Synthesis of Inorganic Solids

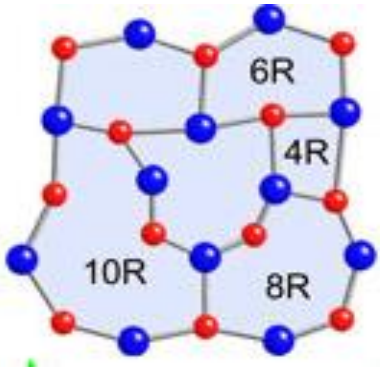
Classification

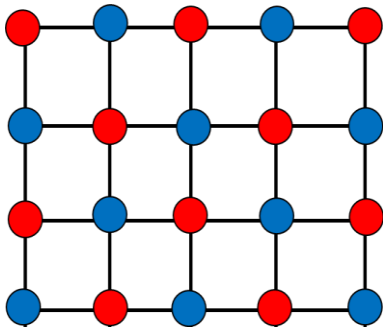
Inorganic Solids

Amorphous

Irregular arrangement of atoms
Non periodic, disorder structure

Natural amorphous
Solution processed (RT or low temp)
Quenching from melts





Crystalline

regular arrangement of atoms
periodic, highly order structure

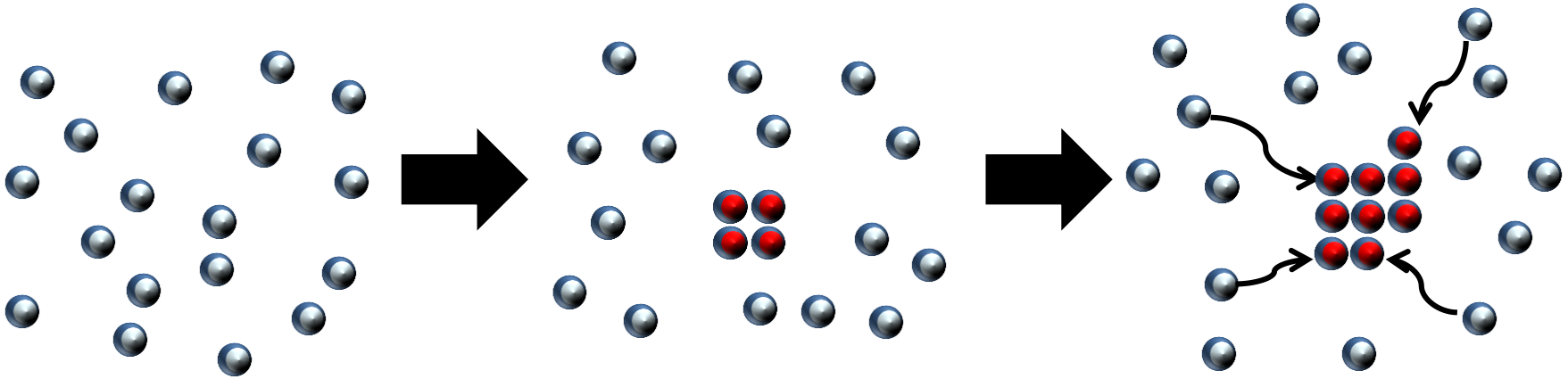
Solid state synthesis
Flux techniques (salt or metals)
Chemical vapor transport
Solution combustion
Hydro/solvothermal synthesis
Bridgman crystal growth
Czochralski process

Crystal Growth

Mobile atoms

Nucleation

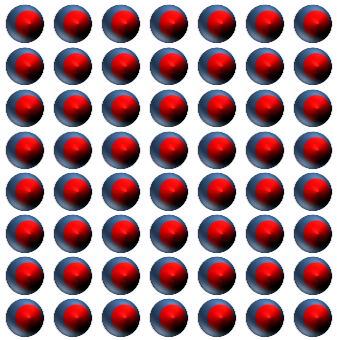
Growth

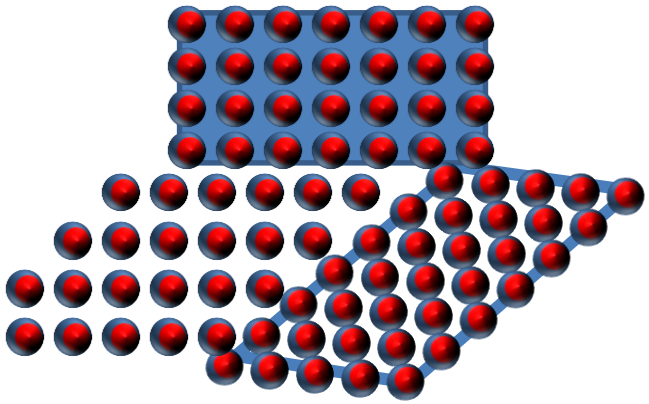


Single crystal

vs.

polycrystalline





Solid state synthesis

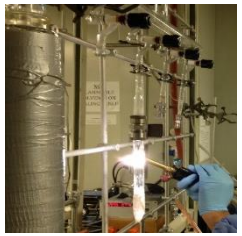
- Reaction among the ions of the solids
- The most useful method for the synthesis of inorganic solids, oxides, nitrides, phosphates, silicates, chalcogenides, etc.
- Reaction: $CaO + TiO_2 = CaTiO_3$ ($\geq 1300^oC$)

  # Homogeneous mixture of the solids

  # Pressed into pellets

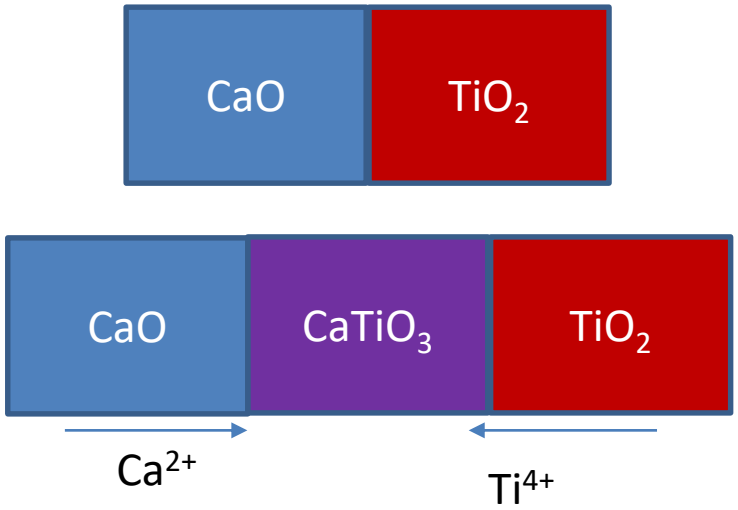






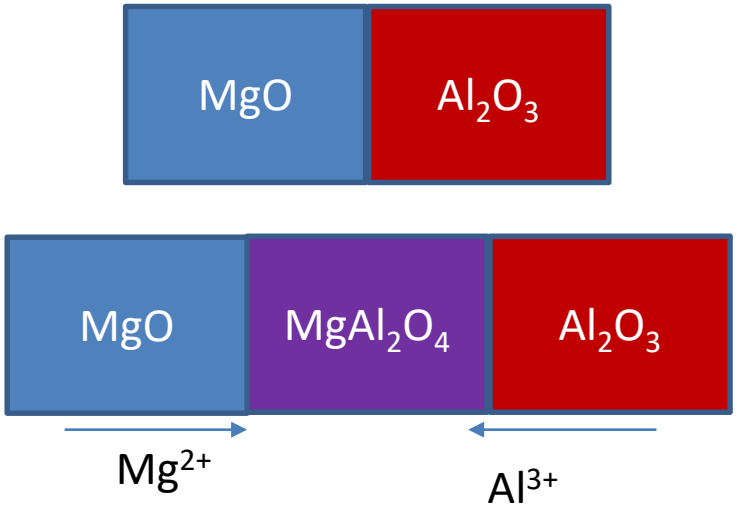
Mechanism of Solid State Reaction

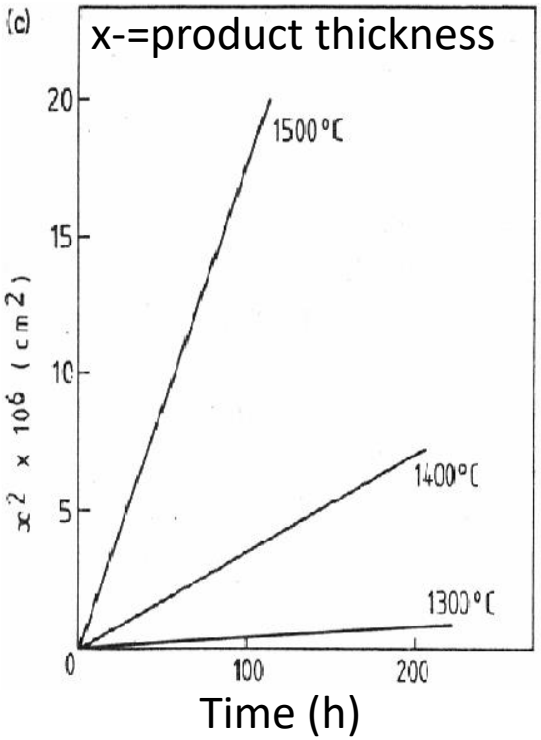
Reaction mechanism: $CaO + TiO_2 = CaTiO_3$



Reaction only occurs at the contact of the grains of CaO and TiO_2
Get nucleation at the contact point and then get diffuses to grow products
Diffusion control
Require high Temperature (≥500^{o}C), use absolute temperature that is > 2/3 of the MP of lowest melting reactant
Often leads to inhomogeneity
Reaction is very sow

Mechanism of Solid State Reaction





Interdiffusion of cations to form single crystals of MgO and Al_2O_3, Thickness, x of $MgAl_2O_4$ product layer as a function of temperature and time. (Pettit, Randklevand Felton, 1966)

The Phase Rule

- The phase rule; Gibbs phase rule (1875), relates the number of components and the number of degrees of freedom in a system at equilibrium by the formula

$$F = C - P + 2 \quad \text{or} \quad F + P = C + 2$$

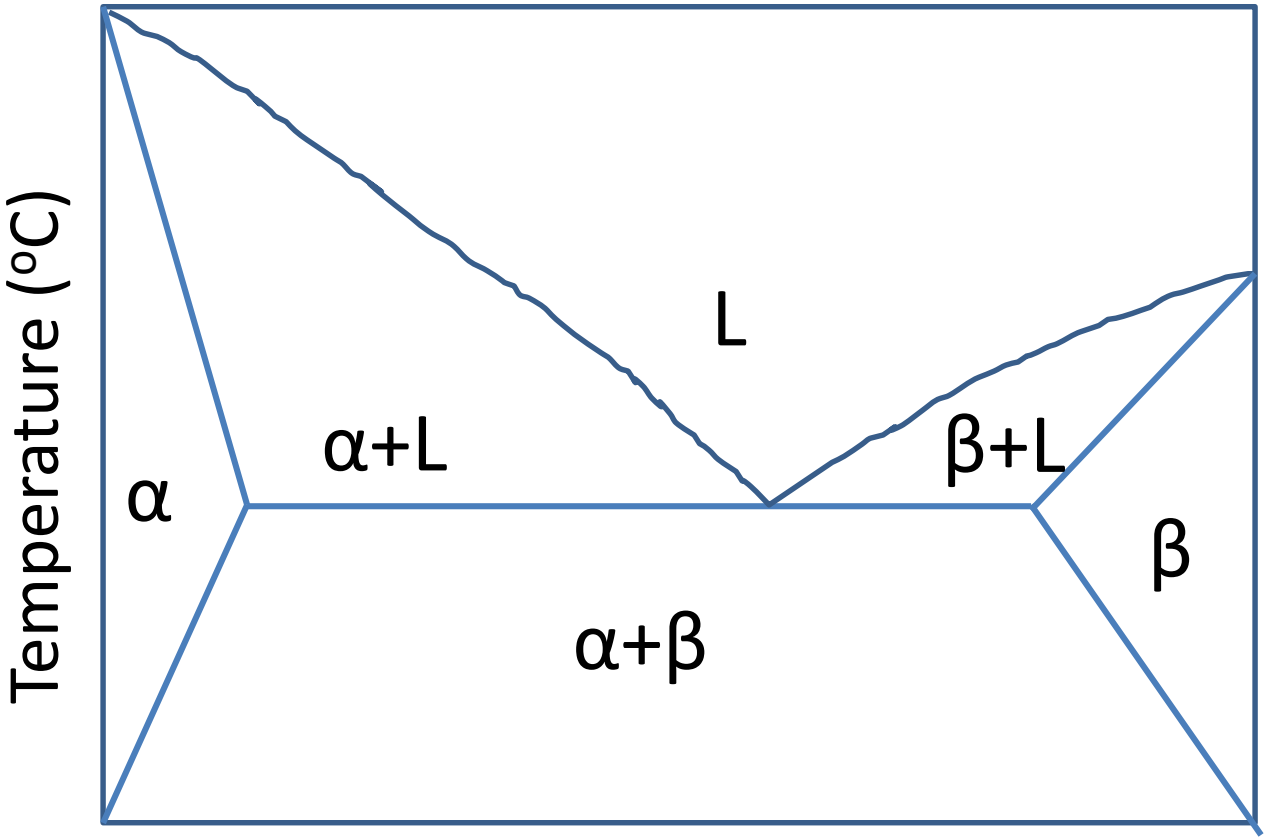
F equals the number of degrees of freedom or the number of independent variables

