materials at high temperatures. (iii) The oxygen content $7 - \delta$ of the YBCO product is variable and must be controlled to optimise T_c .

Solutions: (i) React in a CO_2 -free atmosphere, with $\text{Ba}(\text{NO}_3)_2$ as a source of BaO . (ii) Make pellets of reaction mixture [after decomposition of $\text{Ba}(\text{NO}_3)_2$] and react these on a bed of pre-prepared YBCO. (iii) After reaction at $\sim 950^\circ\text{C}$, carry out final heating at $\sim 350^\circ\text{C}$ to allow O_2 uptake to occur and achieve the desired stoichiometry, $\text{YBa}_2\text{Cu}_3\text{O}_7$.

High-pressure chemistry (1)

See [Solid State Chemistry Wiki](#)

- High pressures ($> 1 \text{ GPa} = 10\,000 \text{ atm}$) enable the synthesis of huge number of new materials that are unattainable in the atmospheric pressure
- In ultra-high pressures (Mbar range, $> 100 \text{ GPa}$), 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)

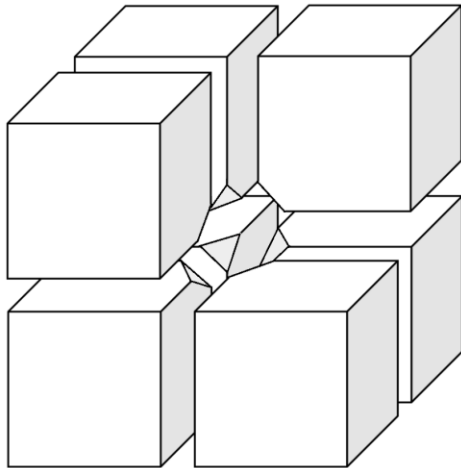
- Ultimately, most substances should become metallic at the most extreme pressures, as the close approach of atoms results in electronic overlap
- In moderate pressures (< 10 GPa), the pressure effects are not as extreme as in ultra-high pressures and typical phenomena are e.g. the increase of coordination 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
		<i>P</i> /kbar	<i>T</i> /°C	
C	Graphite, 3	130	3000	Diamond, 4
CdS	Wurtzite, 4:4	30	20	Rock salt, 6:6
KCl	Rock salt, 6:6	20	20	CsCl, 8:8
SiO ₂	Quartz, 4:2	120	1200	Rutile, 6:3
Li ₂ MoO ₄	Phenacite, 4:4:3	10	400	Spinel, 6:4:4
NaAlO ₂	Ordered	40	400	Ordered
	Wurtzite, 4:4:4			Rock salt, 6:6:6

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

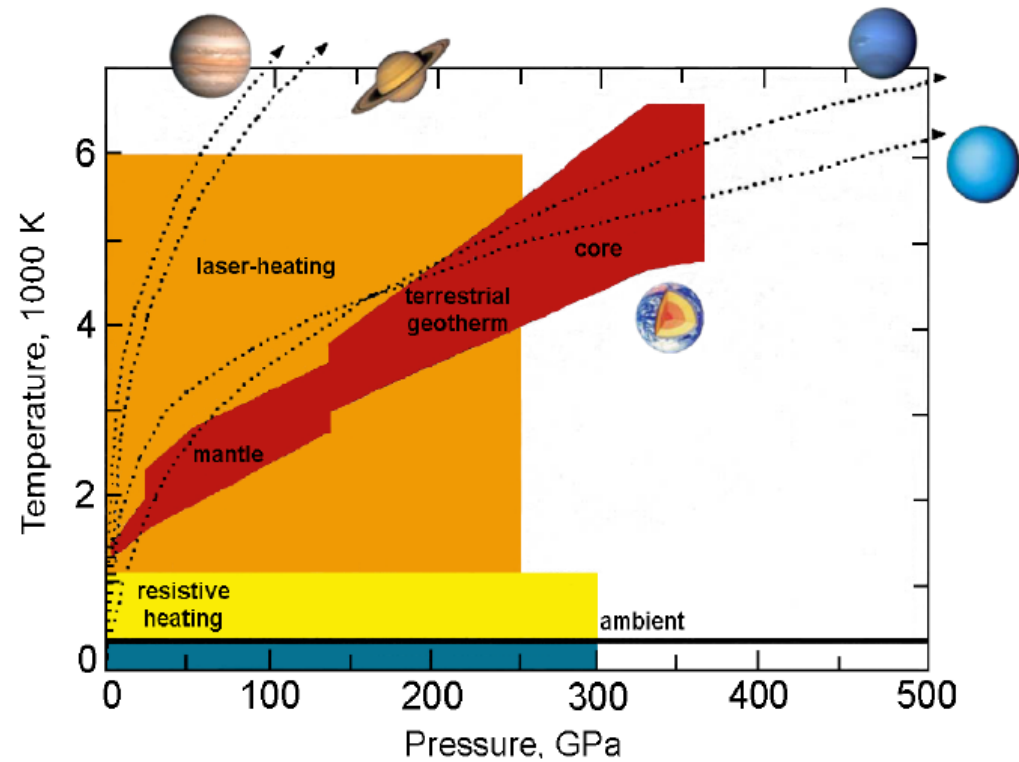
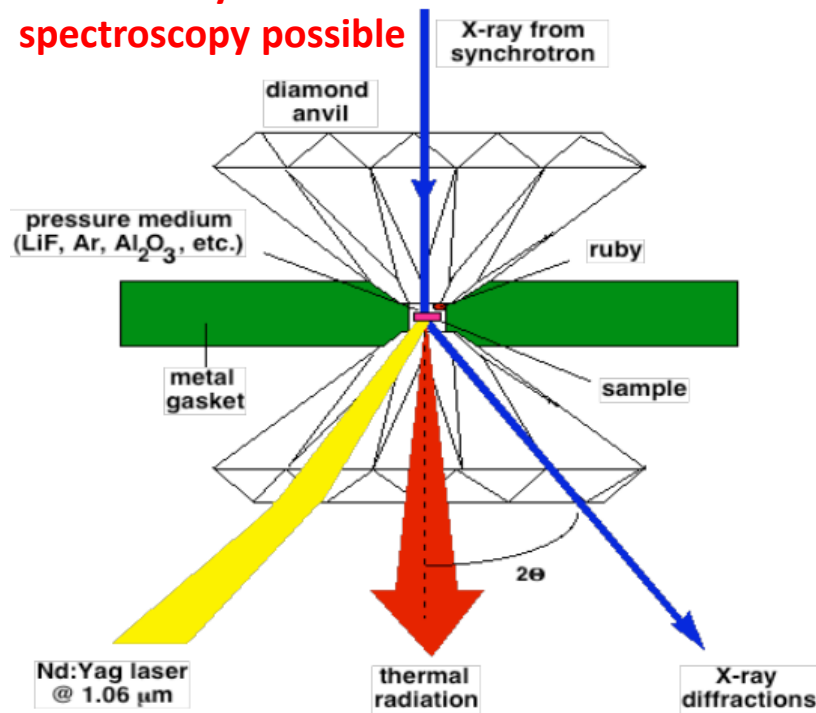


