# Lecture 5: Phase Diagrams and crystal growth

- Phase diagrams
  - Phase rule
  - One-component systems (unary)
  - Two-component systems (binary)
  - Three-component systems (ternary)

- Single crystal growth (*extra material*)
  - Czochralski method
  - Bridgman and Stockbarger methods
  - Zone melt methods
  - Flux methods

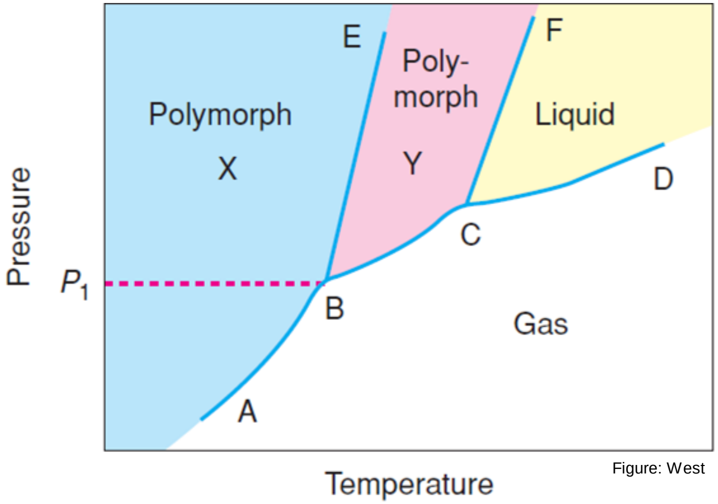


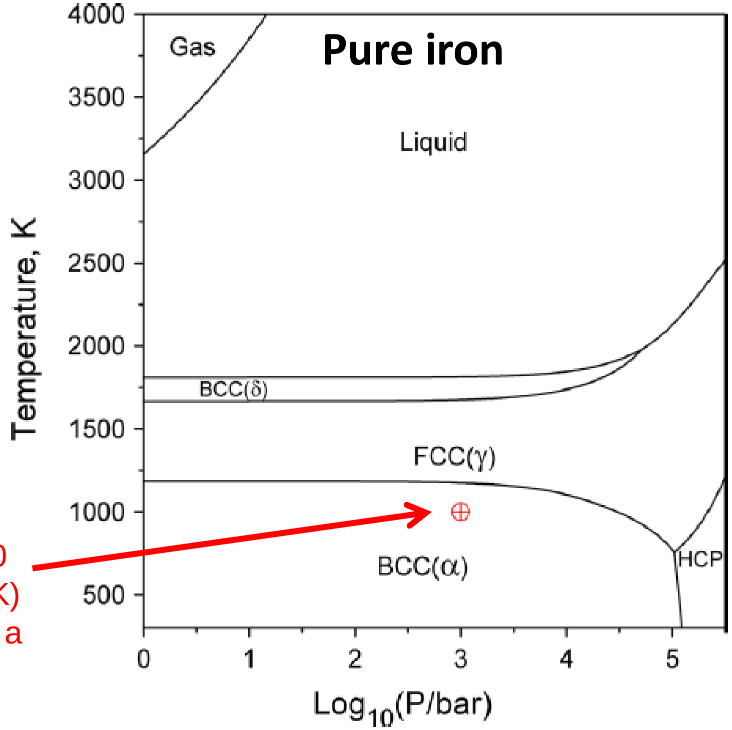
Figure: West

13 gram single crystal of $Ba_8Ga_{16}Ge_{30}$ (Christensen et al. *Nature Mater.* **2008**, *7*, 811)

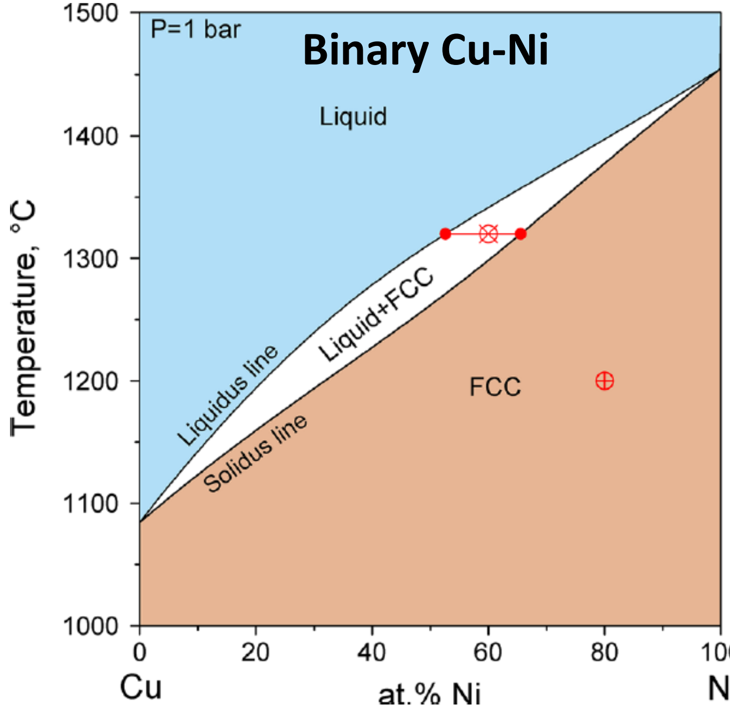
*Solid State Chemistry CHEM-E4155, Antti Karttunen, Aalto University, 2023*

# Phase diagrams

- *"Phase diagrams are the beginning of wisdom - not the end of it"* - [William Hume-Rothery]() (English metallurgist and materials scientist)
- For a comprehensive introduction to phase diagrams: MyCourses -> Materials -> Scientific papers -> Schmid-Fetzer 2014 Phase Diagrams
- Phase diagrams are a **roadmap** for understanding the conditions for phase formation or transformation in any material system
- Phase diagrams are a starting point for materials design and process optimization



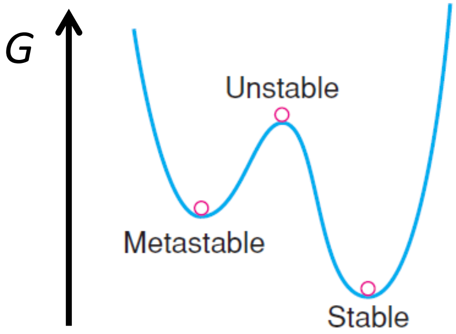
One state point (1000 bar, 1000 K) marked by a crosshair



Figures: [JPEDAV (2014) 35:735–760]() (CC-BY).

