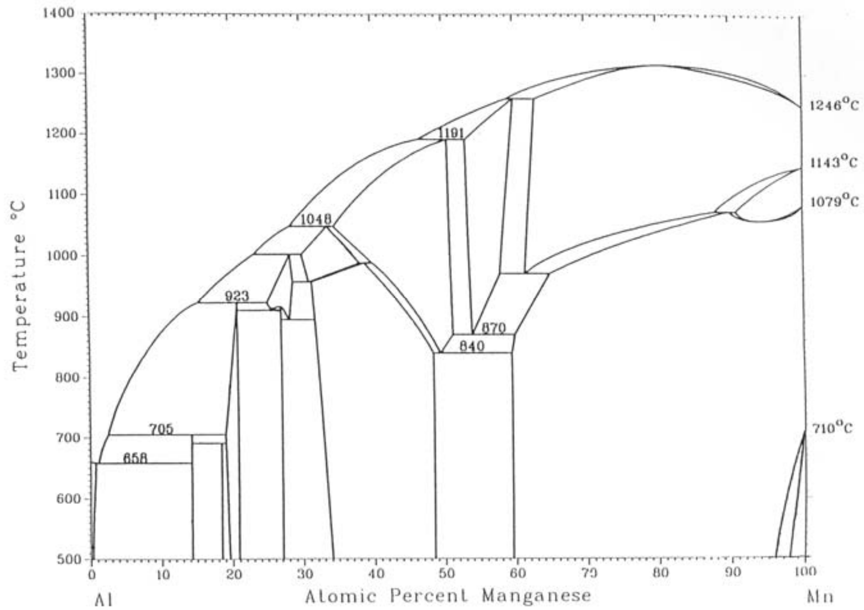
Kap. 4
Phase diagrams

Phasediagrams



Gibbs phase rule

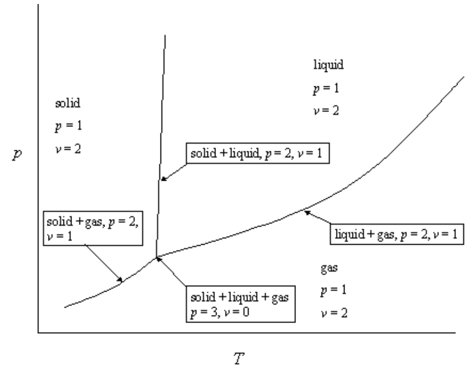
P + F = C + 2

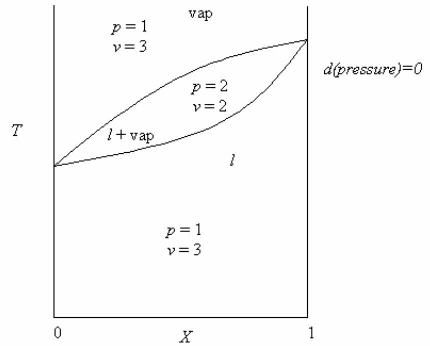
The **Degrees of Freedom** [F] or **Variance** [v] is the number of independent intensive variables (i.e. those that are independent of the quantity of material present) that need to be specified in value to fully determine the state of the system. Typical such variables might be temperature, pressure, or concentration.

A **Phase** [P] is a component part of the system that is immiscible with the other parts (e.g. solid, liquid, or gas); a phase may of course contain several chemical constituents, which may or may not be shared with other phases. The number of phases is represented in the relation by **P.**

The **Chemical Constituents** [C] are simply the distinct compounds (or elements) involved in the equations of the system. (If some of the system constituents remain in equilibrium with each other whatever the state of the system, they should be counted as a single constituent.) The number of these is represented as **C**.

Gibbs phase rule





Thermodynamic stability

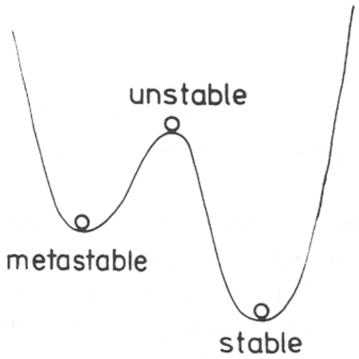


Fig. 6.2 Schematic diagram showing stable, unstable and metastable conditions

Phase diagrams only show the thermodynamically stable plhases.
If they show metastable compounds they are called existence or dominance diagrams.

One component diagrams

P + F = 1 + 2

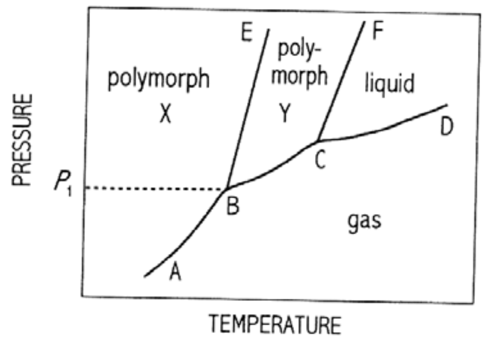


Fig. 6.3 Schematic pressure versus temperature phase diagram of a one-component system

One component diagrams

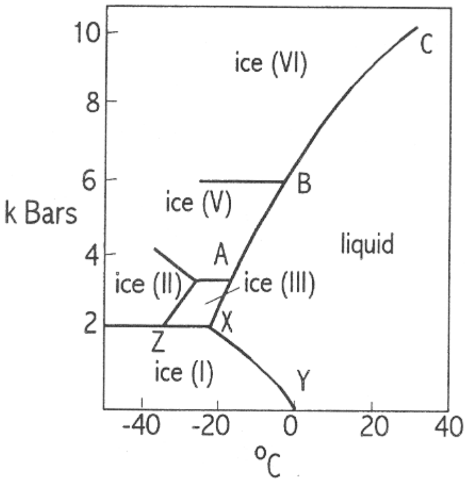


Fig. 6.4 The system H_2O

One component diagrams

P + F = 1 + 2

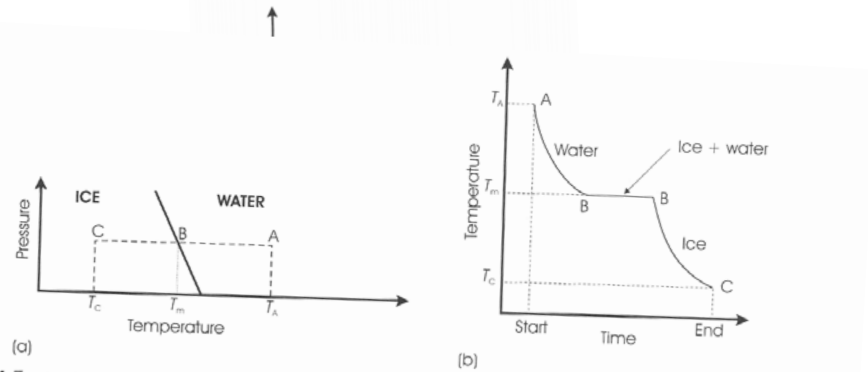


Figure 4.3 (a) A small part of the water phase diagram and (b) the cooling curve generated as a uniform sample of water cools from temperature A (liquid) to temperature C (solid; ice)

