Crystal Growth by Floating Zone Technique

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Outline

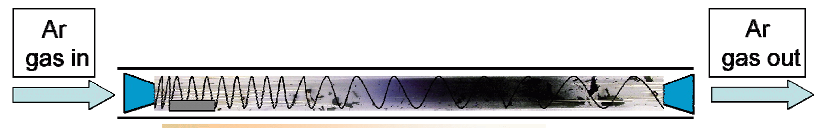
- Introduction to Crystal Growth Techniques
  - Polycomponents
  - Monocomponent
- Liquid-Solid Monocomponent Growth Techniques
- Floating-Zone Technique
  - Description of the Equipment
  - Sample Preparation
  - Growth Preparation
  - Sample Growth
- Characterization
  - Crystallinity
  - Determination of composition
- Bibliography
- Conclusions

Crystal Growth Techniques (1)

- Polycomponents
  - Solid-Solid
    - Precipitation from solid solution
  - Liquid-Solid
    - Growth from solution (evaporation, slow cooling, temperature differential)
    - Growth by reaction (same media, temperature change, concentration change)
  - Gas-Solid
    - Growth by reversible reaction (temperature change, concentration change)
    - Growth by irreversible process (epitaxial process)

Crystal Growth Techniques (2)

- Monocomponent
  - Solid-Solid
    - Strain annealing
    - Devitrification
    - Polymorphic-phase change
  - Gas-Solid
    - Sublimation / Condensation
    - Sputtering



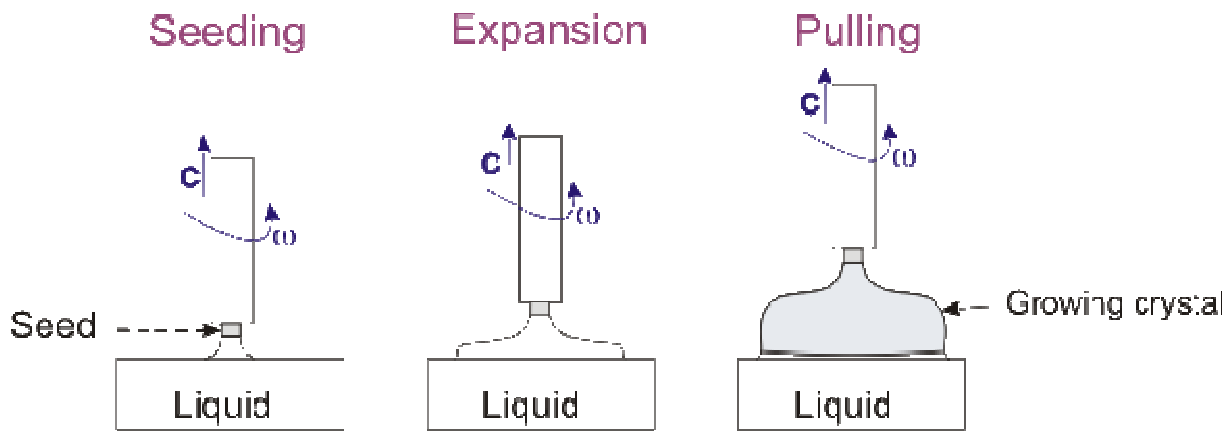
  - Liquid-Solid (melt)
    - Directional solidification
    - Cooled seed
    - Pulling
    - Zoning
    - Verneuil

Directional solidification, Cooled seed, Pulling: Conservative

Zoning, Verneuil: Non-conservative

Melt Growth (1)

Czochralski



Advantages

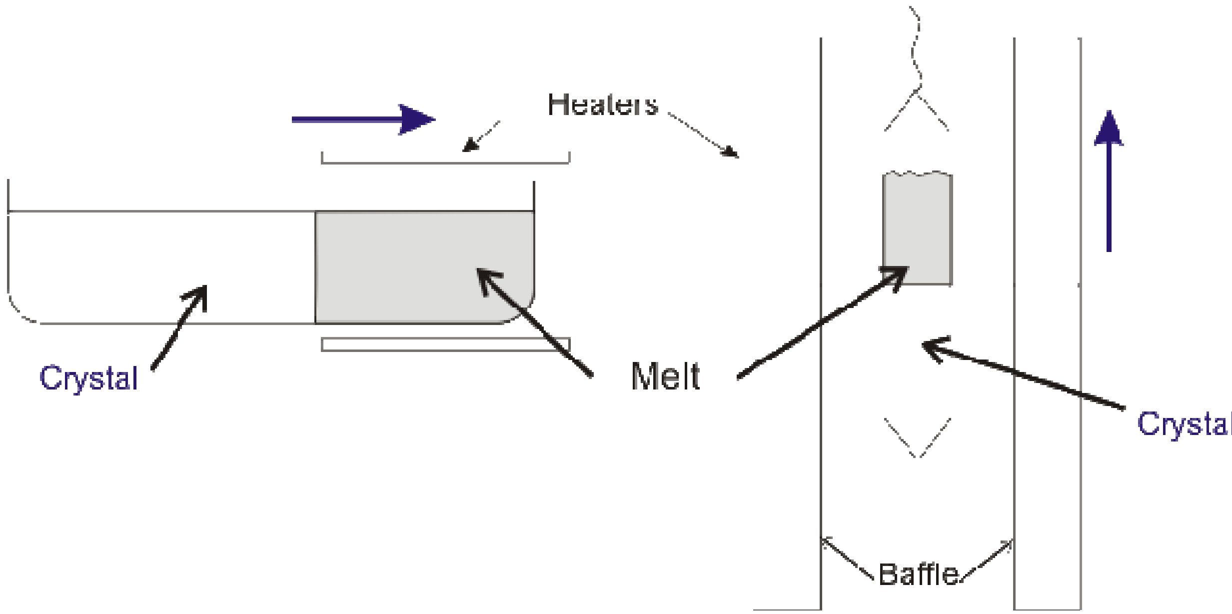
- Growth from free surface
- Growth of large *oriented* single crystals
- Convenient chemical composition
- Control of atmosphere

Limitations

- High vapor pressure materials
- Liquid phase encapsulation
- Possible contamination of the melt by the crucible
- No reproducibility of the crystal shape

Melt Growth (2)

Bridgman



Advantages

- Simple technique
- Control of vapor pressure
- Containers can be evacuated and sealed
- Control of shape and size of crystals
- Stabilization of thermal gradients