# Equilibrium

- In using phase diagrams, it is important to understand what is meant by **thermodynamic equilibrium**
- The equilibrium state is always the state with the lowest Gibbs free energy *G*
  - Other minima may exist but they are not as deep as the equilibrium well
  - If there is a considerable energy barrier involved in moving from a **metastable** state to the stable state, the reaction product may stay in its metastable state
- **Important**: phase diagrams give no information concerning **kinetics** of reactions or transformations!
- A good example of a thermodynamically metastable but kinetically stable state is the metastability of diamond (C) relative to graphite (C) at room temperature



Schematic diagram showing stable, unstable, and metastable conditions

Ref: West p. 329

# Definitions

- **Phase** is a physically separable part of a system with distinct physical and chemical properties.
- A **system** consists of one or more phases
- For example, $NaCl$–$H_2O$ system:
  - If all of the salt is dissolved: one phase (salt solution).
  - If all salt is not dissolved: 2 phases, solid NaCl and solution.
  - If system is heated under sealed conditions: 3 phases (solid + solution + gas)
- Each phase in the system is composed of one or more **components**.
  - The $NaCl$–$H_2O$ system has two components NaCl and $H_2O$ (**binary** system)
  - All other combinations can be described with these formula.
- Pure water would be an **unary** (one-component) system
- Three components -> **ternary** system
- Four components -> **quaternary** system

# Gibbs Phase Rule

- Applies to non-reactive multi-component heterogeneous systems in **thermodynamic equilibrium**
  - Pressure $p$ and temperature $T$ are constant in the system
  - The chemical potentials of the components are the same in each phase

- $F = C - P + 2$
  - $P$ is the number of phases present in equilibrium
  - $C$ is the number of components needed to describe the system
  - $F$ is the number of degrees of freedom or independent variables taken from temperature, pressure, and composition of the phases present

- In many cases, pressure is constant and the *condensed phase rule* is used:
  - $F = C - P + 1$

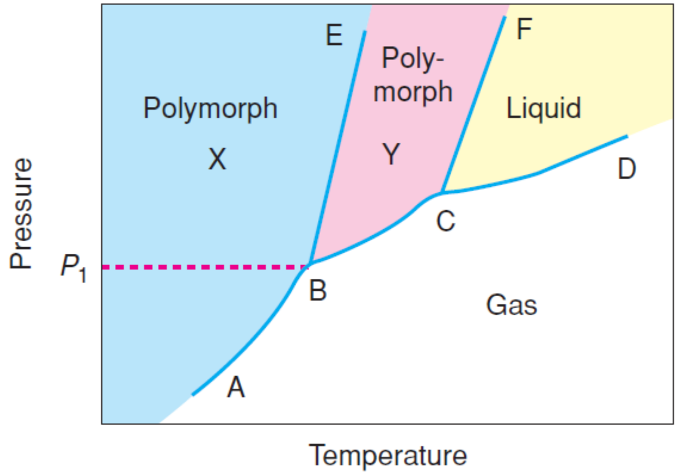
# Simple examples of phase rule

1. A partially melted solid (ice) in a **one-component** system ($H_2O$), in equilibrium at its melting point (ignoring pressure):
   - $F = C - P + 1 = 1 - 2 + 1 = 0$
   - If the temperature changes, the number of phases must change

2. Boiling water = $H_2O$ (l) and $H_2O$ (g) in equilibrium ($C = 1$)
   - $F = C - P + 2 = 1 - 2 + 2 = 1$
   - Boiling point depends on vapor pressure (only one degree of freedom).
   - For example, Mount Everest: 8848 m; p = 34 kPa -> boiling point of $H_2O$ = 71 °C

# One-component systems (1)

- The composition is fixed at $C = 1$ and the independent variables are $T$ and $p$
  - $F = C - P + 2 \iff F + P = 3$
  - The system is **bivariant** ($F = 2$) if one phase is present, **univariant** ($F = 1$) if two are present and **invariant** ($F = 0$) if three are present
- In the schematic example below, the possible phases are two solid-state polymorphs (X and Y), liquid, and gas
- When $P = 1$, $F = 2$ and each phase occupies an area or **field** on the diagram
  - Both $p$ and $T$ are needed to describe a point in one of these fields



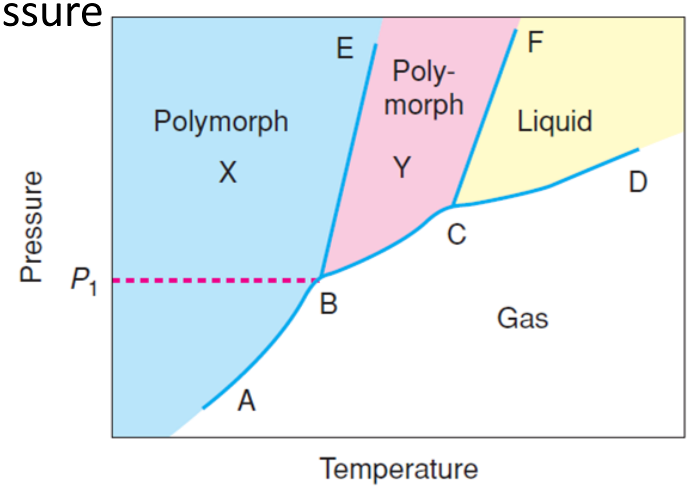
Ref: West p. 331

*Figure 7.3* Schematic P versus T phase diagram of a one-component system.

# One-component systems (2)

- $F + P = 3$
- Each single-phase region is separated from neighboring single-phase regions by **univariant** curves ($P = 2$ and $F = 1$): If $p$ is fixed then $T$ is fixed and vice versa
- The univariant curves on the diagram represent the following equilibria:
  - BE – transition temperature between polymorphs X and Y (the change of transition temperature with pressure)
  - FC – change of melting point of polymorph Y with pressure
  - AB, BC – sublimation curves for X and Y, respectively
  - CD – change of boiling point of liquid with pressure

- On heating, X can either sublime at a pressure below $P_1$ or transform to polymorph Y at pressures above. It **cannot** melt directly.
- B and C are **invariant** points ($P = 3$ and $F = 0$)
- They are also called *triple points*.



