How to use a binary phase diagram to grow crystals of (i) a congruently and (ii) an incongruently melting materials?
Why single crystals?

• In a crystal, the constituent atoms are arranged in an orderly repeating pattern extending in all three spatial dimensions.

❖ Single crystals are crucial for plethora of different motives e.g.

• Structure determination

• Intrinsic property measurements (are preferably, sometimes exclusively, carried out on single crystals)

• For certain applications, most notably those which rely on optical and/or electronic properties (laser crystals, semiconductors, etc.)
Issues with some techniques:
1. Some of the processes need transport agents or a substrate or seed
2. Crystals formed can be really small
3. Side reaction with crucible because of really high temperature requirement > 2000 °C

Advantages of solution growth method:
- Grow congruently and incongruently melting materials
- Has short growth-time scales

Gibbs Phase Rule: \( F = C - P + 2 \)

\( F \) = # degrees of freedom (independent \textit{intensive variables}) among \( T, p, \) composition.
Composition given as mole fractions, \( x_i^{(\nu)} (i = 1, \ldots, C), (\nu = 1, \ldots, P) \)

\( P \) = # phases present at equilibrium; are physically distinct, separable (in principle)
A phase is uniform throughout, in both chemical composition and physical state.

H\(_2\)O\((s)\) vs. H\(_2\)O\((l)\), MgSiO\(_3\)(\(s\)) vs. Mg\(_2\)SiO\(_4\)(\(s\)), \(\alpha\)-Fe\((s)\) vs. \(\gamma\)-Fe\((s)\).
A \textit{homogeneous mixture} is a single phase: N\(_2\)(\(g\)) and O\(_2\)(\(g\)), NaCl\((aq)\)
A \textit{solid solution} is single phase: \(\alpha\)-Al\(_2\)O\(_3\) / Cr\(_2\)O\(_3\) = Al\(_{2-x}\)Cr\(_x\)O\(_3\) or (Al\(_{1-x}\)Cr\(_x\))\(_2\)O\(_3\)

\( C \) = # constituents that can undergo \textit{independent} variation in different phases;
minimum number of constituents needed to completely describe the composition of the system
A and B form a **homogeneous** mixture in the **liquid phase**; At constant $p$, $F = 3 - P$

A and B form a **heterogeneous** mixture in the **solid phase**;

1. Heat 50:50 A:B mixture into **Liquid** region...
2. On cooling, B(s) precipitates when $T = T_1$ (liquidus curve)...
3. More cooling, B(s) forms, **Liquid** follows liquidus curve (gets richer in A)
4. Further cooling gives mixture of A(s) and B(s).
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.

AB is a compound in each phase diagram:

**Congruent Melting:**
\[ AB(s) \xrightarrow{T_1} AB(l) \]

**Eutectic Points:**
\[
\begin{align*}
A_{0.30}B_{0.20} & \quad \xrightarrow{T_1} 0.60 A(s) + 0.20 AB(s) \\
A_{0.22}B_{0.78} & \quad \xrightarrow{T_3} 0.22 AB(s) + 0.56 B(s)
\end{align*}
\]

**Incongruent Melting:**
\[ AB(s) \xrightarrow{T_3} 0.53 A(s) + 1.47 A_{0.32}B_{0.68}(l) \]

**Eutectic Points:**
\[
\begin{align*}
A_{0.22}B_{0.78} & \quad \xrightarrow{T_4} 0.22 AB(s) + 0.56 B(s)
\end{align*}
\]
- Growth by cooling the stoichiometric melt: congruent melting substances
- Growth by cooling melt solution (flux)
The lever rule

From William’s lecture of PHYS 590B
Describe how you would prepare crystals of Al$_2$Gd if you only had access to a furnace that could achieve 1200°C as its highest temperature?

The temperature is too high to use a silica container. At high temperatures, Al reacts with alumina to give oxide side product, which will affect the Al composition in the product.

Answer: Take a 52% Gd and 48% Al mixture, heat to 1200°C in Ta, then slow cool to 1100°C as GdAl$_2$ solidifies.
Thank You