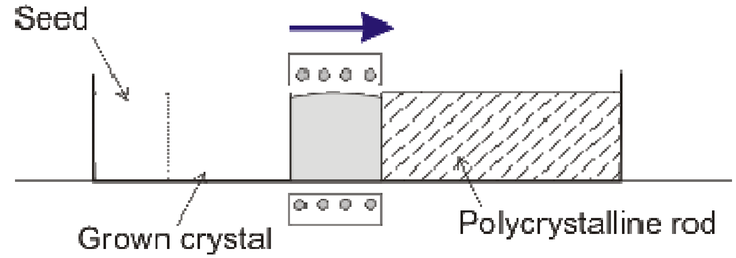
Limitations

- Confinement
- Thermal expansion container vs crystal
- Crystal perfection is not better than the one of the seed
- No visibility

Melt Growth (3)

Zone-melting

- Traveling Zone
- T Gradient close to the growth interface
- Pfann (1952), purification technique



Advantages

- Control of impurities while growth
- Reduce contamination of the melt by the crucible
- Less heater power
- Uniform doping obtained by zone-refining
- Increase of grain size by zone refining

Limitations

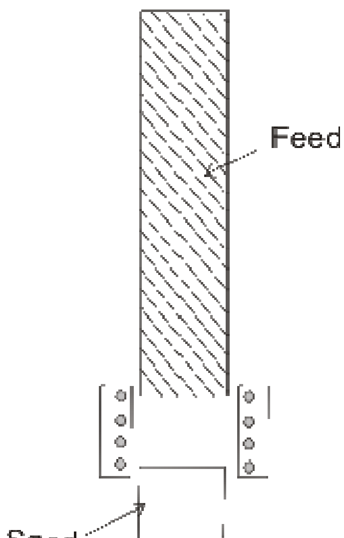
- Contamination from crucible
- Thermal and Volume expansion

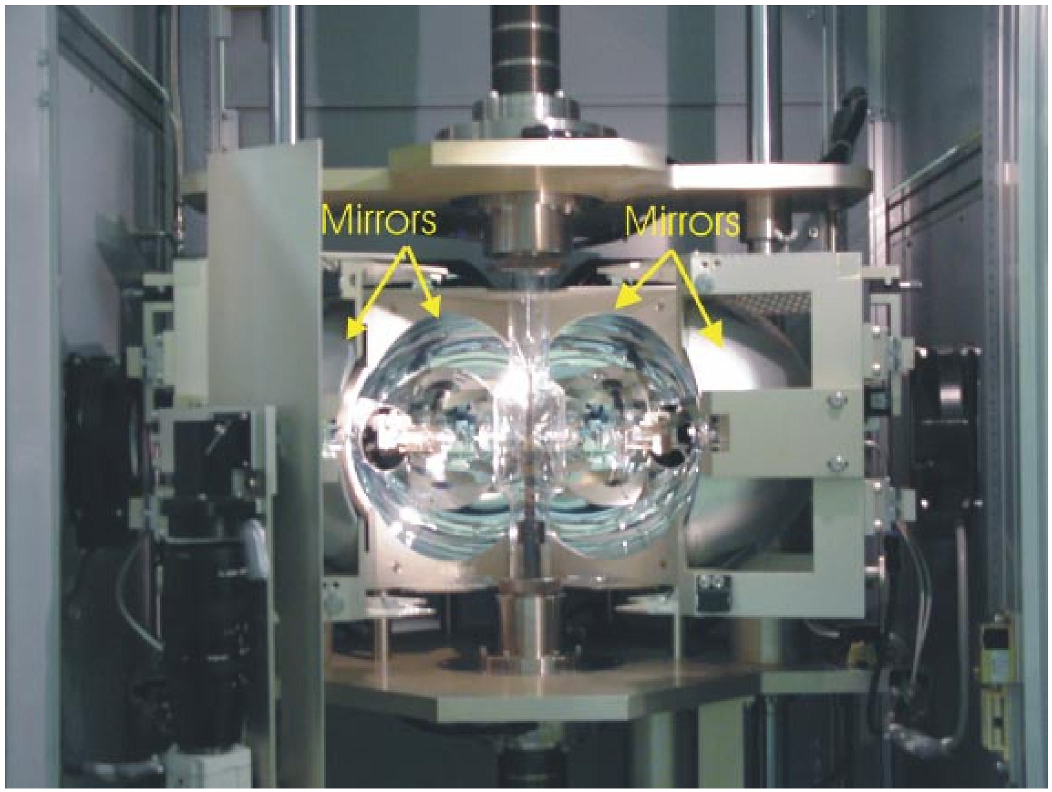
Float Zone Technique

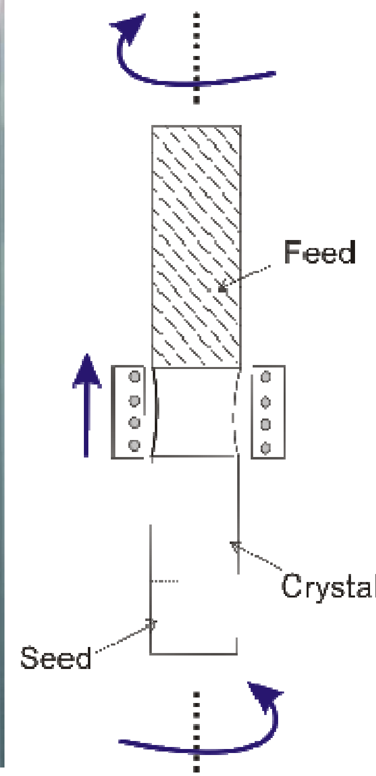
(FZT)

FZT (1)

Setup







FZT (2)

Setup

2-mirror Halogen lamps furnace

Max. Pressure = 3 atm

Max grown size: 80 mm length, 8 mm diameter

Growth rates: 0.25 - 10 mm/hr

Power: 400 W - 3500 W (2150°C)

4-mirror furnace

Halogen lamps (Uniform heating, better spatial definition of the hot zone)	**Xenon HP lamp** (Uniform radial illumination; very well defined vertical power profile)
Power: 800 – 6000 W (2200°C)	Power: 5.4 kW (2800°C)

Max. Pressure = 10 atm → Growth of materials with higher vapor pressures.

