Single Crystal Growth from Melt
(for sample preparation purposes)

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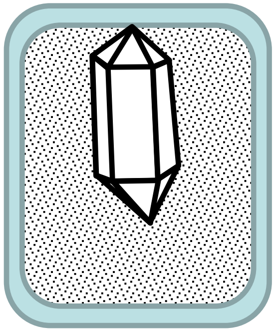
May 2013

Methods of crystal growth:

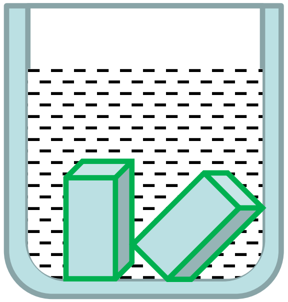
From gas phase:

- ❑ Chemical Vapor Deposition (CVD)
- ❑ Vapor transport



From supercritical fluid:

- ❑ Hydrothermal solution growth

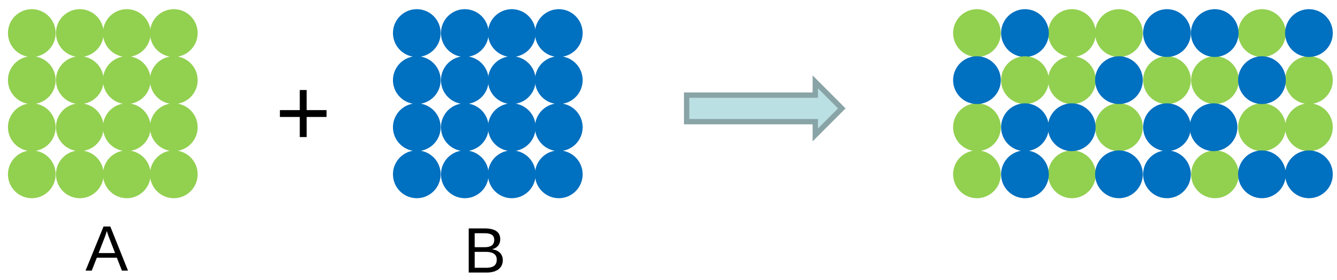


From liquid(melt) phase:

- ❑ Slow cooling melt (flux) growth
- ❑ Top-seeded melt growth
- ❑ Bridgman method
- ❑ Floating zone method
- ❑ Czochralski method

1. Phase equilibria and phase diagrams

(1) Free energy of atomic-level mixing

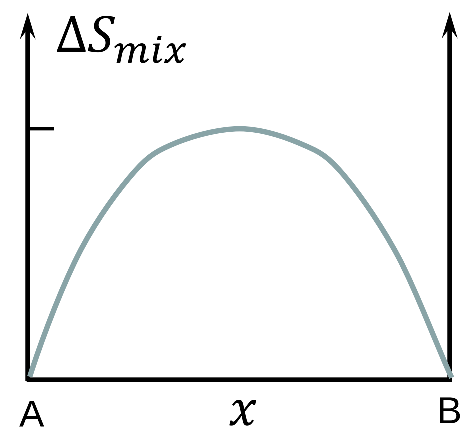


$$G = x_A G_A + x_B G_B + \Delta G_{mix}$$

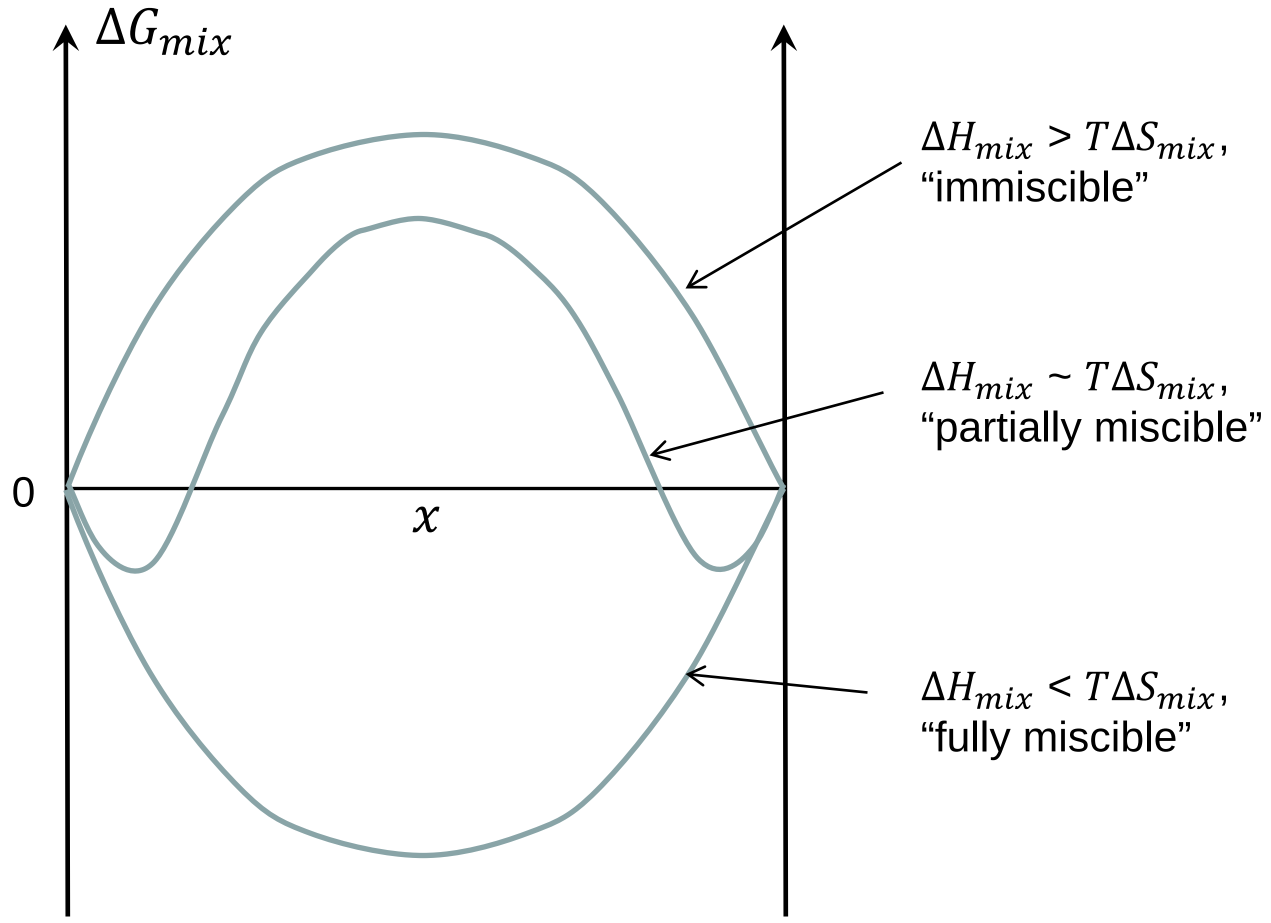
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta S_{mix} = -R(x_A ln x_A + x_B ln x_B)$$

(for ideal materials)

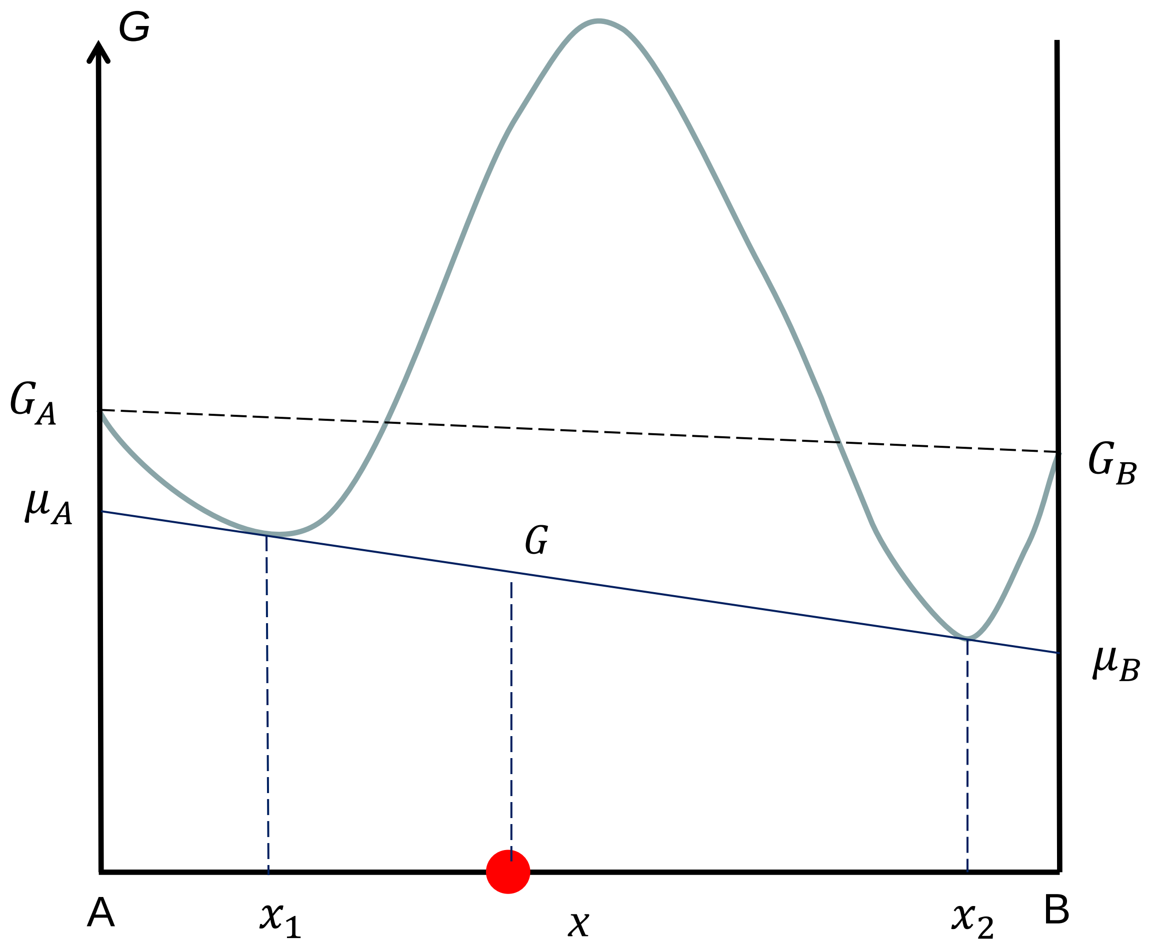


(2) Three types of ΔG_{mix} curve

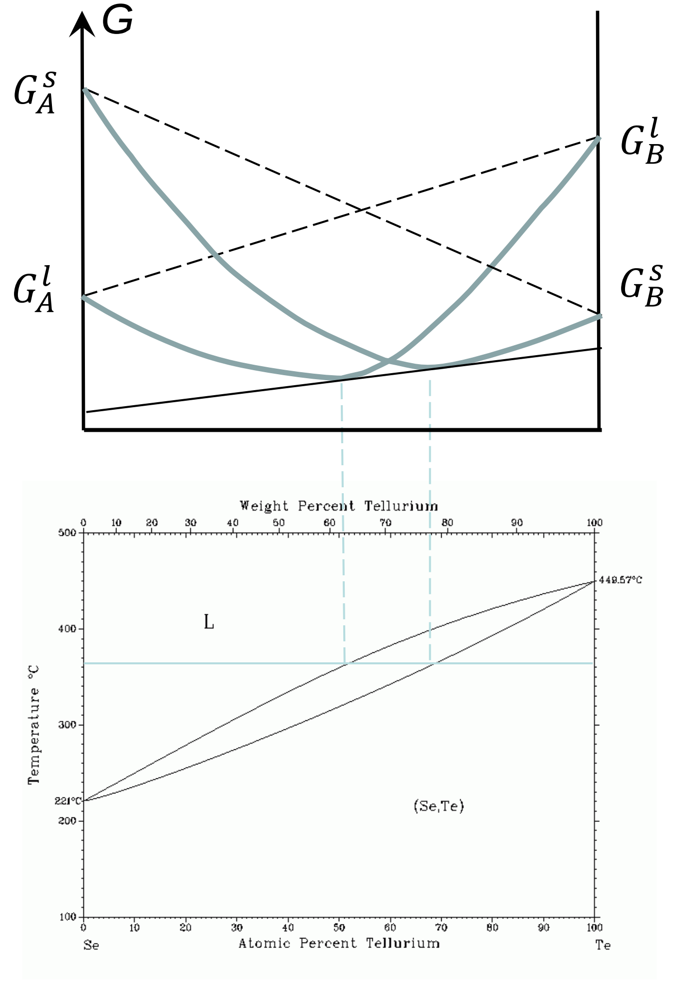


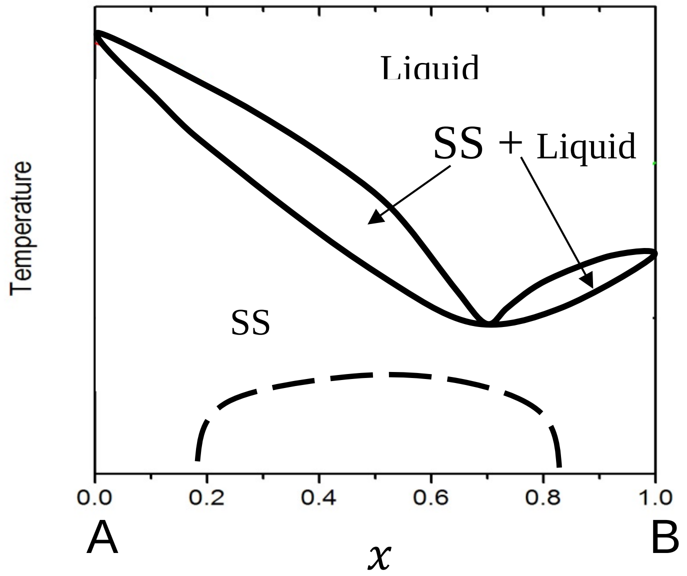
Phase equilibrium:

