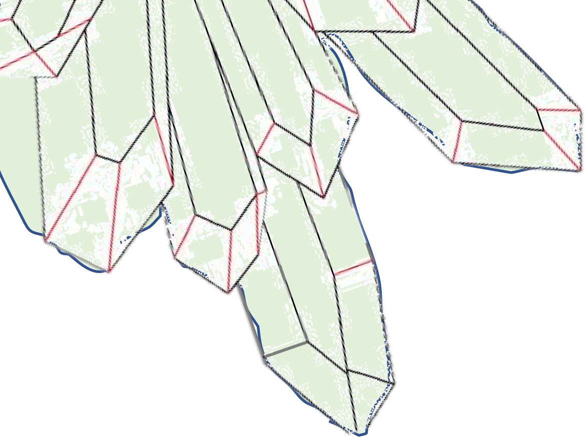
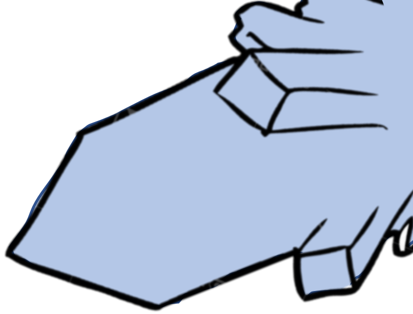


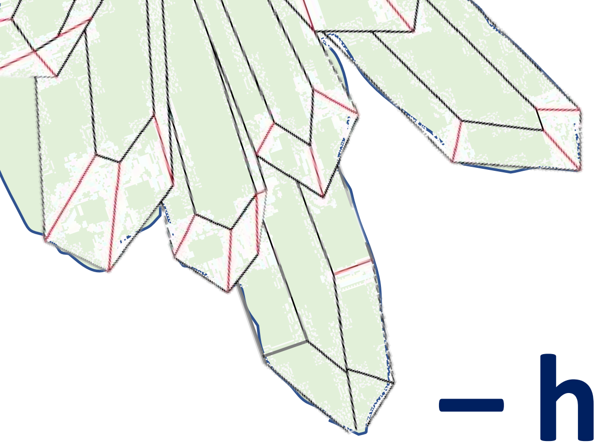


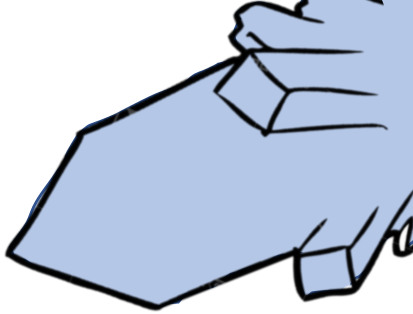
Czech-Bavarian Mini-School 2020

on Large Scale Facilities and Open Data

Sample (Crystal) Growth

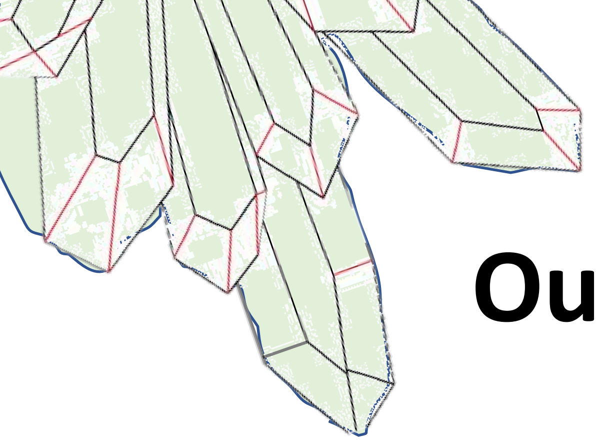
Dr. Ross Colman



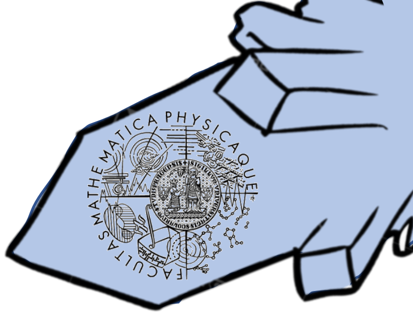


Crystal Growth
– has been around for a while

Buddhist scripture from mid 5th C BC describe crystallisation of sea salt



Outline



1. Motivation for Growing Single Crystals

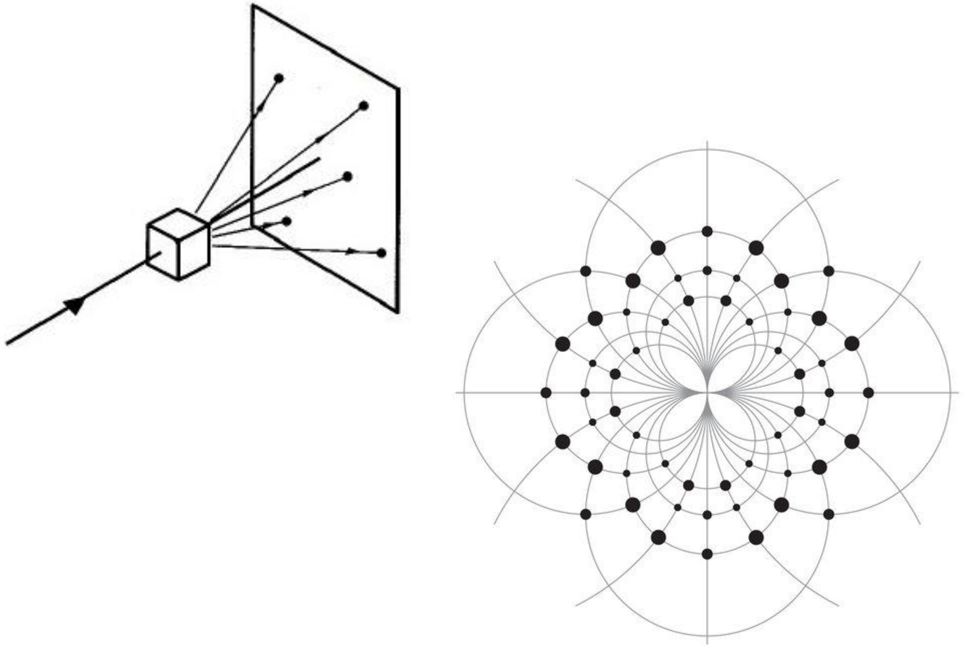
2. Getting Atoms Moving

3. Practical Growth Methods

Motivation for Growing Single Crystals

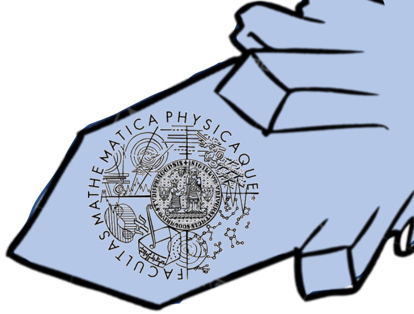
Structure Solution

Single Crystal



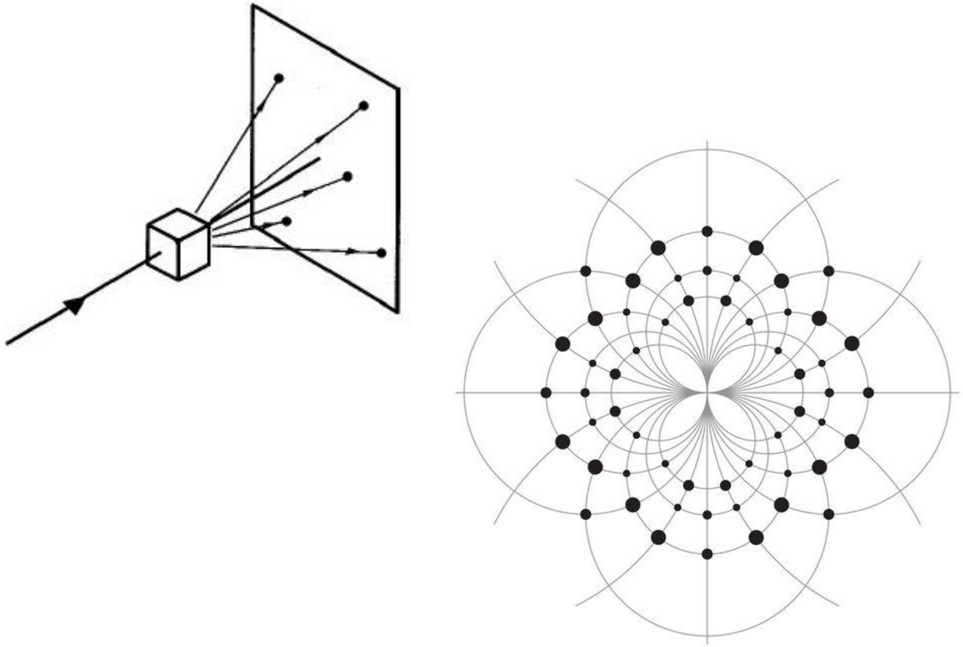
Polycrystalline (powder)

Motivation for Growing Single Crystals

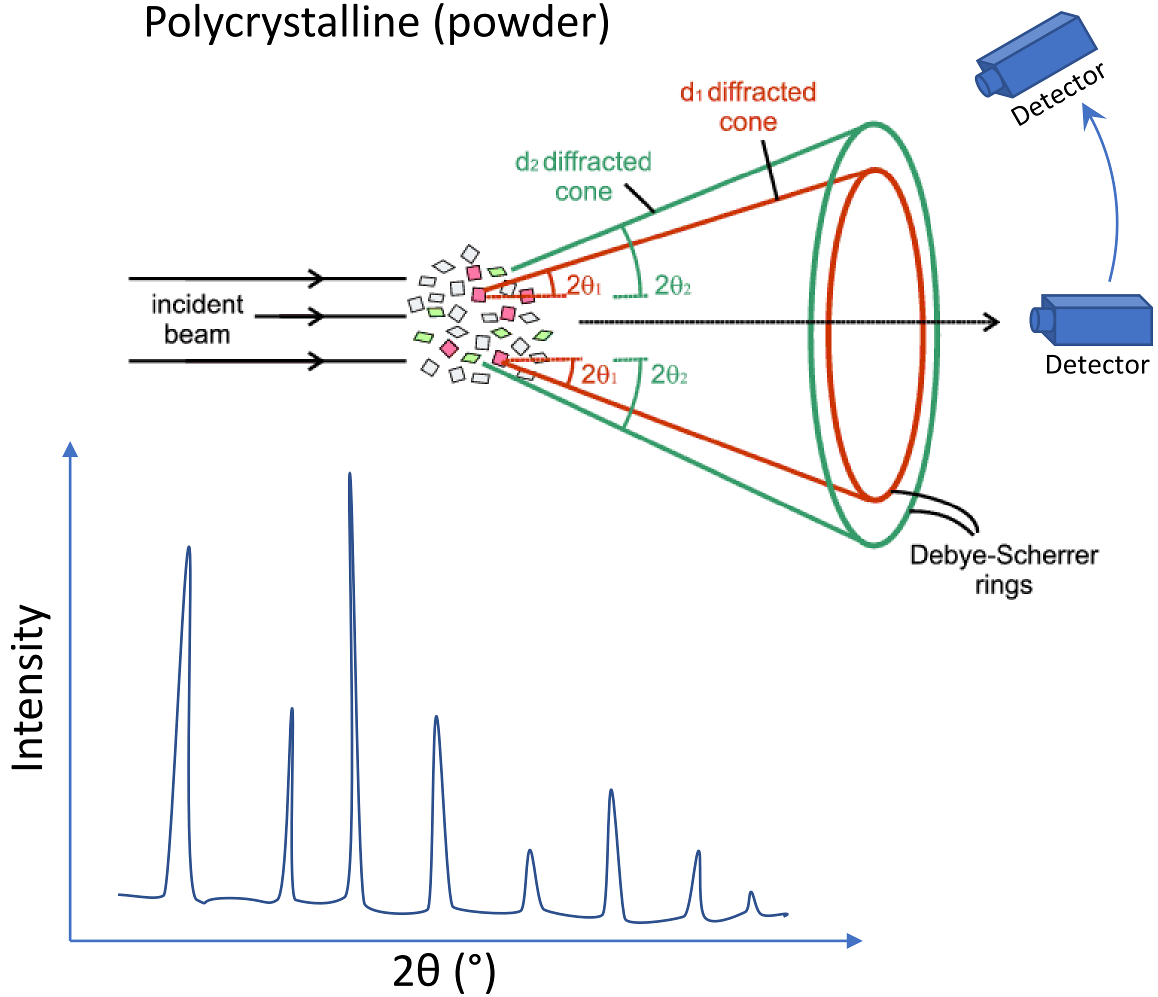


Structure Solution

Single Crystal



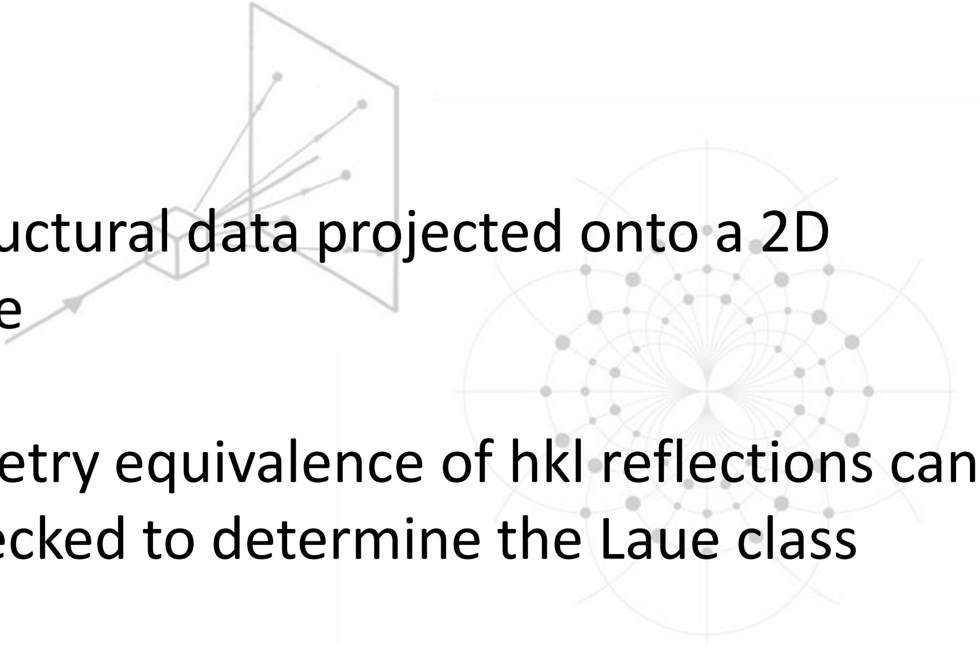
Polycrystalline (powder)



Motivation for Growing Single Crystals

Structure Solution

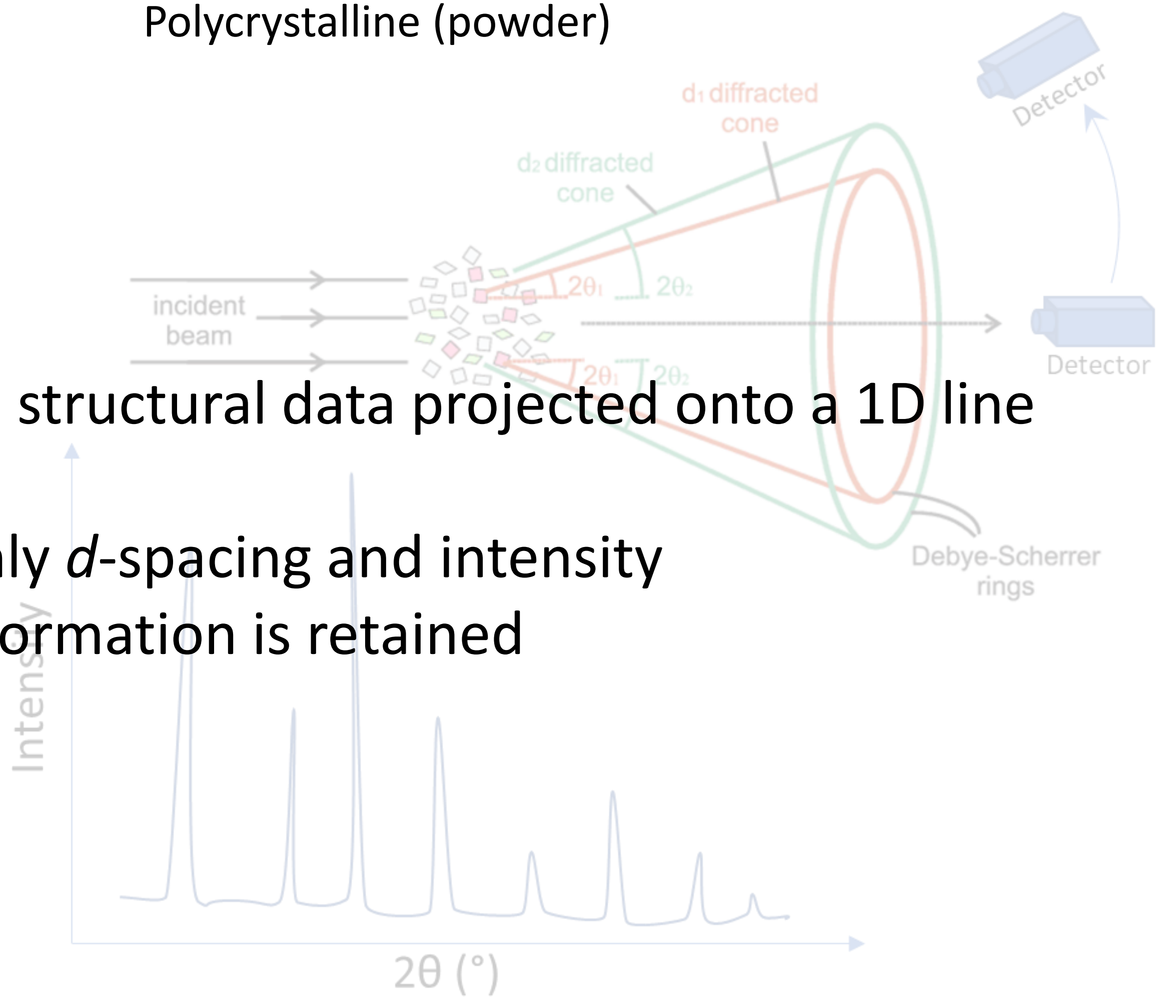
Single Crystal



3D structural data projected onto a 2D surface

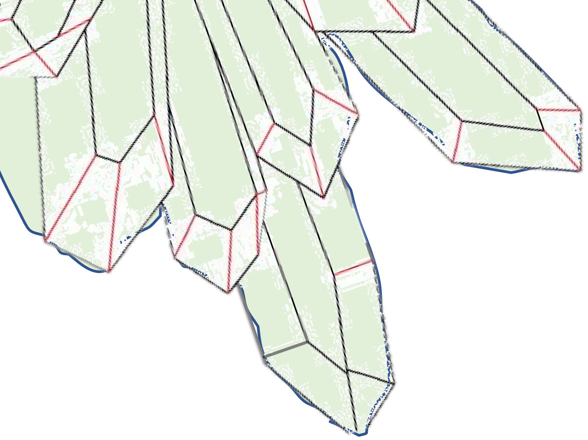
Symmetry equivalence of hkl reflections can be checked to determine the Laue class

Polycrystalline (powder)



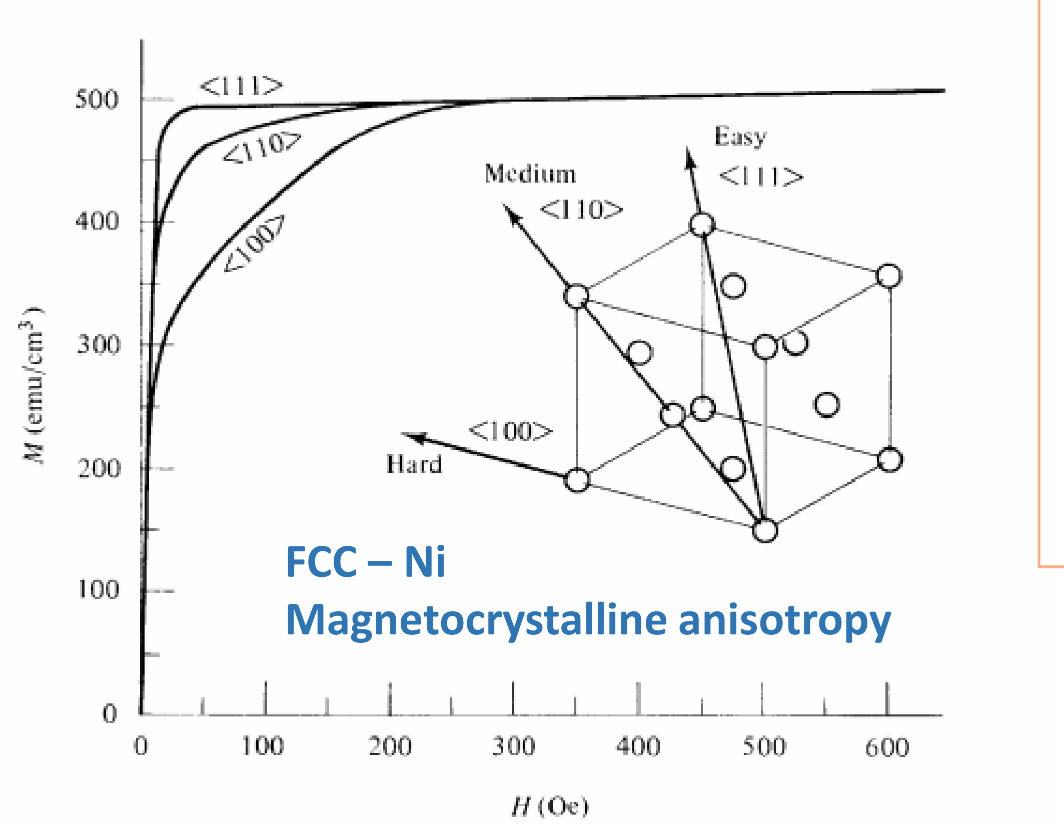
3D structural data projected onto a 1D line