Max grown size: 150 mm length, 10 mm diameter (more for Xe-lamp)

Growth rates: From 0.1 to 20 mm/hr

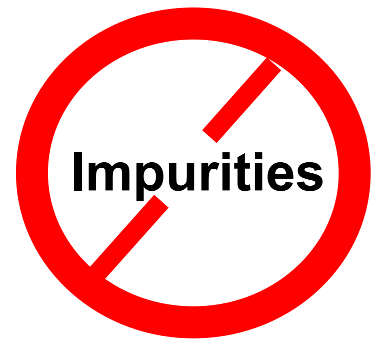
Turbo pump → Vacuum down to 10^{-6} mbar

Sample chamber can be filled with inert, reductive, oxidizing atmospheres

FZT (3)

Sample Preparation

- Starting material:
  - ≈ 20g of thoroughly ground powder
  - Raw compound ($RTiO_3$)
  - Annealed material ($RMnO_3$)
  - Partially annealed material (RVO_3)



- Feed rod preparation:
  - Fill a rubber tube of desired diameter with the powder
  - Slightly tight the end of the tube, make sure the diameter of the rod is constant
  - Pump (progressively) the air remaining in the tube
  - Seal the rubber tube
  - Press the rod with an isostatic press (500 ~ 600 bar)
  - Remove the rubber band

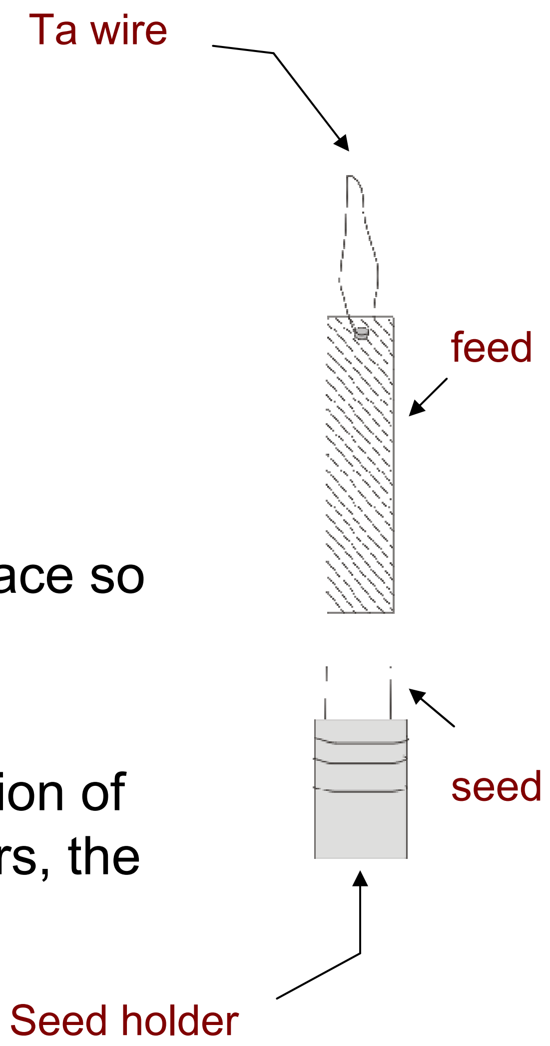
FZT (4)

Sample Preparation

- Seed preparation:
  - Single crystal from a previous growth
  - Polycrystal from a previous growth
  - Part of the feed
  - Single crystal from a similar compound
  - Necking

- Rods of seed and feed are mounted in the furnace so as to be perfectly aligned.

- A very clean work environment for the preparation of the rods, the mounting in the furnace, the mirrors, the lamps, the quartz tube is extremely important



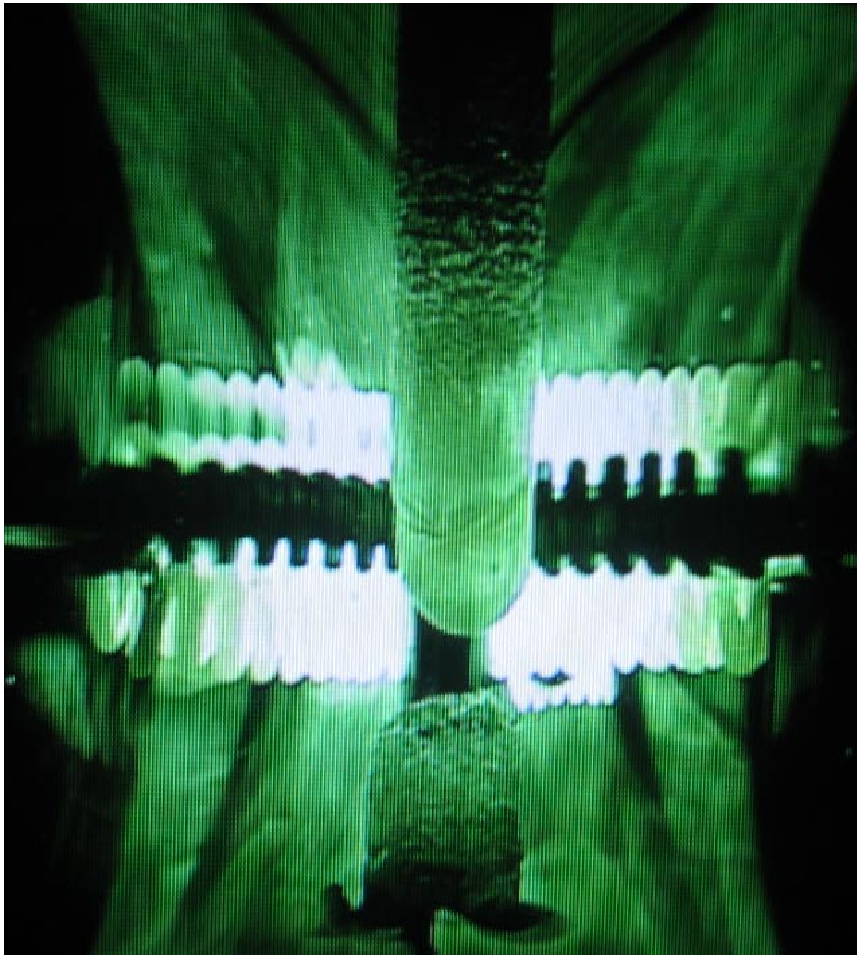
FZT (5)

Growth Preparation

- Evacuation of the sample chamber (10^{-6} mbar)

- Choice of atmosphere and pressure
  - $RTiO_3$: 2 atm 95% Ar, 5%H_2
  - $RMnO_{3\ hex.}$: 1 atm air + 0.5 atm O_2
  - $RMnO_{3\ orth.}$: no evacuation, no flushing
  - RVO_3: 1.5 atm Ar
  - $TbMn_2O_5$: 6 atm O_2.