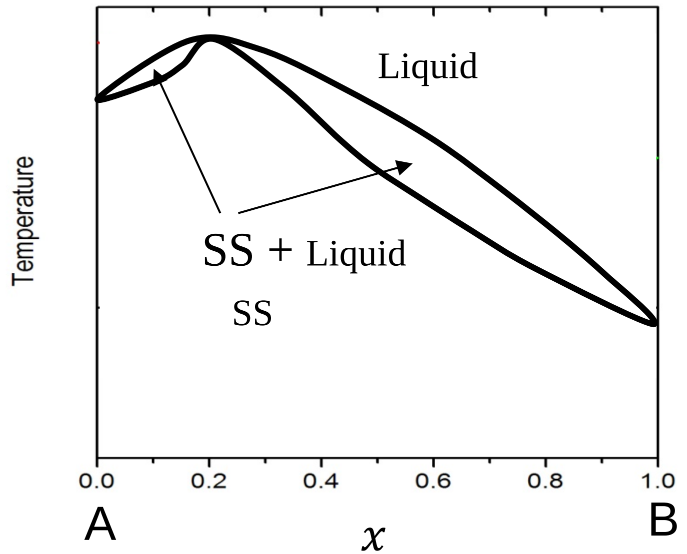
$$\mu_A^1 = \mu_A^2\,, \quad \mu_B^1 = \mu_B^2$$

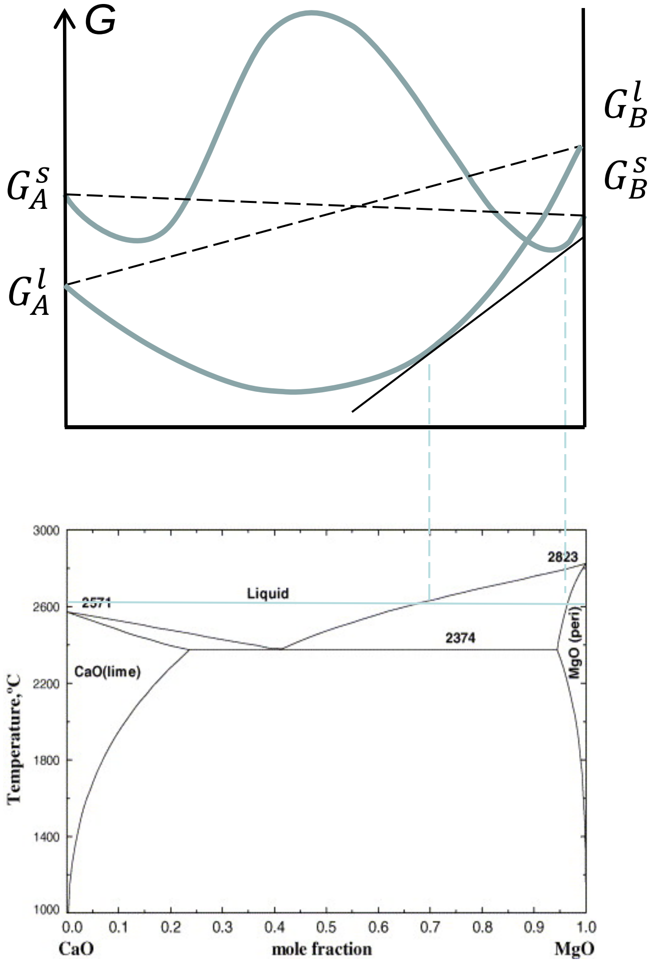


(3) Binary phase diagram and ΔG_{mix} curves

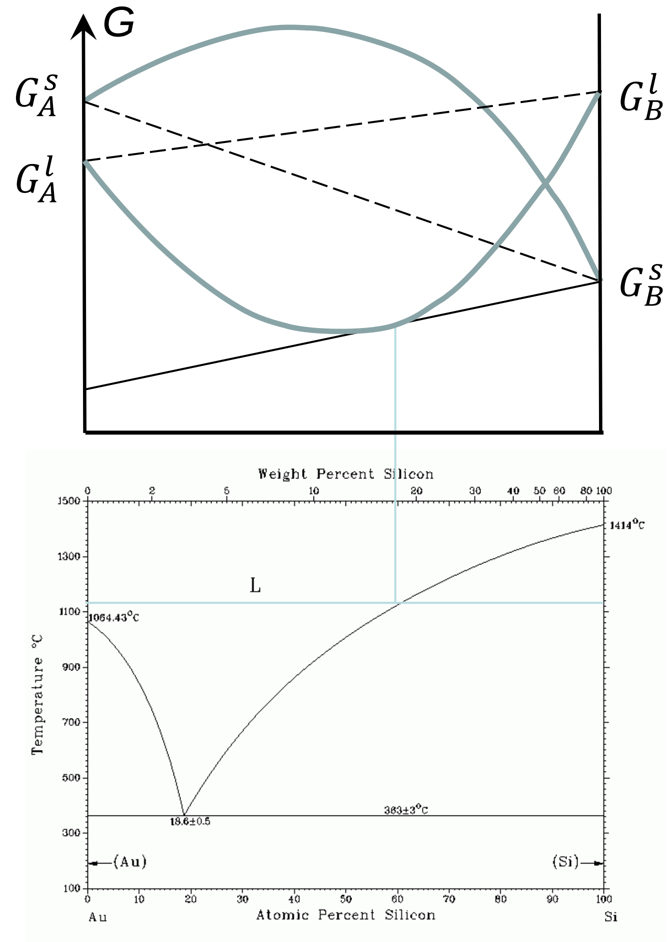




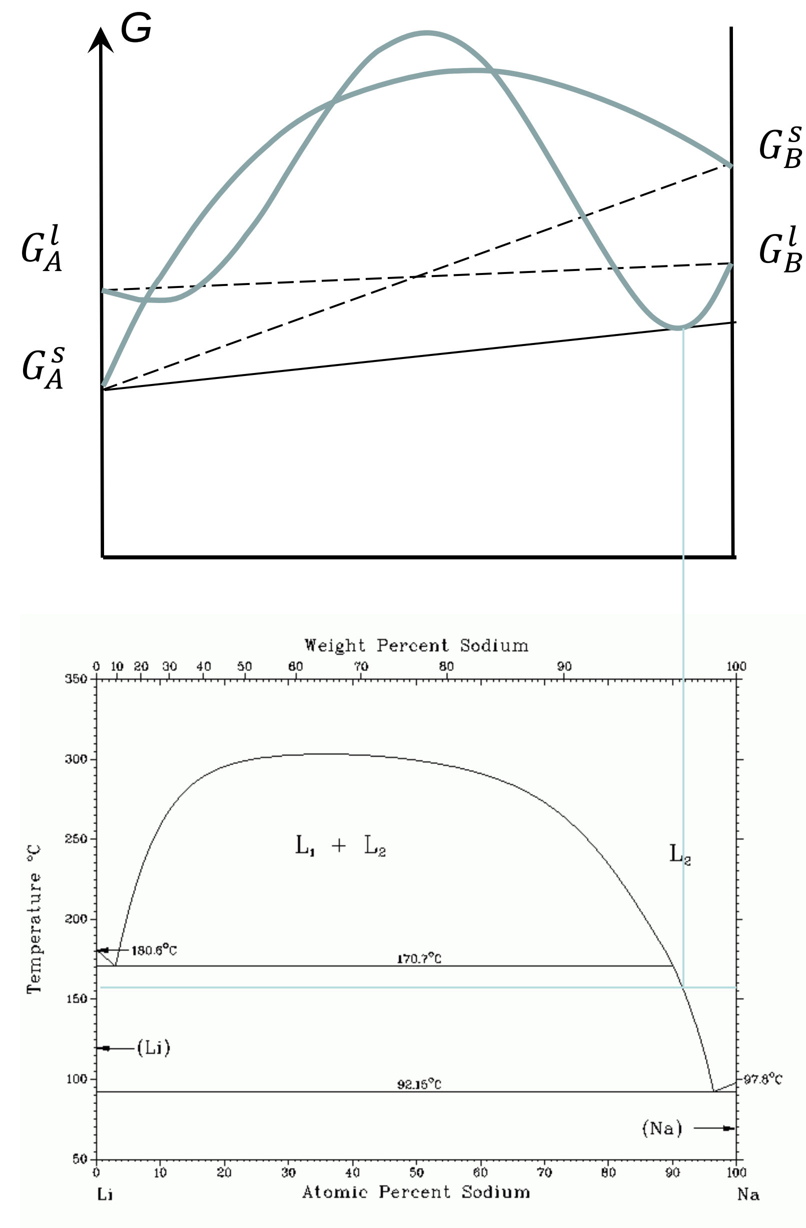




G
G_A^s
G_A^l
G_B^l
G_B^s
3000
2600
2200
1800
1400
1000
Temperature, °C
2823
2571
Liquid
2374
CaO(lime)
MgO (peri)
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
CaO
mole fraction
MgO



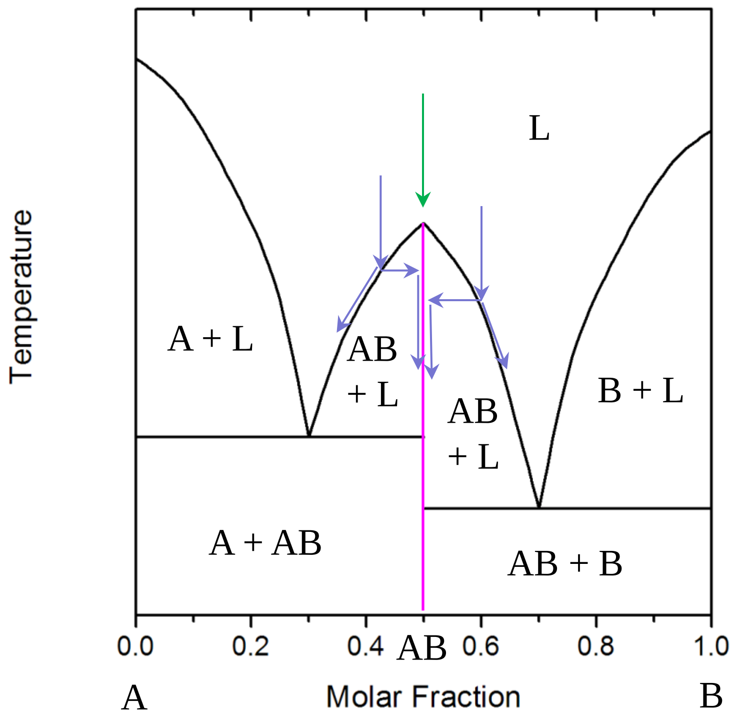
G
G_A^s
G_A^l
G_B^l
G_B^s
Weight Percent Silicon
0 2 5 10 20 30 40 50 60 80 100
1500
1300
1100
900
700
500
300
100
Temperature °C
L
1414°C
1064.43°C
18.6±0.5
363±3°C
(Au)
(Si)
0 10 20 30 40 50 60 70 80 90 100
Au
Atomic Percent Silicon
Si

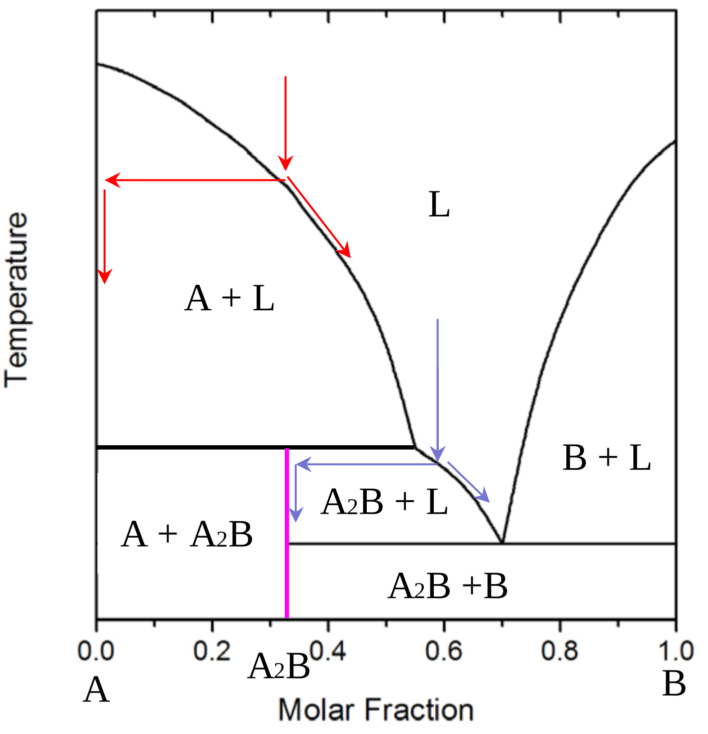


G
G_A^l
G_A^s
G_B^s
G_B^l
Weight Percent Sodium
0 10 20 30 40 50 60 70 80 90 100
350
300
250
200
150
100
50
Temperature °C
$L_1 + L_2$
L_2
180.6°C
170.7°C
(Li)
92.15°C
97.8°C
(Na)
0 10 20 30 40 50 60 70 80 90 100
Li
Atomic Percent Sodium
Na

