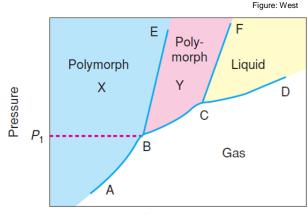# Lecture 5: Phase Diagrams and crystal growth

Figure: West

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

- Single crystal growth
  - Czochralski method
  - Bridgman and Stockbarger methods
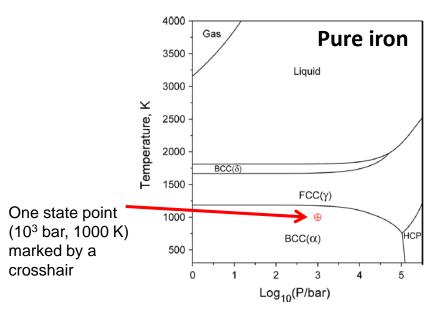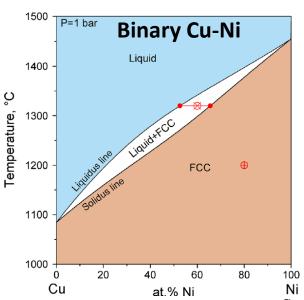 - Zone melt methods
  - Flux methods

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

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, see the following paper in MyCourses -> Materials -> Scientific papers:

  - Schmid-Fetzer 2014 Phase Diagrams - The Beginning of Wisdom

- Phase diagrams are a road map to understand the conditions for phase formation or transformation in any material system

- One can use phase diagrams as the starting point for materials design and process optimization

One state point
(10^3 bar, 1000 K)
marked by a
crosshair

2

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
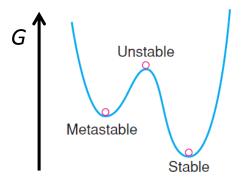

Figure 7.2   *Schematic diagram showing stable, unstable and metastable conditions.*

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
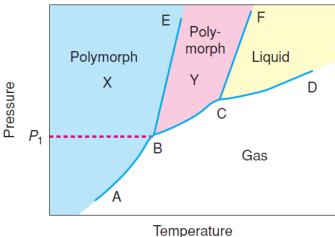- Four components -> **quaternary** system

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:
  - $F = C - P + 1$

Phase rule in practice

1. A solid solution in the system Al_2O_3–Cr_2O_3 (C = 2) has one composition variable because the Al_2O_3:Cr_2O_3 ratio can be varied
   - If a sample has $x\%$ of Al_2O_3, then the Cr_2O_3 content is fixed as $(100 - x)\%$
   - The temperature of the **single-phase** solid solution can also be varied
   - $F = C - P + 1 = 2 - 1 + 1 = 2$ (Al_2O_3:Cr_2O_3 ratio and T)
   - If pressure is taken into account, $F = 3$
2. A partially melted solid (e.g. ice) in a **one-component** system (e.g. 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
3. 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).
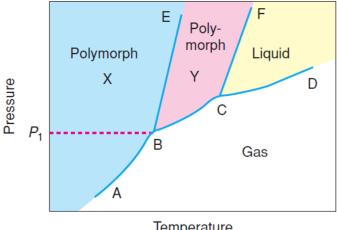   - For example, Mount Everest: 8848 m; p = 34 kPa -> boiling point of H_2O=71 °C

One-component systems (1)

- The composition is fixed at $C = 1$ and the independent variables are T and p
  - $F = C - P + 2 <=> F + P = 3$
  - 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

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

One-component systems (2)

- 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.
- Two invariant points B and C for which $P = 3$ and $F = 0$ are also called *triple points*.

H_2O

Figure: Wikipedia

SiO$_2$

- Silica is the main component of many ceramic materials in addition to being the most common oxide in the Earth's crust

- Complex polymorphism at atmospheric pressure:

α-quartz $\xrightarrow{\text{573}\,°\text{C}}$ β-quartz $\xrightarrow{\text{870}\,°\text{C}}$ β-tridymite $\xrightarrow{\text{1470}\,°\text{C}}$ β-cristobalite $\xrightarrow{\text{1710}\,°\text{C}}$ liquid

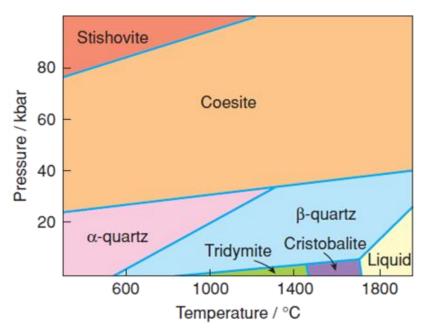- With increasing pressure, the polymorphs with higher density are favored