C equals the number of components in a system in equilibrium

P equals the number of phases

The digit 2 stands for the two variables, temperature and pressure

Phase Rule



At α

F=C-P+2

F=2-1+2=3

Pressure, Temp, mole fraction

At α+β

F=C-P+2

F=2-2+2=2

At constant pressure

The Lever rule

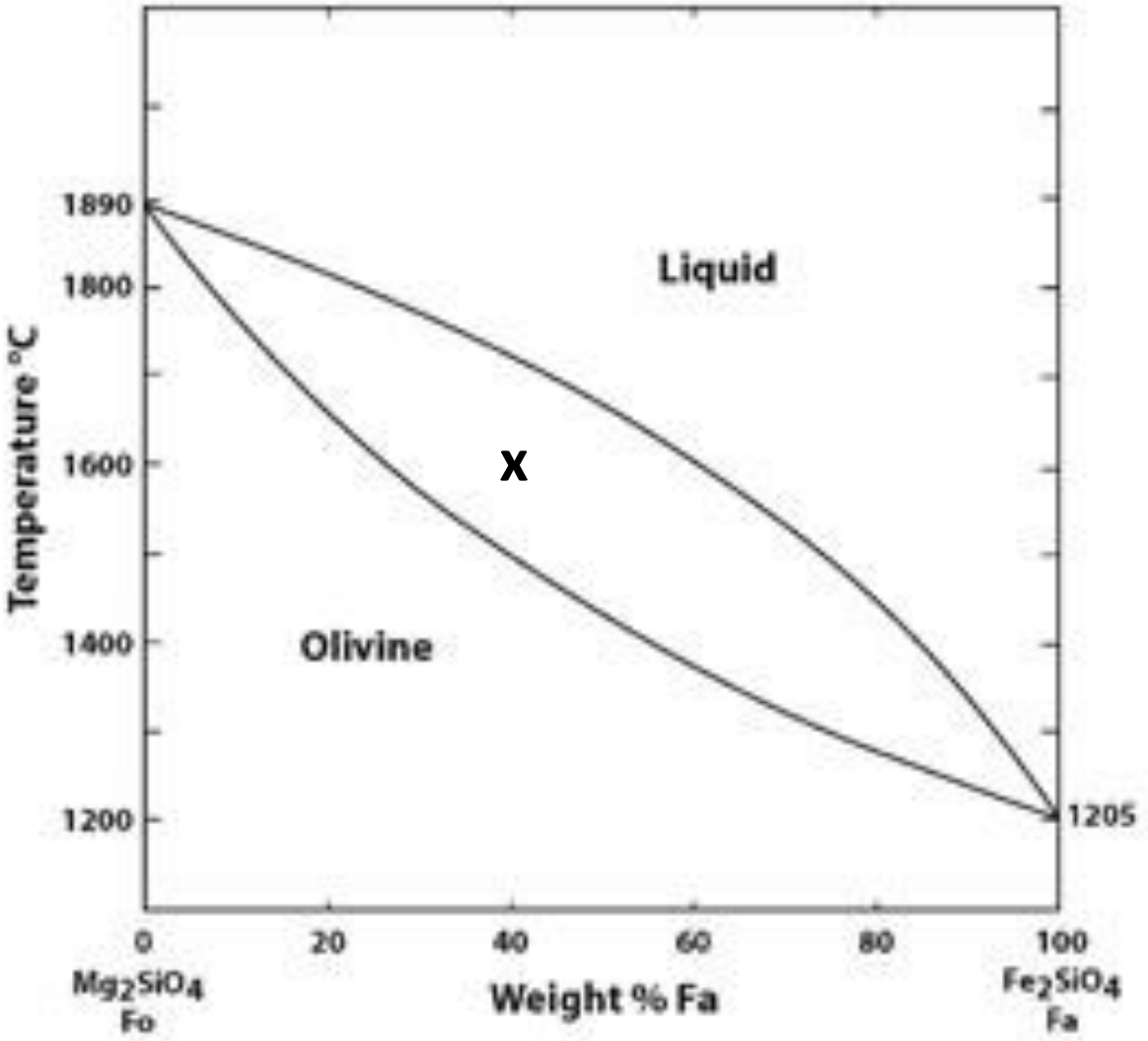
Finding the amounts of phases in a two phase region:

Step 1: Locate composition and temperature in diagram

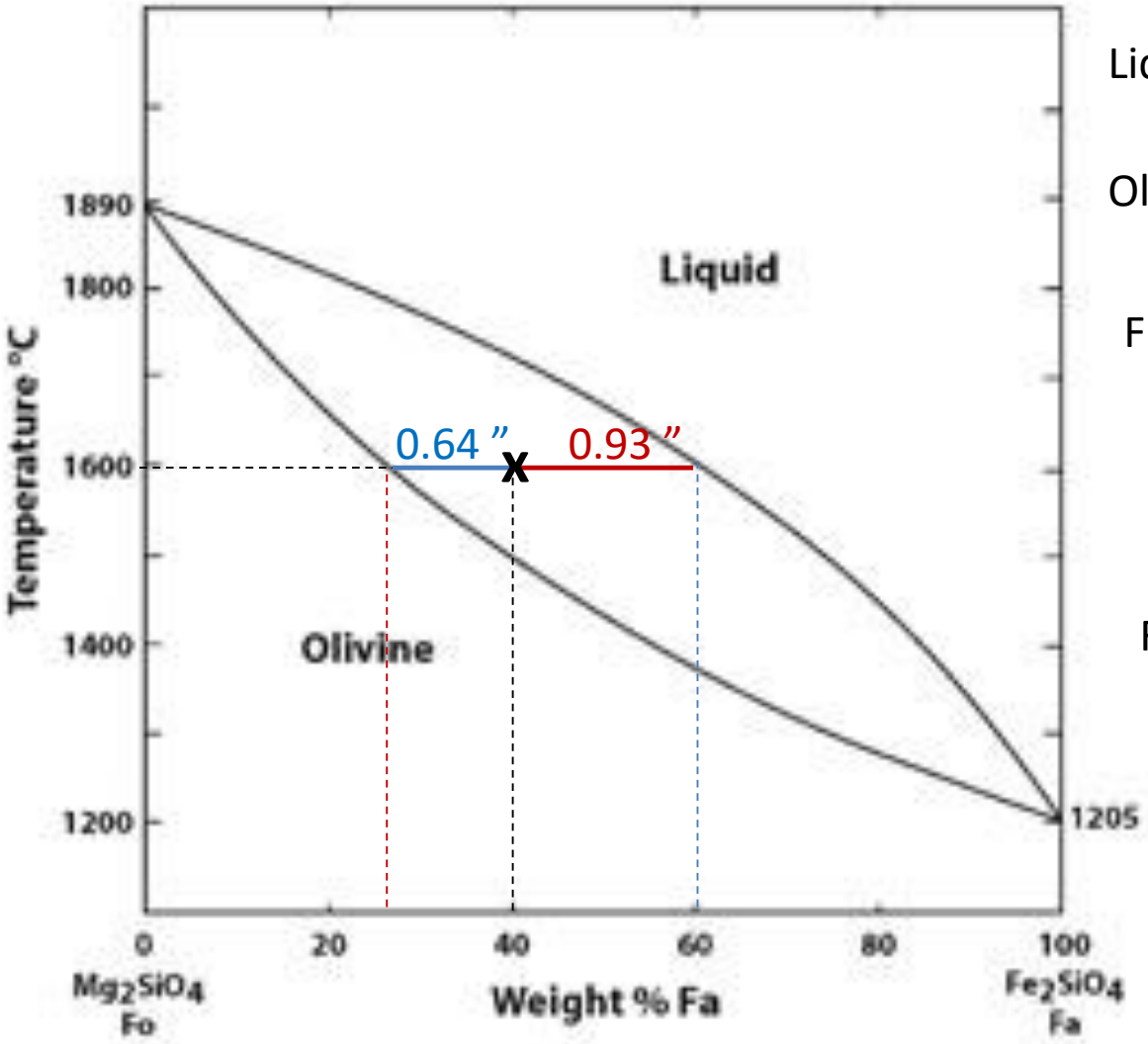
Step 2: In two phase region draw the tie line or isotherm

Step 3: Fraction of a phase is determined by taking the length of the tie line to the phase boundary **for the other phase** and dividing by the total length of tie line.

2-Component System



2-Component System



Liquid Composition = 60% Fe_2SiO_4

Olivine Composition = 27% Fe_2SiO_4

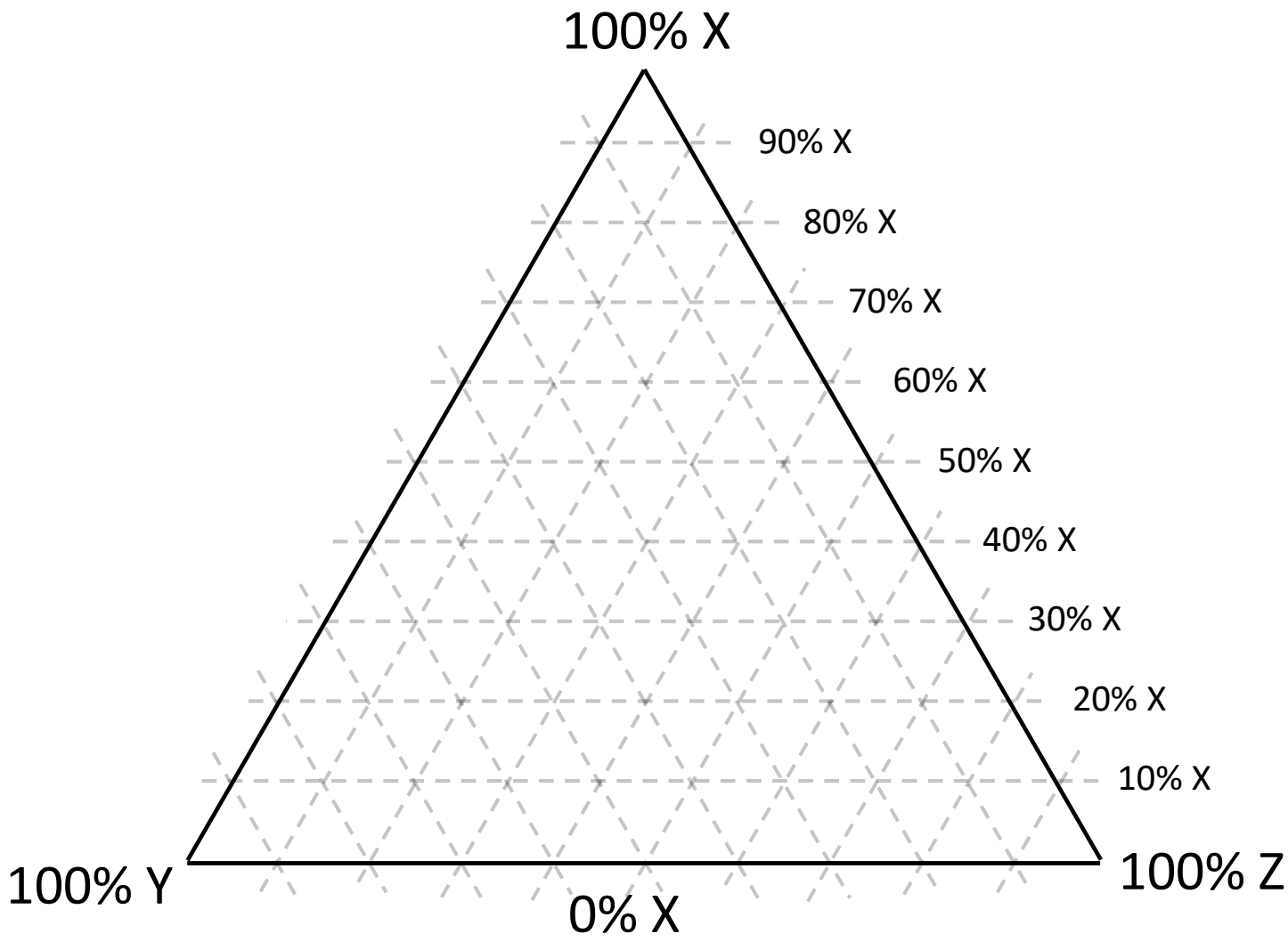
Fraction Olivine = $\frac{0.93}{0.64 + 0.93}$

