Introduction of Solid State Synthesis Methods

Part 1. Solid State Reaction Processing

Part 2. Ceramics —— From Solid State Reactions

Part 3. Important Methods for Solid State Materials

Part 3: Important Methods for Solid State Materials

1. Soft Chemistry
   - (1)Intercalation and De-intercalation
   - (2)Dehydration
   - (3)Ion Exchange
   - (4)Precursor Routes: Coprecipitation, Sol-gel Process
2. Molten Salt Fluxes
3. High-Pressure Synthesis
   - (1)dry high pressure synthesis
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4. CVT (Chemical Vapor Transport)
   CVD (Chemical Vapor Deposition)
5. Single Crystal Growth

1. Soft Chemistry

- Approach : Soft chemistry reactions are carried out under moderate conditions (typically T < 500°C). Soft Chemistry reactions are topotactic, meaning that structural elements of the reactants are preserved in the product, but the composition changes.
- Advantages : Soft chemistry methods are very useful for the following applications:
- Modifying the electronic structure of solids (doping)
- Design of new metastable compounds (structural motif can be selected by choice of precursor, may have unusual properties)
- Preparing reactive and/or high surface area materials used in heterogeneous catalysis, batteries and sensors
- Disadvantages : First of all, one must find the appropriate precursor in order to carry out soft chemistry. Secondly, metastable products are often unstable in applications where high temperatures are used or single crystals are needed.

(1) Intercalation

- Involves inserting ions into an existing structure, this leads to a reduction (cations inserted) or an oxidation (anions inserted) of the host.
- Typically carried out on layered materials (strong covalent bonding within layers, weak van der Waals type bonding between layers, i.e. graphite, clays, dicalchogenides, etc.).
- Performed via electrochemistry or via chemical reagents as in the n-butyl Li technique.
- Examples :

$$TiS_2 + nBu\text{-}Li \longrightarrow LiTiS_2$$

De-intercalation

- The reverse of intercalation, also performed using either electrochemical methods or with reactive chemical species
- Examples :

$$NiMo_3S_4 \longrightarrow Mo_3S_4$$

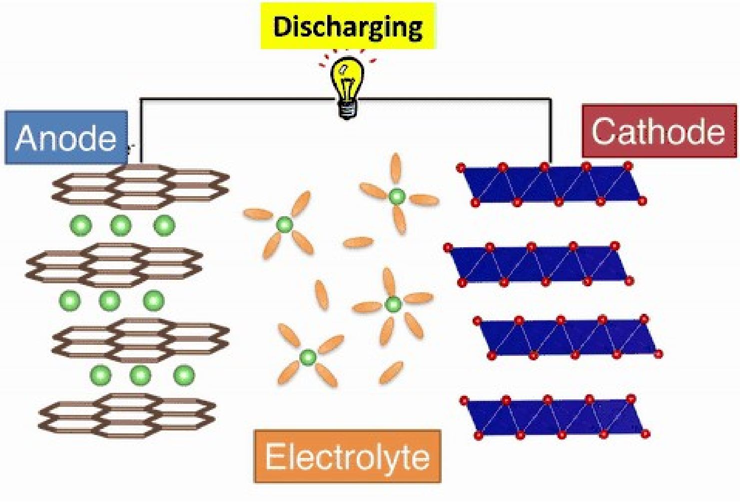
$$In_2Mo_6S_6 + 6HCl\,(g) \longrightarrow Mo_6S_6 + 2InCl_3\,(g) + 3H_2\,(g)$$

This approach can often lead to new phases (polymorphs) of previously known compounds

$$CuTi_2S_4 \longrightarrow \text{cubic } TiS_2$$

$$KCrSe_2 \longrightarrow \text{layered } CrSe_2$$

$$Li_2FeS_2 \longrightarrow FeS_2$$



(2) Dehydration

- By removing water and/or hydroxide groups from a compound, you can often perform redox chemistry and maintain a structural framework not accessible using conventional synthesis approaches.
- Examples：

$$Ti_4O_7(OH)_2 \cdot nH_2O \xrightarrow{500^0C} TiO_2(B)$$

$$2KTi_4O_8(OH) \cdot nH_2O \xrightarrow{500^0C} K_2Ti_8O_{17}$$

(3)Ion Exchange

- Exchange charge compensating, ionically bonded cations (easiest for monovalent cations)
- Examples：

$$LiNbWO_6 + H_3O^+ \longrightarrow HNbWO_6 + Li^+$$

$$cubic-KSbO_3 + Na^+ \longrightarrow cubic-NaSbO_3 + K^+$$

(4)Precursor Routes

- Approach：Decrease diffusion distances through intimate mixing of cations.
- Advantages：Lower reaction temperatures, possibly stabilize metastable phases, eliminate intermediate impurity phases, produce products with small crystallites/high surface area.
- Disadvantages：Reagents are more difficult to work with, can be hard to control exact stoichiometry in certain cases, sometimes it is not possible to find compatible reagents (for example ions such as Ta^{5+} and Nb^{5+} immediately hydrolyze and precipitate in aqueous solution).

Precursor Routes

- Methods：With the exception of using mixed cation reactants, all precursor routes involve the following steps:
- Mixing the starting reagents together in solution.
- Removal of the solvent, leaving behind an amorphous or nanocrystaline mixture of cations and one or more of the following anions: acetate, citrate, hydroxide, oxalate, alkoxide, etc.
- Heat the resulting gel or powder to induce reaction to the desired product.

Mixed Cation Synthesis of Na_2ZrTeO_6

- I was attempting to make Na_2ZrTeO_6 from Na_2CO_3, ZrO_2 and TeO_2, using a conventional heat and beat approach. At ~700–750°C, I began to form my desired product, but there was also a considerable amount of ZrO_2 still present, together with some Na_2TeO_4.
- Increasing the annealing temperature (850 – 950°C) did lead to an increase in the Na_2ZrTeO_6 concentration, but before all of the ZrO_2 would react, I began to volatilize a tellurium species.
- To circumvent this problem, I tried pre-reacting the Na_2CO_3 and ZrO_2 to form Na_2ZrO_3 at ~1000°C. I then reacted Na_2ZrO_3 with TeO_2 at 750°C to form single phase Na_2ZrTeO_6.

$$Na_2CO_3 + ZrO_2 \longrightarrow Na_2ZrO_3$$

$$Na_2ZrO_3(s) + TeO_2(s) \longrightarrow Na_2ZrTeO_6(s)$$

Coprecipitation Synthesis of $ZnFe_2O_4$

- Mix the oxalates of zinc and iron together in water in a 1:1 ratio. Heat to evaporate off the water, as the amount of H_2O decreases a mixed Zn/Fe acetate (probably hydrated) precipitates out.

$$Fe_2((COO)_2)_3 + Zn(COO)_2 \longrightarrow Fe_2Zn((COO)_2)_5 \cdot xH_2O$$

- After most of the water is gone, filter off the precipitate and calcine it (1000°C).

$$Fe_2Zn((COO)_2)_5 \xrightarrow{\Delta} ZnFe_2O_4 + 4CO + 4CO_2$$

- This method is easy and effective when it works. It is not suitable when

1. Reactants of comparable water solubility cannot be found.
2. The precipitation rates of the reactants is markedly different.

- These limitations make this route unpractical for many combinations of ions. Furthermore, accurate stoichiometric ratios may not always be maintained.

