# Fundamental methods of single-crystal growth

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# Single-crystal and its growth

- Single-crystal
  - regular arrangement of basic building blocks (atoms, ions, molecules) is preserved on the macroscopic scale → structure anisotropy is mirrored in the physical property anisotropy

- Single-crystal growth
  - solid phase must be created under the physical conditions close to the thermodynamic equilibrium (stacking „atom-by-atom“ on the seed crystal surface)

# Methods of single-crystal growth

Classification by Wilke:

1) From the dispersion phase (solutions, gases,…)
2) From the own melt
3) From the solid phase

# Single-crystal growth from the dispersion phase

- From the gas phase
  - sublimation
  - chemical reaction (e.g. “hot wire” method)

- From the (low temperature) solutions
  - evaporation (isothermal)
  - cooling (speed growth)
  - gradient method
  - chemical reaction

- Hydrothermal

- From the melt solutions (flux)

# Single-crystal growth from the own melt

- Crucible methods
  - stationary crucible methods
  - Czochralski method
  - Bridgman-Stockbarger method
  - Stěpanov method (EFG)
  - zonal melting

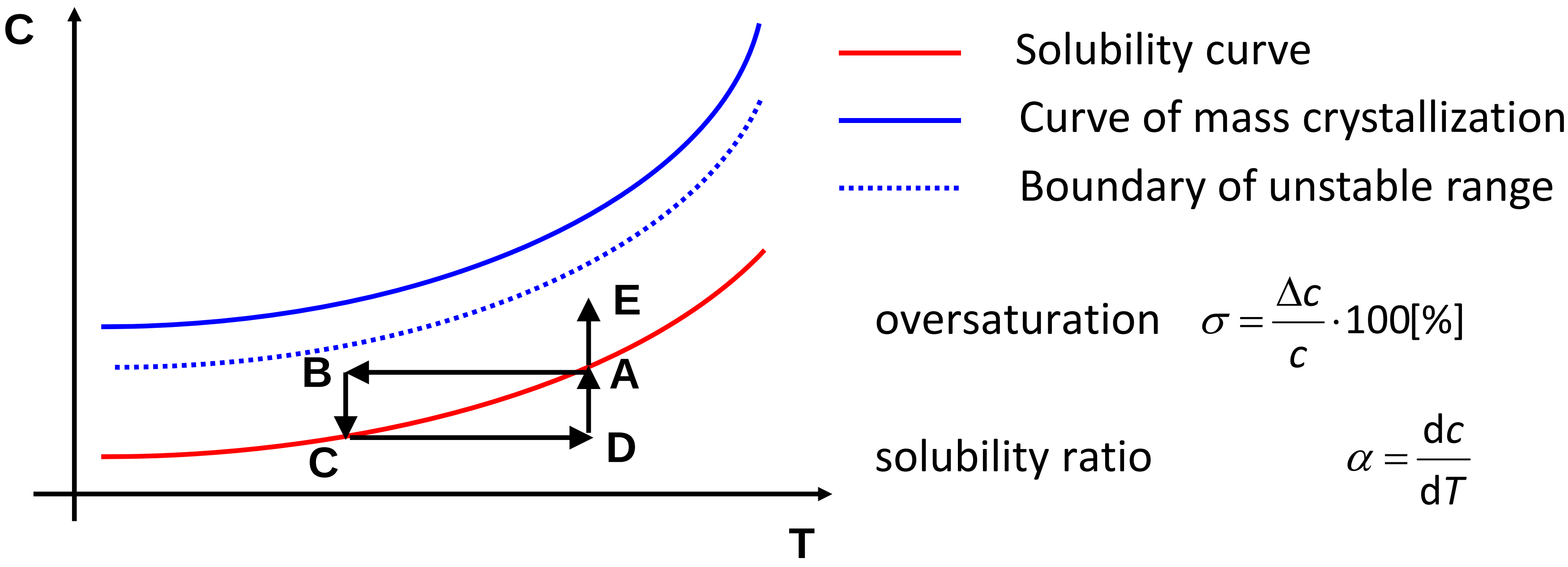
- Methods without crucible
  - Verneuil method
  - „cool crucible“ method

