Bulk Single Crystal Growth of Novel Quantum Materials

Zhiqiang Mao
Department of Physics,
Pennsylvania State University
Outline

1) Basic concepts of crystallization
2) Several crystal growth methods
   -- Solution growth method
   -- Chemical vapor transport method
   -- Bridgeman method
   -- Floating zone method
3) Strategy for the crystal growths of materials with unknown phase diagrams
4) Crystal growth efforts of novel quantum materials of my group
Single Crystals

Constituent atoms arranged in a periodic pattern along x, y and z directions

Examples of single crystals existing in nature

Quartz
Ruby, Al$_2$O$_3$ with 1% Cr
Blue Sapphire, Al$_2$O$_3$ with Ti & Fe inpurities

https://www.mineralminers.com/html/quartz_crystals.stm#quartz-crystals
https://en.israeldiamond.co.il/wikidiamond/birthstones-by-month/ruby-july-gemstone-month/
http://www.healingstoneshealingcrystals.com/Healing_Crystals/Sapphire/BlueSapphire.html
Application of single crystals in industry

Silicon chips
http://www.itpro.co.uk/606099/happy-50th-birthday-to-the-silicon-chip

Nd:Y$_3$Al$_5$O$_{12}$ crystal, Laser

Solar panel
https://asia.nikkei.com/Business/Technology/
Japan-trys-to-chip-away-at-mountain-of-disused-solar-panels

Single crystal solar panel has higher efficiency than polycrystaline panel
Single crystal samples: critically important for revealing underlying physics of quantum materials

- Unconventional superconductors
- Strongly correlated materials
- Magnetic materials
- Low-dimensional materials
- Topological materials
- ...
Crystal Growth Methods

Crystallization techniques:
melt growth, solution growth, vapor phase growth, solid state growth

• **High temperature methods**
  - Czochralski
  - Bridgman
  - Floating-zone
  - Verneuil ...

• **Medium temperature methods**
  - Fluxes (solution method)
  - Electrochemical from melts
  - Vapor phase transfer
  - Sublimation
  - Hydrothermal

• **Low temperature Methods**
  - Solution gel
Driving force for crystallization in solution growth

Two stages of crystallization:

Formation of 3D microscopic nuclei

Development of 3D nuclei to visible crystals

How does crystal nucleation occur?
Driving force for crystallization in solution growth

**Solubility curve:** equilibrium solute concentration

**Supersolubility curve:** the limiting value of solute concentration when instantons nucleation occurs

**Crystallization requires supersaturated solution**

--In undersaturated zone, no nucleation
--In supersaturated unstable zone, nucleation speed and crystal growth speed are too high, producing small and imperfect crystals
--In the metastable nucleation zone, supersaturation is low so that the nuclei formation speed is low, producing large crystals.

Pritula and Sangwal, Bulk Crystal Growth (ELSEVER, edited by Rudolph), 2015
How to create supersaturation?

- Cooling the solution
- Solvent evaporation
- Combination of adiabatic evaporation and cooling

**Crystallization speed**

\[ S = \frac{dN}{dt} = k(c_2 - c_1) \]

\( c_2 - c_1 \), supersaturation

\( N \), the number of nuclei formed per unit of solvent volume.

**Driving force of crystallization:**

supersaturation, measured by concentration difference when \( T \) is reduced,

\[ \Delta c = c_2 - c_1 \]
Driving force for crystallization in solution growth

Gibbs free energy ($\Delta G$)

$$\Delta G = G_i - G_f$$

--Solution growth

$$\Delta G = RT(c_2 - c_1),$$

$c_2 - c_1$, supersaturation,

Melt growth

$$\Delta G \propto \Delta T = T_0 - T$$

$T$, the temperature of melt

$T_0$, the melting temperature of crystal
Nucleation Process I: homogeneous nucleation

Occurring spontaneously and randomly, requiring **supercooling** of the medium.