Sol-Gel Synthesis of Metastable $ScMnO_3$

Begin by dissolving Sc_2O_3 and $MnCO_3$ separately, in heated aqueous solutions of formic acid to form the formate salts:

$$Sc_2O_3 + 6HCOOH + 3H_2O \longrightarrow 2Sc(HCOO)_3 + 3H_2O$$

$$MnCO_3 + 2HCOOH + 2H_2O \longrightarrow Mn(COOH)_2 \cdot 2H_2O + H_2CO_3$$

- Addition of $Sc(HCOO)_3$ and $Mn(COOH)_2$•$2H_2O$ to melted citric acid monohydrate results in the formation of a (Sc,Mn) citrate polymer.
- Heat to 180°C → Removal of excess water and organics
- Heat to 450°C → Formation of an amorphous oxide product
- Heat to 690°C → Formation of crystalline $ScMnO_3$
- Direct reaction of the formates at 700°C simply gives the mixture of the binary oxides:

$$2Sc(HCOO)_3 + 2Mn(COOH)_2 \longrightarrow Sc_2O_3 + Mn_2O_3 + 5CO_2 + 2H_2O + H_2$$

Alkoxide-Hydroxide Synthesis of Sr_2AlTaO_6

- Reflux a mixture of $Ta(OC_2H_5)_5$ and $Al(OC_2H_5)_3$ overnight in a solution of ethanol ⇒ This results in the formation of polymeric (Ta,Al) ethoxide species.
- Add a stoichiometric quantity of $Sr(OH)_2$•$8H_2O$ in acetone, mix well and reflux overnight. The hydroxide ions and water of hydration are sufficient to trigger a slow precipitation.
- Filter off the solution and heat at 120°C to drive off remaining solvent.
- Heat to 1200 – 1400°C to form highly crystalline Sr_2AlTaO_6 or heat to 800 – 1000°C to form high surface area Sr_2AlTaO_6
- Direct reaction of the oxides also results in formation of Sr_2AlTaO_6, but minor Sr/Ta/O impurity phases are always present.
- The alkoxides are often hygroscopic and air sensitive, consequently it can be difficult to weigh out accurate quantities. Furthermore, they are rather expensive.

2. Molten Salt Fluxes

- Solubilize reactants→Enhance diffusion → Reduce reaction temperature
- Synthesis in a solvent is the common approach to synthesis of organic and organometallic compounds. This approach is not extensively used in solid state syntheses, because many inorganic solids are not soluble in water or organic solvents. However, molten salts turn out to be good solvents for many ionic-covalent extended solids.
- Often slow cooling of the melt is done to grow crystals, however if the flux is water soluble and the product is not, then powders can also be made in this way and separated from the excess flux by washing with water.

Molten Salt Fluxes

- **Synthesis needs to be carried out at a temperature where the flux is a liquid. Purity problems can arise, due to incorporation of the molten salt ions in product. This can be overcome either by using a salt containing cations and/or anions which are also present in the desired product (i.e. synthesis of Sr_2AlTaO_6 in a $SrCl_2$ flux) , or by using salts where the ions are of a much different size than the ions in the desired product (i.e. synthesis of $PbZrO_3$ in a B_2O_3 flux).**

Example 1

$$4SrCO_3 + Al_2O_3 + Ta_2O_5 \xrightarrow{SrCl_2\text{ flux, }900°C} Sr_2AlTaO_6$$

Powder sample, wash away $SrCl_2$ with weakly acidic H_2O
Direct synthesis requires T > 1400°C and $Sr_2Ta_2O_7$ impurities persist even at 1600°C

Example 2

$$La_2O_3 + CuO + KOH \xrightarrow{KOH\text{ flux, }380°C} La_{2-x}K_xCuO_4$$

Volatility of potassium plagues direct reaction

Example 3

$$K_2Te_x + Cu \xrightarrow{K_2Te_x\text{ Flux, }350°C} K_2Cu_5Te_5$$

Example of reactive A_2Q_x (A = alkali metal, Q = S, Se, Te) flux. In this approach the flux acts not only as a solvent but also as a reactant. A large number of new compounds have been made in the past decade using this approach.

3.High Pressure Synthesis

- **Approach : By increasing the pressure it allows you to explore regions of the phase diagram not accessible at atmospheric pressure.**
- **Advantages : Often leads to formation of compounds which cannot be formed using any other technique. The presence of high non-metal partial pressures (i.e. high O_2 partial pressure) can be used to stabilize cations in unusually high oxidation states.**
- **Disadvantages : High pressure synthesis equipment tends to be large and expensive. Product volume is often times so small that characterization becomes difficult, and practical application can be impractical.**

•**Methods** : The various high pressure techniques vary primarily in design of the pressure transmitting device, which in turn leads to variations in the accessible pressure and temperature range, as well as the sample volume.

•**Quenching** : A compound that is stable at high pressure may transform back to its ambient pressure phase upon release of the pressure. In order to prevent this, it is important to lower the temperature back to room temperature before releasing the pressure back to ambient pressure. This so-called "quenching" of the high pressure phase is most likely to be successful in cases where considerable structural rearrangement (breaking and making bonds) is involved in the transformation between the low pressure and high pressure phase.

Why Use High Pressures?

- High pressure allows the preparation of new compositions, new structures, unusual oxidation states
- ▸$PbSnO_3$ does not form as a perovskite at ambient pressure, but will at high pressure
- ▸$CaFeO_3$ can only be prepared at high pressures. At ambient pressures, Brownmillerite ($CaFeO_{2.5}$) forms
- ▸Superconducting oxygen excess $La_2CuO_{4+\delta}$ can be prepared at high oxygen pressure
- ▸$La_2Pd_2O_7$ can be prepared at high oxygen pressure. Normally only get Pd^{2+} oxides
- Oxygen Pressure can be generated in-situ by decomposition of $KClO_3$ (or $KMnO_4$)
- However, beware! KCl may be incorporated into the product

The Use of High Pressure Stabilizes Products With the Following Attributes:

(a) Dense packing of ions (Higher cation coordination numbers)

(b) Higher cation oxidation states

(c) Higher symmetry

(A) Dense Packing of Ions (Higher Cation Coordination Numbers)

For example: when prepared under ambient conditions, the compounds Na_2MTeO_6 (M = Ti^{4+}, Sn^{4+}) crystallize with the ilmenite structure. Upon treatment at high temperature (1000°C) and pressure (40–70 kbar) in a multi-anvil device, both of these compounds transform to the perovskite structure, which is one of the most efficiently packed ternary oxide structures known.

Examples of High Pressure Polymorphism for Some Simple Solids

Solid	Normal structure and coordination number	Typical transformation conditions P (kbar)	Typical transformation conditions T (°C)	High pressure structure and coordination number
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_2MoO_4	Phenacite 4:4:3	10	400	Spinel 6:4:4
$NaAlO_2$	Wurtzite 4:4:4	40	400	Rock salt 6:6:6

Pressure vs Structure

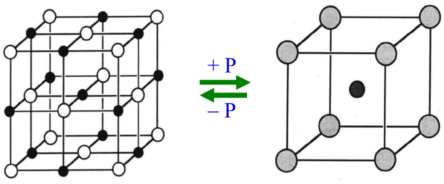
bcc(s) + pressure fcc(s)

less dense more dense

Many metals in bcc structure transform into fcc structure under high pressure

NaCl(rocksalt structure) + P ⋙ NaCl(cesium chloride structure)

less dense more dense



The transformation of sodium chloride from the rocksalt to the cesium chloride structure can be accomplished at 298 K at high P (~10^5 atm).