= 0.59

Fraction Liquid = 0.41

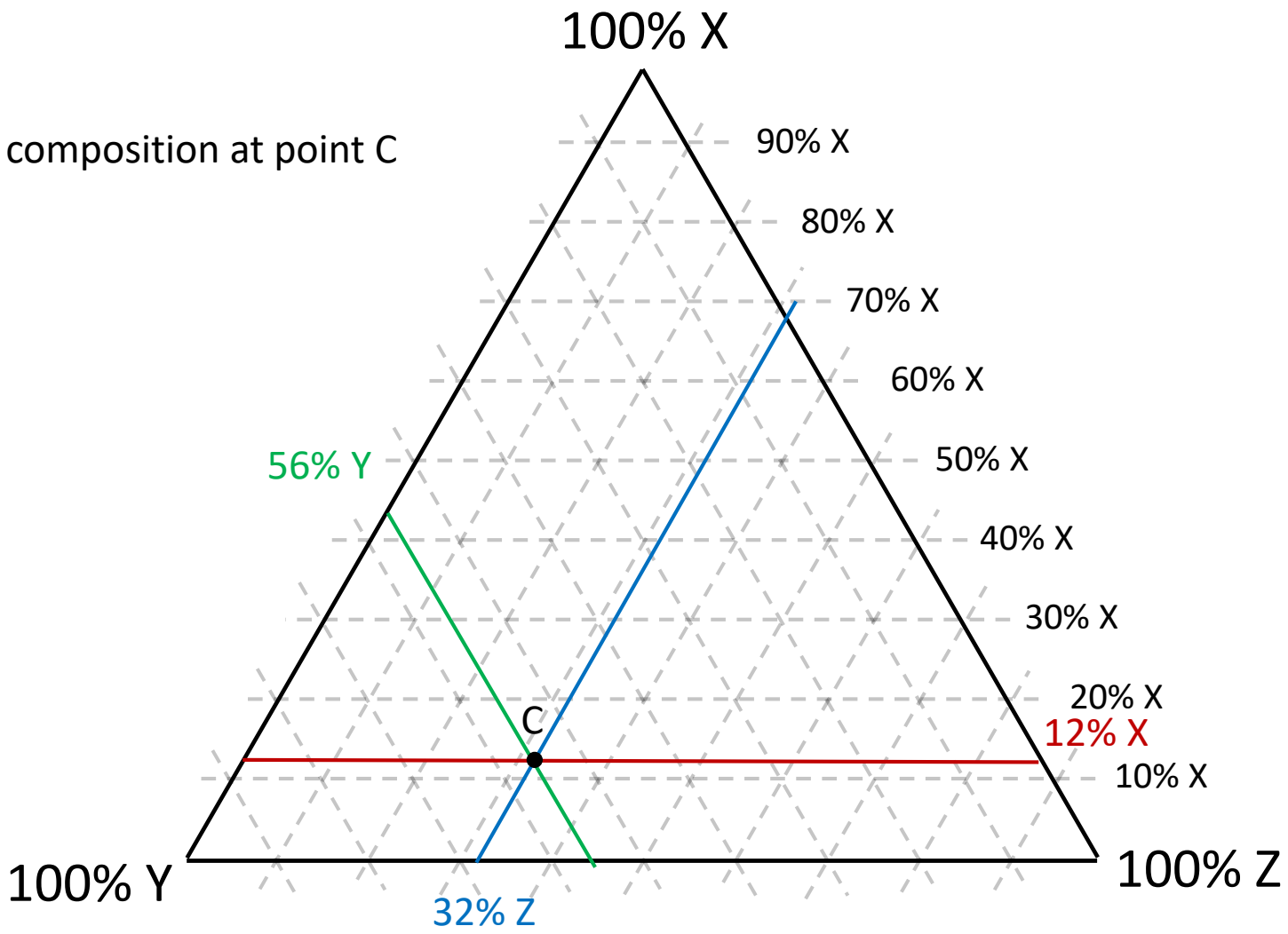
Calculate fraction olivine, liquid composition, and olivine composition at a global composition of 70 % Fe_2SiO_4 at 1450 °C

3-Component Systems



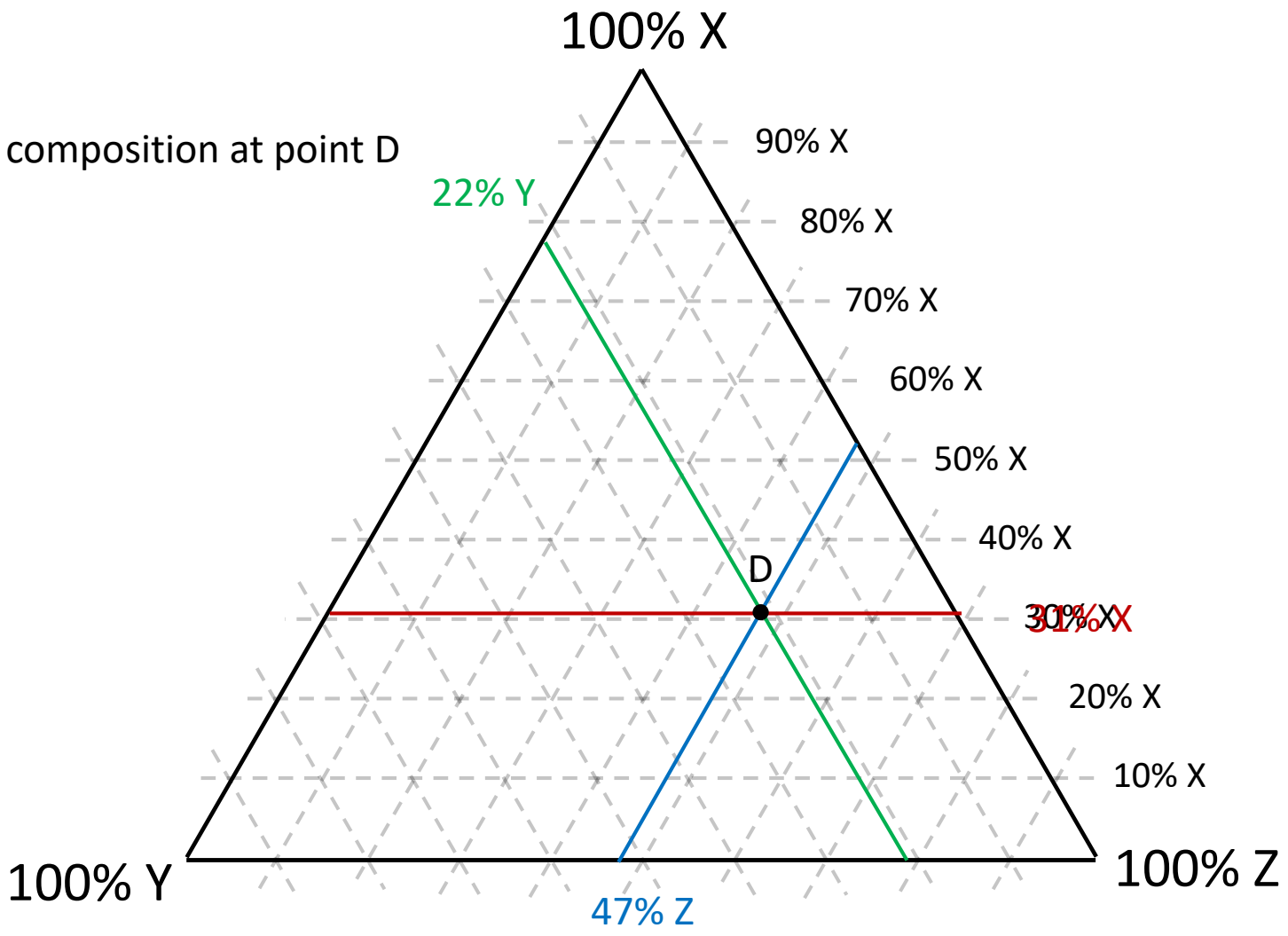
Calculating Compositions

Calculate composition at point C



Calculating Compositions

Calculate composition at point D



Exploring the Y-Ba-Cu System

- Each pair of students will synthesize the $YBa_2Cu_3O_{7-\delta}$ (YBCO) superconducting phase
- You will analyze the products formed via PXRD
- Each pair of students will calculate masses of reagents needed for one additional point on the phase diagram.
- You will draw the phase diagram based on phases we provide you

Y – Ba – Cu

Consider the ratios of Y, Ba, and Cu in $YBa_2Cu_3O_{7-\delta}$ (YBCO) .

1. Calculate the mole fraction of each metal in YBCO.
2. Plot the point on the diagram corresponding to YBCO.
3. Calculate masses of each reagent needed to form 2 grams of YBCO.

Molar Masses

Y_2O_3 – 225.81 g/mol

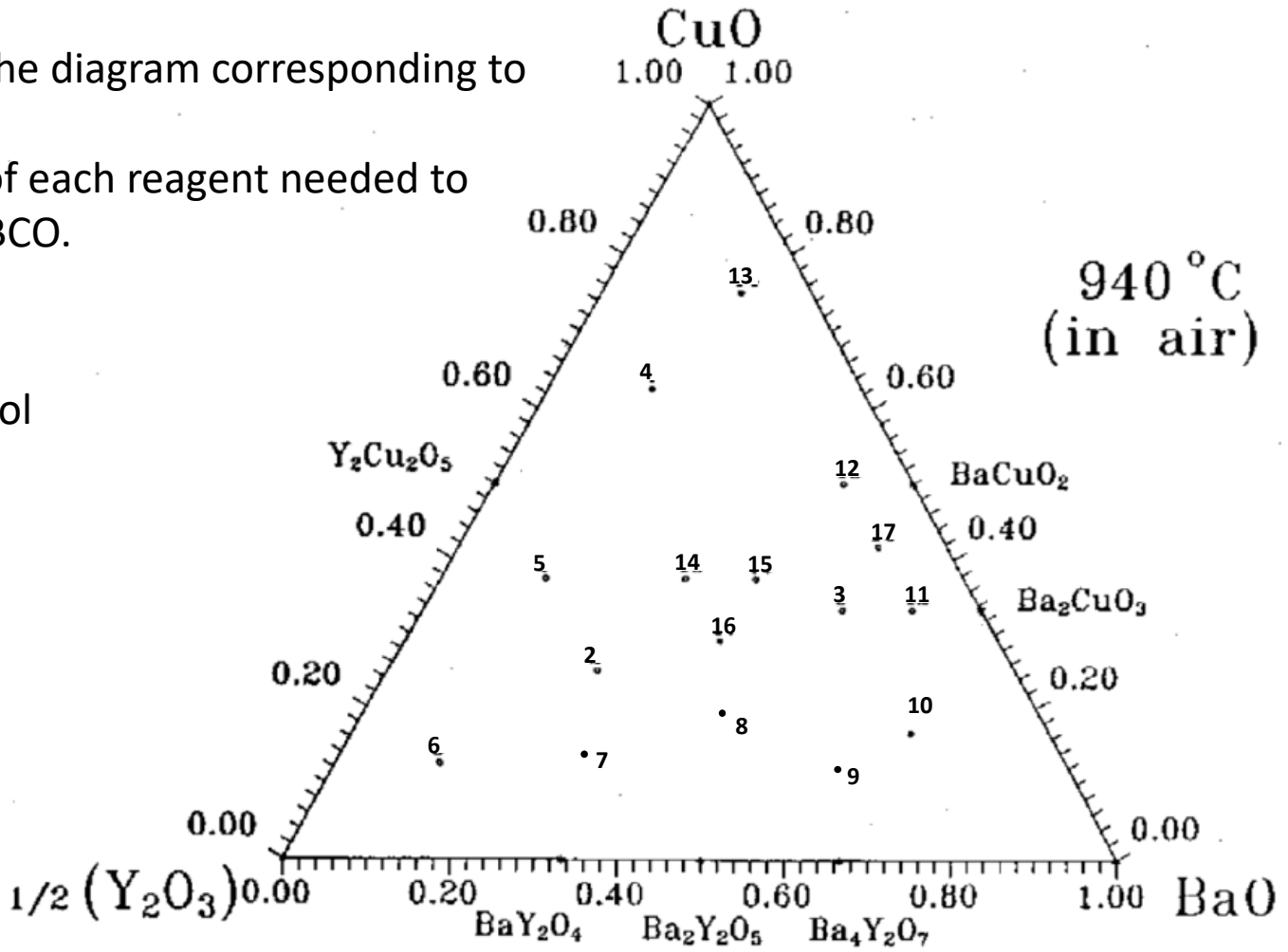
$BaCO_3$ – 197.34 g/mol

CuO – 79.545 g/mol

Y – 88.91 g/mol

Ba – 137.33 g/mol

Cu – 63.55 g/mol



Y – Ba – Cu

4. Choose one other point on the phase diagram and calculate masses of each reagent needed for 2 grams of total product.

You can predict the amount of oxygen in the final product based on the metal oxidation states. For example, a 1 : 1 : 1 ratio would have a hypothetical formula of $YBaCuO_{3.5}$.