Ref: West p. 331

# One-component systems: phase diagram of $H_2O$

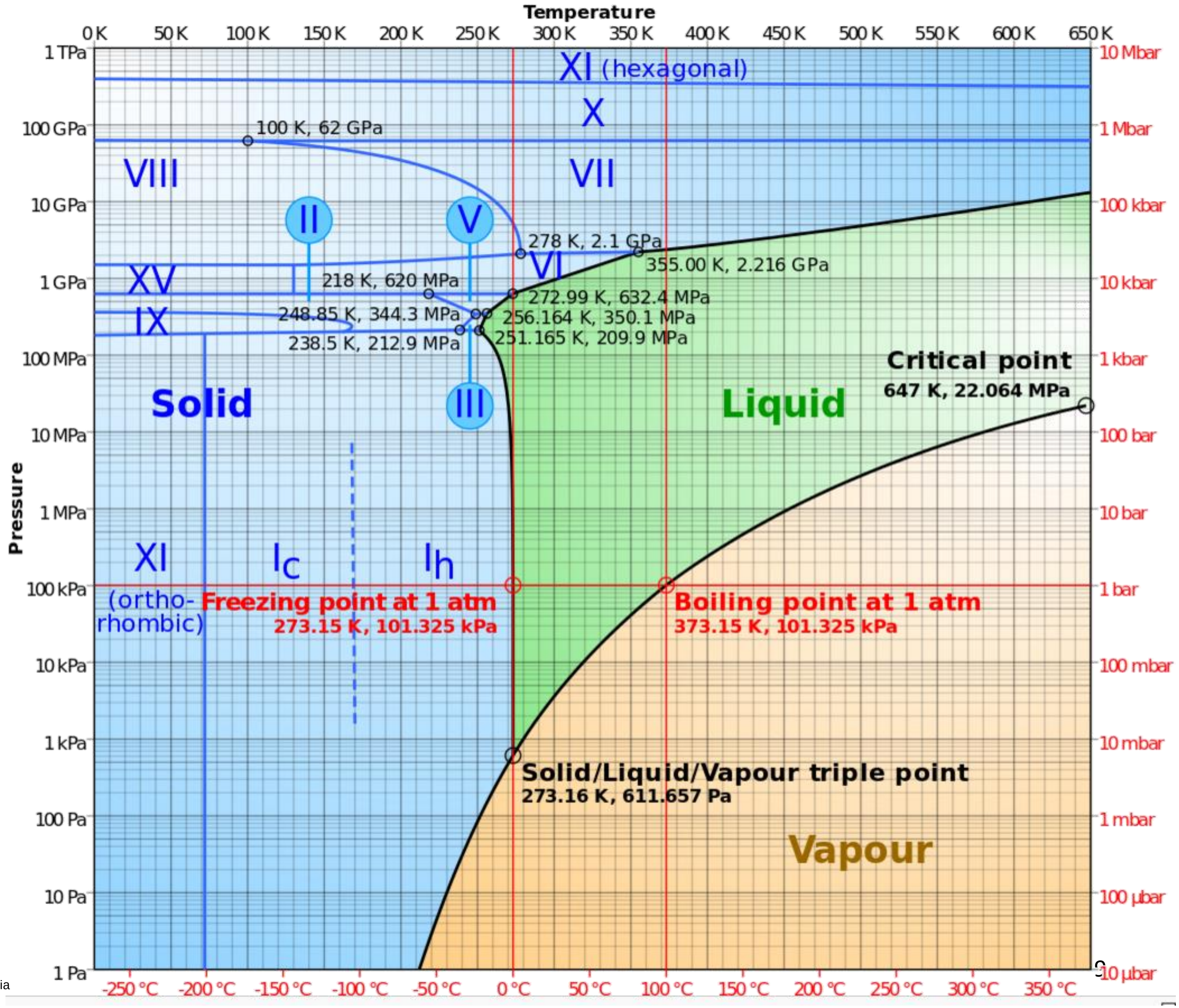


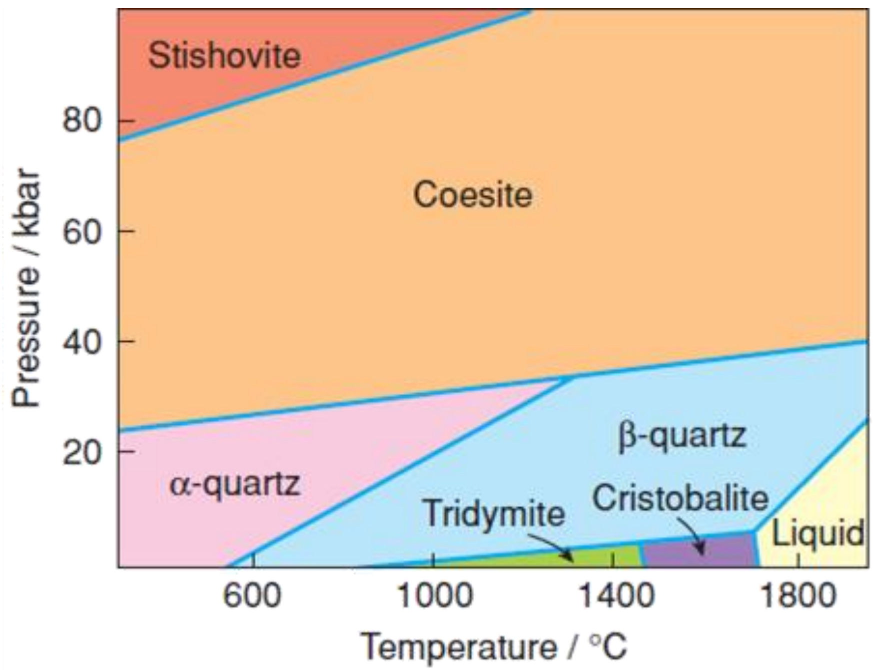
Figure: Wikipedia

# One-component systems: $SiO_2$

- Silica is the most common oxide in the Earth's crust and the main component of many ceramic materials
- It shows complex polymorphism at atmospheric pressure:

$$\alpha\text{-quartz} \xrightarrow{573\,^\circ\mathrm{C}} \beta\text{-quartz} \xrightarrow{870\,^\circ\mathrm{C}} \beta\text{-tridymite} \xrightarrow{1470\,^\circ\mathrm{C}} \beta\text{-cristobalite} \xrightarrow{1710\,^\circ\mathrm{C}} \text{liquid}$$

- With increasing pressure, the polymorphs with higher density are favored



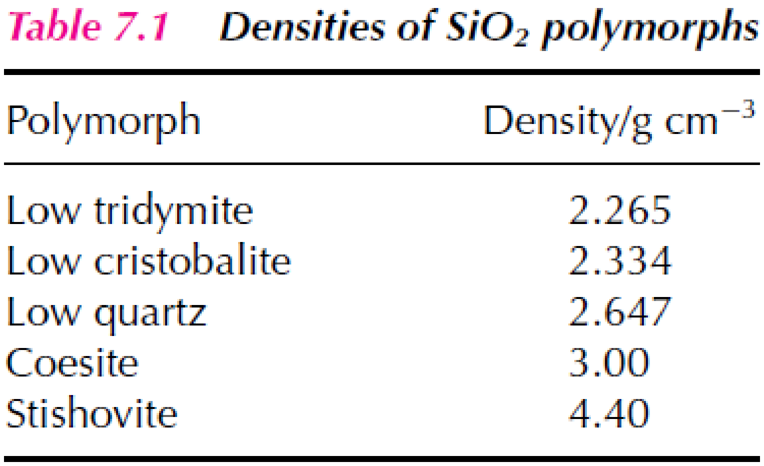


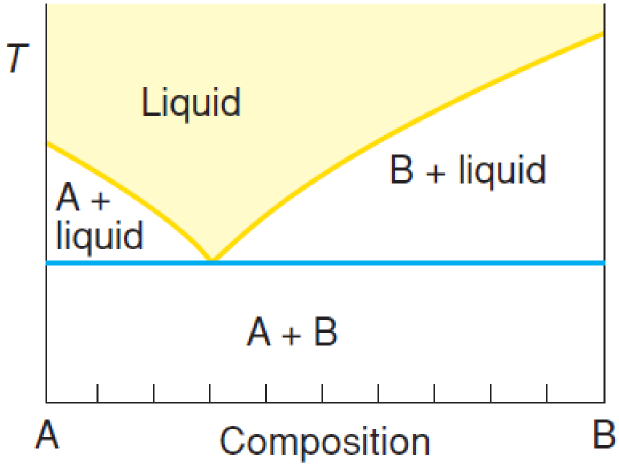
Table 7.1 Densities of $SiO_2$ polymorphs

| Polymorph | Density/g $cm^{-3}$ |
|---|---|
| Low tridymite | 2.265 |
| Low cristobalite | 2.334 |
| Low quartz | 2.647 |
| Coesite | 3.00 |
| Stishovite | 4.40 |