(B) Higher Cation Oxidation States

For example: at ambient pressure the reaction between calcium oxide and iron oxide leads to the formation of $CaFeO_{2.5}$, with the Brownmillerite structure and iron in the +3 oxidation state. But upon treatment with high oxygen pressures in a belt or piston-cylinder device, the perovskite $CaFeO_3$, with iron in the +4 oxidation state is stabilized.

(C) Higher Symmetry

- Since the volume of a polyhedron increases upon distortion, high pressures favor symmetric coordination environments.
- As an example: $PbSnO_3$, with the perovskite structure, can only be made using high pressure. Ambient pressure synthesis leads to a mixture of PbO (with a pronounced Pb^{2+} lone pair effect) and SnO_2.

Dry High Pressure Methods of Solid State Synthesis

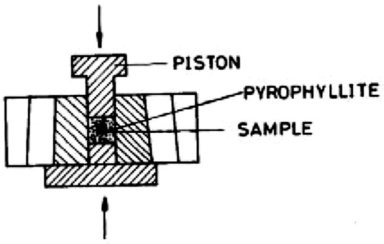
- Pressures up to Gigabars accessible, at high temperatures, and with in – situ observations by diffraction, spectroscopy to probe chemical reactions, structural transformations, crystallization, amorphization, phase transitions and so forth.
- Methods of obtaining high pressures:
  - Anvils, diamond tetrahedral and octahedral pressure transmission
  - Shock waves
  - Explosions
- Pressure techniques useful for synthesis of unusual structures, metastable yet stable when pressure released
- Often high pressure phases have a higher density, higher coordination number

Piston Cylinder Press

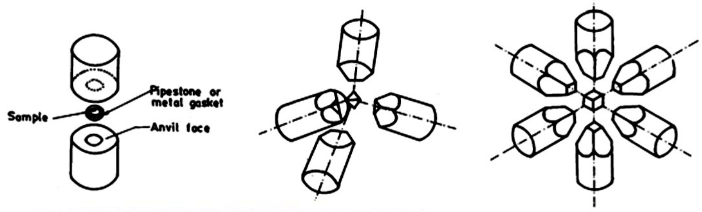
- Can achieve 50 kbar and 1800K
- Sample is placed in container (Pt, Au ..) and the container is embedded in a pyrophyllite block

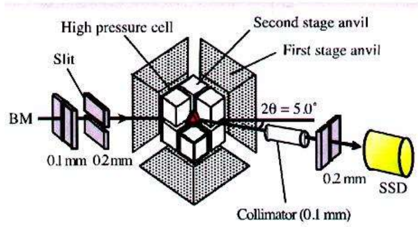
—pyrophyllite acts as a pressure transmitting medium

- Squeeze sample by forcing WC (tungsten carbide) piston into WC (tungsten carbide) cylinder



Multianvil Press





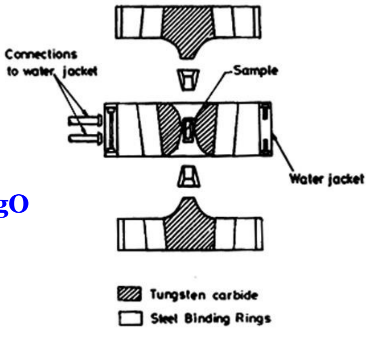
X-ray diffraction under high pressure

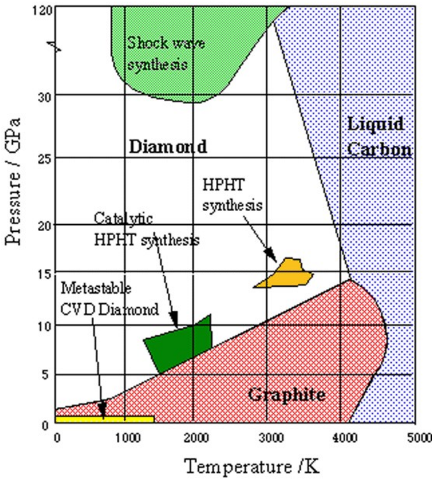
Belt Design

- Can achieve 150 kbar, 2300K

—Relatively large sample volume

—Sample in Au/Pr container or for BN or MgO





The phase diagram for diamond and graphite (from J. Geophys. Res. 1980, 85, B12, 6930.)

The stable condition of diamond: T>2,000°C, P>50,000atm

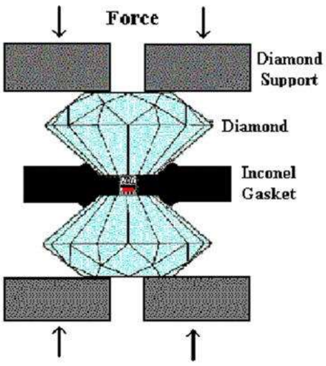
Synthetic Diamond

The production of diamonds

Large synthetic diamonds

Experiments using:

- **Diamond Anvil Cell**
- **Multi-anvil press**
- **Piston cylinder**
- **Laser Heating**
- **Synchrotron Radiation**
- **Shock**



But core pressures and temperatures remain challenging.

Hydrothermal Synthesis

- **Reaction takes place in superheated water, in a closed reaction vessel called a hydrothermal bomb (150 < T < 500°C; 100 < P < 3000 kbar).**
  注意安全！！！！！
- **Seed crystals and a temperature gradient can be used for growing crystals**
- **Particularly common approach to synthesis of zeolites**
- **Example :**

$$6CaO + 6SiO_2 \xrightarrow{150\text{-}350^\circ C} Ca_6Si_6O_{17}(OH)_2$$

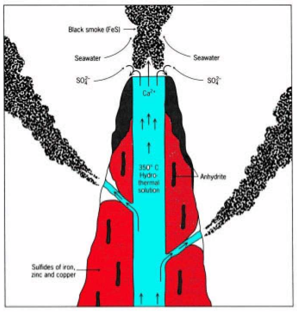
Hydrothermal Chemistry

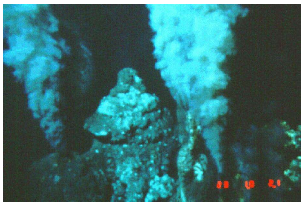
- **When this altered water (~350°C) comes in contact with cold seawater (~2°C), many reactions take place**

$$Fe^{2+} + H_2S \rightarrow FeS \text{ solid}$$

$$2Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4 \text{ solid}$$

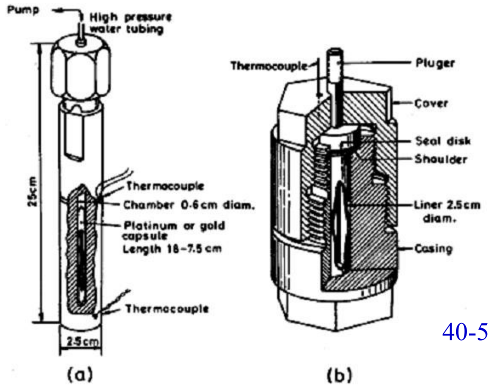
Other reduced metal sulfides form, all insoluble at ambient temperatures





Hydrothermal Reactor Designs

- **Depending on design may be useable to 10 kbar**



40-50 MPa

Applicability and Value of Hydrothermal Synthesis

- Hydrothermal techniques can be used to synthesize a wide variety of materials
  - zeolites and aluminophosphates
  - optical materials like KTP ($KTiOPO_4$)
  - $BaTiO_3$ (widely used ferroelectric)
- Synthesis can be carried out at low temperature (relative to direct reaction of solids)
- High quality samples can be made