- Sintering
  - $RTiO_3$: 80% of growth power
  - $RMnO_{3\ hex.}$: 80% of growth power
  - $RMnO_{3\ orth.}$: 60-75% of growth power
  - RVO_3: 60% Power
  - $TbMn_2O_5$: 60% of growth power



FZT (6)

Growth Preparation

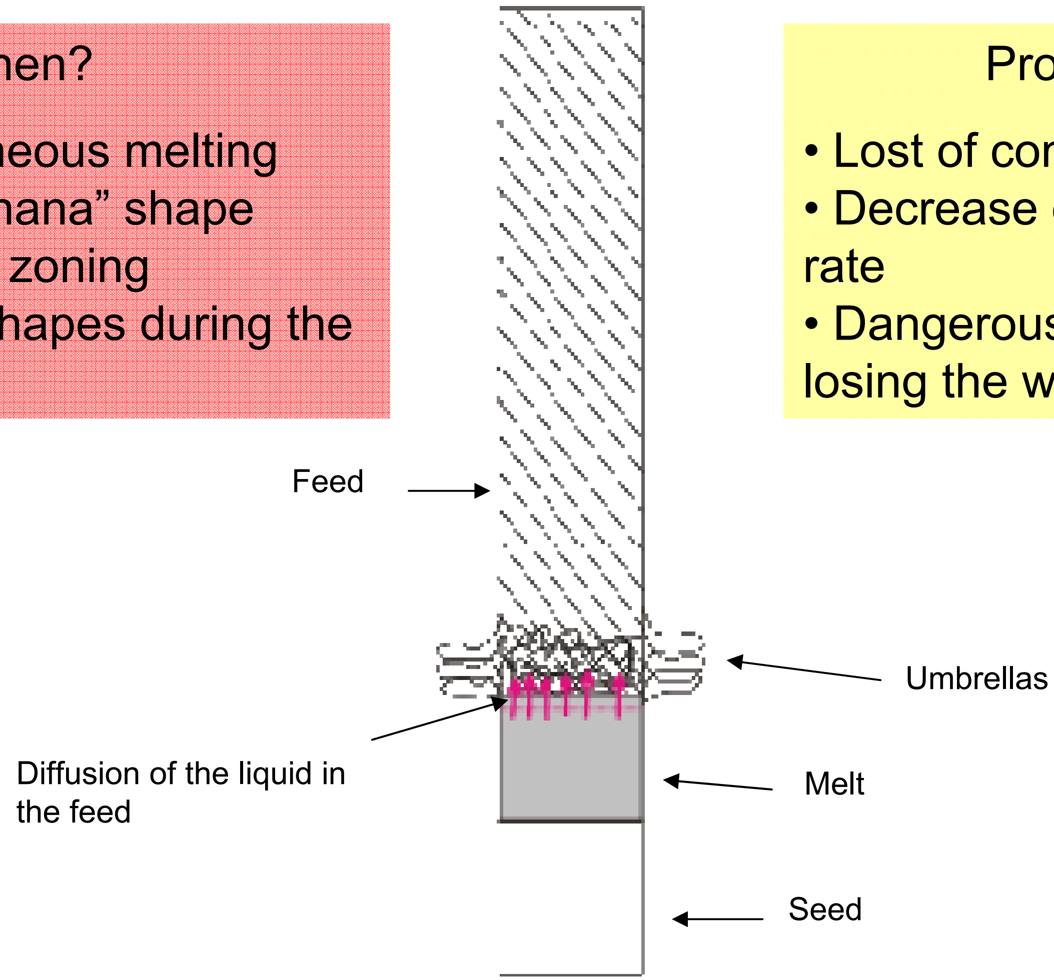
- Fast scanning (~30 mm/hr):

When?

- Inhomogeneous melting
- Rod in "banana" shape
- Insufficient zoning
- Umbrella shapes during the growth

Problem….

- Lost of composition
- Decrease of actual growth rate
- Dangerous, possiblity of losing the whole rod



FZT (7)

Crystal Growth

- Equilibrium in crystal growth

  - The crystal grown must be thermodynamically stable at T and P of crystallization.

  - Dependence of the melting point on pressure:

$$\frac{dP}{dT} > 0 \quad if \;\; \Delta V > 0 \quad and \; \Delta S > 0 \;\; for\ a\ melting\ process$$

$$From \;\; \Delta H = T\Delta S \; , \Delta H > 0 \Rightarrow Melting\ is\ endothermic$$

$$At\ equilibrium, \;\; \Delta G = 0 \Rightarrow T_{eq} = \frac{\Delta H}{\Delta S}$$

Melting point unique for any given pressure

  - Superheating is not possible
  - Very slight supercooling required for growth

FZT (8)

Crystal Growth

- Distribution coefficient

$$k_0 \equiv \frac{a_{s(eq)}}{a_{l(eq)}} \equiv \frac{C_{s(eq)}}{C_{l(eq)}}$$

- k_0 ~ equilibrium constant if the crystal is neither growing nor dissolving
- $a_{s(eq)}$:Equilibrium activity in the solid
- $a_{l(eq)}$:Equilibrium activity in the liquid

During growth, k_{eff} =effective distribution coefficient

Try to reach k_{eff}=1!!!

$$k_{eff} = \frac{C_{s(act)}}{C_{l(act)}}$$

Dependency

- growth rate
- diffusion constant of the material in the melt,
- width of the diffusion layer

FZT (9)

Crystal Growth

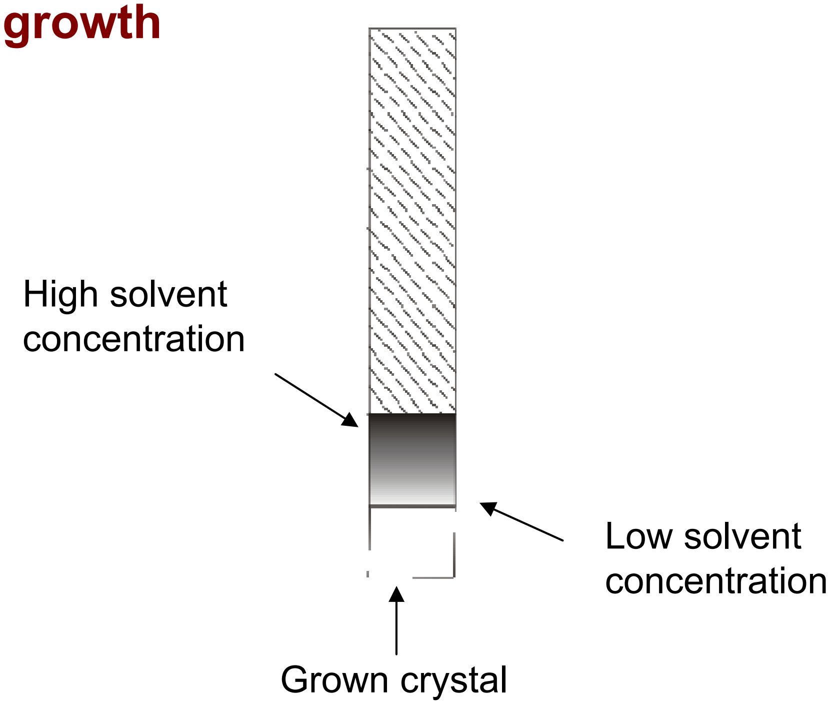
Control of the solvent in Traveling Solvent Float Zone technique:

Solvent used for lowering the melting point, or reduce incongruent melting….