(4) Congruent and incongruent melting: two approaches of crystal growth

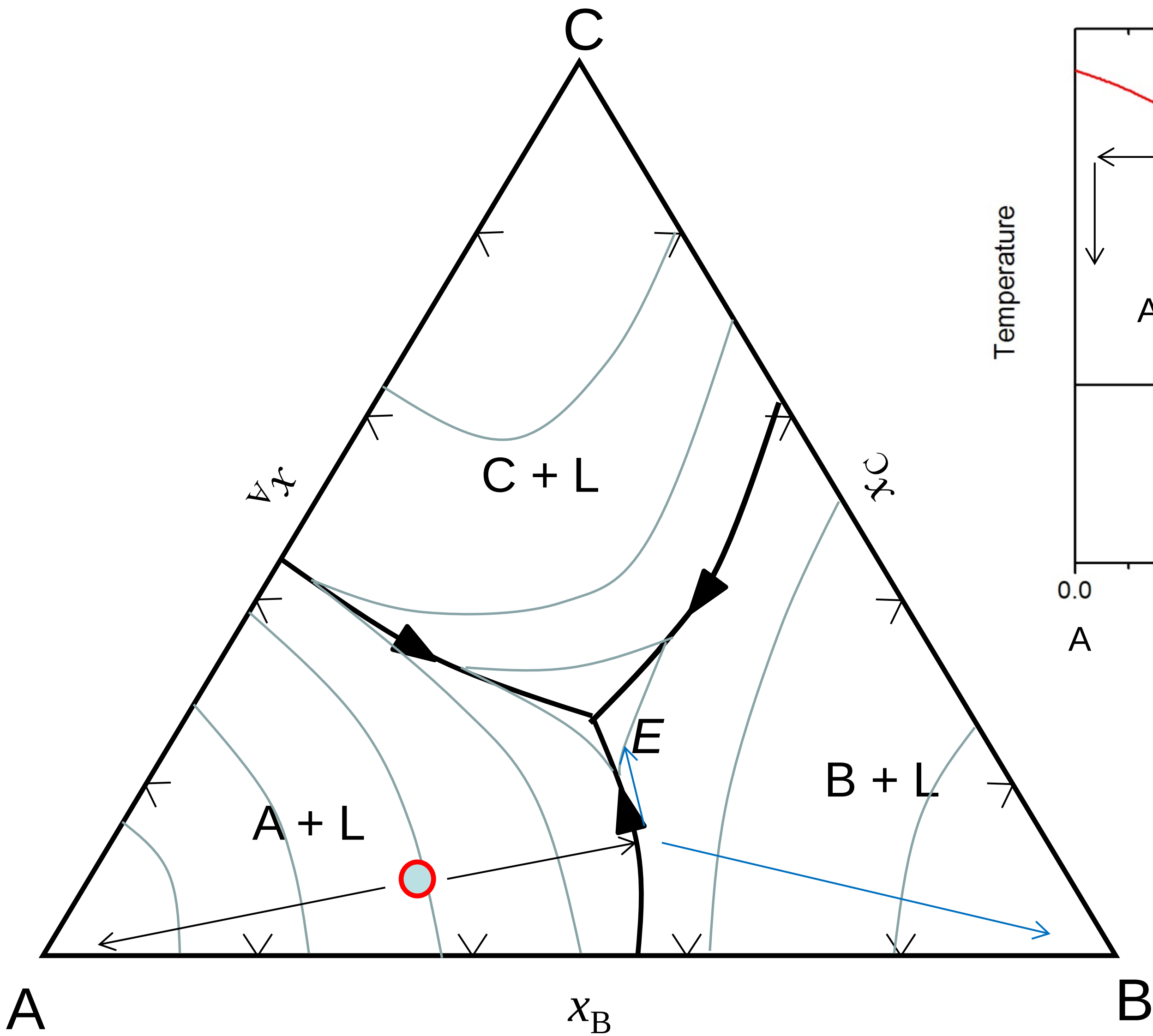
- Congruent melting: A crystalline phase melts into a homogenous liquid phase of the same composition; primary phase region around stoichiometric composition.
- Incongruent melting: A crystalline phase melts into a solid phase (peritectic phase) and a liquid phase of different composition; primary phase region away from stoichiometric composition

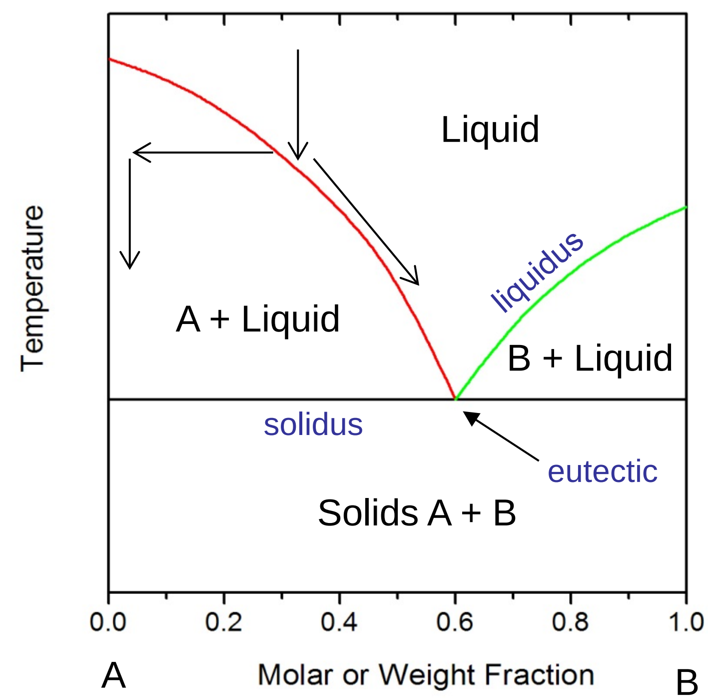


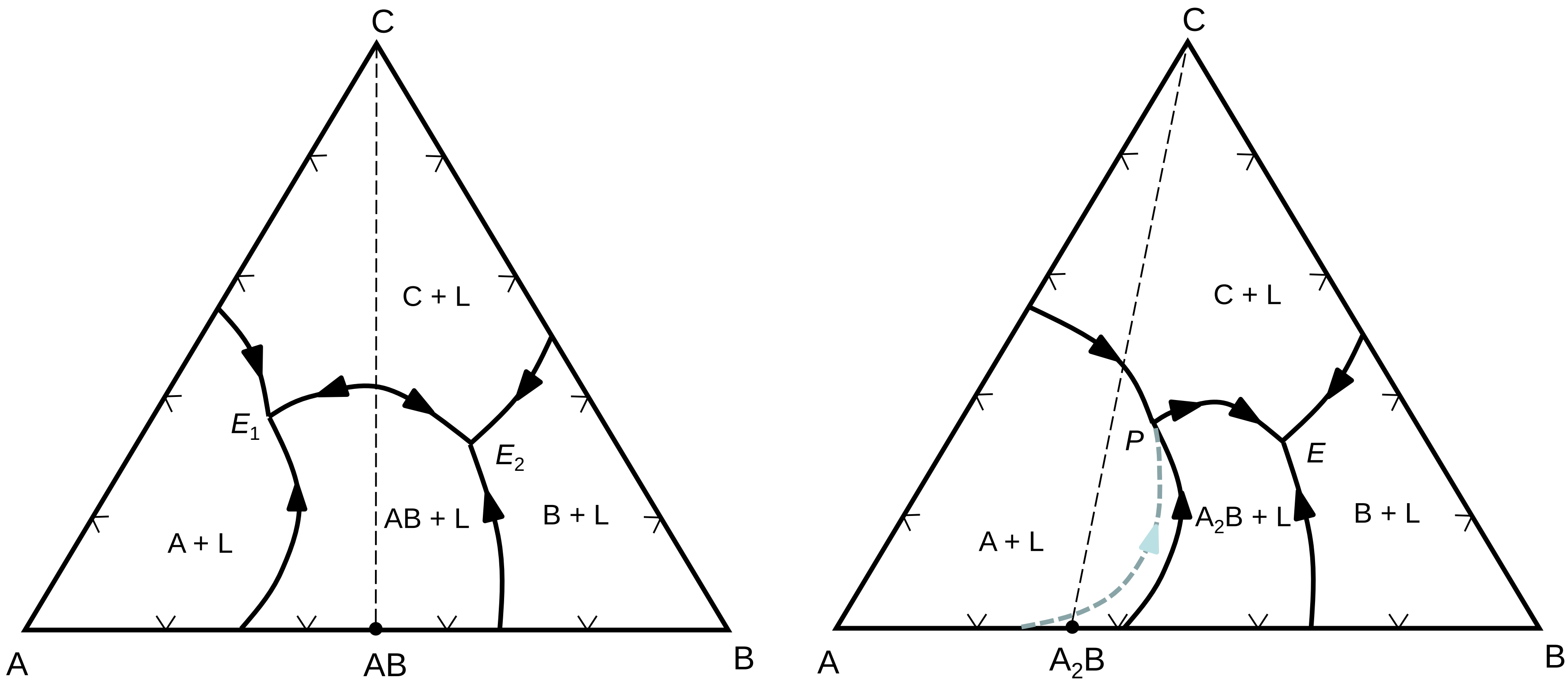


- Growth by cooling the stoichiometric melt: congruent melting substances
- Growth by cooling melt solution (flux)