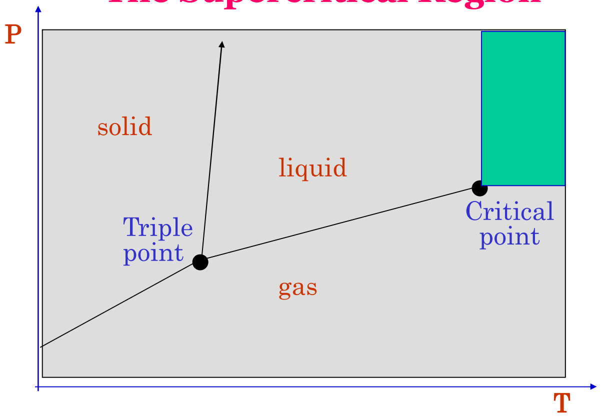
Hydrothermal Synthesis of Crystals

- Basic methodology
- Water medium
- High temperature growth, above normal boiling point
- Water acts as a pressure transmitting agent
- Water functions as solublizing phase
- Often a mineralizing agent is added to assist with the transport of reactants and crystal growth
- Speeds up chemical reactions between solids
- Useful technique for the synthesis and crystal growth of phases that are unstable in a high temperature preparation in the absence of water

Critical Point

- Hydrothermal synthesis necessitates knowledge of what is going on in an autoclave under different degrees of filling and temperature
- Pressure, volume, temperature tables of dense fluids like water are well documented
- The critical point is the point at which the liquid-vapor line ends.
- Physical differences between liquids and gases disappear at the critical point and we speak of a single "fluid" state.
  - Above this point (at higher temperatures or pressures) condensation will not take place.
  - eg. CH_4, T_c = 190 K, CH_4 cannot be liquefied at room temperature, liquid can only be obtained below 190 K.

The Supercritical Region



- Distinction between liquid and gas disappears
- Liquid and gas phase cannot be identified — no meniscus

Critical Temperatures and Pressures

- The super critical region is usually a region of high pressure and temperature

	T_c	T_P/atm
Carbon Dioxide	304.2K	72.8
Water	647.3K	217.6
Ammonia	405.6K	111.3
Ethylene	282.4°C	49.7
Benzene	288°C	48

Properties of Supercritical Fluids

- They are like high density gases and low density liquids (called **fluids** to indicate either form)
- As a high density gas they can penetrate into solids eg: concrete, and undergo reactions internally
- As a low density liquid they can dissolve other compounds, eg. CO_2 can act as a solvent for organic compounds. This property can be used to clean up circuit boards, oil contaminated systems or be a host for organic synthesis.

4. Chemical Vapor Transport

- A polycrystalline sample, A, and a transporting species, B, are sealed together inside a tube.
- Upon heating, the transporting species reacts with the sample to produce a gaseous species AB.
- When AB reaches the other end of the tube, which is held at a different temperature, it decomposes and re-deposits A.
- If formation of AB is endothermic, crystals are grown in the cold end of the tube.

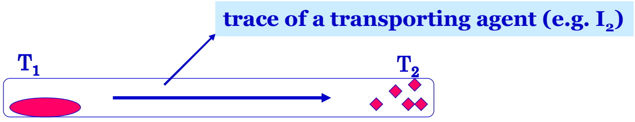
  A (powder) + B (g)→ AB (g) (hot end)
  AB (g) → A (single crystal) + B (g) (cold end)
- If formation of AB is exothermic, crystals are grown in the hot end of the tube.

  A (powder) + B (g) → AB (g) (cold end)
  AB (g) → A (single crystal) + B (g) (hot end)
- Typical transporting agents include:
- I_2, Br_2, Cl_2, HCl, NH_4Cl, H_2, H_2O, $TeCl_4$, $AlCl_3$, CO, S_2
- Temperature gradient is typically created and controlled using a two-zone furnace.
- Tubes are usually SiO_2, unless reactive, in which case metal tubes (Pt, Au, Nb, Ta, W) are used.

Chemical Transport Reaction

A solid is dissolved in the gas phase at one place ($T=T_1$) by reaction with a transporting agent (e.g. I_2). At another place ($T=T_2$) the solid is condensed again.

Whether $T_1 < T_2$ or $T_1 > T_2$ depends on the thermochemical balance of the reaction !
Transport can proceed from higher to lower or from lower to higher temperature



Main application: purification and crystallization of solids

5. Single Crystal Growth

- How do single crystals differ from polycrystalline samples?

Single crystal specimens maintain translational symmetry over macroscopic distances (crystal dimensions are typically 0.1 mm – 10 cm).

- Why would one go to the effort of growing a single crystal?

Structure determination and intrinsic property measurements are preferably, sometimes exclusively, carried out on single crystals.
For certain applications, most notably those which rely on optical and/or electronic properties (laser crystals, semiconductors, etc.), single crystals are necessary.

- What factors control the size and purity of single crystals?

Nucleation and Growth. If nucleation rates are slow and growth is rapid, large crystals will result. On the other hand if nucleation is rapid, relative to growth, small crystals or even polycrystalline samples will result.

Crystal Growth Theory

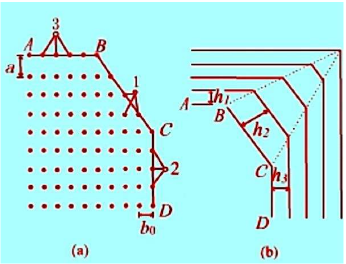
- Initially form a nucleus
  - this is highly dependent upon the presence of impurities and vessel surfaces
- Growth of nucleus
  - growth depends upon the presence of low energy surface sites such as steps
  - presence of additives in solution may alter relative rates for different faces
  - the faces with low surface energy grow more slowly and are therefore larger

Law of Bravais

The faces that appear on a crystal will be parallel to the lattice planes with the greatest density.

Why?

面网密度大
↓
面网间距大
↓
对生长质点吸引力小
↓
生长速度慢
↓
最可能出现和发展的晶面



The crystal planes that grow fastest will grow themselves out of existence, and the lowest ones will preserve.

实际中也存在着偏离布拉威法则的实例

原因：

1. 实际晶体的生长不仅受内部结构控制，而且还受到生长环境因素的影响；
2. 布拉威法则考虑的仅是由抽象的等同点所组成的空间格子，而不是由实在的原子所组成的真实结构，真实结构中原子面的密度及面间距可能与相应面网的面网密度及面间距不一致。如晶体结构中有螺旋轴或滑移面存在时。

Crystal Growth — Practice

generally classified as:

each method has several different versions

solid growth	solid-solid
vapor growth	sublimation-condensation ~ µm/hr
solution growth	supersaturation ~ mm/day
melt growth	directional solidification from the melt ~ mm/hr

(1) Grow from solid phase

Example: Synthetic Diamond

Principle: Solid A → single crystal Solid B (phase change)

The production of diamonds

Large synthetic diamonds

(2) Growth From the Vapor Phase

Principle: Gas (Vapor) → Solid (Condensation)
Chemical Vapor Transport

- Not very common
- Used for some sublimable compounds
- Used where a material can be transported by the addition of an appropriate reagent

$$ZnS(s) + I_2(g) \longrightarrow ZnI_2(g) + 1/8S_8(g)\ \text{(exothermic)}$$

(3) Growth From Solution

- The most common method
- Based on precipitation from a saturated solution
- Saturation can be achieved in many ways
  - – cool solution
  - – evaporate solvent off
  - – add things to solvent to reduce solubility
  - Hydrothermal Growth

Solutions

- Saturated Solution:

A solution containing the maximum amount of dissolved solute at a given temperature.