not to scale

One component diagrams

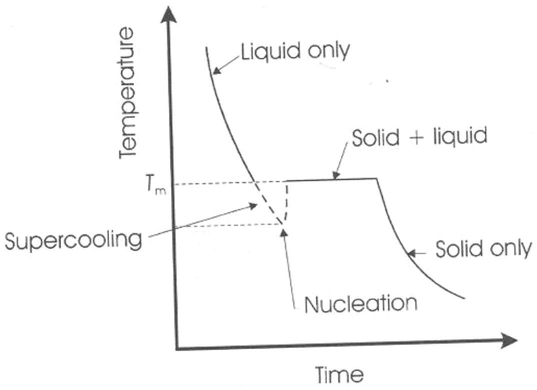


Figure 4.4 A cooling curve showing supercooling

One component diagrams

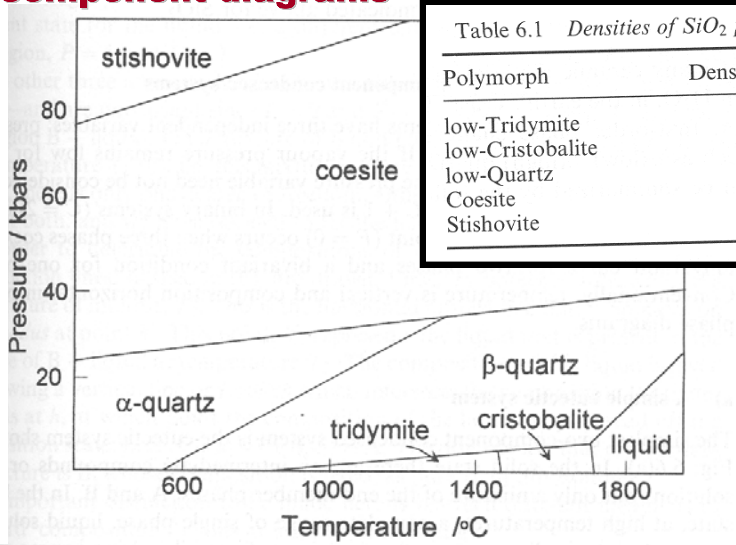


Fig. 6.5 The system SiO_2. (Adapted from Griffin, *Silicate Crystal Chemistry*, Oxford, 1992)

Table 6.1 *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

One component diagrams

P + F = 1 + 2

573 °C 870 °C 1470 °C 1710 °C

α-Quarts → β-Quarts → β-Tridymite → β-Cristobalite → liquid

Simple complete solid solution

P + F = 2 + 2

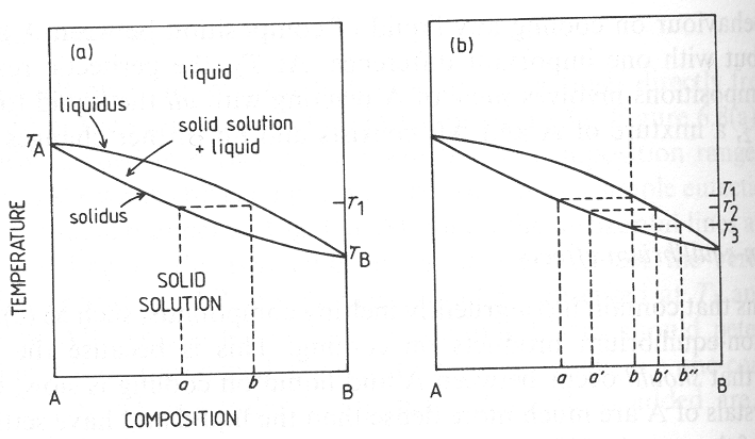


Fig. 6.10 Binary system with a complete range of solid solutions

Simple complete solid solution

P + F = 2 + 2

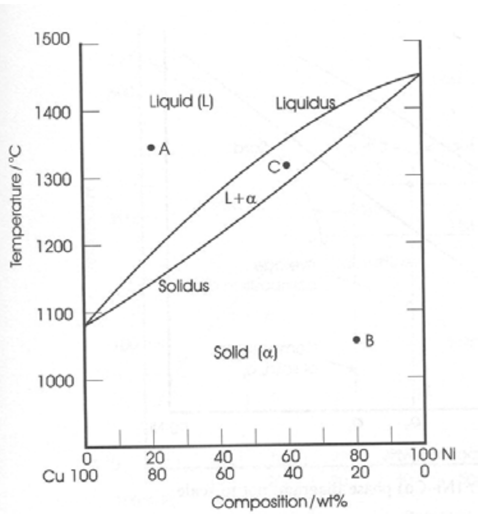


Figure 4.6 The nickel–copper (Ni–Cu) phase diagram at atmospheric pressure

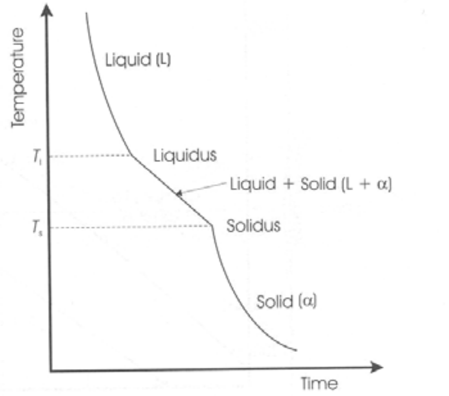


Figure 4.7 A cooling curve for a sample passing through a two-phase liquid + solid region

Simple complete solid solution

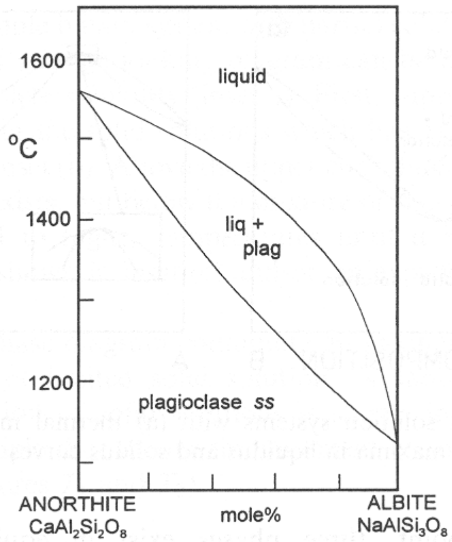


Fig. 6.11 The plagioclase feldspar system, anorthite–albite

Simple complete solid solution

P + F = 2 + 2

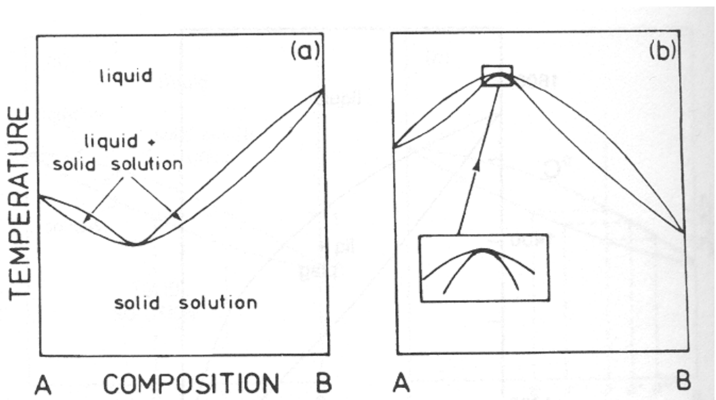


Fig. 6.12 Binary solid solution systems with (a) thermal minima and (b) thermal maxima in liquidus and solidus curves