Molar Masses
Y_2O_3 – 225.81 g/mol
$BaCO_3$ – 197.34 g/mol
CuO – 79.545 g/mol

Y – 88.91 g/mol
Ba – 137.33 g/mol
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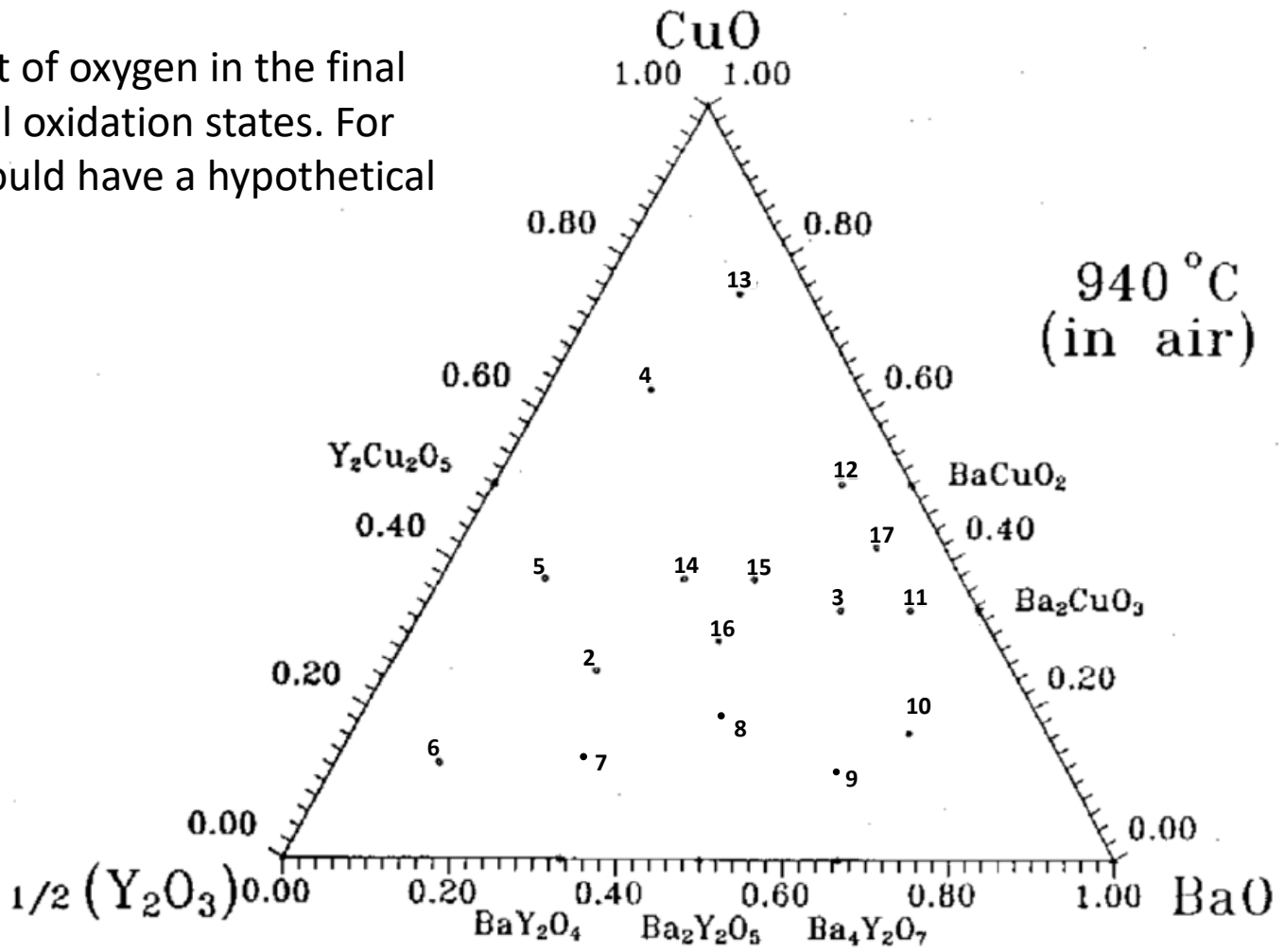


Back to solid state methods

Molten Fluxes Technique

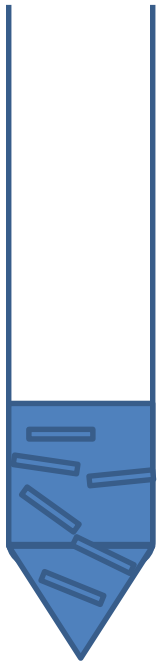
- Solubilize reactants → Enhanced Diffusion rate → Faster Reaction completion.
- Synthesis needs to be carried out at a temperature where the flux is a liquid.

<u>Opportunity</u>

- Lower Temperature than that of solid state reaction
- Growing single crystal
- New compounds
- Stabilization of the metastable compounds

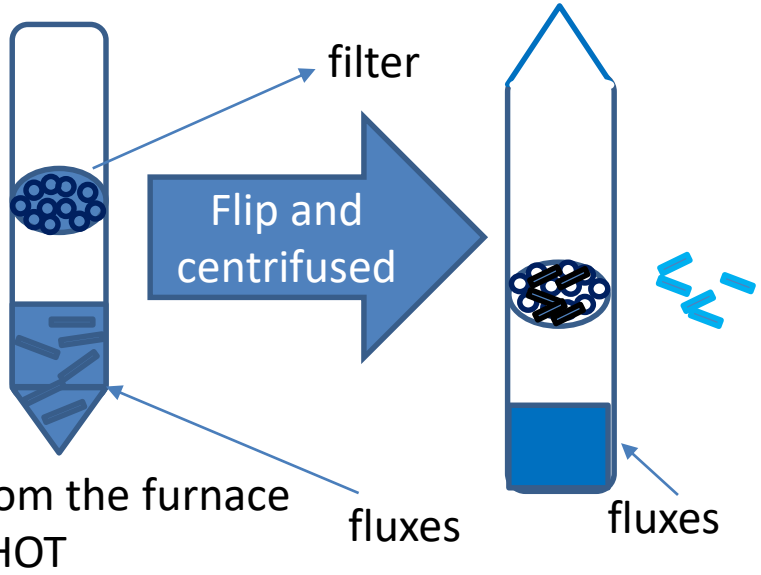
Molten Slats Fluxes

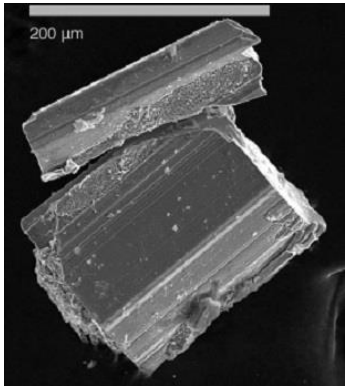
- $4SrCO_3 + Al_2O_3 + Ta_2O_5 = Sr_2AlTaO_6$ ($SrCl_2$ flux, 900°C)
- Powder sample, wash away $SrCl_2$ with weakly acidic H_2O
- Direct synthesis requires T > 1400°C and $Sr_2Ta_2O_7$ impurities persist even at 1600°C



Metal Fluxes

- One of the reactants is metal
- Typical for intermetallic compounds
- Reaction products are unpredictable
- Great technique to obtain new compounds
- Flux metals with low melting and high boiling points; Typical metals are Ga, In, Pb, Sn, Sb, etc





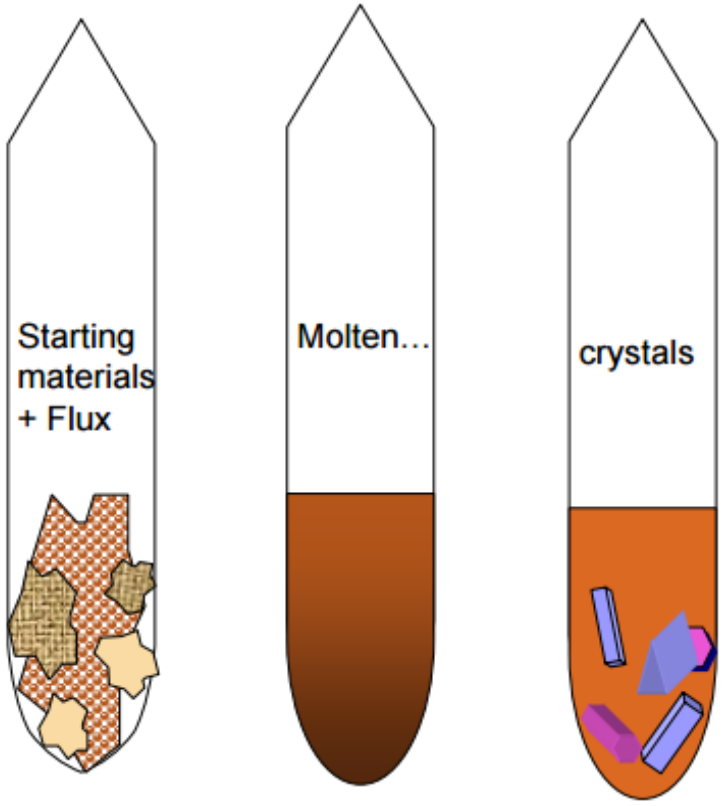
$Y_4Mn_{1-x}Ga_{12-y}Ge$

Polychalcogenides Fluxes

- Molten chalcogenide salts ($A_2Q + Q_x \rightarrow A_2Q_x$) as Reagents and Solvents to synthesize new compounds

ADVANTAGES

- Low temperatures (250 °C < T < 750 °C)
- Can produce compounds not accessible by other methods
  - Kinetic products / Thermodynamic products
- Conducive to large crystal growth
- Ability to produce in pure form more complicated compounds such as ternary: A/Bi/Q or quaternary: A/M/Bi/Q)



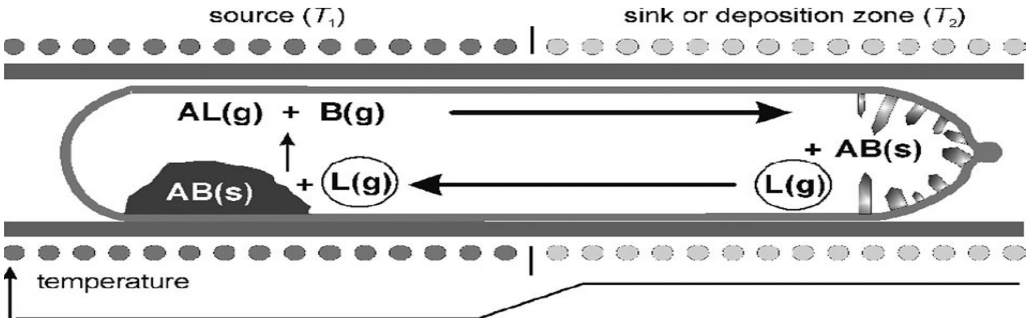
M. G. Kanatzidis and A. Sutorik *Progress in Inorganic Chemistry* **1995**, *43*, 151-265.

Source:http://chemgroups.northwestern.edu/kanatzidis/resources/presentations

Chemical Vapor Transport (CVT)

- CVT is a heterogeneous catalysis process that produced crystals of the desire compounds by the condensation of the supersaturated gaseous substances.
- Bunsen, first described a naturally occurring vapor transport reaction in 1852.
- During the eruption of the volcano *Vesuv* Bunsen noticed the formation of hematite in the presence of hydrogen chloride.

Reaction: $AB_{,S} + L_{,g} = AL_{,g} + B_{,g}$



Two Zone furnace

Chemical Vapor Transport

Endothermic Reaction: $Fe_2O_{3,s} + 6HCl_{,g} \rightleftharpoons Fe_2Cl_{6,g} + 3H_2O_{,g}$

T_2=1000 °C, T_1=750 °C; $\Delta H_{rxn} > 0$ (endothermic)

Exothermic Reaction: $MoO_{2,s} + 2I_{2,g} \rightleftharpoons MoO_2I_{2,g}$

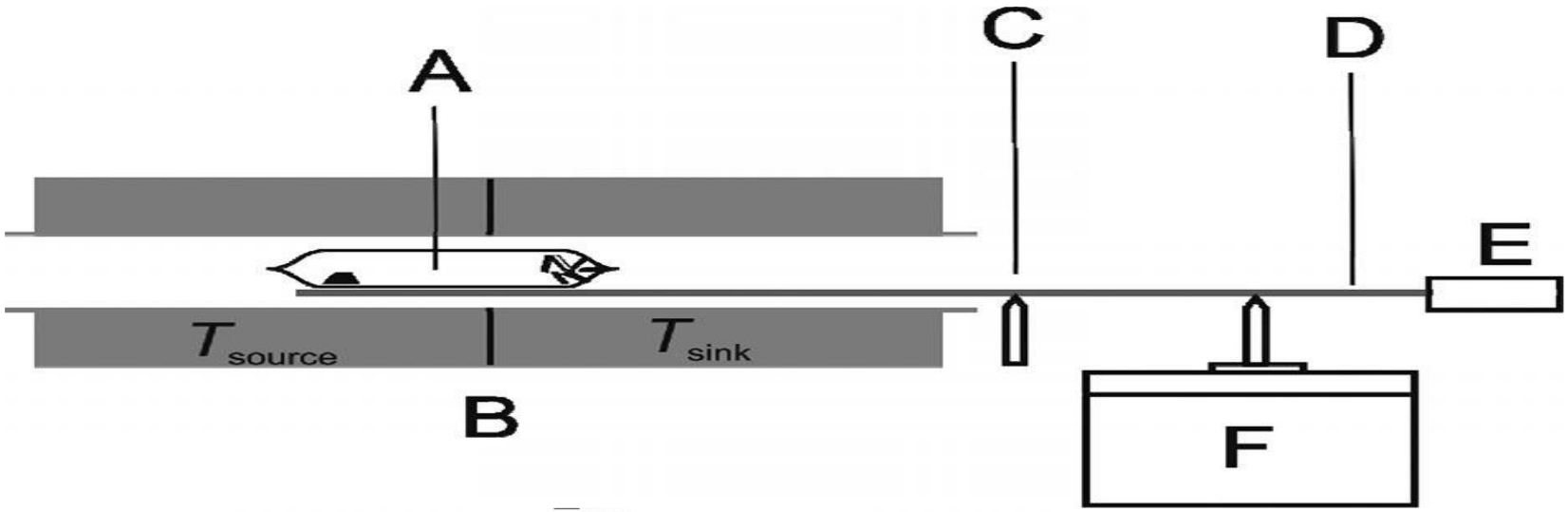
T_2=700 °C, T_1=900 °C; $\Delta H_{rxn} < 0$ (exothermic)

Halogen Lamps Reaction: $WO_{2,s} + 2I_{2,g} \rightleftharpoons WO_2I_{2,g}$

T_2=700 °C, T_1=900 °C; < 0 (exothermic)

Tungsten is evaporated from the filament, converts to WO2I2 (g) with the traces of oxygen and iodine. At the high temperature near filament it decomposes back to W, O2 and I2.