Figure: Choong-Shik Yoo, Washington State University

The most incompressible metal osmium at static pressures above 750 gigapascals

L. Dubrovinsky^{1*}, N. Dubrovinskaia^{2*}, E. Bykova^{1,2}, M. Bykov², V. Prakapenka³, C. Prescher³, K. Glazyrin⁴, H.-P. Liermann⁴, M. Hanfland⁵, M. Ekholm^{6,7}, Q. Feng^{6,7}, L. V. Pourovskii^{6,8}, M. I. Katsnelson^{9,10}, J. M. Wills¹¹ & I. A. Abrikosov^{7,12}

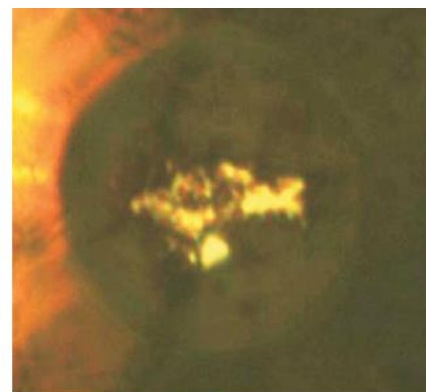
Transparent dense sodium

NATURE | Vol 458 | 12 March 2009

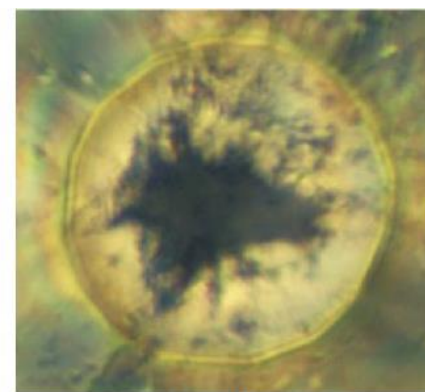
LETTERS

Yanming Ma^{1,2}, Mikhail Erements³, Artem R. Oganov^{2,4†}, Yu Xie¹, Ivan Trojan³, Sergey Medvedev³, Andriy O. Lyakhov^{2†}, Mario Valle⁵ & Vitali Prakapenka⁶

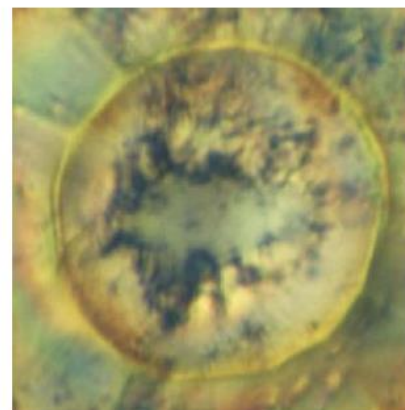
a Under pressure, metals exhibit increasingly shorter interatomic distances. Intuitively, this response is expected to be accompanied by an increase in the widths of the valence and conduction bands and hence a more pronounced free-electron-like behaviour. But at the densities that can now be achieved experimentally, compression can be so substantial that core electrons overlap. This effect dramatically alters electronic properties from those typically associated with simple free-electron metals such as lithium (Li; refs 1–3) and sodium (Na; refs 4, 5), leading in turn to structurally complex phases^{6–8} and superconductivity with a high critical temperature^{9–11}. But the most intriguing prediction—that the seemingly simple metals Li (ref. 1) and Na (ref. 4) will transform under pressure into insulating states, owing to pairing of alkali atoms—has yet to be experimentally confirmed. Here we report experimental observations of a pressure-induced transformation of Na into an optically transparent phase at ~200 GPa (corresponding to ~5.0-fold compression). Experimental and computational data identify the new phase as a wide bandgap dielectric with a six-coordinated, highly distorted double-hexagonal close-packed structure. We attribute the emergence of this dense insulating state not to atom pairing, but to *p*–*d* hybridizations of valence electrons and their repulsion by core electrons into the lattice interstices. We expect that such insulating states may also form in other elements and compounds when compression is sufficiently strong that atomic cores start to overlap strongly.