Supercooling of pure water
--Water can be "supercooled" down to $-48.3^\circ C$.

--Requirement:
pure water and free of nucleation sites.

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Pritula and Sangwal, Bulk Crystal Growth (ELSEVER, edited by Rudolph), 2015

http://www1.lsbu.ac.uk/water/supercooled_water.html
Nucleation Process II: heterogeneous nucleation

Preferential nucleation sites:
- phase boundaries,
- surfaces of container or
- impurities like dust.

Taking place much more often than homogeneous nucleation.

Carbonated water
Nucleation Barrier

- Nucleation Barrier $\Delta G^*$ and Critical size ($r^*$)

\[ \Delta G = G_{\text{Interfacial}} - G_{\text{Volume}} \]

When $r > r^*$, $\Delta G$ is reduced with increasing $r$ such that solidification starts.

**Green regime**: small particles formed and dissolved back to liquid; thermodynamically unstable, homogeneous nucleation.

**Yellow regime**: particles further grow and some of particles pass over barrier.

**Red regime**: growth of particle will be highly favored due to rapid decrease of $\Delta G$, leading to formation of large crystals.
Criteria for selecting appropriate solvent (flux)

- A flux should ensure a **sufficient solubility** of the compound.
- The solubility should show **sufficient change with temperature**.
- The flux material should have low melting point, low vapor pressure, low **viscosity**, low toxicity.
- Not corrode the crucible and furnace
- Easily separated from the grown crystals
- ...

Pritula and Sangwal, Bulk Crystal Growth (ELSEVER, edited by Rudolph), 2015
Commonly used fluxes for high-temperature solution growth

- **Salts** [e.g. NaCl (801 °C), KCl (770 °C), LiCl (605 °C), PbO (888 °C), PbF₂ (824 °C), etc.]
- **Oxides** [e.g. B₂O₃ (450°C), Bi₂O₃ (817 °C), etc.]
- **Hydroxides** (KOH (680 °C), NaOH, (604 °C), etc.)
- **Low melting-point metals** (Sn, Ga, Sb, Bi, etc)
- **Self flux**

**Choice of crucible**
- Very high melting point,
- Not react with the sample and flux
- Commonly used crucibles: Al₂O₃, ZrO₂, Pt, Ta, Nb, etc.
Crystal growth techniques

- Depending the methods of achieving supersaturation in the solution, the techniques of growing crystals from high-temperature solution may be grouped into three types:
  - **Slow cooling of the solution** (often used)
  - **Solvent evaporation** (useful growing crystals that are stable over a narrow temperature range)
  - **Temperature gradient method**

Pritula and Sangwal, Bulk Crystal Growth (ELSEVER, edited by Rudolph), 2015
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Chemical Vapor Transport Method (CVT)

\[ (A/B)L(g) + B/A(g) \]

A, B(s) + L(g)  
Hot

AB(s) + L(g)  
cold


L: Iodine or Bromine
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Growth of Compounds with its Melting Point < 1000 °C

Topological Insulator - Bi$_2$Se$_3$, Bi$_2$Te$_3$, Sb$_2$Te$_3$, (Bi$_x$Sb$_{1-x}$)$_2$Se$_3$, Bi$_{2-x}$Ca$_x$Se$_3$, MnBi$_2$Te$_4$, etc

TMD - SnSe$_2$, In$_2$Se$_3$, InSe

Melt Growth Technique – Vertical Bridgman

- Three zone vertical furnace
- Max temperature up to 1250 °C
- Ampoule diameter up to 2”
- Data logging
- Programmatic linear translation and rotational motion

Growth rate was optimized to maximize size of the Primary grain

Sam Lee, 2DCC postdoc scholar
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Floating Zone Growth of Silicon

Typical impurity concentration in FZ-grown Si is 2-3 orders of magnitude smaller that Czochralski (CZ) crystals.