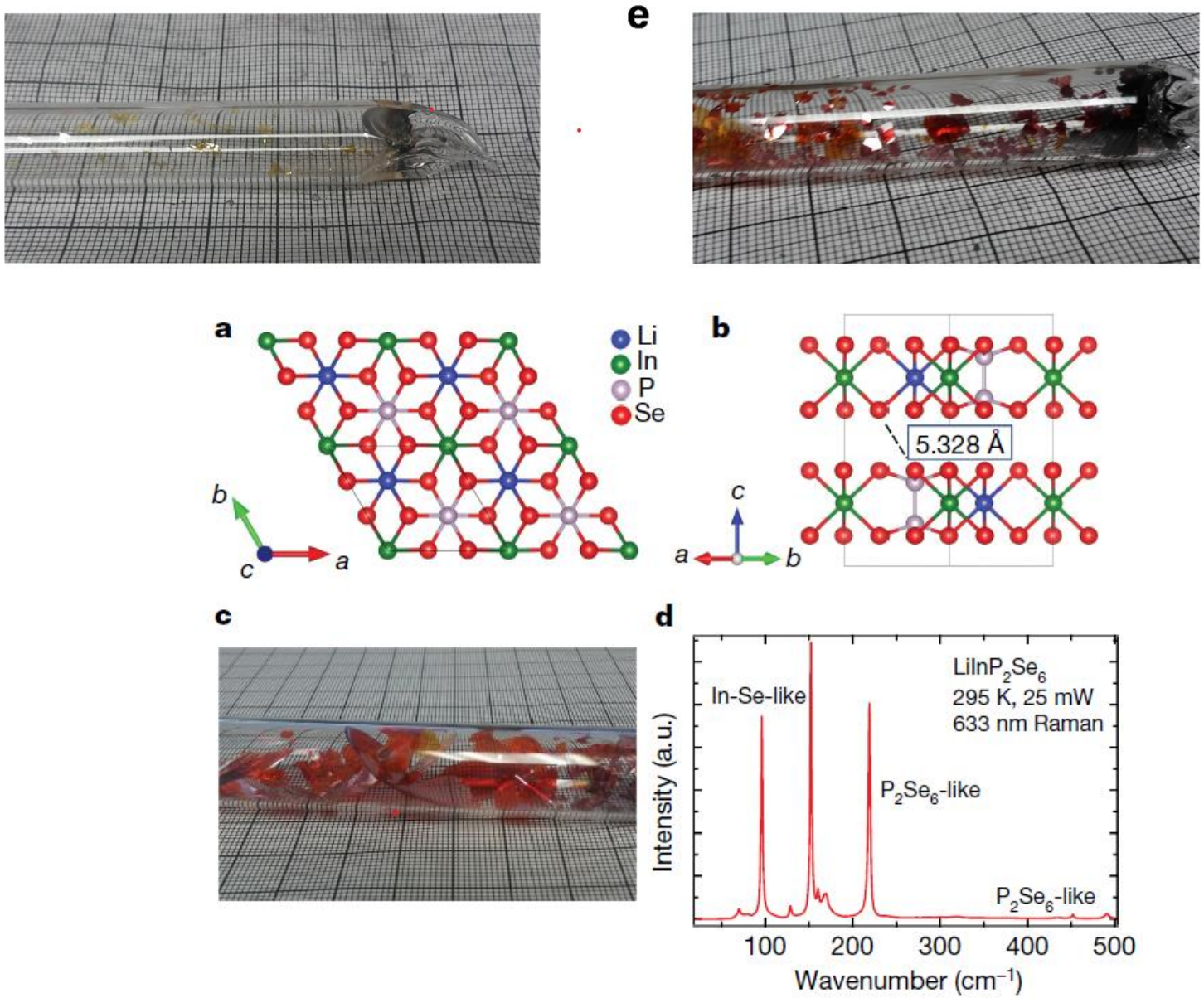
Chemical Vapor Transport



$$\dot{n}(A) = \frac{n(A)}{t'} = \frac{i}{j} \cdot \frac{\Delta p(C)}{\Sigma p} \cdot \frac{\bar{T}^{0.75} \cdot q}{s} \cdot 0.6 \cdot 10^{-4} \ (\mathrm{mol \cdot h^{-1}})$$

$\dot{n}(A)$ = Transport rate (mol·h–1)
i, j = Stoichiometric coefficients in the transport equation
$\Delta p(C)$ = Partial pressure difference of the transport effective species C (bar)
Σp = Total pressure (bar)
$\bar{T}$ = Mean temperature along the diffusion path (K) (practically $\bar{T}$ can be taken as average of $T1$ and $T2$)
q Cross section of the diffusion path (cm2)
s Length of the diffusion path (cm)
t Duration of the transport experiments (h)

Chemical Vapor Transport –recent example



D. Chica et al., *Nature* **2020** *577* 346-253

Czochralski process

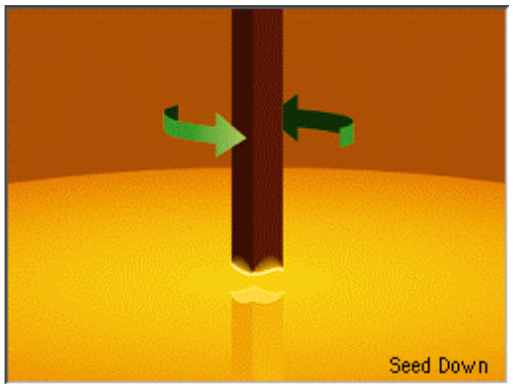
Large single crystals are made by the Czochralski process.

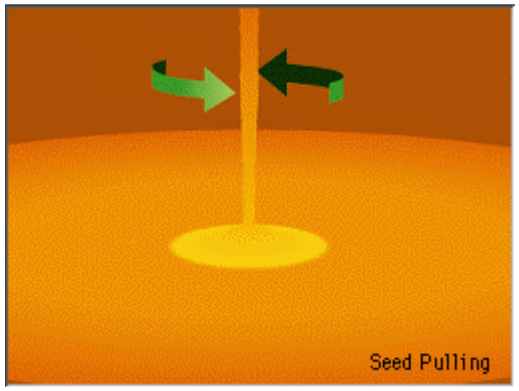
- The silicon is melted in an atmosphere of Ar, then a single crystal seed rod is used as a seed which is dipped into the melt.

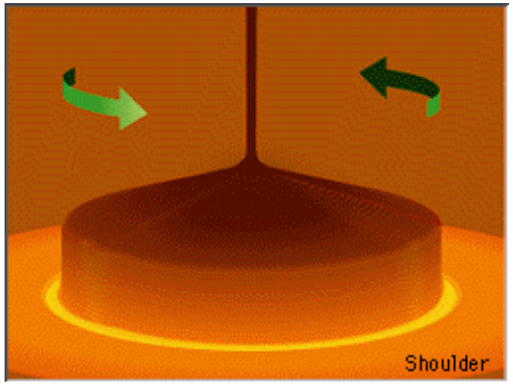
- The crystal is slowly withdrawn, pulling an ever lengthening single crystal in the same orientation as the original seed.

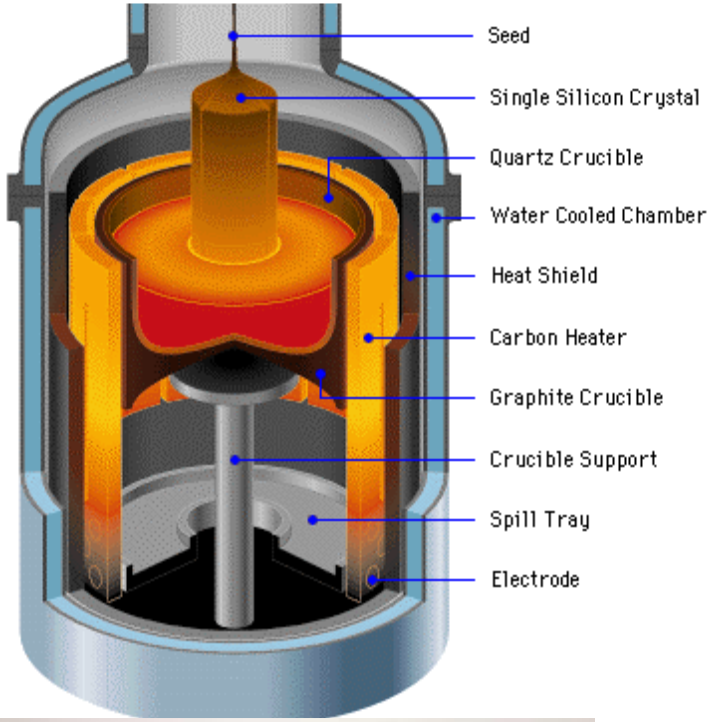
Czochralski process

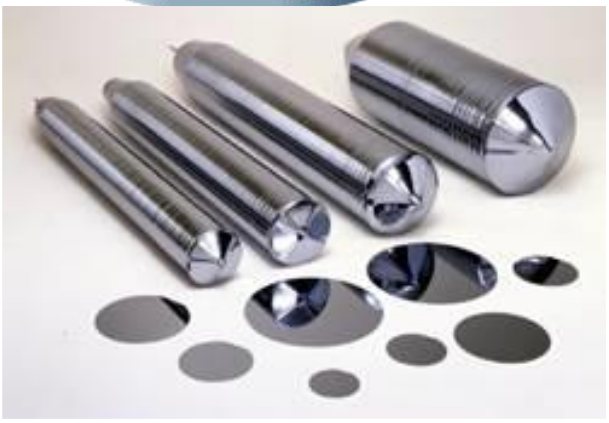
Seed is brought to the contact of the melts
Slowly rotate and pull out from the solution





