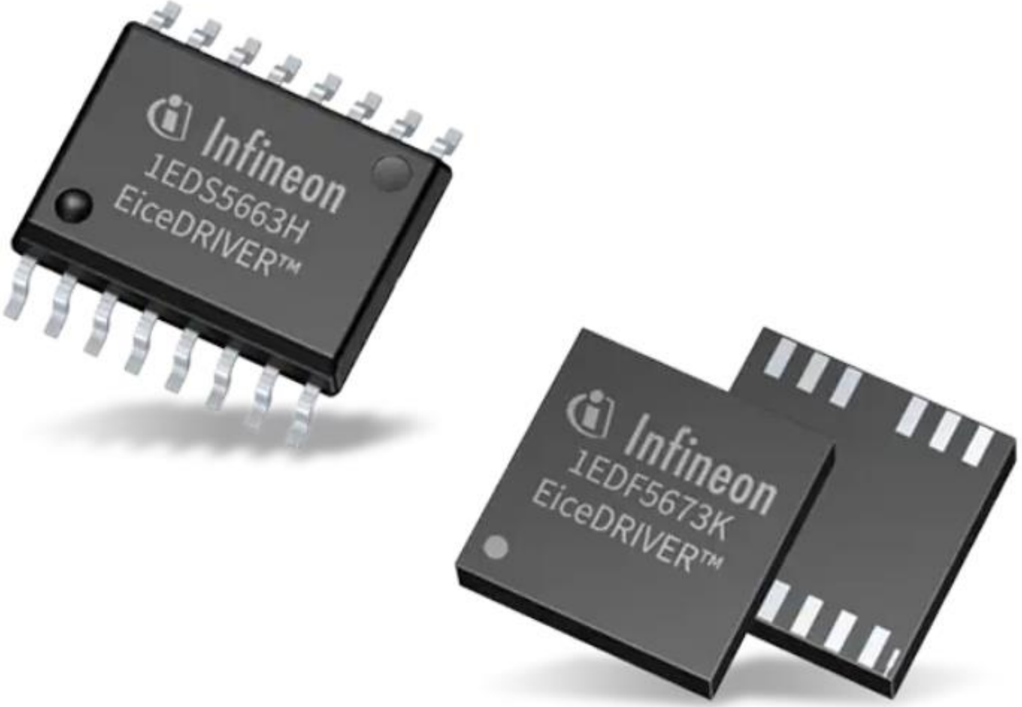
Growth of bulk crystals from the melt or solution

Tomasz Sochacki

Institute of High Pressure Physics Polish Academy of Sciences, Warsaw, Poland,
e-mail: tsochacki@unipress.waw.pl

Why do we grow crystals?

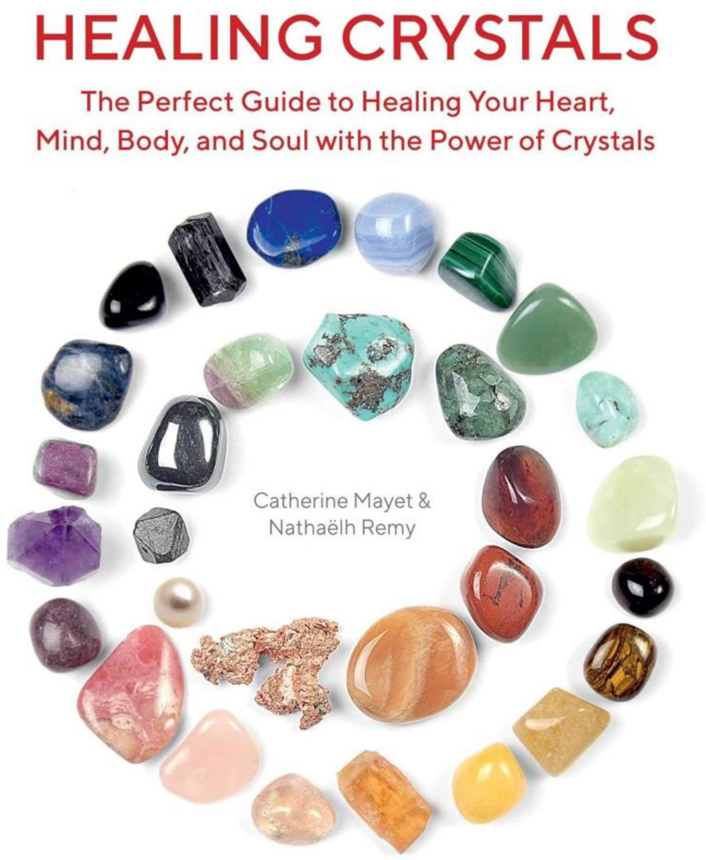
WE LIKE IT



WE NEED IT

Infineon Technologies CoolGaN™ Gallium Nitride e-mode HEMTs

Why do we grow crystals?



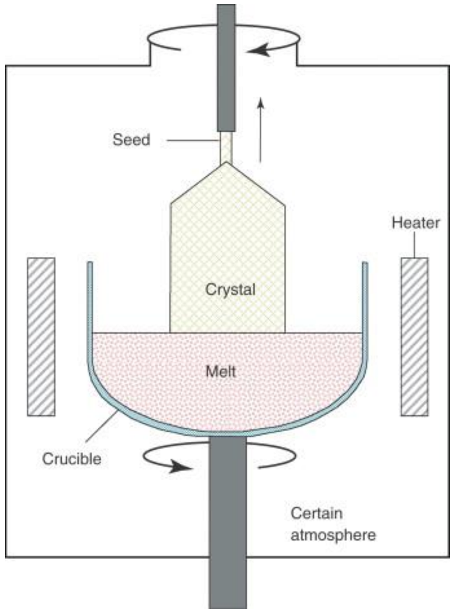
HEALING CRYSTALS

The Perfect Guide to Healing Your Heart,
Mind, Body, and Soul with the Power of Crystals

Catherine Mayet &
Nathaëlh Remy

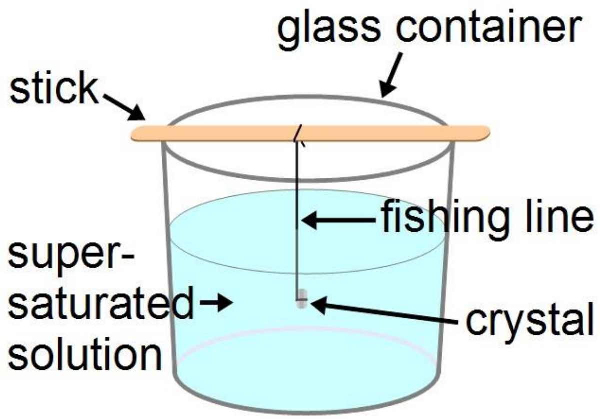
How can we grow crystals and what does it depend on?

Crystal Growth from the Melt



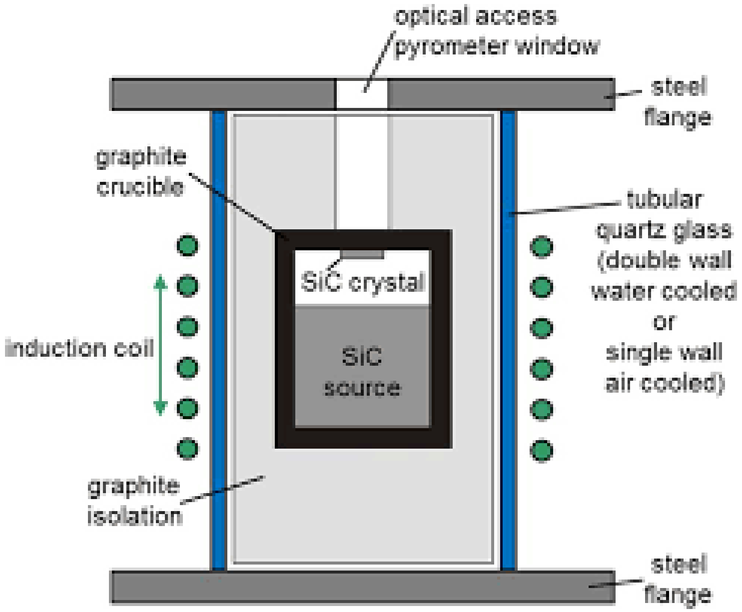
G. Müller, J. Friedrich,
in Encyclopedia of Condensed
Matter Physics, 2005

Crystal Growth from Solution



Make big Rochelle salt crystals from
seeds (rimstar.org)

Crystal Growth from the Gas Phase



P. J Wellmann 2018
Semicond. Sci. Technol. **33** 103001

Growth from the melt

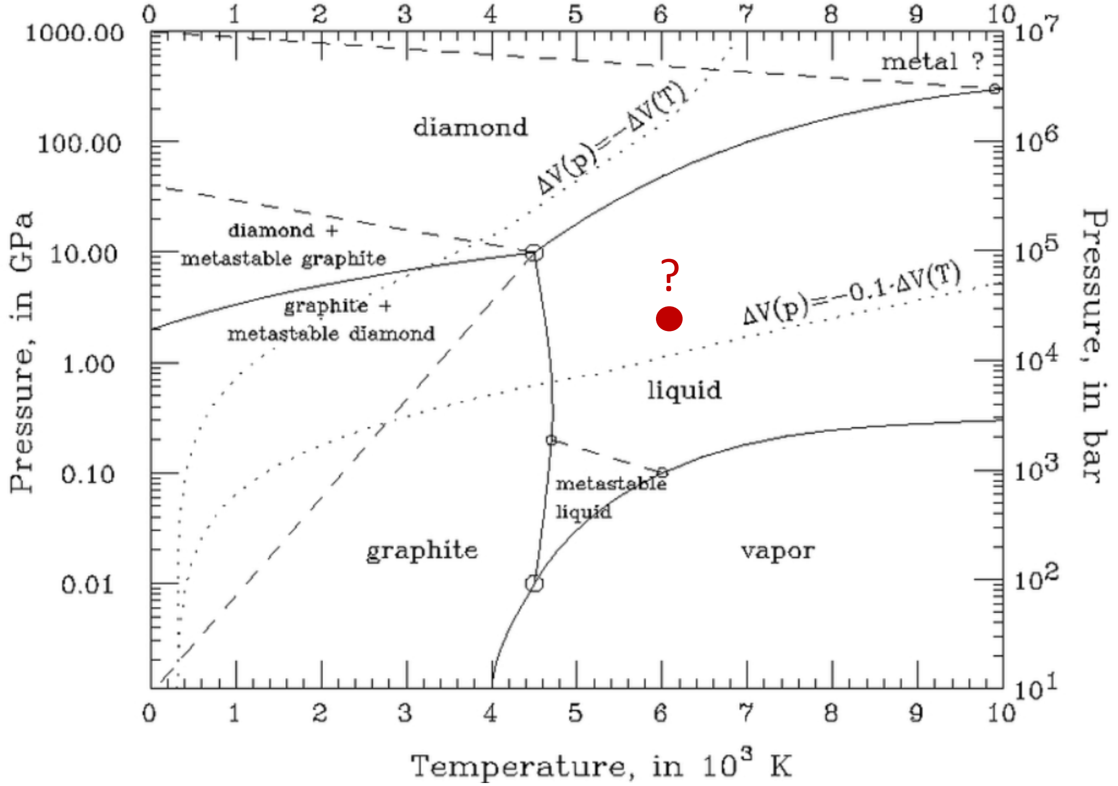
Growth from the melt – realization of phase transition: liquid phase → crystalline solid phase
chemical compositions of liquid and solid are the same (not counting impurities < ~0.1 % at.)

Phase diagrams - decide about a possibility to grow a particular crystal from its melt

Why?
What we are looking for in phase diagrams?

p, T - phase diagrams

Diamond

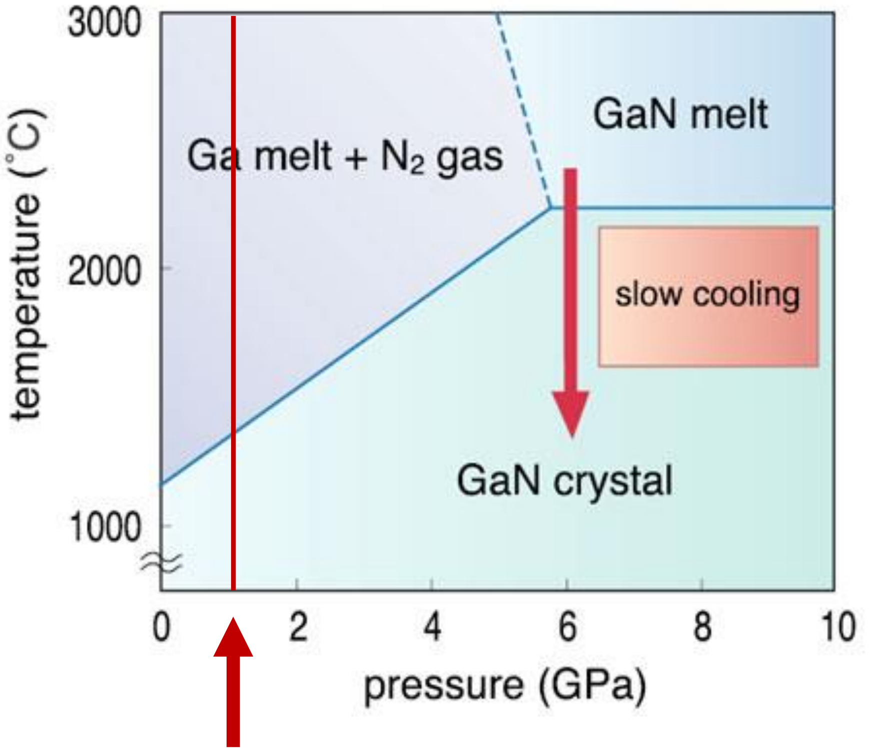


Too ↑p and ↑T

J. M. Zazula, LHC Project Note 78/97

Gallium Nitride

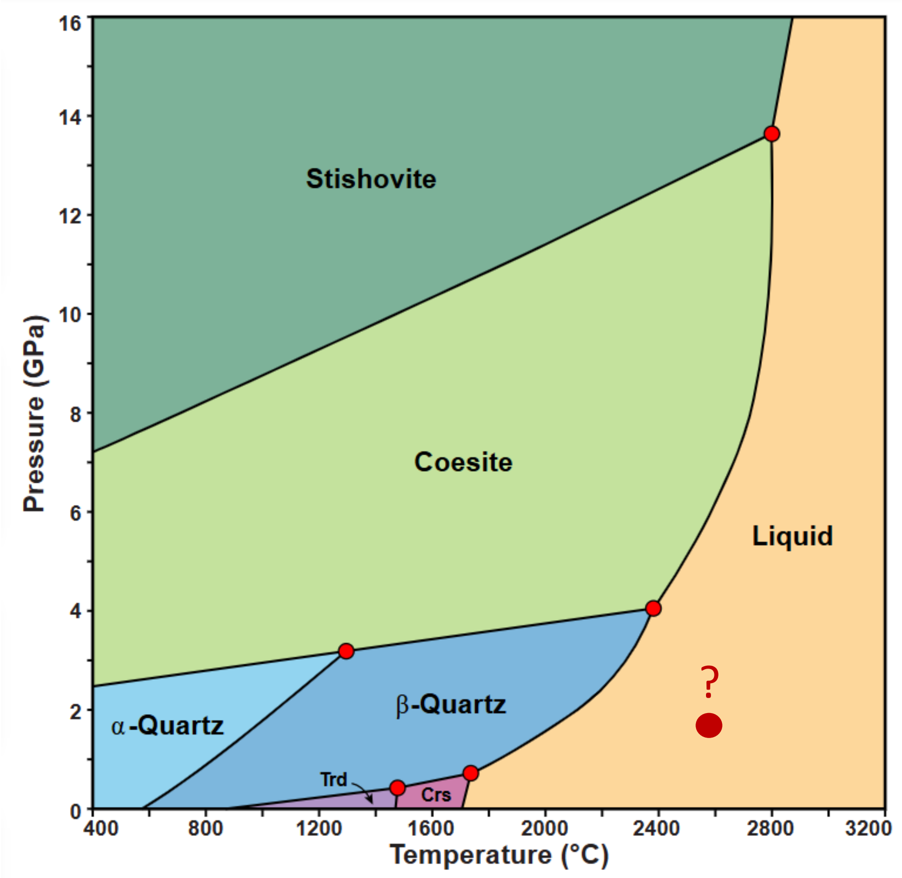
Multi-anvil high-pressure
apparatus Spring-8 synchrotron



Technological limit **Too ↑p**

W. Utsumi et al. Nature Materials 2 (2003) 735

α - SiO_2



From experimental data by Bohlen and Boettcher (1982), Zhang and others (1993), and Fei and Bertka (1999).

What we are looking for in phase diagrams?

p, T – phase diagrams

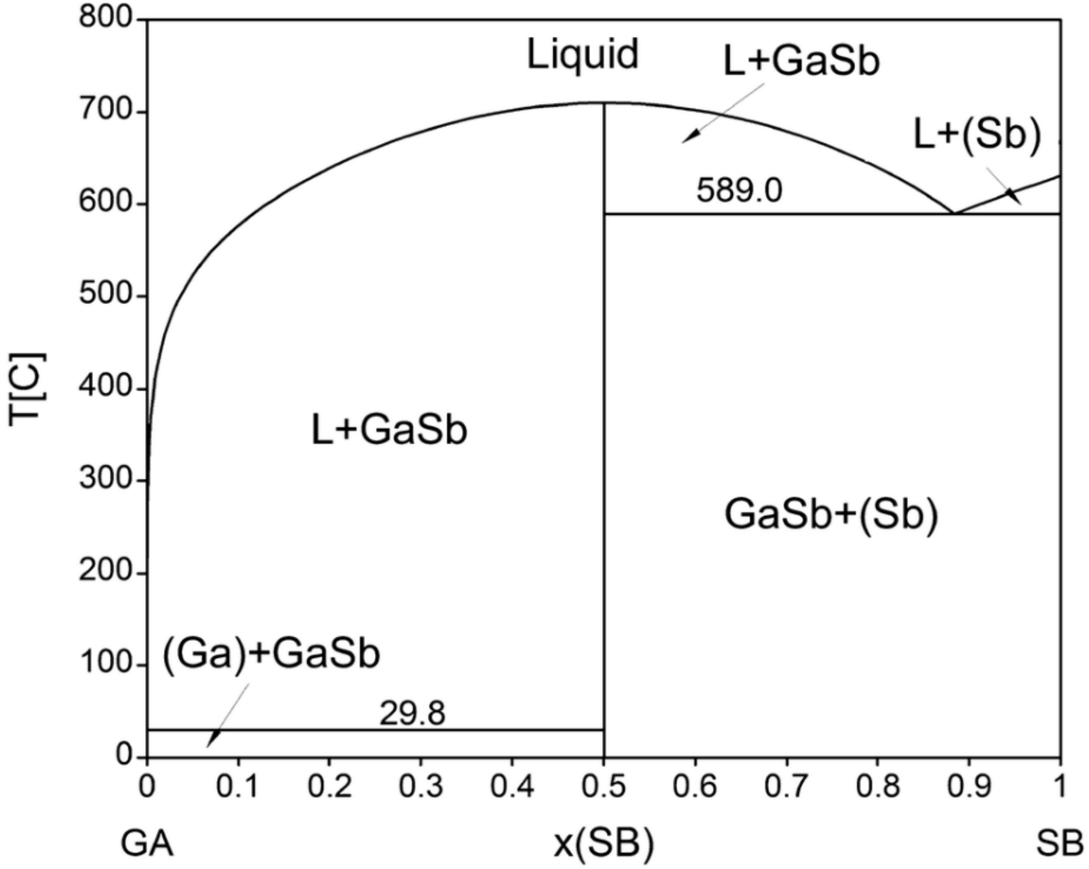
Conditions, the “ path” to go from melt to the desired solid phase.
Conditions for the existence of a stable solid phase

T, x – phase disgrams
T – temperaturę, x – composition at constant p

Thermodynamic equilibrium point between liquid and solid at the same chemical compositions of both phases – existence of the **congruent point**

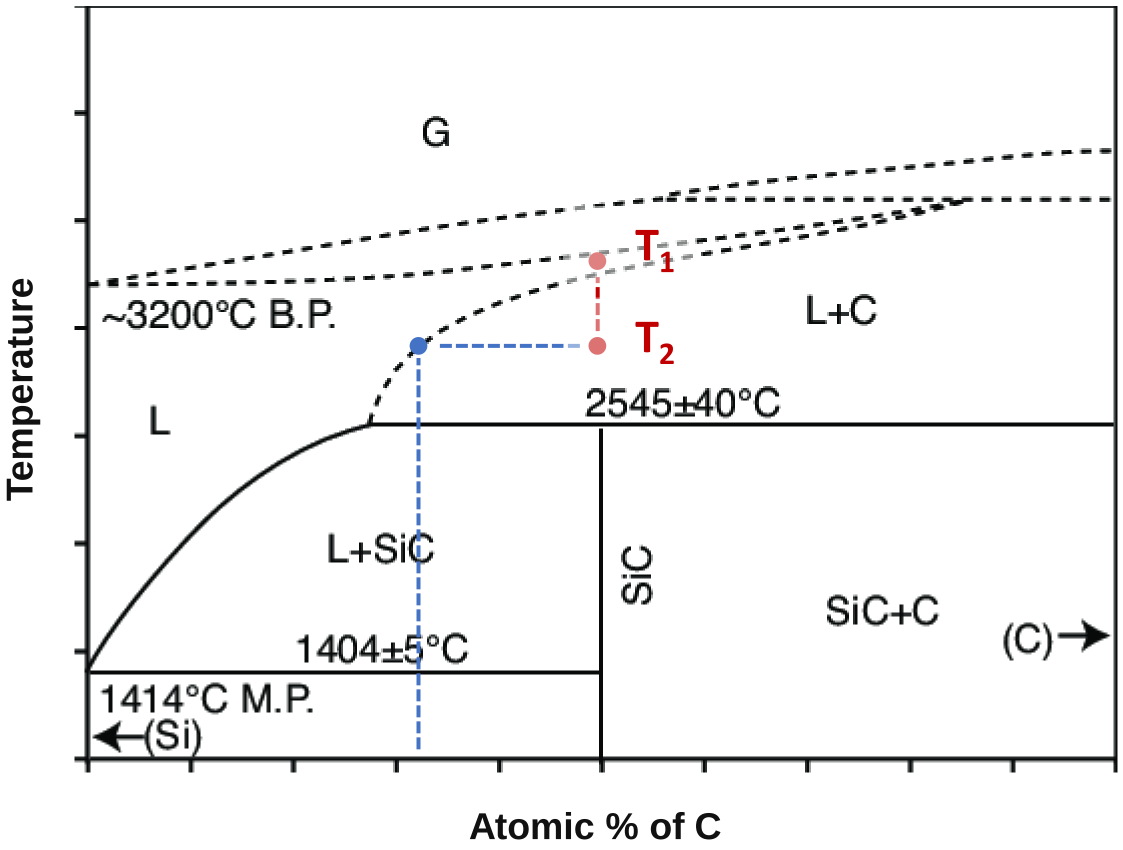
GaSb

Infrared detectors,
infrared LEDs and lasers,
transistors
thermophotovoltaic systems
https://www.matltech.com/gallium-antimonide-gasb-product/