Simple eutectic

L -> A + B

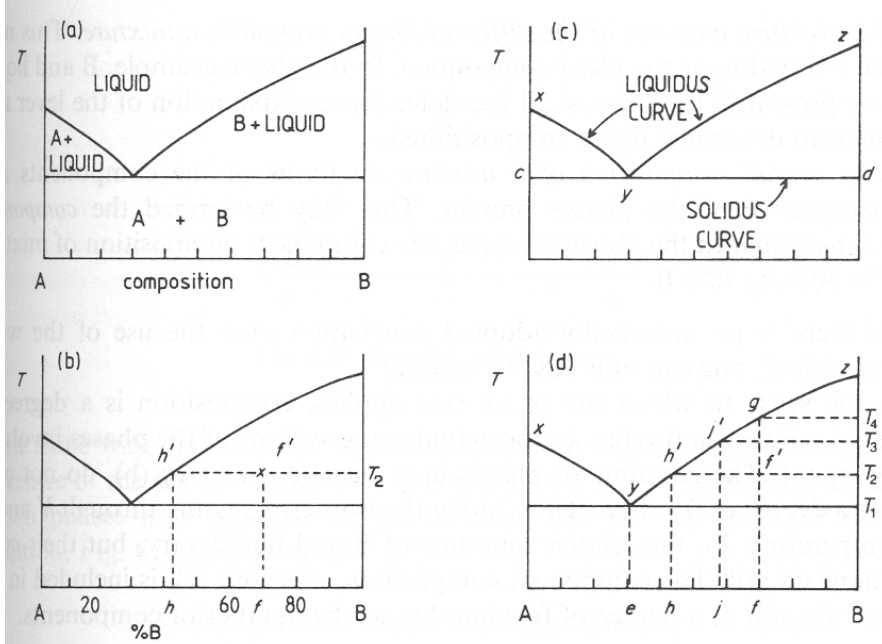


Fig. 6.6 Simple eutectic binary system

Simple eutectic

P + F = 2 + 2

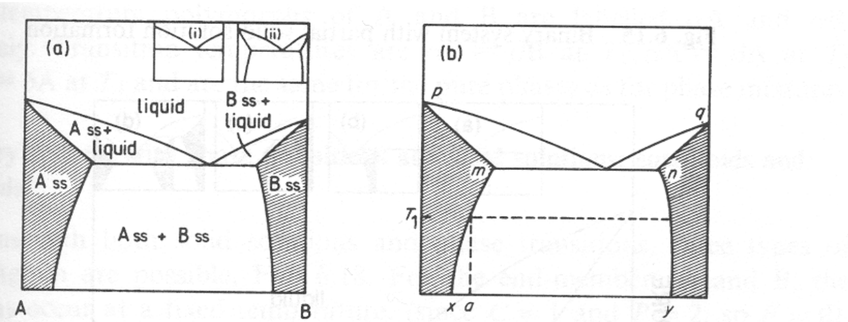


Fig. 6.13 Simple eutectic system showing partial solid solubility of the end members

Simple eutectic

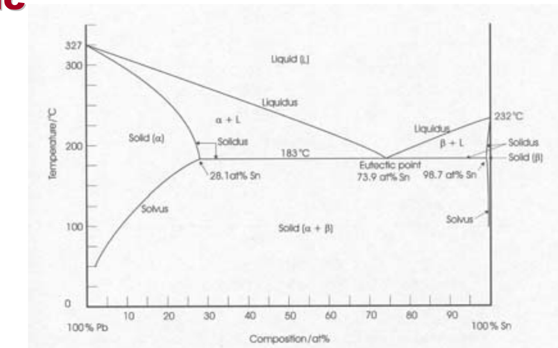


Figure 4.9 The lead-tin (Pb-Sn) phase diagram at atmospheric pressure

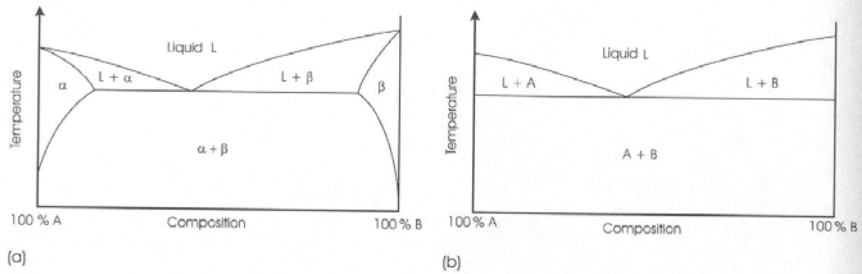


Figure 4.13 (a) A typical binary metallurgical phase diagram; (b) a typical ceramic (nonmetallic) phase diagram

Simple eutectic

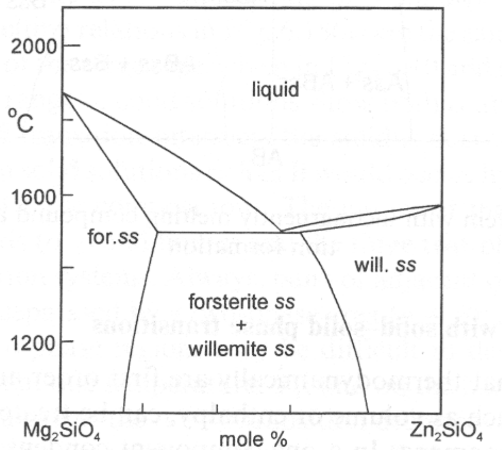
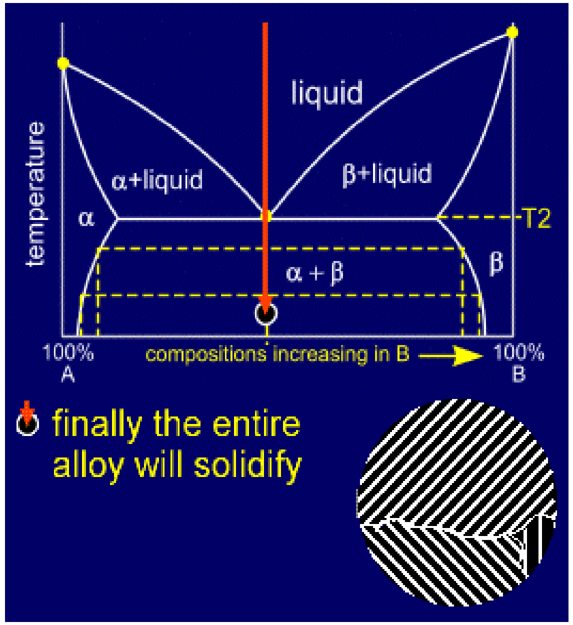
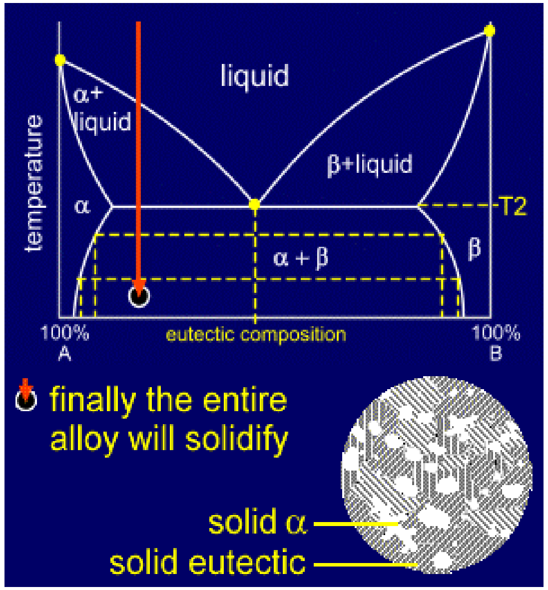