Muiznieks et al., Bulk Crystal Growth (ELSEVER, edited by Rudolph), 2015
Crystal Growth using a optical Floating-method

Akashi and Shindo, 1969

Heat source:
- Halogen lamp
- Xenon arc lamp (more powerful)
- Laser

Advantages:
-- Crucible free
-- high thermal gradient on the crystallization front, which decreases the danger of supercooling and enables fast growth
-- large crystal
-- low impurity level, < 40 ppm.
-- video camera, allowing for in-situ observation of crystal growth

Gained popularity for fast growth of oxides which are difficult to be grown using other methods
Many grains form at the beginning;
-- At later time, the grain with higher radical component of growth velocity continues to grow.
-- The crystal could eventually become a single domain if ideal growth conditions are found.

The quality of grown single crystals depends on the growth stability:
♦ the shape of starting rods
  ideal rod: uniform and straight
♦ the alignment of both seed and feed rods
♦ Viscosity
♦ high pressure needed if the material produces high vapor
♦ the shape of melting-zone
Two mirrors, NEC
Maximum temperature
2150 °C, equipped with
a cold trap,
For oxide growth
Quantum Design
Optical Floating-zone Furnace

Two mirrors,
Cold trap,
Temperature < 2000 °C
Used for growing intermetallic compounds
New Synthesis Lab (under renovation)

- 10 multiple zone tube furnaces for CVT growth
- 10 crucible furnaces and Muffle furnaces for flux/melt growth
- One arc melting furnace for Czochralski growth
- 2DCC equipment
  - One Bridgeman furnace
  - A Ta tube sealer system with a glovebox
Assumption: the polycrystalline material of desired compound can be made using solid state reaction method and show congruent melting.

--melt growth in crucible furnace its melting point is low
----melt growth in a FZ furnace its melting point is high.

If the solid phase exhibits a structural transition, the single crystals of high temperature phase can be obtained through the high temperature crystallization and quenching procedure (along Route 2).

If the melt growth fails, we have to try solution growth.
Examples of binary Ti-Pt alloy growth

Ti₃Pt does not show a structural transition and can be grown by slowly cooling the liquid phase to room temperature.

TiPt exhibits a structural transition near 1000 °C; to grow the β-phase of TiPt, we have to quench the before the temperature reaches the structural transition temperature.
My group’s research interest:
to discover and understand new quantum material properties through material synthesis and characterization

Materials Synthesis
- Bulk Single crystal growth (Flux, CVT, Floating zone)
- 2D crystal preparation (Mechanical exfoliation)

Materials Characterization
- Structure
- Magnetic
- Transport
- Thermodynamic
- Neutron scattering

Material Physics
- Superconductivity
- Magnetism
- Quantum transport
- Topological property
Single Crystals Growth using the melt, solution and CVT methods

### Superconductors
- Fe(\(\text{Te}_{0.5}\text{Se}_{0.5}\))
- FeSe
- \(K_x\text{Fe}\_{2-y}\text{Se}_2\)
- \(\text{Ta}_2\text{PdSe}_5\)
- \(\text{CsBi}_4\text{Te}_6\)

### Topological insulators
- \(\text{Bi}_2\text{Te}_3\)
- \(\text{Sb}_2\text{Te}_3\)
- \(\text{PbTe}\)

### Dirac/Weyl semimetals
- \(\text{TaP}\)
- \(\text{NbP}\)
- \(\text{ZrSiS}\)

### Low dimensional materials
- Black Phosphorus
- \(\text{WSe}_2\)
- \(\text{WTe}_2\)
- \(\text{Nb}_3\text{SiTe}_6\)
- \(\text{Ta}_2\text{PdSe}_6\)
- \(\text{CdPS}_3\)
Layered Magnetic Materials with van der Waals gap

MnPS$_3$  FePS$_3$  NiPS$_3$  CdPS$_3$

Fe$_{1/4}$TaS$_2$  TaFeTe$_3$  FeNbTe$_2$  CrSiTe$_3$

AFM/FM ordering
2D atomic layers of layered ternary materials

  - ZrSiSe/Te
  - Dirac nodal-line semimetal
  - 10 layers

- **Liu et al., Nano Letters, 2016.**
  - Ta_2Pd_3Se_8
  - Semiconductor

- **Yue et al., ACS NANO, 2016**
  - Fe_{1+y}(Te_{1-x}Se_x)
  - superconductor
  - Transition from 3D to 2D SC.