Only *d*-spacing and intensity information is retained



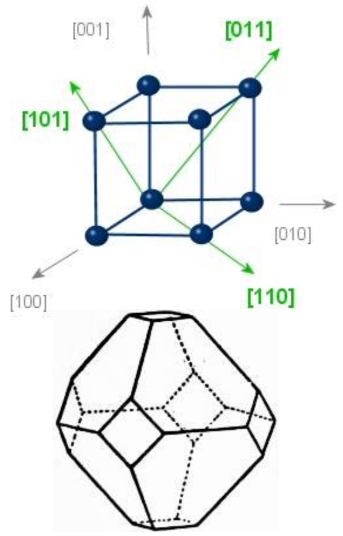
Motivation for Growing Single Crystals

Property Measurements



FCC – Ni
Magnetocrystalline anisotropy

Crystallographic directions

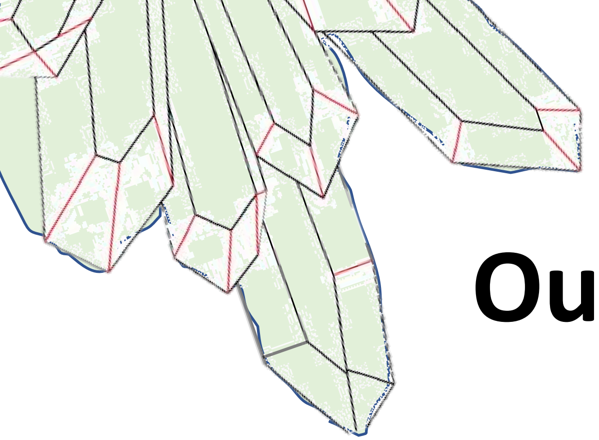


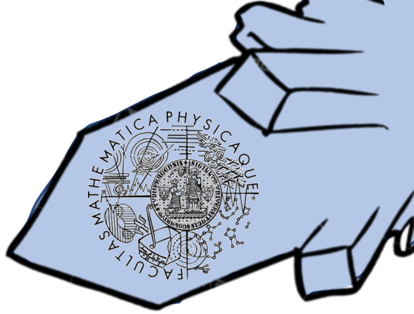
Resistivity,
Magnetoresistance

Hall-effect

Thermal expansion

Thermal conductivity



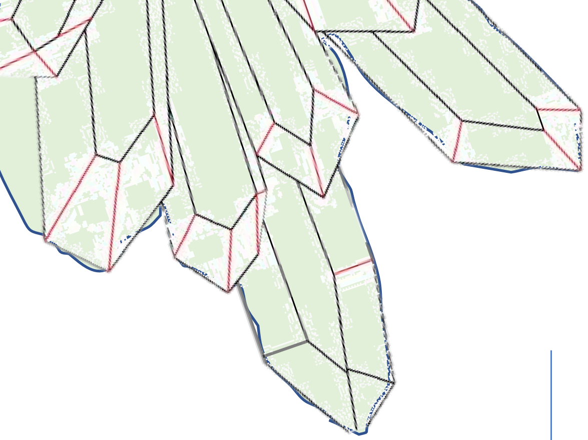


Outline

1. Motivation for Growing Single Crystals

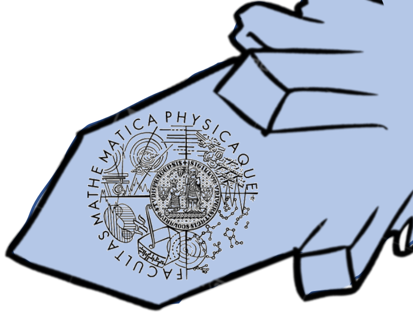
2. Getting Atoms Moving

3. Practical Growth Methods



Getting Atoms Moving

Recrystallisation



Solid

Solid-State Reorganisation
($T < T_{\text{melt}}$)

Liquid

Melting
($T > T_{\text{melt}}$)

Dissolving
($T > T_{\text{solvation}}$)

Flux
(reduced the energy barrier to reorganisation)

$E_{\text{fusion}} > E_{\text{solvation}}$

Gas

Sublimation/Condensation
($T > T_{vap}$)

Chemical transport
($T < T_{vap}$)

Getting Atoms Moving

Heating methods

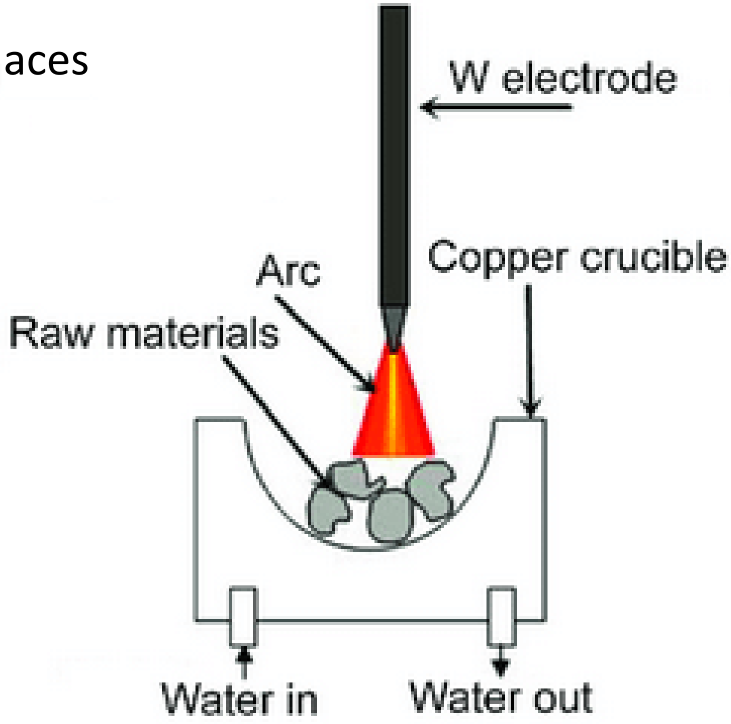
Resistive heating
- Standard box and tube furnaces

Getting Atoms Moving

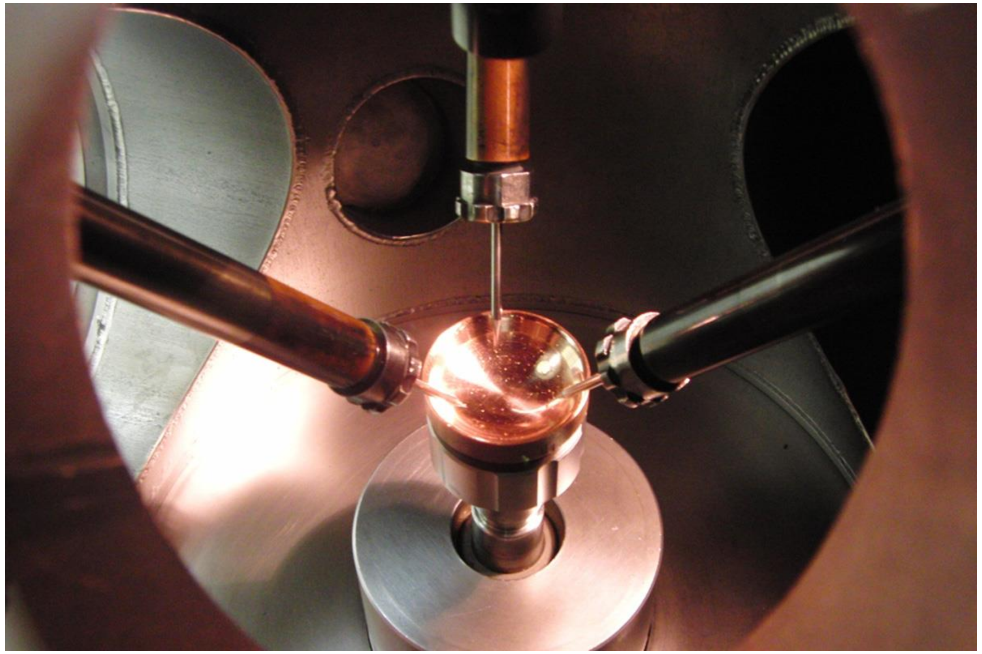
Heating methods

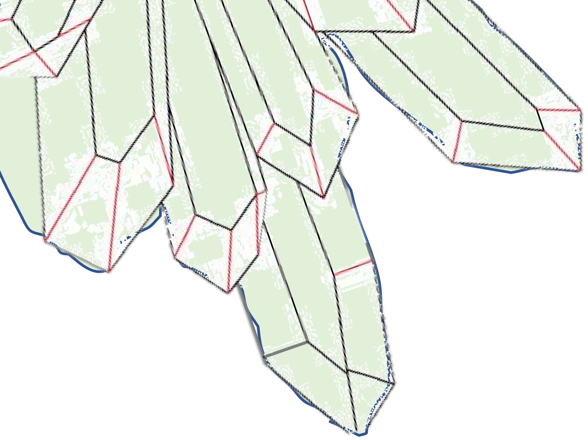
Resistive heating
- Standard box and tube furnaces

Arc discharge



S. Fashu, M. Lototskyy, et al., Mater. Des. **186**, 108295 (2020).





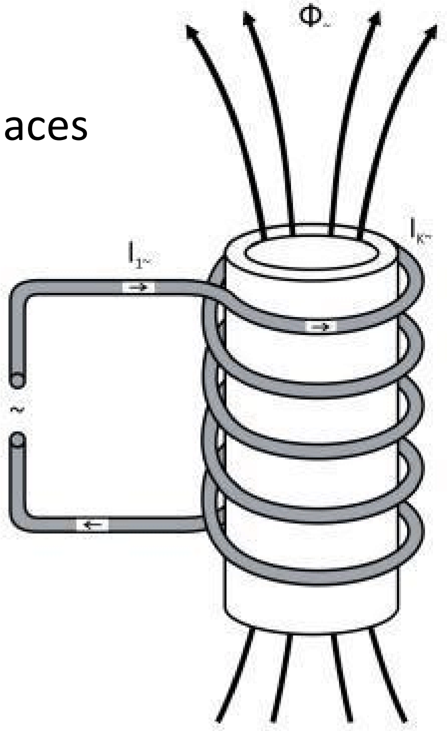
Getting Atoms Moving

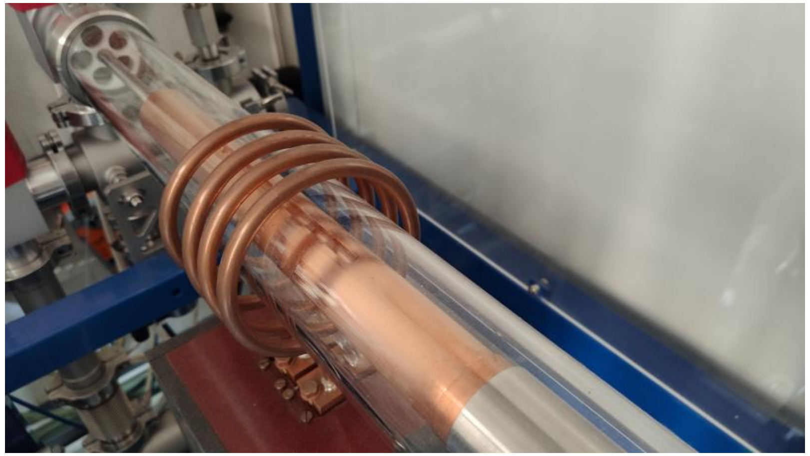
Heating methods

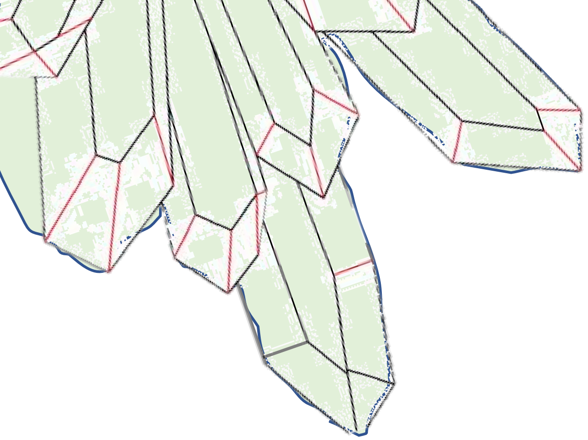
Resistive heating
- Standard box and tube furnaces

Arc discharge

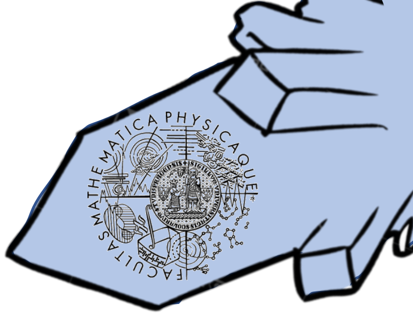
Induction heating







Getting Atoms Moving



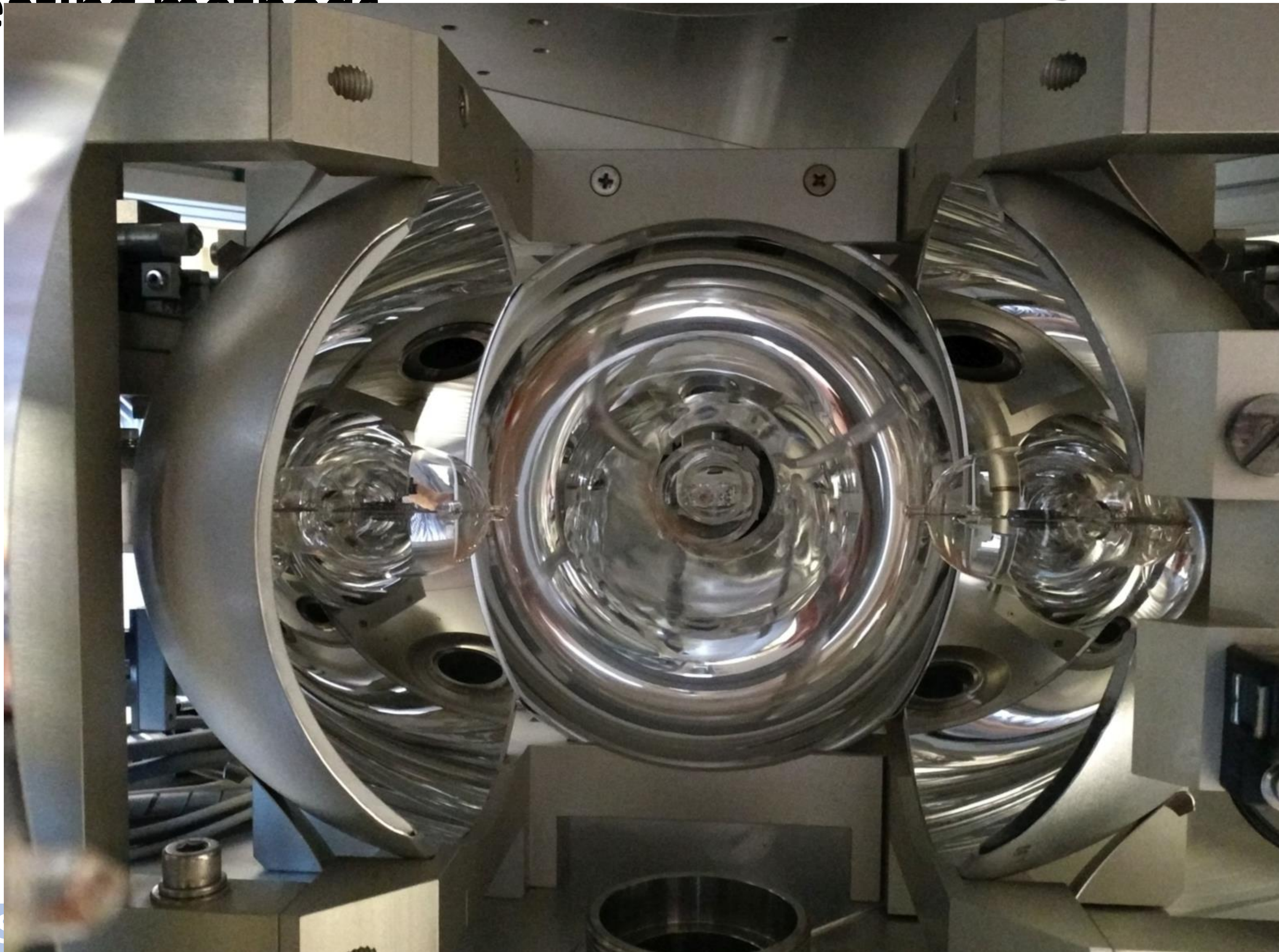
Heating methods

Resistive heating
- Standard box and tube furnaces

Arc discharge

Induction heating

Optical (IR) heating



Getting Atoms Moving

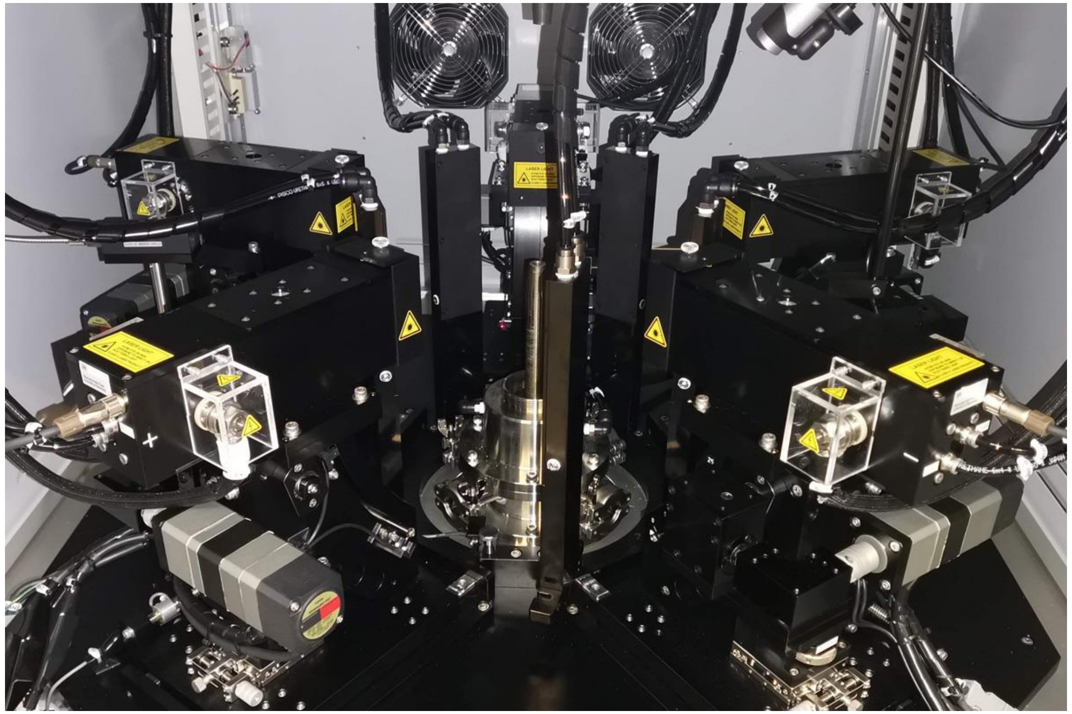
Resistive heating
- Standard box and tube furnaces

Arc discharge

Induction heating

Optical (IR) heating

Laser (IR) heating



Getting Atoms Moving

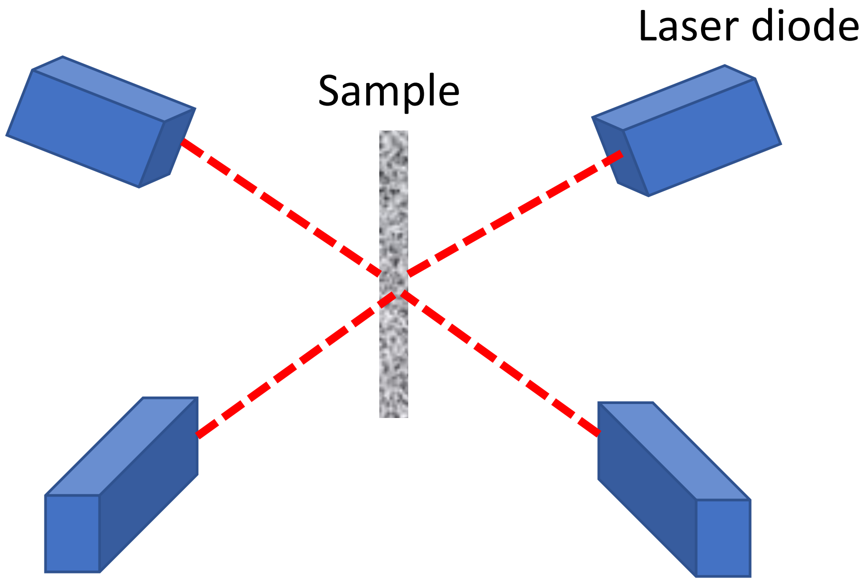
Resistive heating
- Standard box and tube furnaces