Ref: West p. 332

# Binary eutectic system (1)

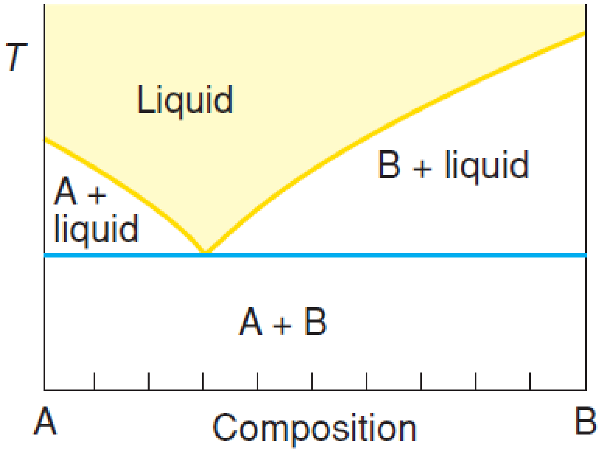
- Binary systems ($C = 2$) have 3 independent variables: $p$, $T$ and composition
- Let's consider condensed phases (ignoring pressure): $F = C - P + 1 = 3 - P$
  - Invariant point occurs when three phases coexist ($F = 0$), a univariant curve for two phases ($F = 1$), and a bivariant condition for one phase ($F = 2$)
- Conventionally, temperature is the vertical axis and composition is the horizontal axis in binary phase diagrams
- The simplest two-component condensed system is the **eutectic** system below
  - Occurs whenever two non-interacting solids, A and B, that can melt without decomposition, are mixed
  - No compounds or solid solutions are formed but the mixtures melt at lower temperatures than either pure solid

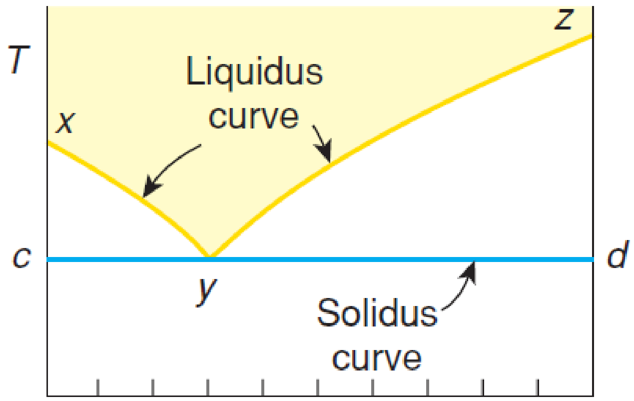


Ref: West p. 334

# Binary eutectic system (2)

- The **liquidus** curve (*xyz*) gives the highest temperatures at which crystals can exist
  - Shows the effect of soluble impurities on the melting points of pure compounds
  - Familiar practical example: In the binary system $H_2O$–NaCl, addition of NaCl lowers the melting point of ice
- The **solidus** *curve* (*cyd*) gives the lowest temperatures at which liquids can exist
- Point *y* is an **invariant point** at which three phases, A, B and liquid, coexist
  - $F = C - P + 1 = 2 - 3 + 1 = 0$
  - Called the **eutectic point** ($H_2O$–NaCl system: –21°C and 23.3% NaCl by mass)
  - The lowest temperature at which a composition can be completely liquid

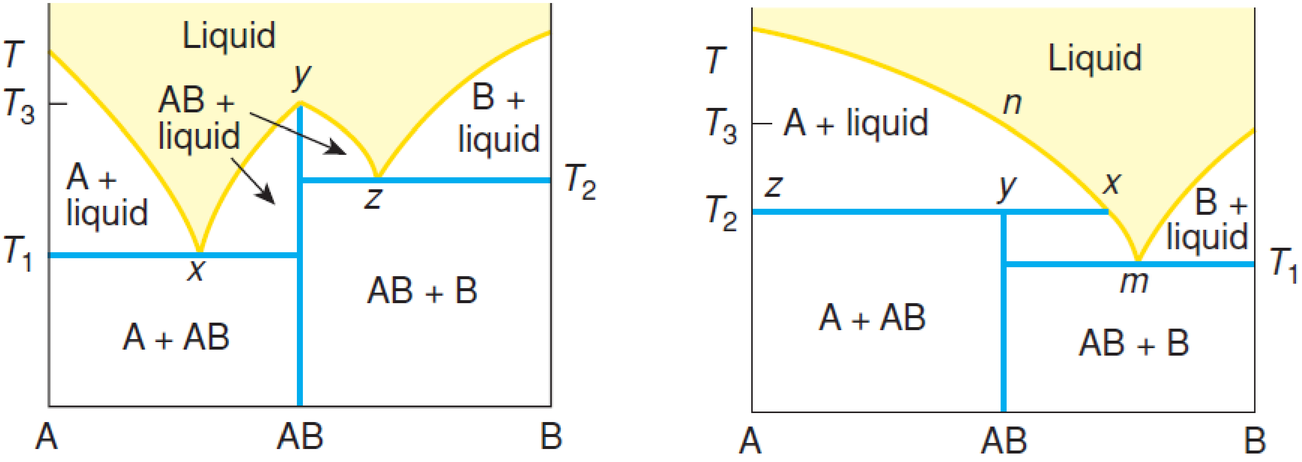




Ref: West p. 334

# Binary system with a compound (1)

- A stoichiometric binary compound such as AB is represented by a vertical line. This shows the range of temperatures over which it is stable
- Compound AB melts **congruently** in Fig. 7.8(a) because it changes directly from solid AB to liquid of the same composition at temperature $T_3$.
  - Important for understanding **crystallization paths**
- In Fig. 7.8(c), compound AB melts **incongruently** at $T_2$ to give a mixture of A and liquid of composition *x*