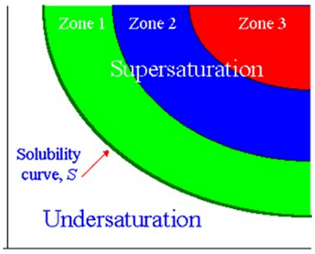
- Unsaturated Solution:

A solution containing less than the maximum amount of dissolved solute at a given temperature.

- Supersaturated Solution:

A solution containing more than the maximum amount of dissolved solute at a given temperature. A non-equilibrium situation.

Solutions



Zone 1 — Metastable zone. The solution may not nucleate for a long time, but this zone will sustain growth. It is frequently necessary to add a seed crystal.

Zone 2 — Nucleation zone. Product crystals nucleate and grow.

Zone 3 — Precipitation zone. Product does not nucleate but precipitate out of solution.

Nucleation

phenomenon whereby a “nucleus”, such as a dust particle, a tiny seed crystal starts a crystallization process.

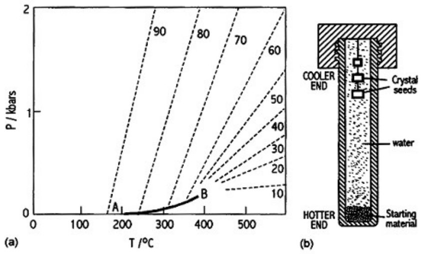
Common difficulties:

1.If supersaturation is too high, too many nuclei form, hence an overabundance of tiny crystals.

2. In supersaturated solutions that don’t experience spontaneous nucleation, crystal growth often only occurs in the presence of added nuclei or “seeds”.

Hydrothermal Growth of Quartz Crystals

- Large quartz crystals are needed as oscillators for timing applications
- Large quartz crystals are grown from basic aqueous solution at high P/T due to improved solubility of SiO_2



Hydrothermally grown quartz

Hydrothermal Growth of Quartz Crystals

- Water medium
- Nutrients region: 400°C
- Seed region: 370°C
- Pressure 1.7 Kbar
- Mineralizer 1M NaOH

▸Uses of single crystal quartz:

- Radar, sonar, piezoelectric transducers, monochromators
- Annual global production hundreds of tons of quartz crystals, amazing

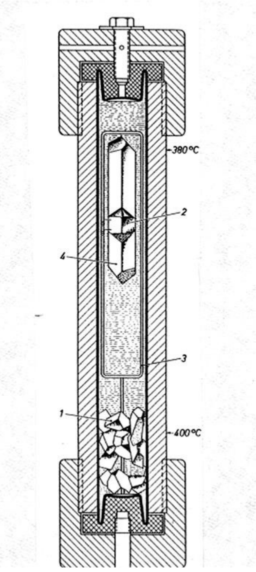
Hydrothermal Synthesis

Chemical transport in supercritical aqueous solution (H_2O: T_k= 374°C, P_k= 217.7 atm)

Autoclave for the growth of SiO_2 single crystals (→ quartz)

1500 bar, T- gradient 400 →370°C

1: nutrient (powder)
2: seed crystal
3: mechanical fixing of crystal
4: product crystal



Hydrothermal Synthesis of Crystals

▸Crystal growth hydrothermally involves:
▸Temperature gradient reactor
▸Dissolution of reactants at one end
▸Transport with help of mineralizer to seed at the other end
▸Crystallization at the other end.
▸Note that because some materials have negative solubility coefficients, crystals can actually grow at the hotter end in a temperature gradient hyrdothermal reactor, counterintuitive but true, good example is α-$AlPO_4$ known as Berlinite, important for its high piezoelectric coefficient (yes larger than α-quartz with which it is isoelectronic) and use as a high frequency oscillator

- Hydrothermal crystal growth is also suitable for growing single crystals of:
- Ruby: Cr^{3+}/Al_2O_3
- Corundum: α-Al_2O_3
- Sapphire: Cr_2^{6+}/Al_2O_3
- Emerald: $Cr^{3+}/Be_3Al_2Si_6O_{18}$
- Berlinite: α-$AlPO_4$
- Metals: Au, Ag, Pt, Co, Ni, Tl, As

Role of the Mineralizer

⌑Consider the growth of quartz crystals

⌑Control of crystal growth rate, through choice of mineralizer, temperature and pressure

Solubility of quartz in water is important

$$SiO_2 + 2H_2O \rightarrow Si(OH)_4$$

Solubility about 0.3 wt% even at supercritical temperatures >374°C
A mineralizer is a complexing agent (not too stable) for the reactants/precursors that need to be solublized (not too much) and transported to the growing crystal
Some mineralizing reactions:

NaOH mineralizer, dissolving reaction, 1.3-2.0 KBar

$$3SiO_2 + 6OH^- \rightarrow Si_3O_9^{6-} + 3H_2O$$

Na_2CO_3 mineralizer, dissolving reaction, 0.7-1.3 KBar

$$SiO_2 + 2OH^- \rightarrow SiO_3^{2-} + H_2O$$

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$$

■NaOH creates growth rates about 2x greater than with Na_2CO_3 because of different concentrations of hydroxide mineralizer

Examples of Hydrothermal Crystal Growth and Mineralizers

- ● Berlinite α-$AlPO_4$
  - ⊕ Powdered $AlPO_4$ cool end of reactor, negative solubility coefficient!!!
  - ⊕ H_3PO_4/H_2O mineralizer
  - ⊕ $AlPO_4$ seed crystal at hot end
- ● Emeralds Cr^{3+}:$Be_3Al_2Si_6O_{18}$
  - ⊕ SiO_2 powder at hot end 600˚C
  - ⊕ NH_4Cl or HCl/H_2O mineralizer, 0.7-1.4 Kbar, cool central region for seed, 500˚C
  - ⊕ $Al_2O_3/BeO/Cr^{3+}$ dopant powder mixture at other hot end 600ºC

$$6SiO_2 + Al_2O_3 + 3BeO \rightarrow Be_3Al_2Si_6O_{18}$$

Beryl contains $Si_6O_{18}^{12-}$ six rings

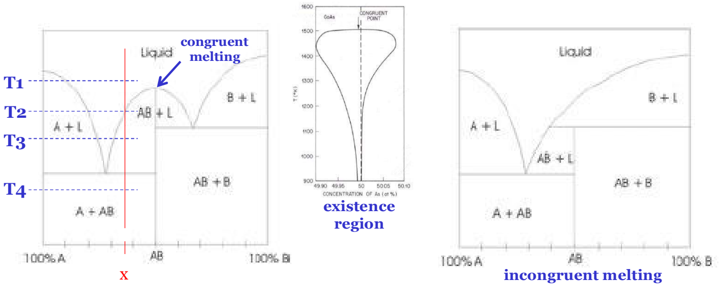
(4) Growth From the Melt

- ■ Very important, but not possible for most materials
- ■ Material must be stable above melting point
- ■ Phase diagram must allow direct crystallization
  - ✸**Czochralski Process**
  - ✸**Bridgman-Stockbarger-Process**
  - ✸**Verneuil Method**
  - ✸**Molten Metal Fluxes Process**
  - ✸**Zone Melting Process**

Growth From the Melt (1)

feasibility conditions:

- **congruent melting**
  - **not trivial in the case of binary or more compounds**



Growth From the Melt (2)

feasibility conditions (continued):

raw material must not decompose before melting

- changes in stoichiometry of the melt due to different evaporation rates are also to be avoided

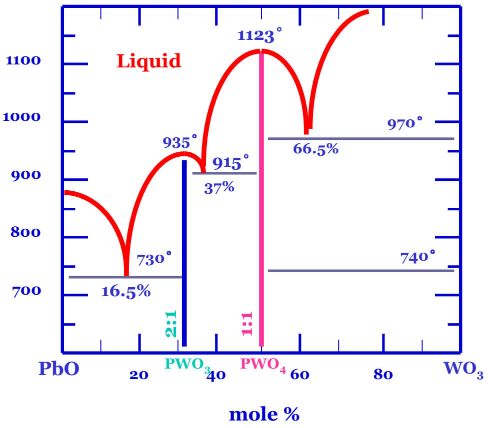
- grown crystal must not undergo a solid state phase transformation when cooled down to room temperature

preliminary detailed study of phase diagram is needed {
thermodifferential analysis
thermogravimetrical analysis
X-ray diffraction analysis
...