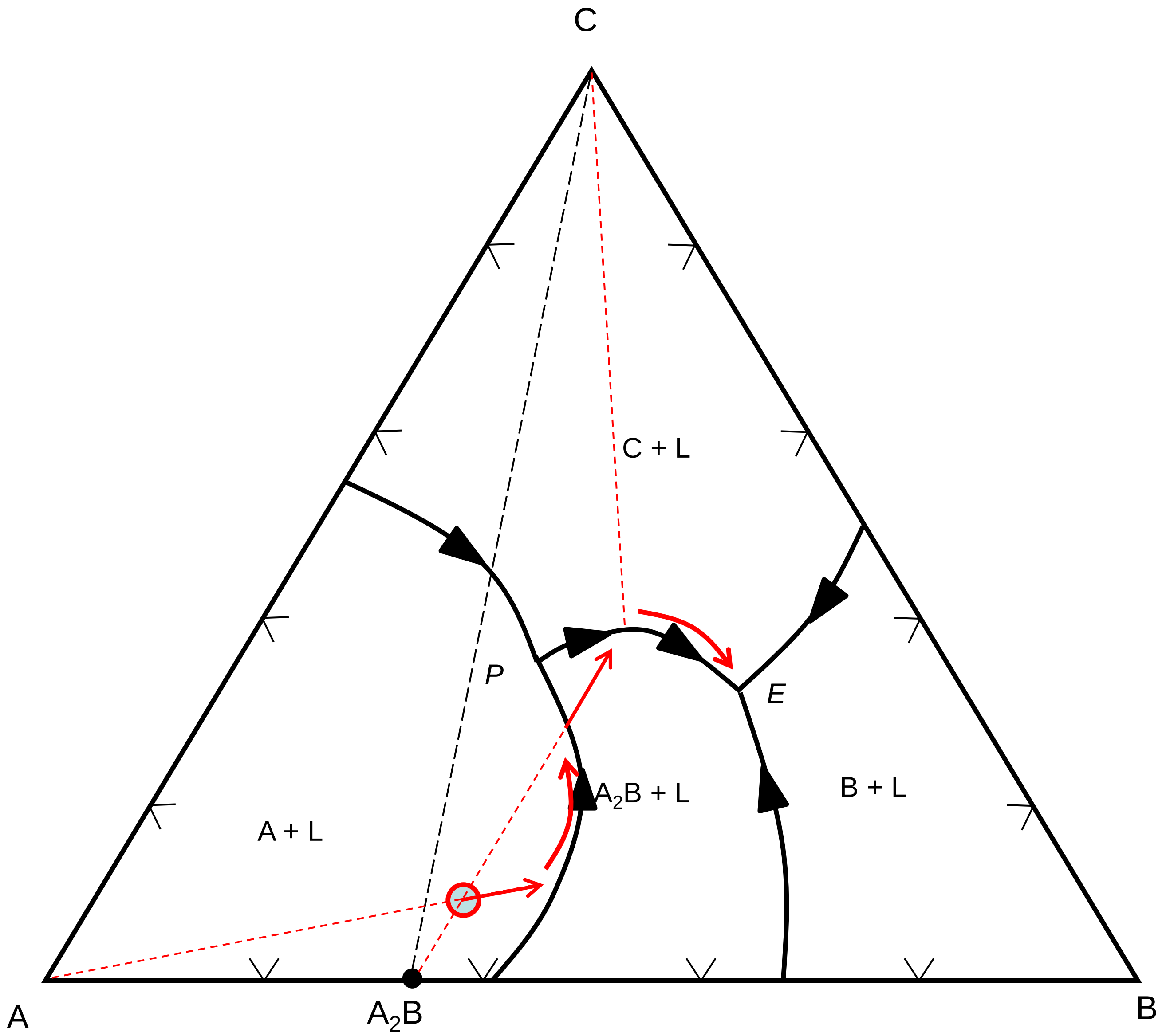
(3) Ternary phase diagrams

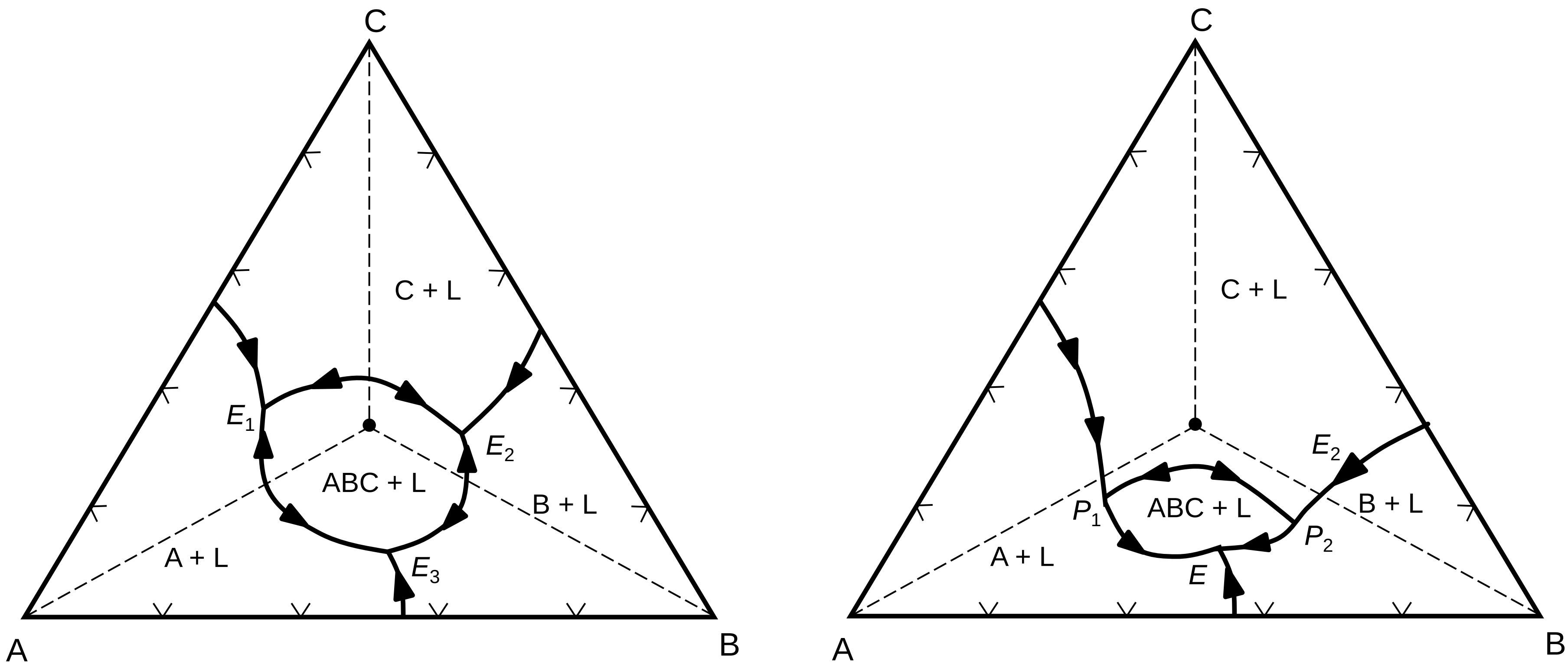






C
C + L
A + L
AB + L
B + L
E_1
E_2
A
AB
B
C
C + L
A + L
A_2B + L
B + L
P
E
A
A_2B
B


C
C + L
P
E
A + L
A_2B + L
B + L
A
A_2B
B


C
C + L
E1
E2
ABC + L
B + L
A + L
E3
A
B
C
C + L
E2
P1
ABC + L
B + L
P2
A + L
E
A
B

(6) Where to find phase diagrams?

Oxides, borides, nitrides, chalcogenides, carbides and salts:

Phase Equilibria Diagrams (book, CD, online, formerly Phase diagrams for Ceramist) by The American Ceramic Society

Alloy and intermetallic compounds

Alloy Phase Diagram Database by ASM International
(many diagrams can be purchased about $20/ea)

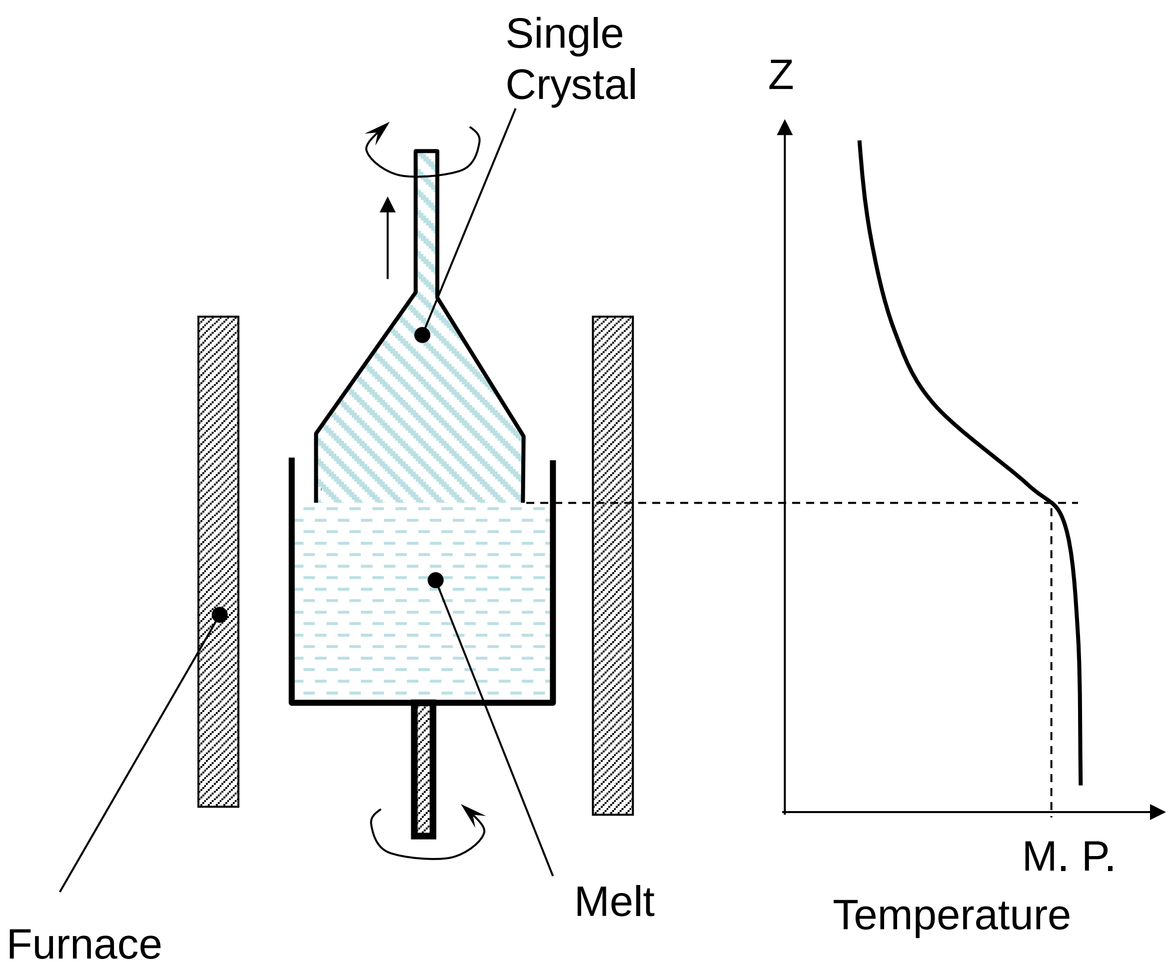
Binary alloy phase diagrams

http://www.himikatus.ru (Russian)

2. Methods of crystal growth from melt

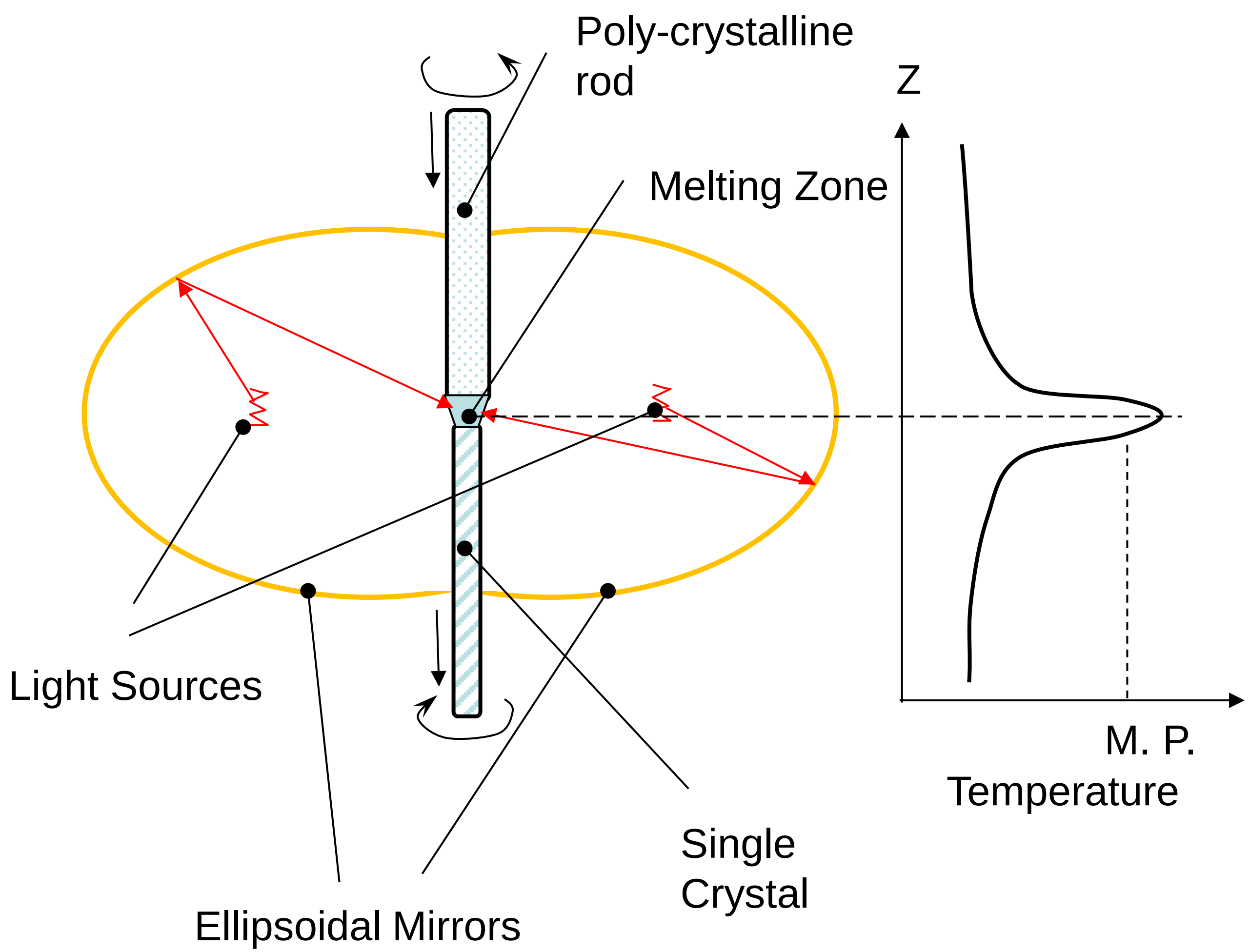
(1) Czochralski Method

- Congruent melting substances
- Stoichiometric melt



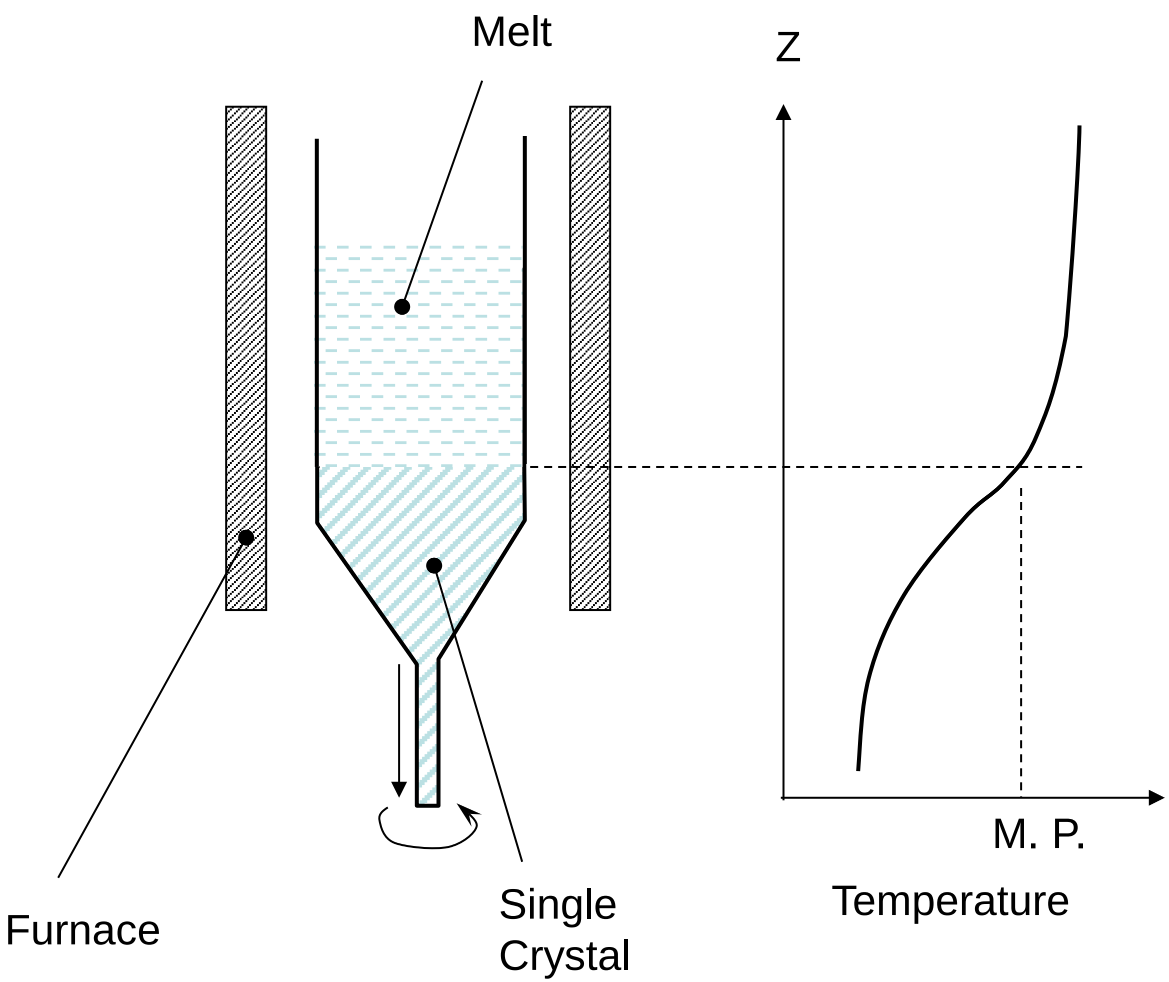
(2) Floating zone method

- Congruent or incongruent melting substances
- Stoichiometric melt or flux (TSFL)