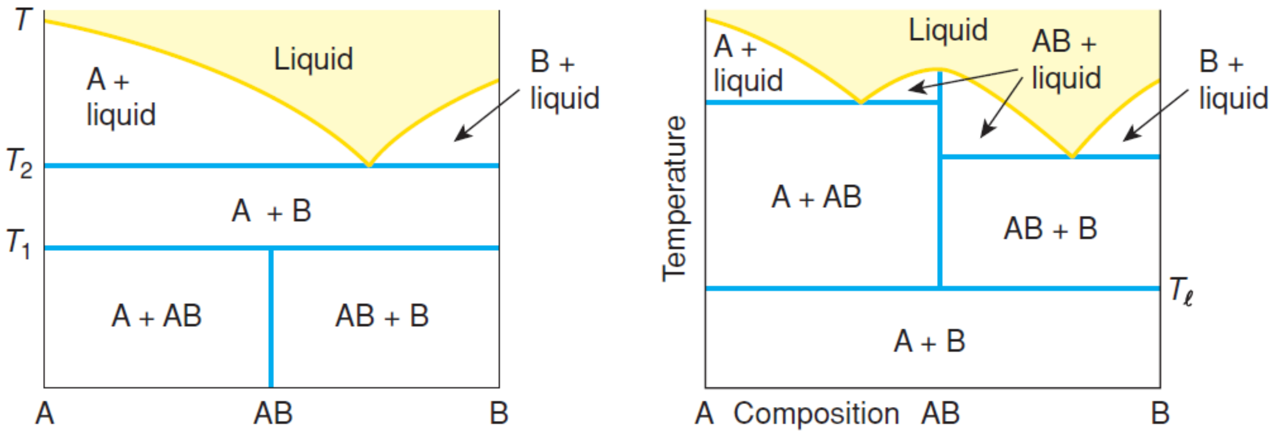
(a) (c)

Ref: West p. 338

**Figure 7.8** *Binary systems showing a compound AB melting congruently (a) and incongruently (c)*

# Binary system with a compound (2)

- Sometimes, compounds decompose before melting, as shown for AB in Fig. 7.9(a)
  - In this case, compound AB has an **upper limit of stability**
  - At temperature $T_1$ it disproportionates into a mixture of A and B;
  - At higher temperatures the system is simple eutectic in character
- There are also systems containing compounds with a **lower limit of stability**
  - Below a certain temperature, AB decomposes into a mixture of A and B



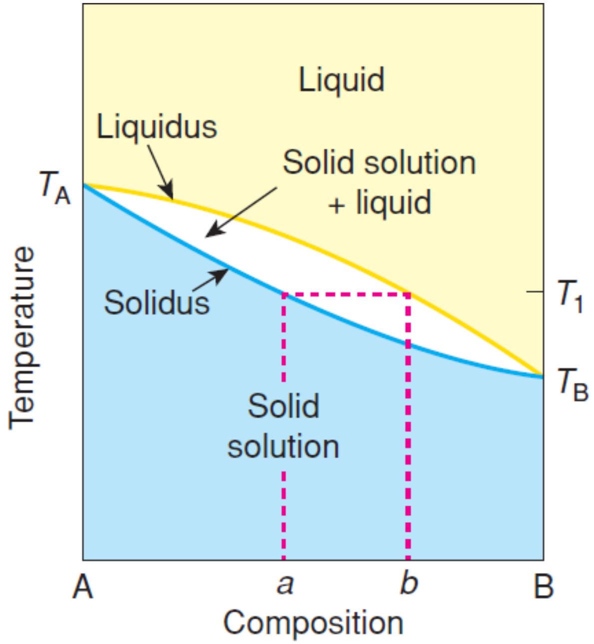
(a) (b)

Ref: West p. 339

*Figure 7.9* ***Binary system showing compound AB with (a) an upper limit of stability and (b) a lower limit of stability.***

# Binary systems with solid solutions

- The simplest **solid solution** system is one that shows complete miscibility in both solid and liquid states
- The melting point of one end member, A, is depressed by addition of the other end member, B
- The liquidus and solidus are smooth curves which meet only at the end-member compositions A and B
- At low temperatures, a single-phase solid solution exists and is bivariant ($C$ = 2, $P$ = 1, and $F$ = C – P + 1 = 2)
- At high temperatures, a single-phase liquid solution exists and is similarly bivariant
- At intermediate temperatures, a two-phase region of solid solution + liquid exists



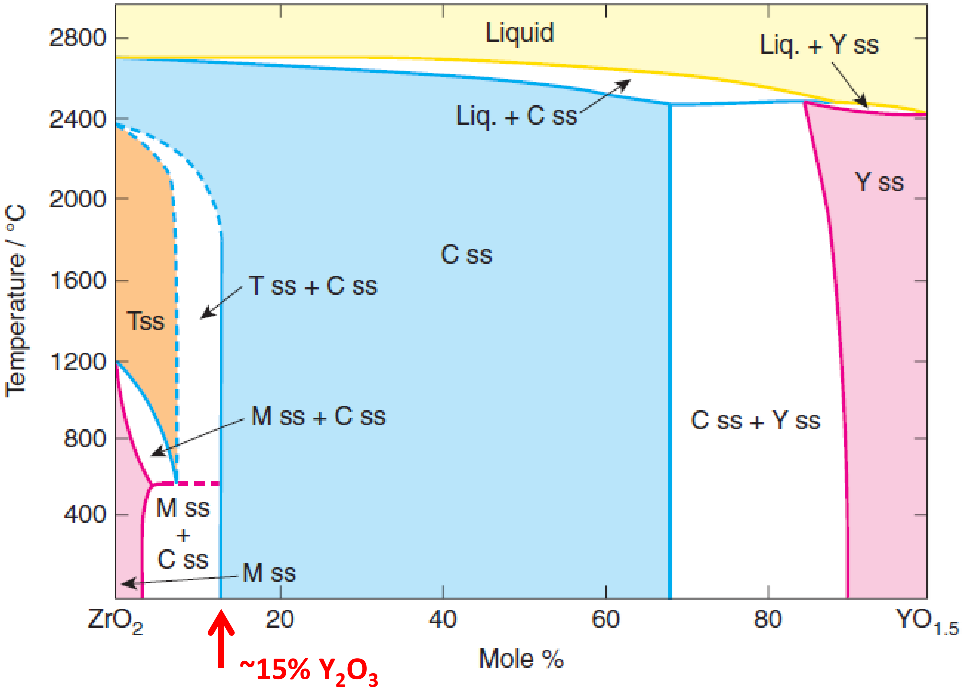
Ref: West p. 340

# Yttria-stabilized Zirconia (YSZ)

- Zirconia, $ZrO_2$, is potentially a very useful ceramic material with a high melting point of ~2700 ◦C but on cooling it undergoes a series of phase transitions:

$$\text{cubic (fluorite)} \xrightarrow{2400\,^{\circ}\text{C}} \text{tetragonal} \xrightarrow{1050\,^{\circ}\text{C}} \text{monoclinic (baddeleyite)}$$

- The tetragonal to monoclinic transition is associated with an increase in unit cell volume by ~9% -> ceramic bodies fabricated at high *T* shatter on cooling
- The transitions can be avoided by creating a solid solution $ZrO_2$–$Y_2O_3$