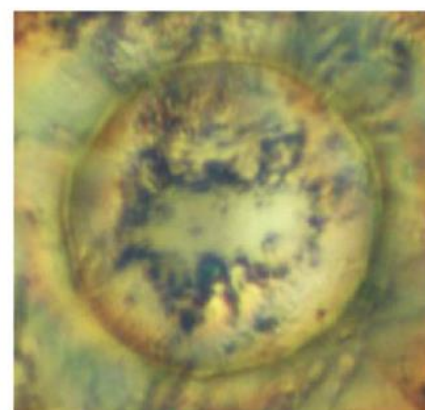
199 GPa



156 GPa

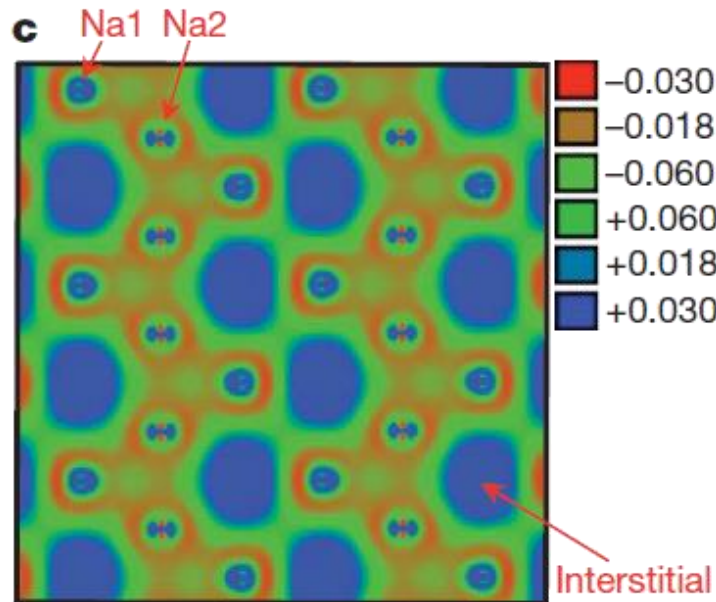
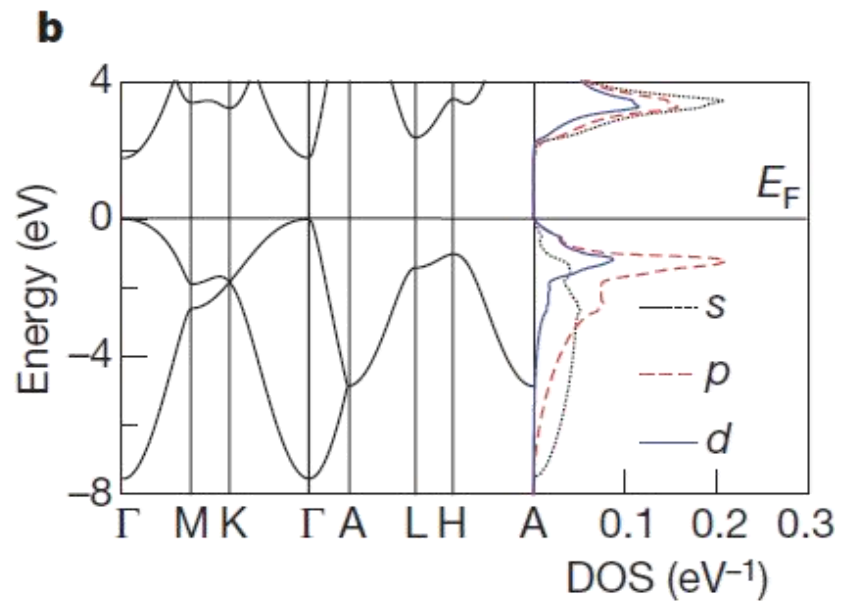
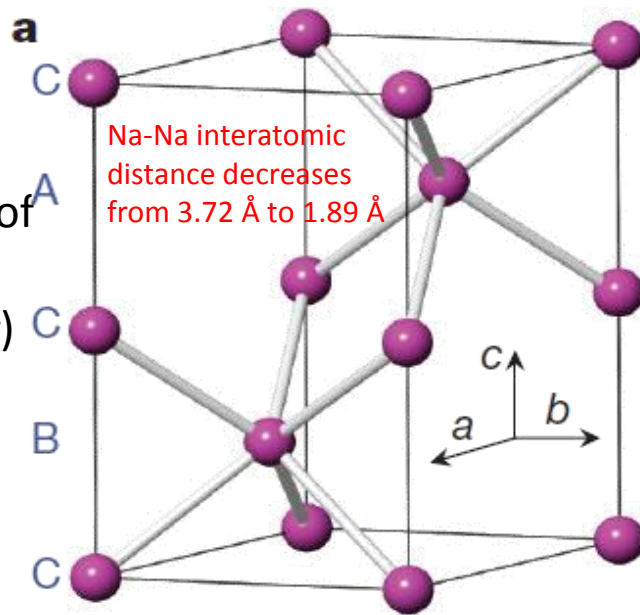


124 GPa



120 GPa

Crystal structure of Na-hP4 ($P6_3/mmc$)



d

Energy (eV)

The theoretical calculations performed by Ma and colleagues elucidated the reason for the dramatic transformation on sodium. At pressures of more than 2 million atm, sodium is strongly (5-fold) compressed so that the **atoms overlap** and **force their outer electrons** into the **interstitials** between the atoms, where electron density strongly localizes. This is responsible for the collapse of the metallic state. Sodium thus transforms to an **elemental ionic solid** where sodium atoms play the role of cations while the localized electrons behave as anions (source: Argonne National Laboratory) 15