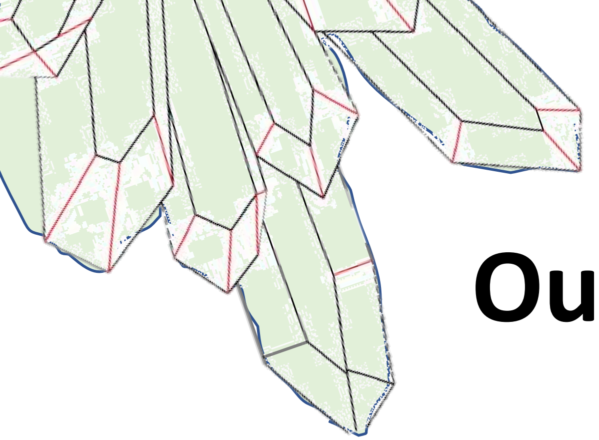
Arc discharge

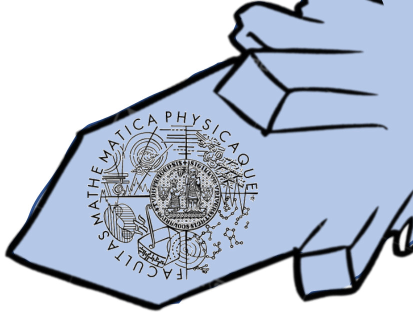
Induction heating

Optical (IR) heating

Laser (IR) heating







Outline

1. Motivation for Growing Single Crystals

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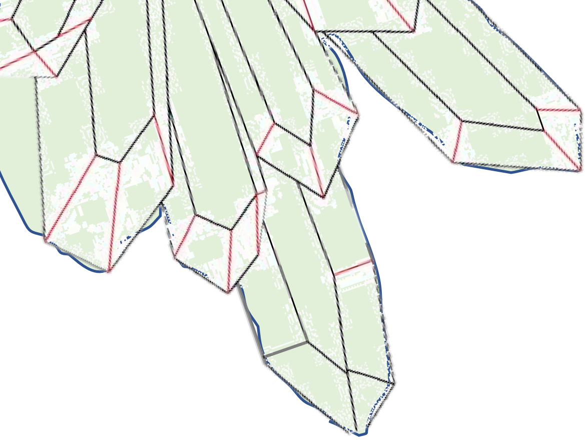
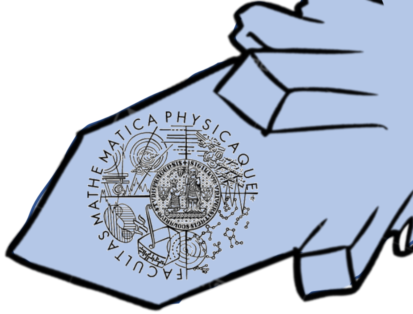
3. Practical Growth Methods



Practical Growth Methods



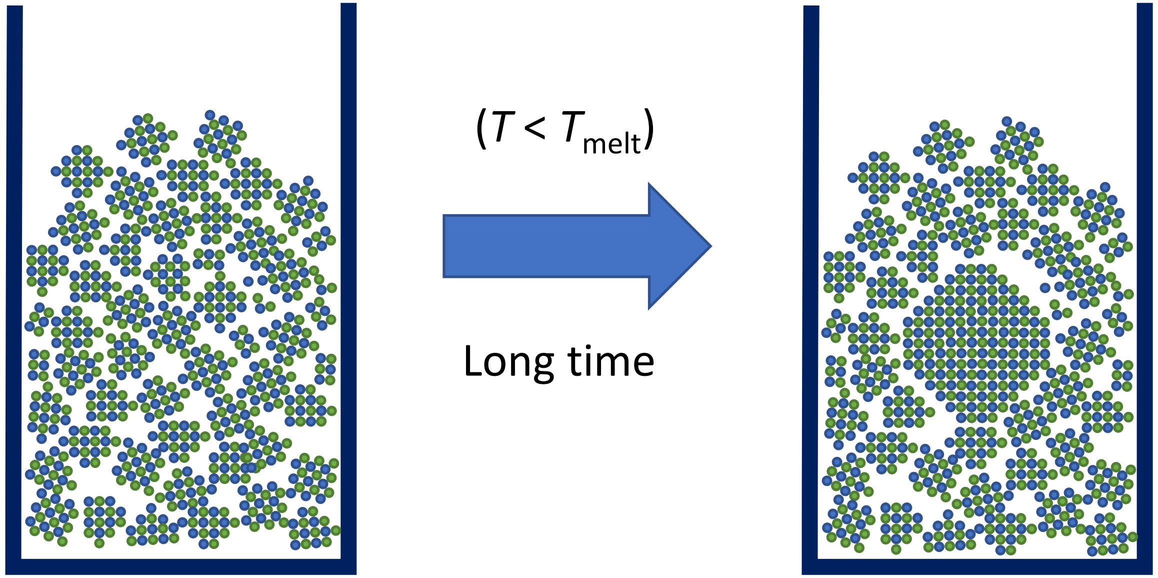
Solid State Sintering

Pros:
Relative simplicity

Cons:
Long times required

Small crystals

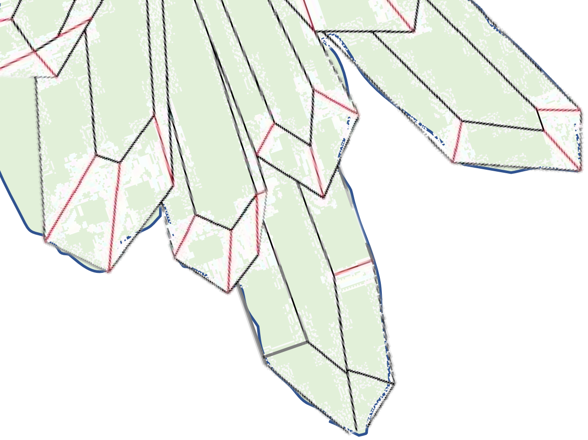
Crystal isolation is tricky



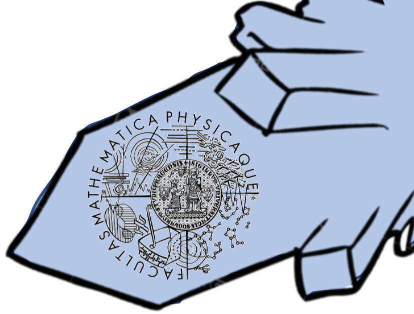
$(T < T_{melt})$

Long time

Mn_3GaC
F. Scheibel, B. Zingsem, et al.,
Phys. Rev. Mater. **3**, 54403 (2019).



Practical Growth Methods



Recrystallising from a melt

Pros:

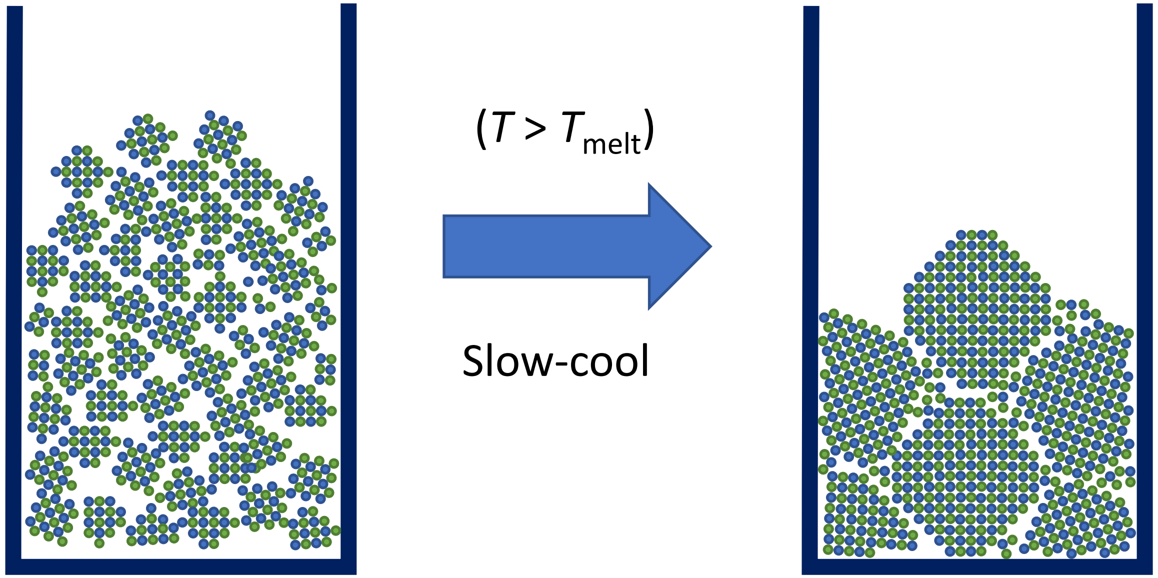
Relative simplicity

Cons:

Limited control of nucleation

Orientation control not possible

Only works for congruently melting materials



($T > T_{melt}$)

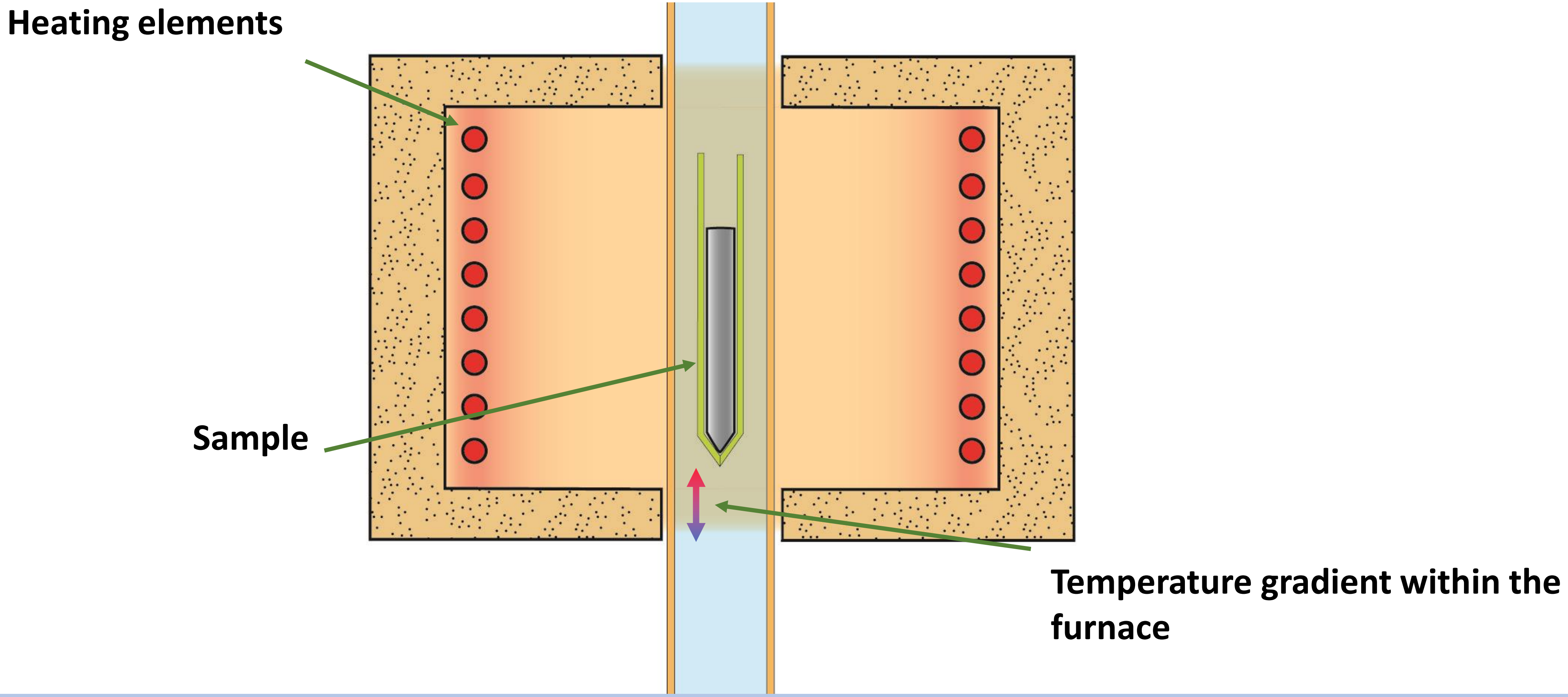
Slow-cool

CuMnAs

J. Volný, D. Wagenknecht, et al., *Electrical Transport Properties of Bulk Tetragonal CuMnAs*, Phys. Rev. Mater. **4**, 064403 (2020).

Practical Growth Methods

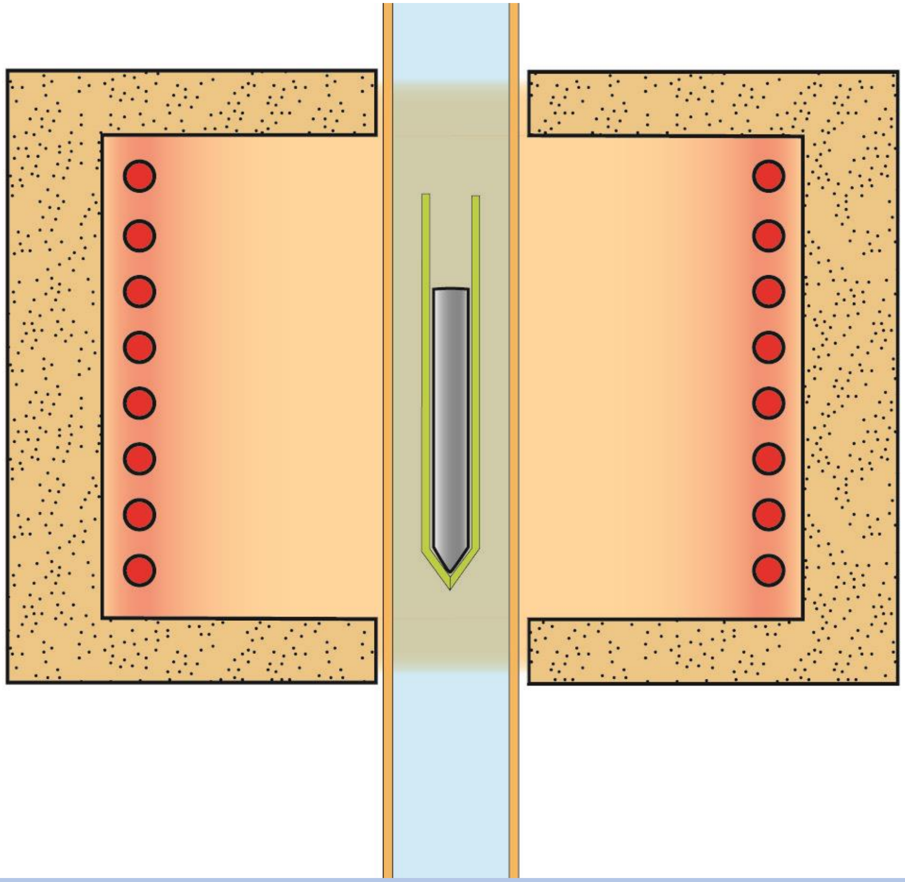
Recrystallising from a melt:
Directional solidification: Bridgeman-Stockbarge

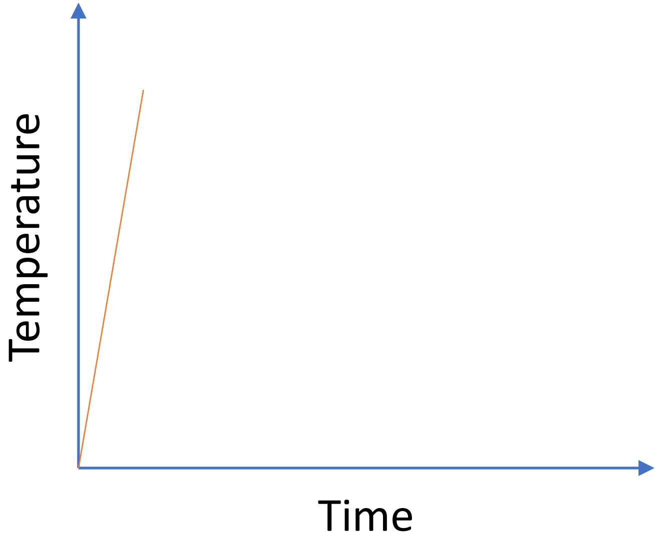


Practical Growth Methods

Recrystallising from a melt:

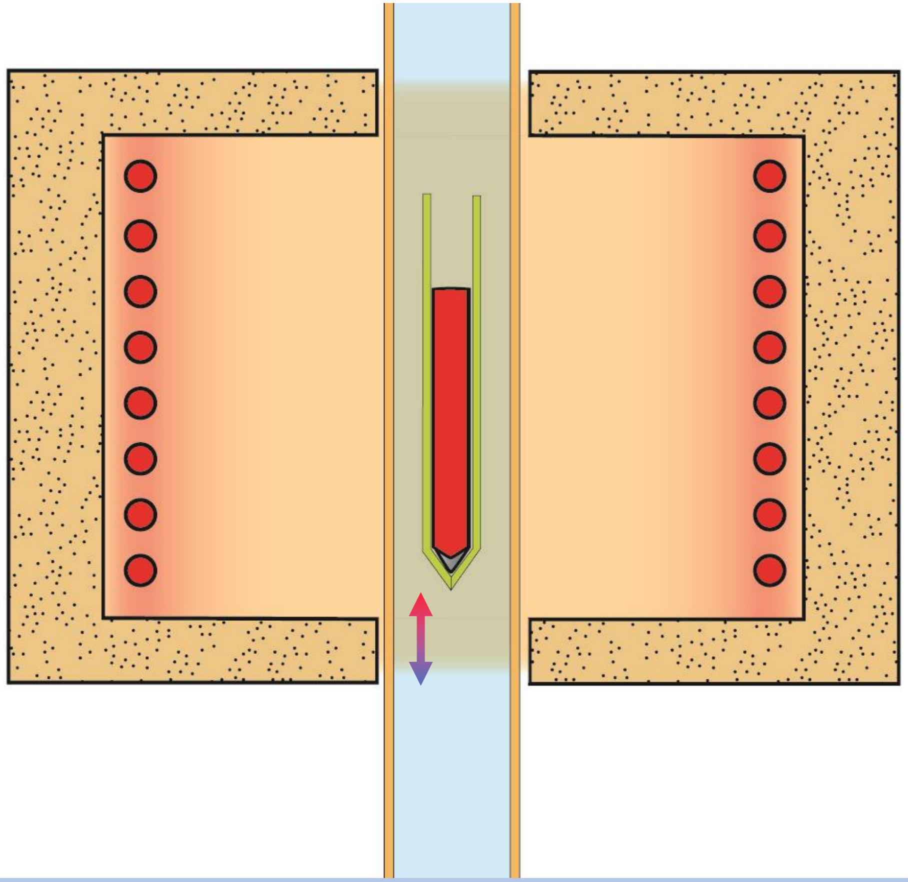
Directional solidification: Bridgeman-Stockbarge