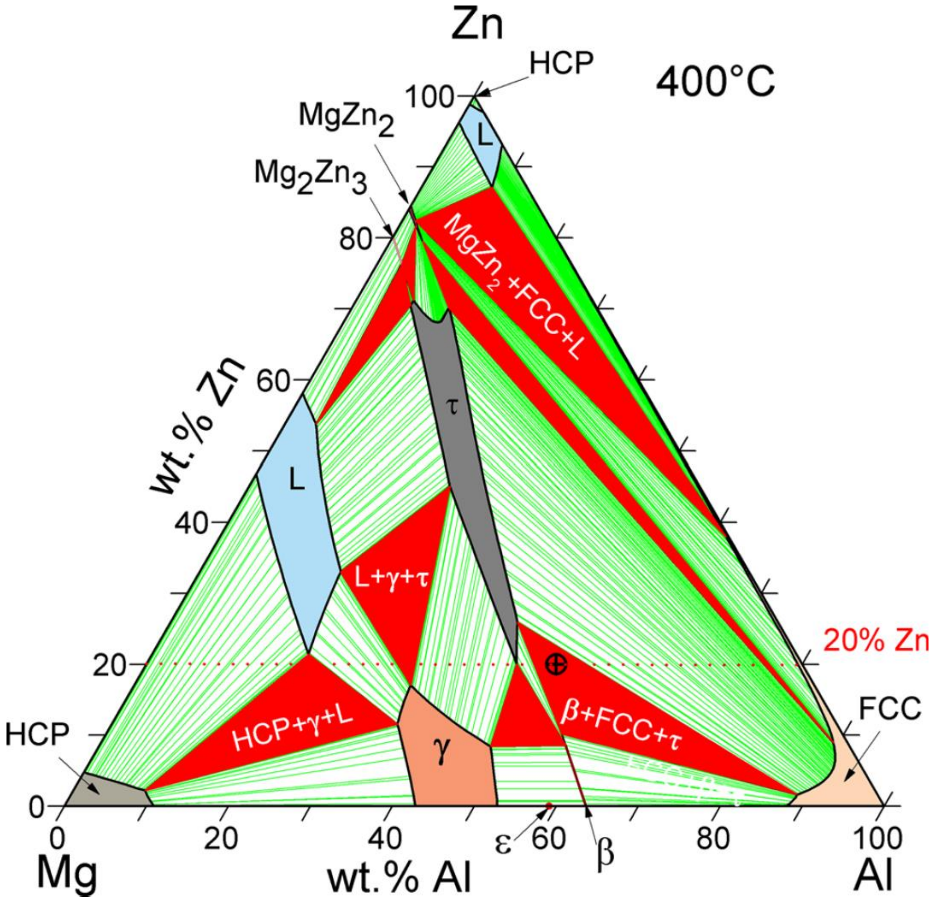
~15% $Y_2O_3$

Ref: West p. 355

*Figure 7.28* *$ZrO_2$–$Y_2O_3$ phase diagram. M, T and C refer to the monoclinic, tetragonal and cubic polymorphs of zirconia, and their solid solutions, ss. Y = yttria, $Y_2O_3$.*

# Ternary phase diagrams

- Ternary phase diagrams are much more complicated than binary diagrams
- One reasonable visualization is to show the diagram just for one temperature



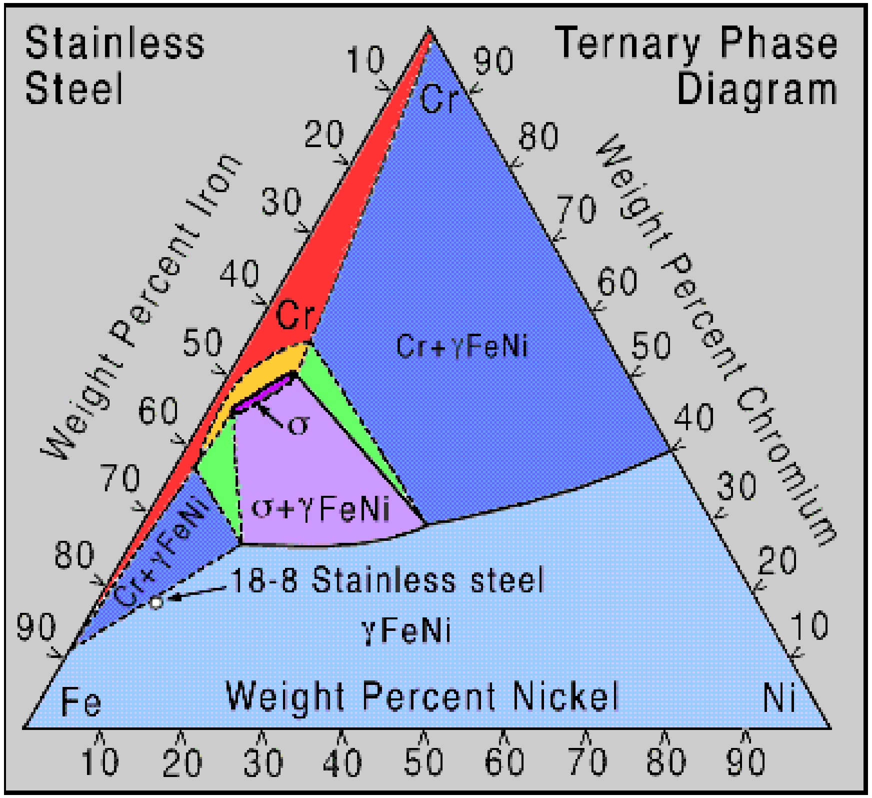
Isothermal section of the **Mg-Al-Zn** phase diagram at 400 °C.

The state point of the alloy "Mg30Al50Zn20" (wt. %), marked by ⊕, is located in the three-phase region β + FCC + τ

Figure: JPEDAV (2014) 35:735–760 (CC-BY).

# Phase diagram resources

- Resources for phase diagrams (require subscription):
  - https://phaseonline.ceramics.org
  - https://www.asminternational.org/materials-resources/online-databases
- Journal of Physical and Chemical Reference Data is a very good resource
  - MyCourses -> Materials -> Phase diagrams includes few useful papers



Stainless steel phase diagram **at 900°C** (ASM 1-27)

Figure: ASM Handbook of Alloy Phase Diagrams

# Extra slides

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

Methods for obtaining single crystals (SSC Wiki)

# Crystal Growth

- Crystals may be grown from vapor, liquid, or solid phases
  - Usually, only the vapor and liquid routes give crystals of sufficient size for applications or physical property measurements
  - The concepts of congruent and incongruent melting are important for understanding crystallization pathways (see the slide “Binary system with a compound (1)” above)
- Czochralski method
- Bridgman and Stockbarger methods
- Zone melting method
- Precipitation from solution or melt: flux method
- Single crystal growth in gel medium (SSC Wiki)

13 gram single crystal of $Ba_8Ga_{16}Ge_{30}$ (Christensen et al. *Nature Mater.* **2008**, *7*, 811)

# Czochralski method

- https://wiki.aalto.fi/display/SSC/Czochralski+method
- A crystal is grown from a melt of the same composition by starting with a seed crystal in contact with the melt, whos temperature is maintained slightly above its melting point
- As the seed is gradually pulled out of the melt, the melt solidifies on the surface of the seed to give a rod-shaped crystal in the same crystallographic orientation as the original seed
- The melt and growing crystal are usually rotated counter-clockwise during pulling
- Widely used for semiconducting materials: Si, Ge, GaAs, etc.