Thin film techniques

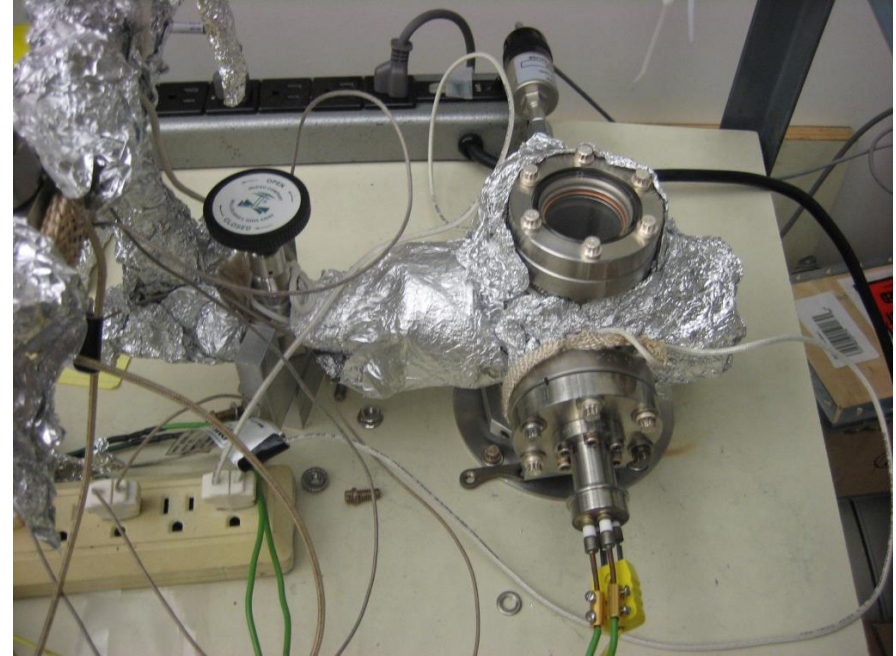
- Physical Vapor Deposition
 - Sputtering and evaporation
- Chemical Vapor Deposition (CVD)
- Atomic Layer Deposition (ALD)

Figure: [Zaera Group at UC Riverside](#)



Figure: [MPA industrie](#)

CVD reactor for TiC, TiCN, Al₂O₃, TiN deposition on hard metals and steels



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 °C. 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 °C 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 $10^{-1} \dots 10^{-2}$ 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

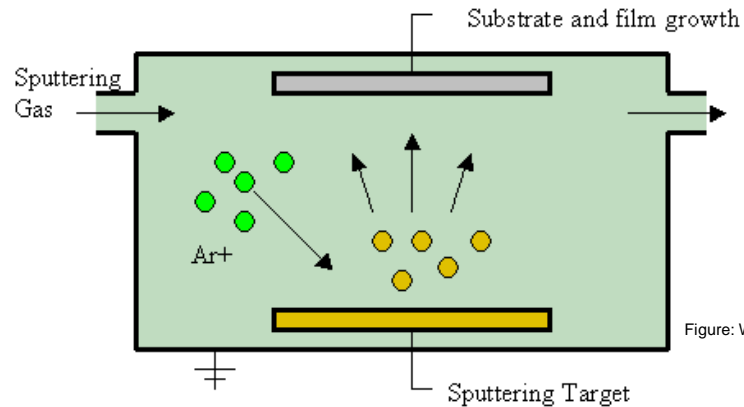
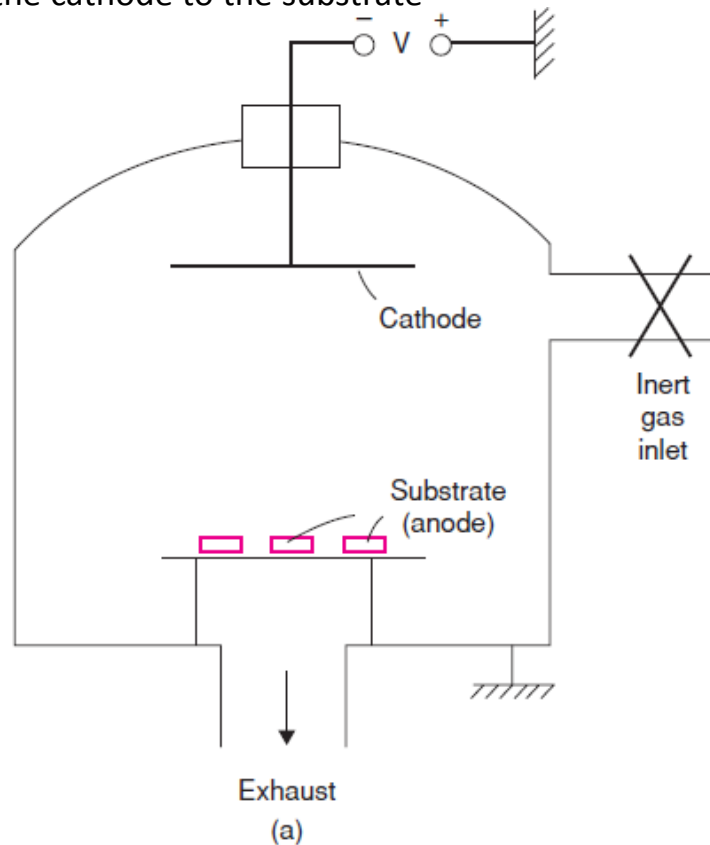
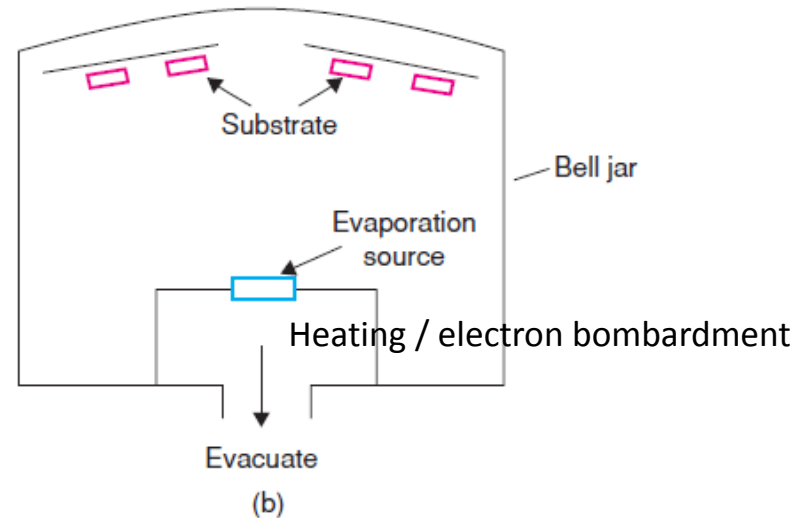