Table 7.1 *Densities of SiO$_2$ polymorphs*
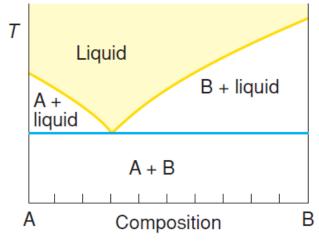
Polymorph	Density/g cm^{-3}
Low tridymite	2.265
Low cristobalite	2.334
Low quartz	2.647
Coesite	3.00
Stishovite	4.40

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 ($F = 0$) occurs when three phases coexist, a univariant curve for two phases and a bivariant condition for one phase
- 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
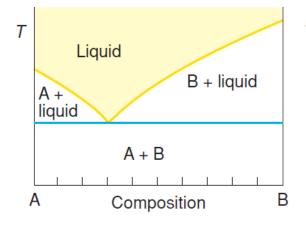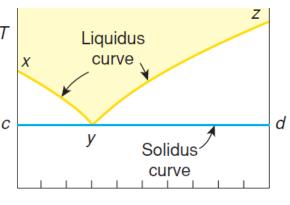
Binary eutectic system (2)

- 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 as the system contains an eutectic at –21°C.
- 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**
  - 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
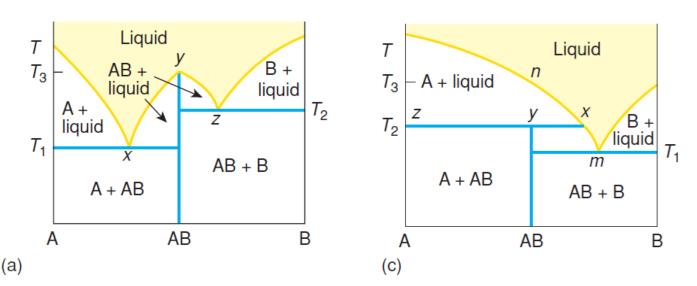
Figure 7.8 *Binary systems showing a compound AB melting congruently (a) and incongruently (c)*

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**
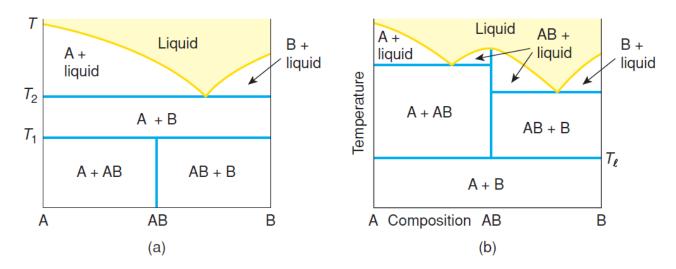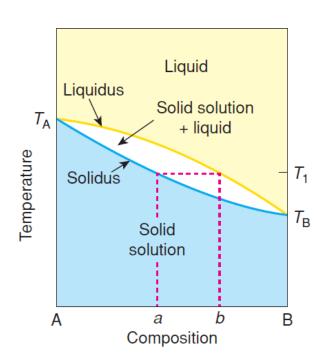 - Below a certain temperature, AB decomposes into a mixture of A and B

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.*

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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
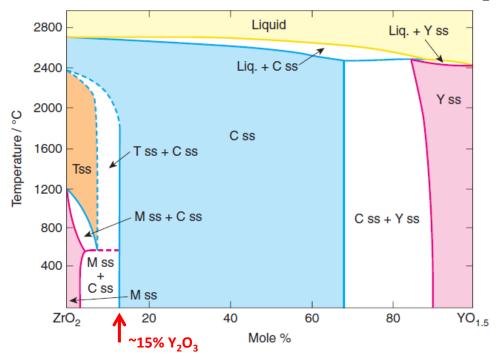
Yttria-stabilized Zirconia (YSZ)

- 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:

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

- 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
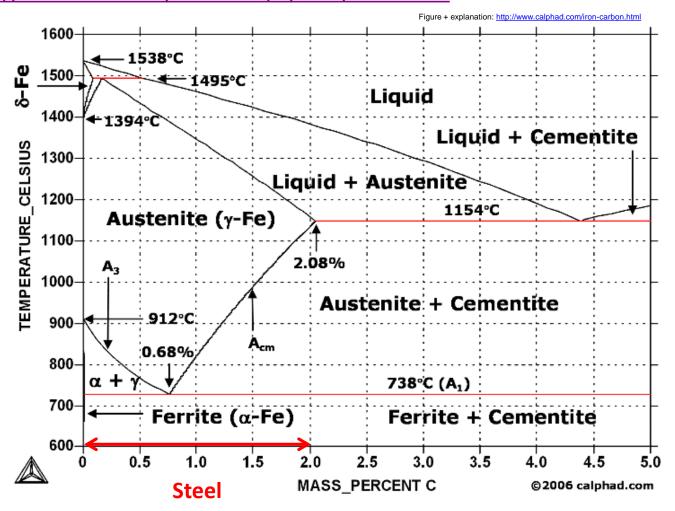