Fig. 6.14 The system Mg_2SiO_4–Zn_2SiO_4. (E.R. Segnit and A.E. Holland, *J. Amer. Ceram. Soc.*, **48**, 412, 1965)

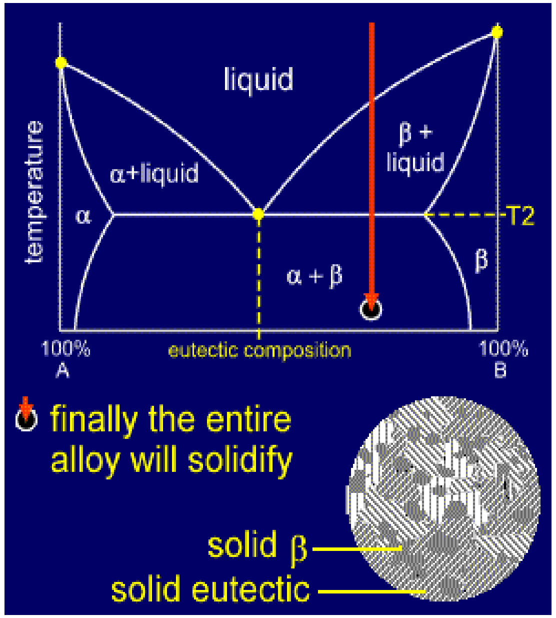
Simple eutectic



Simple eutectic



Simple eutectic



Complex eutectic

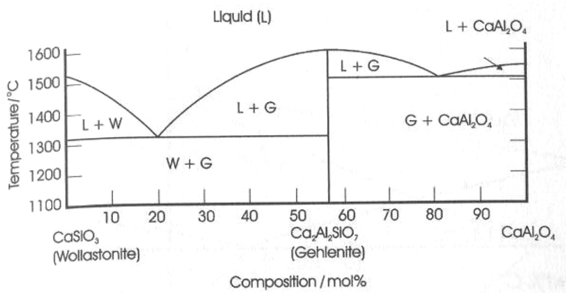
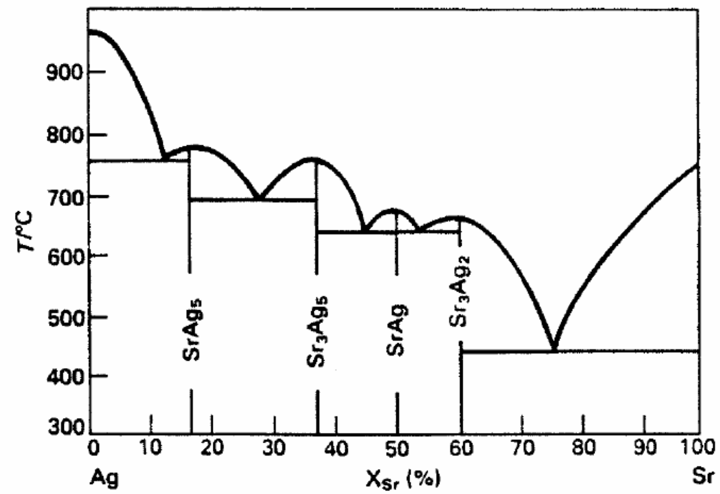


Figure 4.14 The wollastonite–calcium aluminate ($CaSiO_3$–$CaAl_2O_4$) phase diagram showing the intermediate phase gehlenite, $Ca_2Al_2SiO_7$

Complex eutectic



Simple peritectic

L + A -> B

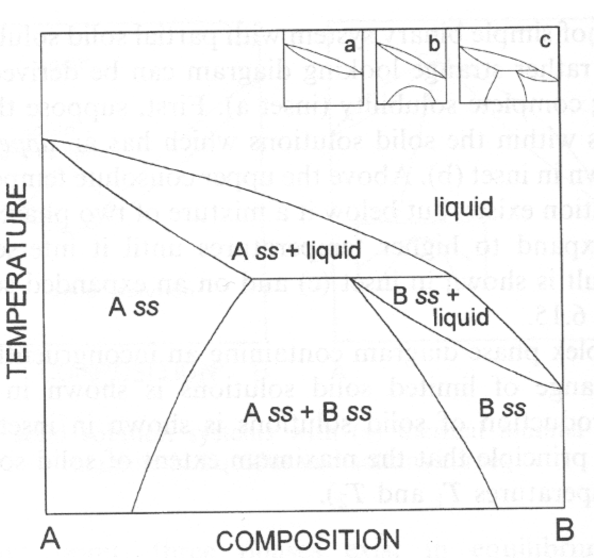


Fig. 6.15 Binary system with partial solid solution formation

Simple peritectic

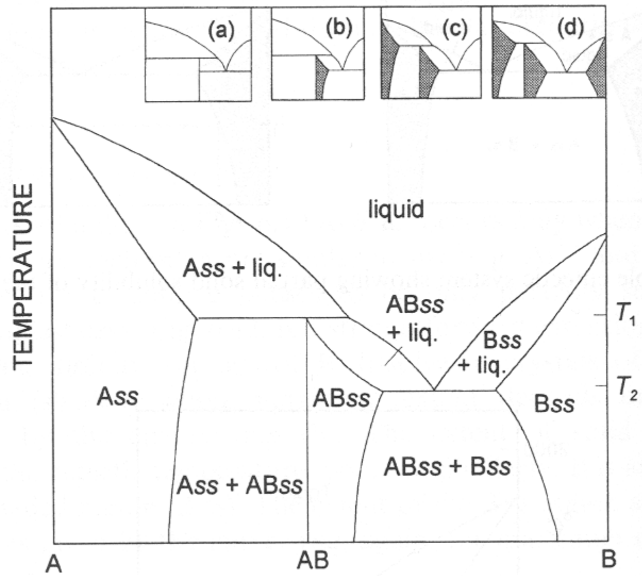


Fig. 6.16 Binary system with incongruently melting compound and partial solid solution formation