Figure: Wikipedia

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



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:
 - $\text{SiH}_4 \rightarrow \text{Si (polycrystalline)} + 2\text{H}_2$
- To deposit compounds, e.g. 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

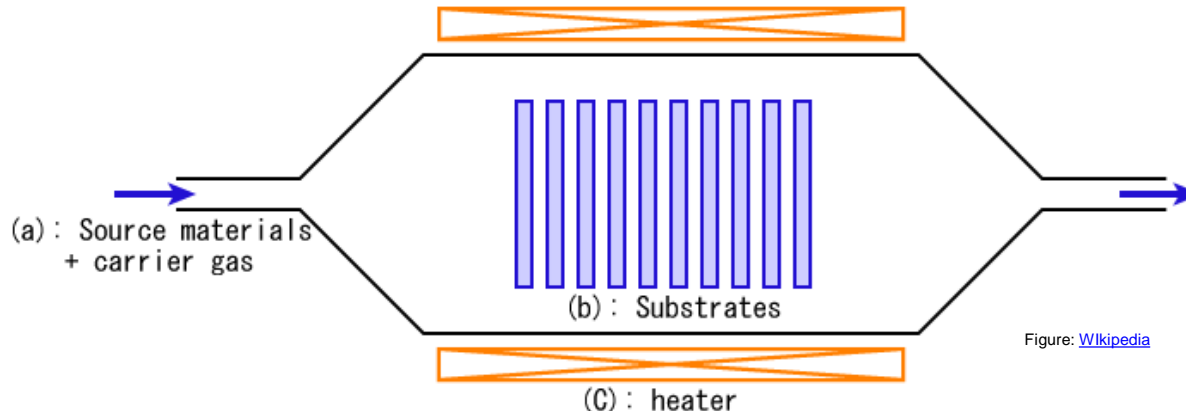
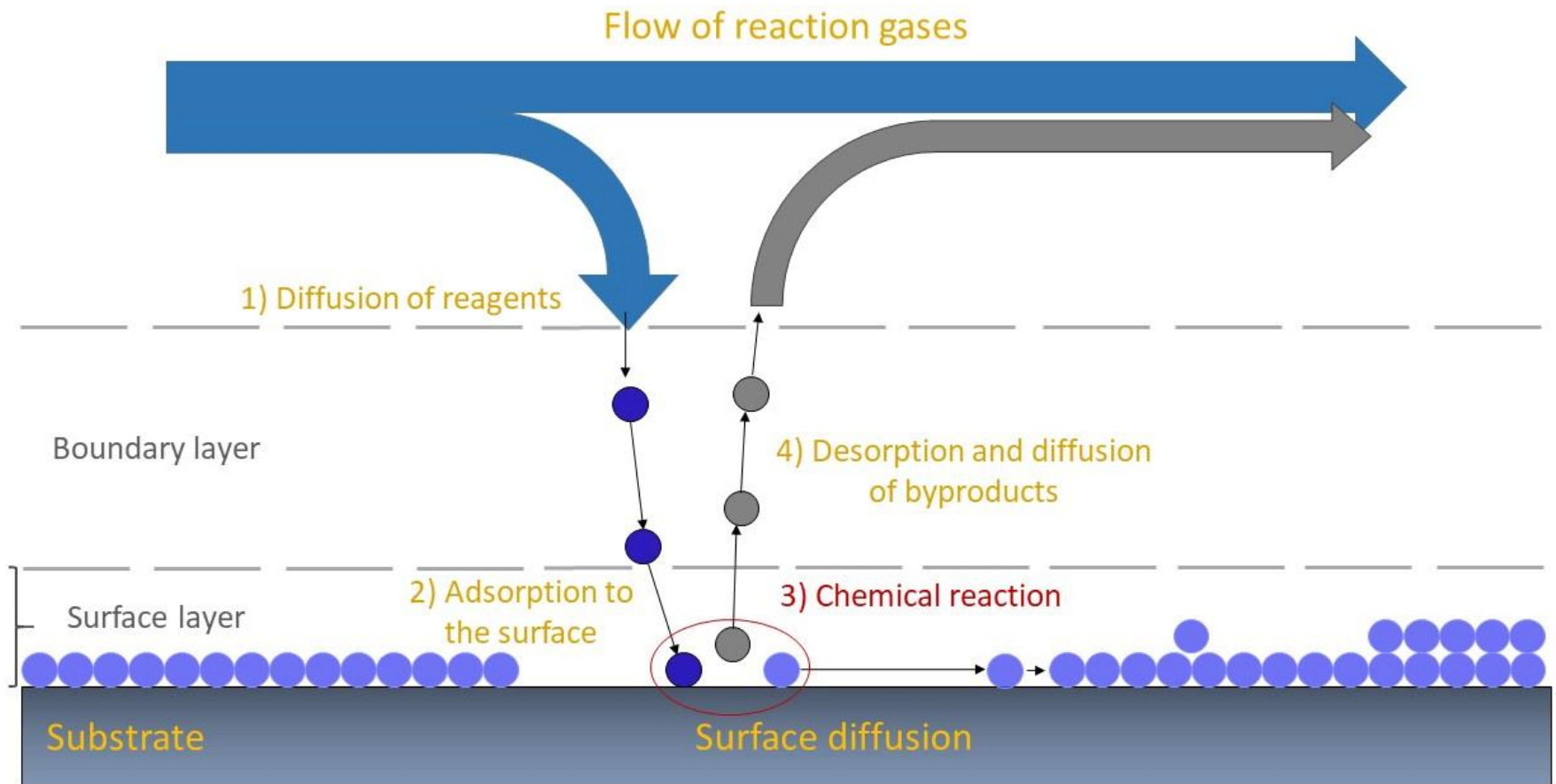