Goal: keep the solvent all along the growth

If $k_{eff} > 1$

- Depletion of the solvent concentration close to the growing crystal
- Bulk of melt richer in solvent than growth region



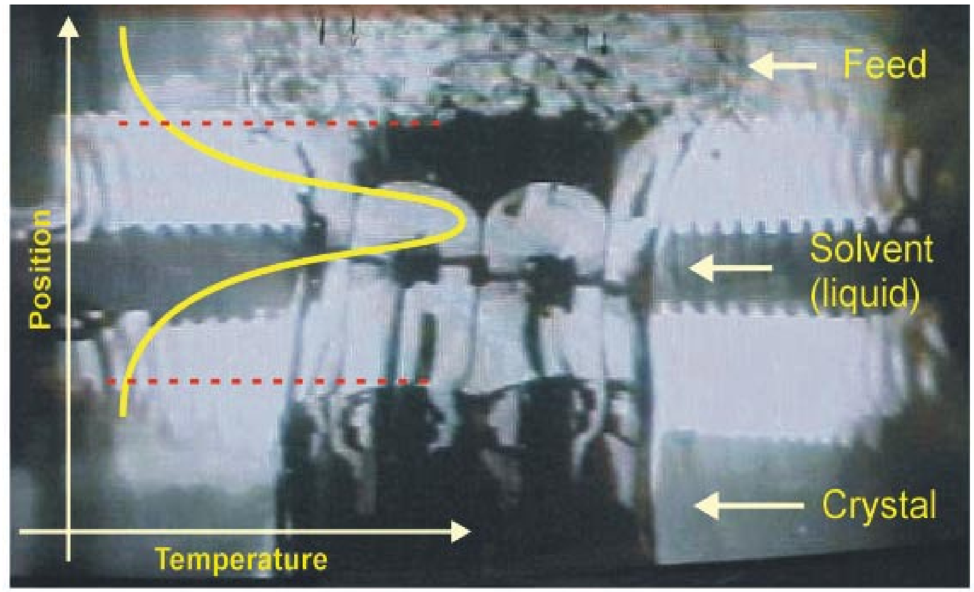
FZT (10)

Crystal Growth

- Stability conditions
  (Heywang-1956).

Include:

- ✓ surface tension,
- ✓ gravitational field,
- ✓ melt wetting the solid completely,
- ✓ negligible volume change



$$\lambda = l\sqrt{\frac{dg}{\sigma}} \quad and \quad \rho = r\sqrt{\frac{dg}{\sigma}}$$

- l= maximum zone length
- r= rod diameter
- d= density of liquid
- g= gravitational field
- σ= surface tension

As r ↗ λ approaches 2.7

If l > r : difficult to control melt zone

Stability: l~r and $l = \frac{1}{2.7}\sqrt{\frac{\sigma}{dg}}$

FZT (11)

Crystal Growth

- Stirring
  - Function of the melt viscosity
  - Rotation of the feed > seed (20 vs 15 mm/hr)
- Stability of the solid phase
  - Is the crystal to be grown the most stable phase?
  - Is the melting congruent?

YVO_3: incongruent melting when doped with Calcium

$TbMn_2O_5$: decomposes in $TbMnO_3$ and Mn_3O_4

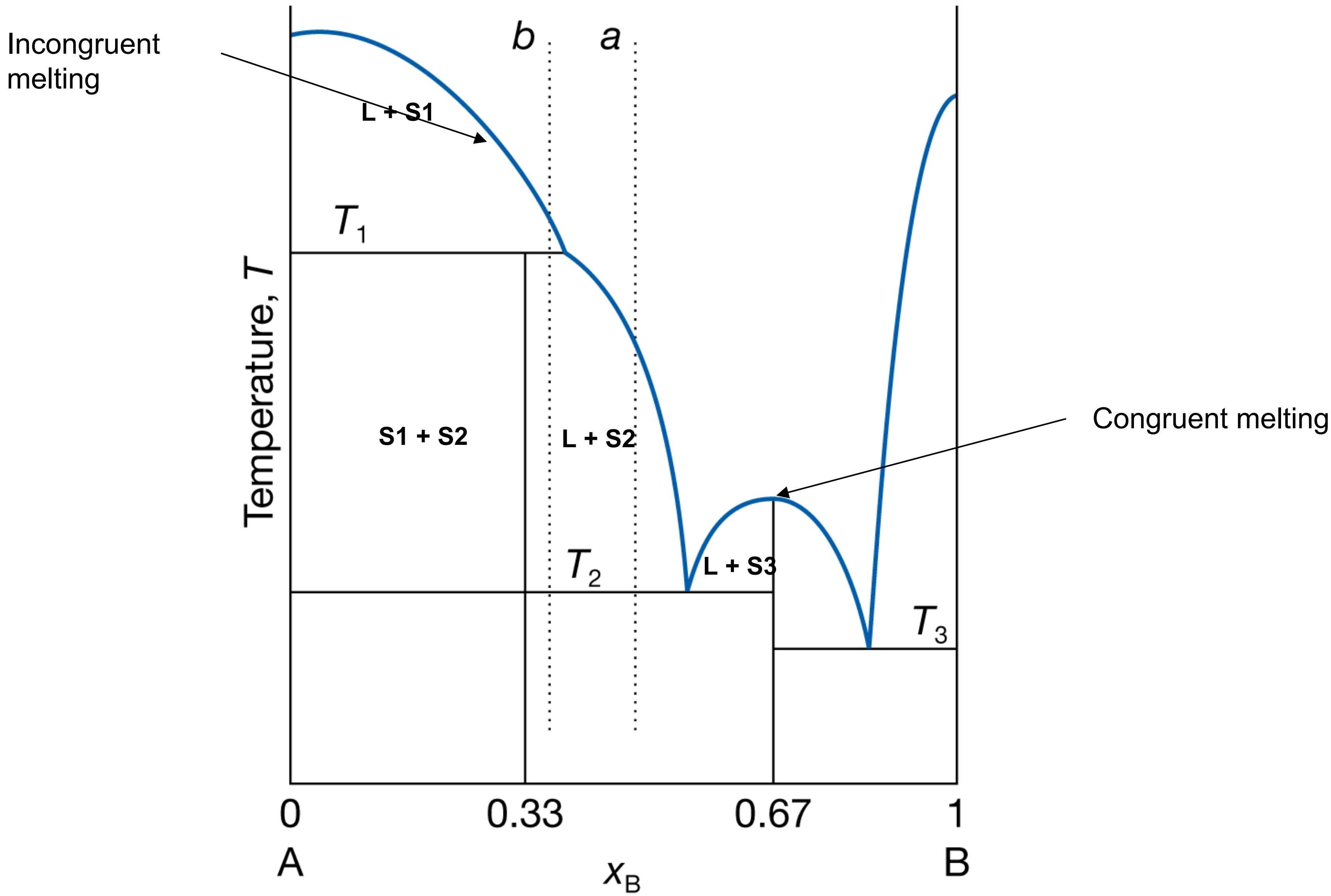
$BiFeO_3$: $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$ stable phases

→ Observation of the phase diagram

→ XRD of the melt and of the solid phase

FZT (12)

Crystal Growth



FZT (13)

Crystal Growth

- Vapor pressure
  - Increase the pressure of the sample chamber
  - Excess of the compound with the highest vapor pressure
- Power control and overflow

- Nucleation
  - Heterogeneous nucleation (seed polycrystalline, or monocrystalline neighbor material)

Nucleation ~~particles aggregation

Precursors of nuclei large enough to grow are formed by association of particles in the system.