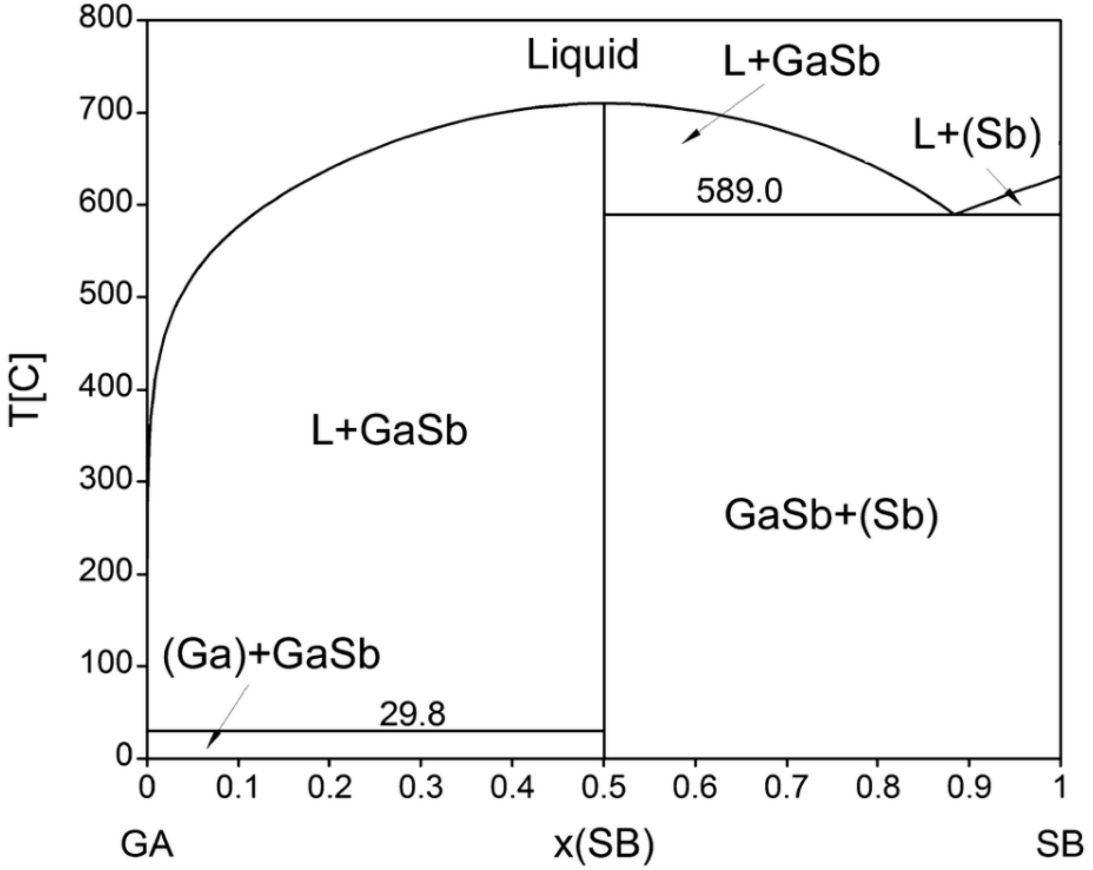


I. Ansara, C eta al. A Binary Database for III–V Compound Semiconductor Systems, *Calphad*, 1994, **18**(2), p 177-222

SiC

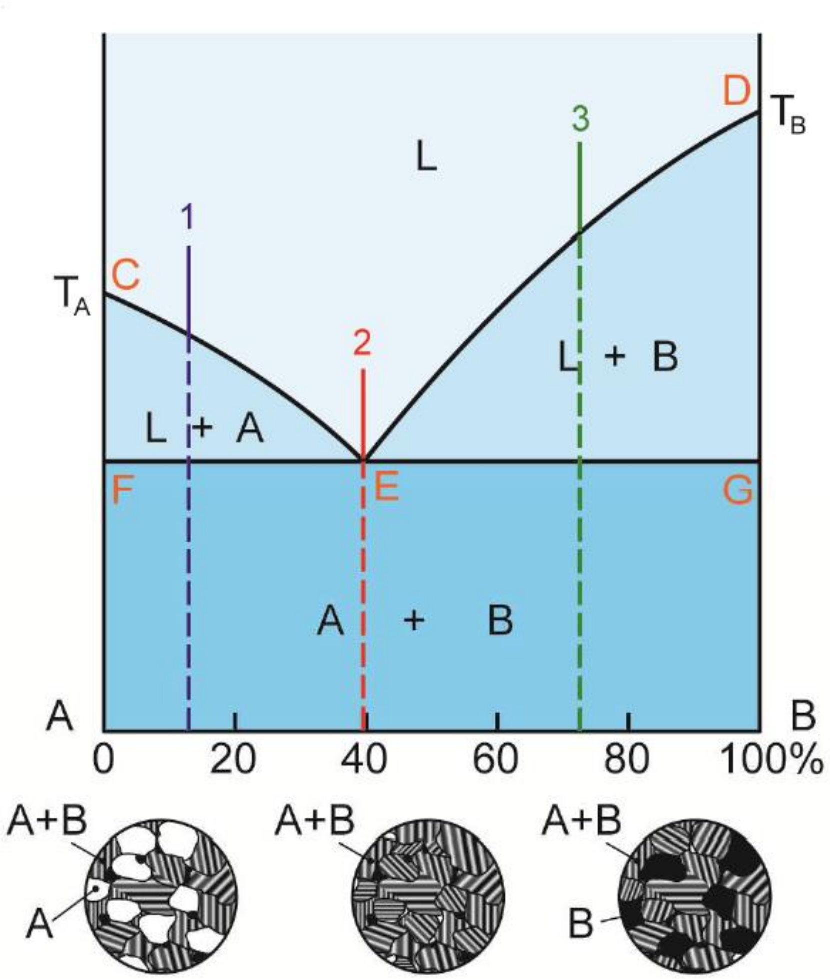


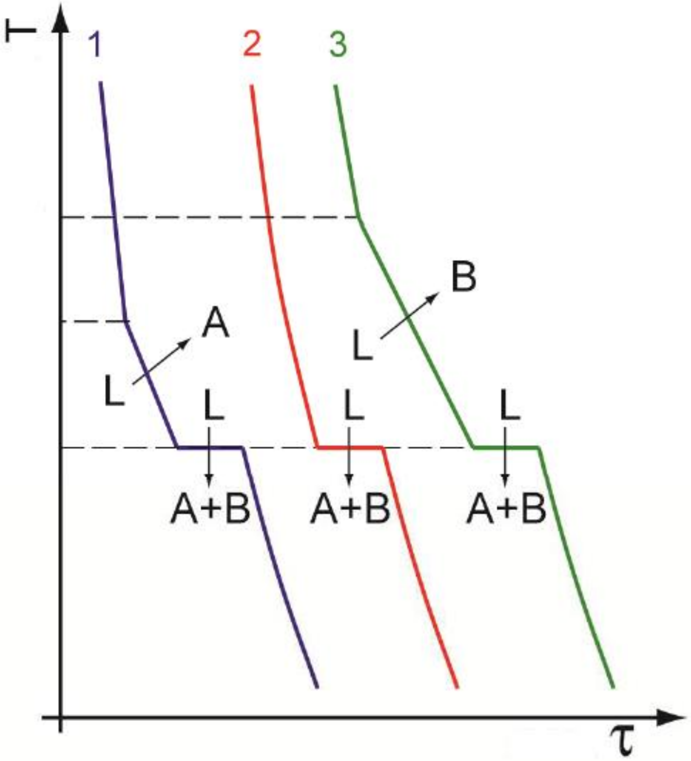
Si-C binary system (Olesinski & Abbaschian, 1996)



I. Ansara, C eta al. A Binary Database for III–V Compound Semiconductor Systems, *Calphad*, 1994, **18**(2), p 177-222

Crystalization of alloys





Prof. Marcin Kazimierz Leonowicz

Short Summary

What we are looking for in phase diagrams?

p, T – phase diagrams

Conditions, the “ path” to go from melt to the desired solid phase.
Conditions for the existence of a stable solid phase

T, x – phase disgrams
T – temperature, x – composition at constant p

Thermodynamic equilibrium point between liquid and solid at the same chemical compositions of both phases – existence of the **congruent point**

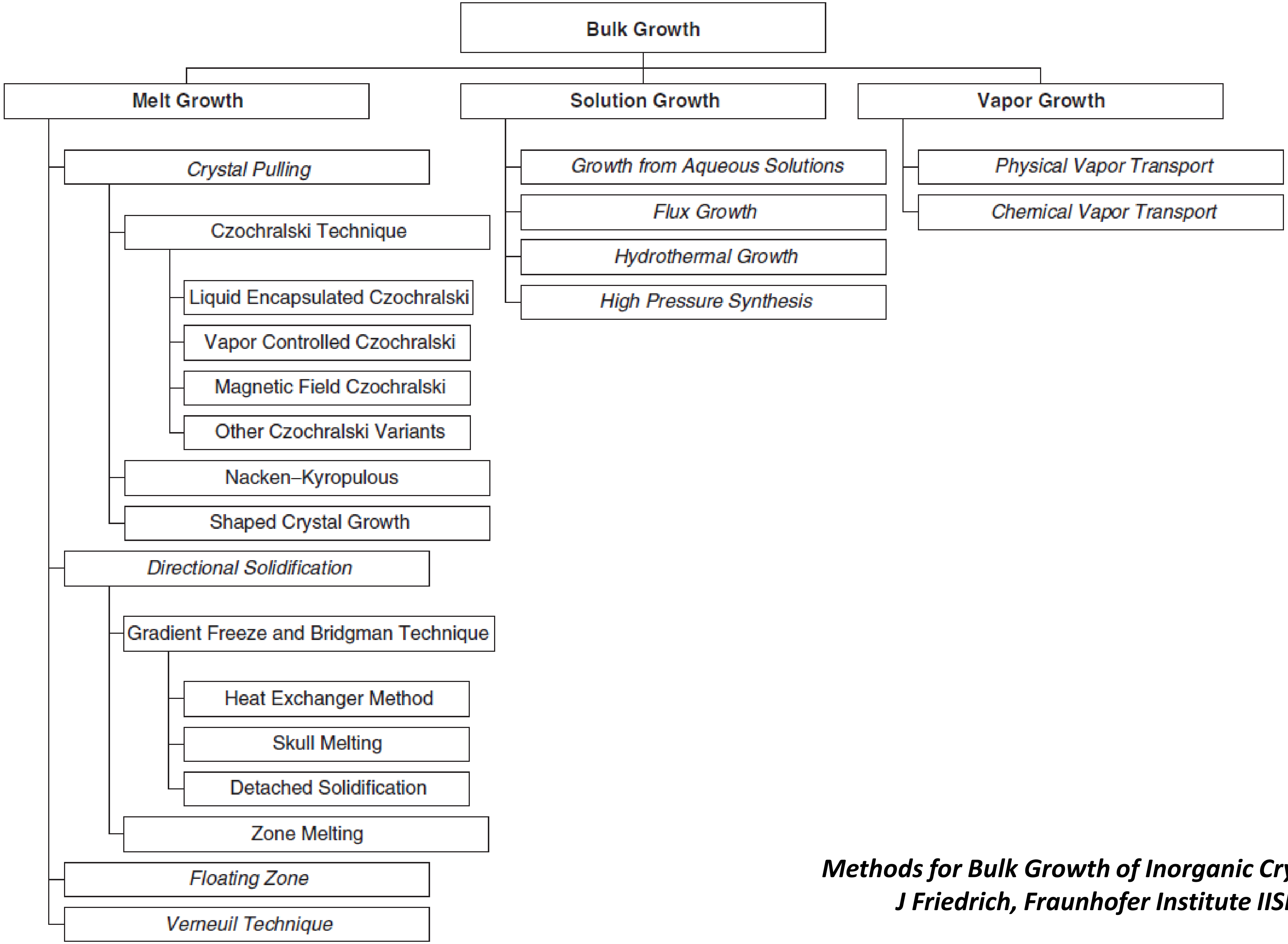
Crystals and Their Applications

- **Semiconductors for diodes, transistors**, IC's, LED's, etc., (e.g. **Si**, **GaAs**, **GaN**, **SiC**, $Hg_{1-x}Cd_xTe$ (MCT), and **ZnO**).
- **Optical materials for windows, lenses, polarizers, laser hosts, magneto-optics, electro-optics and nonlinear devices, etc.**, (e.g. sapphire, **CaF_2**, **$Y_3Al_5O_{12}$ (YAG), $LiNbO_3$, and KDP**),
- **Magnetic materials** (e.g. ferrites and garnets (**$Y_3Fe_5O_{12}$**),
- **Piezoelectric crystals** (e.g. **SiO_2**, $LiTaO_3$, **AlN**),
- **Pyroelectrics** (e.g. **$Sr_xBa_{1-x}Nb_2O_6$** (SBN),
- **Gemstones**, (e.g. emerald, ruby, diamond and cubic zirconia),
- **Radiation detectors** (e.g. Eu:SrI_2, Ce: $Lu_{2(1-x)}Y_{2x}SiO_5$ (LYSO), and Tl:NaI),
- **Collimators and focusing elements** (**SiO_2**).

Growth from the: melt, solution, vapor phase

Growth from the melt

Methods



- Bulk Growth
  - Melt Growth
    - *Crystal Pulling*
      - Czochralski Technique
        - Liquid Encapsulated Czochralski
        - Vapor Controlled Czochralski
        - Magnetic Field Czochralski
        - Other Czochralski Variants
      - Nacken–Kyropulous
      - Shaped Crystal Growth
    - *Directional Solidification*
      - Gradient Freeze and Bridgman Technique
        - Heat Exchanger Method
        - Skull Melting
        - Detached Solidification
      - Zone Melting
    - *Floating Zone*
    - *Verneuil Technique*
  - Solution Growth
    - *Growth from Aqueous Solutions*
    - *Flux Growth*
    - *Hydrothermal Growth*
    - *High Pressure Synthesis*
  - Vapor Growth
    - *Physical Vapor Transport*
    - *Chemical Vapor Transport*

Methods for Bulk Growth of Inorganic Crystals: Crystal Growth
J Friedrich, Fraunhofer Institute IISB, Erlangen, Germany
2016 Elsevier Inc.

First announcement about Chochralski method

I15. Growth of Germanium Single Crystals. G. K. Teal and J. B. Little, *Bell Telephone Laboratories* (*To be read by title*).—The growth in the number of ideas of possible conduction mechanisms of practical value that might be realized in germanium has emphasized the importance of developing specific methods of producing germanium single crystals in which the relevant properties of the material are controlled. In the present study germanium single crystals of a variety of shapes, sizes, and electrical properties have been produced by means of a pulling technique distinguished from that of Czochralski and others in improvements necessary to produce controlled semiconducting properties. Germanium is a solid that expands markedly on solidifying and is very sensitive to factors, such as physical strain, which give rise to twinning. The method of pulling the germanium single crystal progressively from the melt at such a rate as to have a stationary interface between the solid and the liquid only slightly above the liquid surface is very well suited to the material since it avoids the constraints inherent in solidifying the germanium within inflexible walls and provides a simple planar thermal gradient in the neighborhood of the interface thereby minimizing thermally induced strains. Single crystal rods up to 8 inches in length and $\frac{3}{4}$ inch in diameter and having a high degree of crystalline lattice perfection have been produced. Measurements in these Laboratories have shown the bulk lifetimes of injected carriers in these materials to be greater than 200 microseconds.

Phys. Rev. **78**, 637 – **Published 1 June, 1950**

Germanium single crystals

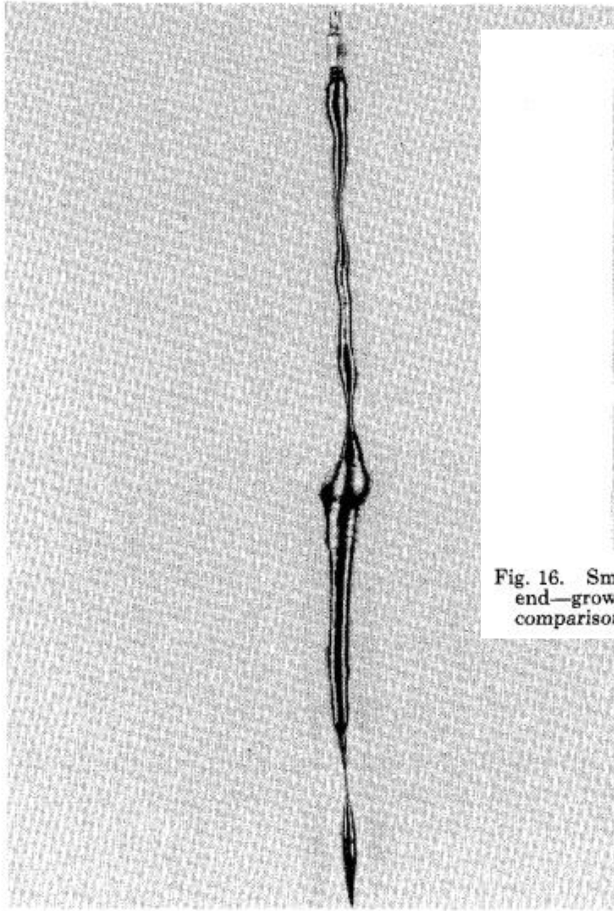


Fig. 2. An early germanium single crystal grown in the type I crystal puller equipment by G. K. Teal and John Little.

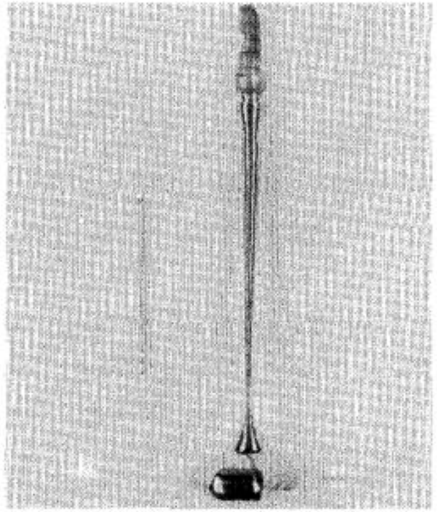


Fig. 16. Small diameter germanium single crystal with bulbar lower end—grown in the type II machine with rotating seed. Small pin for comparison.

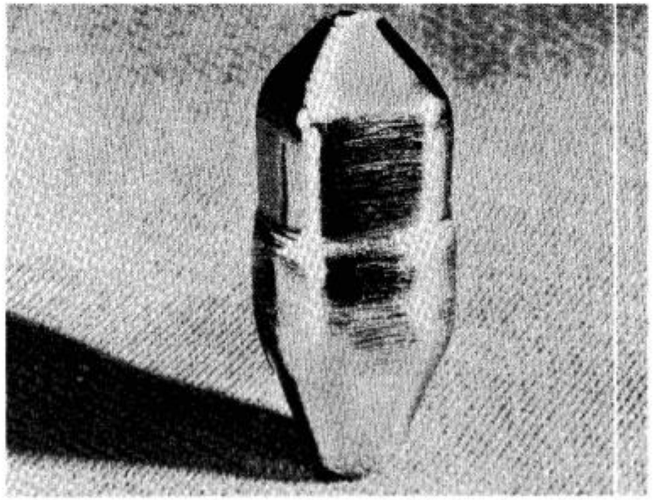


Fig. 22. Germanium single crystal grown in the type II crystal pulling machine by Teal and Little and often used in Bell system advertisements.

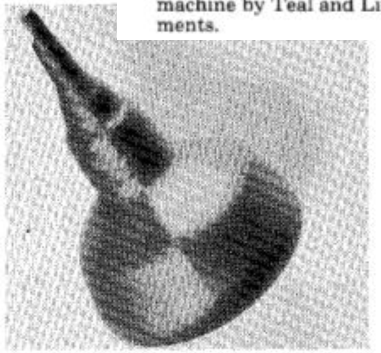


Fig. 18. 1¼-in-diam germanium single crystal grown in the (111) direction and at a very slow rate.

G. K. Teal, "Single crystals of germanium and silicon – Basic to the transistor and integrated circuit," in *IEEE Transactions on Electron Devices*, vol. 23, no. 7, pp. 621-639, July 1976, doi: 10.1109/T-ED.1976.18464.

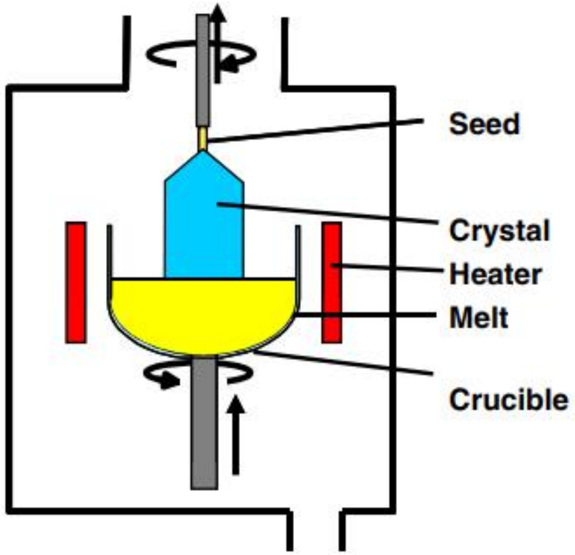
Why it was so important? – dislocation free sillicon crystals

The most important technical application of the Cz method is the growth of **dislocation – free silicon crystals with diameters up to 300mm and a weight up to 300kg** in industrial production.