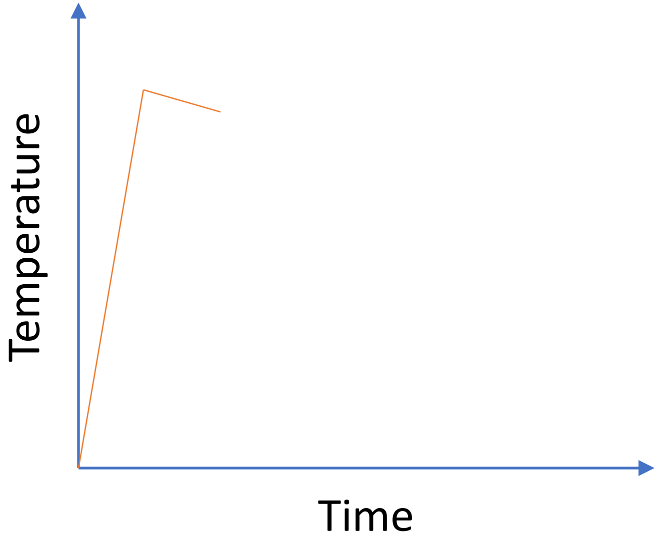




Practical Growth Methods

Recrystallising from a melt:
Directional solidification: Bridgeman-Stockbarge





Practical Growth Methods

Recrystallising from a melt:
Directional solidification: Bridgeman-Stockbarge

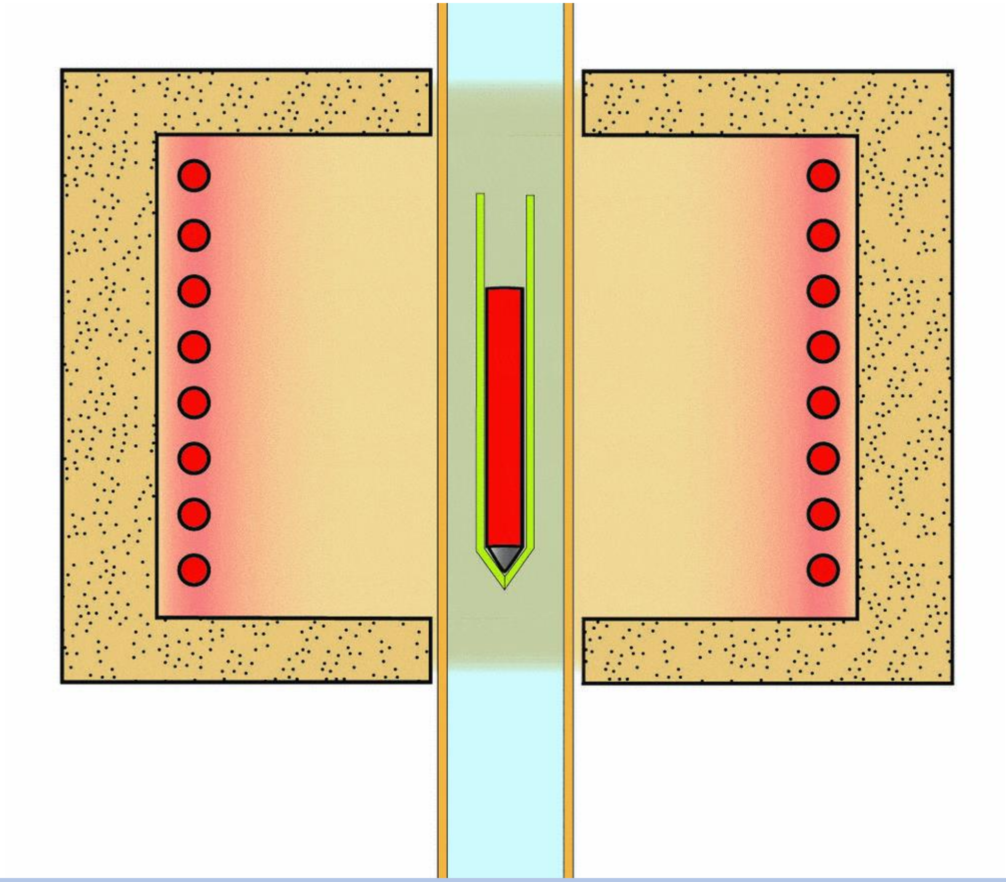
Pros:
Relative simplicity

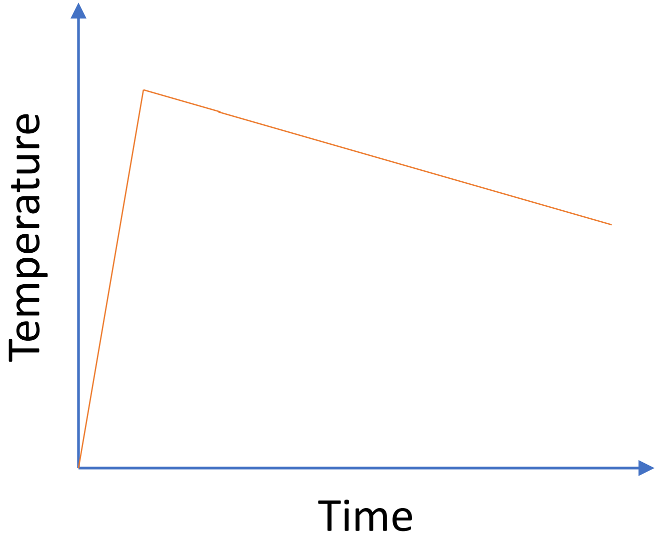
Some control of nucleation

Large crystals possible

Cons:
Orientation control not possible

Only works for congruently melting materials



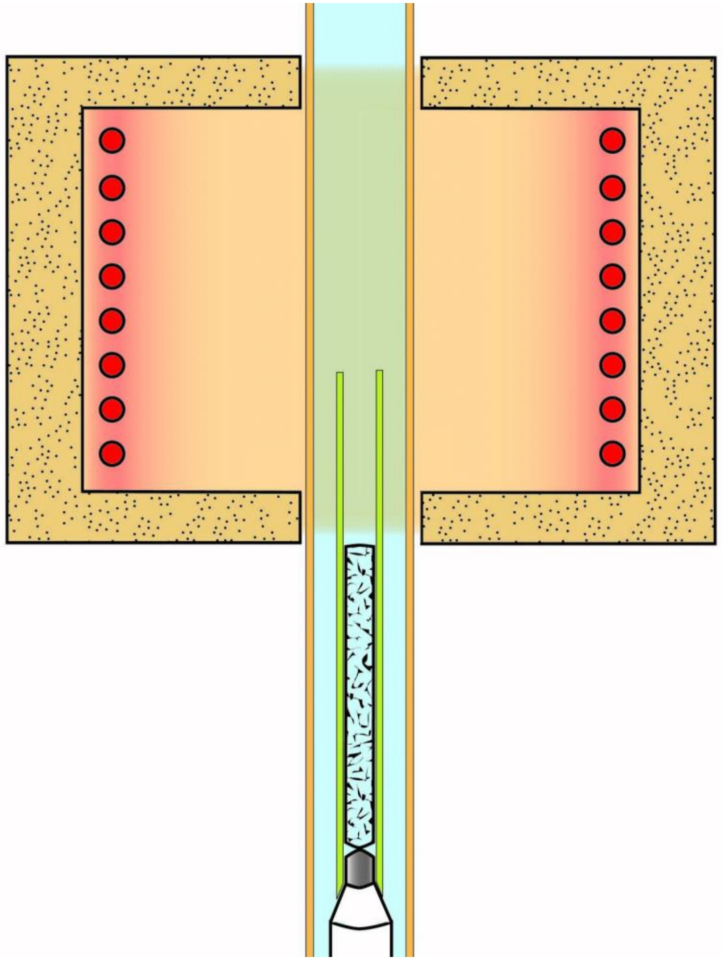


Practical Growth Methods

Recrystallising from a melt:

Directional solidification: Bridgeman-Stockbarge

(with seed)

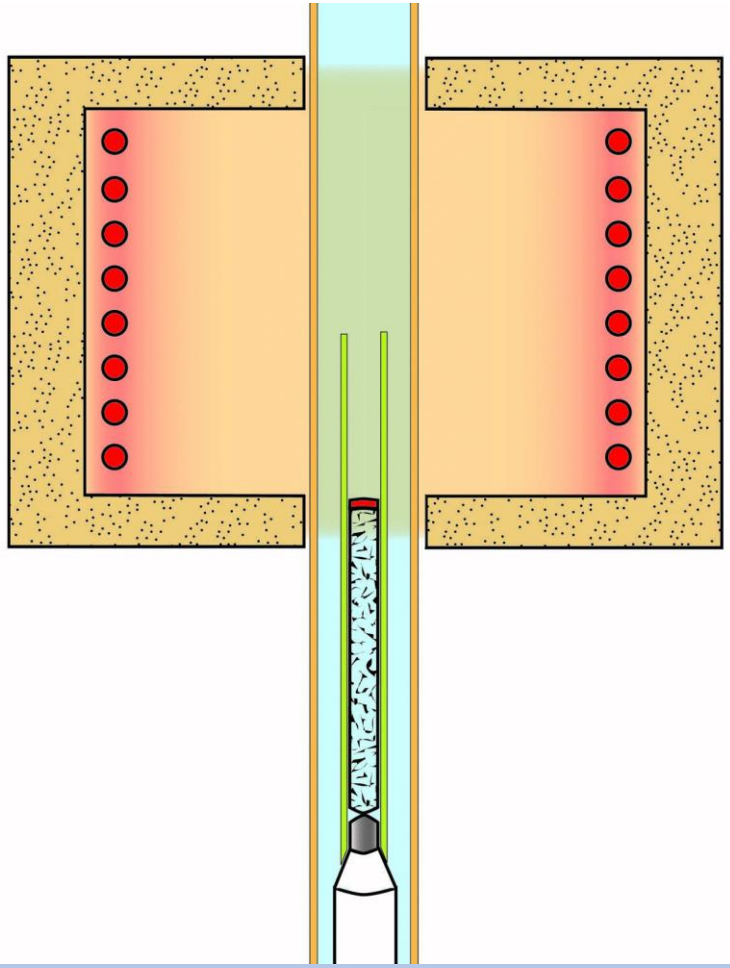


Practical Growth Methods

Recrystallising from a melt:

Directional solidification: Bridgeman-Stockbarge

(with seed)



Practical Growth Methods

Recrystallising from a melt:
Directional solidification: Bridgeman-Stockbarge

(with seed)

Pros:

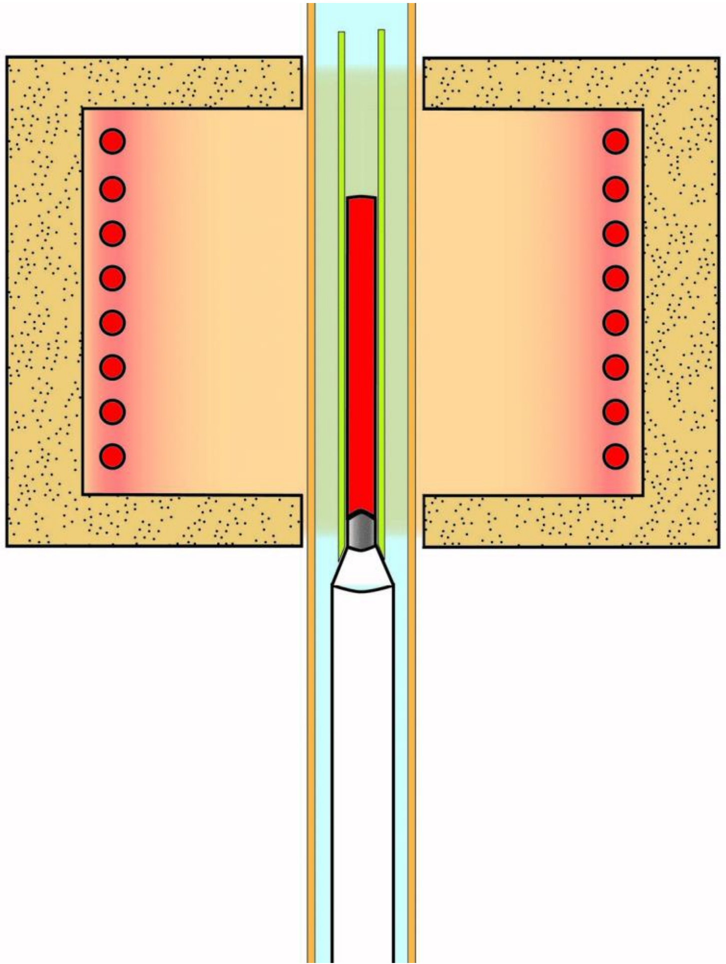
Seed orientation control

Large crystals possible

Cons:

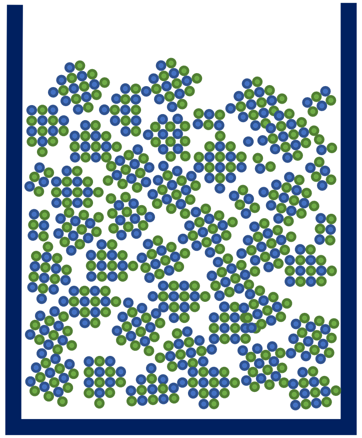
Only works for congruently melting materials

Complexity is increased



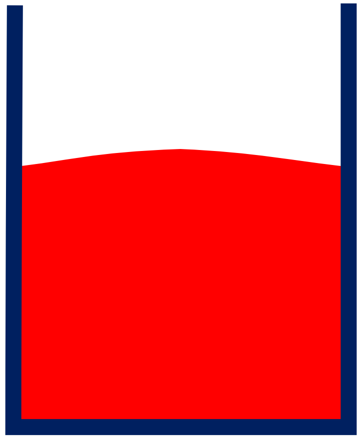
Practical Growth Methods

Recrystallising from a melt:
Czochralskii pulling



Practical Growth Methods

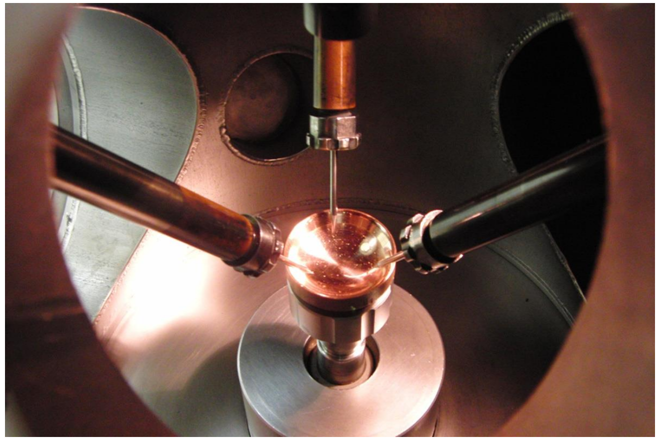
Recrystallising from a melt:
Czochralskii pulling

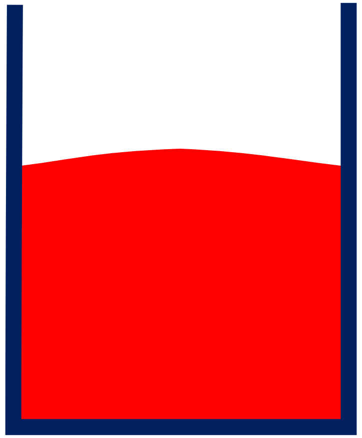


Practical Growth Methods

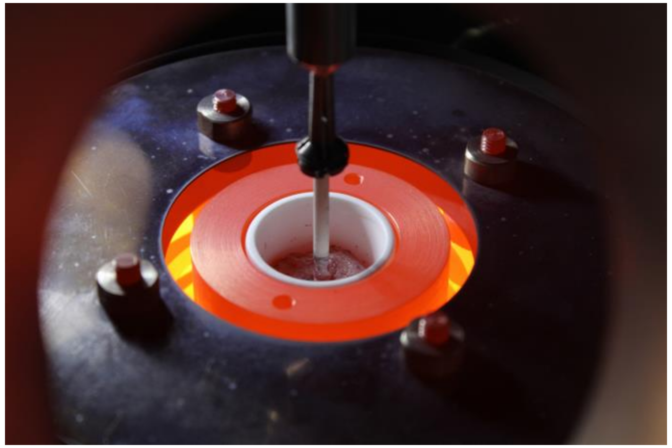
Recrystallising from a melt:
Czochralskii pulling

Tri-Arc melting





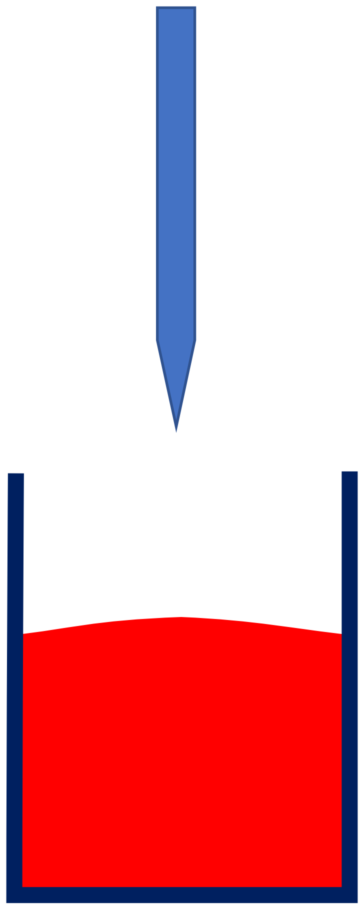
Resistance heater melting



Practical Growth Methods

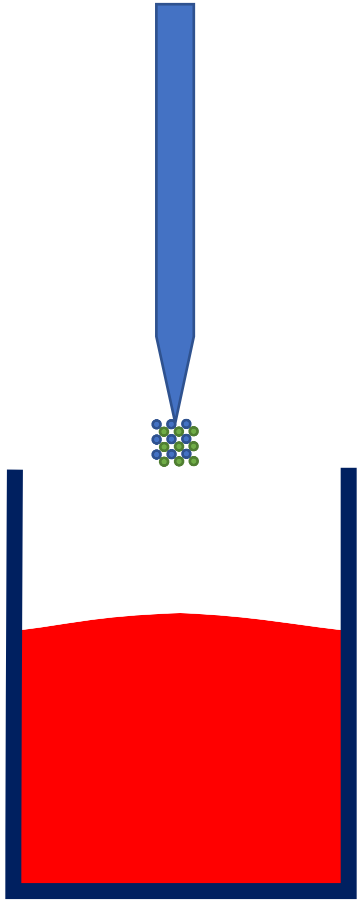
Recrystallising from a melt:

Czochralskii pulling



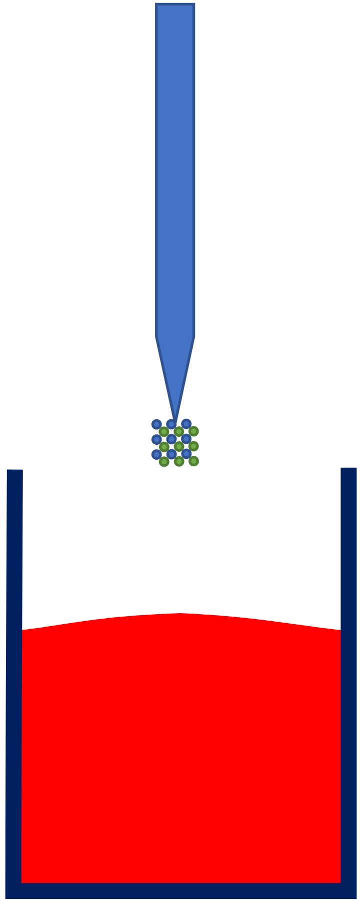
Practical Growth Methods

Recrystallising from a melt:
Czochralski pulling



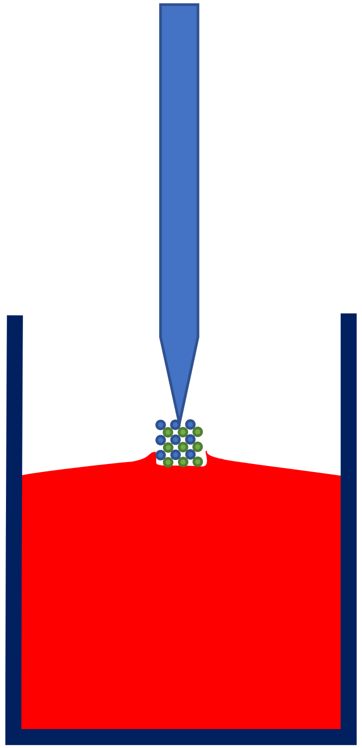
Practical Growth Methods

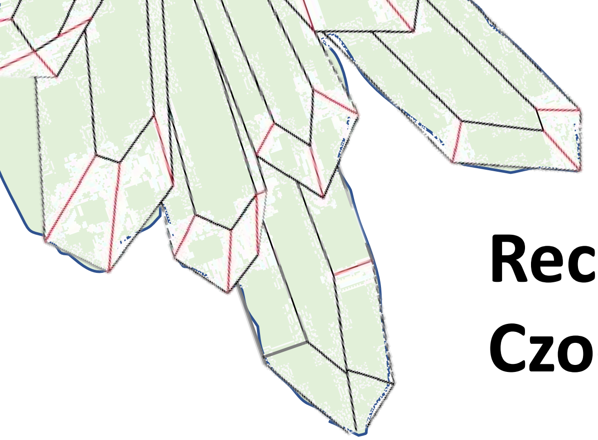
Recrystallising from a melt:
Czochralski pulling



Practical Growth Methods

Recrystallising from a melt:
Czochralski pulling





Practical Growth Methods

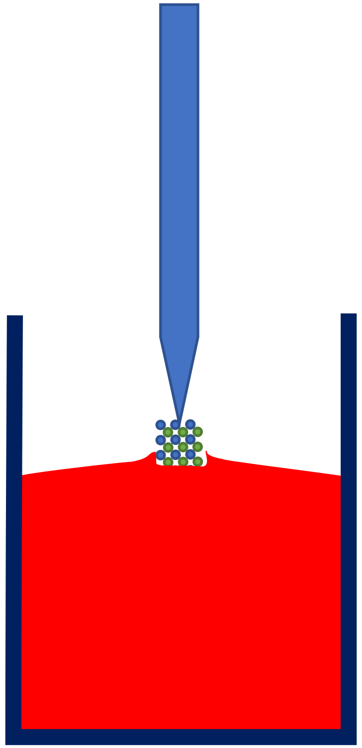
Recrystallising from a melt: Czochralski pulling

Pros:

Seed orientation control

Large (long) crystals possible

Minimised vessel contamination



Cons:

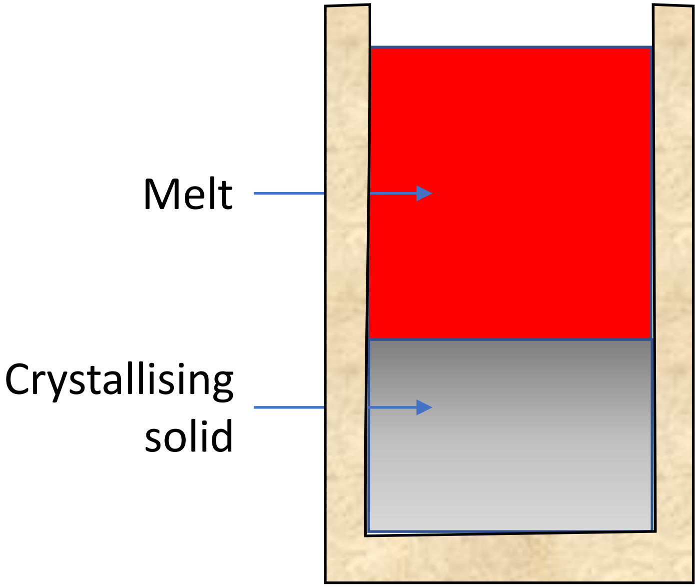
Time consuming and complex

Not suitable for incongruently melting materials

Practical Growth Methods

A material is described as incongruently melting

- if the solid crystallises with a different composition from the melt.



e.g. If the melt has composition

$\mathbf{Ni_{50}Mn_{28.5}Ga_{21.5}}$

the crystallising solid will have composition

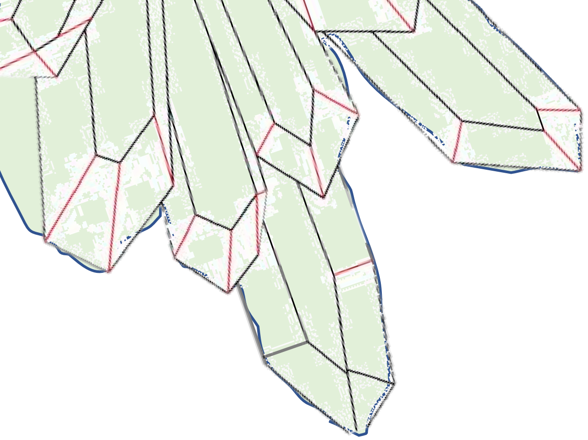
$\sim \mathbf{Ni_{50.5}Mn_{26.8}Ga_{22.7}}$

The ratio between melt concentration and solid concentration is known as the partition coefficient,

$$k = \frac{c_{solid}}{c_{melt}}$$

For Ni-Mn-Ga, these are known to be:

$k_{Ni} \sim 1.04$
$k_{Mn} \sim 0.88$
$k_{Ga} \sim 1.09$



Practical Growth Methods

As the solid forming has a different composition to the melt, the composition of the melt changes during the growth.