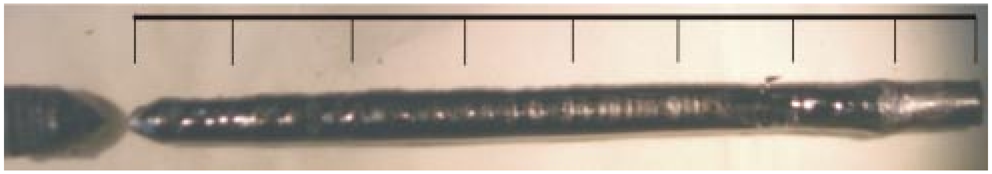
For a nucleating material A: $mA \leftrightarrow A_m$

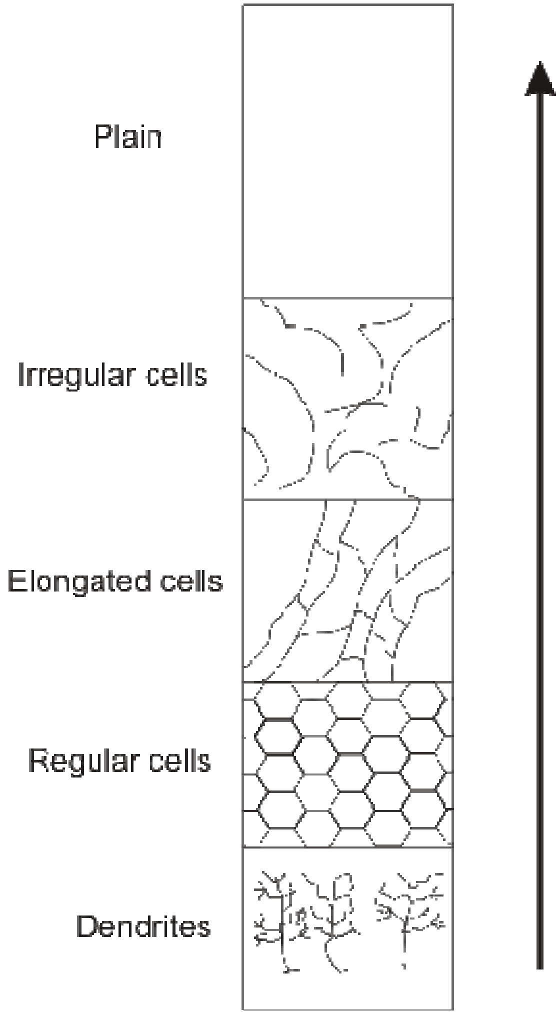
For large m and equilibrium constants: growth of nucleation!

FZT (14)

Crystal Growth

- Formation of cells
- Growth rate
  - $RTiO_3$: 5 mm/hr
  - $RMnO_{3\ orth.}$: 10 mm/hr
  - $RMnO_{3\ hex.}$: 4 mm/hr ; 1.5 mm/hr if doped with Ca.
  - RVO_3: 2 mm/hr
  - $TbMn_2O_5$: 1.5mm/hr