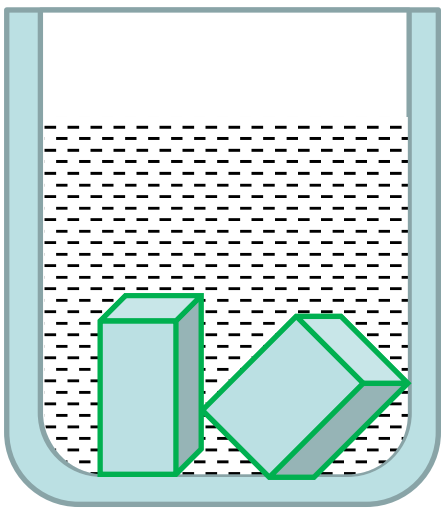
(3) Bridgman method

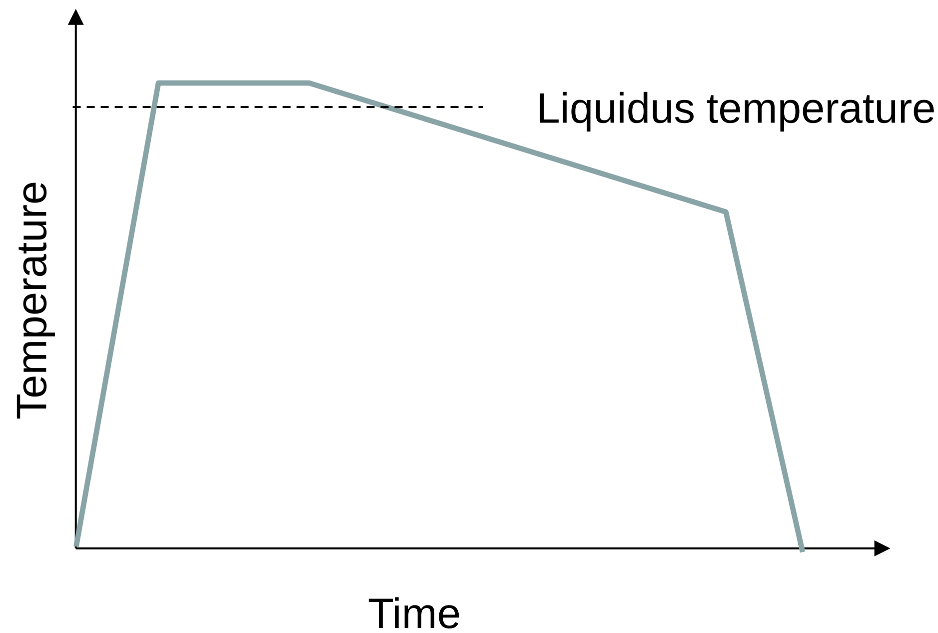
- Congruent melting substances
- Stoichiometric melt



(4) Flux method

- Congruent or incongruent melting substances
- Melt solution (flux)





(5) How to chose the right crystal growth method? (for sample preparation purpose)

1) Properties of the compound
   - ❑ Melting point
   - ❑ Congruent or incongruent melting
   - ❑ Phase diagram
   - ❑ Vapor pressure of the components
   - ❑ Toxicity of the components
2) Priorities: crystal perfection or sizes?
3) Availability of suitable crucible materials
4) Usage of the crystals: widely used or not?

(6) Crucible materials

Metal and semi-metal melts: High melting point oxide/nitride crucibles

- ❑ Quartz glass (up to 1500℃)
  - Unsuitable for melts of alkali and alkali earth metals
- ❑ Alumina
- ❑ Calcia or yittria-stabilized zirconia
- ❑ Boron nitride, silicon nitride

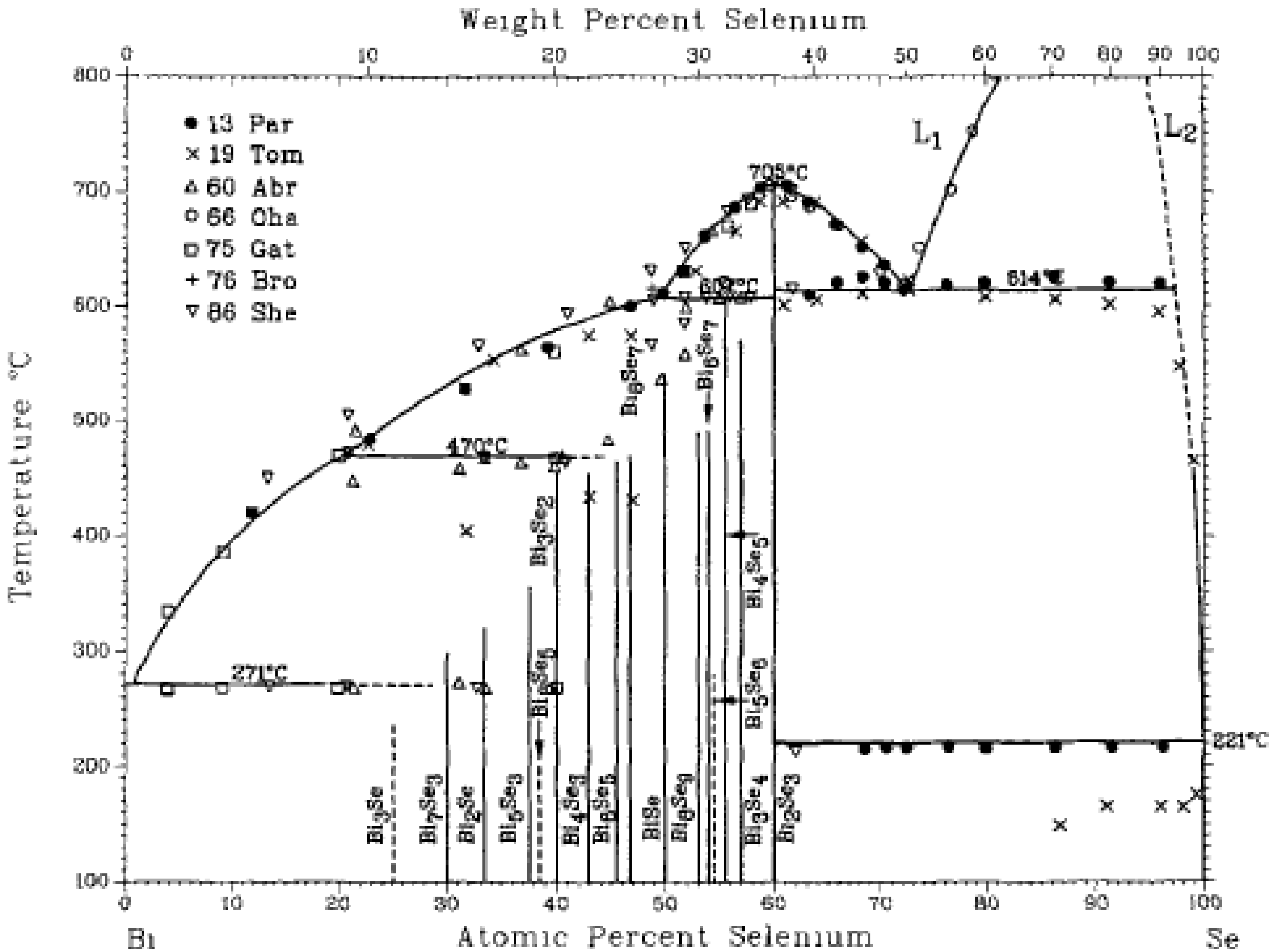
Oxide melts: metal crucibles

- ❑ Inert metals (Au, Pt)
- ❑ High melting point metals, such as Ir, W, Mo and Nb (inert atmosphere)

3. Examples of single crystal growth

(1) Bi_2Se_3

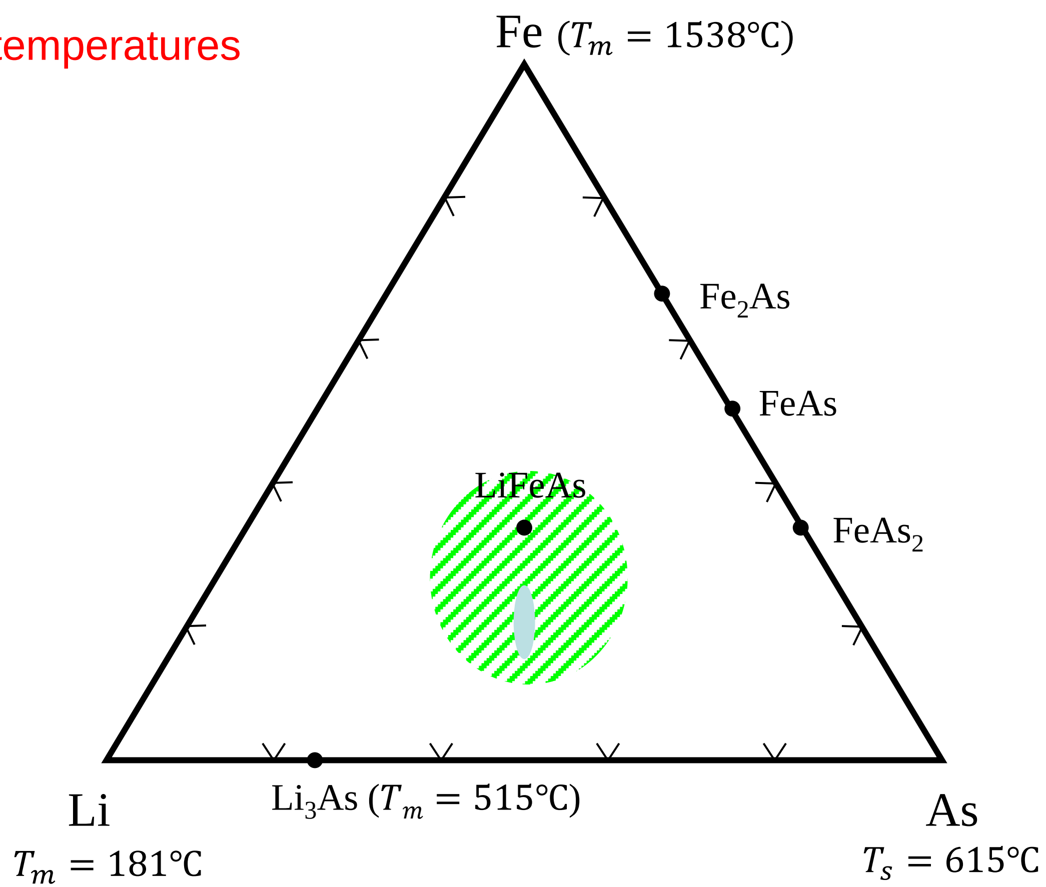
- Detailed Bi – Se phase diagram available
- Growth conditions are refined to obtain best crystals



H. Okamoto, J. Phase Eq. 15, 195 (1994)

(2) LiFeAs

- ❑ Congruent melting under Li vapor pressure, $T_m \cong 1400°C$
- ❑ Li and As volatile at elevated temperatures
- ❑ As poisonous
- ❑ Li reacts with quartz glass

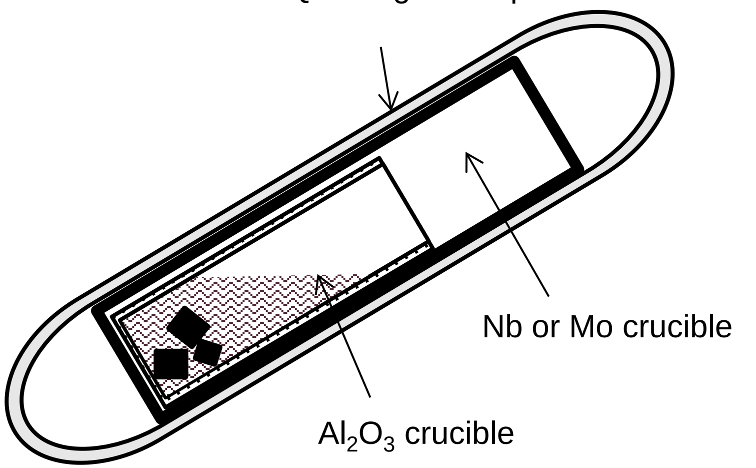


LiFeAs crystal growth: growth techniques

Bridgman technique (1):
- BN crucible, Li excess, sealed in tungsten tube
- Growth temperature 1500℃