A formula to describe the composition change was put forward by Scheil in 1942 – now known as the Scheil-Gulliver equation:

Partition coefficient

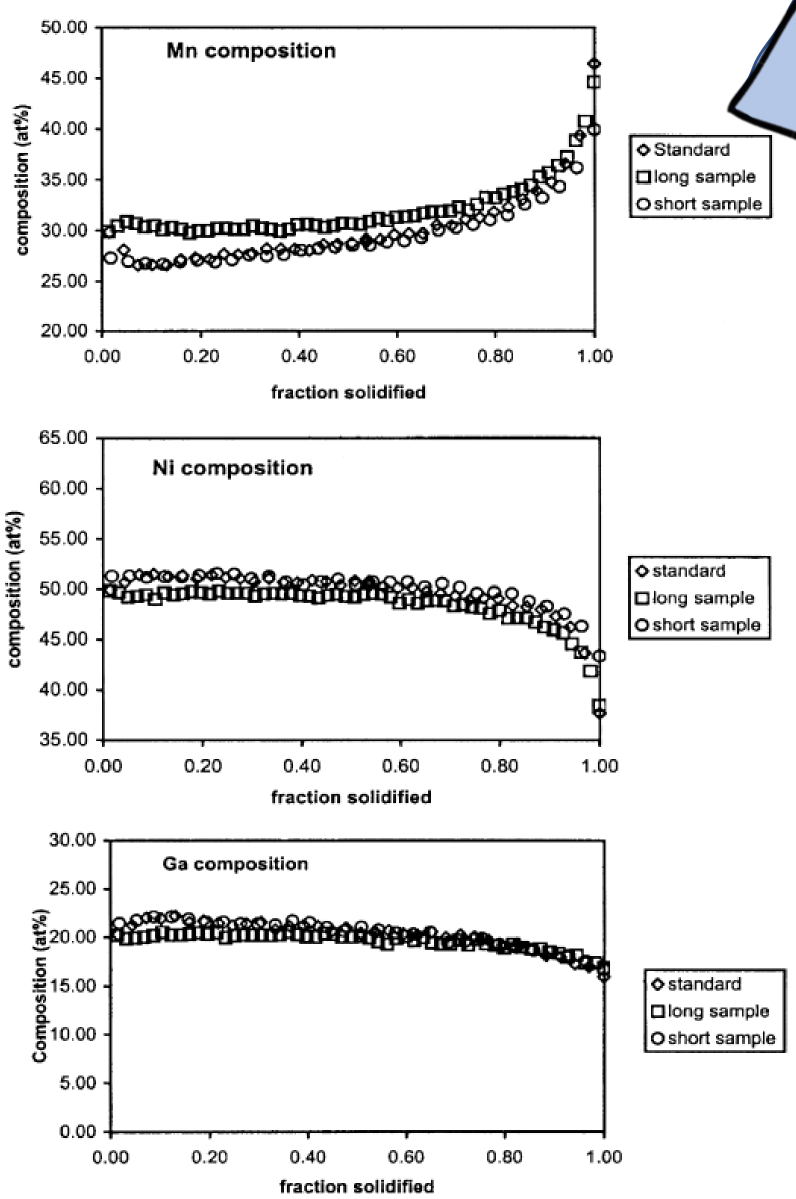
Crystalizing concentration

$$c_s(f) = kc_0(1-f)^{k-1}$$

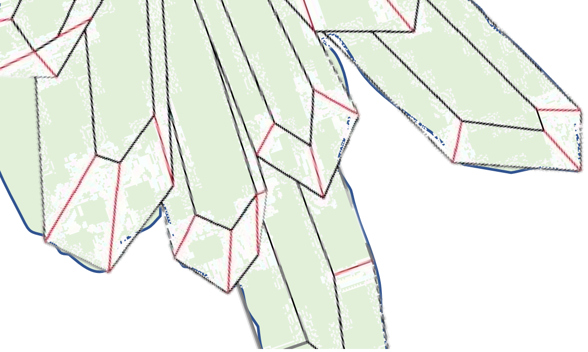
Initial concentration

Fraction solidified

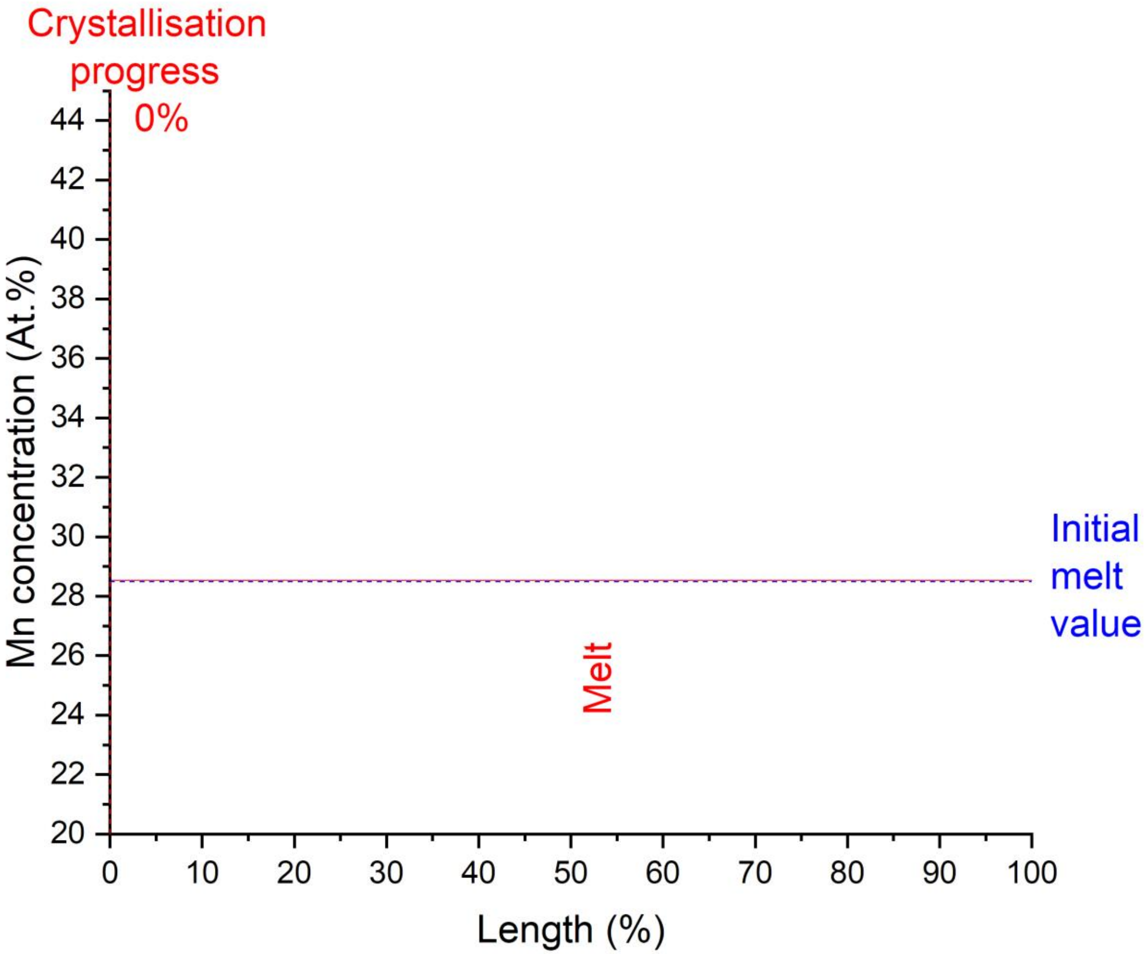
Scheil E. *Z Metall* 34 (1942) 70.

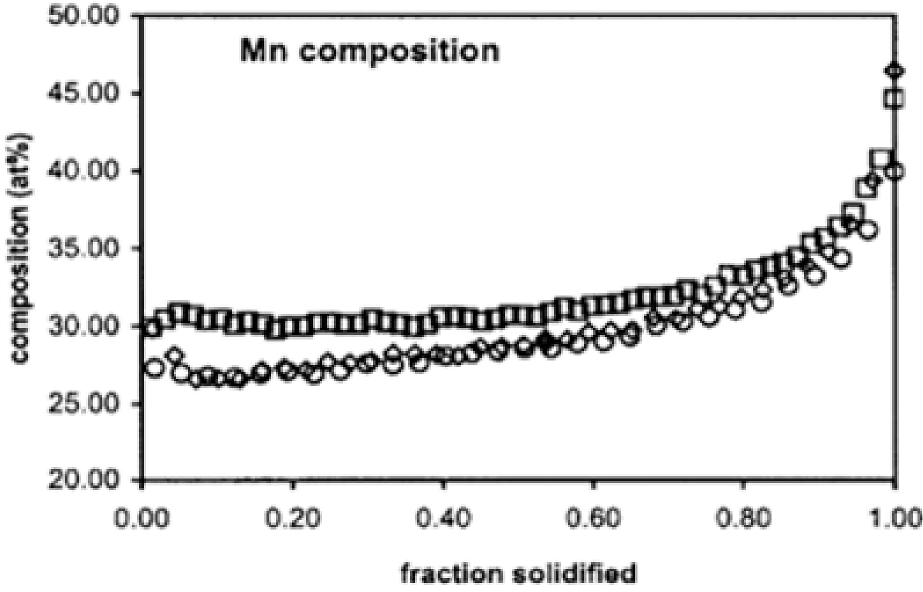


D. L. Schlagel et al. *J. Alloys Compd*. **312**, 77 (2000).



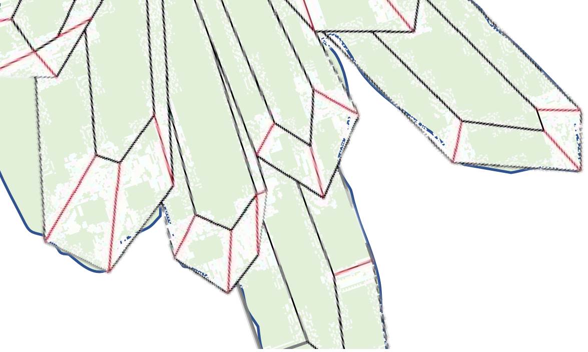
Practical Growth Methods



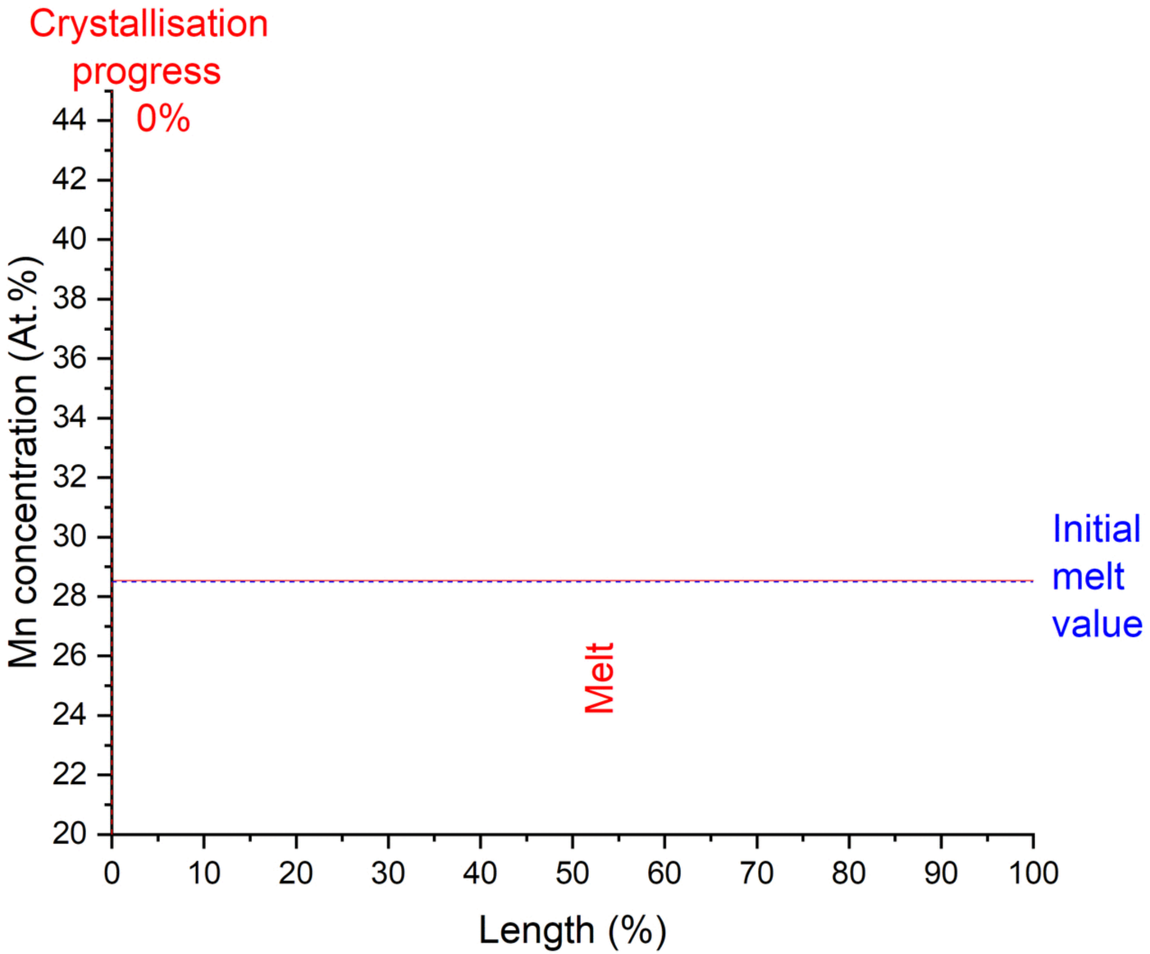


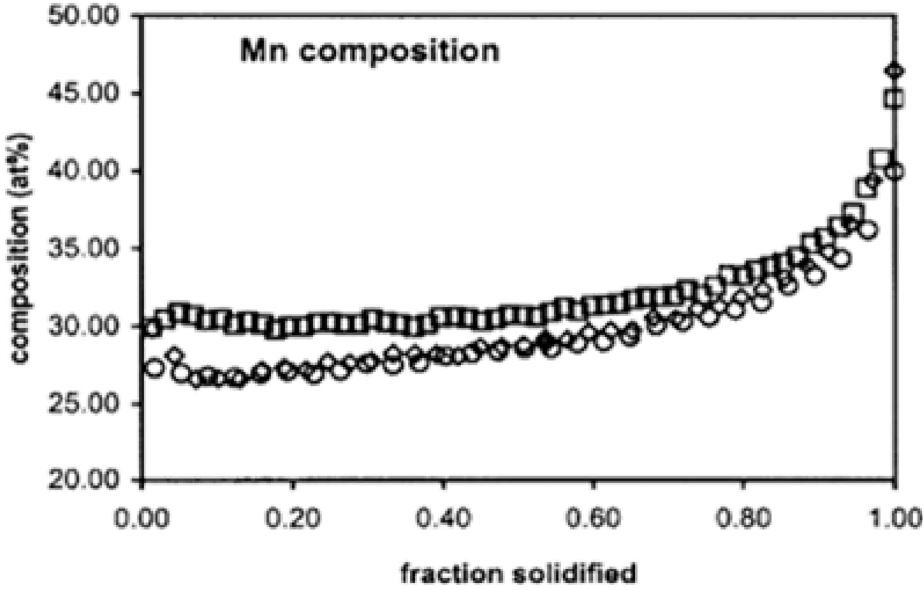
D. L. Schlagel et al. *J. Alloys Compd.* **312**, 77 (2000).

$k_{\mathrm{Mn}} = 0.88$



Practical Growth Methods





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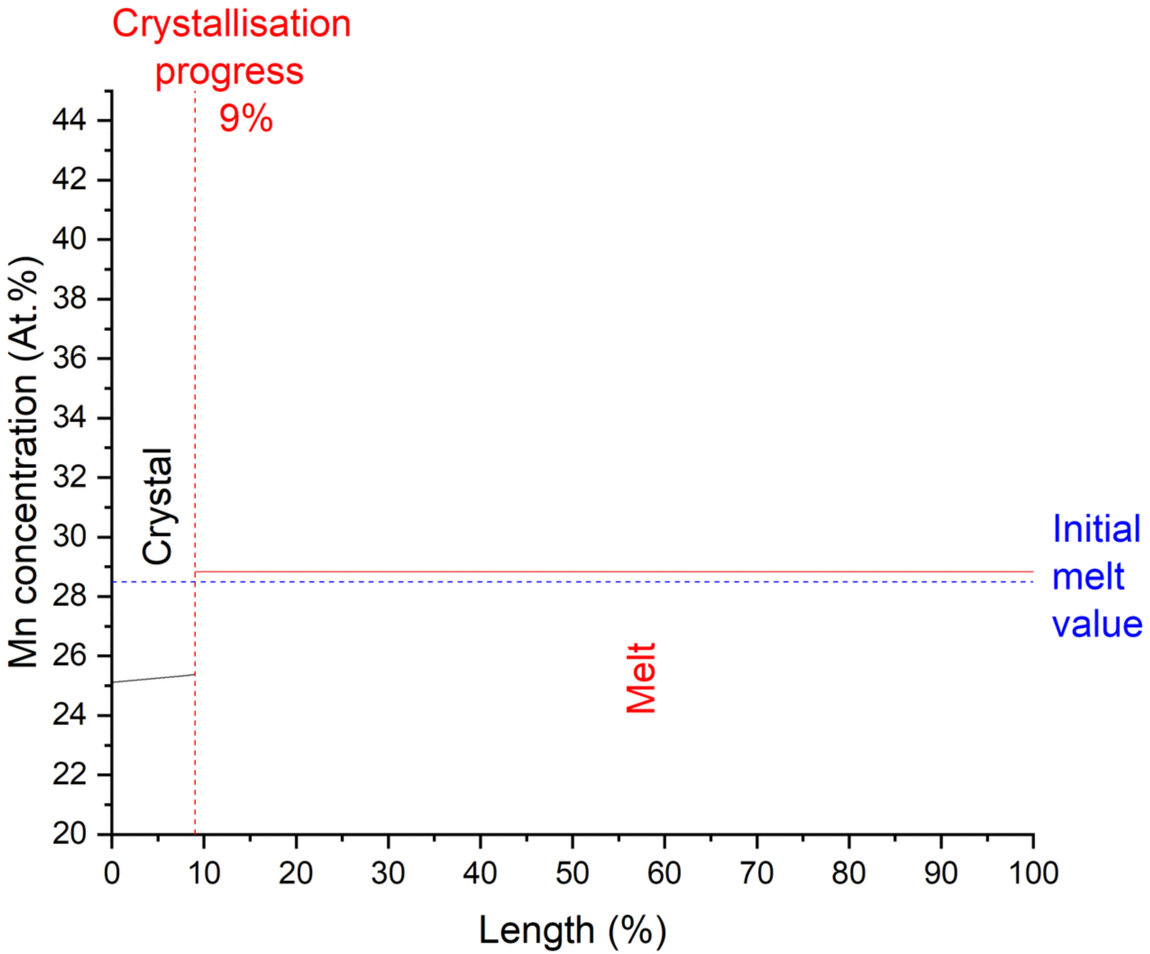
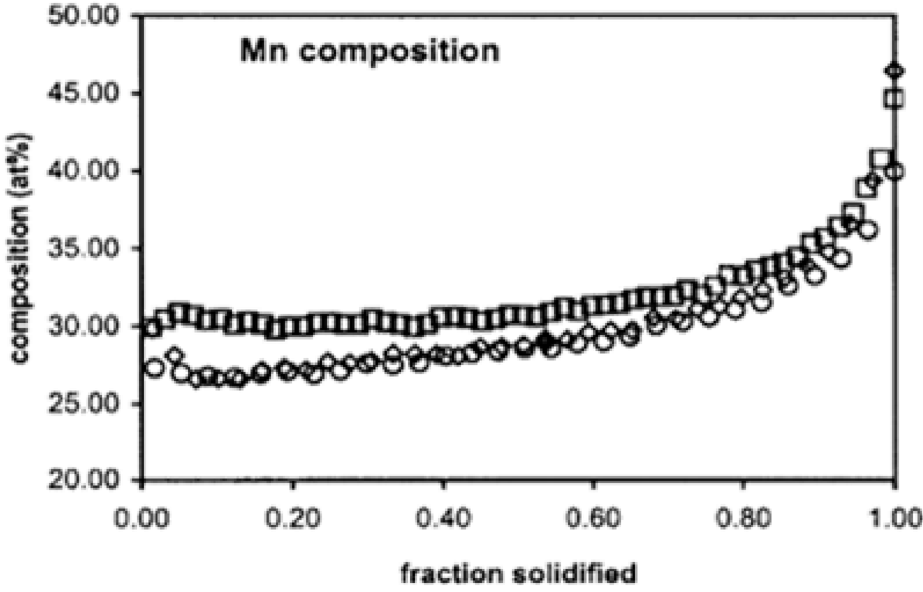
Practical Growth Methods





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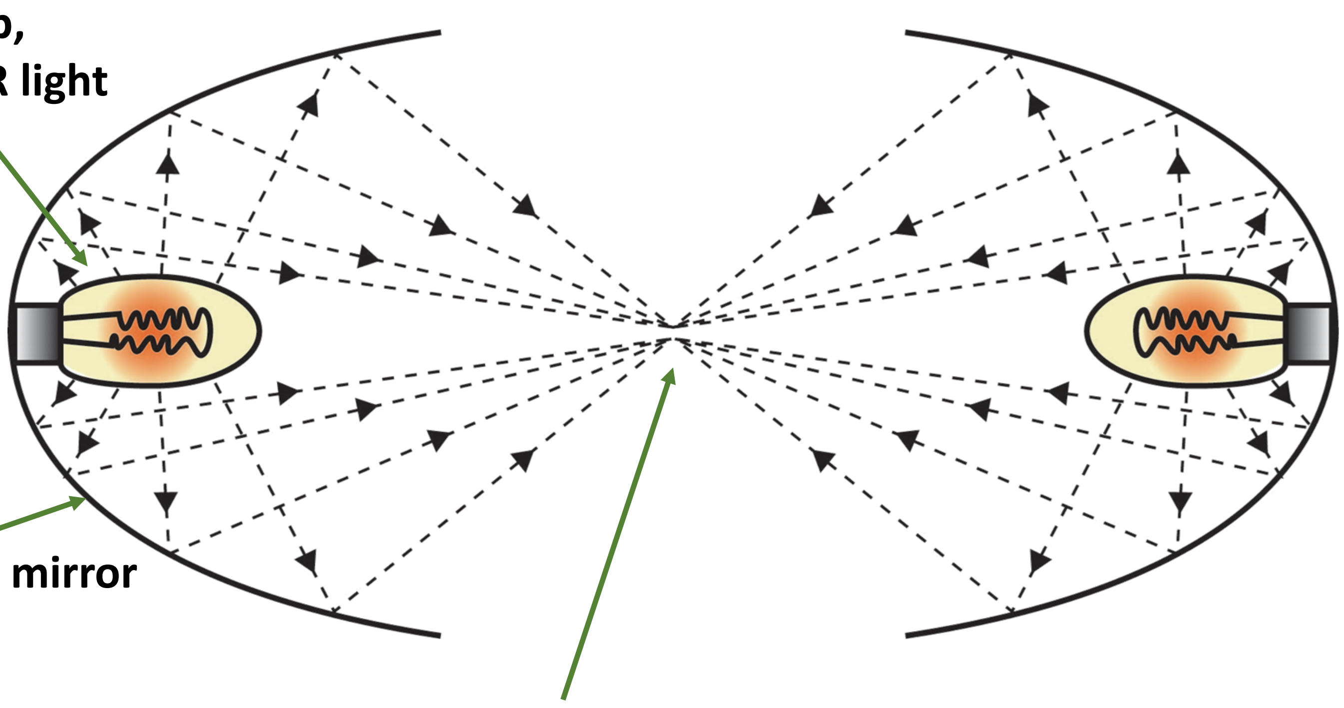
Practical Growth Methods