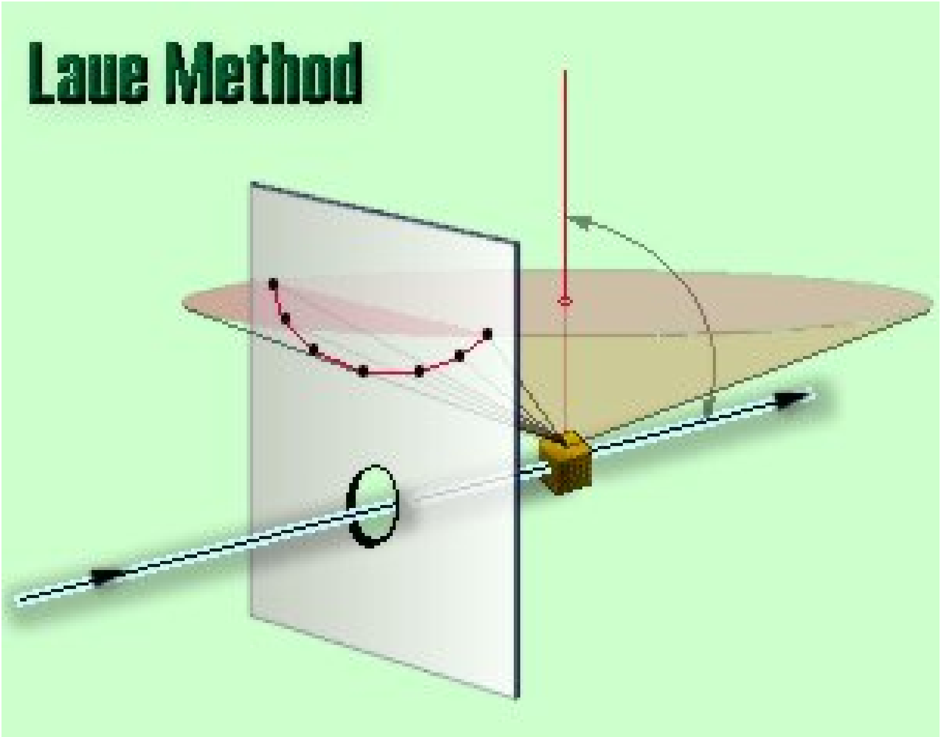




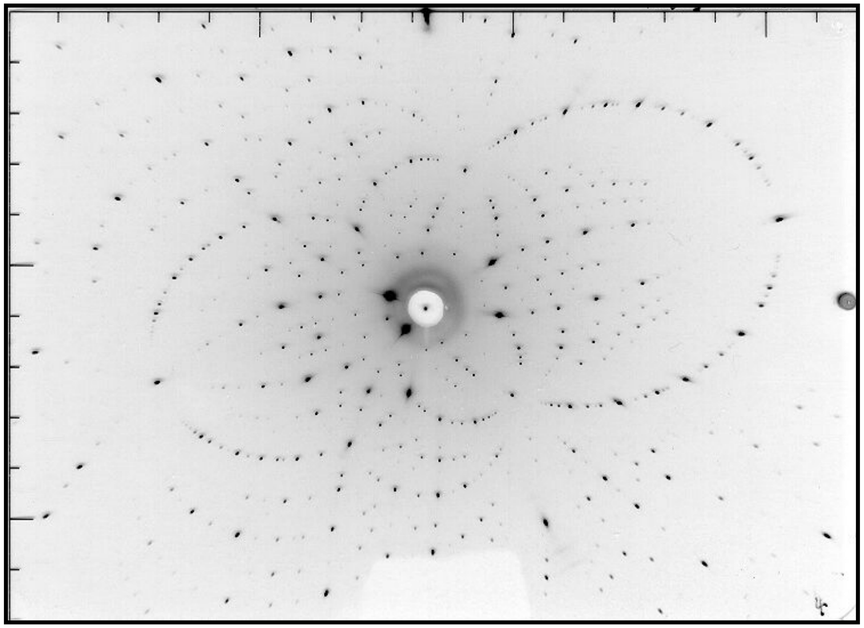
Characterization (1)

- Crystallinity

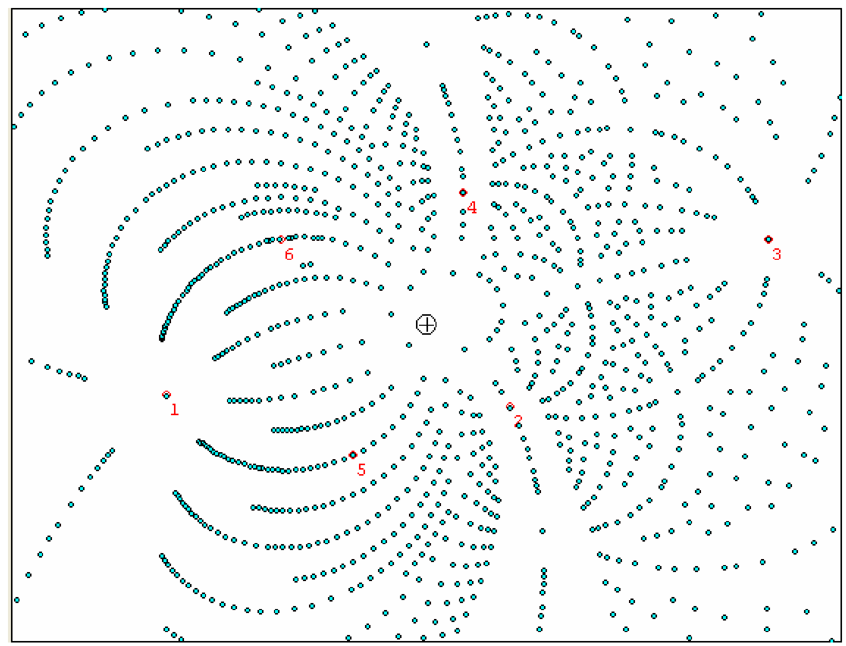
- Back-reflection Laue method.
- Diffracted beams form arrays of spots.
- Bragg angle fixed for every set of planes in the crystal.
- The positions of the spots on the film depend on the orientation of the crystal relative to the incident beam.
- Determine crystallinity, orientation and perfection, from size and shape of spots.



Characterization (2)



- Input supposed crystal structure
- Input coordinates (manually or by scanning the film)
- Chose the most important coordinates
- Simulate a Laue pattern



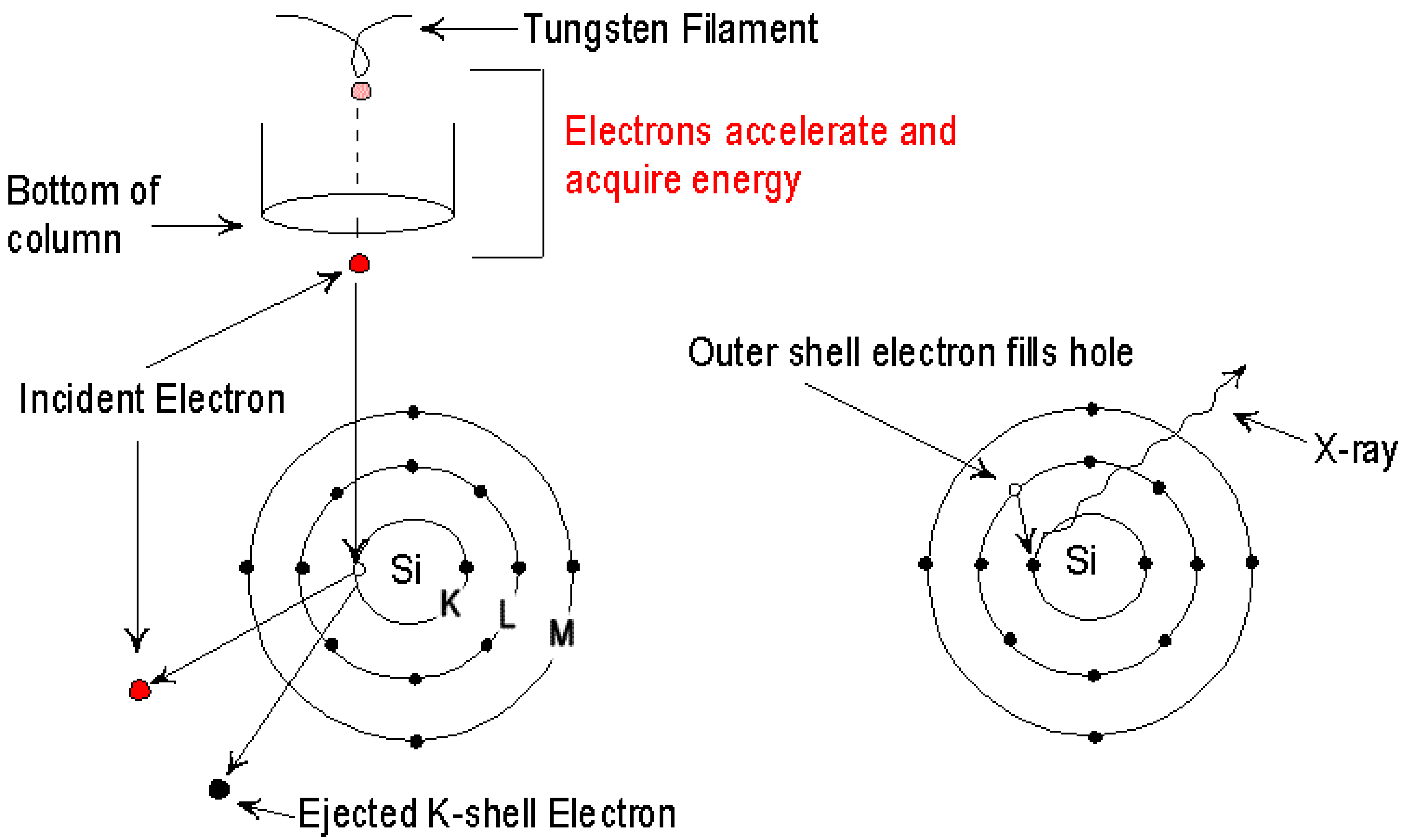
- Find a good simulation match
- Index hkl’s , simulate rotations in order to get the desired orientation for the crystal
- Take another Laue picture after necessary changes
- Check the validity of the orientation by same process