# Single-crystal growth from the solid phase

- Recrystallization
  - mechanical
  - by annealing

# Low temperature solutions

- materials solvable at room temperature in suitable solvent (water, ethanol, aceton, …), e.g. TGS ($(NH_2CH_2ClOH)_3 \cdot H_2SO_4$), KDP ($KH_2PO_4$), ADP ($NH_4H_2PO_4$), …




oversaturation $\sigma = \frac{\Delta c}{c} \cdot 100[\%]$

solubility ratio $\alpha = \frac{\mathrm{d}c}{\mathrm{d}T}$

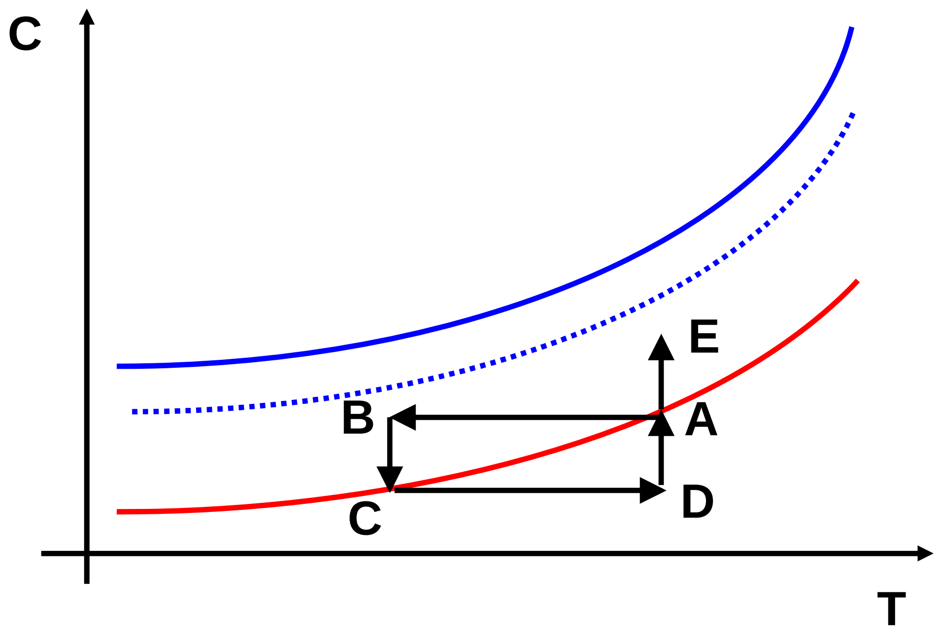
for the most materials $\alpha > 0$

T ϵ (15°C – 60°C)

# Low temperature solutions

Principles of methods:

- AE – evaporation
- AB – cooling
- ABCD – gradient method



# Evaporation

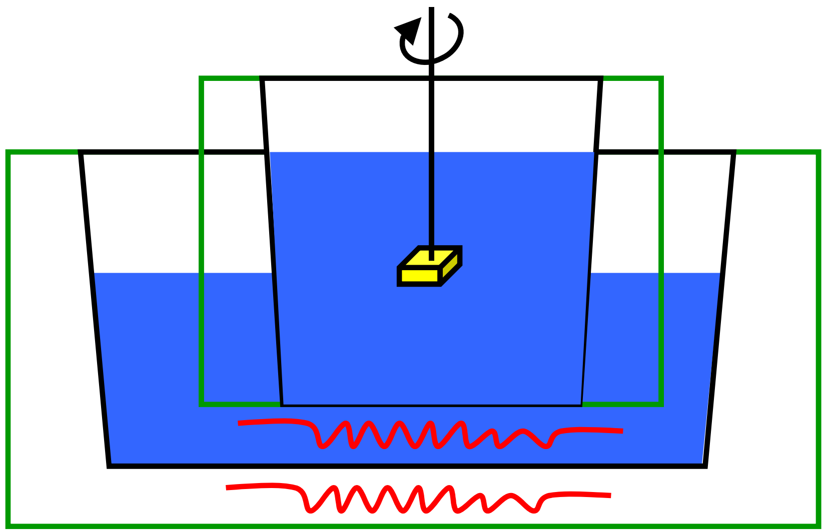
- Advantages
  - simple isothermal method
  - independent from α

- Drawback
  - difficult control of evaporation speed → growth fluctuation → defects and parasitic crystal occur

Suitable method for the easy tentative laboratory single-crystal growth (e.g. $CuSO_4 \cdot 5(H_2O)$).