Photograph of a silicon CZ puller with 200 mm crystal

Wacker Siltronic AG

Growth stages in the Czochralski method



J. Friedrich, Methods for Bulk Growth of Inorganic Crystals: Crystal Growth, Reference Module in Materials Science and Materials Engineering, Elsevier, 2016,

Growth stages in the Czochralski method

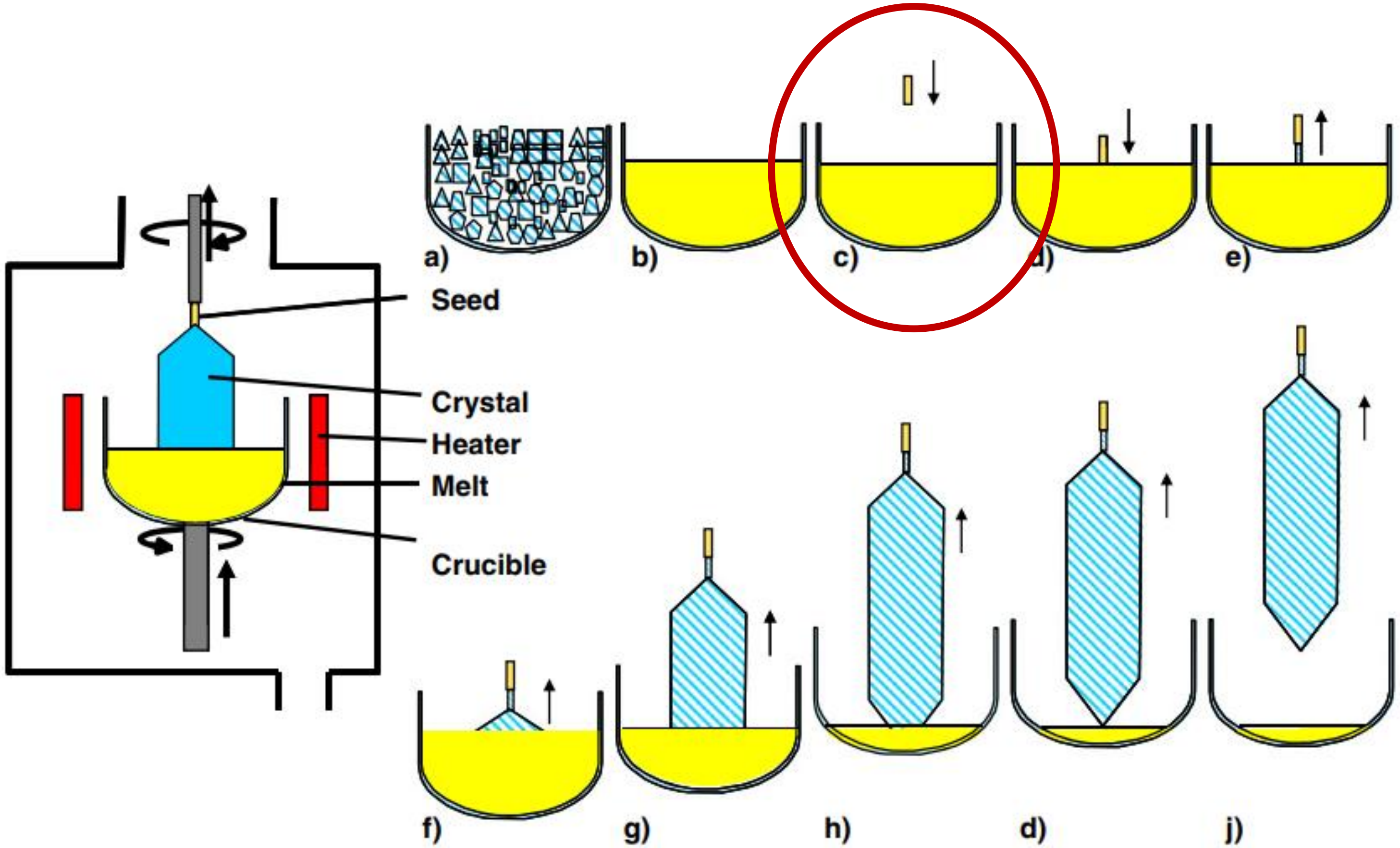


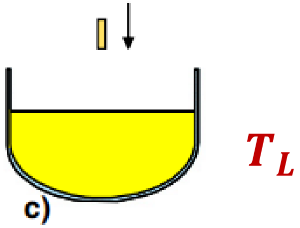
Figure 2 Schematic of the principle of the Czochralski method (left) and illustration of the different steps (a–j) of the Cz process for growing a Si crystal. (a) The polycrystalline feedstock is melted (b) in a crucible. (c, d) Seeding procedure: The seed crystal is dipped into the melt, followed by Dash necking (e), shouldering (f), cylindrical growth (g), growth of end cone (h), lift off (i), cooling down and removing of the crystal (j).

J. Friedrich, Methods for Bulk Growth of Inorganic Crystals: Crystal Growth, Reference Module in Materials Science and Materials Engineering, Elsevier, 2016,

Growth stages in the Czochralski method

How do we know that the melting temperature is appropriate? (T_L)

$$T_L \cong T_{eq}$$



We have:
View of the melt,
Seed/crystal weight,
Position of the seed,

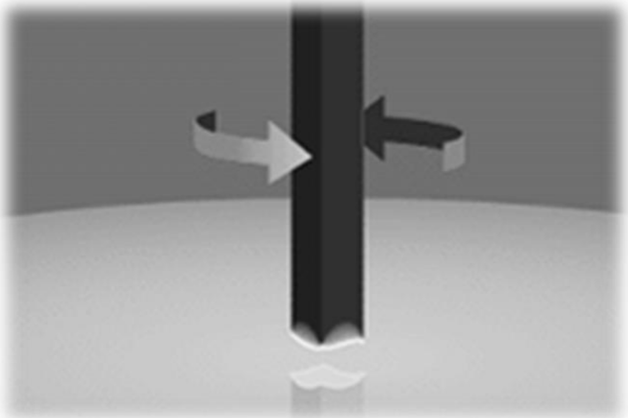
We can see:
Convection lines,

Dripping of material from the seed.

The mass loss is too small.

We can calculate the contact position with the melt (melt density + crucible volume).

If the calculated contact position matches the actual one, we are very close to equilibrium.



Growth stages in the Czochralski method

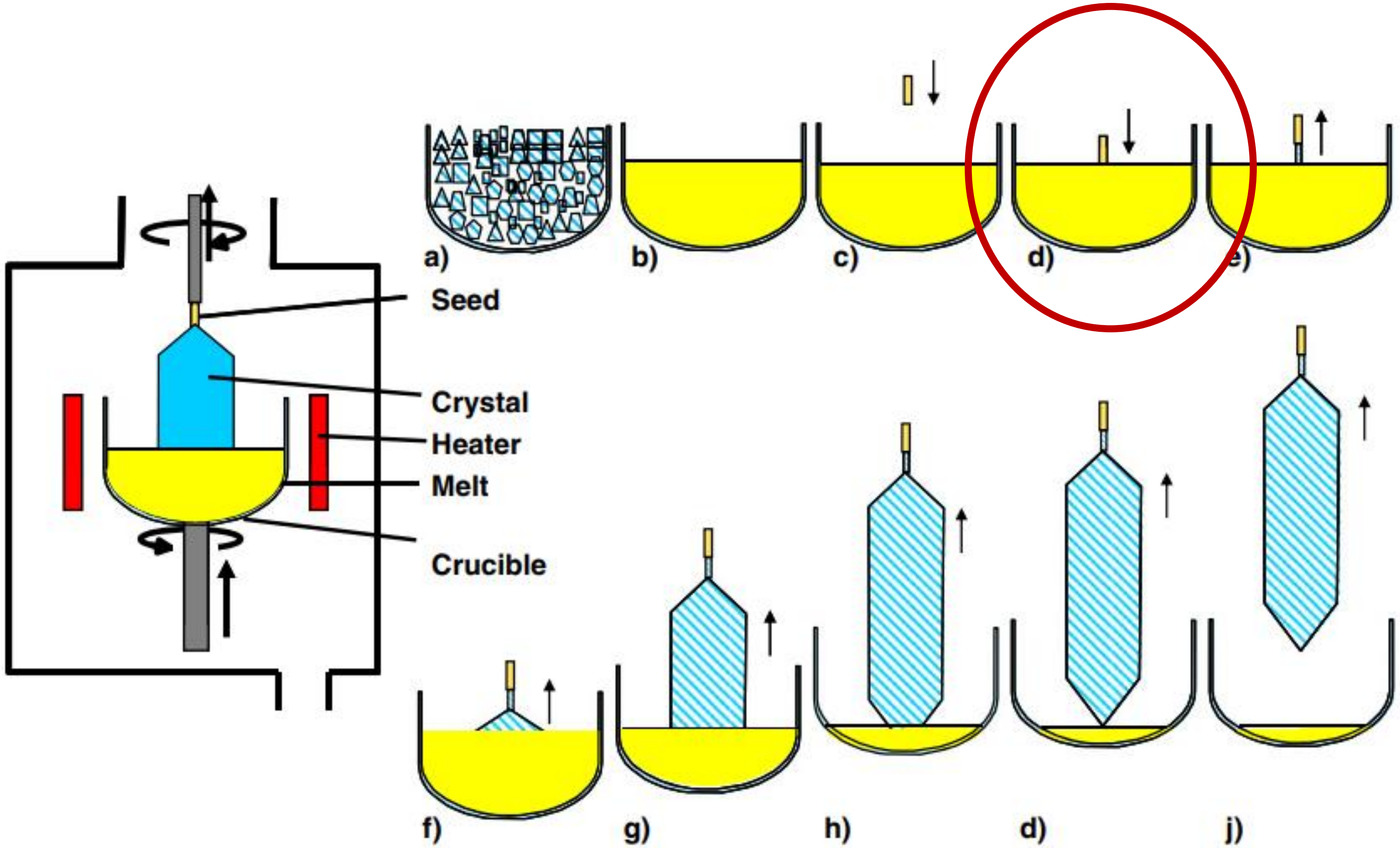


Figure 2 Schematic of the principle of the Czochralski method (left) and illustration of the different steps (a–j) of the Cz process for growing a Si crystal. (a) The polycrystalline feedstock is melted (b) in a crucible. (c, d) Seeding procedure: The seed crystal is dipped into the melt, followed by Dash necking (e), shouldering (f), cylindrical growth (g), growth of end cone (h), lift off (i), cooling down and removing of the crystal (j).

J. Friedrich, Methods for Bulk Growth of Inorganic Crystals: Crystal Growth, Reference Module in Materials Science and Materials Engineering, Elsevier, 2016,

Growth stages in the Czochralski method - seeding

How do we know that the melting temperature is appropriate? (T_L)

$$T_L \cong T_{eq}$$

If we lift the seed:

and the meniscus will decrease

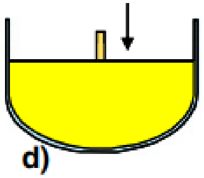
$$T_L > T_{eq}\ ;$$

and the meniscus will increase

$$T_L < T_{eq}$$

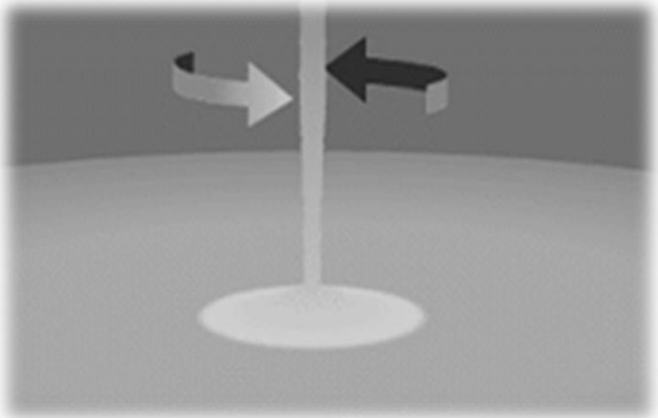
If we lift the seed and the meniscus width does not change:

$$T_L \cong T_{eq}$$



We have:
View of the melt,
Seed/crystal weight,
~~Position of the seed~~,

We can see:
Convection lines,
Meniscus around the seed.



Growth stages in the Czochralski method

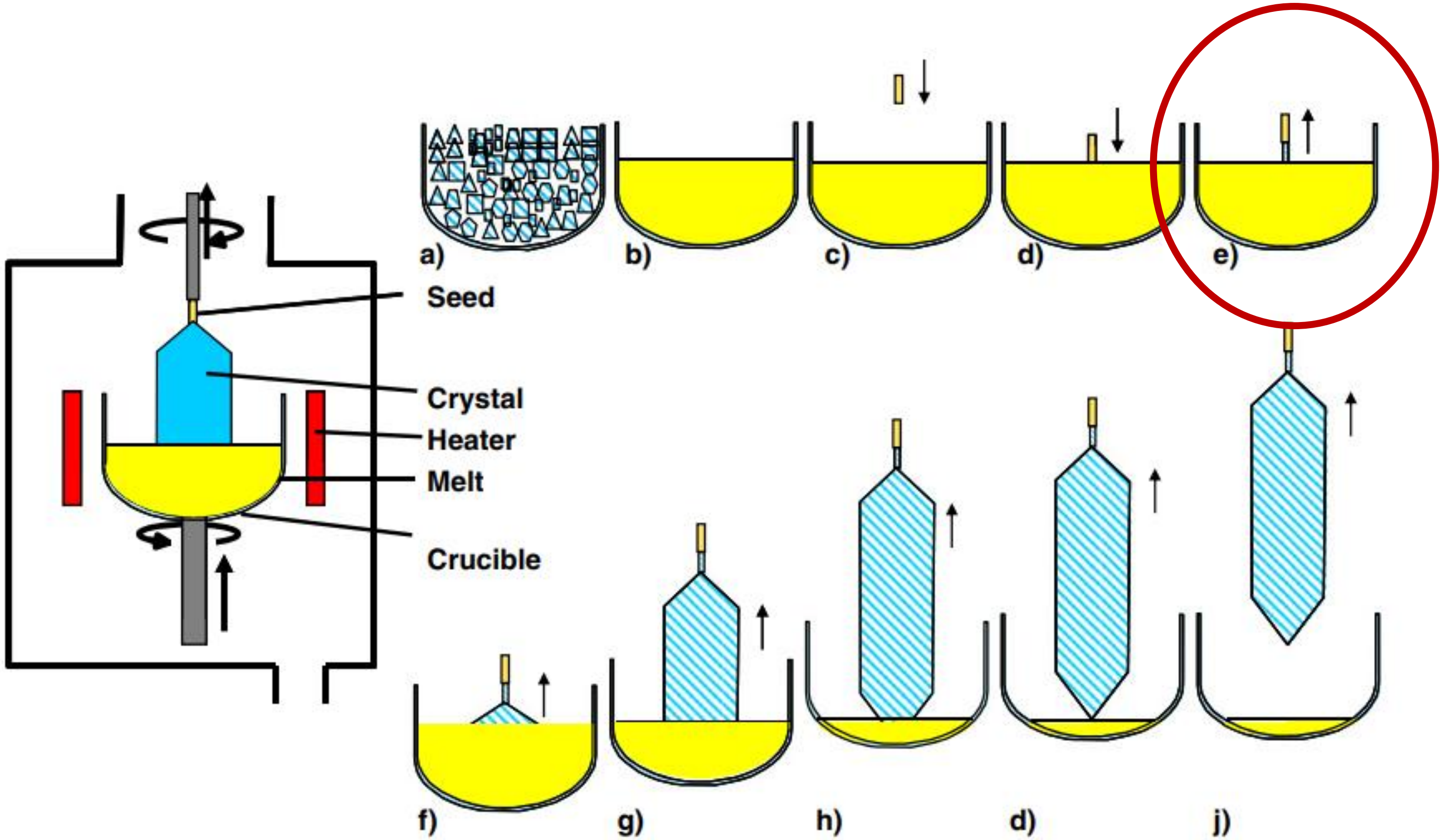
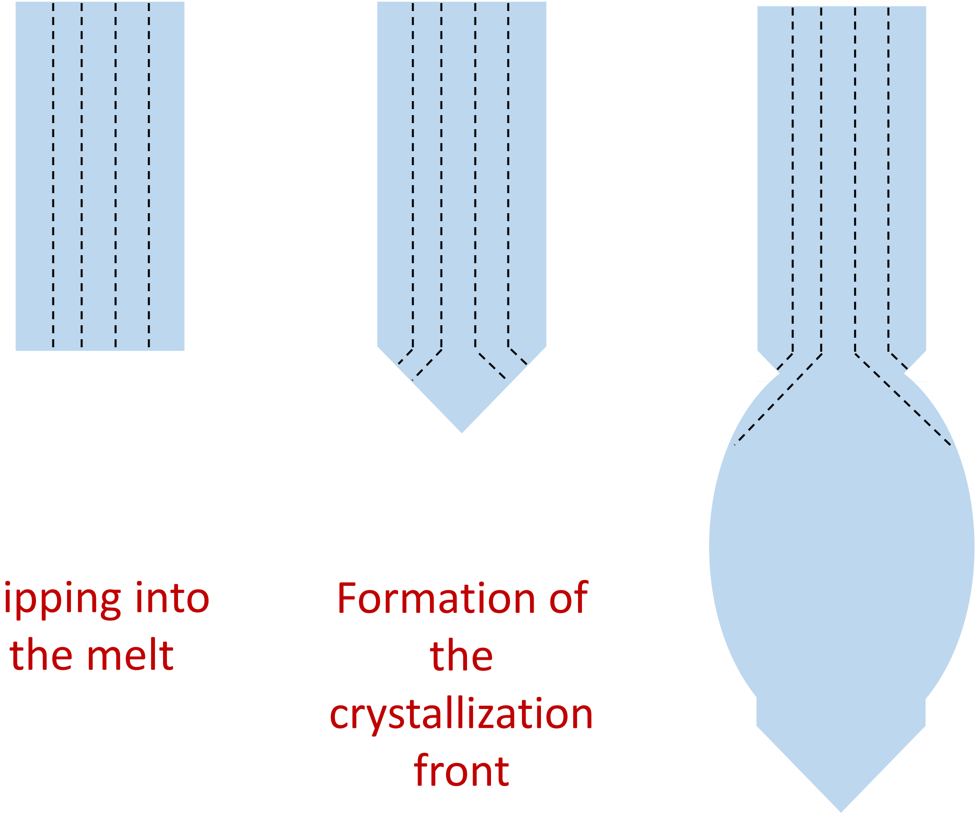


Figure 2 Schematic of the principle of the Czochralski method (left) and illustration of the different steps (a–j) of the Cz process for growing a Si crystal. (a) The polycrystalline feedstock is melted (b) in a crucible. (c, d) Seeding procedure: The seed crystal is dipped into the melt, followed by Dash necking (e), shouldering (f), cylindrical growth (g), growth of end cone (h), lift off (i), cooling down and removing of the crystal (j).

J. Friedrich, Methods for Bulk Growth of Inorganic Crystals: Crystal Growth, Reference Module in Materials Science and Materials Engineering, Elsevier, 2016,

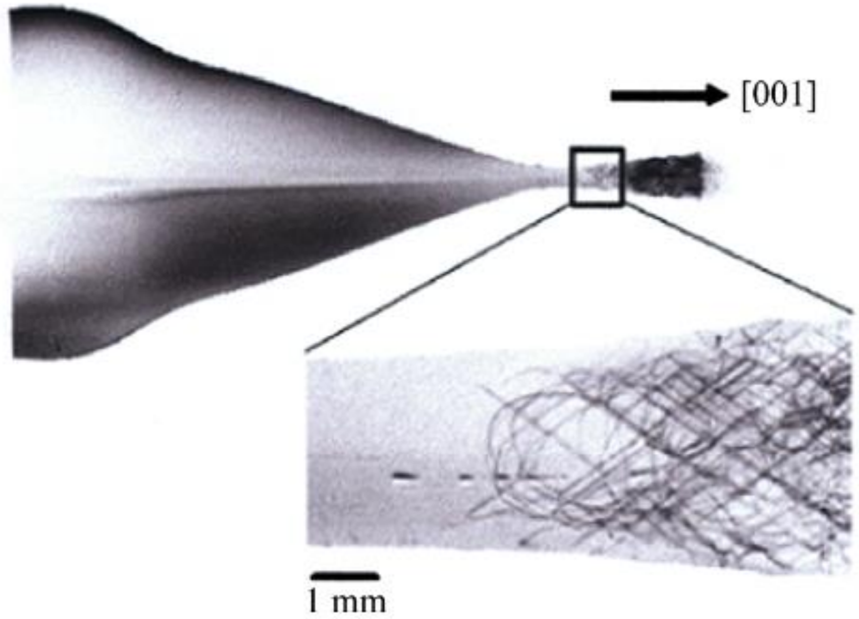
Growth stages in the Czochralski method - shouldering



Dipping into the melt

Formation of the crystallization front

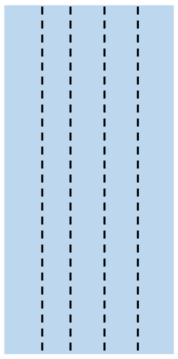
Dislocation reduction



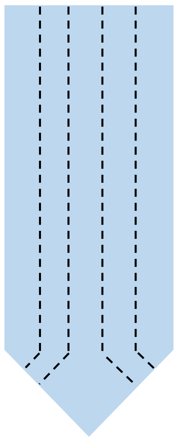
Longitudinal section of the seed and cone region of a Cz-grown Si crystal. Dislocation lines are visualized by X-ray topography. Enlargement (right): dislocations are eliminated within the neck.