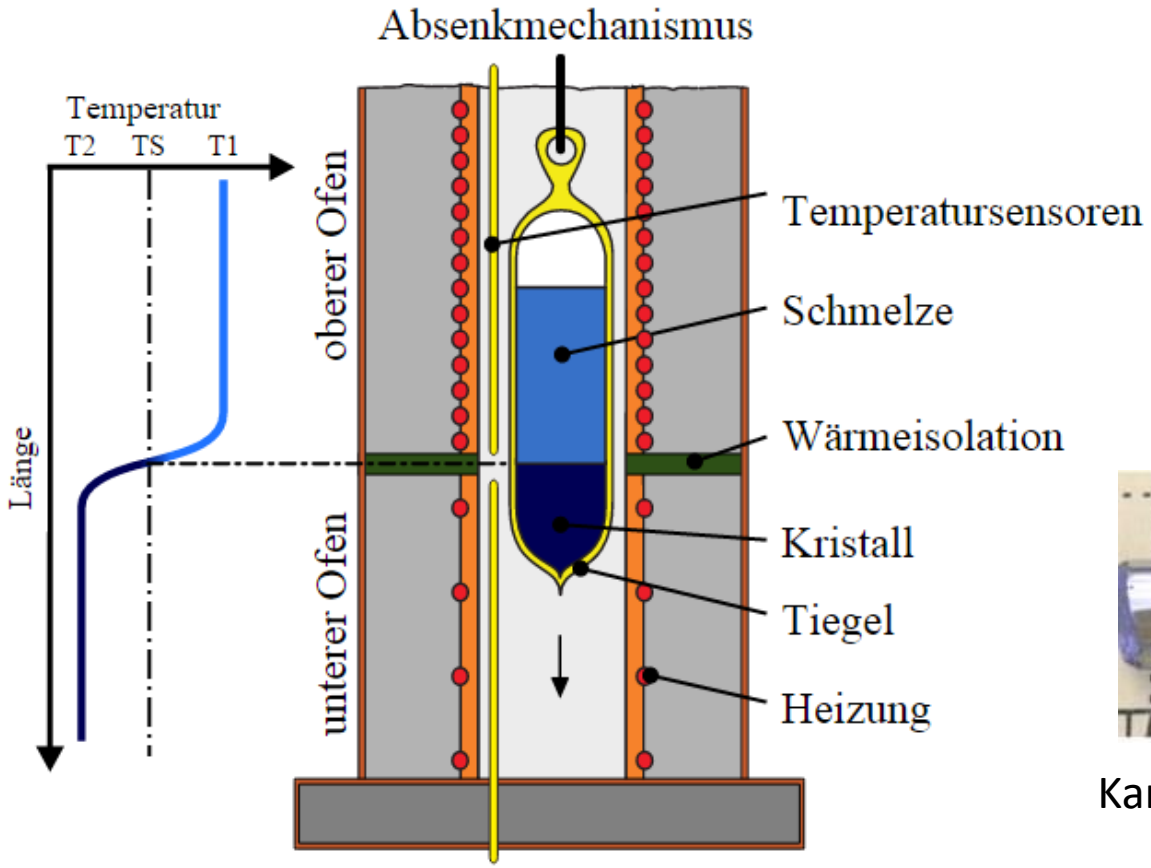


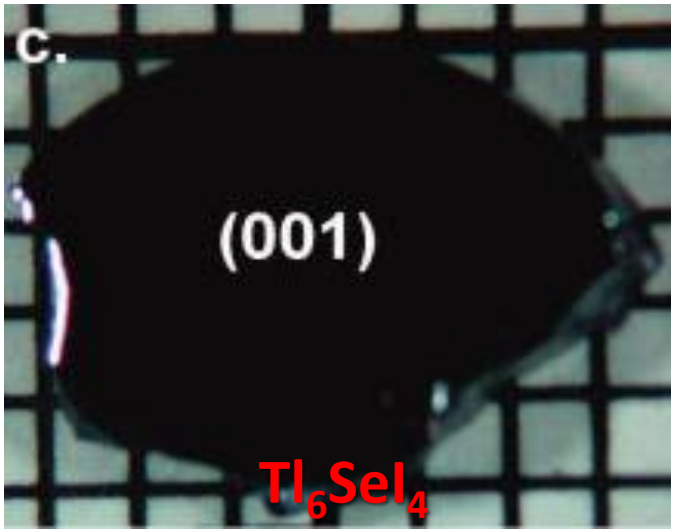




Bridgeman Crystal growth

Crystallization from melts
High purity large crystals





Kanatzidis,et al. J. Am. Chem. Soc. 2011, 133, 10030

Kanatzidis, et al., *Nature,* **2014**, 508, 373

Bridgemann Crystal Growth

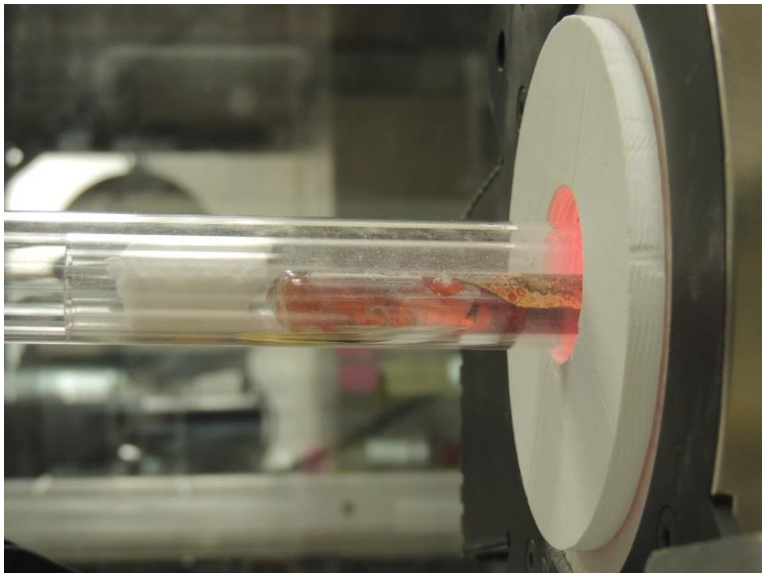
Crystal Growth

Single-Crystal Growth

- **Bridgman method**
- Growth from the melt

-Purification of raw materials

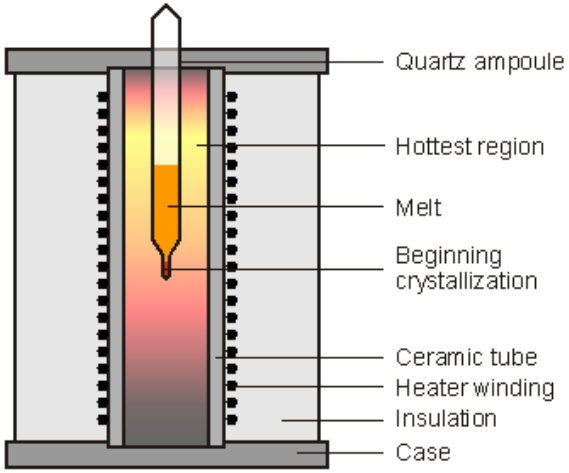
- **Zone refining**



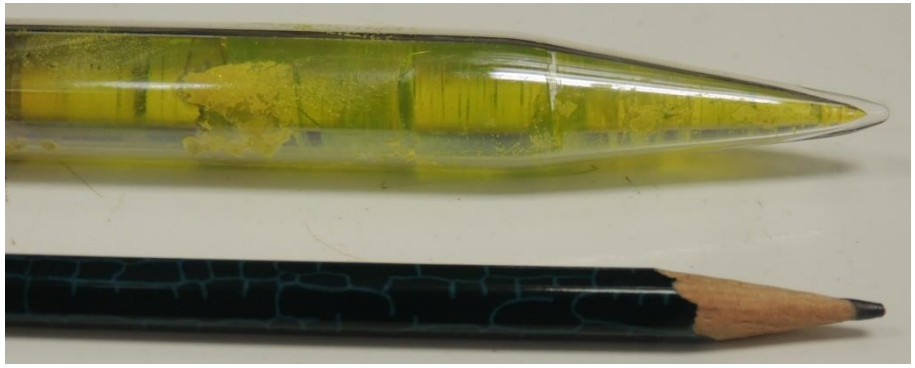
Bridgman Furnace

(Cross section)

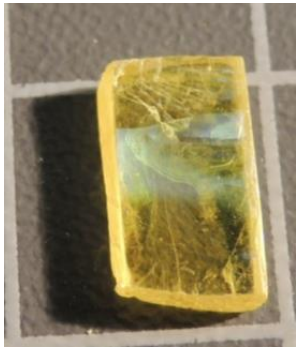
Growing Crystals by the "Bridgman Technique"

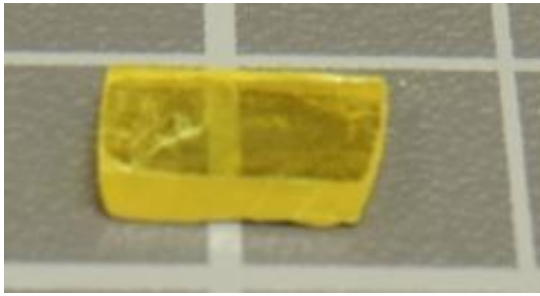


Crystal Growth and Processing



$Cs_3Bi_2Br_9$





$CsPbBr_3$

$Cs_3Bi_2I_9$

Solution Combustion Synthesis (S)

- Combustion synthesis is a **self-propagating high temperature synthetic** method.

- CS uses highly exothermic (ΔH < -170 kJ/mol) and even explosive reactions to maintain a self-propagating high reaction temperature.
- Reactants are mixed to together, formed into a pellet, and ignited (laser, electric arc, heating coil) at high temperature.
- Once ignited, the reaction propagates as a synthesis wave, the reaction must lose less heat than it generates, or it will quench.
- Temperatures up to 3000 K are maintained during the fast reaction.

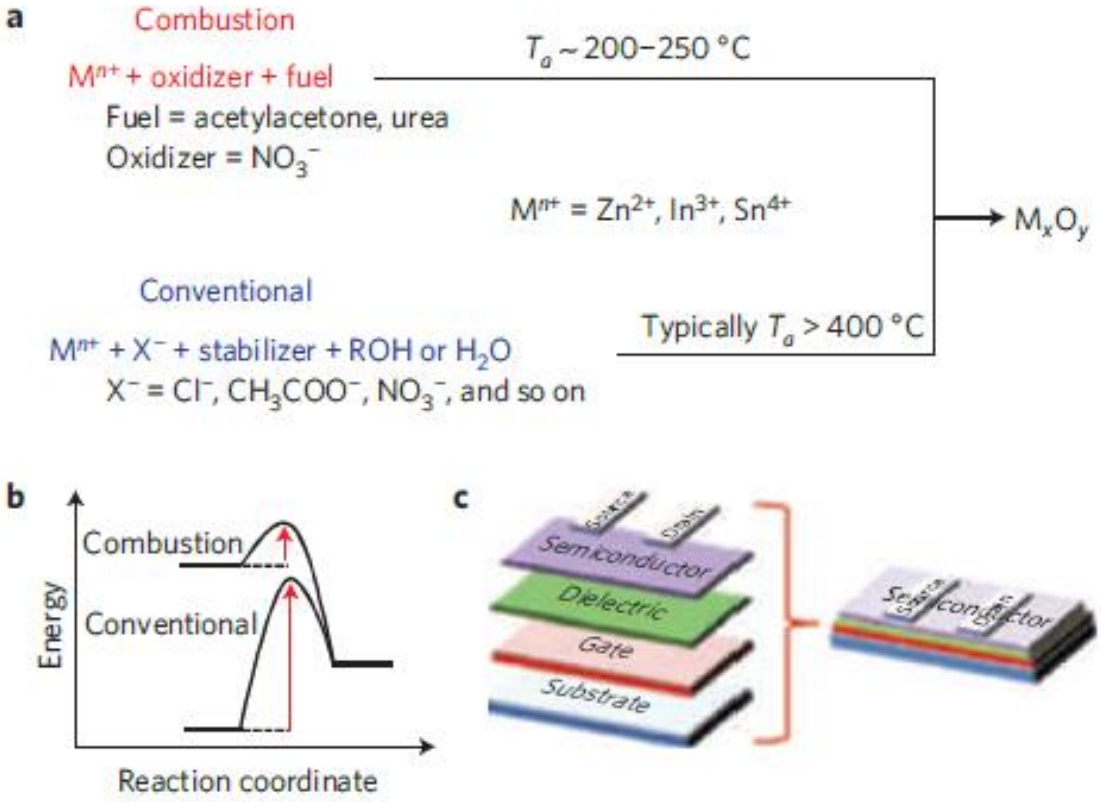
Reactants + Fuel → exothermic energy

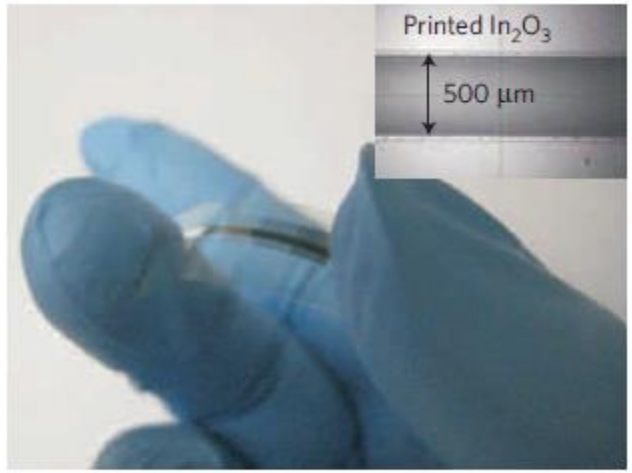
Usually Nitrates

Organic compounds

Very short reaction time
Generation gaseous stuffs

http://www.sciencedirect.com/science/article/pii/S0008884609000775





$$3Zn(NO_3)_2 \cdot 6H_2O_{(s)} + 5 \quad \underset{H_2N}{\overset{O}{\diagup\!\!\diagdown}}\!\!\underset{}{} \quad NH_{2\ (s)} \longrightarrow$$

$$3ZnO_{(s)} + 8N_{2(g)} + 28H_2O_{(g)} + 5CO_{2(g)}$$

$$\Delta H_{298\ K} = -2320.4\ kJ \text{ and } T_{ad} \sim 700\ °C \qquad (1)$$

M.-K. Kim *Nat. Mater.* **2011** *10* 382

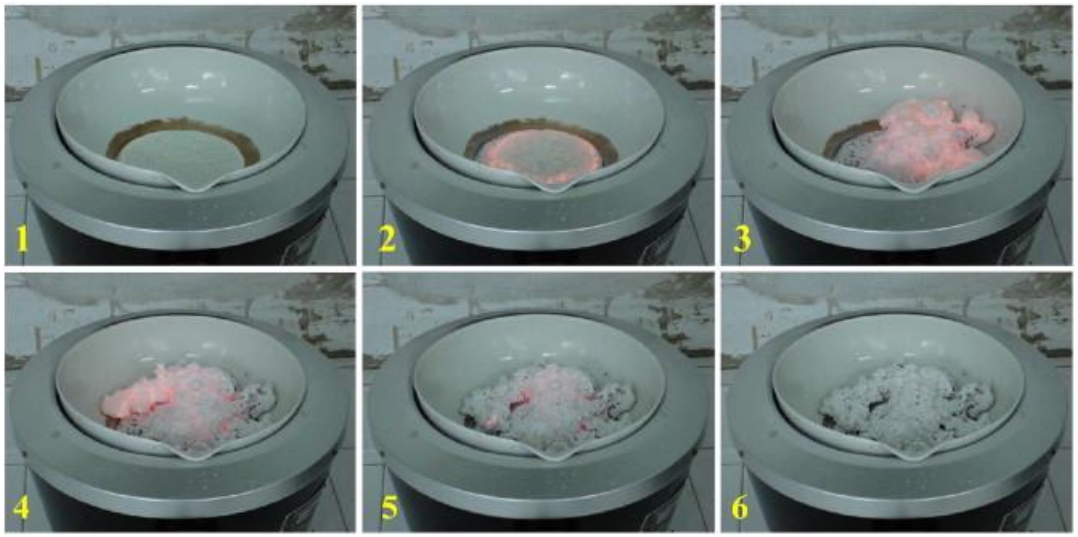
Solution combustion

Synthesis of $Ca_3Al_2O_6$

$3Ca(NO_3)_2 + 2Al(NO_3)_3 + 10CH_4N_2O \rightarrow Ca_3Al_2O_6 + 10CO_2 + 20H_2O + 16N_2$

$3Ca(NO_3)_2 + 2Al(NO_3)_3 + 4C_3H_7NO_2 \rightarrow Ca_3Al_2O_6 + 12CO_2 + 14H_2O + 8N_2$

$3Ca(NO_3)_2 + 2Al(NO_3)_3 + 2C_3H_7NO_2 + 5CH_4N_2O \rightarrow Ca_3Al_2O_6 + 11CO_2 + 17H_2O + 12N_2$



http://www.sciencedirect.com/science/article/pii/S0008884609000775

Hydro(Solvo)thermal Synthesis

- Water as solvent or any solvent
- Temperatures close or above 100 °C
- Pressures above 1 bar
- Sealed vessels
- Dissolve otherwise insoluble materials
- Properties of water/solvent change

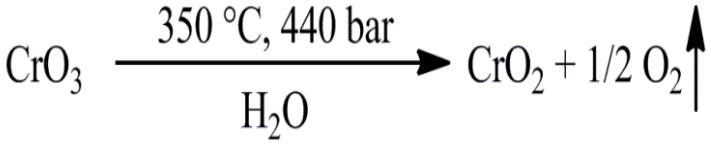
Properties of water

- Viscosity – lowered to 10% of value in normal conditions at 100 bar and 500 °C
  - Increase mobility
- Autoionization
  - $pK_w = 7.85 \pm 0.3$ at 1000 °C and 10 kbar

Seward, T.M. *Phys. Chem. Earth*. **1981**, *13-14*, 113.
Rabenau, A. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1026.
Hamann, S.D. *Phys. Chem. Earth*. **1981**, *13-14*, 89.