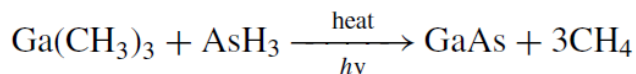
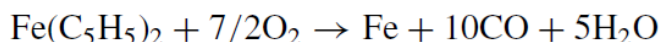
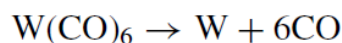
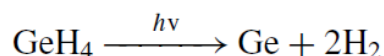
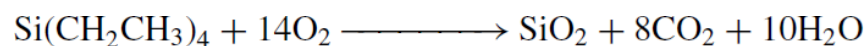
Figure: [Wikipedia](#)

Chemical Vapor Deposition (2)



Chemical Vapor Deposition (3)

- Examples of CVD processes:



- New single-source precursors are being continually developed for **metal-organic CVD (MOCVD)**

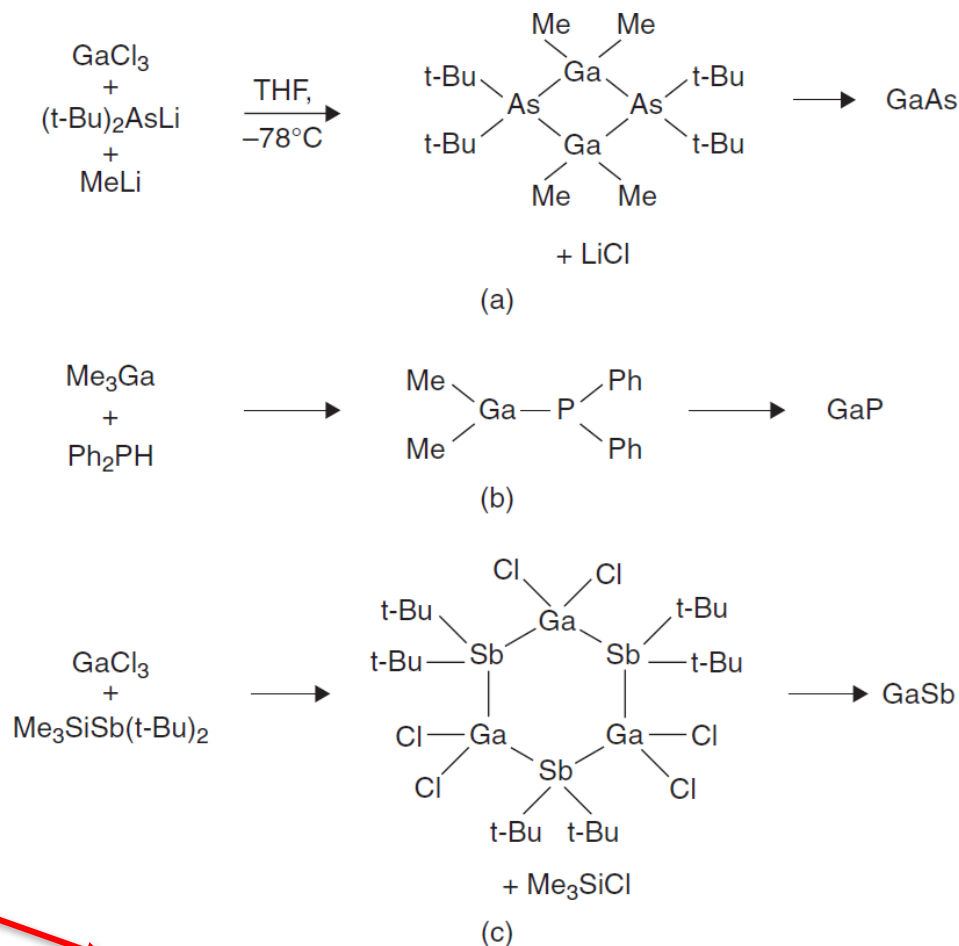


Figure 4.14 Single-source precursor molecules for MOCVD.