# Cooling

- highly demanding temperature stability, fluctuation <0,01K
- typical temperature changes ≈0,1–1K/day
- slow crystal growth (approx. 0,5mm/day)
- quality crystals

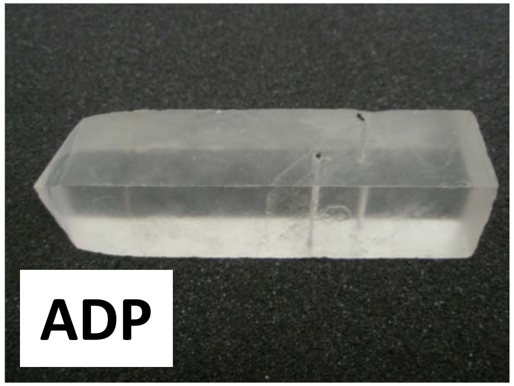


# Speed crystal growth

- “cooling” method variant
- process is closer to the unstable boundary range
- measurement of crystal growth and feedback for the growth parameters
- growth speed approx. 50mm/day
- large and quality crystals

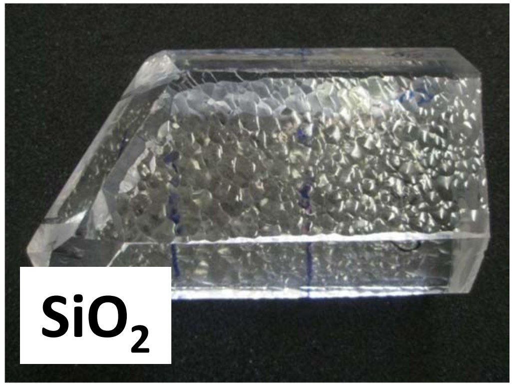
# Gradient method

- two-stage or three-stage crystallizer
- solution saturation (high temperature) and crystal growth at different places, necessary to filter the solution
- large and quality crystals
- expensive technology



# Hydrothermal growth

- similar principle like for the low temperature solutions
- solubility is increased by the high pressure and temperature (autoclave)
- crystallization by cooling
- suitable for single-crystal growth of $SiO_2$, ZnO, ...



# Solutions of melts (flux)

- applicable also for the materials melted non-congruently
- usually smaller crystals with defects (inclusions of flux particles)
- problem is the proper flux choice (e.g. PbO, $Bi_2O_3$, $B_2O_3$, PbF)
- grown single-crystal separation problems
- modifications of the growth from the own melt (especially Schmidt-Viechnicki and Bridgman-Stockbarger method) are growing methods
- material examples:

– YIG ($Y_3Fe_5O_{12}$)
– PZN-PT ($Pb(Zn_{1/3}Nb_{2/3})O_3 – PbTiO_3$)
– PMN-PT ($Pb(Mg_{1/3}Nb_{2/3})O_3 – PbTiO_3$)

# Growth from the own melt

- General conditions
  - congruent melting of the material
  - technically achievable melting temperature

- Heating methods
  - resistive
  - inductive

# Crucible methods

- stationary crucible methods
- Czochralski method
- Bridgman-Stockbarger method
- Stěpanov method (EFG)
- zonal melting

