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 ((NH₂CH₂ClOH)₃ · H₂SO₄), KDP (KH₂PO₄), ADP (NH₄H₂PO₄), ...

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

\[
\text{solubility ratio } \alpha = \frac{dc}{dT}
\]

for the most materials \( \alpha > 0 \)

\( T \in (15^\circ C – 60^\circ C) \)
Low temperature solutions

Principles of methods:

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

• Advantages
  – simple isothermal method
  – independent from $\alpha$

• Drawback
  – difficult control of evaporation speed $\rightarrow$ growth fluctuation $\rightarrow$ defects and parasitic crystal occur

Suitable method for the easy tentative laboratory single-crystal growth (e.g. $\text{CuSO}_4 \cdot 5(\text{H}_2\text{O})$).
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$_2$O$_3$, B$_2$O$_3$, 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$_3$Fe$_5$O$_{12}$)
  – 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

- PGO
- LiNbO$_3$
- PbWO$_4$
- Rubín
- YAP
Bridgman-Stockbarger method

- temperature field gradient
- descent of the crucible with growing single-crystal
Bridgman-Stockbarger method – materials

- material examples:
  - BGO white \((\text{Bi}_4\text{Ge}_3\text{O}_{12})\)
  - \(\text{CaF}_2\)
  - \(\text{CeF}_3\)
  - \(\text{NaI}:\text{Tl}\)
  - \(\text{LiF}\)
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 Al₂O₃ 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:
- Al₂O₃ 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:
  – ZrO₂