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

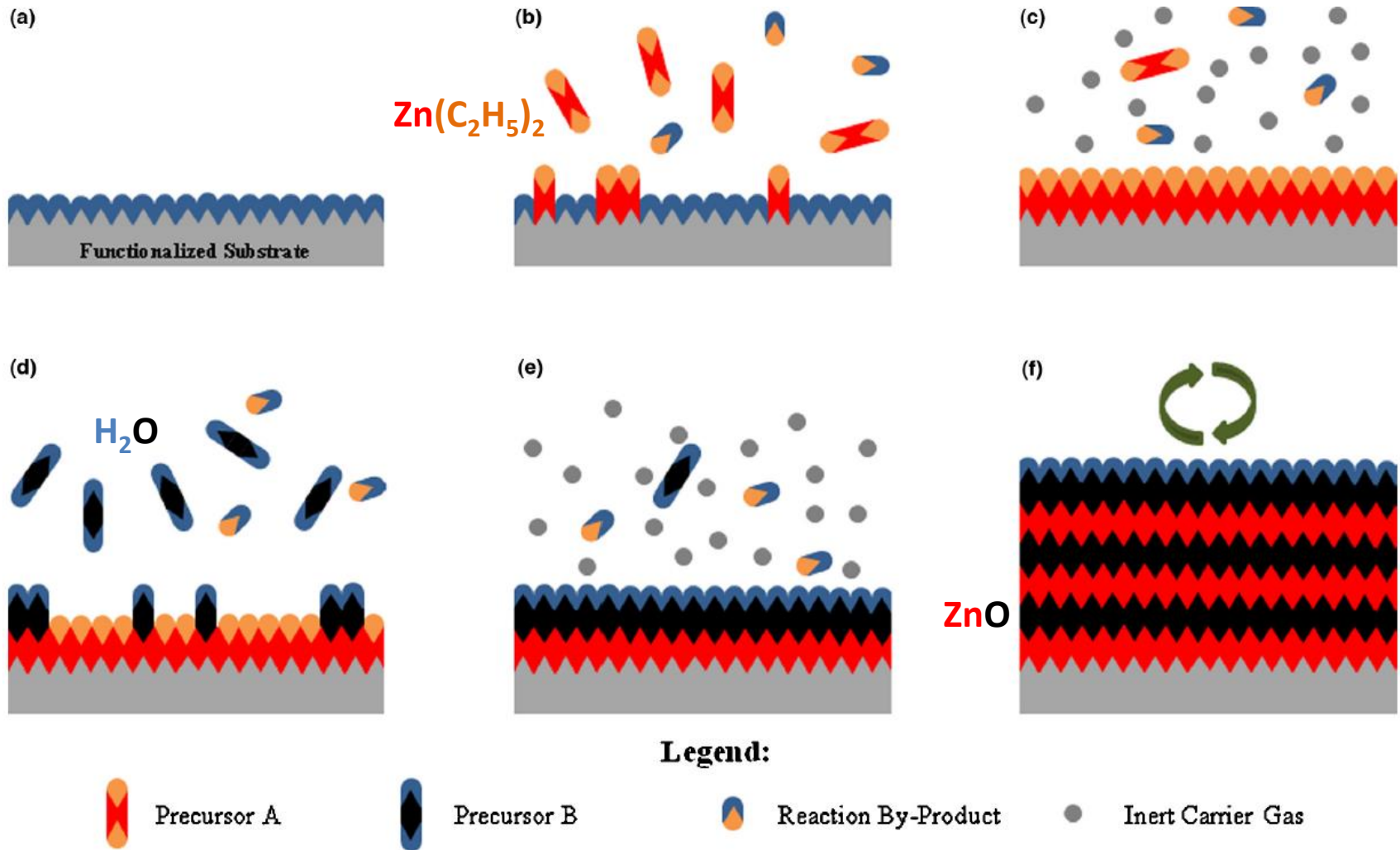


FIGURE 1

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

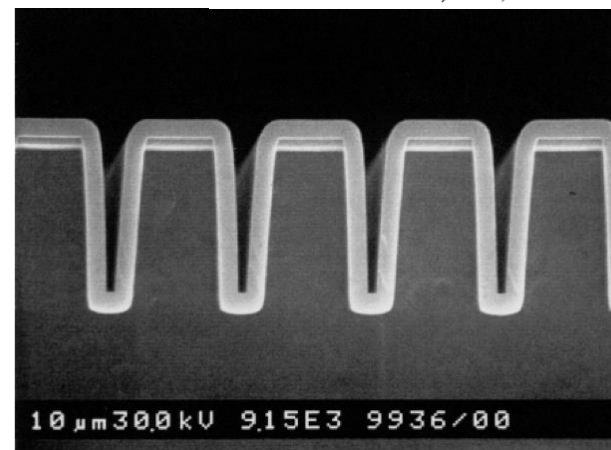


Figure 3. Cross-sectional SEM image of an Al_2O_3 ALD film with a thickness of 300 nm on a Si wafer with a trench structure.

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

Low temperature methods (1)

- 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-T 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

Alkoxide sol–gel method (1)

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.
- Organometallic precursors, particularly alkoxides, are widely used for the small-scale synthesis of known or new materials
 - Alkoxide: $R-O^-M^+$ (e.g. $CH_3-O^-Na^+$; $Si(OCH_2CH_3)_4$ – source of SiO_2)
- The alkoxide-based sol–gel method is extremely versatile and can incorporate most elements of the periodic table

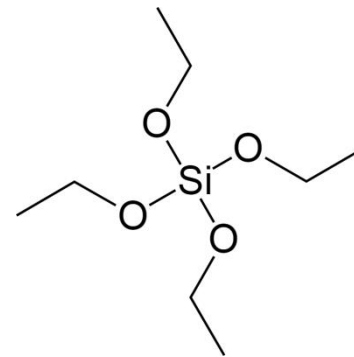
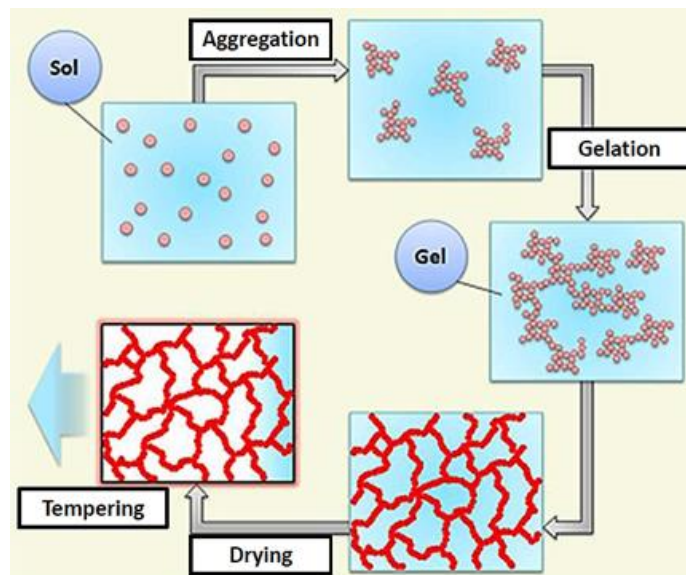
Alkoxide sol–gel method (2)

4.3.1.1 Synthesis of MgAl_2O_4

Appropriate reagents are $\text{Mg}(\text{OCH}_3)_2$ and $\text{Al}(\text{O}^i\text{Bu})_3$. 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 $\sim 1700^\circ\text{C}$). 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 .