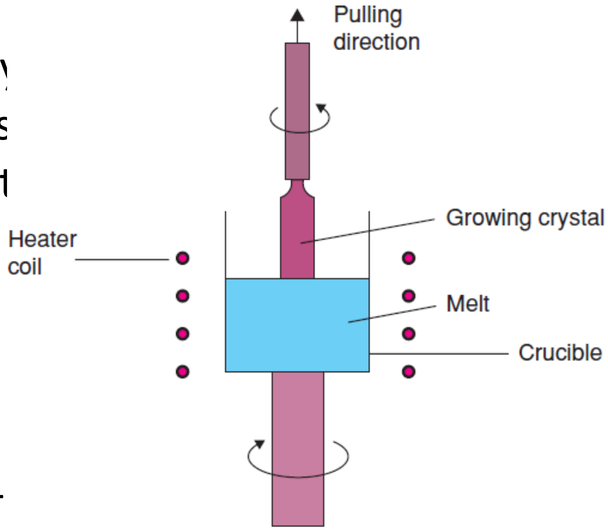
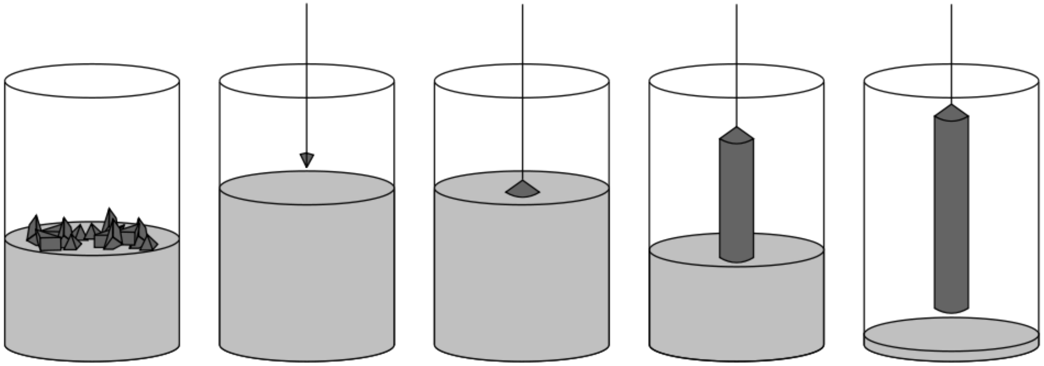


*Figure 4.22* *Czochralski method for crystal growth.*



Melting of polysilicon, doping

Introduction of the seed crystal

Beginning of the crystal growth

Crystal pulling

Formed crystal with a residue of melted silicon

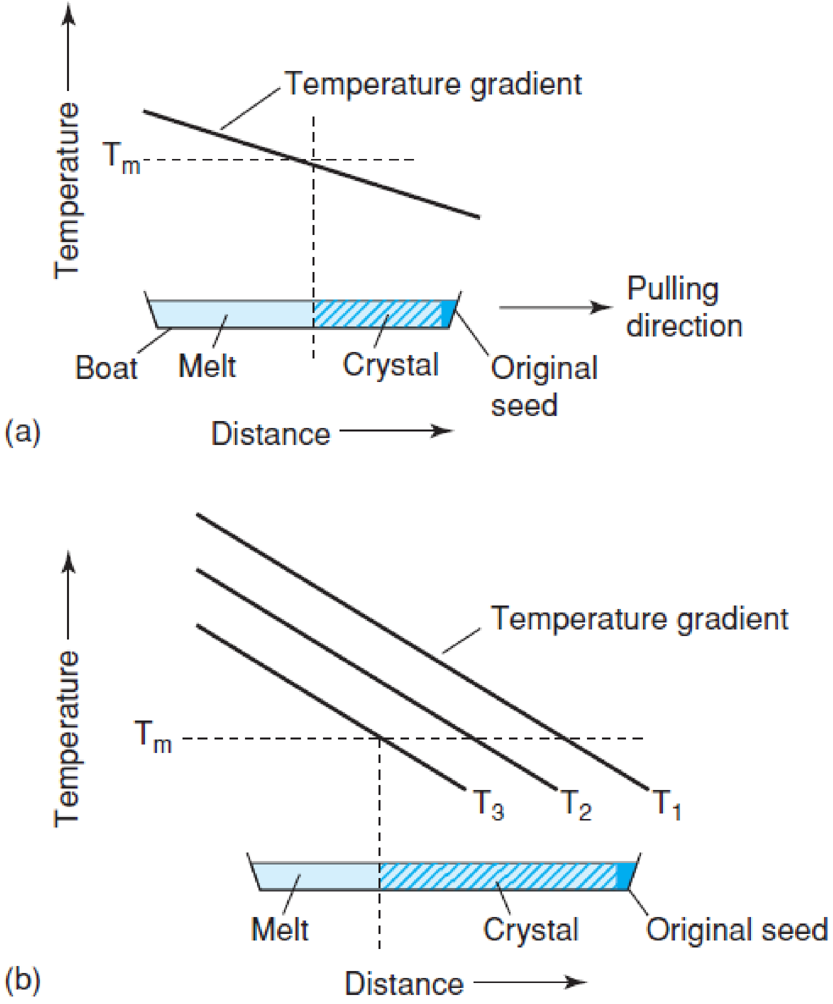
Figure: Wikipedia

Ref: West p. 226

# Bridgman and Stockbarger methods

https://wiki.aalto.fi/display/SSC/Bridgman+and+Stockbarger+methods

- Based on the solidification of a stoichiometric melt
- Crystallisation is controlled by passing the melt through a temperature gradient such that crystallization occurs at the cooler end
- This is achieved in the Stockbarger method by arranging displacement of the melt within a temperature gradient
- In the Bridgman method, the melt is inside a temperature gradient furnace and the furnace is gradually cooled so that solidification begins at the cooler end
- In both methods, it is advantageous to use a seed crystal