Recrystallising from a melt:
Directional solidification: Floating-zone



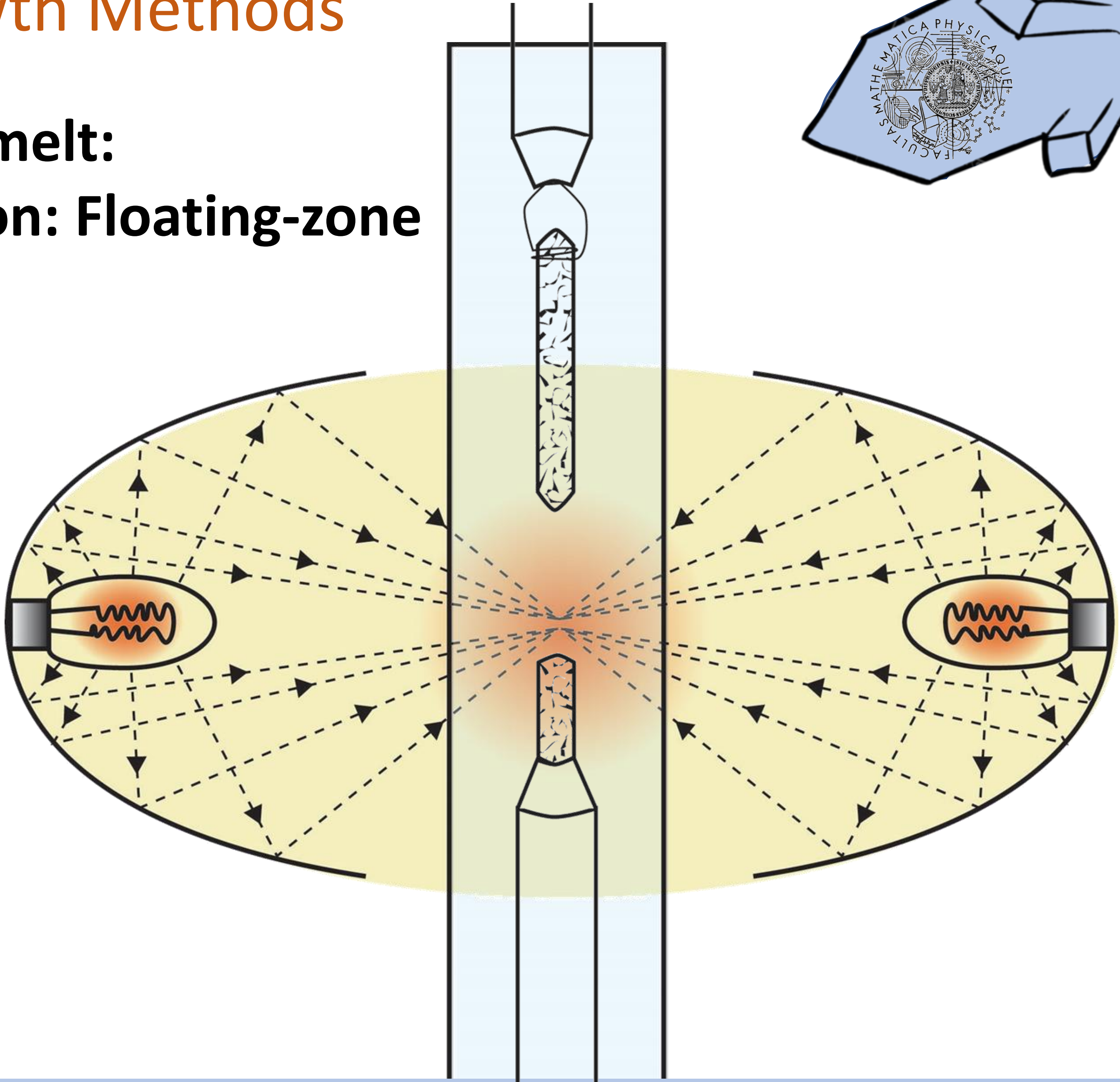
Halogen bulb, heating by IR light

Parabolic mirror

Focal point of 4x bulbs and mirrors

Practical Growth Methods

Recrystallising from a melt:
Directional solidification: Floating-zone



Practical Growth Methods

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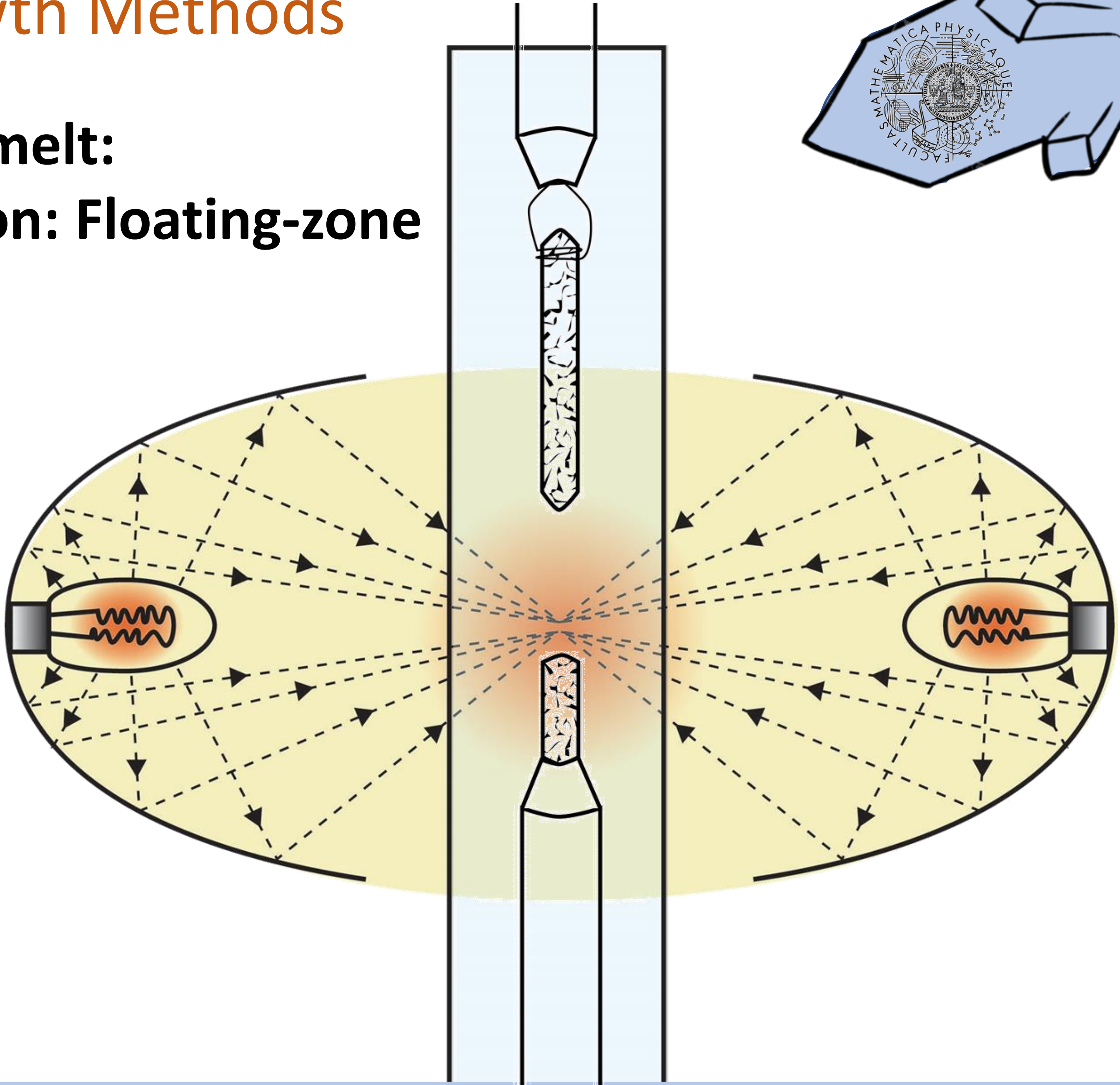

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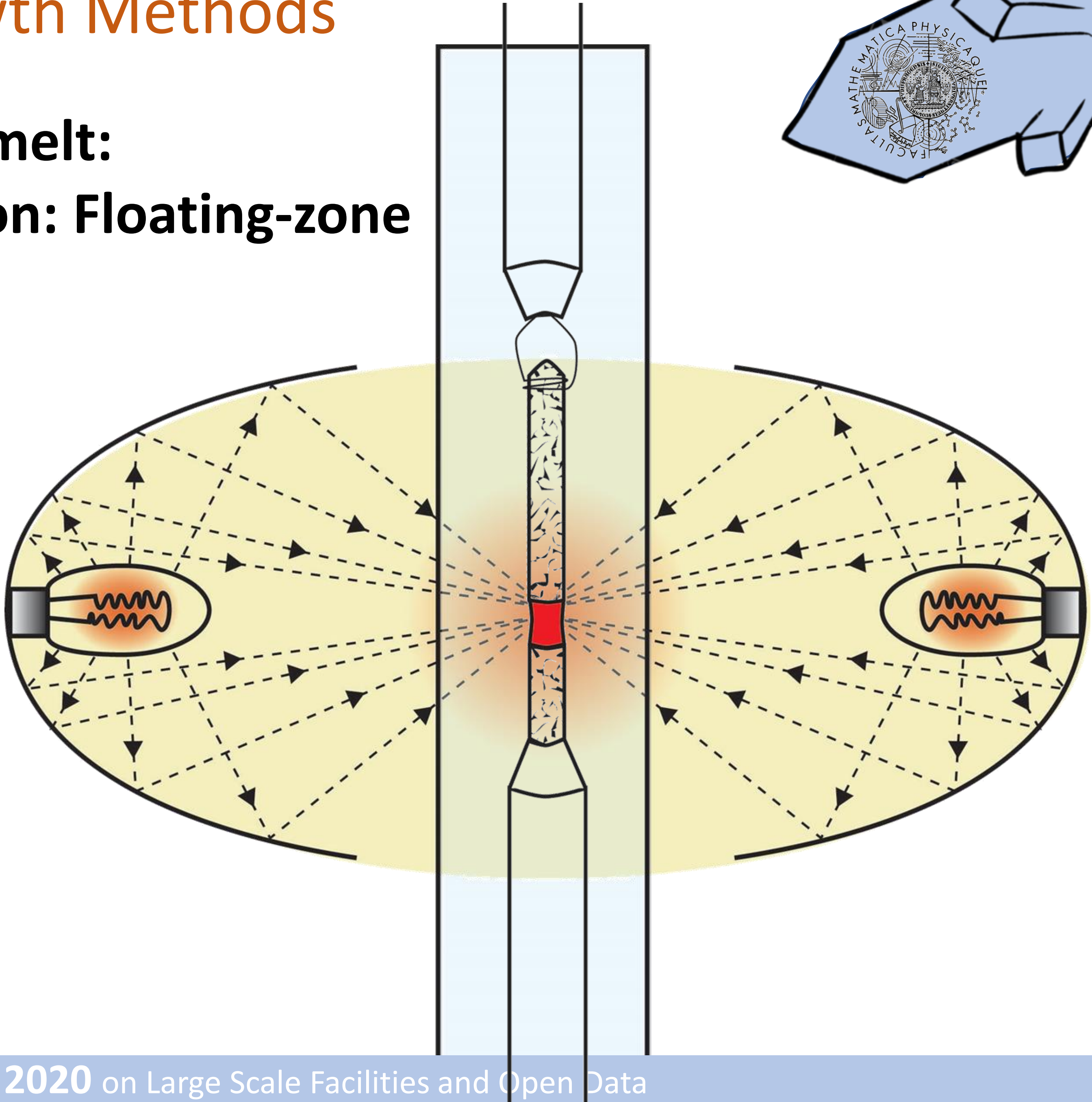
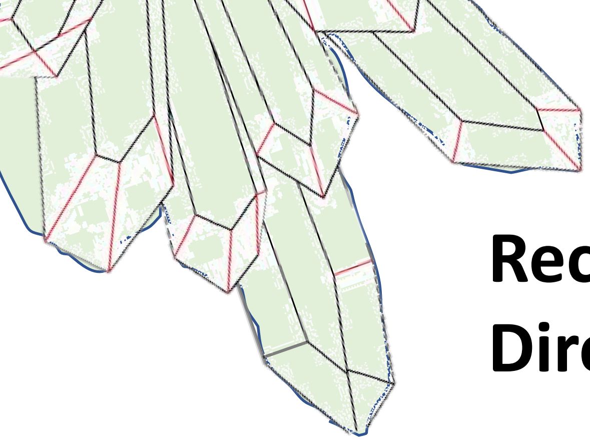




Practical Growth Methods

Recrystallising from a melt:
Directional solidification: Floating-zone

Pros:

Orientation control possible

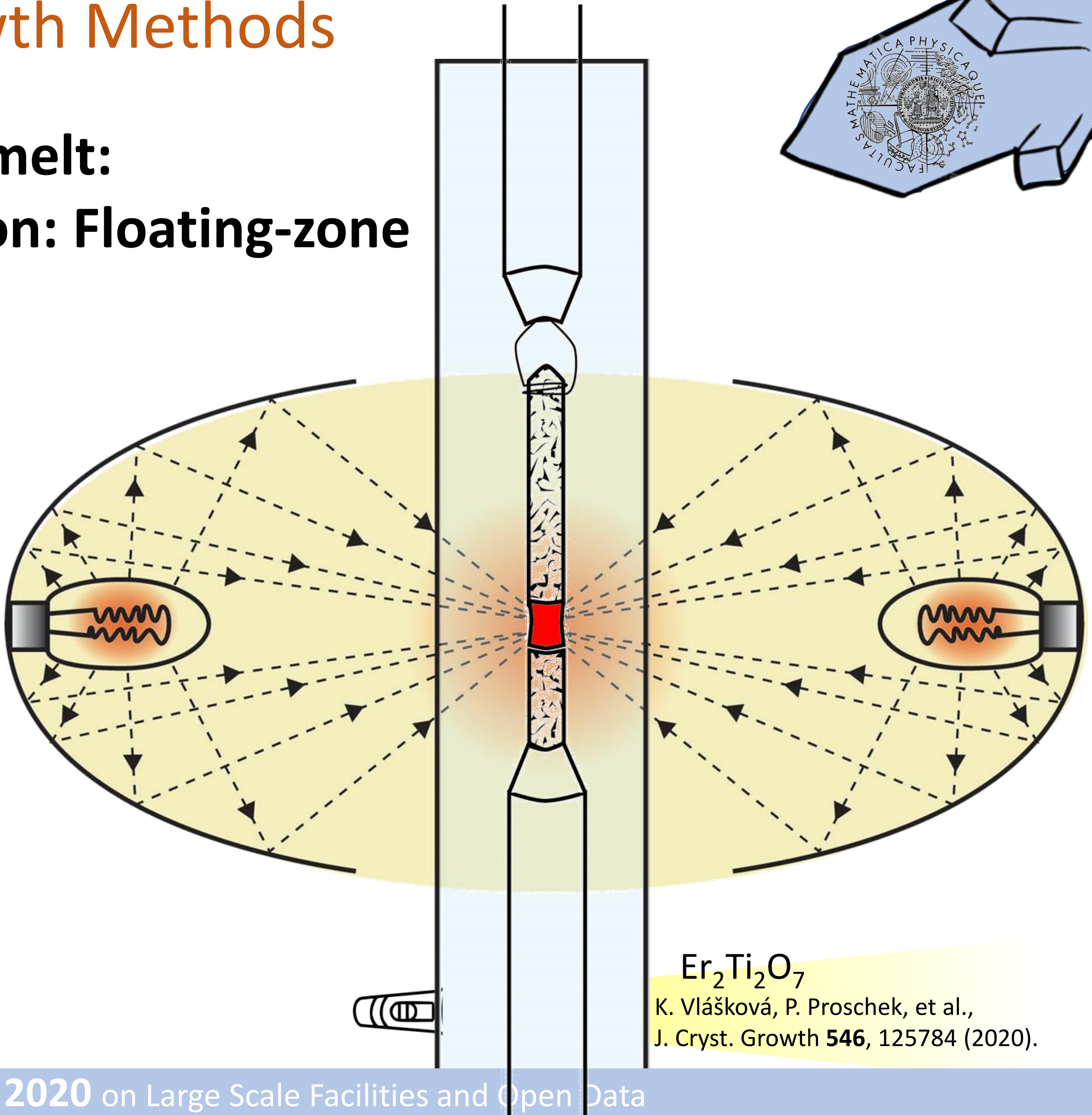
Suitable for incongruently melting materials

Minimal vessel contamination

Cons:

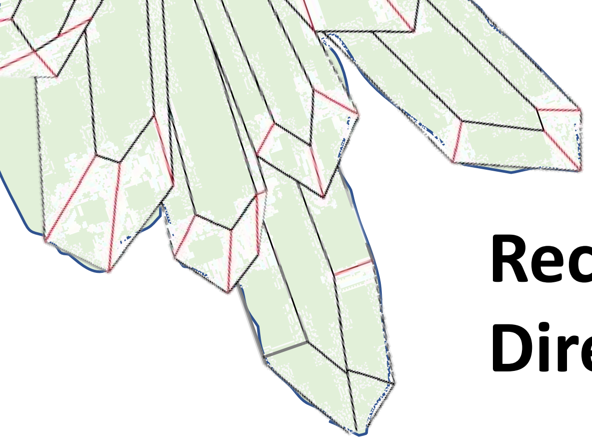
Complex setup

Not possible for volatile compounds



$Er_2Ti_2O_7$

K. Vlášková, P. Proschek, et al.,
J. Cryst. Growth **546**, 125784 (2020).



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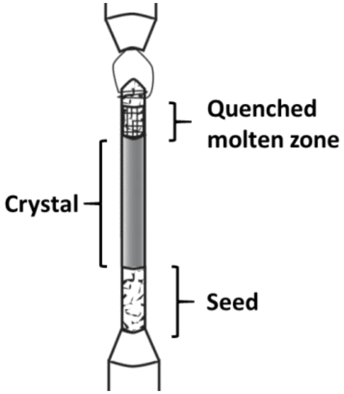
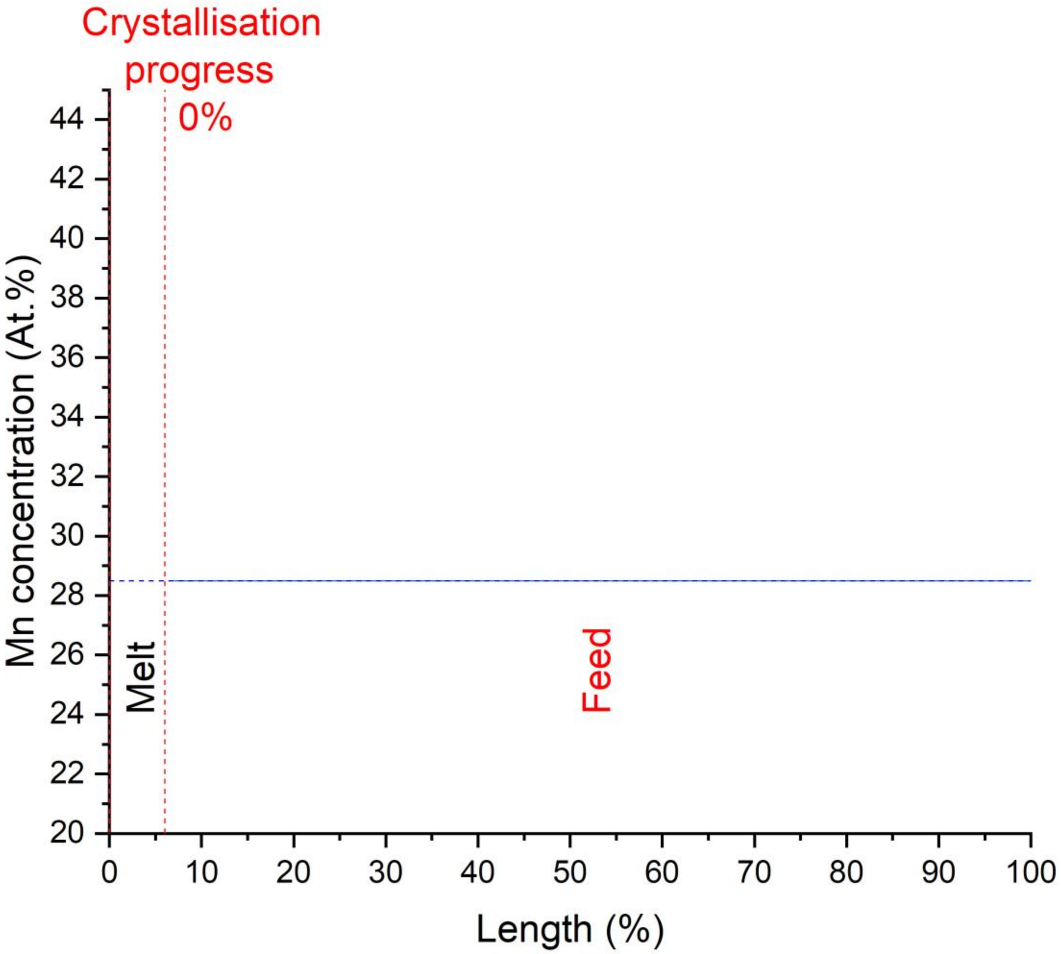
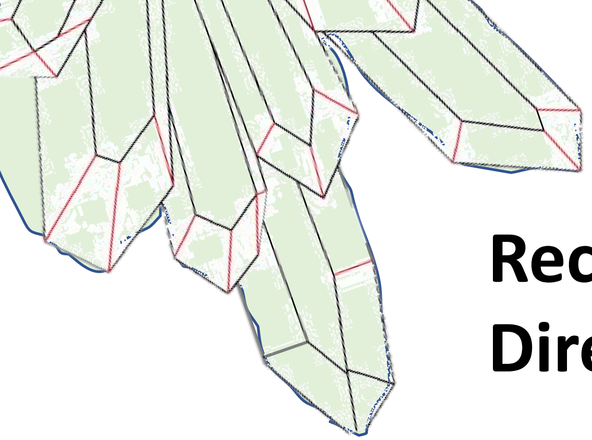


$$c_s(f) = c_0\left[1-(1-k)e^{\left(-k\frac{f}{l}\right)}\right]$$





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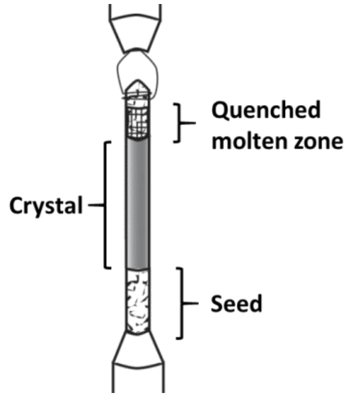