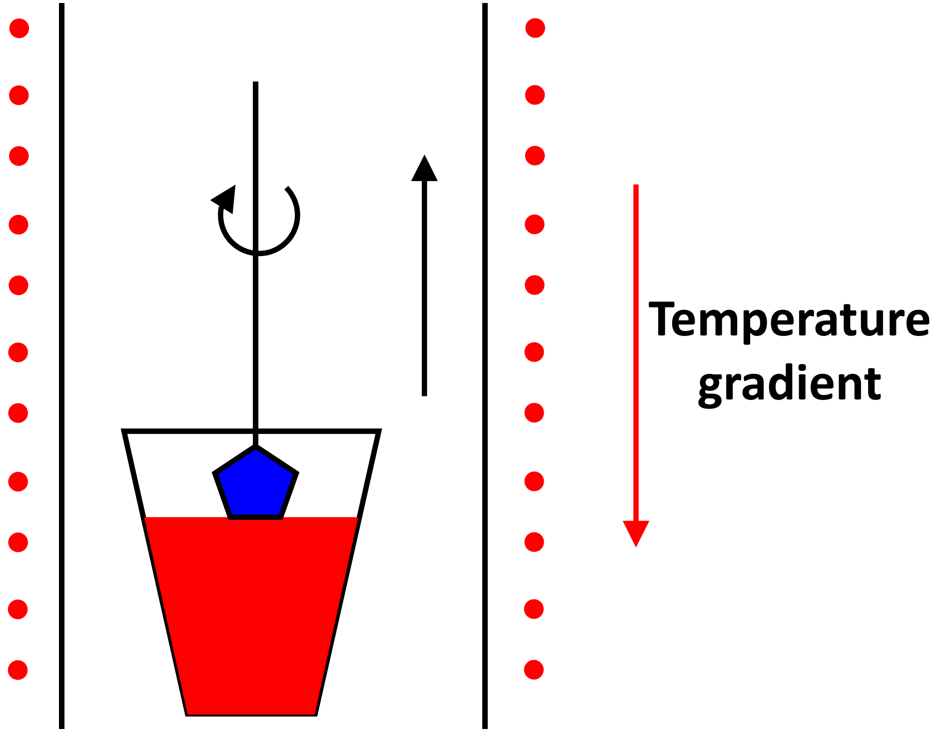
# Stationary crucible methods

- Nacken-Kyropoulos method
  - stationary growth in the crucible
  - seed crystal on the surface with the possibility of its rotation
  - heat outlet by the seed bar
  - melt cooling

- Schmidt-Viechnicki method
  - stationary growth in the crucible
  - seed crystal at the crucible bottom
  - melt cooling

# Czochralski method

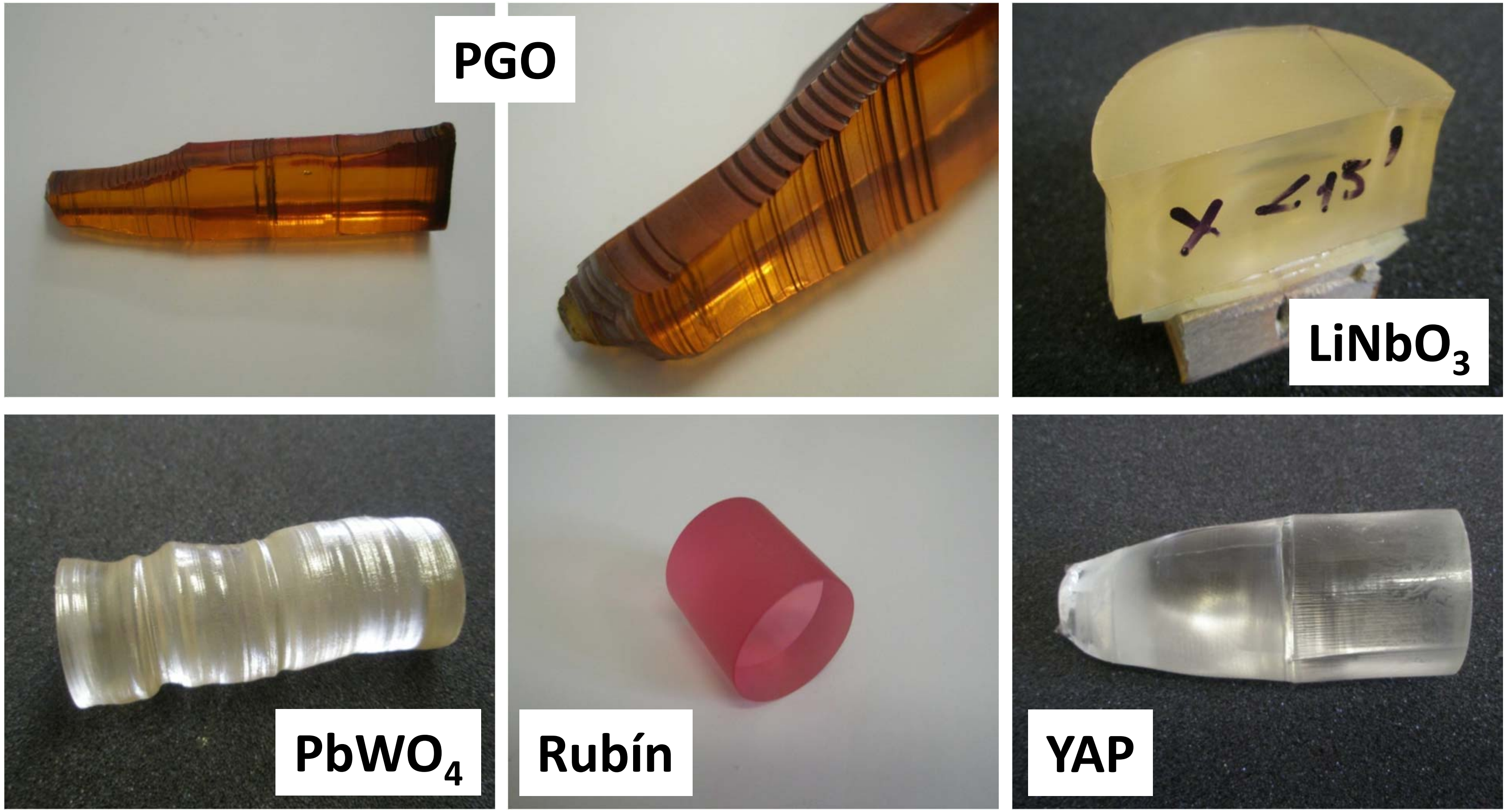
- temperature field gradient
- pulling of growing single-crystal