Simple peritectic

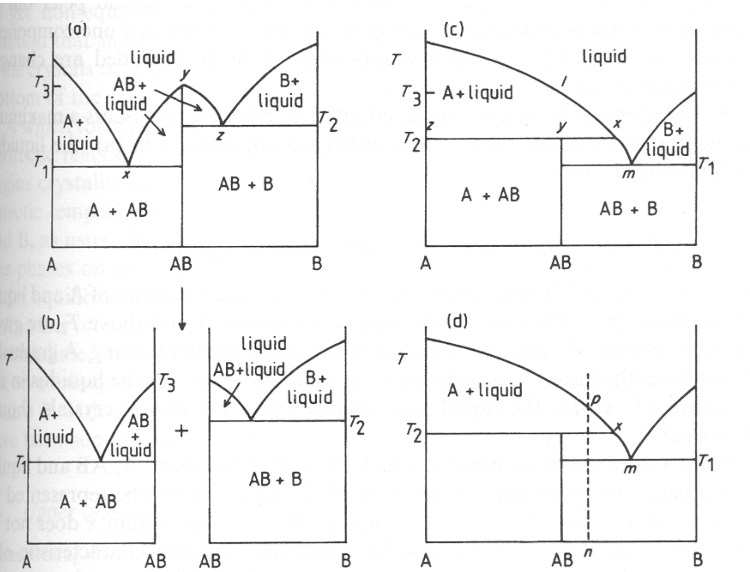


Fig. 6.8 Binary systems showing a compound AB melting congruently (a) and incongruently (c), (d). In (b), the diagram in (a) is separated into two self-contained, simple eutectic systems

Simple peritectic

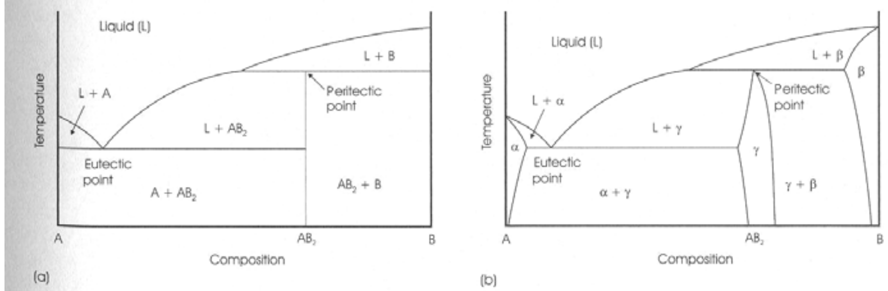


Figure 4.15 (a) A hypothetical ceramic (nonmetallic) phase diagram containing a peritectic point and (b) a hypothetical metallurgical phase diagram containing a peritectic point

Lever rule

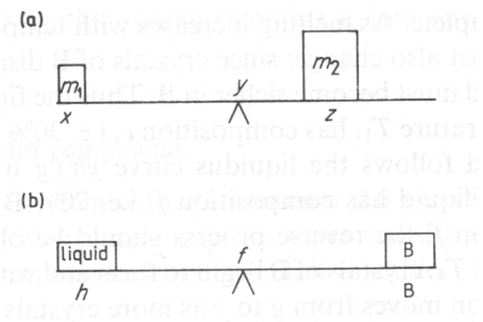
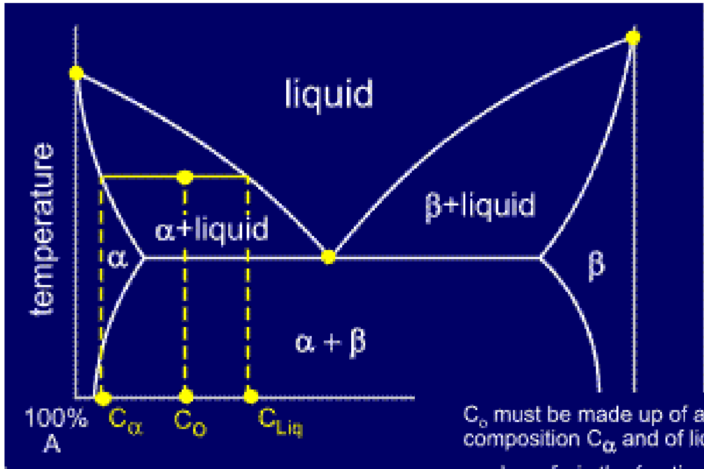


Fig. 6.7 Principle of moments



C_o must be made up of appropriate amounts of α at composition C_α and of liquid at composition C_{Liq},

where f_α is the fraction of α in the sample:

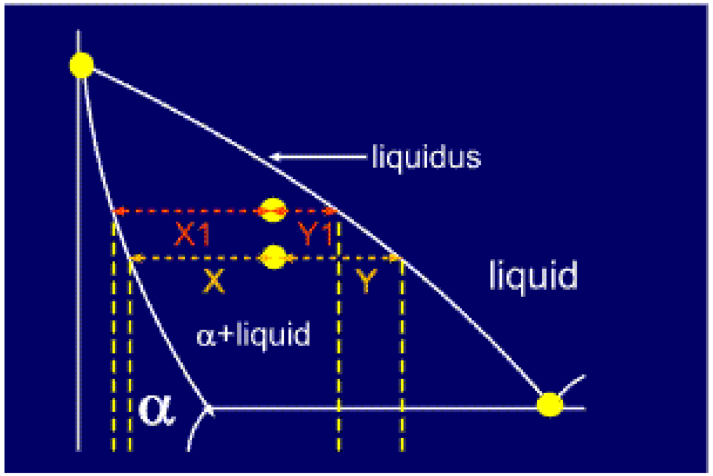
$$C_o = f_\alpha C_\alpha + (1 - f_\alpha) C_{Liq}$$

and by rearranging:

$$C_o - C_{Liq} = f_\alpha (C_\alpha - C_{Liq})$$

and finally:

$$f_\alpha = \frac{C_o - C_{Liq}}{C_\alpha - C_{Liq}}$$



Demixing

L -> L' + L"