Kawado S, Taishi T, Iida S, Suzuki Y, Chikaura Y, Kajiwara K. J Phys D Appl Phys 2005;38:A17

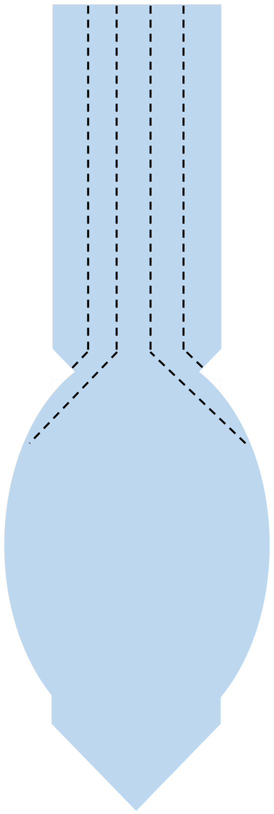
Growth stages in the Czochralski method - shouldering



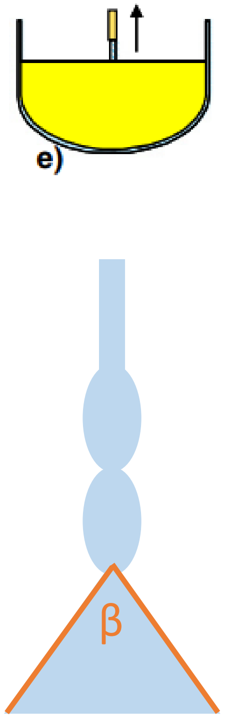
Dipping into the melt



Formation of the crystallization front

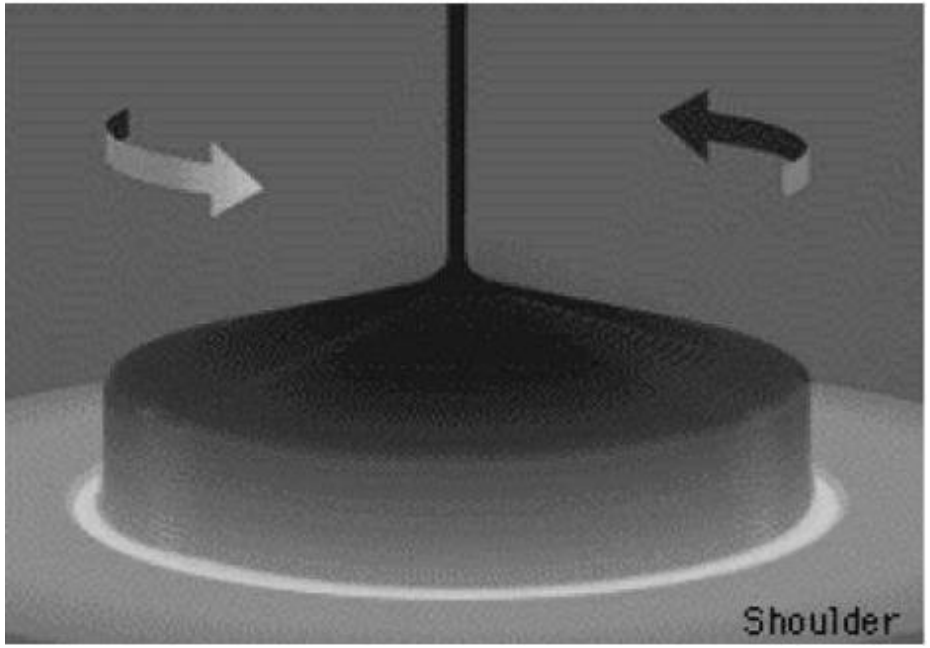


Dislocation reduction



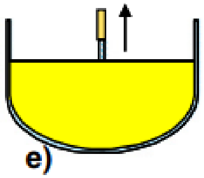
Shouldering

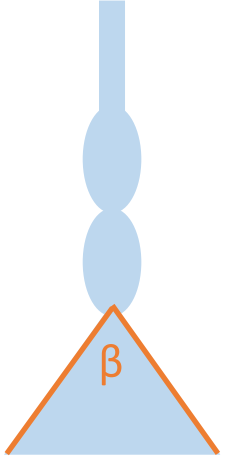
Growth stages in the Czochralski method - shouldering



curvature of meniscus is seen (brighter ring)

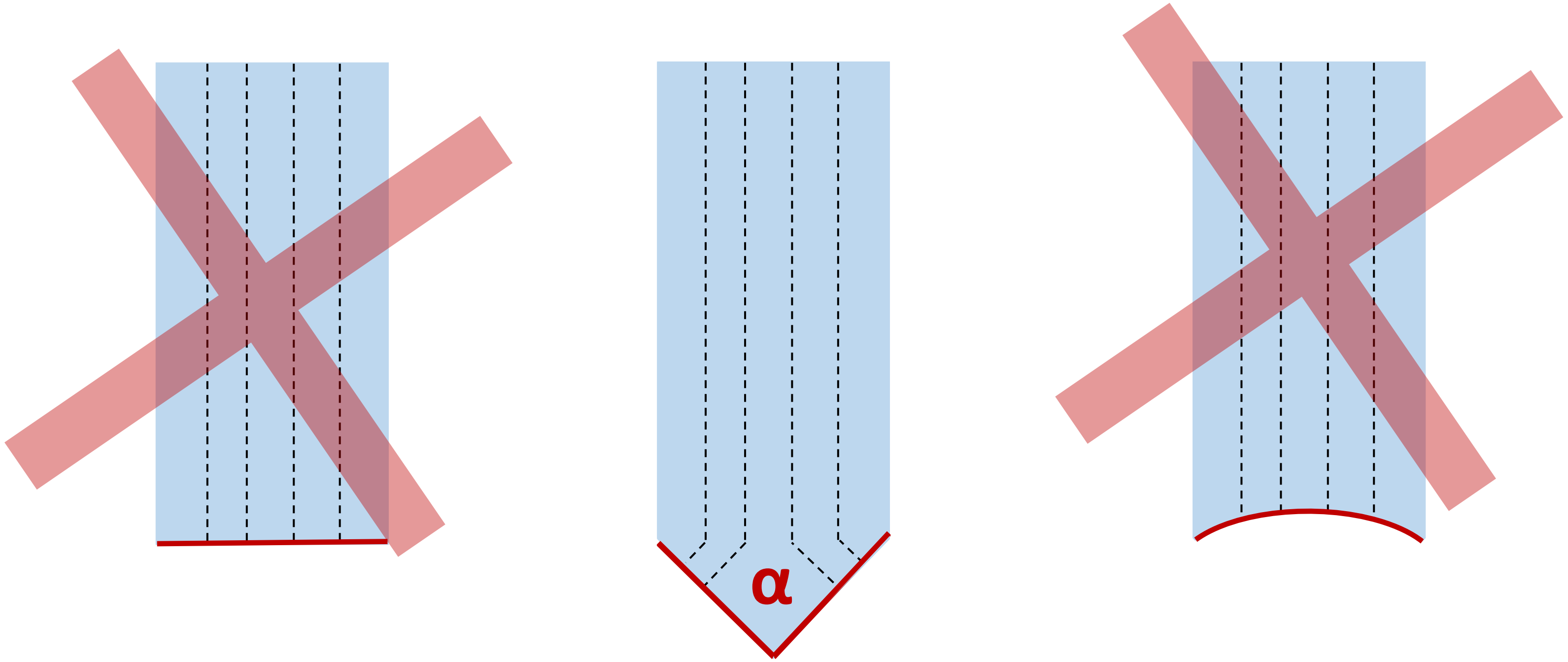
Actual diameter can be determined by optical means (detecting lighter ring of meniscus) using automated methods of image recognition. Another method is continuous weighting of crystal or crucible. Some difficulties arise due to meniscus forces.





Shouldering

Shape of crystallization front



α - constant

Flat

Convex

Concave

Growth stages in the Czochralski method

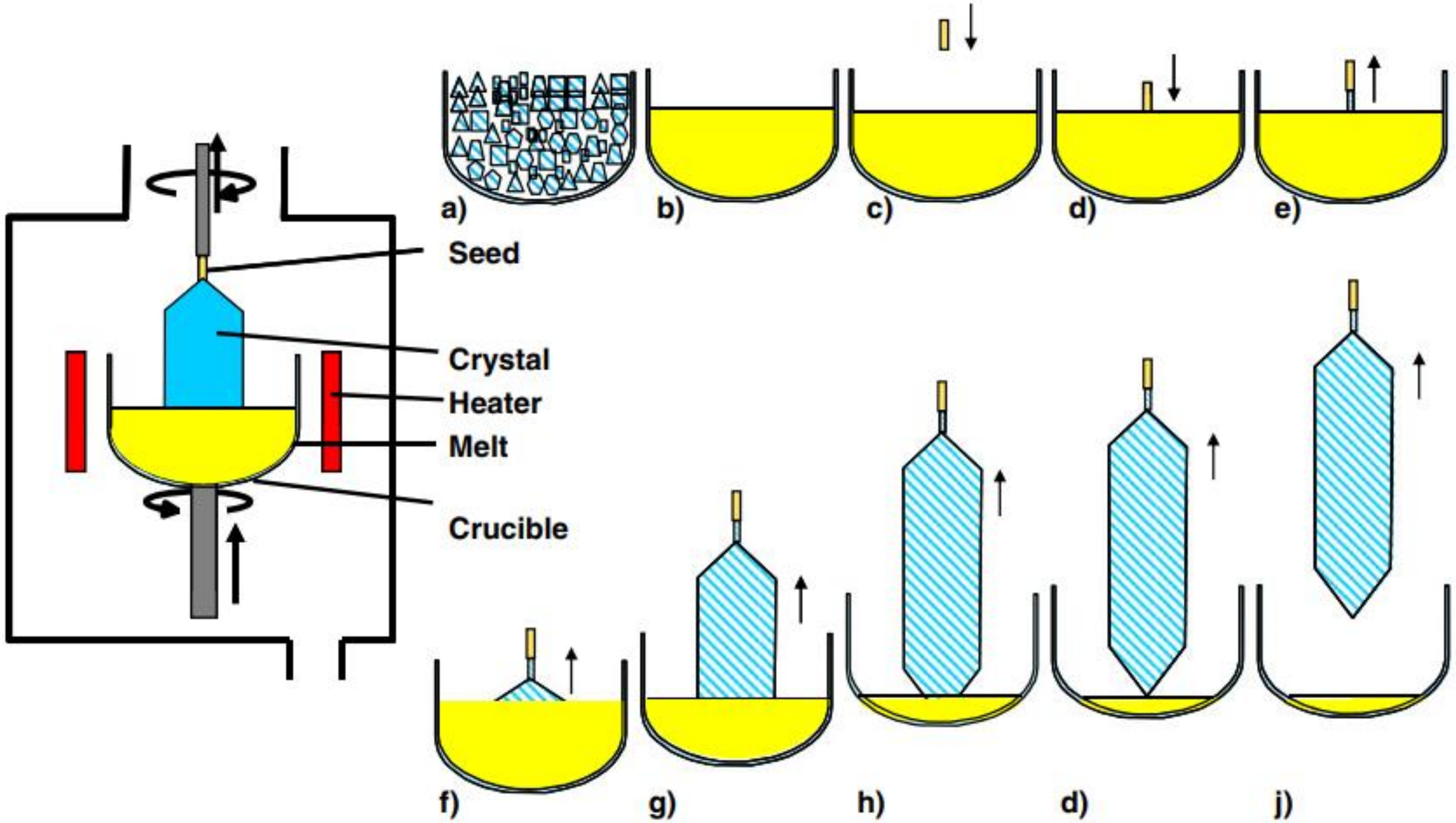


Figure 2 Schematic of the principle of the Czochralski method (left) and illustration of the different steps (a–j) of the Cz process for growing a Si crystal. (a) The polycrystalline feedstock is melted (b) in a crucible. (c, d) Seeding procedure: The seed crystal is dipped into the melt, followed by Dash necking (e), shouldering (f), cylindrical growth (g), growth of end cone (h), lift off (i), cooling down and removing of the crystal (j).

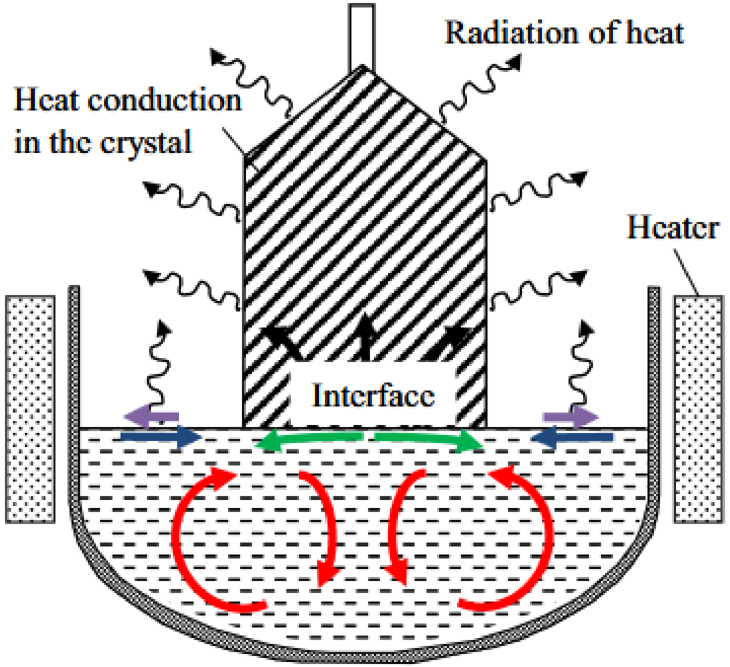
J. Friedrich, Methods for Bulk Growth of Inorganic Crystals: Crystal Growth, Reference Module in Materials Science and Materials Engineering, Elsevier, 2016,

Role of heat transport

$$\lambda_s \left(\frac{\partial T}{\partial z}\right)_s = \lambda_l \left(\frac{\partial T}{\partial z}\right)_l + \rho V L$$

λ_s , λ_l – thermal conductivity
V– growth rate
L – latent heat of crystallization

Temperature gradient in the crystal must be much larger than in the melt
$\lambda_l > \lambda_s$



Growth rate V itself is not limited by growth kinetics, but rather by the rate of heat transfer.
(for one component crystal)

(multi component crystals?)

Role of heat transport

$$\lambda_s \left(\frac{\partial T}{\partial z}\right)_s = \lambda_l \left(\frac{\partial T}{\partial z}\right)_l + \rho V L$$

λ_s , λ_l – thermal conductivity
V – growth rate
L – latent heat of crystallization

Temperature gradient in the crystal must be much larger than in the melt
$\lambda_l > \lambda_s$

Growth rate V itself is not limited by growth kinetics, but rather by the rate of heat transfer.
(for one component crystal)

(multi component crystals?)

V_{max} - depends on crystal diameter
High R – cooling of the crystal is less efficient

Limiting factors for V_{max}

Heat transfer
Incorporation of point defects
Thermal stress

Role of heat transport

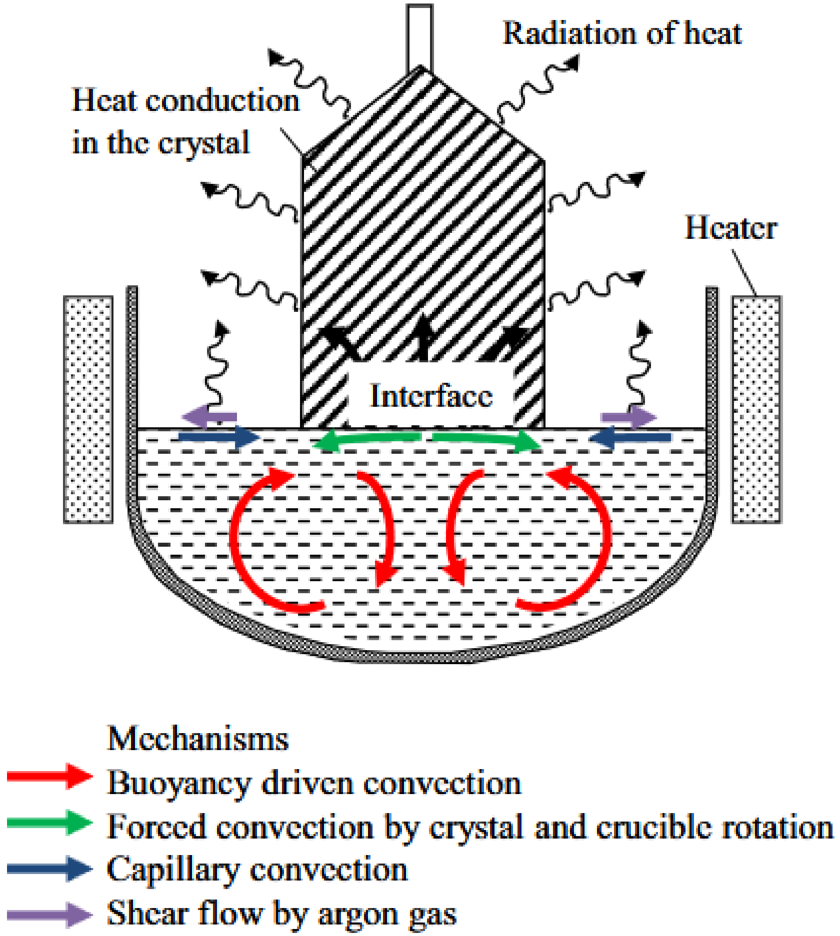
The convection can be classified into two categories.
One is related to temperature gradients,
and the other is related to the movements of crystal and crucible.

The driving force for the melt flowing can be represented by Grashof number (Gr)

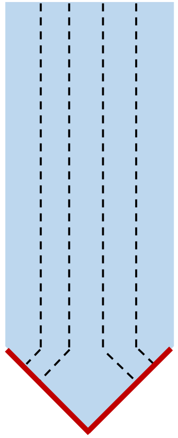
$$Gr = \frac{g\ \beta\ \Delta T_m\ L^3}{\nu_k}$$

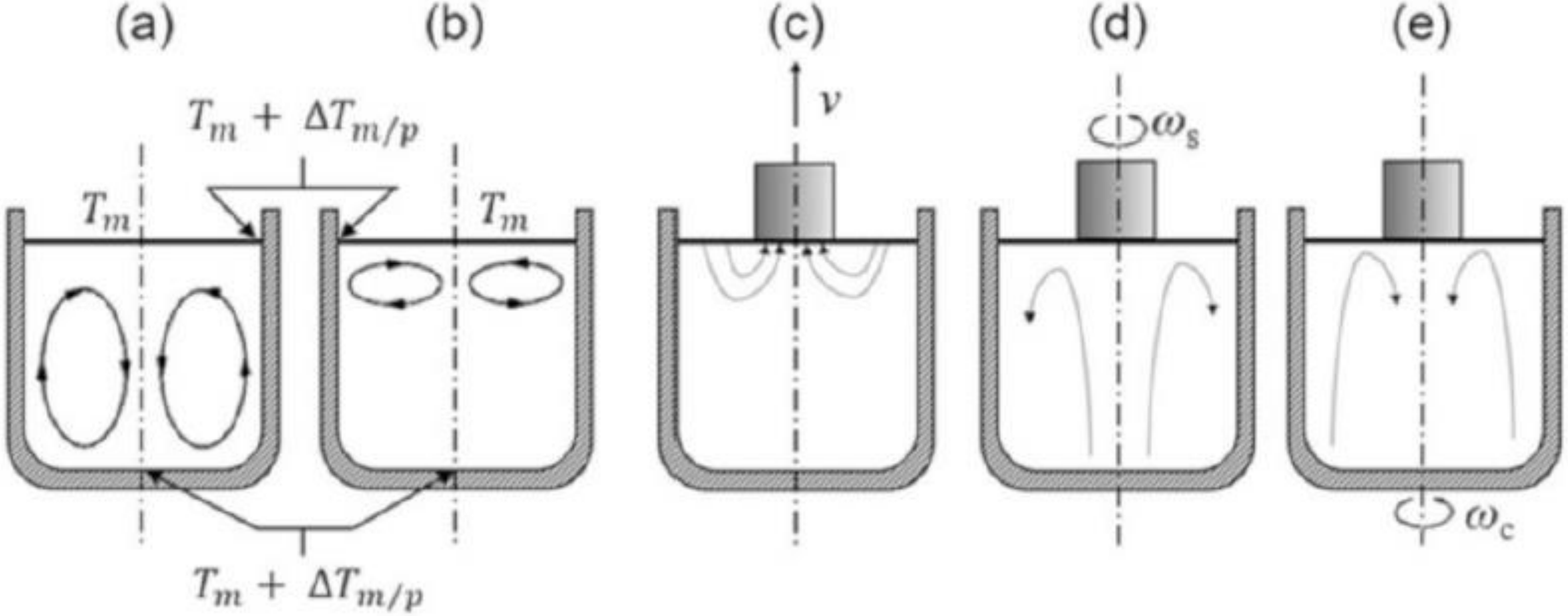
g – gravity acceleration
β – thermal expansion coefficient
ΔT_m – temperature difference in the melt over a specific length (L),
L – specific length
ν_k – kinematic viscosity

The thermal convection of the melt is suppressed by decreasing the value of Gr



Rotation





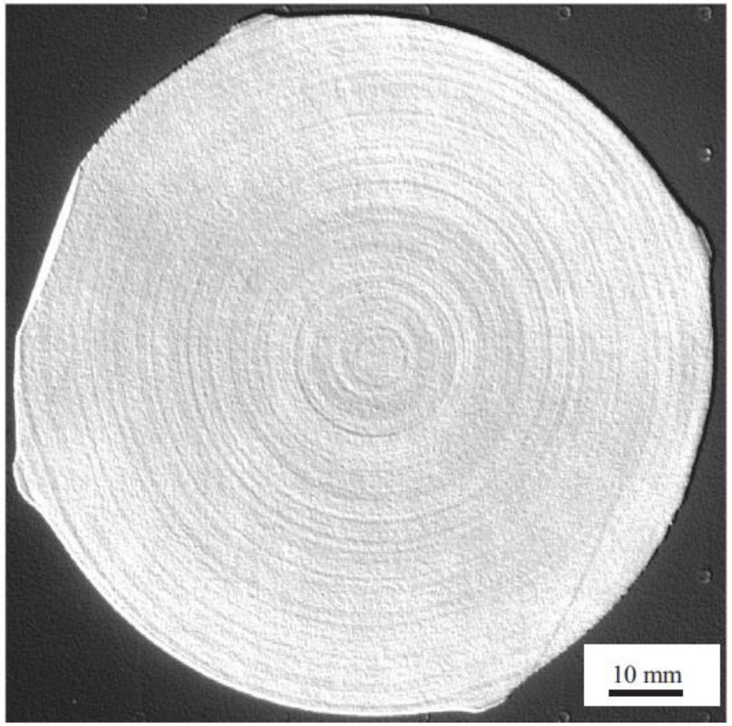
Crystal rotation: In a Cz melt, forced convection is induced by the rotation of the crystal with a certain rotation rate ω_S. The Si melt sticks to the crystal interface, which transfers its rotational movement to the melt region below the interface by the viscous forces in the melt.