Growth From the Melt (3)

example

PbO-WO_3 compounds



Slow Cooling of the Melt

- With congruently melting materials (those which maintain the same composition on melting) one simply melts a mixture of the desired composition then cools slowly (typically 2 – 10°C/hr) through the melting point.
- More difficult with incongruently melting materials, knowledge of the phase diagram is needed.
- Often times the phase diagram is not known, consequently there is no guarantee that crystals will have the intended stoichiometry.
- Molten salt fluxes are often used to facilitate crystal growth in systems where melting points are very high and/or incongruent melting occurs.
- Crystals grown in this way are often rather small, thus this method is frequently used in research, but usually not appropriate for applications where large crystals are needed.

Growth From the Melt (4)

characteristics

- fast (~mm/hr) growth rate is limited by heat transfer, not by mass transfer
- allows for a large variety of techniques
  - Czochralski
  - Bridgman-Stockbarger
  - Verneuil
  - zone melting and floating zone

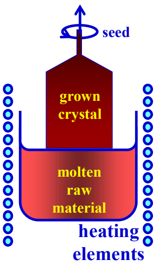
Czochralski Method


Jan Czochralski
(1885 - 1953)

A seed crystal mounted on a rod is dipped into the molten material. The seed crystal's rod is pulled upwards and rotated at the same time. By precisely controlling the temperature gradients, rate of pulling and speed of rotation, a single-crystal cylindrical ingot is extracted from the melt. The process may be peformed in controlled atmosphere and in inert chamber.

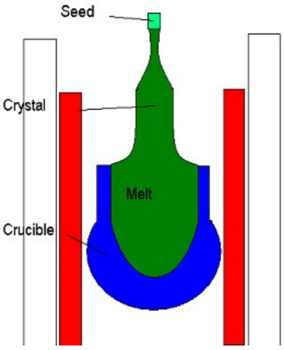
characteristics:

- charge and seed are separated at start
- no material is added or removed (conservative process)
- charge is held at temperature slightly above melting point
- crystal grows as atoms from the melt adhere to the seed



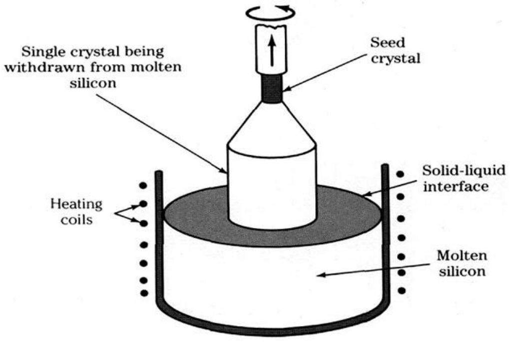
Czochralski Process

- Start with a single crystal seed of known orientation.
- Somewhere along its length will be the interface of the melt to air. In other words, melt half of it.
- Slowly pull up into air.
- Crucible material will reintroduce some impurities at the surface of boule.



Czochralski process: Si

— a rotating seed crystal is raised slowly from a melt with equal composition



Czochralski Crystal Growth Technique

- This technique originates from pioneering work by Czochralski in 1917 who pulled single crystals of metals. Since crystal pulling was first developed as a technique for growing single crystals, it has been used to grow germanium and silicon and extended to grow a wide range of compound semiconductors, oxides, metals, and halides. It is the dominant technique for the commercial production of most of these materials.

- One step in the production of semiconductor devices involves the growth of a large (10 or more inches in diameter!) single crystal of silicon by the Czochralski process. In this process, a solid seed crystal is rotated and slowly extracted from a pool of molten Si.
  - A pure silicon seed crystal is now placed into the molten sand bath.
  - This crystal will be pulled out slowly as it is rotated.
  - The result is a pure silicon tube that is called an ingot

Commercial $LiNbO_3$ Crystals

Gadolinium Gallium Garnet
Used as substrate for growth of devices

Czochralski Method

advantages

- growth from free surface (stress free)
- crystal can be observed during the growth process
- forced convection easy to impose
- large crystals can be obtained
- high crystalline perfection can be achieved
- good radial homogeneity

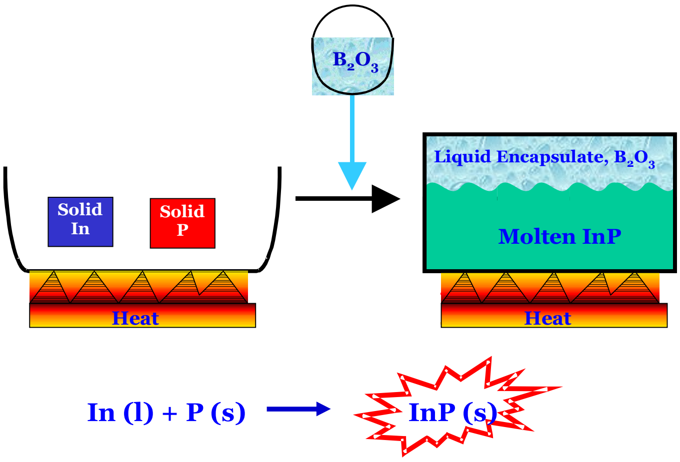
drawbacks

- delicate start (seeding, necking) and sophisticated further control
- delicate mechanics (the crystal has to be rotated; rotation of the crucible is desirable)
- cannot grow materials with high vapor pressure
- batch process (axial segregation, limited productivity)

Growing GaAs Crystal Requires a Modification of the Czochralski Method

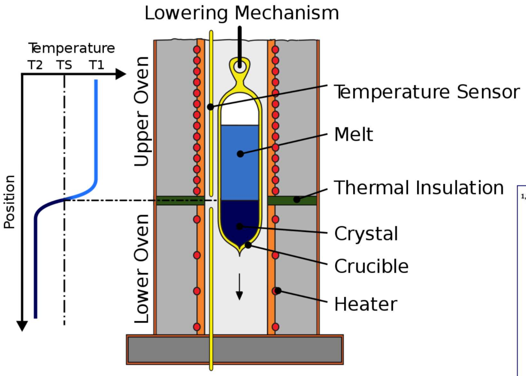
- **Layer of molten inert oxide like B_2O_3 was spread on to the molten feed material to prevent preferential volatilization of the both volatile component of Ga and As, this is critical for maintaining precise stoichiometry. For example $Ga_{1+x}As$ and $GaAs_{1+x}$ which are respectively rich in Ga and As, become p-doped and n-doped .**
- **The Czochralski crystal pulling technique has proven invaluable for growing many large single crystals in the form of a rod, which can subsequently be cut and polished for various applications, some important examples: Si, Ge, GaAs, $LiNbO_3$, $SrTiO_3$, $NdCa(NbO_3)_2$**

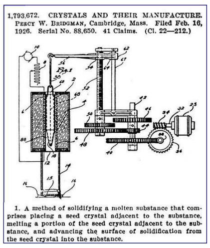
Liquid Encapsulated Czochralski Technique



In (l) + P (s) → InP (s)

Bridgman-Stockbarger-Process (Moving Temperature Gradient)





1,793,672. CRYSTALS AND THEIR MANUFACTURE. Percy W. Bridgman, Cambridge, Mass. Filed Feb. 16, 1926. Serial No. 88,650. 41 Claims. (Cl. 22—212.)