# Czochralski method – materials

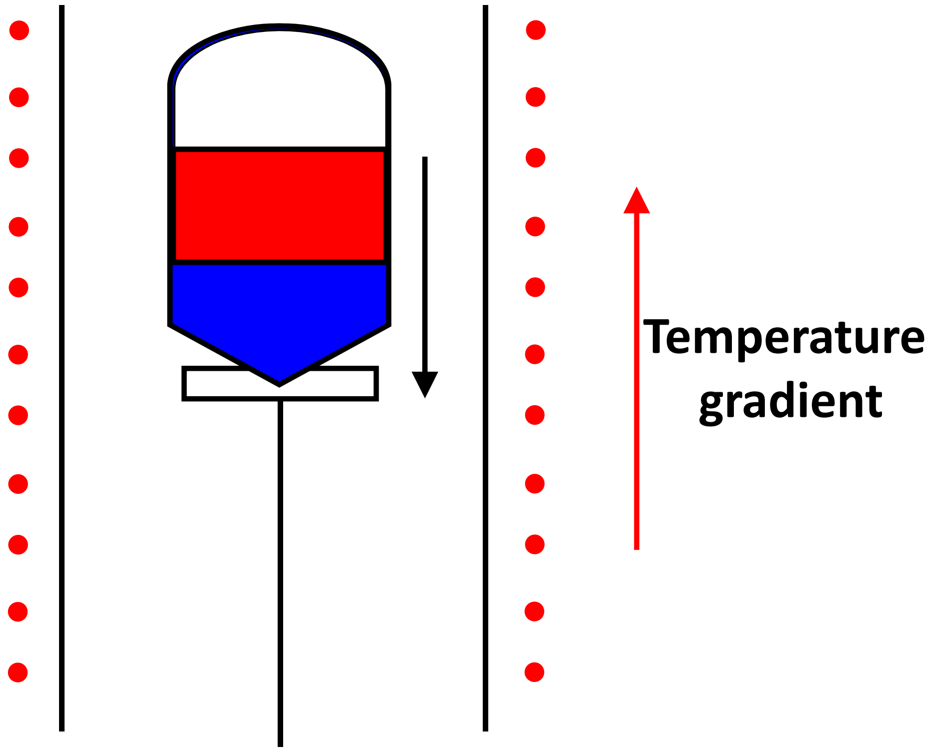
- material examples:
  - YAG ($Y_3Al_5O_{12}$) with dopants, e.g. YAG:Nd, YAG:Ce
  - YAP ($YAlO_3$) with dopants, e.g. YAP:Nd, YAP:Ce
  - LN ($LiNbO_3$)
  - BGO white ($Bi_4Ge_3O_{12}$)
  - BGO brown ($Bi_{12}GeO_{20}$)
  - PGO ($Pb_5Ge_3O_{11}$)
  - $Al_2O_3$ with dopants, e.g. $Al_2O_3$:Cr (ruby), $Al_2O_3$:Ti
  - $PbWO_4$