Crucible rotation (ω_C): Similarly to the crystal rotation, the crucible rotation generates a contact force at the melt–crucible interface, leading to forced convection in the form of a primary azimuthal flow.

Heat transport - striations

X-ray topography of a longitudinal section of a silicon Cz crystal grown under the influence of a cusp magnetic field. The nonuniform incorporation of dopants causes the occurrence of growth striations displaying the shape of the solid–liquid interface.

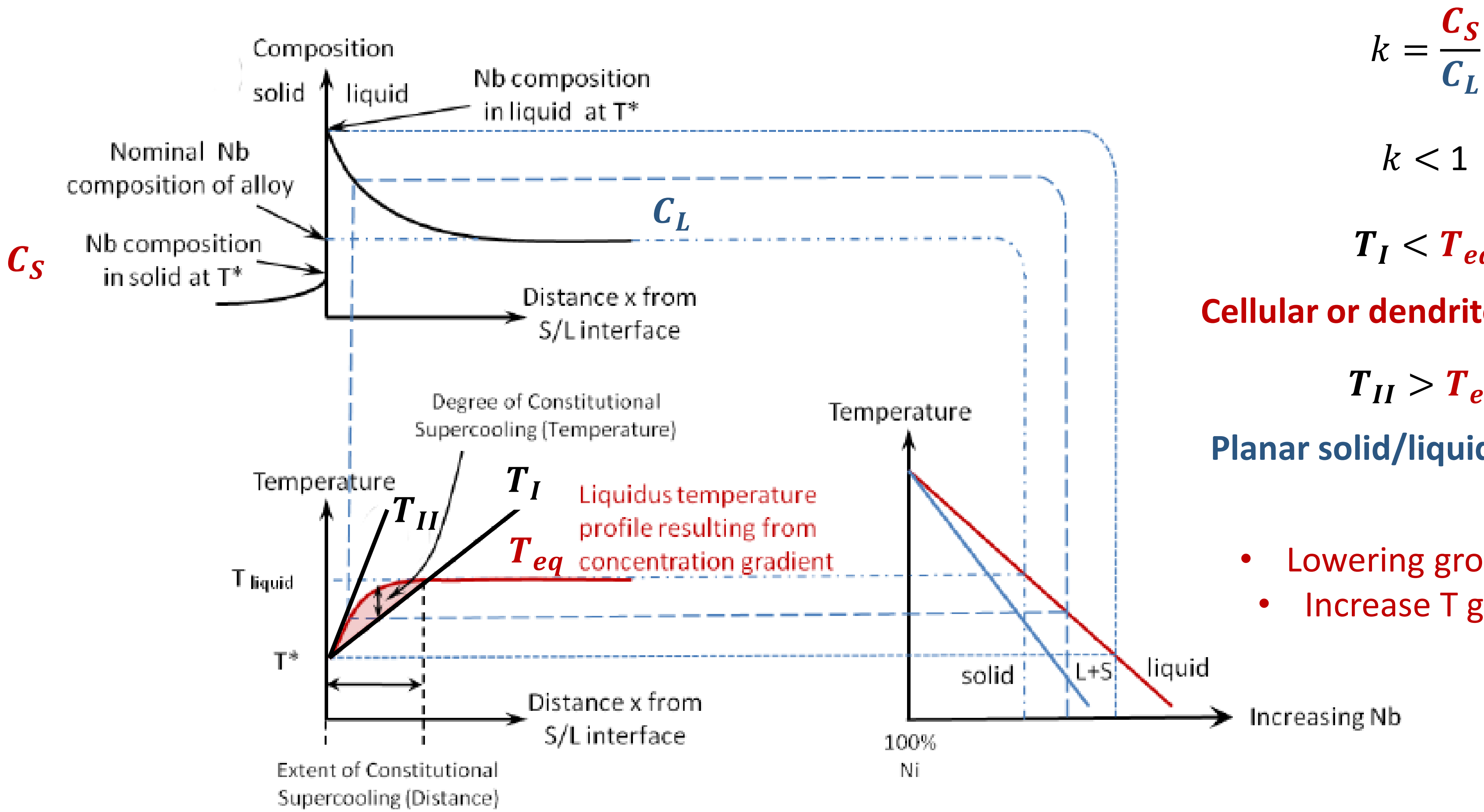
Watanabe M, Eguchi M, Hibiya T. J Cryst Growth 1998;193:402.



Visualization of rotational striations in a highly arsenic-doped silicon wafer (diameter approximately 100 mm) using a photoluminescence technique.

Courtesy of Fraunhofer IISB.

Constitutional supercooling (NiNb alloy)



$$k = \frac{C_S}{C_L}$$

$$k < 1$$

$$T_I < T_{eq}$$

Cellular or dendrite structure

$$T_{II} > T_{eq}$$

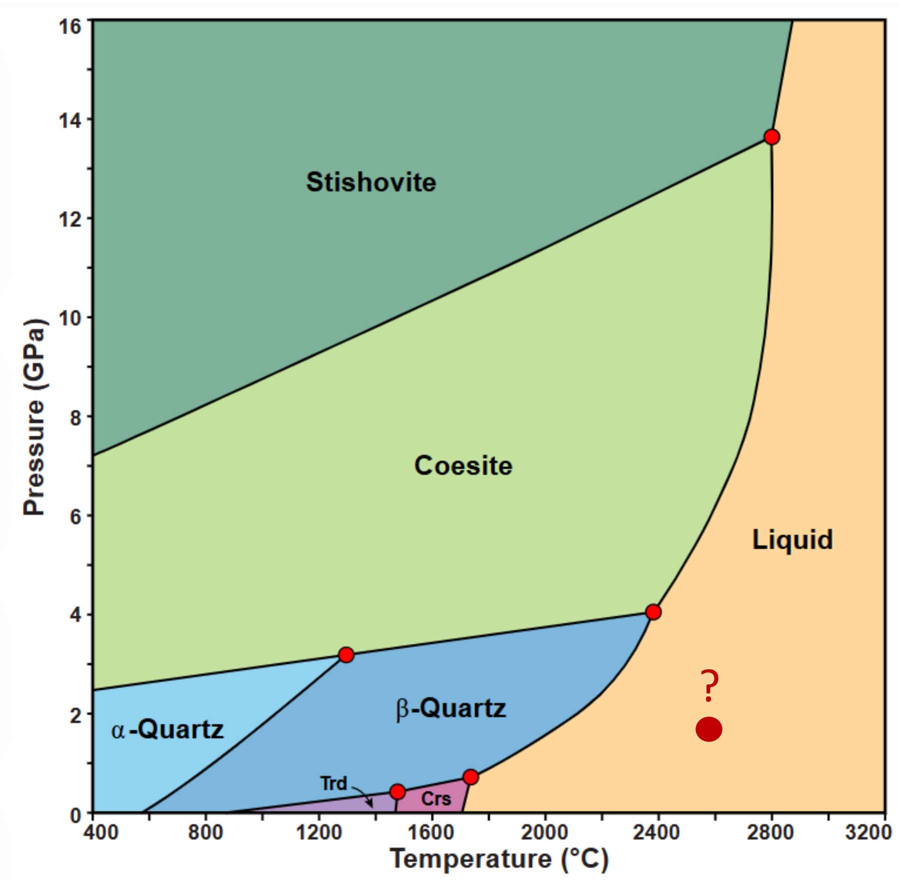
Planar solid/liquid interface

- Lowering growth rate
- Increase T gradient

Growth from the solution

When we have to use growth form solution method?

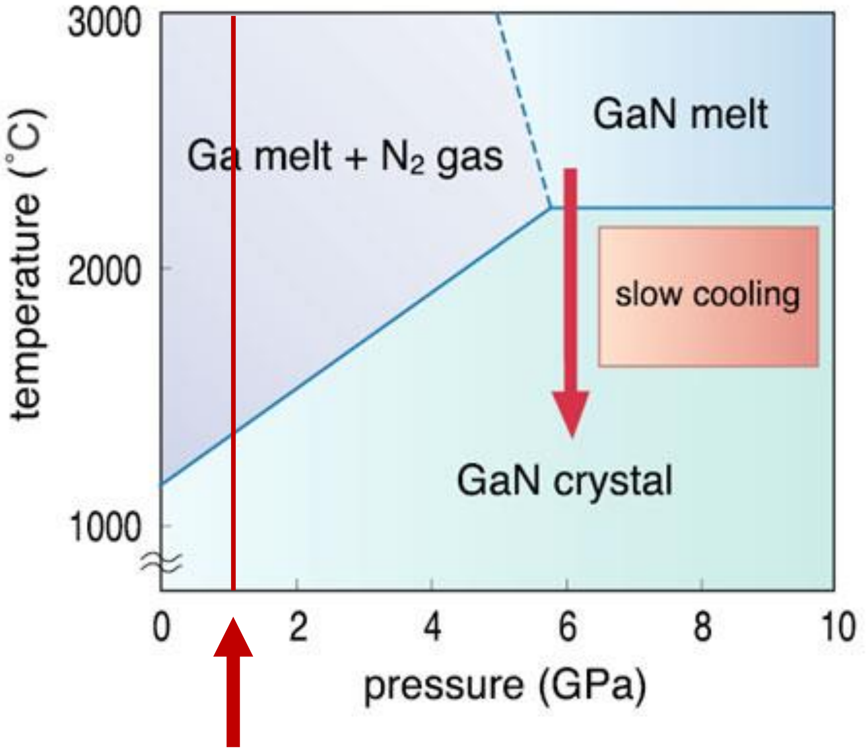
α - SiO_2



From experimental data by Bohlen and Boettcher (1982), Zhang and others (1993), and Fei and Bertka (1999).

Gallium Nitride

Multi-anvil high-pressure
apparatus Spring-8 synchrotron



Technological limit **Too ↑p**

W. Utsumi et al. Nature Materials 2 (2003) 735

- Bulk Growth
  - Melt Growth
    - *Crystal Pulling*
      - Czochralski Technique
        - Liquid Encapsulated Czochralski
        - Vapor Controlled Czochralski
        - Magnetic Field Czochralski
        - Other Czochralski Variants
      - Nacken–Kyropulous
      - Shaped Crystal Growth
    - *Directional Solidification*
      - Gradient Freeze and Bridgman Technique
        - Heat Exchanger Method
        - Skull Melting
        - Detached Solidification
      - Zone Melting
    - *Floating Zone*
    - *Verneuil Technique*
  - Solution Growth
    - *Growth from Aqueous Solutions*
    - *Flux Growth*
    - *Hydrothermal Growth*
    - *High Pressure Synthesis*
  - Vapor Growth
    - *Physical Vapor Transport*
    - *Chemical Vapor Transport*

Methods for Bulk Growth of Inorganic Crystals: Crystal Growth
J Friedrich, Fraunhofer Institute IISB, Erlangen, Germany
2016 Elsevier Inc.

Growth from solution

The methods of growing crystals from solutions are classified into several groups based on the principle by which supersaturation is achieved.

- Crystallization by changing the solution temperature.

This includes methods where the solution temperature varies in different parts of the crystallization vessel (**temperature-difference methods**) as well as isothermal crystallization, where the entire volume of the solution is cooled or heated (**cooling method**).

- Crystallization by changing the composition of the solution (e.g., **solvent evaporation**).
- Crystallization by **chemical reaction**.

The choice of method depends on the solubility of the substance and the temperature solubility coefficient $\partial C_0/\partial T$. A few rules can be formulated to serve as guidelines in selecting the appropriate method

Temperature Solubility Coefficient $\partial C_0/\partial T$

Solubility $mol_{solute}/mol_{solvent}$

Growth from solution - criteria

The choice of method depends on the **solubility** of the substance and the **temperature solubility coefficient** (TCS) $\partial C_0/\partial T$.

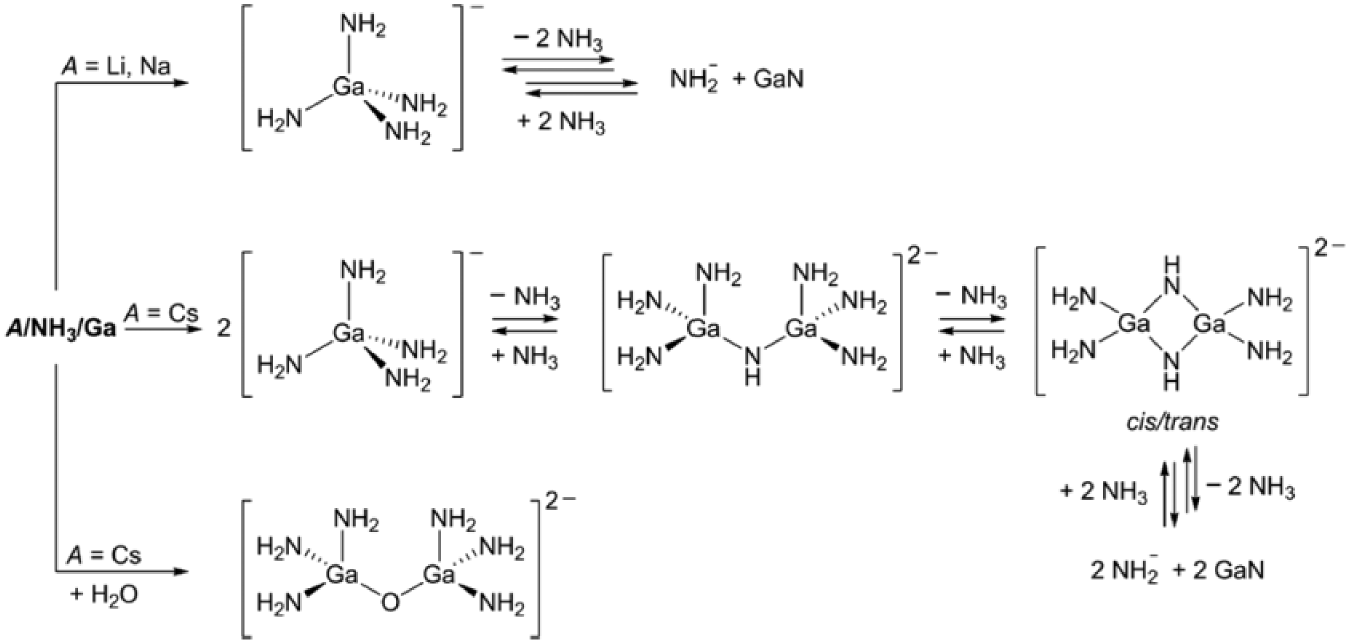
1. TCS > 0 - crystallization by temperature-difference method may be used.
   - TCS i low (0.01-0.1 g/l deg) continuous growth of crystals in one part of the crystallization vessel as a result of continuous dissolution of the substance in the other part or cooling method.
   - TCS is high (over 1 g/l deg), Low absolute solubility of the substance is low (several weight percent).
   - TCS i high, solubility is high – cooling method (difficult to control)
2. TCS is very low, crystallization can be achieved by solvent evaporation or by chemical reaction. The absolute solubility is not particularly important here, but it must not be too low in evaporation methods.
3. Solubility is low, crystallization by chemical reaction is expedient.
4. Growth at a constant temperature and at a constant supersaturation in the growth zone is best ensured by feed-up methods. The temperature-difference method can be considered a version of the feed-up method. In other versions a supersaturated solution is added to the crystallizer making use of various techniques and forced convection of the solution is realized.

Chemistry…

Crystal growth from solutions always occurs under conditions in which the solvent and the crystallizing substance interact.

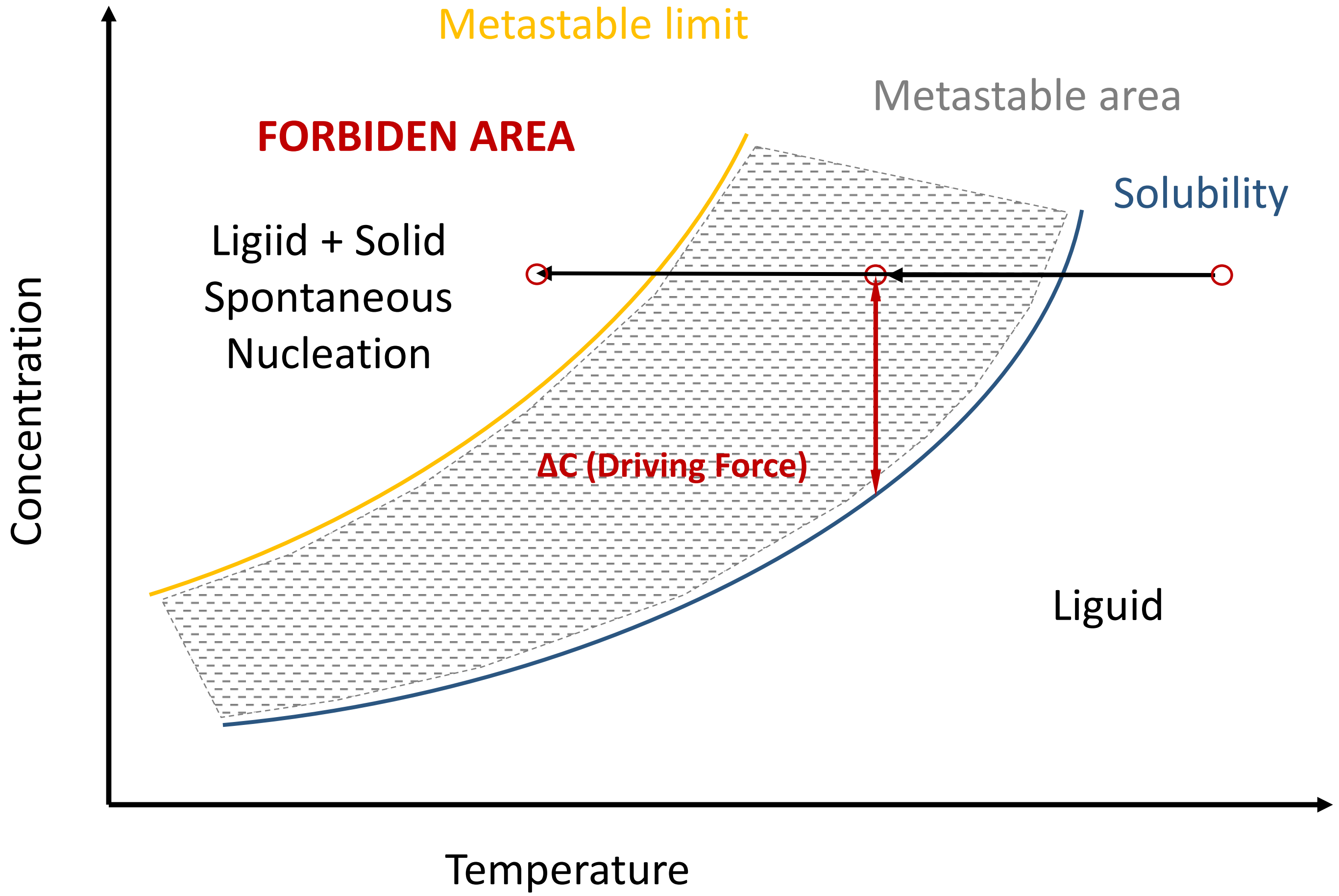
This interaction manifests itself in the formation of complexes between solvent molecules (or ions) and solute molecules in the bulk of the liquid phase, as well as in the solvation (hydration in aqueous solutions) of the crystal faces.

Scheme 1. Reactions under Ammonothermal Conditions with Different Alkali Metal Amides Serving as Mineralizer and Occurring Equilibria of Ga-Containing Complex Species[a]



[a]Double arrows for GaN formation represent possible multi-step processes.

Driving force for crystal growth



Supersaturation and Crystallization for Nucleation and Growth (mt.com)

The crystallization process should be carried out in the metastable area!