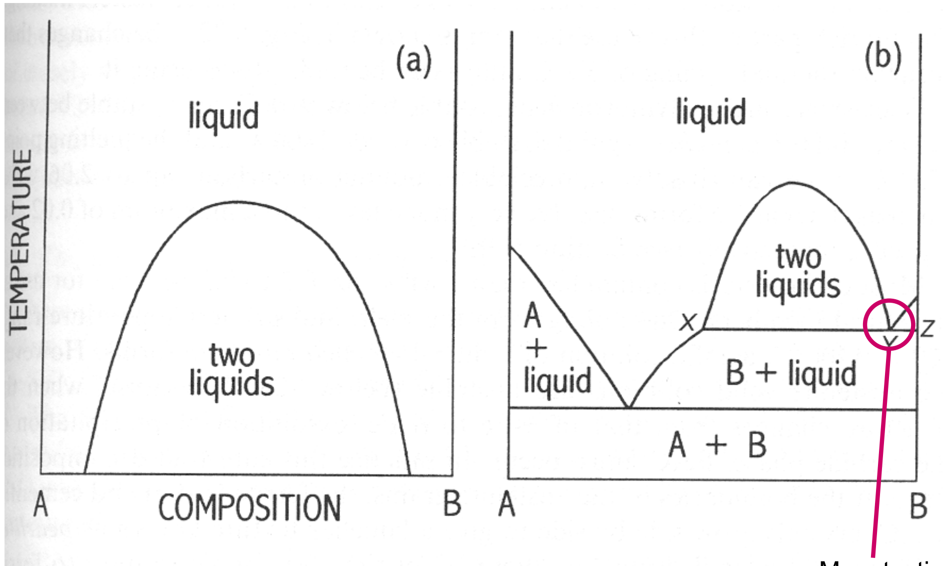


Fig. 6.20 Liquid immiscibility domes in phase diagrams

Monotectic
L -> L' + B

Demixing

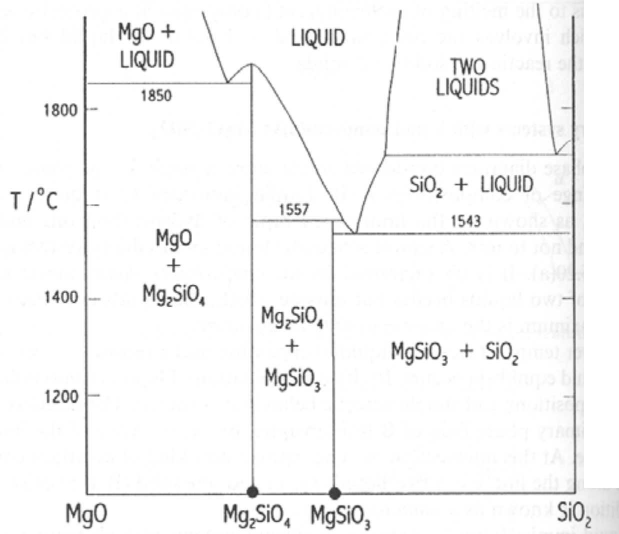
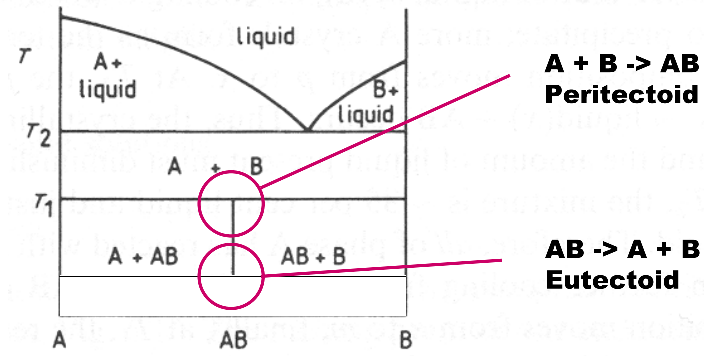


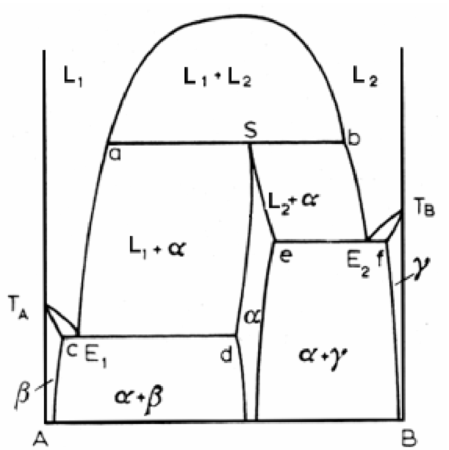
Fig. 6.21 Phase diagram MgO–SiO_2

-oid



Binary system showing compound AB with an upper limit of stability

Synthetic reaction



$L_1 + L_2 \rightarrow \alpha$

K-Zn, Na-Zn, K-Pb, Pb-U and Ca-Cd

Polymorphs

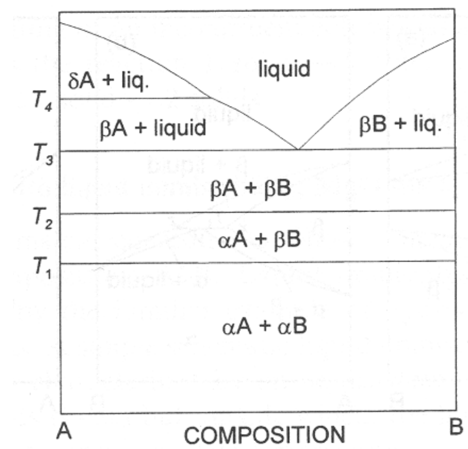


Fig. 6.17 Simple eutectic system with solid–solid phase transitions

Polymorphs

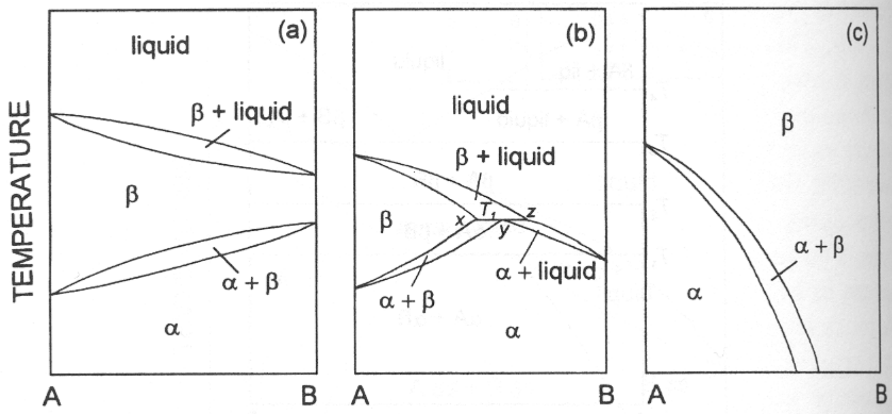


Fig. 6.18 Binary solid solution systems with polymorphic phase transitions

Polymorphs

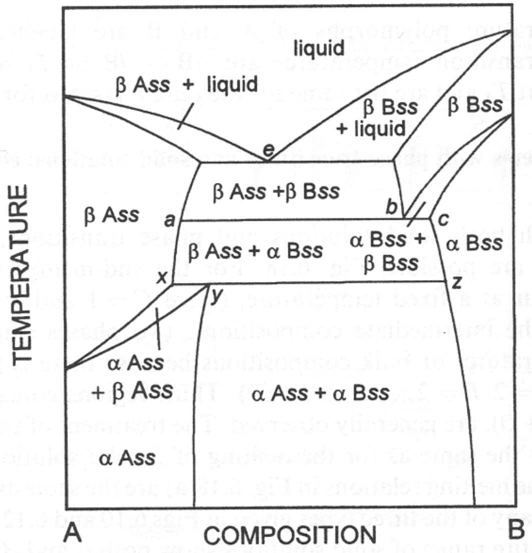
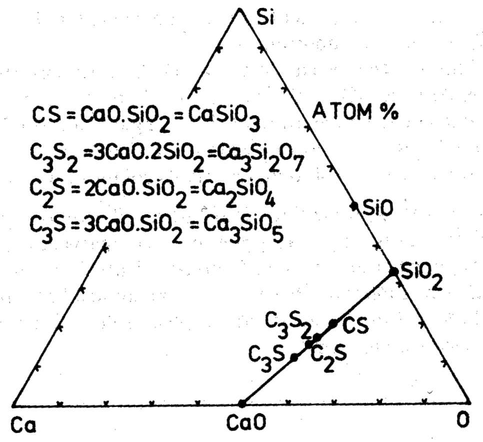


Fig. 6.19 Binary eutectic system with polymorphic transitions and partial solid solution formation

Terneary diagrams



6.1 Binary join CaO–SiO$_2$ in the ternary system Ca–Si–O. Note the method used the labelling of phases, C=CaO, etc. This type of abbreviation is widely used in oxide chemistry