Characterization (3)

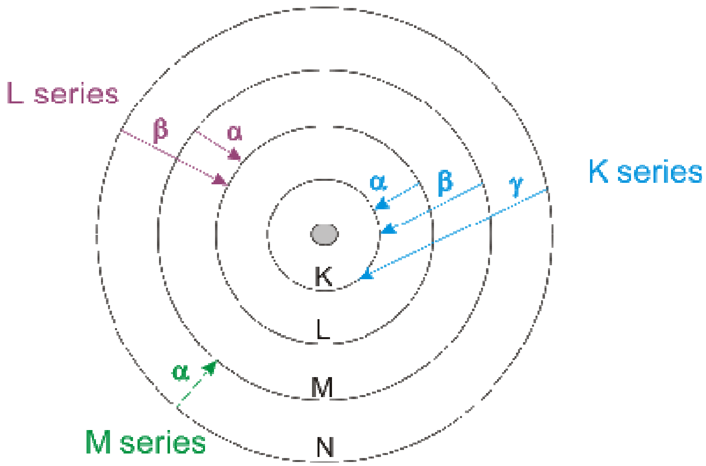
- Composition
  - Powder X-Ray diffraction
    - Crushed single crystal ⟶ use of sieve
    - Evidence for extra crystalline phases
    - Structural refinements
  - Single Crystal X-Ray diffraction
    - Size dependence
    - Evidence for extra crystalline phases
    - Evidence for twinning
    - Orientation
    - Structural refinements

Characterization (4)

– Energy / Wavelength dispersive X-Ray analysis (EDX / WDX)



Characterization (5)



- Electron beam energy up to 40 keV
- Area : from 0.5 microns
- Depth: 0.5 to 2 microns ⟶ Not surface technique!
- Detector

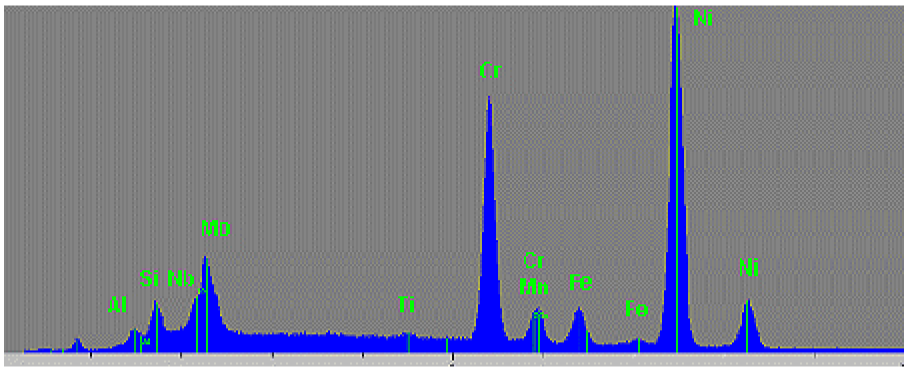
WDX

- Classifies and counts impinging X-Rays of characteristic wavelengths
- Tuned for a single wavelength at a time

Advantages	Limitations
• Very high energy resolution, • Better accuracy • Lower background noise: more accurate quantification	• Very high time consumption • Chamber contamination because of high beam current • Very high costs

Characterization (6)

Quantification



Standard less

•Calculation of the area under each peak

•Accounts for acceleration voltage

• Sensitivity factors that convert area into weight/ atomic %

•Gaussian fit + ZAF algorithm

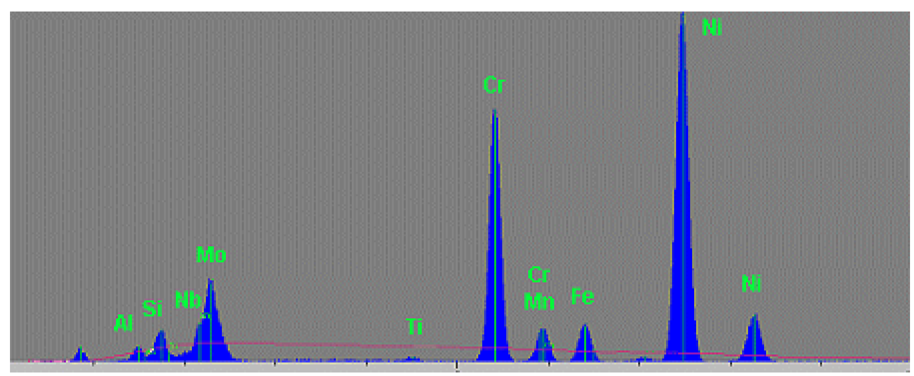
Standard

• No ZAF algorithm

•Comparison to standard files

•Standard files taken in EXACT same conditions

•Better in case of overlapping peaks or trace elements



Conclusions

- Melt growth is one of the most controllable process
- FZT / TSFZT

Advantages

- No crucible contamination
- Shape control
- Impurity control
- Surface tension control
- Vapor pressure control
- Atmosphere control
- Large growth rates
- Large grown crystals

Limitations

- High melting compounds
- Expensive technique
- Incongruent melting
- Phase separation and stability
- Sensitivity of control parameters
- Overflows

- Widely available and powerful characterization techniques

Bibliography

- W. Bardslay, D.T.J. Hurle, J.B. Mullin, Crystal Growth: a tutorial approach, North Holland, (1979)
- P. Hartman, Crystal growth: an introduction, North Holland, (1973)
- J.C. Brice, The growth of Crystals from the melt, North Holand, (1965)
- Laudise, The growth of single crystals, Prentice Hall, (1970)
- W.G. Pfann, Zone melting, John Wiley & sons, (1966)
- P.H. Keck, M.J.E. Golay, Crystallization of silicon from a floating liquid zone, PRL89, 6, (1953)
- W. Heywang, Zeitschrift für Naturforschung A11, 3, (1956)
- Laue diffraction software [Orient Express]: http://www.ccp14.ac.uk/ccp/web-mirrors/lmgp-laugier-bochu/orientex.zip

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