Opportunity

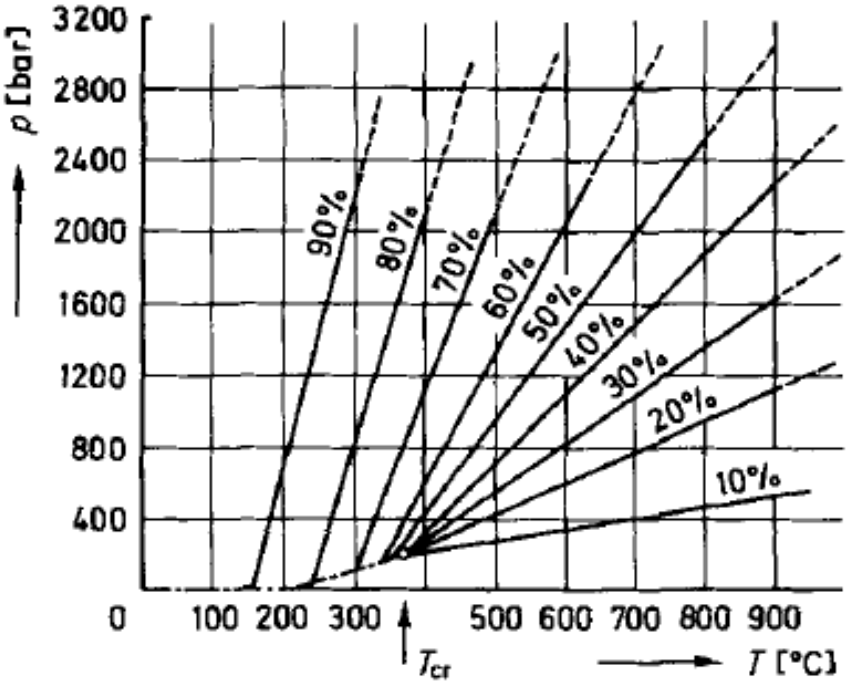
- To grow crystal with unusual oxidation states



- Produce low temperature phases
  - γ-phase of CuI (390 °C) – p-type semiconductor
- Isolate metastable phases
  - h-MoO_3
- Low temperature synthesis
- Synthesis of nano crystal to large single crystals,
- High purity single crystal
- Accessible compounds which other techniques does not permit such as certain MOF and Zeolites

Autogenous Pressure

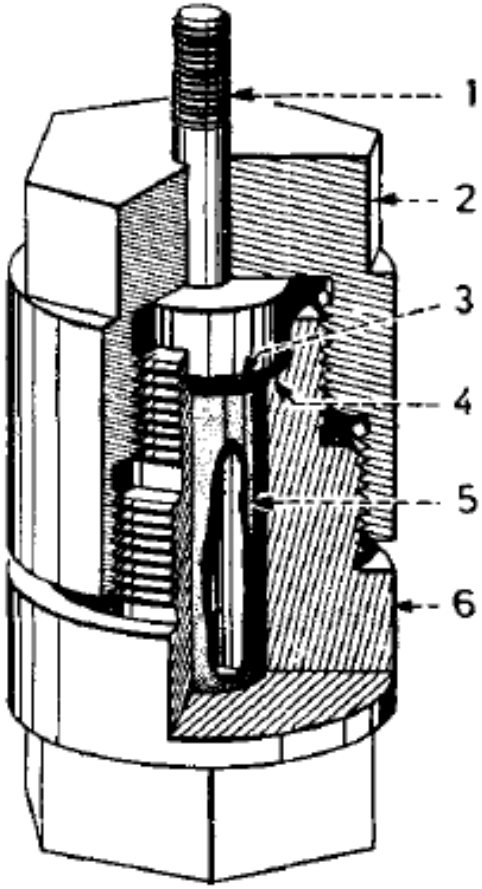
- Closed systems (reaction vessel is closed)
- Pressure is self-produced
- Increases boiling point of water



Pressure-Temperature diagram of water

Rabenau, A. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1026.

Autoclaves



1 - plunger-shaped lock

2 – hexagonal lock

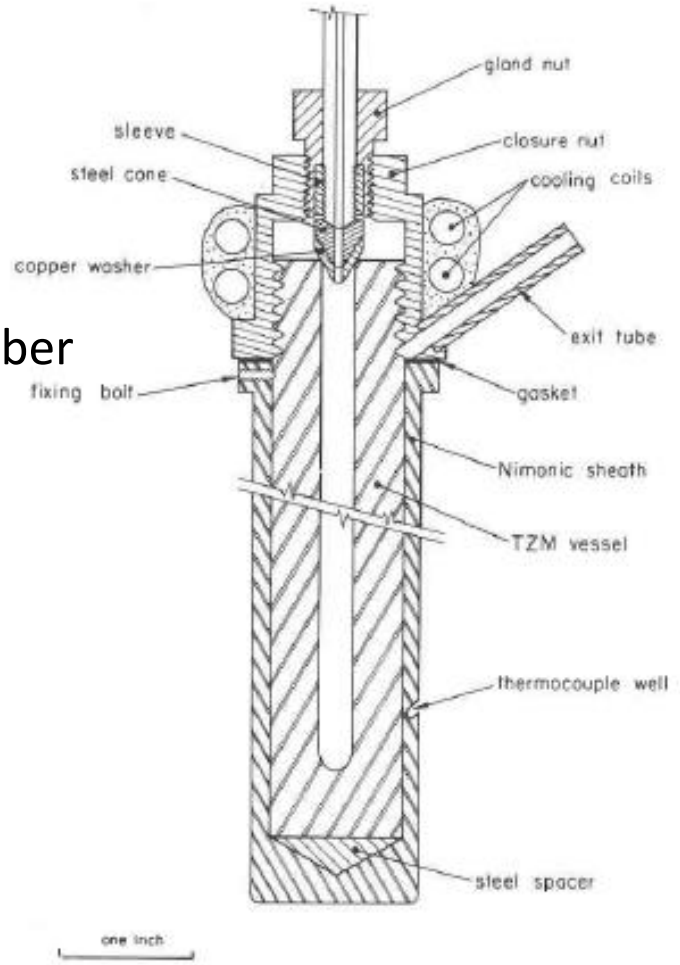
3 – O-ring

4 – O-ring support on chamber

5 – reaction chamber

6 – mantle

400 °C and 400 bar



1100 °C and 3 kbar

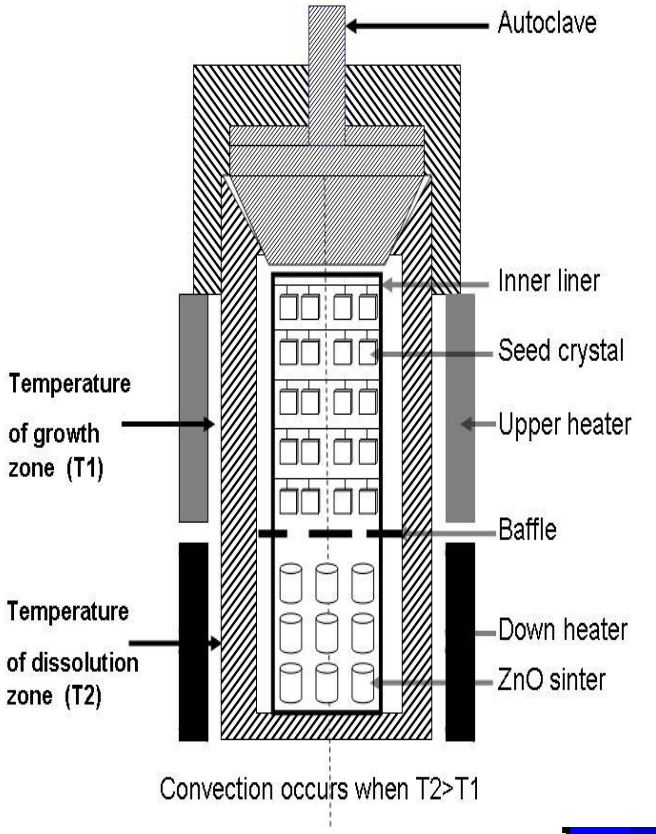
Externally regulated pressure

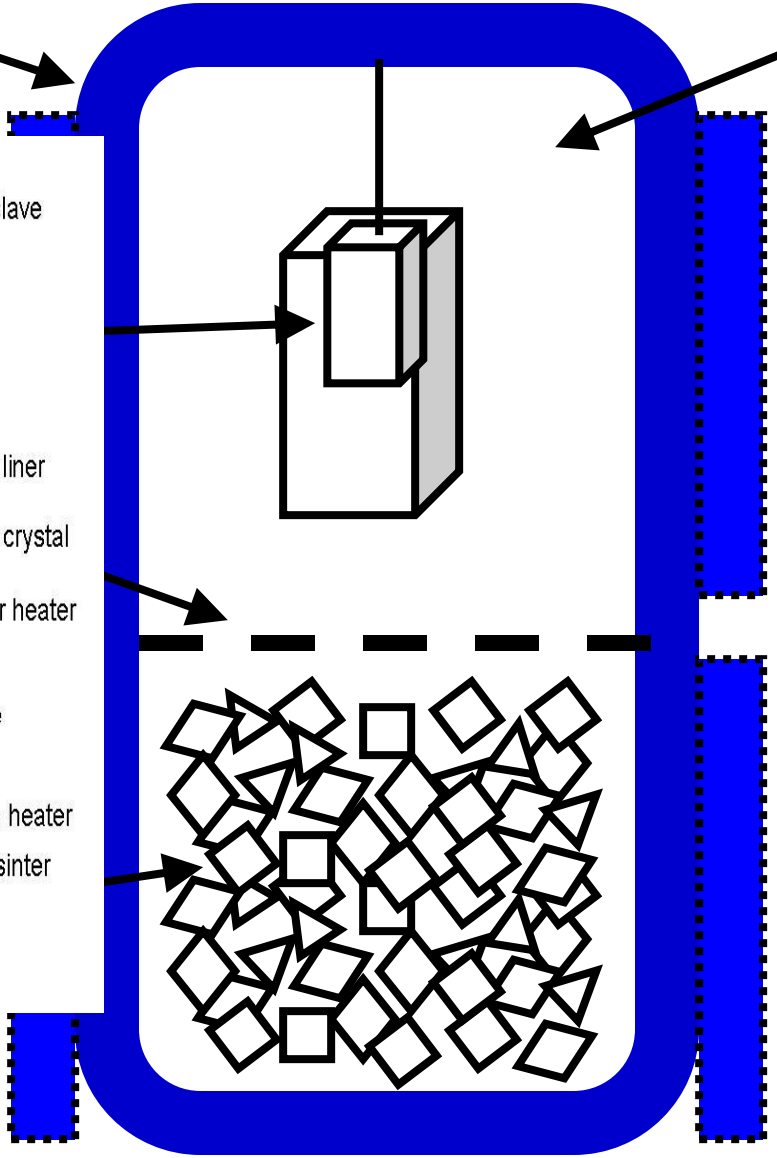
Morey, G.W. *J. Am. Chem. Soc.* **1914**, *36*, 215.
Rabenau, A. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1026.

Hydrothermal Growth: Methods and Instrument

High pressure Autoclave

Mineralizer Solution



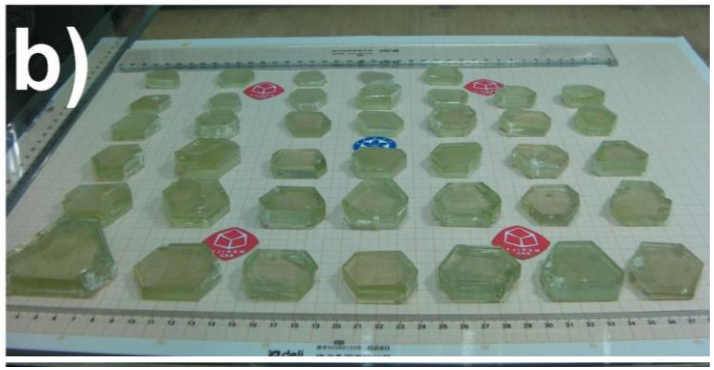


Upper heater:
Low temp.