# Czochralski method – materials



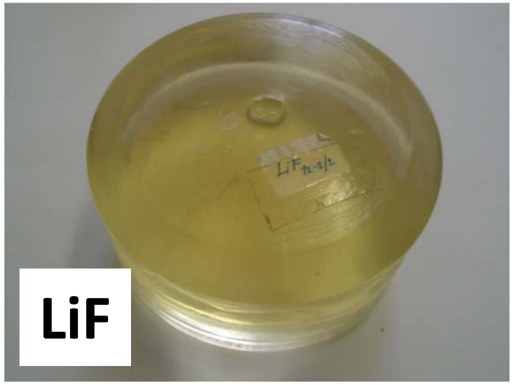
# Bridgman-Stockbarger method

- temperature field gradient
- descent of the crucible with growing single-crystal



# Bridgman-Stockbarger method – materials

- material examples:
  - BGO white ($Bi_4Ge_3O_{12}$)
  - $CaF_2$
  - $CeF_3$
  - NaI:Tl
  - LiF



# Comparison of mostly used crucible methods

- Czochralski method
  - growth of the best quality crystals from the own melt
  - melt may not be volatile
  - atmosphere problems

- Bridgman-Stockbarger method
  - Crucible could be hermetically sealed
  - Multiple growth possible

Both methods have many variants (different types of heating, atmosphere, crucible material etc.).

# Stěpanov method (EFG)

- growth of profile single-crystals
- pulling the seed crystal without rotation through the dies
- necessary condition – melt capillarity on the dies material surface

Profile single-crystals of $Al_2O_3$ are mostly grown by this method.

# Zonal melting

Method principle:

- horizontal pulling of sintered (polycrystalline) material in the crucible of elongated shape (boat) through the zone with the temperature above melting point → recrystallization (macroscopic single-crystal growth at the optimum conditions) and refining of the material

Method is mostly applied for the single-crystal growth of semiconductor materials (Si, Ge).

# Growth methods without crucible

- Verneuil method
- “cool crucible” method

Growth methods without crucible are suitable for the materials with the high melting temperature.

# Verneuil method

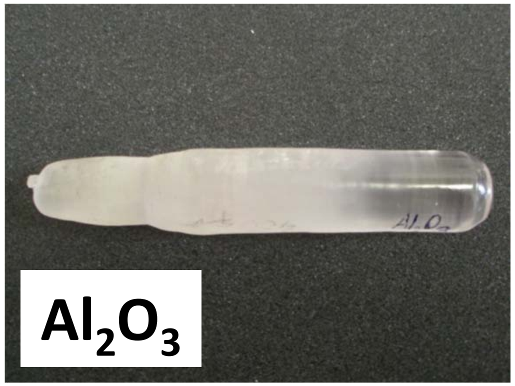
Method principle:

- melting of the powder material in the flame and melt droplets deposition onto the surface of crystal inside the temperate chamber

- Drawbacks
  - growth conditions are far from the thermodynamic equilibrium
  - structural defects occur

- Advantage
  - high concentration of dopants possible

- Material examples:
  - $Al_2O_3$ with different dopants



# „Cool crucible“

Method principle:

- inductive heating, conductive melt × non-conductive solid, starting conductive material, cooled inductor keeps the crust of melted material

- Drawback
  - generation of larger quantity of smaller single-crystals

- Material examples:
  - $ZrO_2$