Critical radius

$\Delta G_r = \Delta G_S + \Delta G_V$

$\Delta G_S = 4\pi r^2 \gamma > 0$

γ - surface tension (always positive)

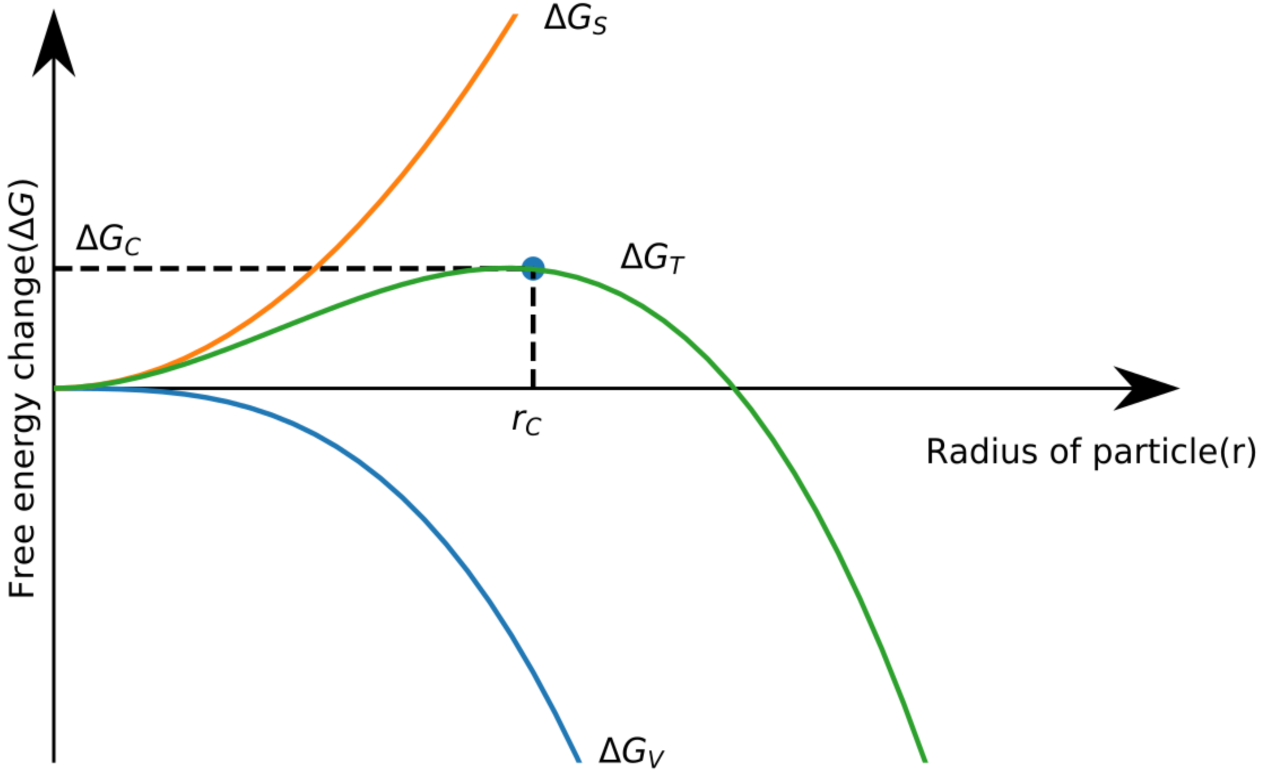
$\Delta G_V = \frac{4}{3}\pi r^3 \Delta g_V$

Δg_V - Gibbs free energy per volume

It is defined as the energy difference between one system at a certain temperature and the same system at the fusion temperature and it depends on pressure, the number of particles and temperature:
$\Delta g_V\ (T, p, N)$

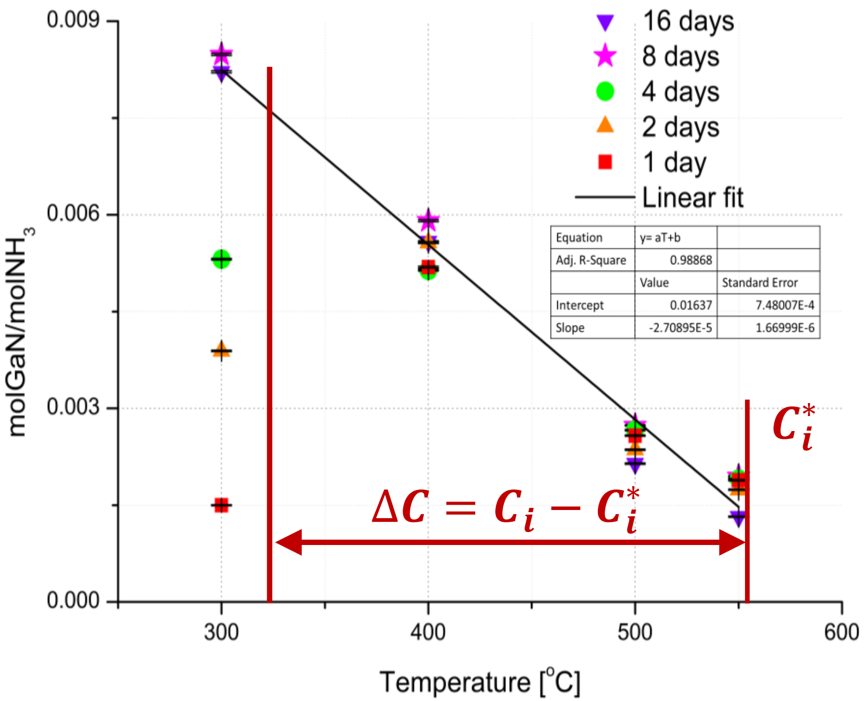
Temperature, far from the fusion point - big (it is more difficult to change the phase) and

Temperature close to the fusion point - small (the system will tend to change its phase).



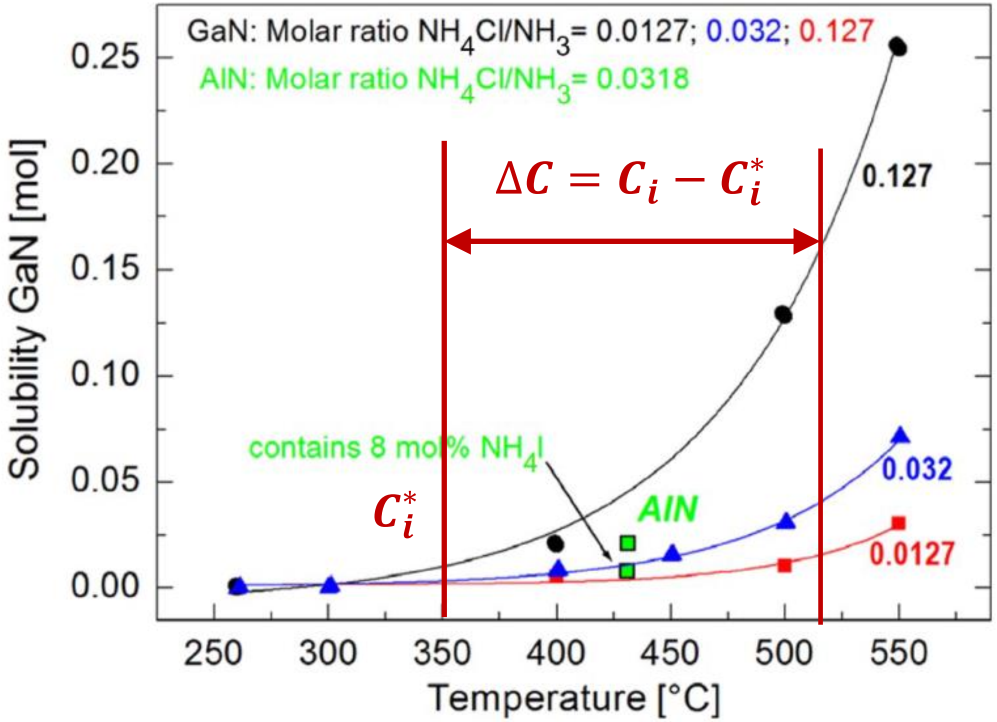
Solubility and Driving Force – GaN crystalization

Ammonothermal - Basic



K. Grabianska et al., submitted to J. Cryst. Growth.

Ammonothermal - Acidic



Ehrentraut, Dirk & Fukuda, Tsuguo. (2010). The Ammonothermal Crystal Growth of Gallium Nitride—A Technique on the Up Rise. Proceedings of the IEEE. 98. 1316 - 1323. 10.1109/JPROC.2009.2029878.

Solubility – strange situation? ☺

Na_2ZnGe0_4 in the NaOH solution

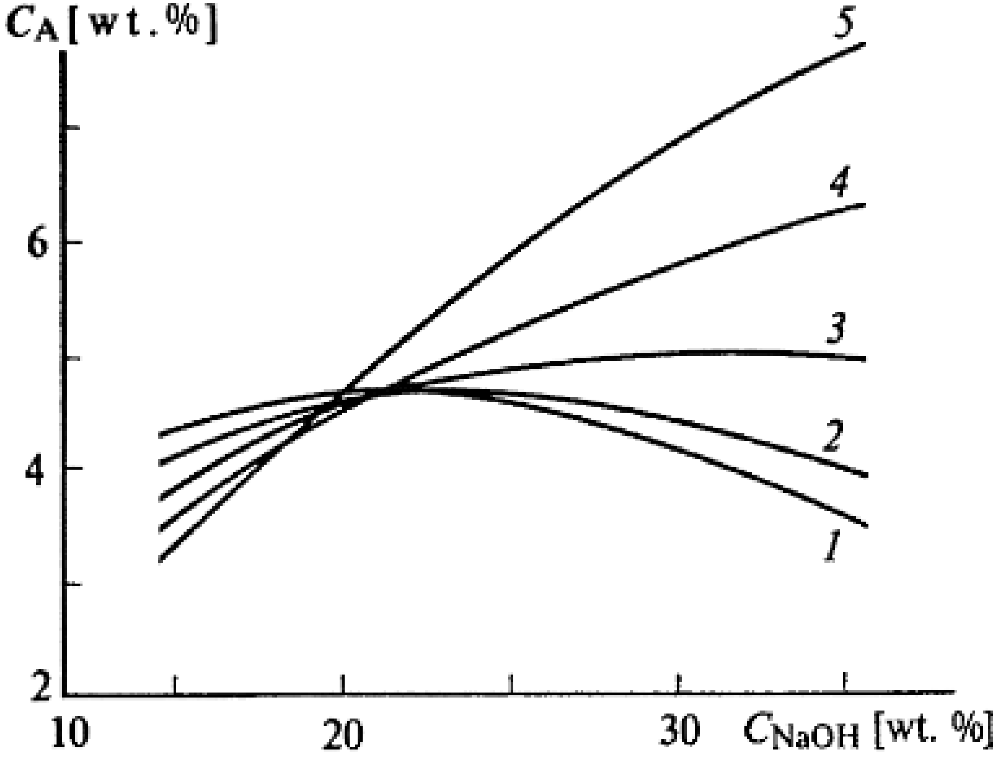


Fig.9.29. Solubility of sodium zinc germanate in aqueous solutions of sodium hydroxide vs solvent concentration [9.59]. (*1*) 200°C, (*2*) 220°C, (*3*) 250°C, (*4*) 300°C, (*5*) 350°C

Growth from solution - criteria

For a large number of substances, the solubility in water at low temperatures (below 100°C), where the vapor pressure over the solution is significantly lower than atmospheric pressure.

For those substances, growing crystals from aqueous solutions becomes impracticable.

One way to increase solubility is by raising the solution temperature and pressure.

High pressure + high temperature water → Hydrothermal (SiO_2)

High pressure + high temperature ammonia → Ammonothermal (GaN)

Additional compound: Mineralizer

Ammonia properties…

$NH_{3\ (l)}$

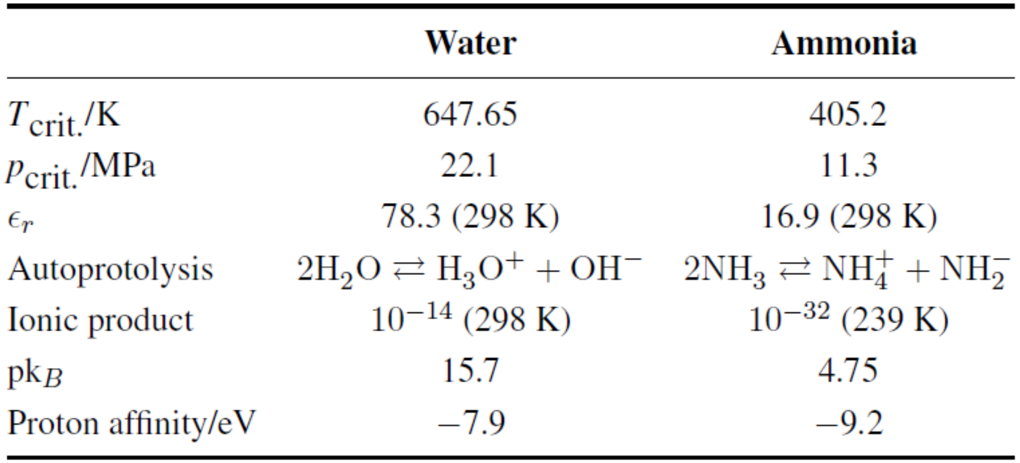
Less protic and polar then H_2O, at ambient p, T,
Liquid ammonia shows small solubilities for inorganic compounds,
Higher vapor pressures at high T,

Solubility condition
$\epsilon_r > \Delta U_{lattice}$ (lattice Energy of the solid)

$NH_{3(sc)}$

p_{crit}, T_{crit}

$\uparrow p \rightarrow \uparrow \rho_{fluid} \rightarrow \uparrow \epsilon_r \rightarrow \uparrow$ Solubility

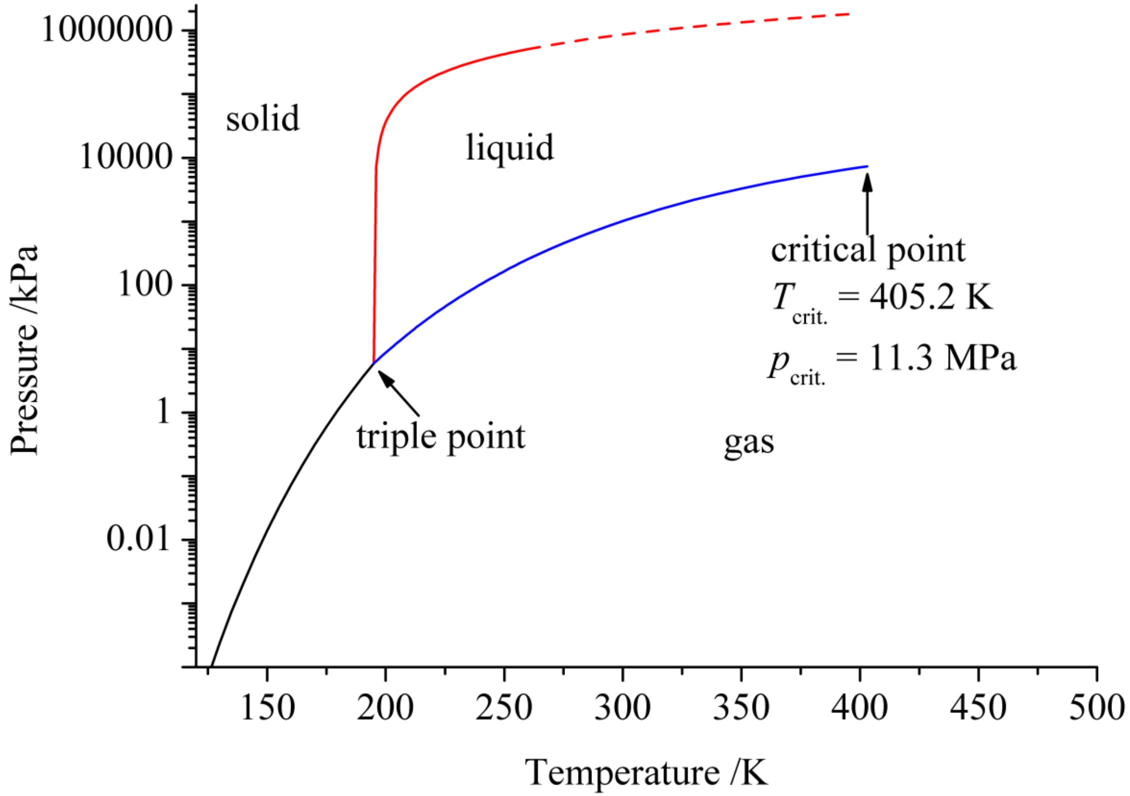


	Water	Ammonia
$T_{crit.}$/K	647.65	405.2
$p_{crit.}$/MPa	22.1	11.3
ϵ_r	78.3 (298 K)	16.9 (298 K)
Autoprotolysis	$2H_2O \rightleftarrows H_3O^+ + OH^-$	$2NH_3 \rightleftarrows NH_4^+ + NH_2^-$
Ionic product	10^{-14} (298 K)	10^{-32} (239 K)
pk_B	15.7	4.75
Proton affinity/eV	−7.9	−9.2

ε_r - relative permittivity (dielectric constant)

Glasser, L. Equations of state and phase diagrams of ammonia. J. Chem. Educ. 2009, 86, 1457–1458.

Ammonia as solvent



	Water	Ammonia
$T_{\text{crit.}}$/K	647.65	405.2
$p_{\text{crit.}}$/MPa	22.1	11.3
ϵ_r	78.3 (298 K)	16.9 (298 K)
Autoprotolysis	$2H_2O \rightleftarrows H_3O^+ + OH^-$	$2NH_3 \rightleftarrows NH_4^+ + NH_2^-$
Ionic product	10^{-14} (298 K)	10^{-32} (239 K)
pk_B	15.7	4.75
Proton affinity/eV	−7.9	−9.2

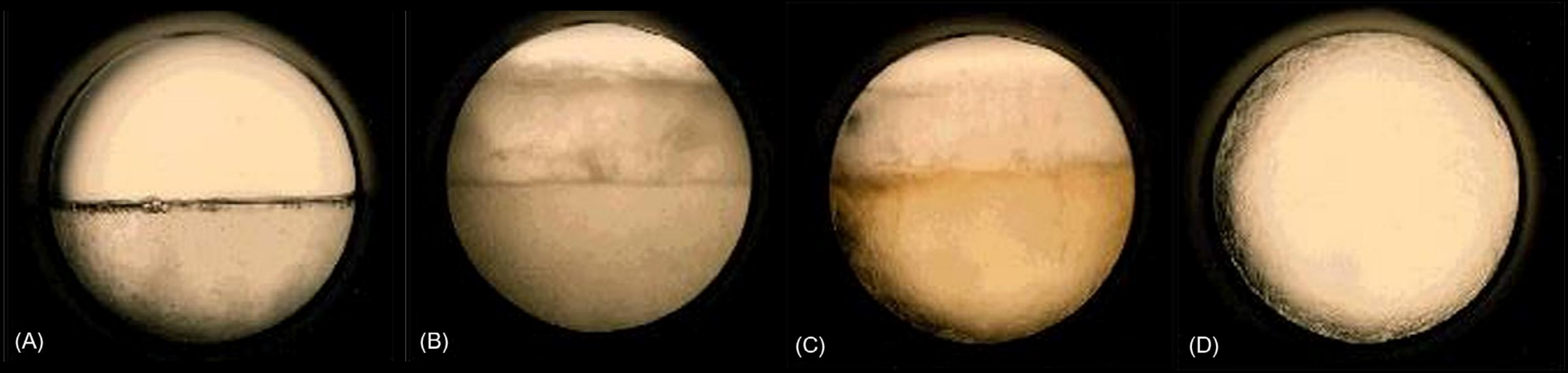
ε_r - relative permittivity (dielectric constant)

Glasser, L. Equations of state and phase diagrams of ammonia. J. Chem. Educ. 2009, 86, 1457–1458.

Phase transfer of CO_2

↑p, ↑T

SCF state



vapor-liquid phase equilibrium

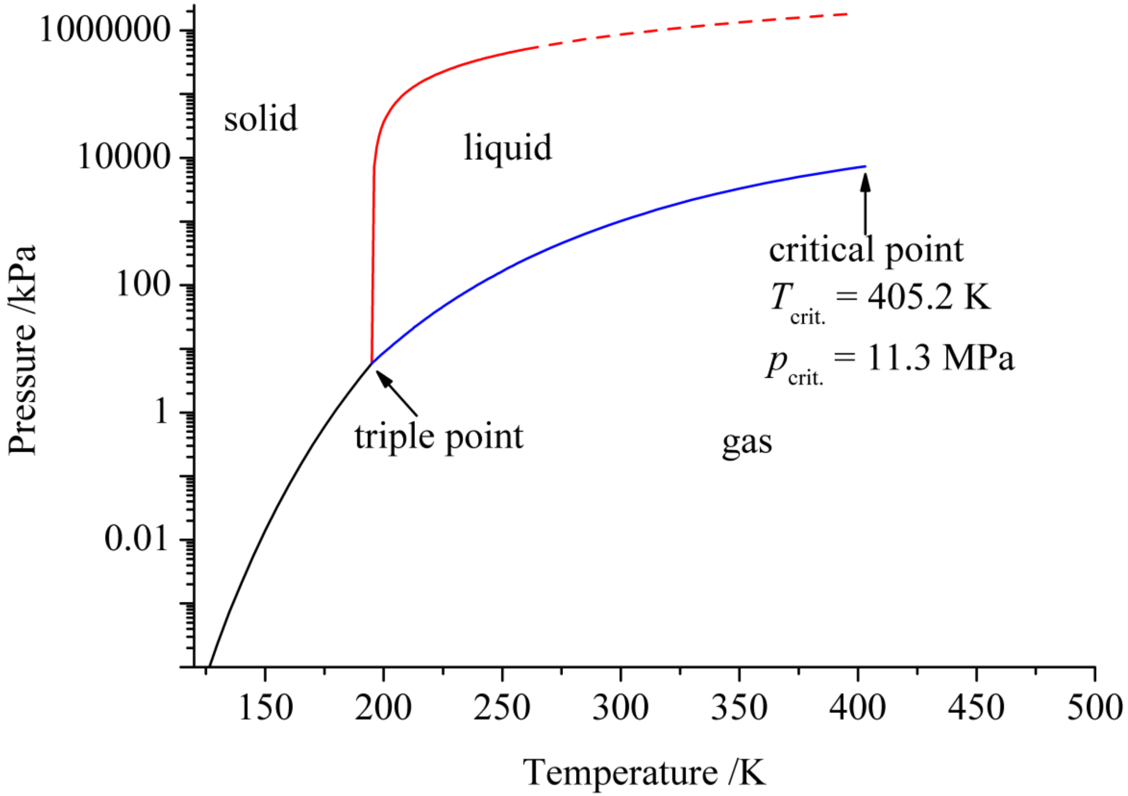
meniscus begins to disappear

the densities of the liquid and vapor phases are more similar

two phases are no longer distinguishable

University of Leeds, School of Chemistry, http://www1.chem.leeds.ac.uk/ (accessed February, 2016)

Ammonia at supercritical state



“gas-like” viscosity

“liquid-like” density

low viscosity inherently leads to fast diffusivity

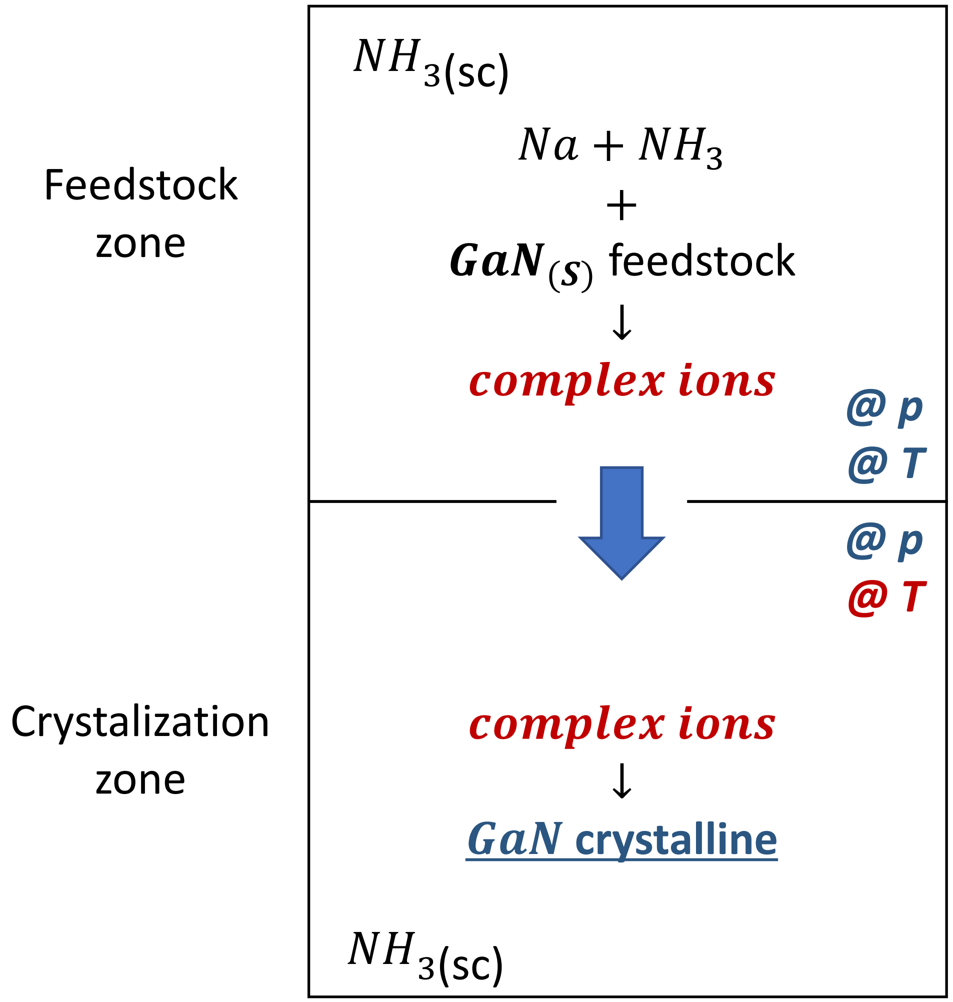
compressibility of an SCF is much larger than that of a liquid,

relatively small change in pressure leads to a quite large change in volume and density.

solubility can easily be tuned by changing temperature and pressure.