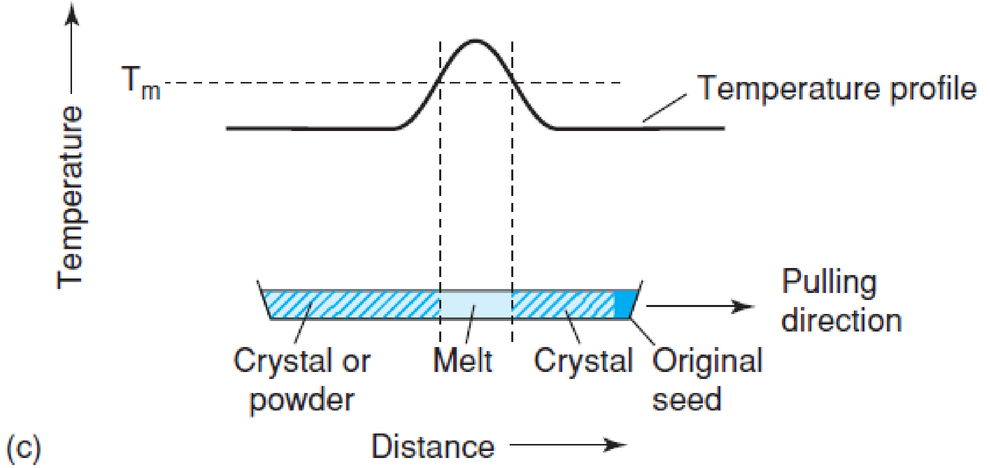
(a) Stockbarger method. $T_m$ = crystal melting point.
(b) Bridgman method

Ref: West p. 228

# Zone melting method

https://wiki.aalto.fi/display/SSC/Zone+melt+methods

- Related to the Stockbarger method but the thermal profile through the furnace is such that only a small part of the charge is molten at any one time
- Initially that part of the material in contact with the seed crystal is melted
- As the boat is pulled through the furnace, oriented solidification onto the seed occurs and, at the same time, more of the charge melts
- A well-known method for purification of solids, the zone-refining technique
- Makes use of the principle that impurities usually concentrate in the liquid rather than in the solid phase
- Impurities are "swept out" of the crystal by the moving molten zone
- State-of-the-art techniques: **Optical floating zone** (see *e.g.* S. M. Koohpayeh, D. Fort, J. S. Abell, *Prog. Cryst. Growth Charact. Mater.* **2008**, *54*, 121-137 (DOI))



Ref: West p. 228

# Precipitation from solution or melt: Flux method

- https://wiki.aalto.fi/display/SSC/Flux+methods
- In contrast to the above methods in which crystals have the same composition as the melt, precipitation methods involve the growth of crystals from a solvent of different composition
- The solvent may be one of the constituents of the desired crystal,
  - e.g. crystallization of salt hydrate crystals from water,
  - or the solvent may be an entirely separate liquid in which the crystals of interest are partially soluble, e.g. various high-melting silicates may be precipitated from low-melting borate or halide melts
- In these cases, the solvent melts are often referred to as **fluxes** since they effectively reduce the melting point of the crystals by a considerable amount.

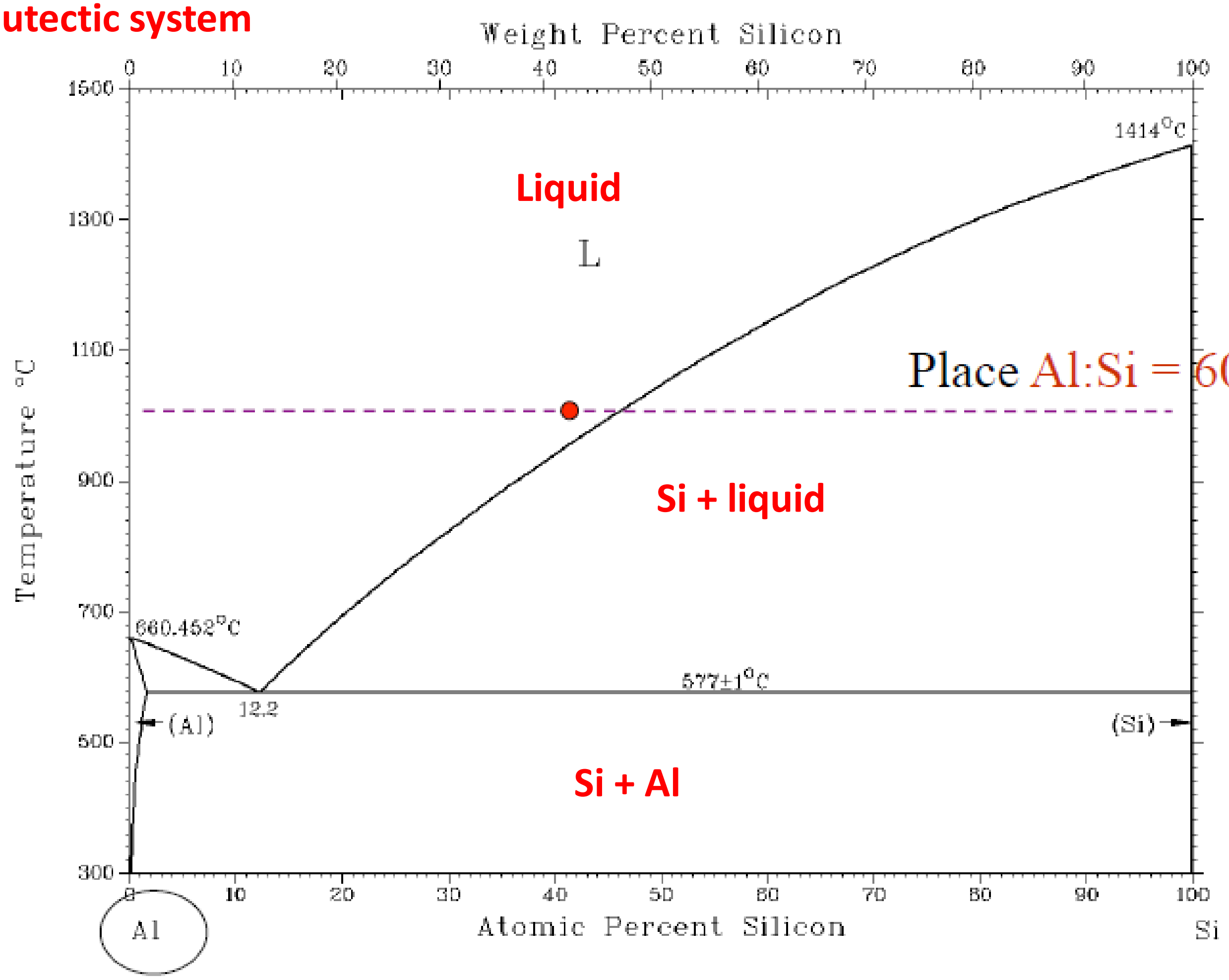
# (1) How to make Si? ($T_{melt}$ = 1412 °C)

Let’s aim for max temperature of our furnace of ~ 1000 °C

Look up solvents that are low melting: Bi, Sn, Zn, Ga, Al

Best solvent

**Binary eutectic system**



Place Al:Si = 60:40 into $Al_2O_3$

**Growing Si single crystals at lower temperature with the help of Al flux**

Figure: Athena S. Sefat, Oak Ridge