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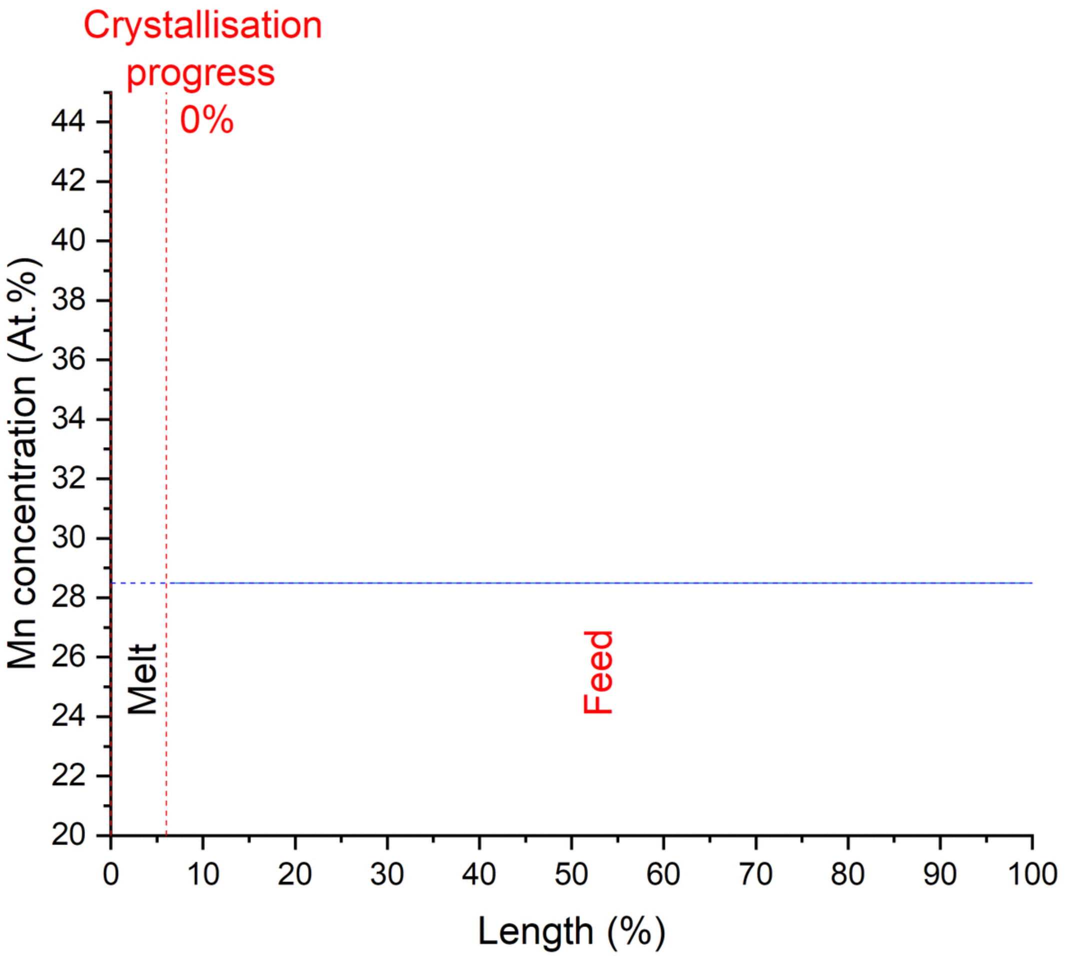

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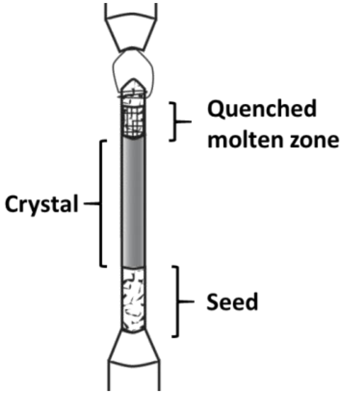

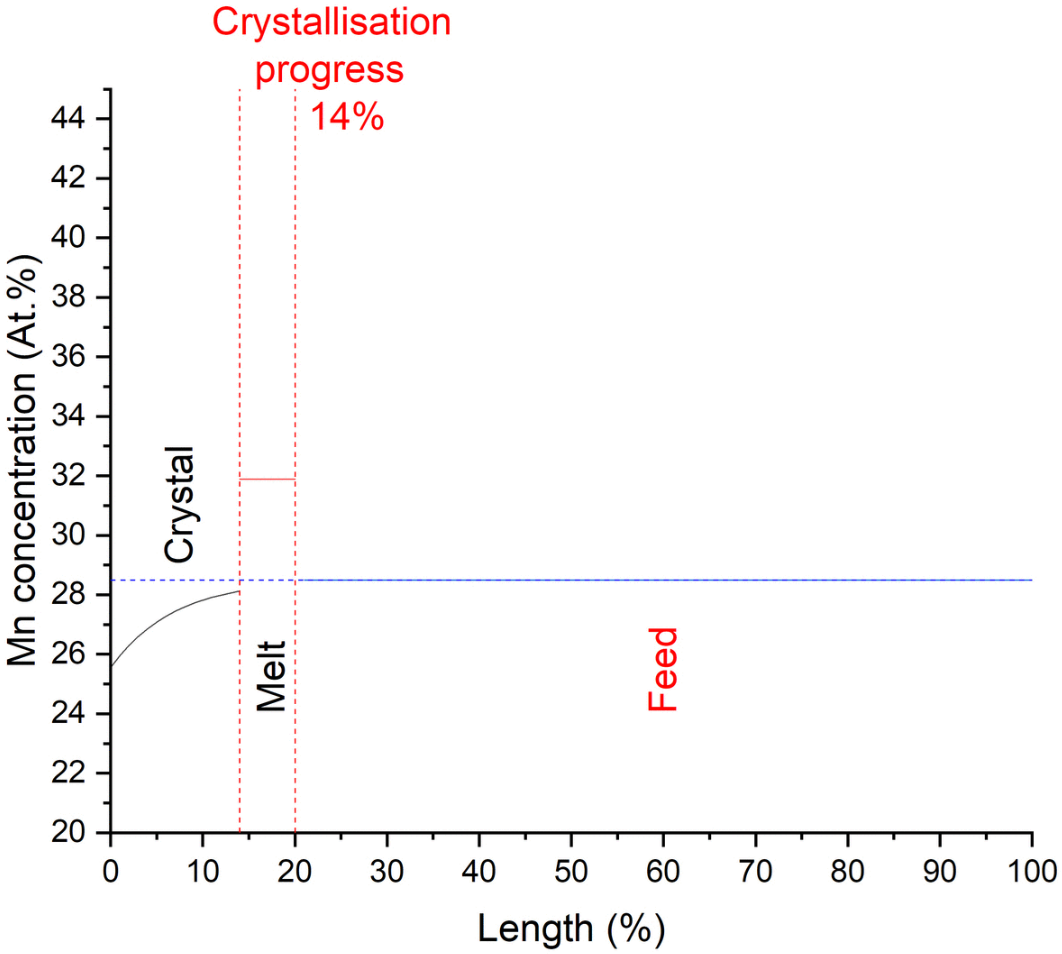

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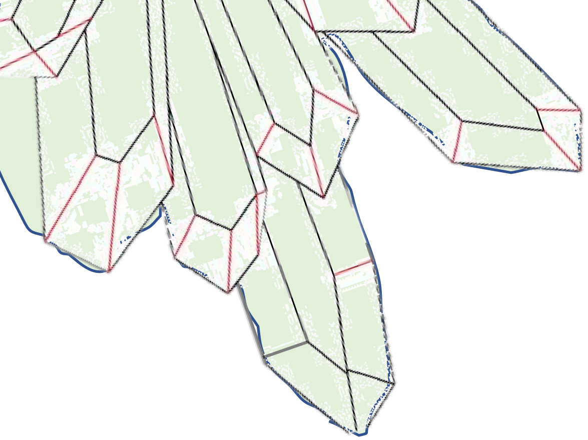
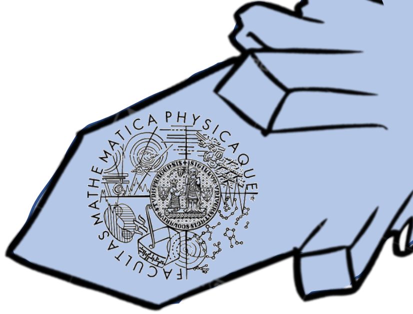


Practical Growth Methods



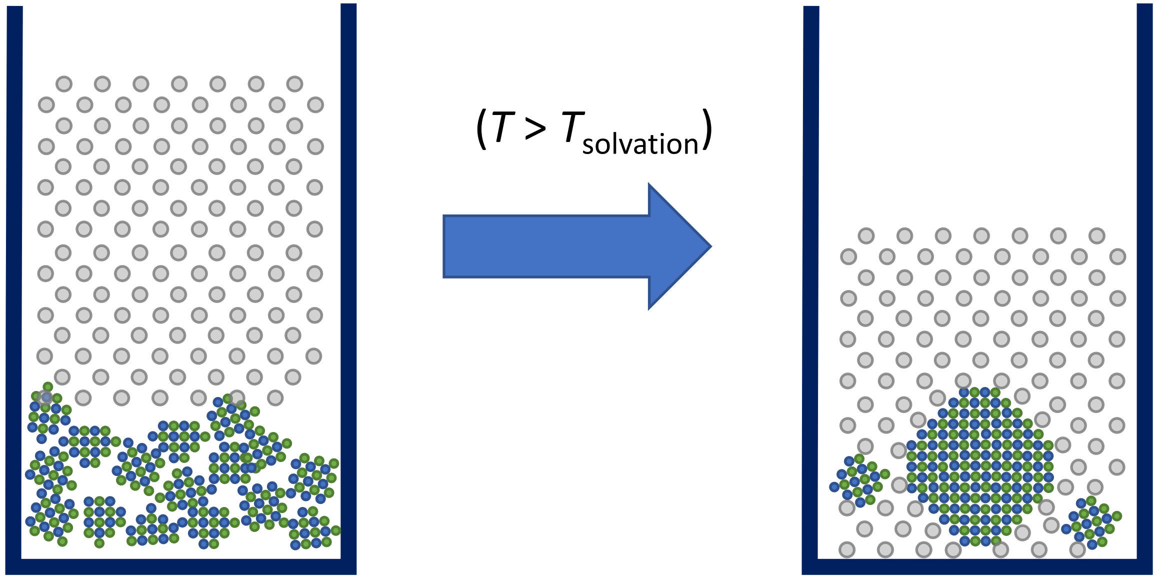
Flux growth

Flux choice:

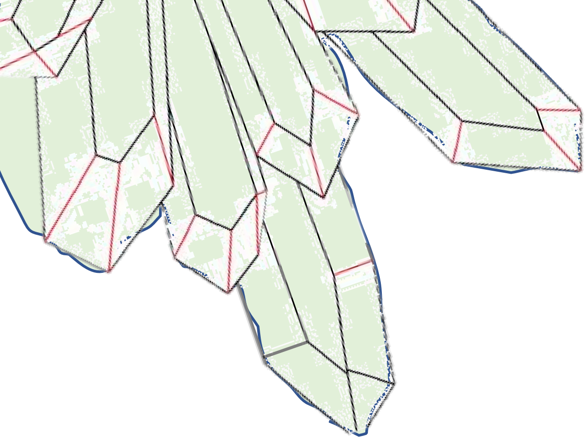
Low melting point

Capable of dissolving chosen material

Un-reactive (towards compound)



($T > T_{\text{solvation}}$)



Practical Growth Methods

Flux growth

Pros:
Simple

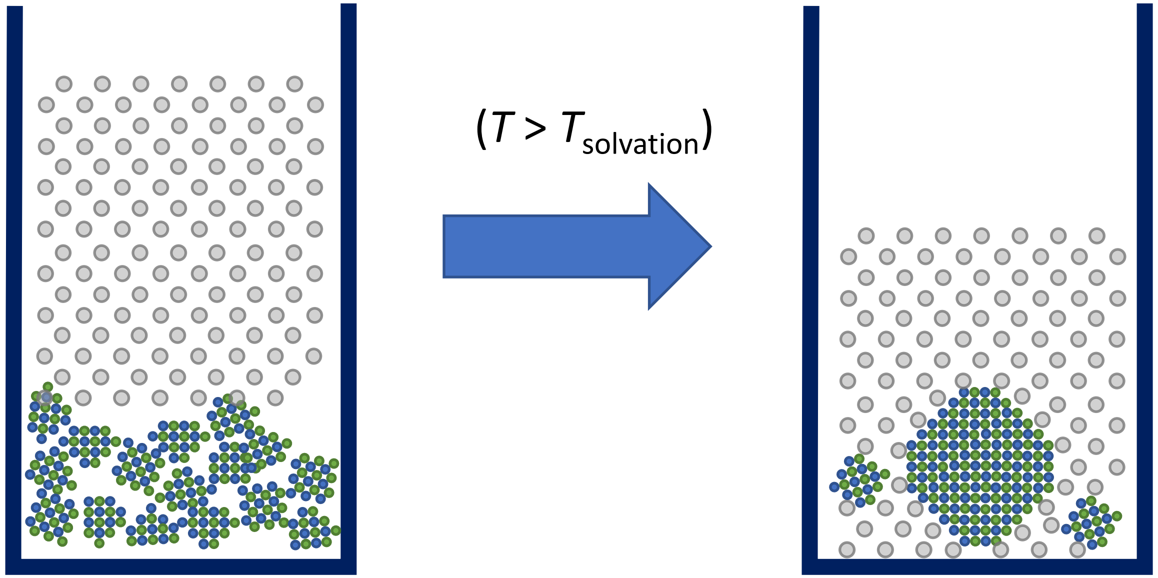
Incongruently melting materials can be prepared

Cons:
Flux choice can be difficult

Nucleation is not controlled

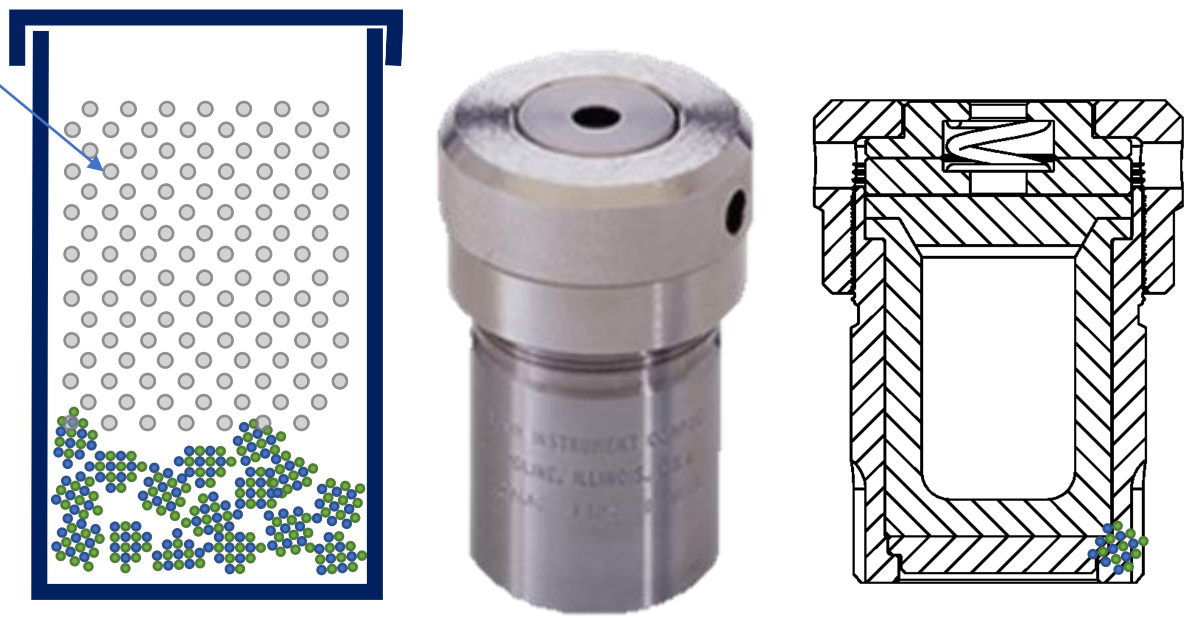
Sample must be separated from the flux

Sample can be contaminated by flux



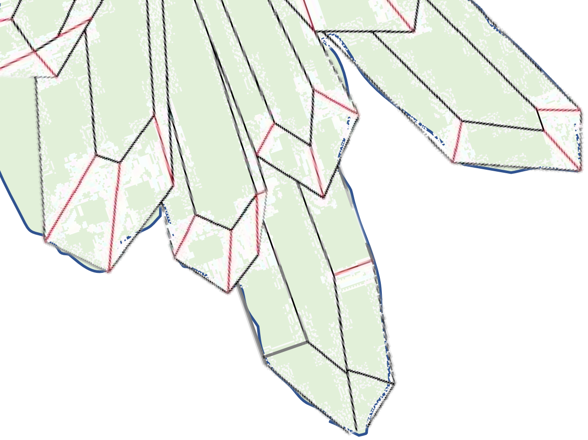
Practical Growth Methods

Hydrothermal (Flux = water) growth



Water (+ mineralising agent)

γ-$Cu_3Mg(OH)_6Cl_2$
R. H. Colman, A. Sinclair, et al., Chem. Mater. **23**, 1811 (2011).