Glasser, L. Equations of state and phase diagrams of ammonia. J. Chem. Educ. 2009, 86, 1457–1458.

Minealizers…



Feedstock zone

$NH_{3(\text{sc})}$

$Na + NH_3$

$+$

$\mathbf{GaN}_{(s)}$ feedstock

$\downarrow$

complex ions

@ *p*

@ *T*

@ *p*

@ ***T***

Crystalization zone

complex ions

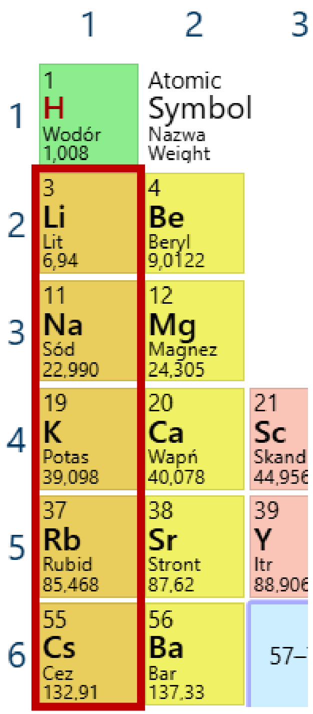
$\downarrow$

GaN **crystalline**

$NH_{3(\text{sc})}$

$$2Na + 2NH_3 \rightarrow \mathbf{2NaNH_2} + H_2$$

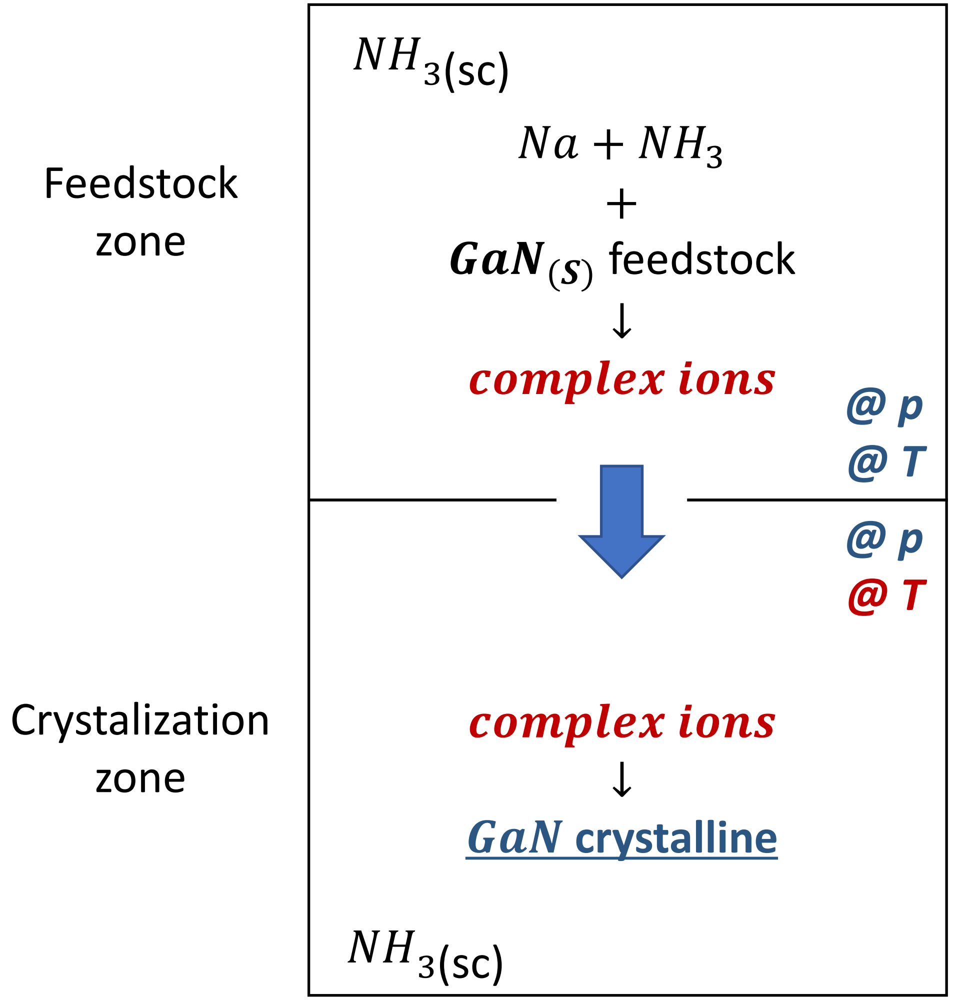
$$LiNH_2, KNH_2, NaNH_2, RbNH_2, CsNH_2$$



	1	2	3
1	1 H Wodór 1,008	Atomic Symbol Nazwa Weight	
2	3 Li Lit 6,94	4 Be Beryl 9,0122	
3	11 Na Sód 22,990	12 Mg Magnez 24,305	
4	19 K Potas 39,098	20 Ca Wapń 40,078	21 Sc Skand 44,956
5	37 Rb Rubid 85,468	38 Sr Stront 87,62	39 Y Itr 88,906
6	55 Cs Cez 132,91	56 Ba Bar 137,33	57–

Solubility of the metal and complex ions in NH_3 increases with increasing atomic weight

Minealizers…



Feedstock zone

$NH_{3(sc)}$

$Na + NH_3$

$+$

$\boldsymbol{GaN_{(s)}}$ feedstock

$\downarrow$

complex ions

@ p

@ T

@ p

@ T

Crystalization zone

complex ions

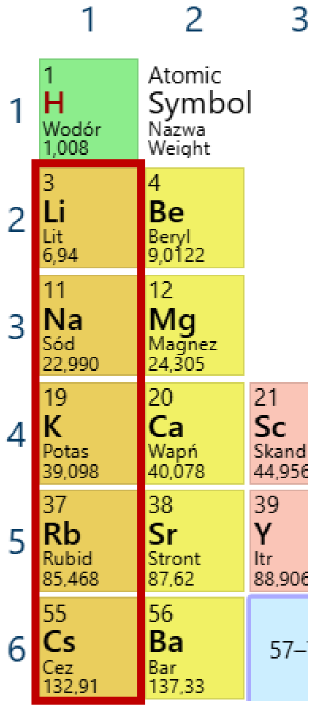
$\downarrow$

GaN **crystalline**

$NH_{3(sc)}$

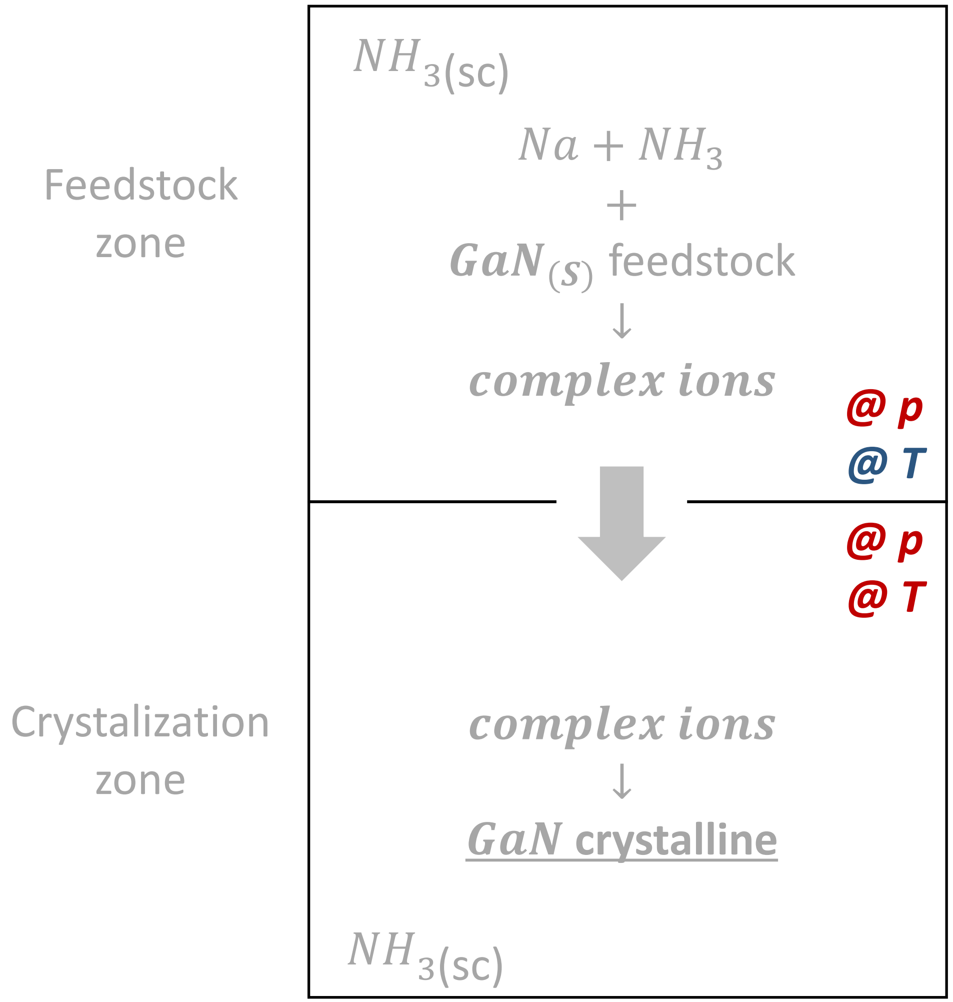
$$2Na + 2NH_3 \rightarrow \mathbf{2NaNH_2} + H_2$$

$$LiNH_2, KNH_2, NaNH_2, RbNH_2, CsNH_2$$



	PLN / 100g
Li	1 500
Na	100
K	1 800
Rb	370 000
Cs	140 000

Crucial parameters of the process



Feedstock zone

$NH_{3(sc)}$

$Na + NH_3$

$+$

$GaN_{(s)}$ feedstock

↓

complex ions

@ *p*

@ *T*

@ *p*

@ *T*

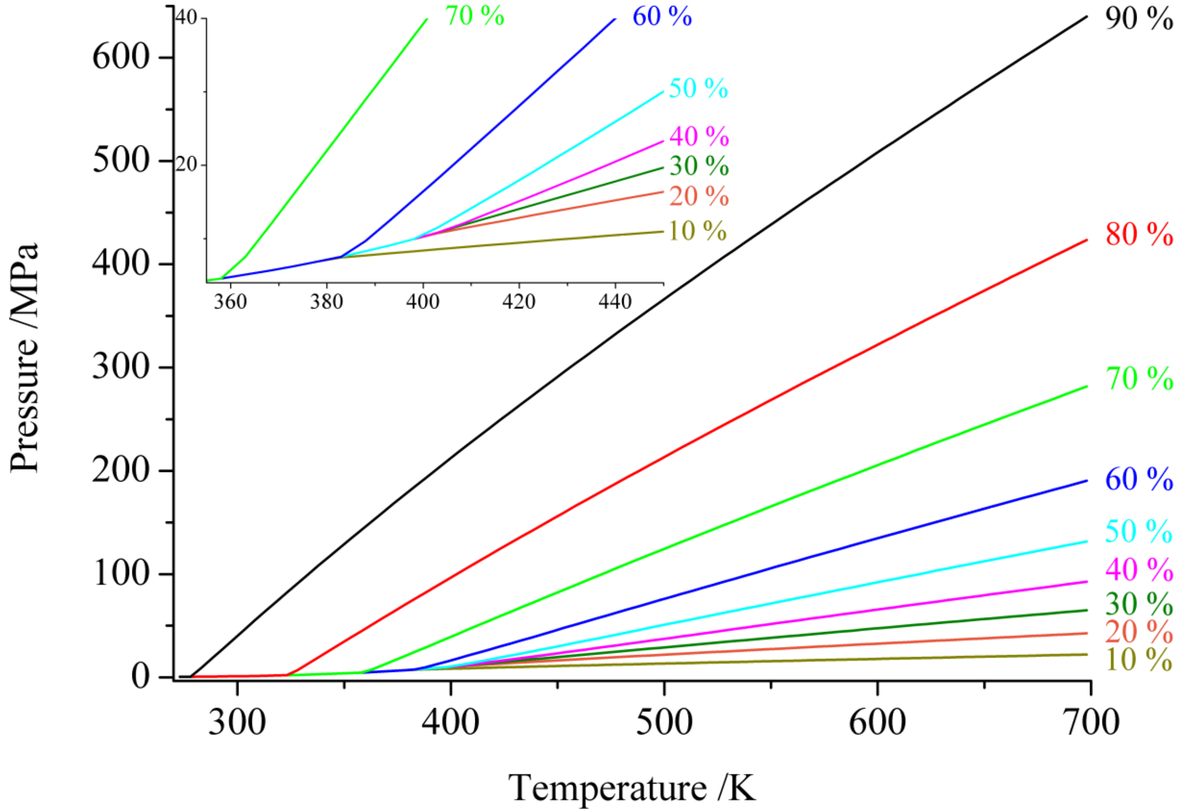
Crystalization zone

complex ions

↓

$\underline{GaN}$ **crystalline**

$NH_{3(sc)}$

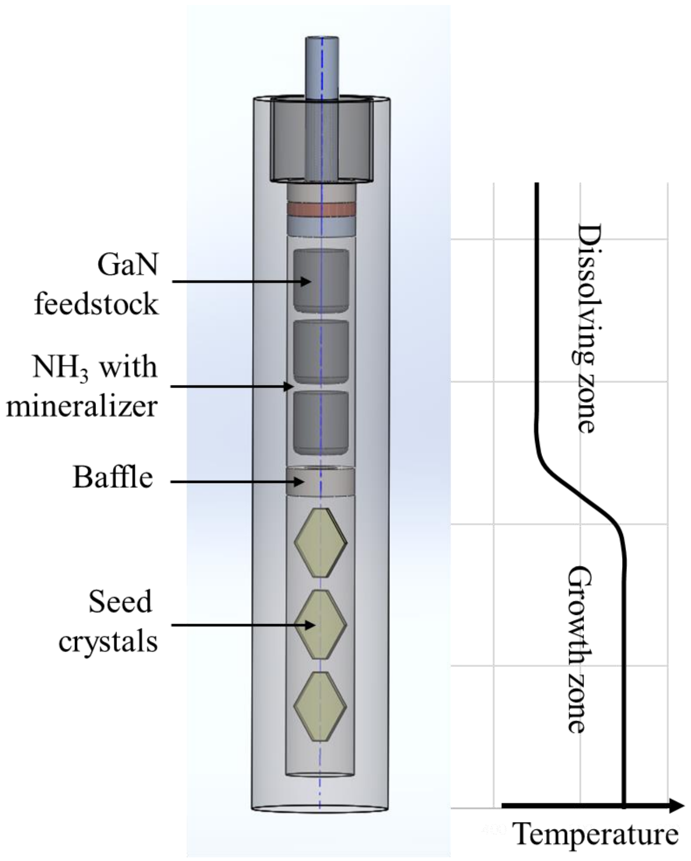


Pressure-temperature diagram of ammonia in dependence on the filling degree of the reaction vessel (in %).

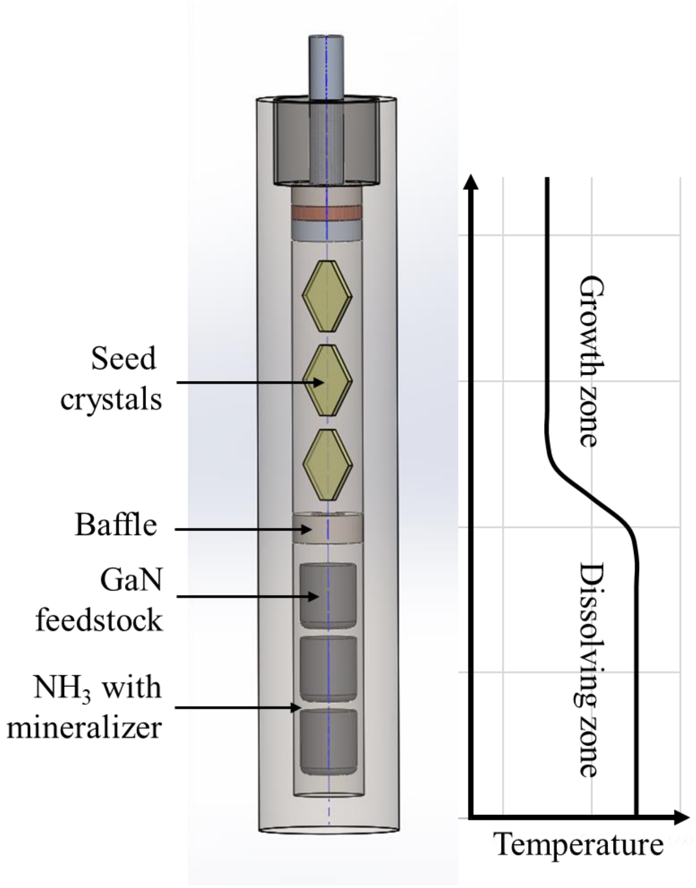
Lemmon, E.W.; McLinden, M.O.; Friend, D.G. Thermophysical properties of fluid systems, NIST standard reference data. Available online: http://webbook.nist.gov/chemistry/fluid/

Ammonothermal Method (GaN crystalization)

Basic



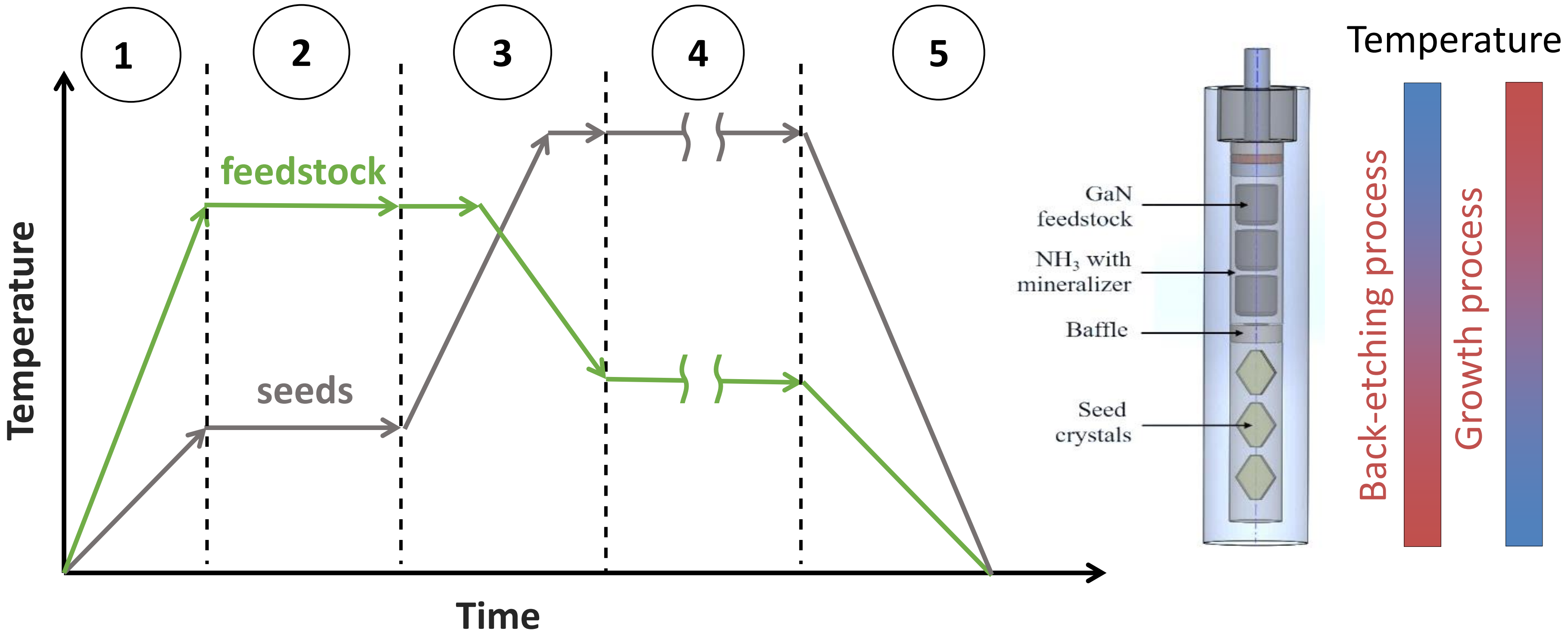
Acidic



Mineralizers: Alkali metals | Halide compounds

Basic Ammonothermal Method

1. Heat-up
2. Back-etching of the seeds at lower temperature - coupling of the solution with seeds
3. Temperature transition
4. Growth at higher temperature/dissolution of the feedstock at lower temperature
5. Cool-down