Sn flux growth (2):
- Growth temperature below 850℃
- Sn substitution in Fe site

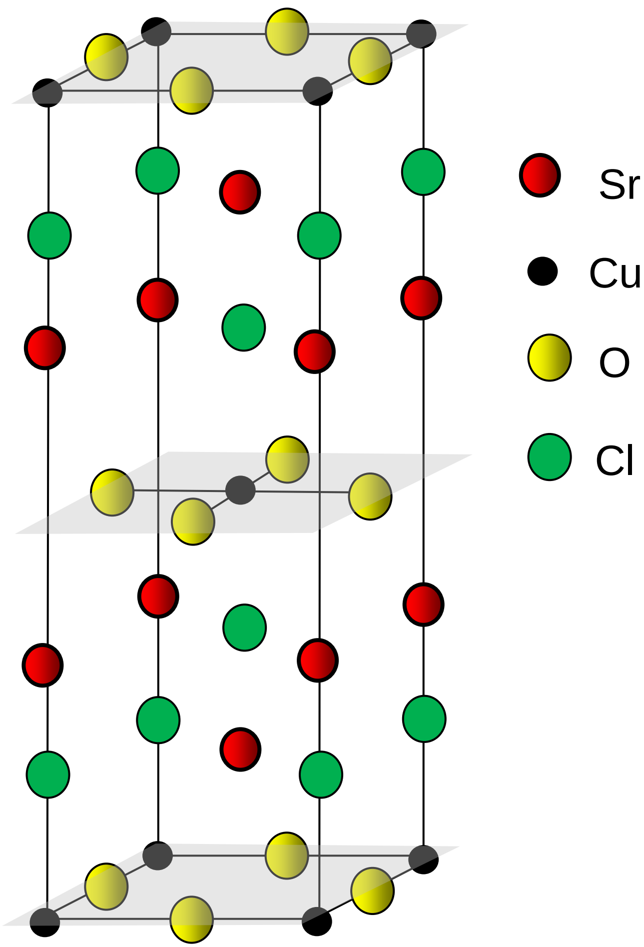
Self flux growth (3):
- Li-As flux
- Growth temperature below 1100℃

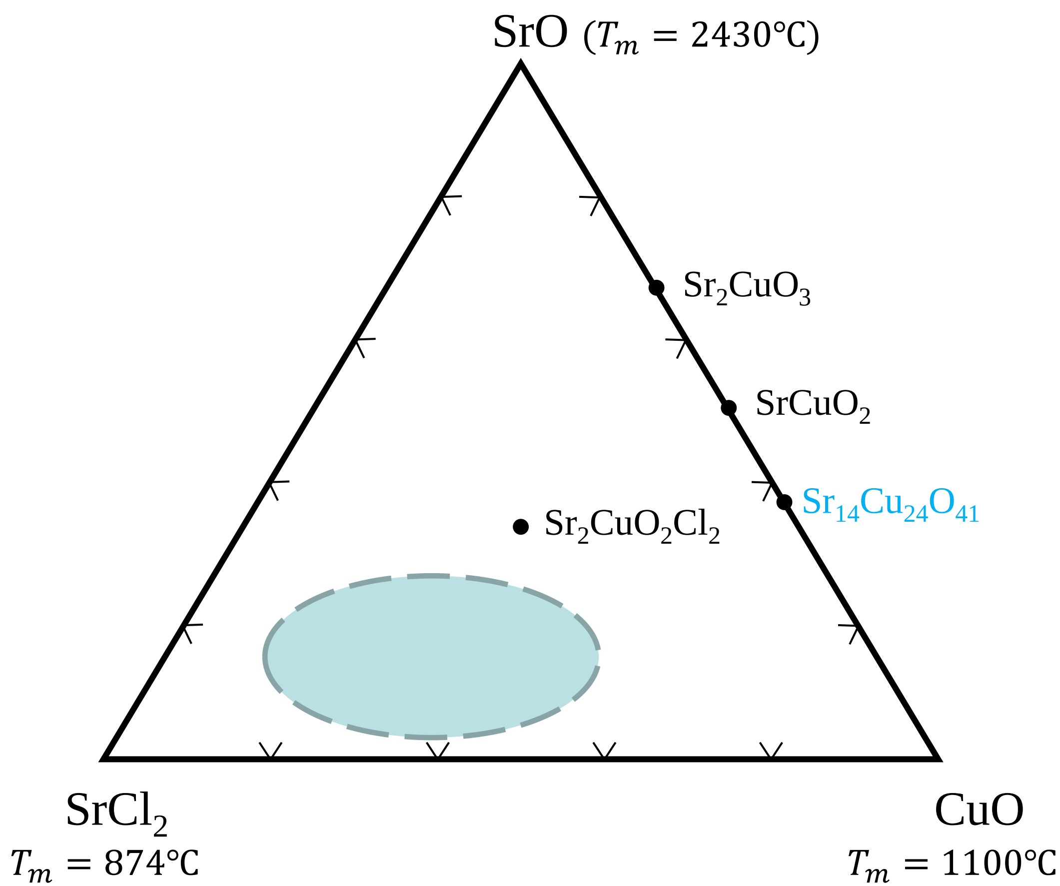


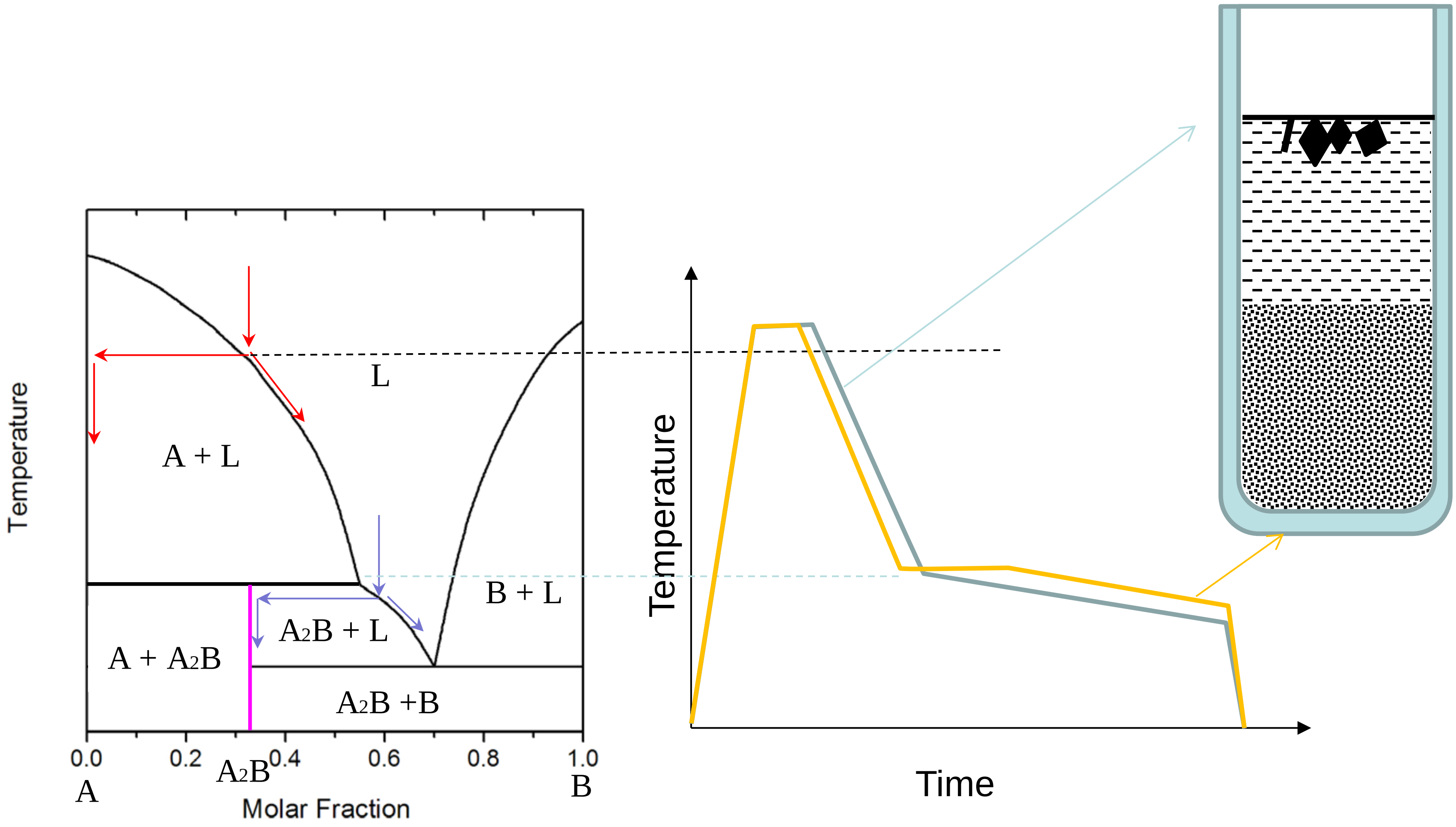
Song et al, Appl. Phys. Lett. 96, 212508 (2010)
Lee et al, Appl. Phys. Lett. 91, 27002 (2010)
Morozov et al, Cryst. Growth Des. 10, 4428 (2010)