~15% Y_2O_3

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.*

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Fe-C phase diagram

- "The most important phase diagram in the history of civilization"(?)
- For some hands-on exercises on phase diagrams, see: http://www.southampton.ac.uk/~pasr1/index.htm

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
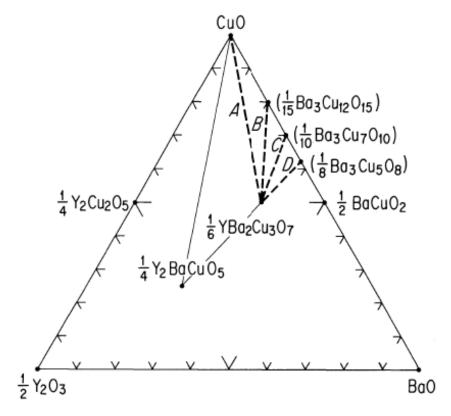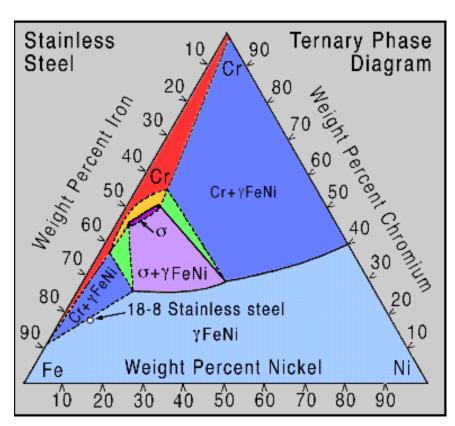

Fig. 1. Y_2O_3–BaO–CuO ternary phase diagram. The phase-equilibrium measurements were carried out along A, B, C and D directions (shown by bold dots). The coefficients before the molecular formulae are for normalization.

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

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
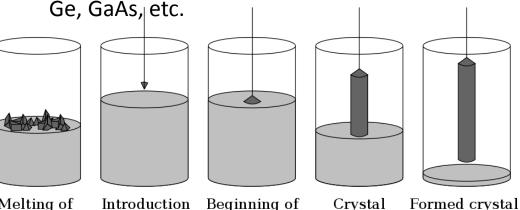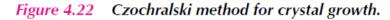- Precipitation from solution or melt: flux method

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

Czochralski method

- A crystal is grown from a melt of the same composition by starting with a seed crystal in contact with the melt, whose 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.*

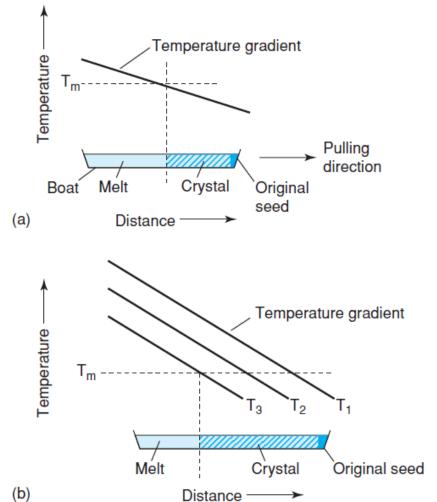| Melting of polysilicon, doping | Introduction of the seed crystal | Beginning of the crystal growth | Crystal pulling | Formed crystal with a residue of melted silicon |

Ref: West p. 226
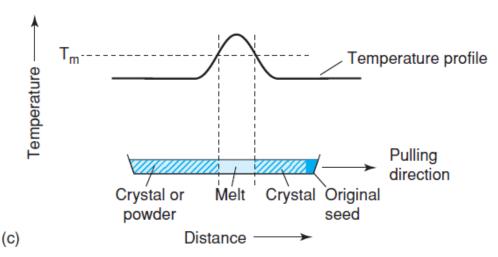
Bridgman and Stockbarger methods

- 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

Zone melting method

- 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

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Precipitation from solution or melt: Flux method

- 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

Liquid

Si + liquid

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

Si + Al

Figure: Athena S. Sefat, Oak Ridge

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