Practical Growth Methods

Hydrothermal (Flux = water) growth

Pros:

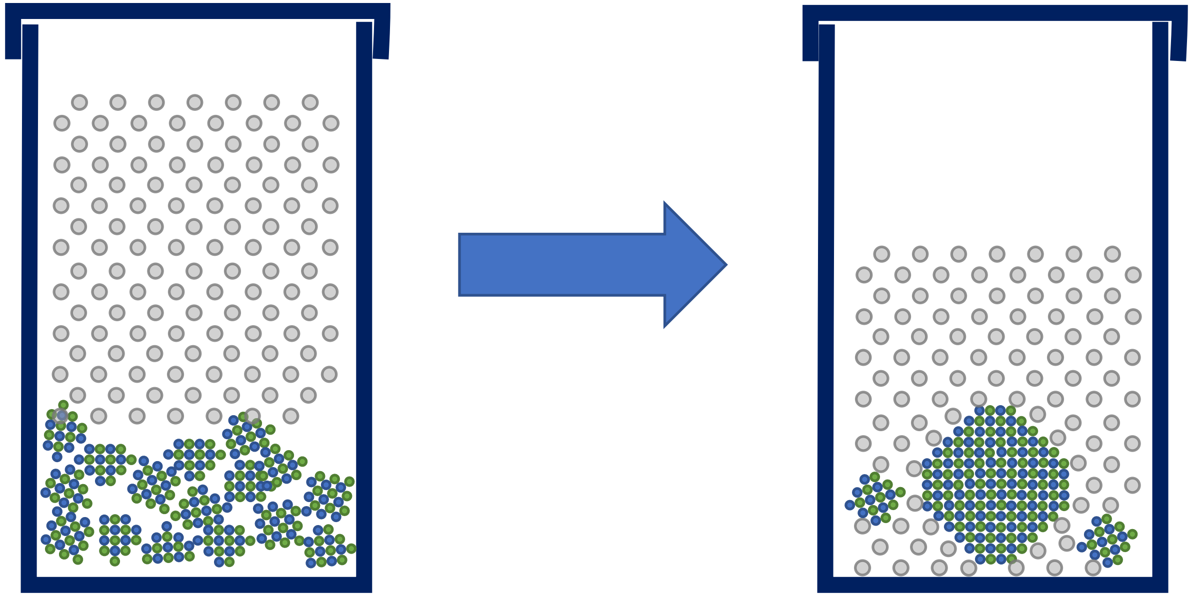
Simple

Materials that decompose before melting can be prepared

Cons:

Many parameters to test:

- Temperature (and ramp)
- Concentration(s)
- Mineralising agent
- Fill level (pressure)



γ-$Cu_3Mg(OH)_6Cl_2$

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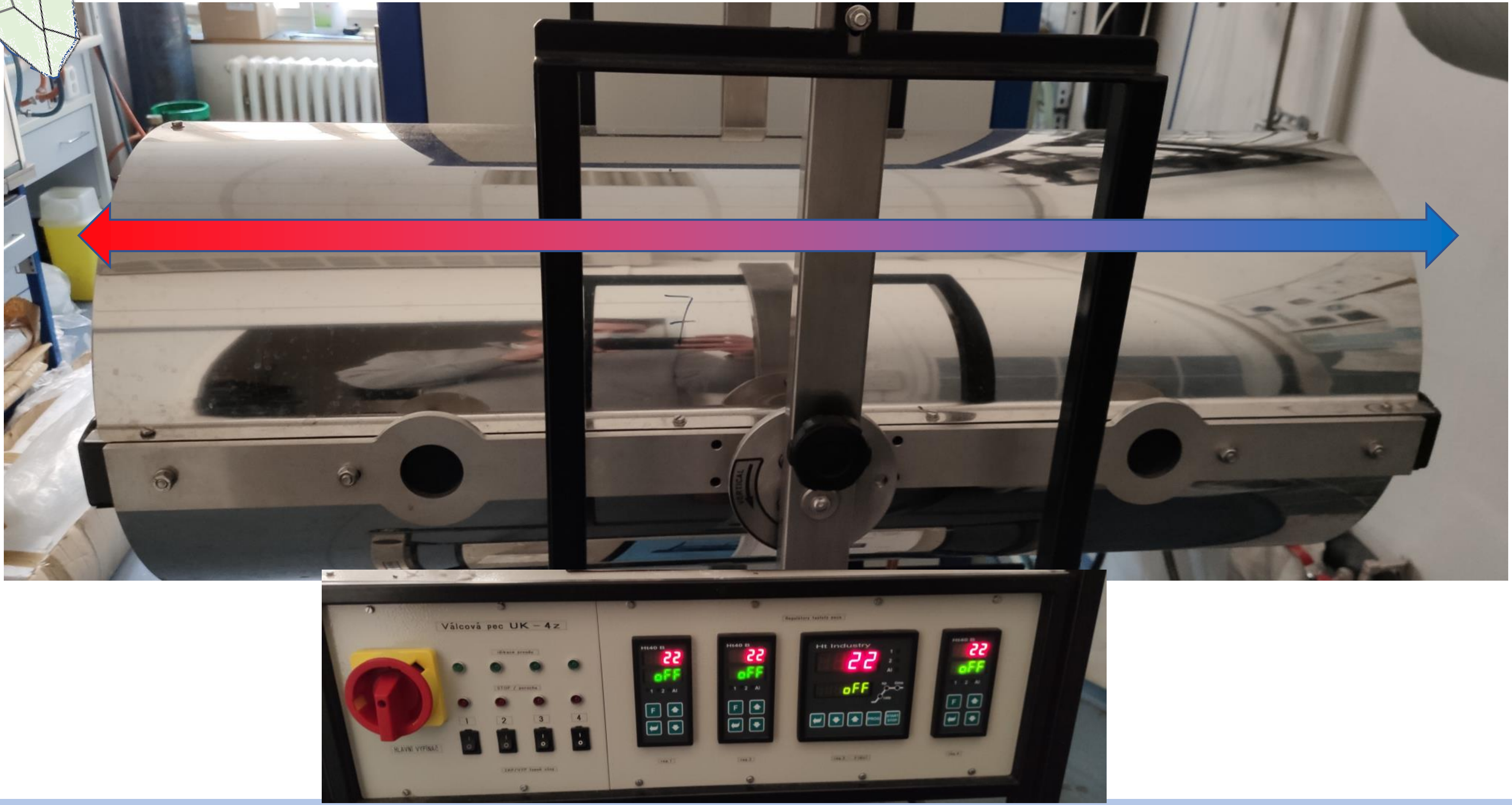
Practical Growth Methods

Chemical transport



Practical Growth Methods

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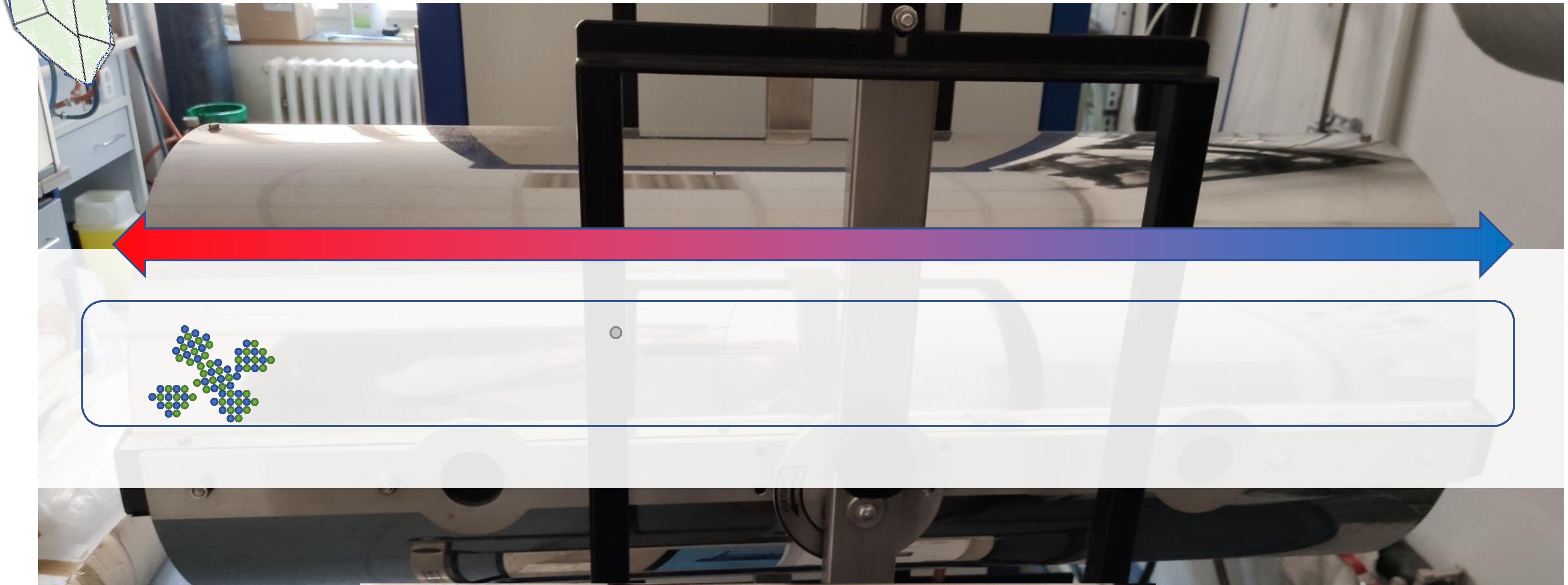

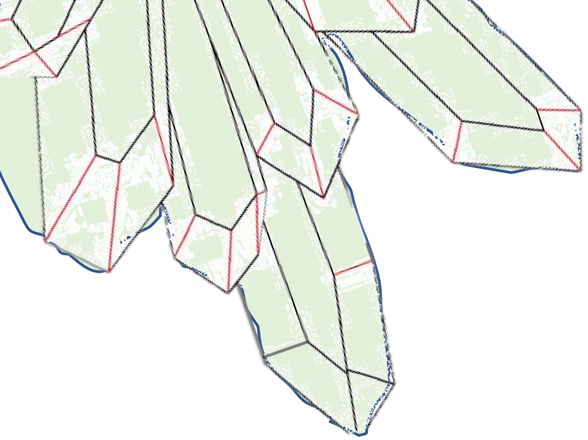

Practical Growth Methods

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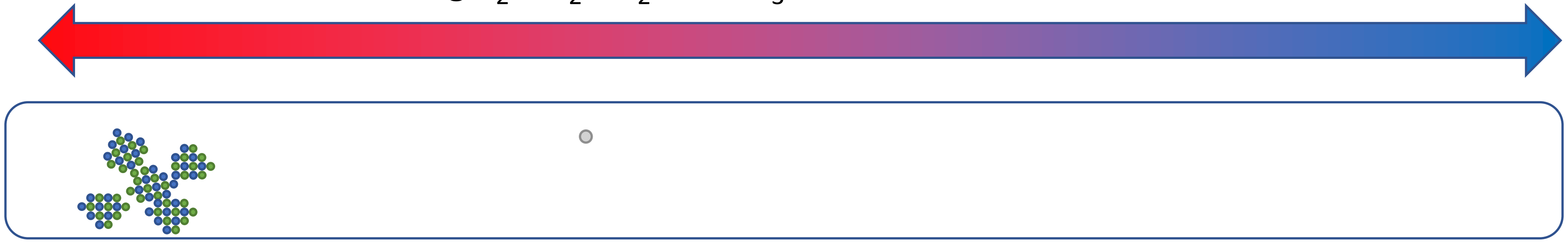
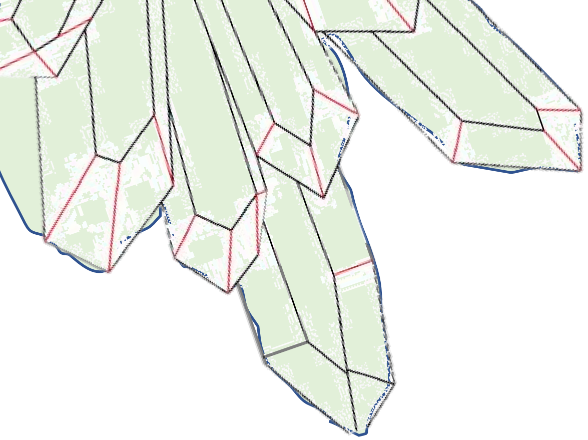


Transport agent
e.g. I_2 , Cl_2 , O_2, S, $AlCl_3$



Practical Growth Methods

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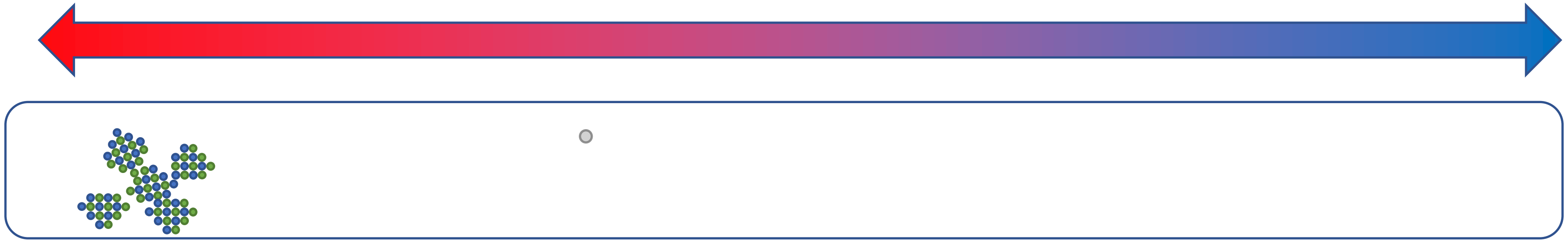
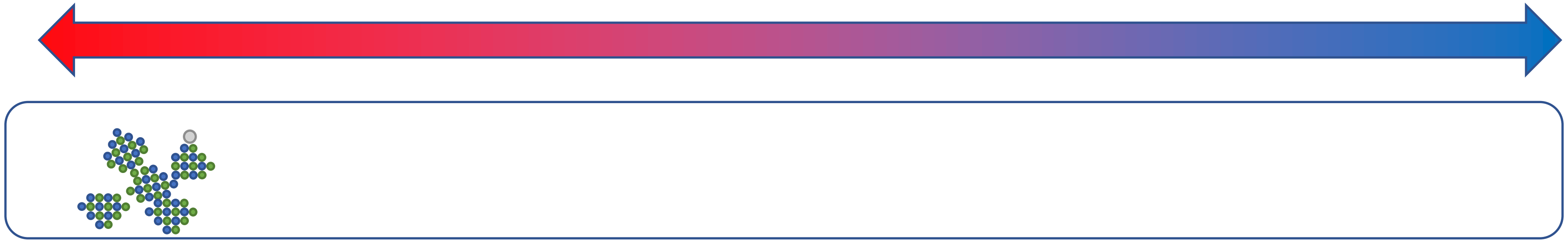
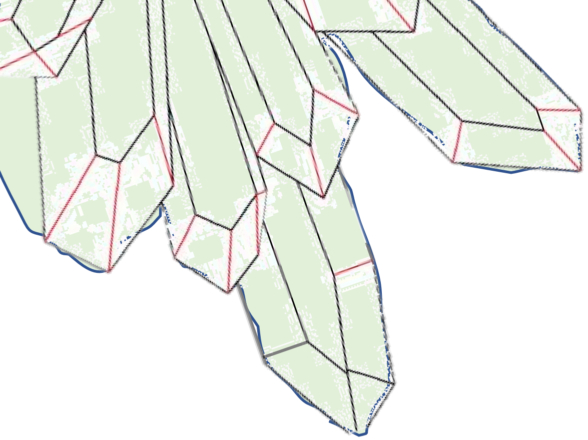


Practical Growth Methods

Chemical transport





Practical Growth Methods

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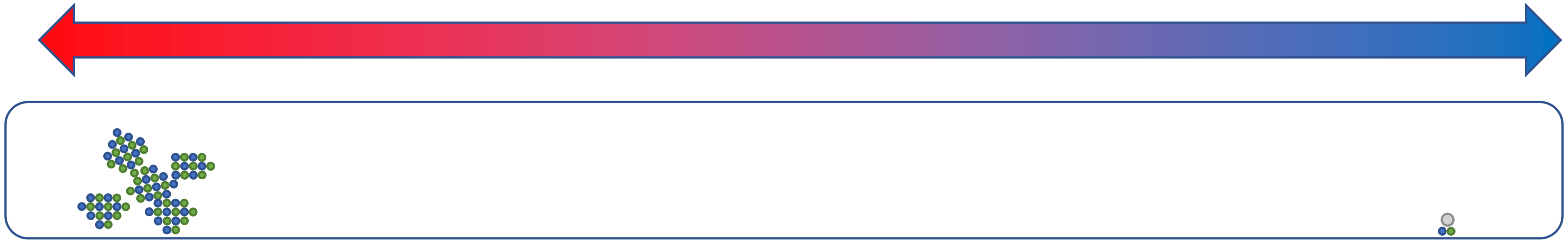
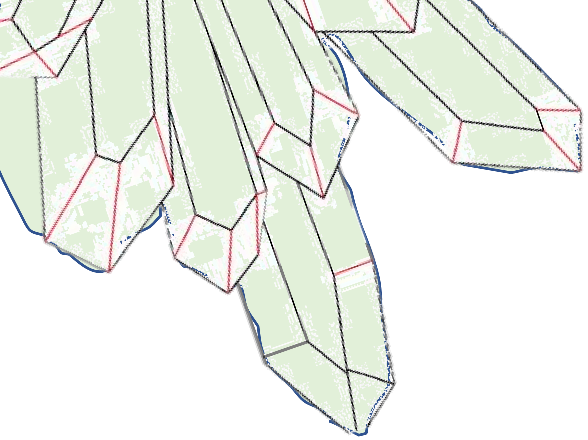
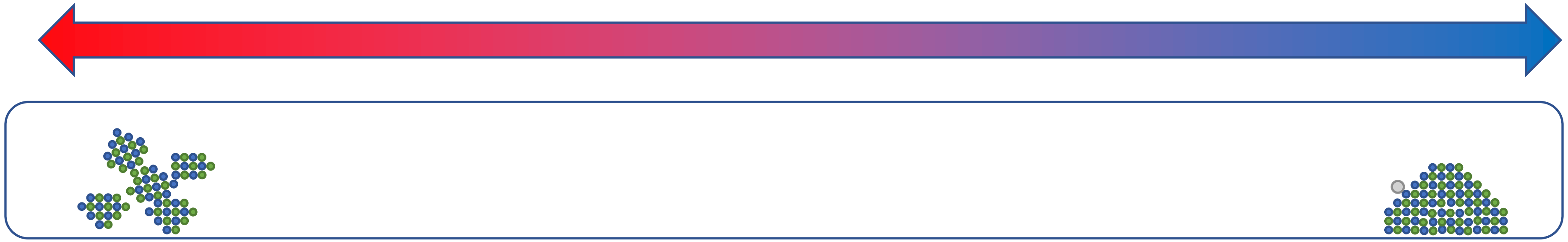
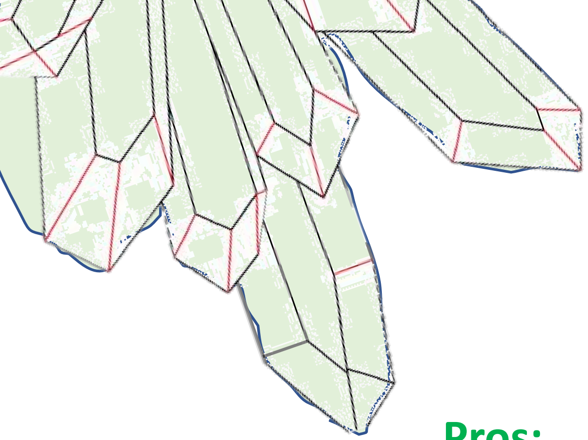




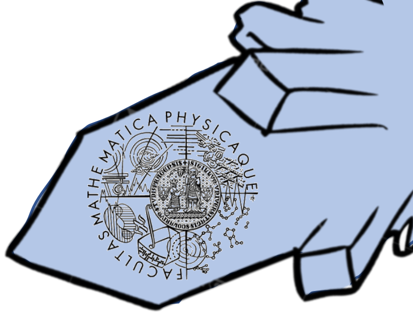
Practical Growth Methods

Chemical transport





Practical Growth Methods

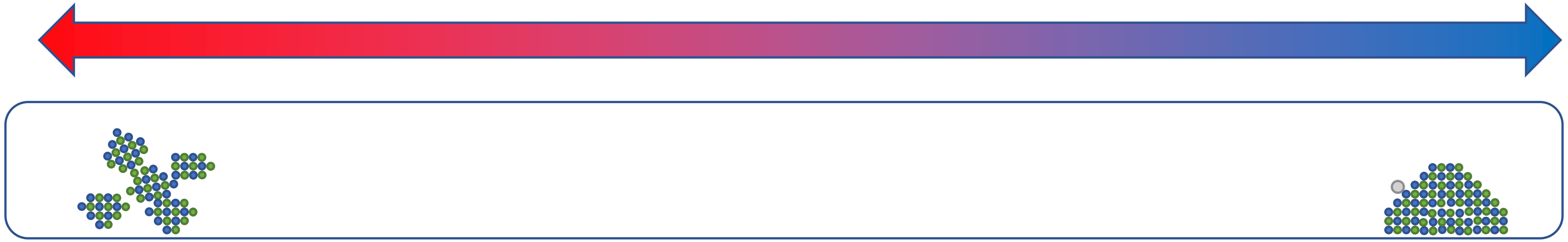


Chemical transport

Pros:

Large, high quality crystals

Compounds can be volatile

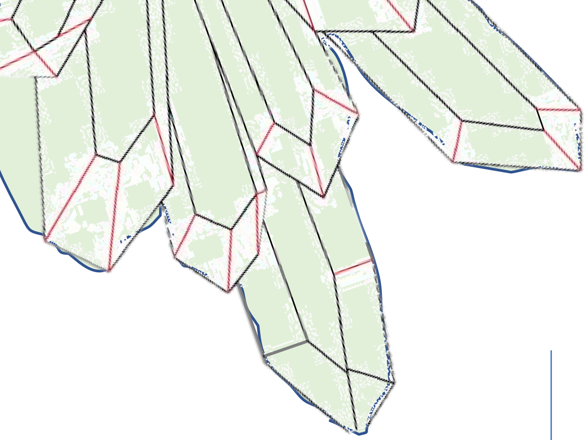


Cons:

Many parameters to test:

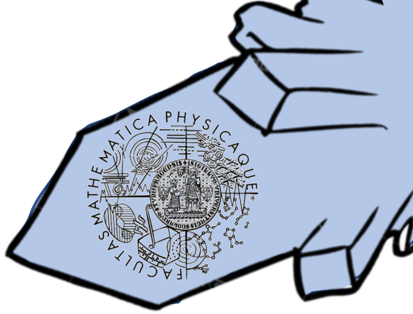
- Temperature (and gradient)
- Concentration(s)
- Transport agents

Slow process



Getting Atoms Moving

Recrystallisation



Solid

Solid-State Reorganisation
($T < T_{melt}$)

Liquid

Melting
($T > T_{melt}$)

Dissolving
($T > T_{solvation}$)

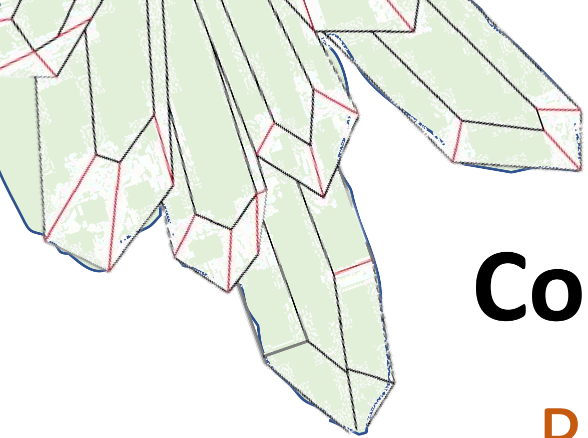
Flux
(reduced the energy barrier to reorganisation)

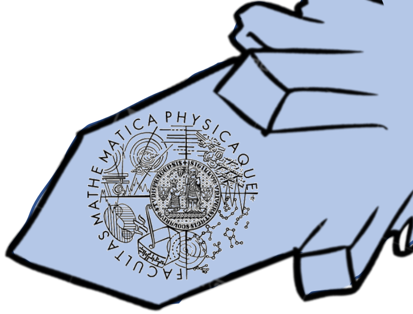
$E_{fusion} > E_{solvation}$

Gas

Sublimation/Condensation
($T > T_{vap}$)

Chemical transport
($T < T_{vap}$)





Conclusions

Practical Growth Methods

Solid

- Solid state reorganisation

Liquid

- Melt
- Bridgeman-Stockbarge
- Czochralskii
- Floating zone
- Flux
- Hydrothermal

Gas

- Chemical transport
- Condensation