(3) $Sr_2CuO_2Cl_2$

- Incongruent melting, $T_p \cong 990°C$
- Phase diagram unknown

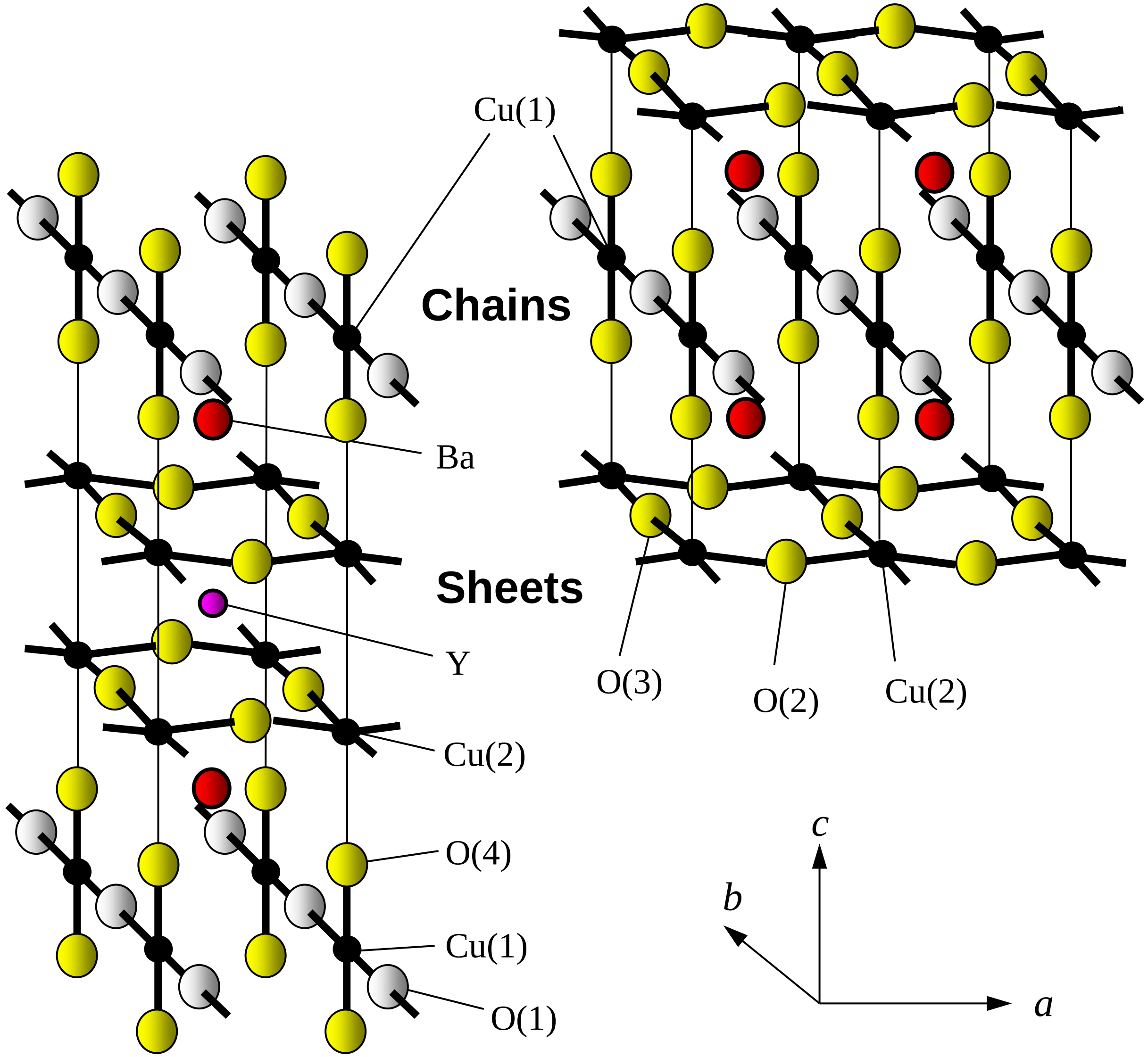




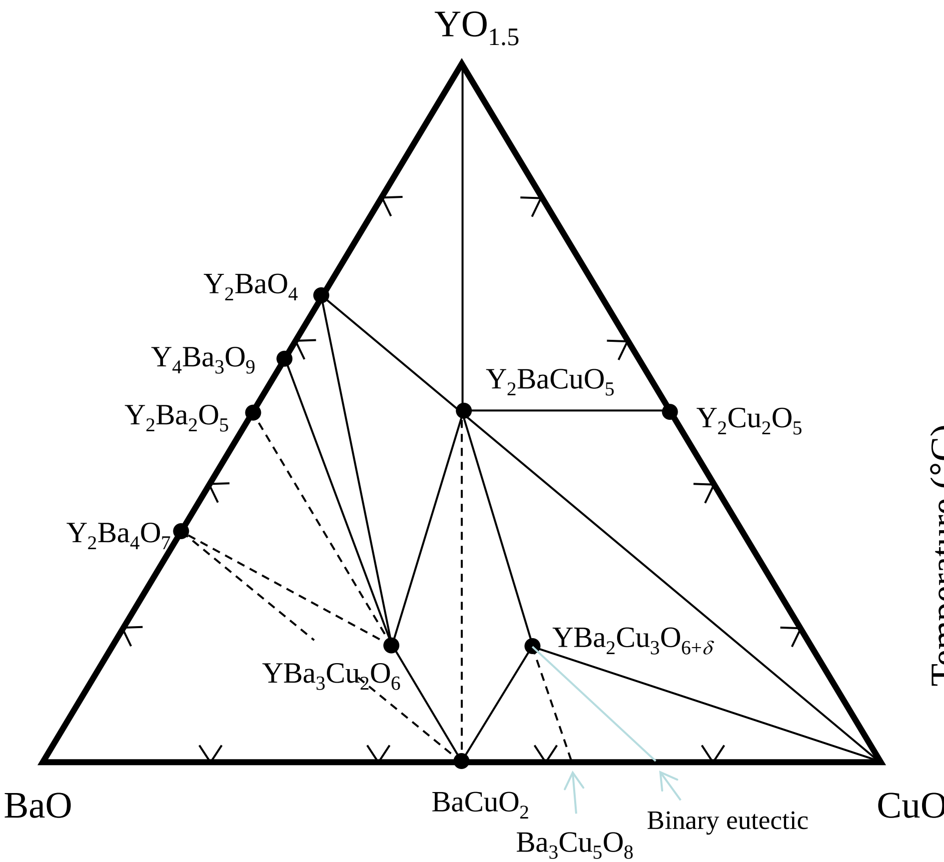


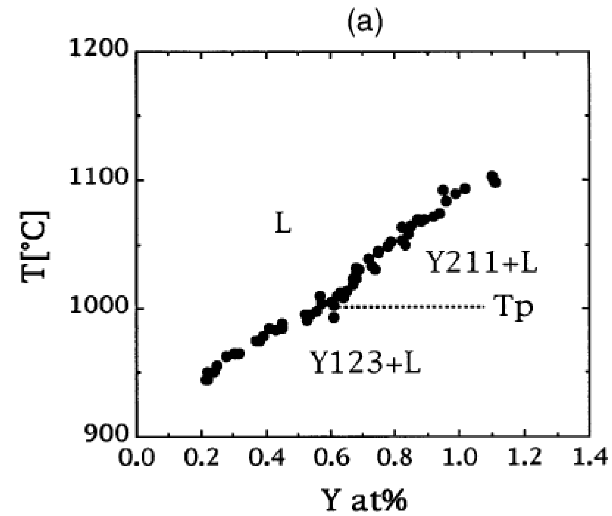
Temperature
L
A + L
B + L
A2B + L
A + A2B
A2B +B
0.0
0.2
0.4
0.6
0.8
1.0
A
A2B
B
Molar Fraction
Temperature
Time

(4) $YBa_2Cu_3O_{6+x}$ (YBCO)

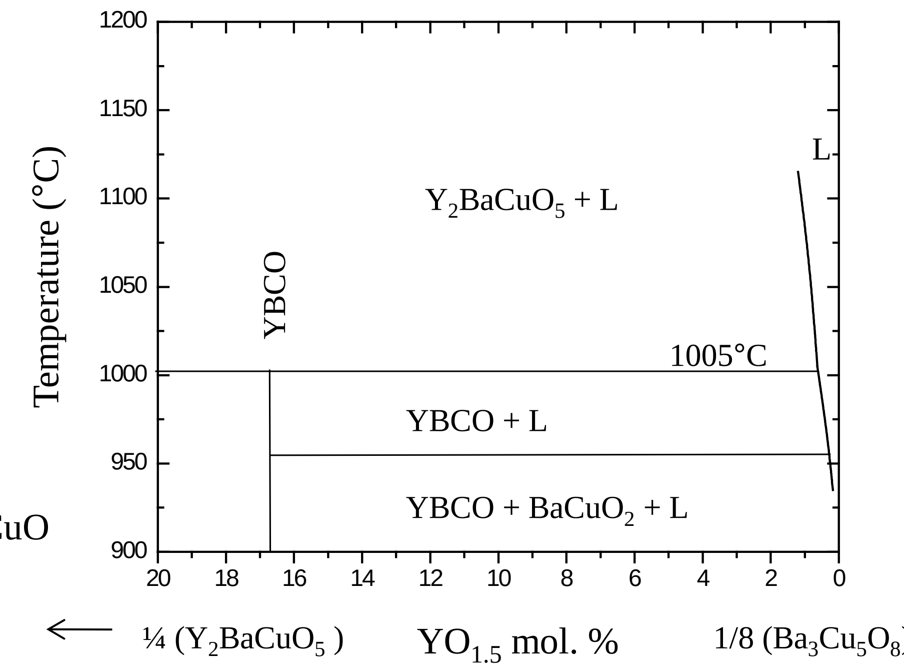


- Incongruent melting, $T_p \cong 1005$°C
- Peritectic phase: Y_2BaCuO_5





M. Nakamura et al, J. Mater. Res. **11**, 1076 (1996)



YBCO crystal growth: Choice of growth technique

- ❑ Low solubility in BaO-CuO melt
- ❑ Narrow growth temperature range

TSFL technique:

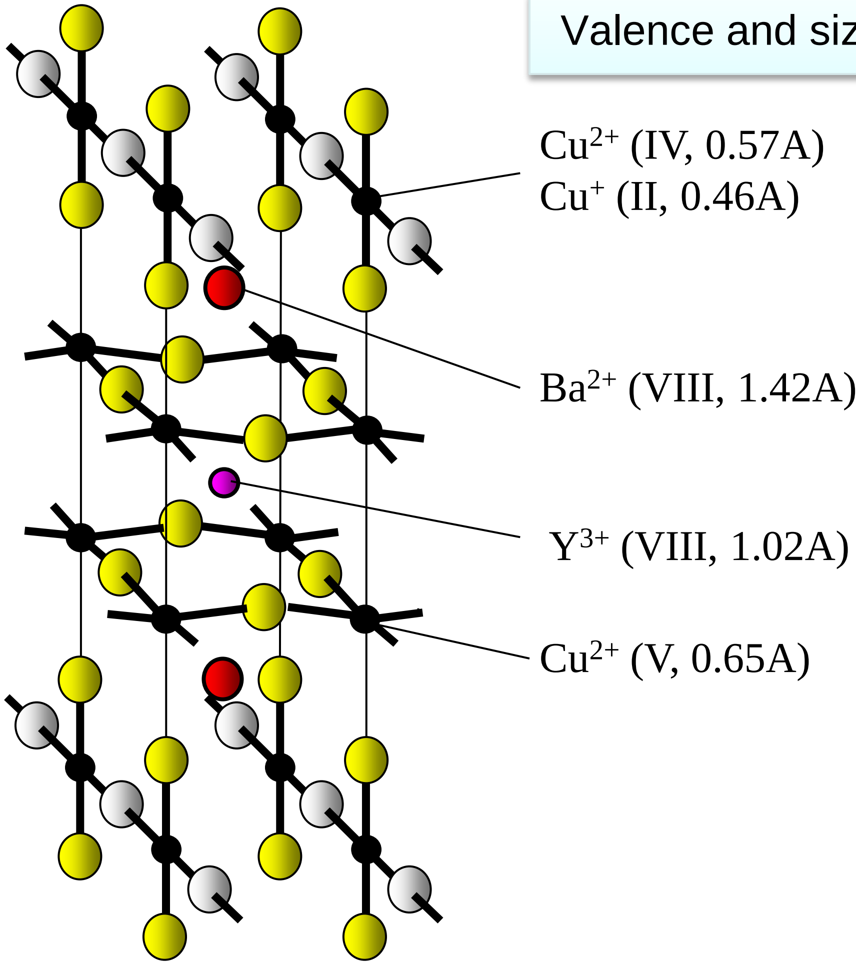
- ❑ Difficult to precisely control the melt temperature
- ❑ Crystals with peritectic phase inclusion

Self-flux growth technique:

- ❑ Need to find a suitable crucible material

- ❑ Growth in oxidizing atmosphere, non-inert metals unusable.
- ❑ Growth temperature close to melting point of gold – gold slightly miscible in YBCO lattice.
- ❑ BaO-CuO-Y_2O_3 melt reacts with platinum and forms $Y_2Ba_2CuPtO_8$ and $Ba_4CuPt_2O_9$.
- ❑ BaO-CuO-Y_2O_3 melt reacts to boron nitride and silicon nitride.

Crucible material: find an oxide immiscible in YBCO



Valence and size of cations:

Mg^{2+} (IV, 0.57A; V, 0.66)

Al^{3+} (IV, 0.39A; V, 0.49A; VI, 0.54A)

Ti^{4+} (VI, 0.61A)
Sn^{4+} (VI, 0.69A)
Zr^{4+} (VI, 0.72A)
Th^{4+} (VI, 0.94A, VIII, 1.05A)

Melting point:

TiO_2 1843℃
SnO_2 1630℃
ZrO_2 2715℃

$$ZrO_2 + BaO = BaZrO_3$$

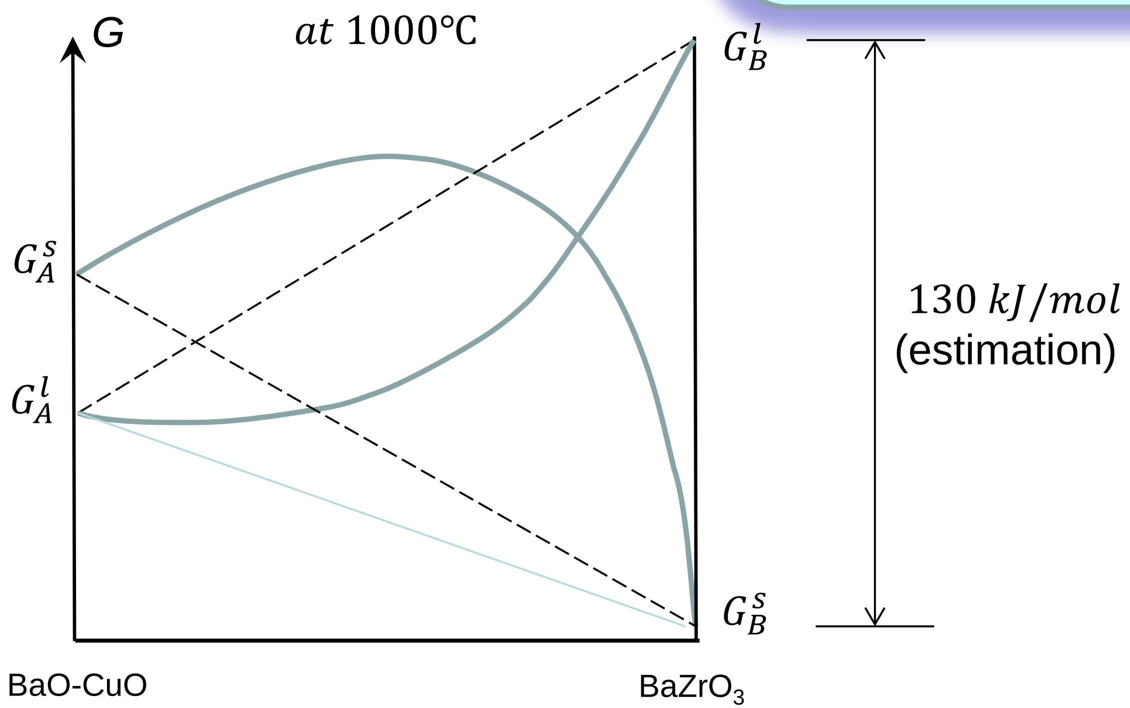
$$\Delta H^\circ = -128\ kJ/mol$$

$$\Delta S^\circ = 1.8\ J/mol$$

- Cubic ABO_3 perovskite structure

  Tolerance factor $t = \dfrac{R_A + R_O}{\sqrt{2}(R_B + R_O)} = 1.01$

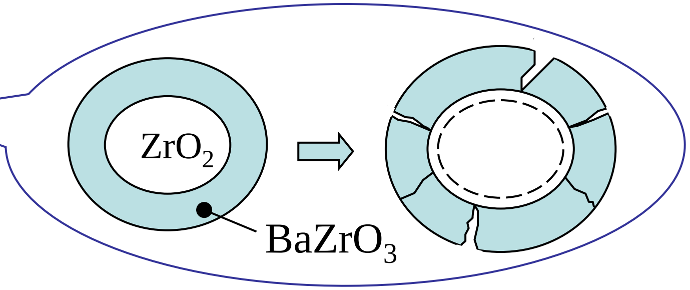
- Melting Point >2700°C
- $\Delta H_m \cong 240\ kJ/mol$ (estimation)