Important phase diagrams

Fe-C

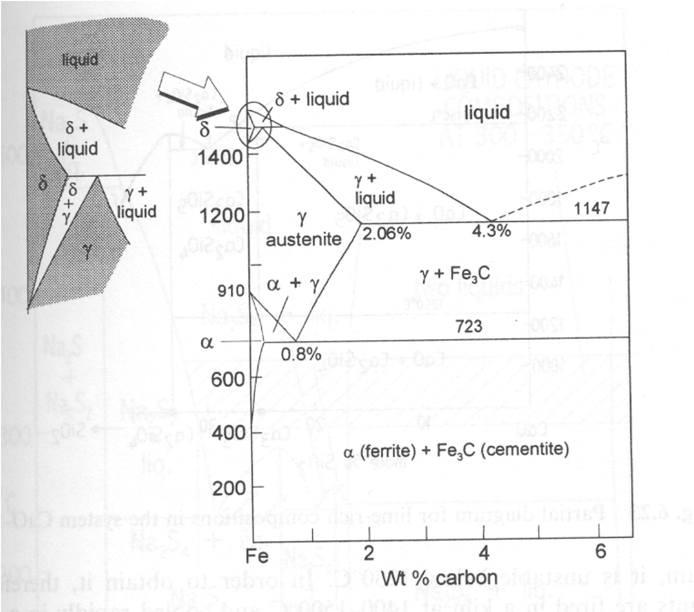
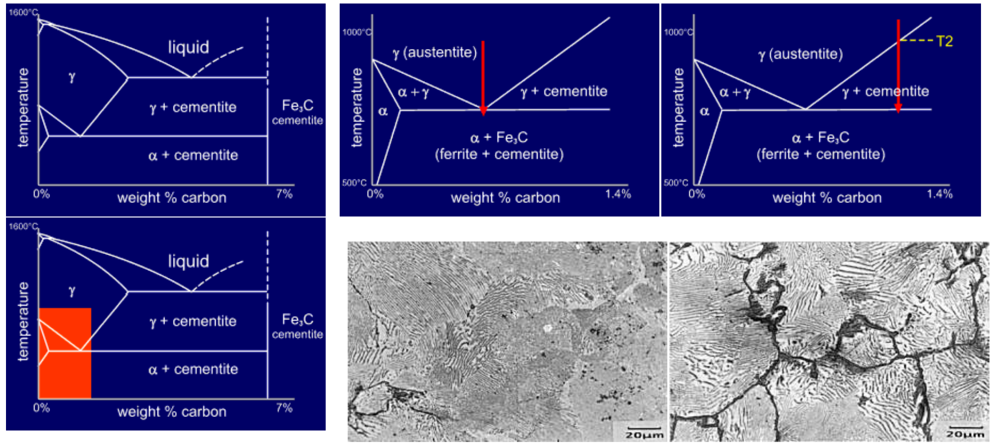


Fig. 6.22 The Fe–C diagram

Fe-C



0.83

1.3

CaO-SiO_2

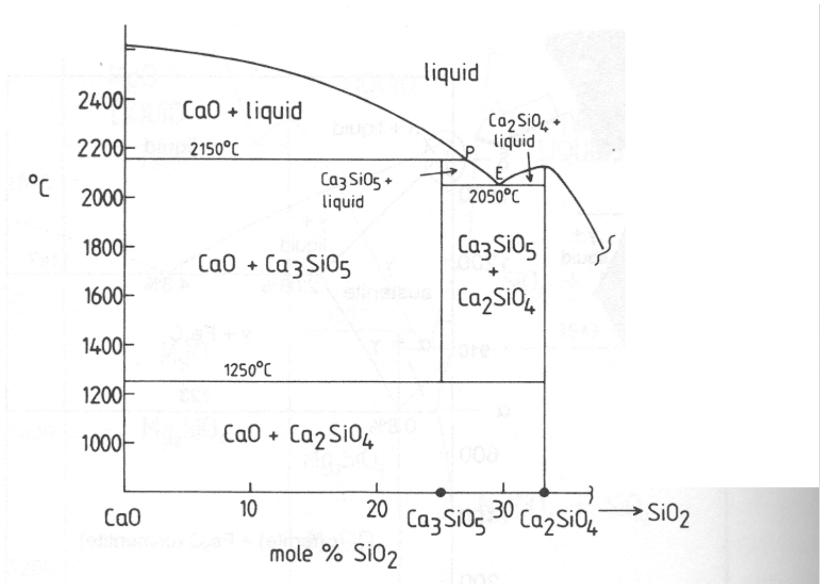


Fig. 6.23 Partial diagram for lime-rich compositions in the system CaO–SiO_2

Na_2O-SiO_2

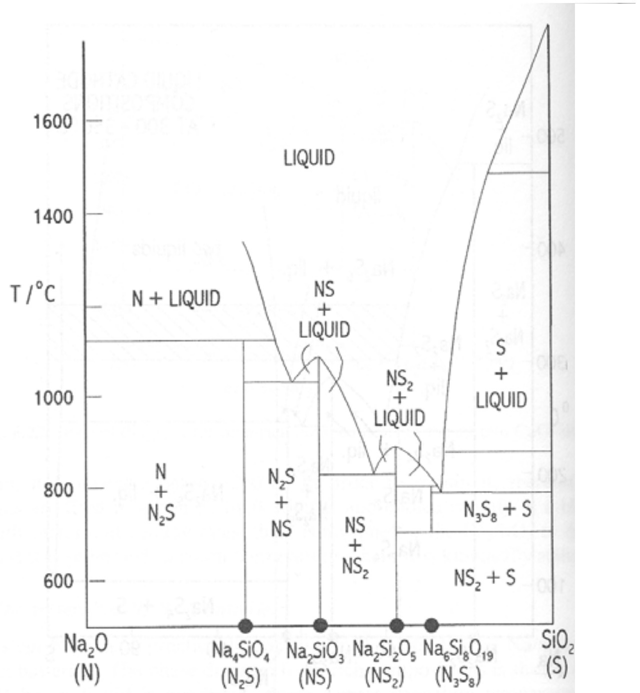


Fig. 6.25 Phase diagram Na_2O–SiO_2. N = Na_2O, S = SiO_2, N_2S = Na_4SiO_4, NS = Na_2SiO_3, NS_2 = $Na_2Si_2O_5$ N_3S_8 = $Na_6Si_8O_{19}$