1. A method of solidifying a molten substance that comprises placing a seed crystal adjacent to the substance, melting a portion of the seed crystal adjacent to the substance, and advancing the surface of solidification from the seed crystal into the substance.

advantages

- the shape of the crystal is defined by the container
- no radial temperature gradients are needed to control the crystal shape.
- low thermal stresses result in low level of stress-induced dislocations.
- crystals may be grown in sealed ampules (easy control of stoichiometry)
- relatively low level of natural convection
- easy control and maintenance

drawbacks

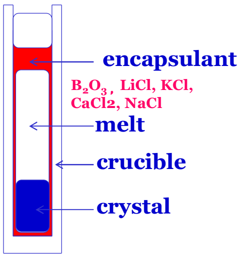
- confined growth (crucible may induce stresses during cooling)
- difficult to observe seeding and growing processes
- changes in natural convection as the melt is depleted
- delicate crucible and seed preparation, sealing, etc.

applications

- melts with volatile constituents:
  - III-V compounds (GaAs, lnP, GaSb)
  - II-VI compounds (CdTe)
- ternary compounds:
  - $Ga_{1-x}ln_xAs$, $Ga_{1-x}ln_xSb$, $Hg_{1-x}Cd_xTe$

improvement example (liquid encapsulation)

- reduced nucleation
- reduced thermal stresses
- reduced evaporation
- prevents contact between crucible and melt



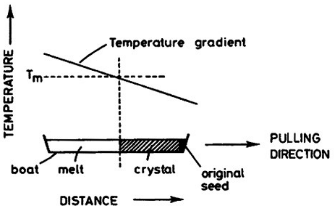
encapsulant characteristics

- low vapor pressure
- melting temperature lower than the crystal
- density lower than the density of the melt
- no reaction with the melt or crucible

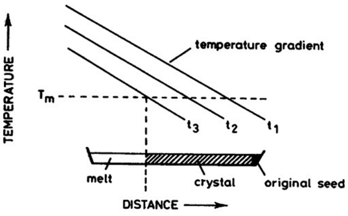
Stockbarger Method

Move the crucible containing a seed and the melt through a temperature gradient so that the melt crystallizes onto the seed crystal

Stockbarger method is based on a crystal growing from the melt, involves the relative displacement of melt and a temperature gradient furnace, fixed gradient and a moving melt/crystal

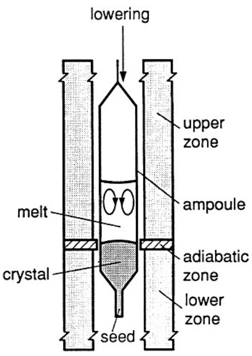


Bridgman Method



Bridgman method is again based on crystal growth from a melt, but now a **temperature gradient furnace is gradually cooled** and crystallization begins at the cooler end, fixed crystal and changing temperature gradient

Vertical Bridgman Crystal Growth Process



The furnace consists of three zones:

(1) the upper zone (temperature>T_{mp}; melting point of the crystal),

(2) the lower zone (temperature<T_{mp})

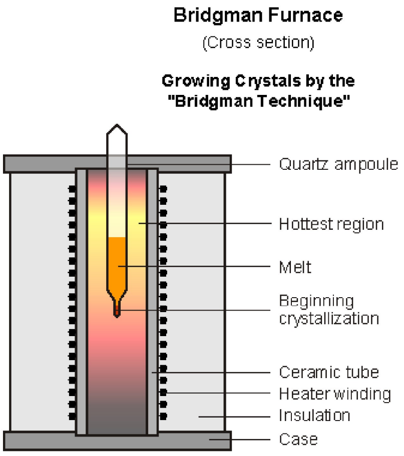
(3) an adiabatic zone (a baffle) between the two.

The ampoule is raised into the upper zone until only the lower portion of the single crystal seed remain unmelted in the lower zone. After the temperature stabilizes, the ampoule is lowered slowly into the lower zone to initiate crystal growth from the seed.

Stockbarger and Bridgman Methods

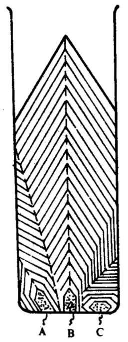
- Stockbarger method is based on a crystal growing from the melt, involves the relative displacement of melt and a temperature gradient furnace, fixed gradient and a moving melt/crystal
- Bridgman method is again based on crystal growth from a melt, but now a temperature gradient furnace is gradually cooled and crystallization begins at the cooler end, fixed crystal and changing temperature gradient
- Both methods are founded on the controlled solidification of a stoichiometric melt of the material to be crystallized
- Enables oriented solidification
- Melt passes through a temperature gradient
- Crystallization occurs at the cooler end
- Both methods benefit from seed crystals and controlled atmospheres

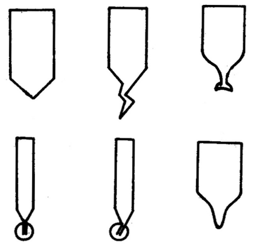
Bridgman-Stockbarger Crystal Growth Technique



Bridgman Technique

Geometry Elimination Rule





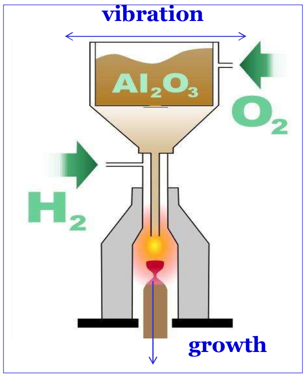
Different crucible shape for controlling the orientation of seed crystals

Verneuil Method

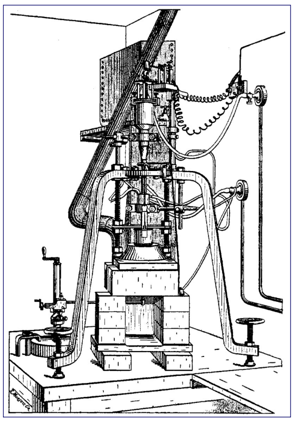
- Used for growing large crystals of high melting point solids

For example:

- Ruby from Cr^{3+}/Al_2O_3 powder
- Sapphire from Cr_2^{6+}/Al_2O_3 powder



1902, Auguste Verneuil



characteristics:

- no crucible contamination
- highly pure starting material (>99.9995%)
- strict control of flame temperature
- precise positioning of melted region

Verneuil Fusion Flame Method

- 1902 first recorded use of the method
- Useful for growing crystals of extremely high melting metal oxides
- Starting material fine powder
- Passed through O_2/H_2 flame or plasma torch (ouch, they are hot!)
- Melting of the powder occurs in the flame
- Molten droplets fall onto the surface of a seed or growing crystal

---

Flux Growth

growth from solutions

- melt non congruently
- decompose before melting
- have very high melting point
- undergo solid state phase transformation between melting point and room temperature

molten salt (flux) growth

- oxides with very high melting points

key requirement

high purity solvent insoluble in the crystal

flux:

a liquid reaction medium that dissolves the reactants and products, but do not participate in the reaction

typical solvents:	PbO, PbF_2, B_2O_3, KF
main advantage:	carried on at much lower temperature than melting point
limitations:	very slow, borderline purity, platinum crucibles, stoichiometry hard to control