Preparation of $BaZrO_3$ powder: $BaCO_3 + ZrO_2 = BaZrO_3 + CO_2$

Starting materials: $BaCO_3$ (99.995%), ZrO_2 (99.99%)

Mixing ZrO_2 and $BaCO_3$ in 1:0.5 molar ratio



Calcination at 1200 °C for 12 h

Add $BaCO_3$ to Zr:Ba = 1:1

Repeated calcination at 1200 °C for 12 h

Confirm completion of reaction by monitoring weight loss (CO_2 ↑)

Ball mill in ethanol with PVA
Yttria-partially-stabilized ZrO_2 balls

$BaZrO_3$ Powder
<1μm particle size

Preparation of $BaZrO_3$ crucibles

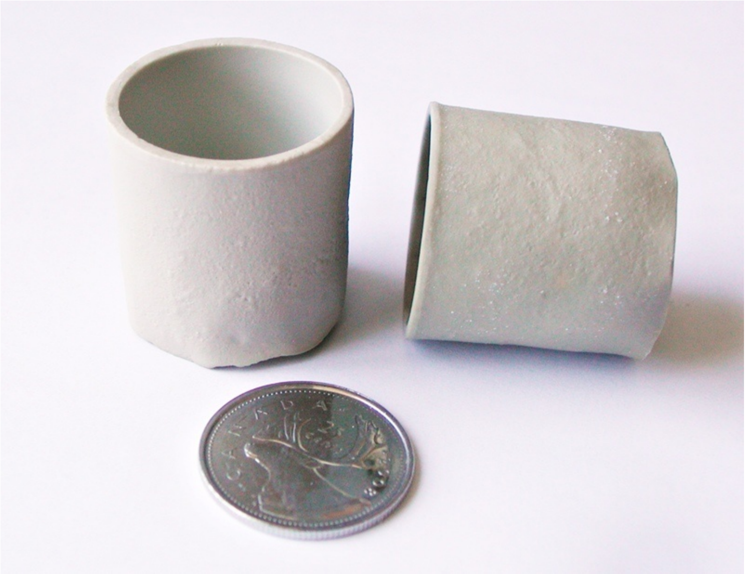
$BaZrO_3$ Powder
<1μm particle size

↓

Pressing into crucible at 2500 atm hydrostatic pressure

↓

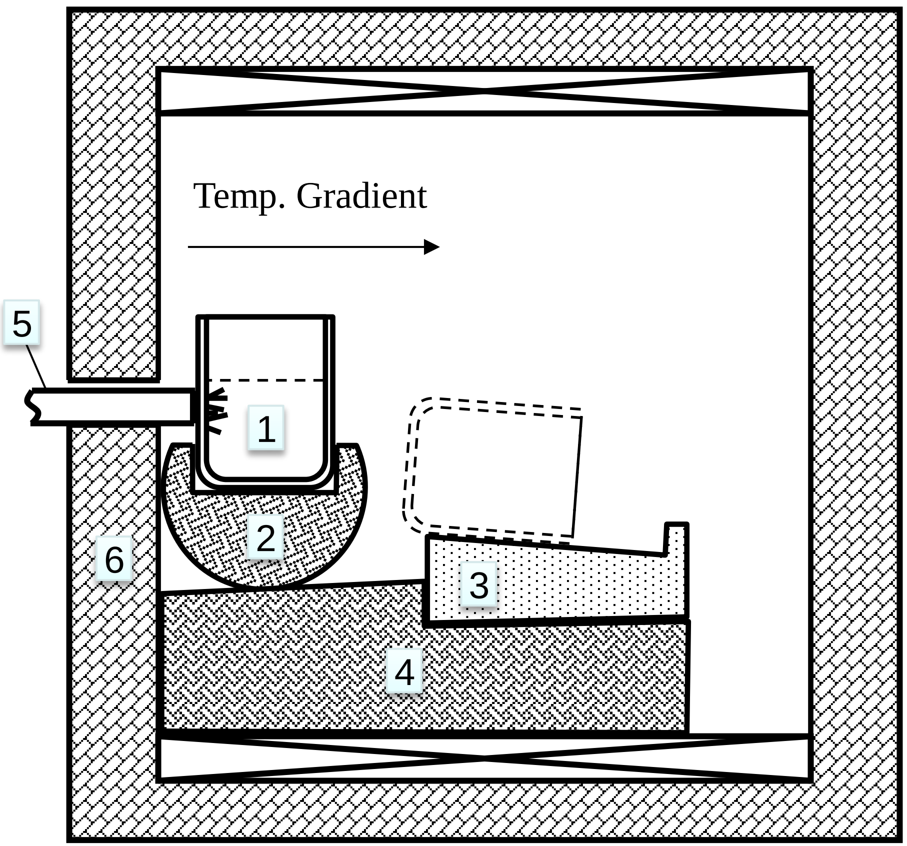
Sintering
at 1680 °C for 48 h

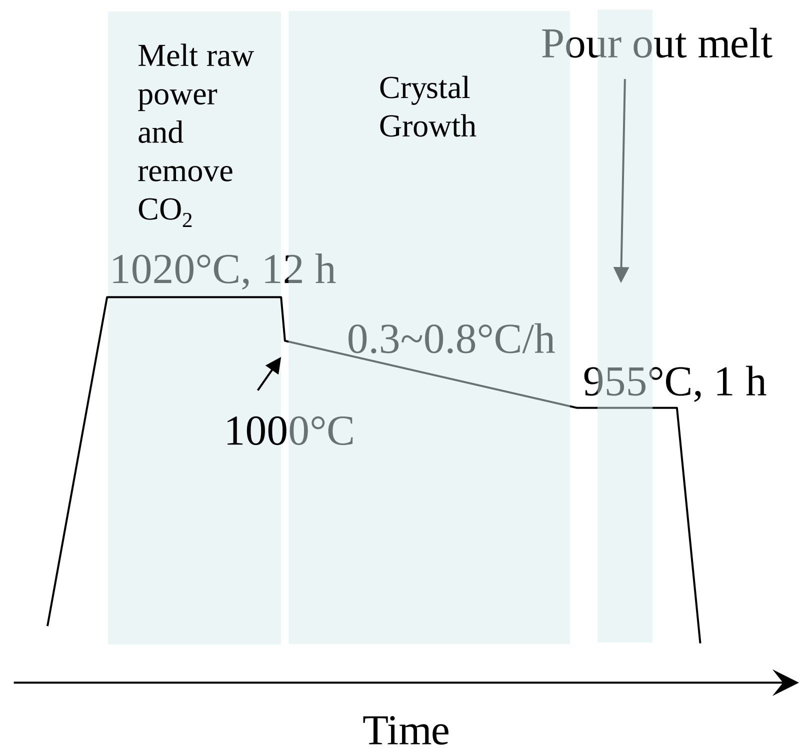


$BaZrO_3$ ceramic crucibles:

- 95 to 97% of theoretical density
- Grain size 1 to 4 μm

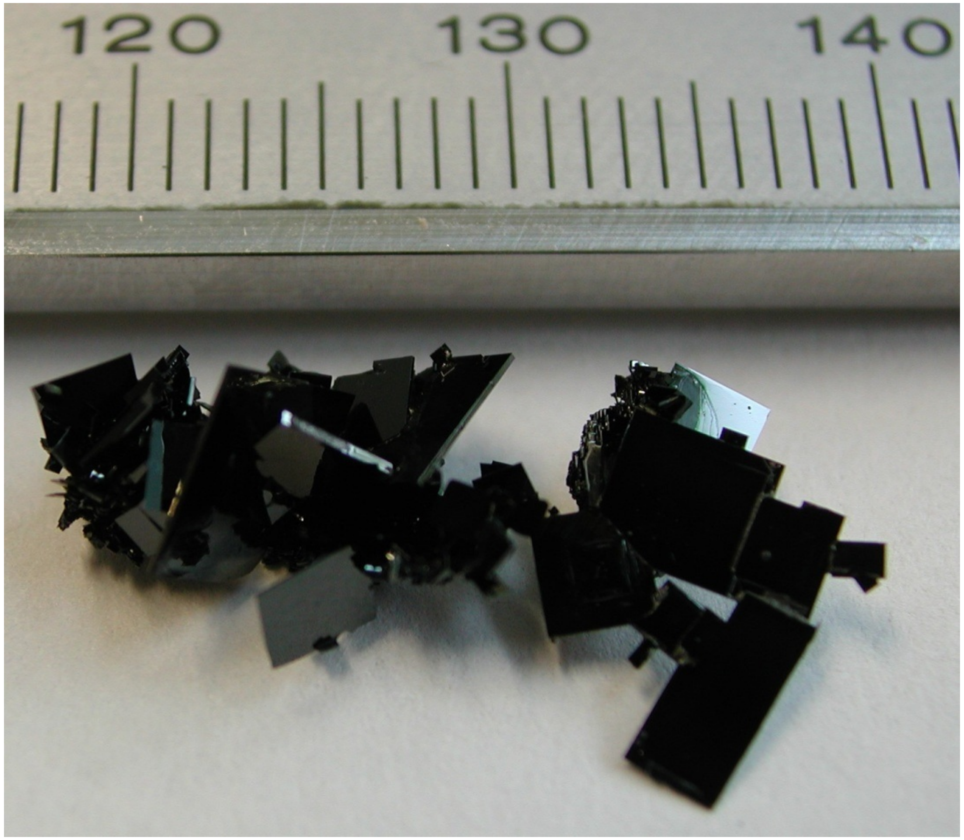
YBCO crystal growth





1. BaZrO3 crucible; 2. Ceramic roll; 3. Porous ceramic;
4. Ceramic support; 5. Quartz glass rod; 6. Furnace

YBCO single crystals



YBCO single crystals: post growth

(1) Slow cooling after growth

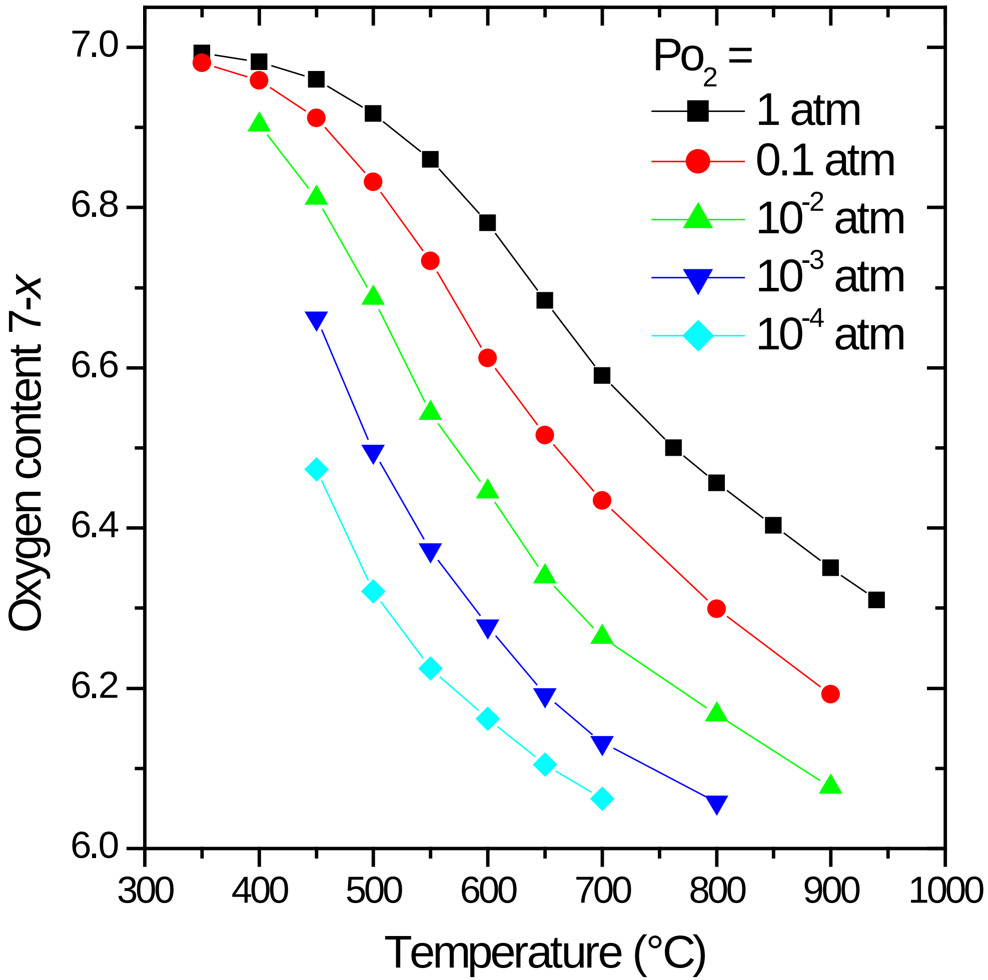
- YBCO absorbs oxygen and undergoes the tetragonal to orthorhombic phase transition.
- Fast cooling generates cracks in the crystals.

(2) Annealing at temperatures slightly below the growth temperature.

- To release stress in the crystals.

(3) Setting of oxide content to various desired values.

(4) Removing twins



Oxygen nonstoichiometry in YBCO

YBCO chain oxygen ordering phase diagram

M. von Zimmermann (HASYLAB, Germany) et al. PRB 68, 104515 (2003)