$Li_2SiO_3 - SiO_2$

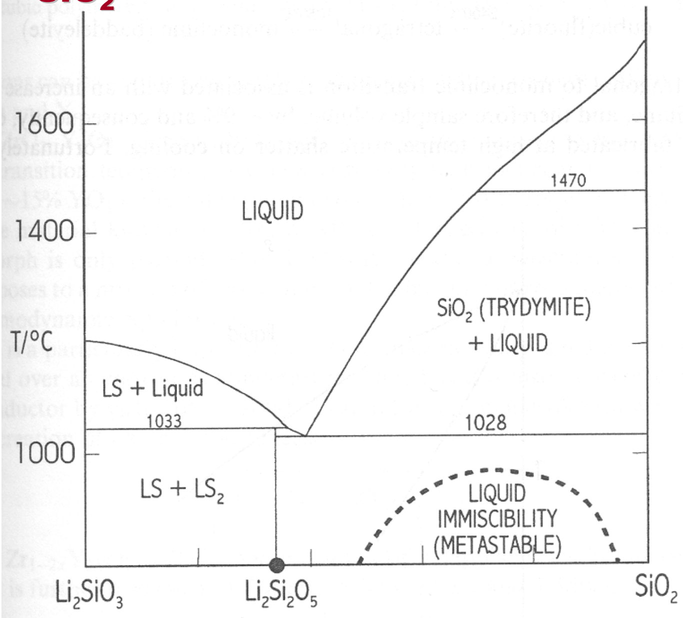


Fig. 6.26 Phase diagram Li_2SiO_3–SiO_2. LS = Li_2SiO_3, LS_2 = $Li_2Si_2O_5$. The existence of a metastable immiscibility dome in rapidly-cooled liquids that have avoided crystallization is shown schematically, dashed

Na-S

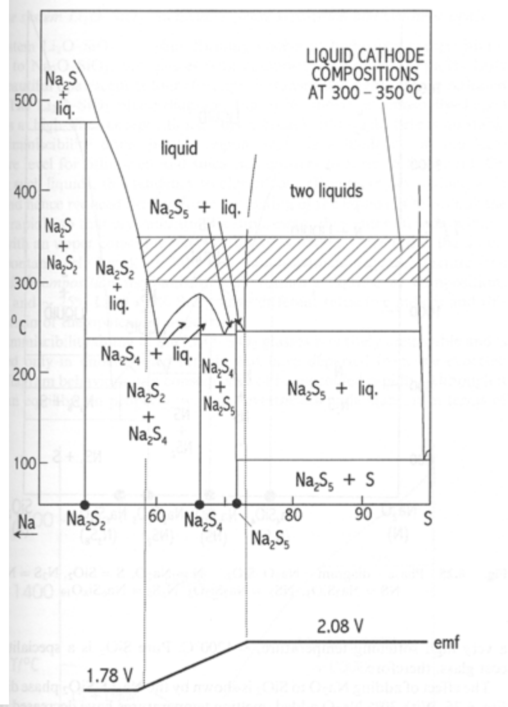


Fig. 6.24 Na–S phase diagram and open circuit cell voltage as a function of degree of discharge/cathode composition for the Na/S cell

$ZrO_2 - Y_2O_3$

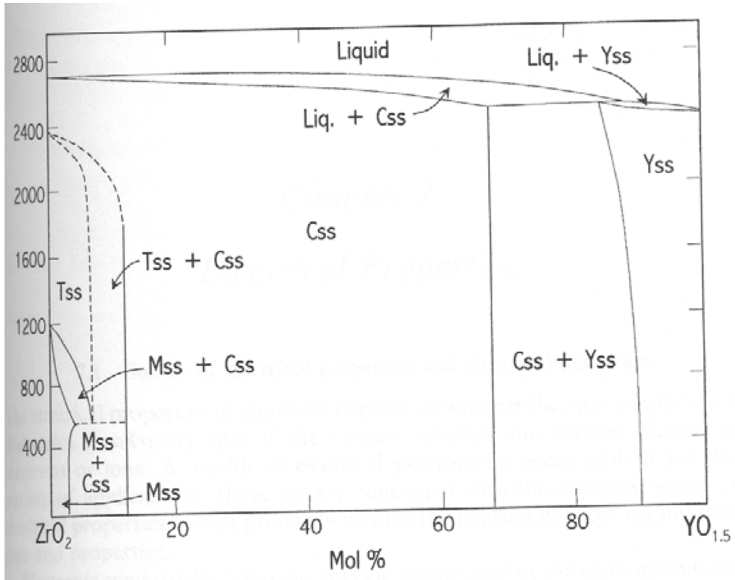
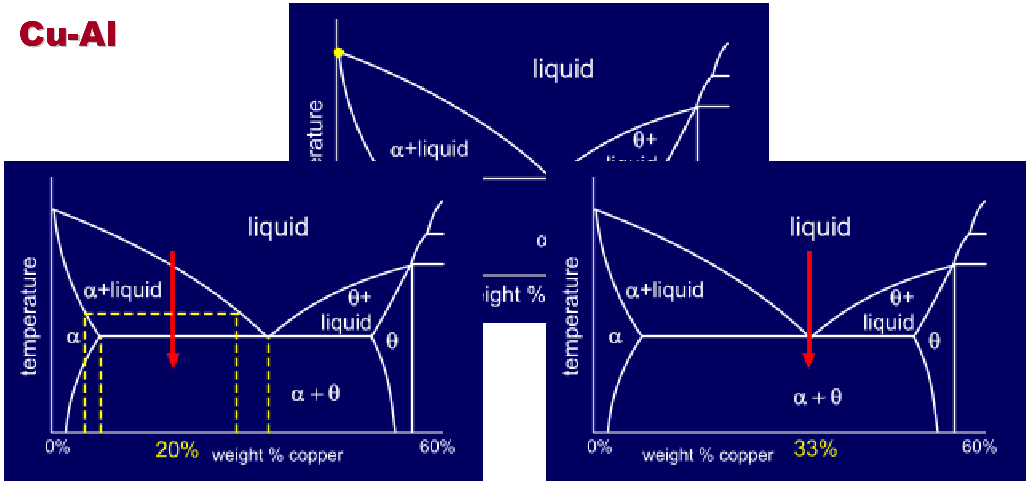
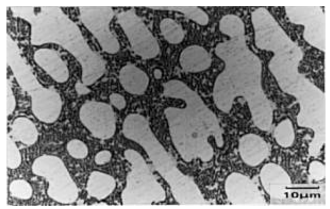
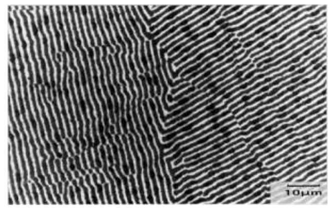


Fig. 6.28 Phase diagram ZrO_2–Y_2O_3. M, T and C refer to the monclinic, tetragonal and cubic polymorphs of zirconia, and their solid solutions, ss. Y = yttria, Y_2O_3

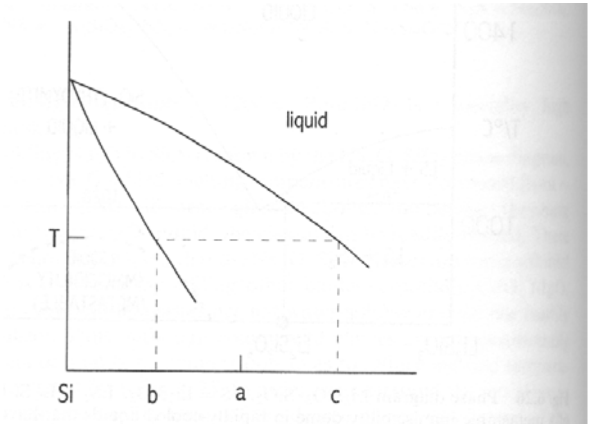
Cu-Al







Zone refinement



Purification of Si by zone refining: impurities concentrate in melt