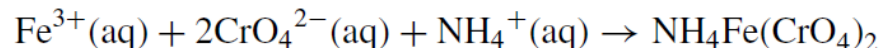
TEOS = Tetraethyl orthosilicate

Use of homogeneous, single-source precursors

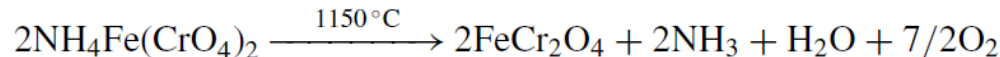
- A solid-state analogue of the sol-gel method is to prepare a crystalline, homogeneous, single-phase precursor material that contains all the required cations in the correct ratio
- This precursor should not be particularly stable and on heating decomposes to give the desired product

(a) $\text{NH}_4\text{Fe}(\text{CrO}_4)_2$ precursor to FeCr_2O_4 :

The precursor is synthesised by precipitation from aqueous solution:

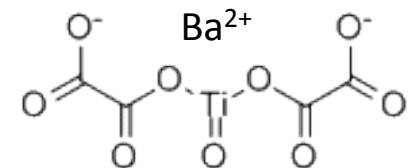
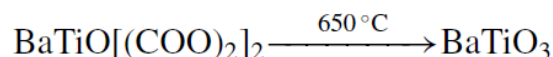
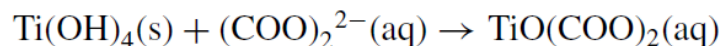
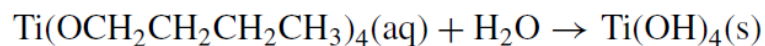


It decomposes on heating:



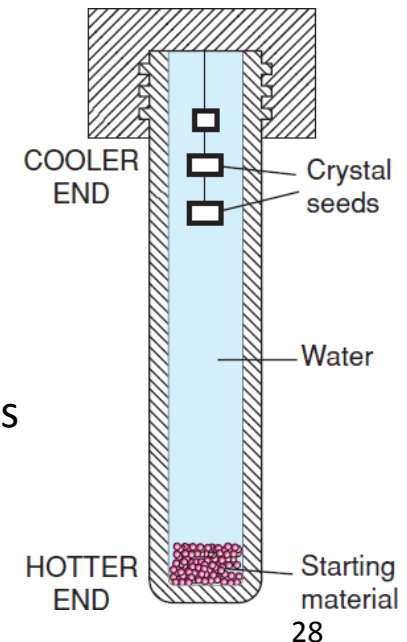
(c) $\text{Ba}(\text{TiO})[(\text{COO})_2]_2$ precursor to BaTiO_3 :

Barium titanyl oxalate is prepared by a multistep route and decomposed by heating:



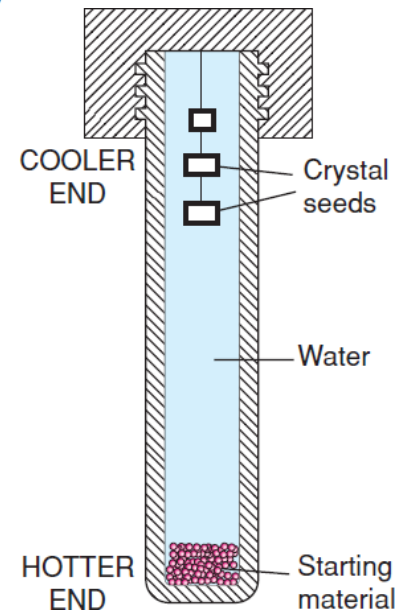
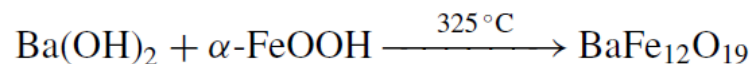
Hydrothermal and solvothermal synthesis (1)

- 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 a temperature in the range 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



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, $\text{BaFe}_{12}\text{O}_{19}$, would require heating of the oxide components, BaCO_3 and $\alpha\text{-Fe}_2\text{O}_3$, at e.g. 1250°C but hydrothermally can be carried out at a much lower temperature:



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

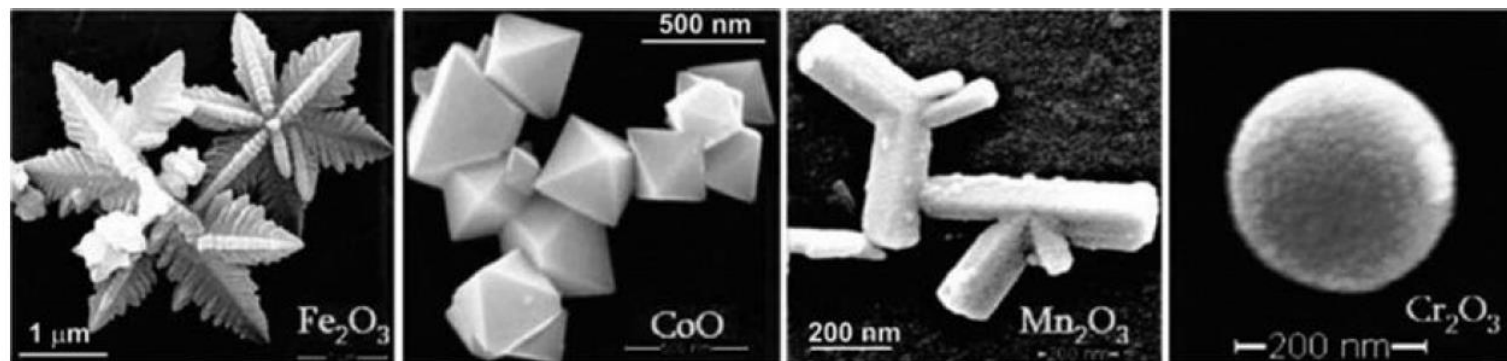


Figure 4.9 SEM images of various metal oxide nanostructures. Reproduced with permission from I. Bilecka and M. Niederberger, *Nanoscale*, 2, 1358, © 2010 Royal Society of Chemistry.