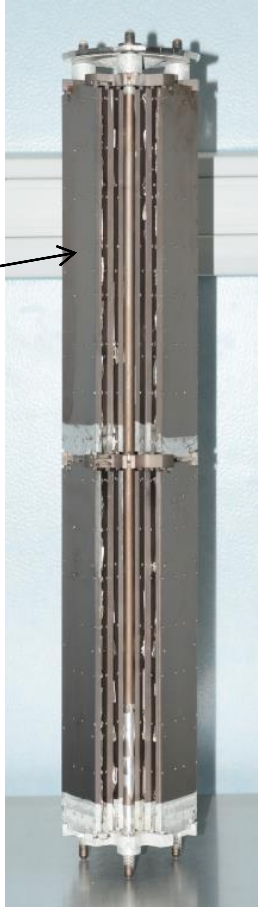


Basic Ammonothermal GaN Crystals

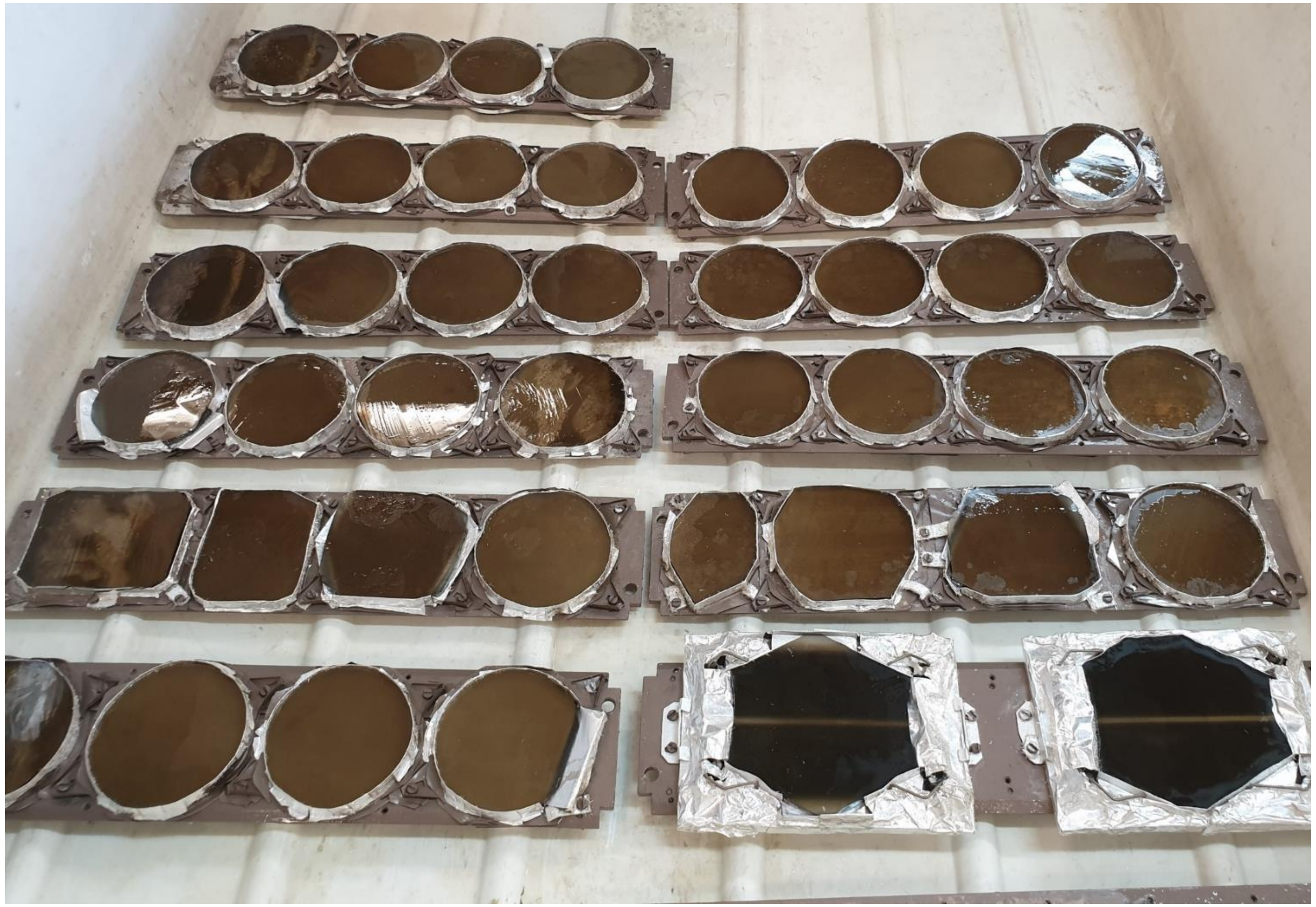
Seed selection

Mounting
on metal plate

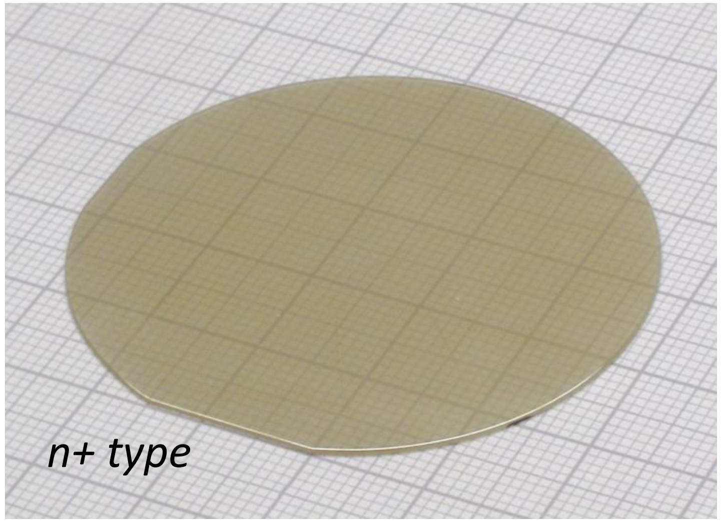
Growth zone

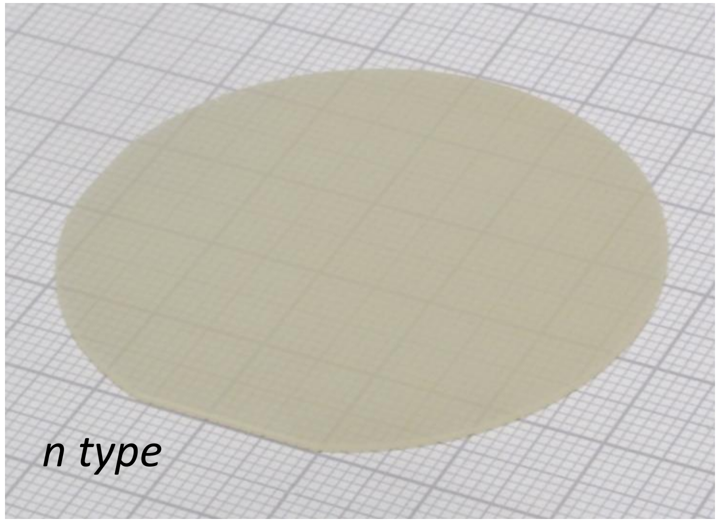


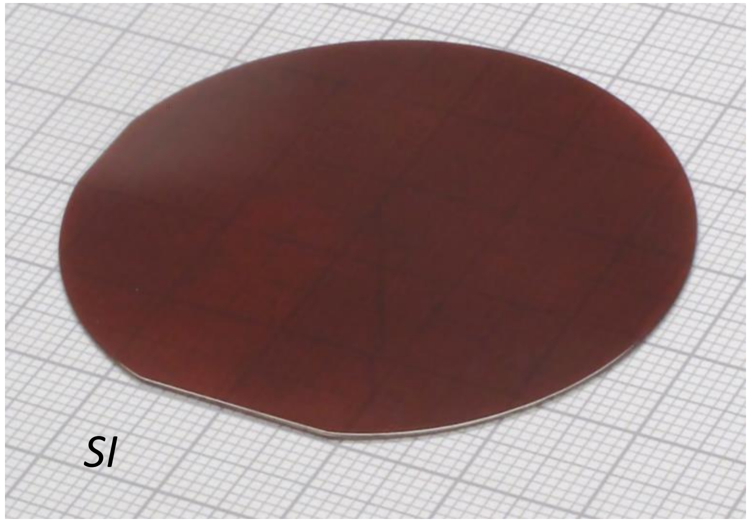
After growth process

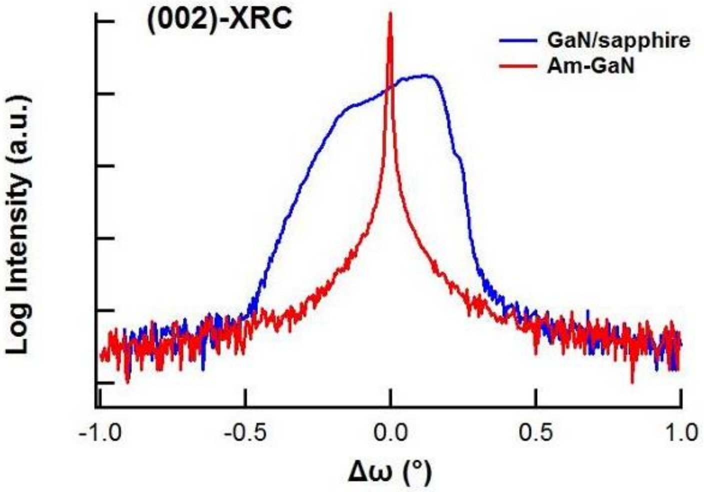


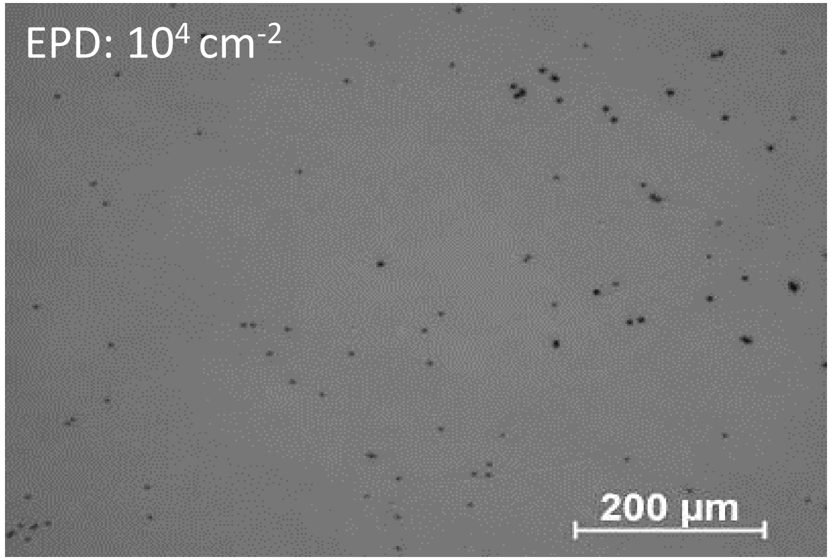
AM-GaN substrates – electrical properties


n+ type


n type

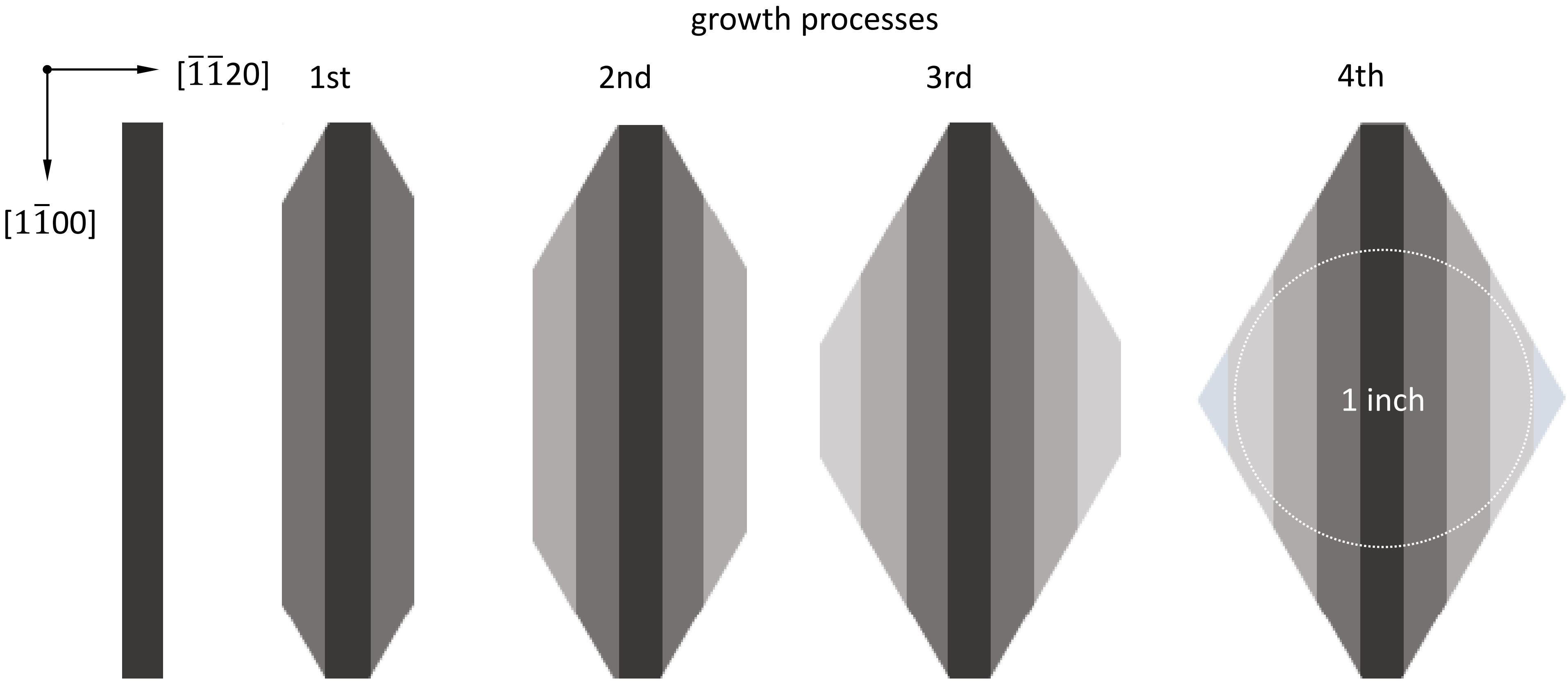

SI




EPD: 10^4 cm^{-2}

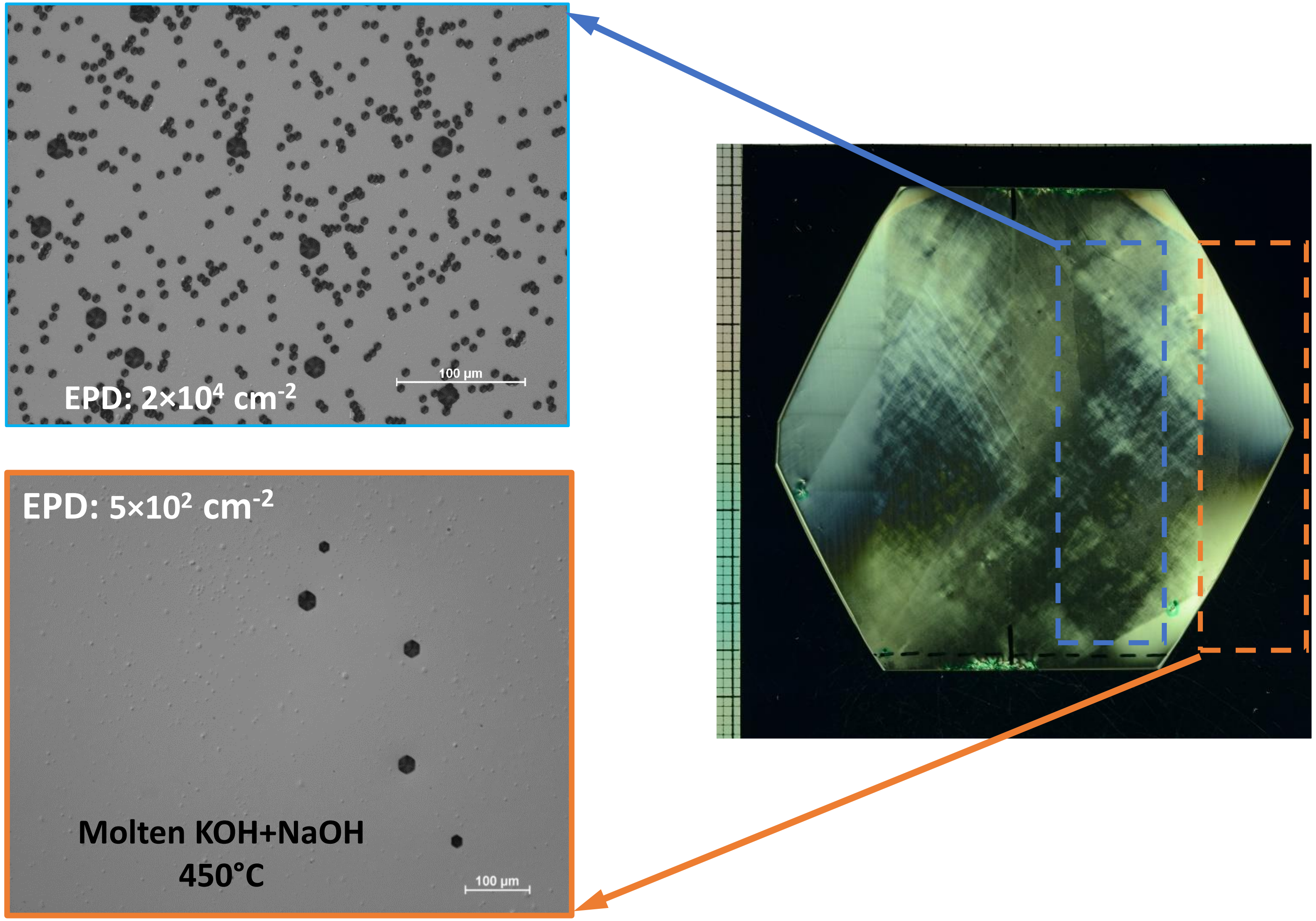
Dopping in GaN
n-type: O, Ge, Si, Sn
SI: Mn, Fe, C, Mg*
p-type: Mg, C*

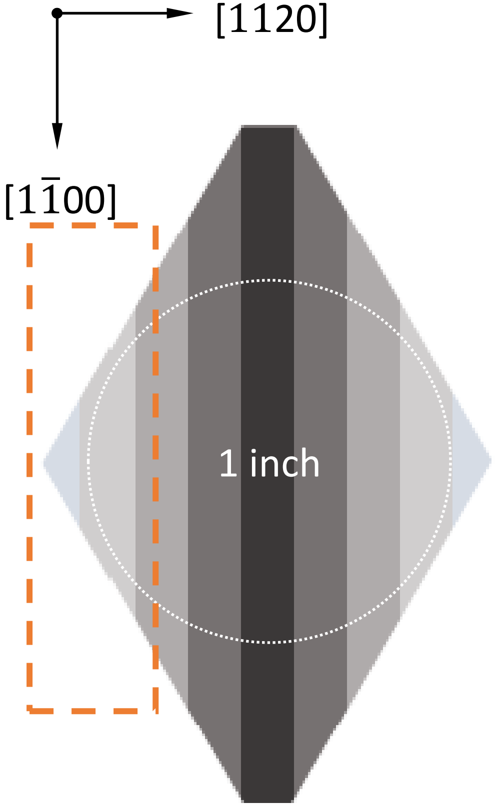
Crystal enlargement (looks familiar?)



[000-1]: (40 µm/day)
[11-20]: (80 µm/day)
[10-10]: (2 µm/day)

Crystal enlargement (dislocation reduction)





unipress

Crystal growth from the melt vs growth from the solution

Growth from melt:

- available only for materials which melts congruently (= the same composition of liquid and solid phase at equilibrium), and under the conditions that termodynamical parameters are technically accessible,
- high growth rates,
- supercooling is the factor which controls the growth,
- precise control of temperature field in growth zone is required,
- good control of impurities is possible (impurities < ~0.1 %at.), but may require a proper care.

Growth from solution:

- for many various materials providing the chemically proper solvent can be found,
- dissolution reaction must be reversible and possible to control (p, T),
- small growth rates, but simple control of
- Growth
- supersaturation is the factor which
- controls the growth
- a precise controll of components transport
- conditions from dissolution zone to growth
- zone is required.

unipress

Thank you for your attention