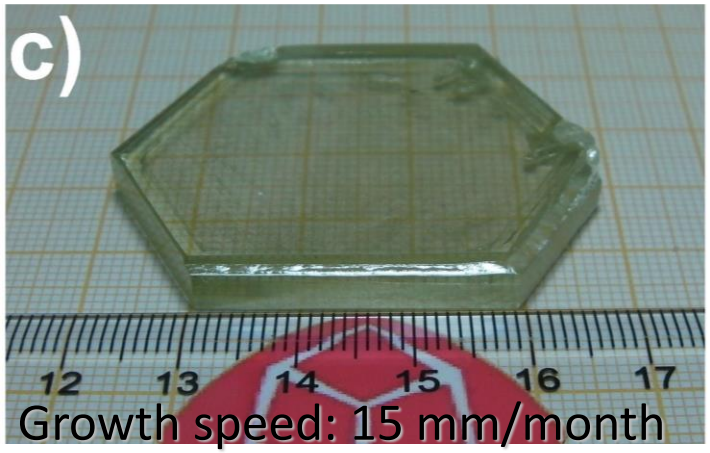
Lower heater:
High temp.

Mass Production of Inches Sized ZnO by a Low-cost Hydrothermal Method

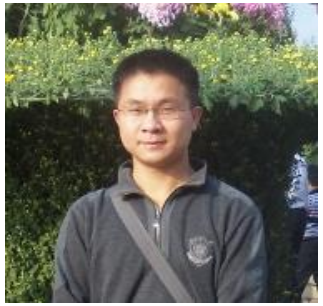
Homemade autoclave. It can accommodates 100 1’ sized or 36 2’ sized seed wafers.



One third of crystals grown in one autoclave after 14 days’ growth.



Growth speed: 15 mm/month



Dr. Wenwen Lin

T2=350C
T1=300C
P=1000 bar

Fujian Institute of Research on the structure of Matter, Chinese Academy of Sciences

Industrial Growth

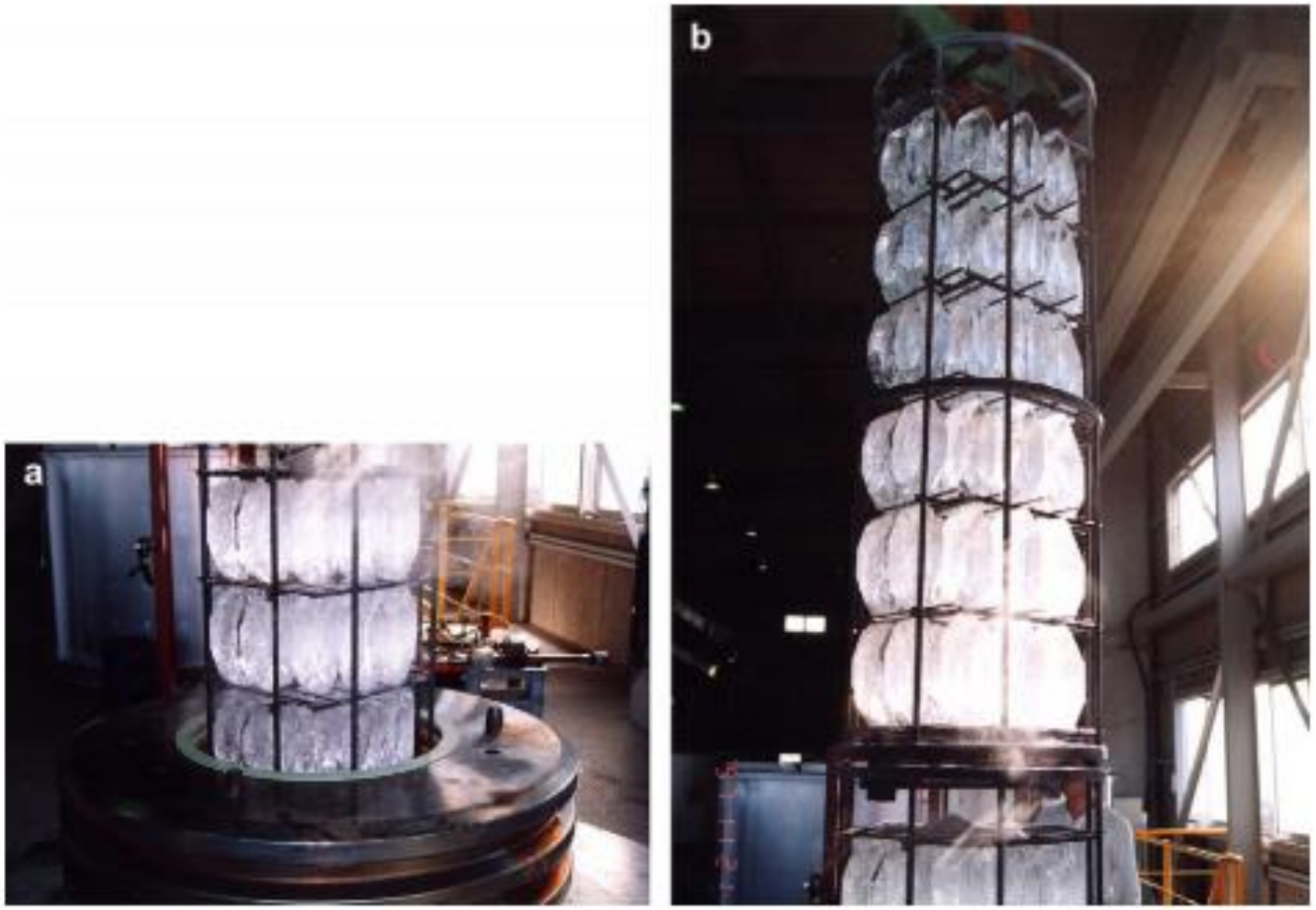


Fig. 2. (a) Quartz crystals being withdrawn from the autoclave of 0.65 m inner diameter and 14 m length; (b) crystal holder with about 25 cm large quartz crystals.

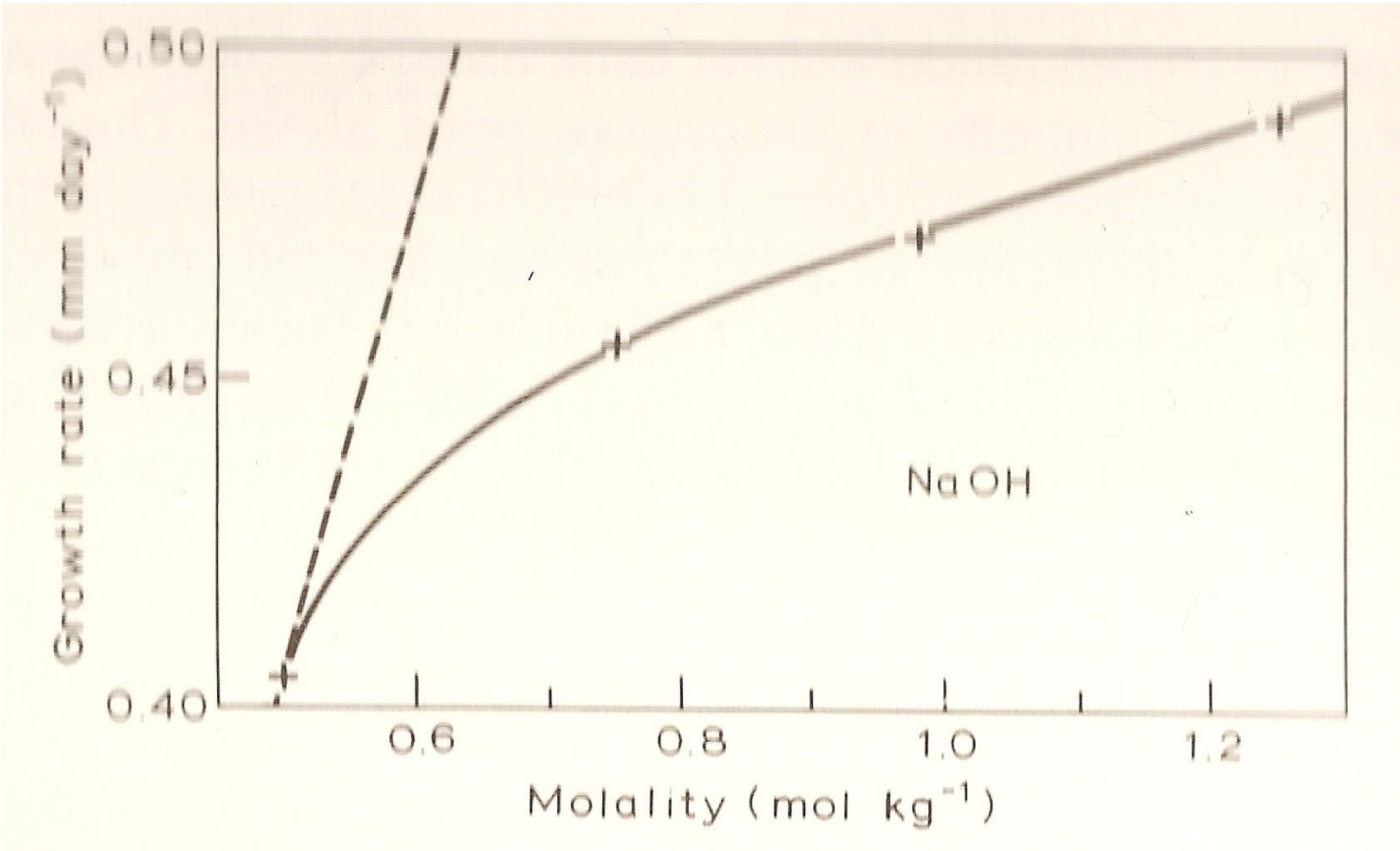
D. Ehrentraut et al. / Progress in Crystal Growth and Characterization of Materials 301 52 (2006) 280e335

Growth Rate Variables

- Concentration of the mineralizer
- Degree fill of the vessel
- Crystallization temperature
- Temperature difference between the nutrient and growth zones

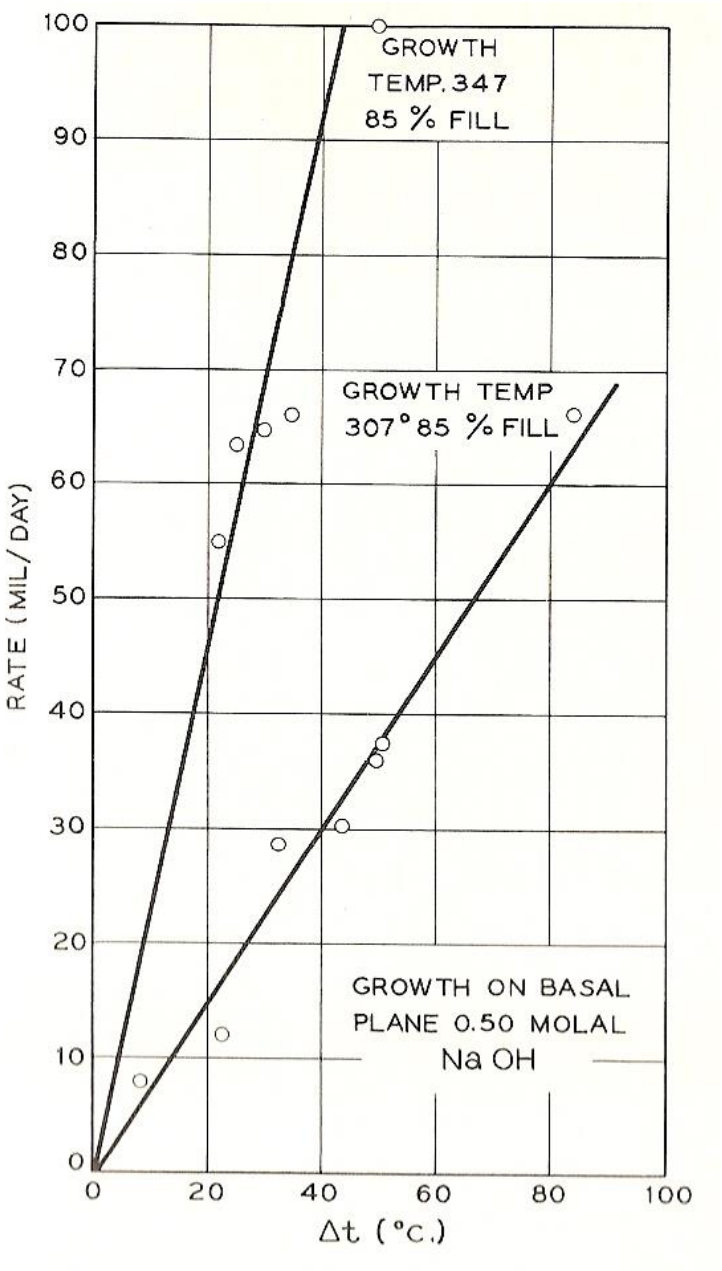
Laudise, R.A. Hydrothermal Growth. In *Crystal Growth: an introduction*; Hartman, P., Ed.; North-Holland Publishing Company: Amsterdam, 1973

Mineralizer Concentration



Brice, J.C. *Crystal Growth Processes.* Blackie & Son Limited: Glasgow, 1986.

Temperature Gradient



Laudise, R.A. Hydrothermal Growth. In *Crystal Growth: an introduction*; Hartman, P., Ed.; North-Holland Publishing Company: Amsterdam, 1973

Hydrothermal Timeline