---

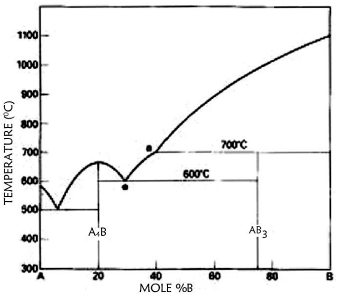
Flux Growth

- Oxides like Bi_2O_3 and PbO have low melting points and may be used as solvents
  - – $PbTiO_3$ can be crystallized from PbO/PbF_2 mixtures
  - – need to pick a flux that is compatible with the desired product
- Alkali and alkaline earth metal hydroxides and halides are also frequently used as fluxes

---

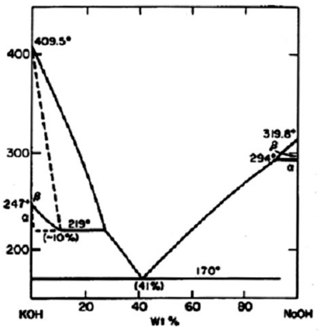
Phase Diagram Can Give Problems

- Crystal growth of an incongruently melting phase can be very difficult
- Can not just go straight from a stoichiometric melt ⇒ may need to use flux or other method
- A_4B can be grown directly from stoichiometric melt AB_3 can not



Growing From Wet KOH/NaOH

- Many superconducting copper oxides have been grown by this method
- Synthesis of $EuBa_2Cu_3O_{7-\delta}$
  - take stoichiometric amounts of CuO, Eu_2O_3 and $Ba(OH)_2 \cdot 8H_2O$ and dissolve in molten KOH/NaOH at 450°C
  - gives clear blue solution
  - solution held at 450°C under flowing dry air
  - as water is lost, the product crystallizes out



Molten Metal Fluxes

- Molten metals can sometimes be used as solvents. However, metal should not form stable compounds with reactants

$$Mn + 2Si \xrightarrow{\text{liquid Cu,1200°C}} MnSi_2$$

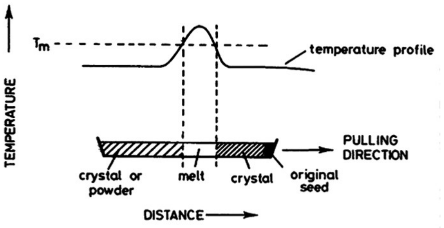
Heat materials in sealed ampoule. Using a Cu solvent avoids Mn loss due to heating at high temperatures

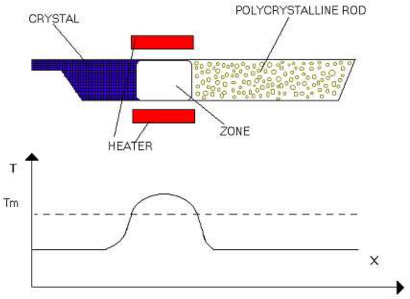
$$Ru + P \xrightarrow{\text{liquid Sn}} RuP_2$$

1:2:100 ratio of Ru, P and Sn sealed evacuated quartz tube. Heated to 1200°C and then slow cooled. Crystals recovered from Sn by washing with HCl.

Zone Melting

- Sweep a molten zone through the crucible in such a way that the melt crystallize onto a seed
- Method used for purifying existing crystals as impurities tend to stay with the liquid
- Method related to the Stockbarger technique
- Thermal profile furnace employed





characteristics:

- only a small part of the charge is molten
- material is added to molten region (nonconservative process)
- molten zone is advanced by moving the charge or the gradient
- axial temperature gradient is imposed along the crucible

advantages

Charge is purified by repeated passage of the zone (zone refining).
Crystals may be grown in sealed ampules or without containers (floating zone).
Steady-state growth possible.
Zone leveling is possible; can lead to superior axial homogeneity.
Process requires little attention (maintenance).
Simple: no need to control the shape of the crystal.
Radial temperature gradients are high.

drawbacks

Confined growth (except in floating zone).
Hard to observe the seeding process and the growing crystal.
Forced convection is hard to impose (except in floating zone).
In floating zone, materials with high vapor pressure can not be grown.

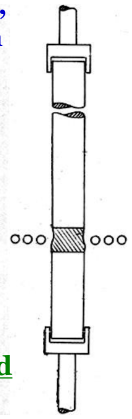
Floating Zone Melting

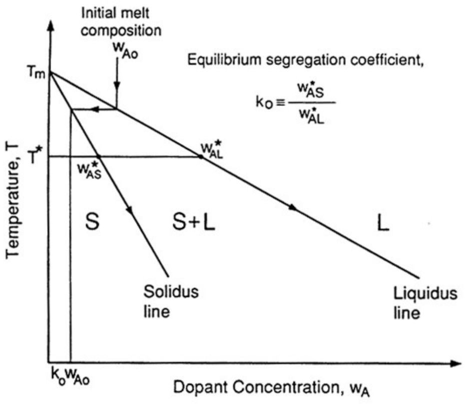
- When a small slice of the sample is molten and moved continuously along the sample, impurities normally dissolve preferably in the melt. (!! icebergs in salt water don't contain any salt !!)
- segregation coefficient k:

  $k = C_{solid}/C_{liquid}$

  (c: concentration of an impurity)

- Zone melting was first used as a purification technique. It, however, can also be used for crystal growth.
- only impurities with k < 1 can be removed by zone melting !!

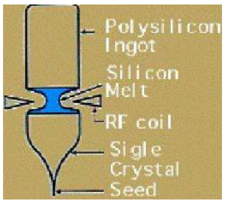


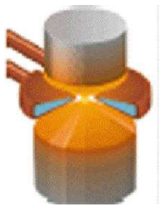


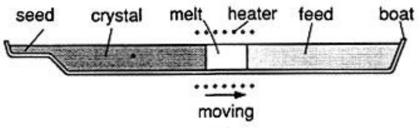
A phase diagram for studying dopant segregation

Floating Zone Growth of Silicon

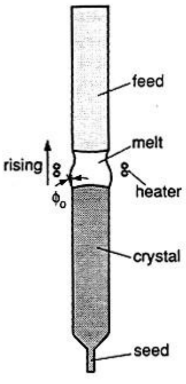
- Trace amount of impurities in inter-metallic compounds have a considerable influence on the physical properties of the material. Zone melting is a powerful technique for purification, as it passes the material through a thermal gradient melting only a small part of the batch. Impurities usually concentrate in the liquid rather than in the solid phase.
- Move polycrystalline ingot into hot zone a seed formation of single crystal.







(a)



(b)

Zone melting crystal growth:

(a) horizontal

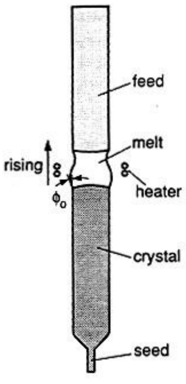
(b) floating zone

Zone melting crystal growth can also be conducted without a crucible, as in the floating-zone process.

The molten zone is sustained by the surface tension of the melt, and also by electromagnetic levitation if an induction heater is used.

The advantage of the floating-zone process is that it is free from contamination by the crucible material, which is particularly significant when growing single crystals from high-melting-point or reactive materials.

The disadvantage, however, is that the molten zone has a tendency to collapse under gravity.



(b)