- **J. Hu et al, Nature Physics 2015**
  - Nb_3SiTe_6
  - Anisotropic metal

- **G. Long et al., to appear in ACS Nano**
  - MnPS_3
  - AFM insulator

  - Ta_2Pd_3Se_8
  - Nanowire
  - 1.2nm

- **ZrSiSe/Te**
  - Nanowire
  - 8.6nm

- **Ta_2Pd_3Se_8**
  - Nanowire
  - 1.2nm

- **Fe_{1+y}(Te_{1-x}Se_x)**
  - Superconductivity
  - Transition from 3D to 2D SC.

- **CrSiTe_3**
  - FM insulator
  - 9nm

Rich opportunities to seek functional properties in low dimensions.
Strongly correlated oxides grown using floating-zone technique

$\text{Sr}_3\text{Ru}_2\text{O}_7$

$\text{Sr}_2\text{RuO}_4$

$\text{Ca}_3\text{Ru}_2\text{O}_7$

$\text{Fe}_3\text{O}_4$
Unconventional superconductors

- Liu, J. Hu et al, *Nature Materials* 9, 716 (10)
- Yi et al., *Nature Communications* 6, 7777 (15).
- Liu et al., *Physical Review Letters*. 110, 037003 (13)
- Hanke et al., *Nature Communications* 8, 13939 (16).

Topological semimetals


Exotic phenomena of strongly correlated materials

- Hooper et al., *Physical Review Letters* 92, 257206 (04).
- Zhu et al., *Physical Review Letters* 116, 216401 (16)
- Ying et al., *Nature Communications* 4, 2596 (13).
- Stoger et al., *Physical Review Letters*. 113, 116101 (14)
- Bliem et al., ACS NANO 8, 7531 (14).

2D ternary transition metal chalcogenides

- Liu et al., Nano Lett. 16, 6188 (16)
- C.L.Yue. et al, ACS nano 10, 429(16).
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Jin Hu  Jinyu Liu  Yanglin Zhu

(Material synthesis, bulk characterization, material physics, Tulane)

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New members:
Yangling Zhu (from Tulane)
Sam Lee (2DCC postdoc)
Lujin Min (co-advised with Prof. Gopalan)
Jingyang He (co-advised with Prof. Gopalan)
Dipesh Timsina

.....
Collaboration network (more than 50 groups)

2D materials
Wei (Tulane); Samarth (PSU); Natelson (Rice); Hebard (Unin. Of Florida); Wang (UCLA); Lau (Ohio Sate); Li (Vanderbilt); Feng (Case Western); Xiang (Sicun Univ.)
Xiao (Argonne); Chen (Purdue); Suen (Hong Kong Univ. of Sci. and Tech); Wang (RMIT Univ. Australia); Politano (Univrsity of Calabria, Italy); Chen (Laboratoire National des Champs Magnétiques Intenses-CNRS, France); Jin (Zhejiang Univ) Tian (Hefei Institutes of Physical Sci. High Magnetic Field alb, China)

Photoemission spectroscopy
Shen (Stanford); Zhou (Institute of Physics, Beijing); Feng (Univ. St. Andrews).

Neutron Scattering
Broholm (Johns Hopkins); Bao (Renming Univ., China); Cao (ORNL); Dai (Rice Univ.); Ke (Michigan State Univ.); DiTusa and Plummer (LSU); Argyriou (HZB, German); Qiu (NIST)

High magnetic field experiments
Jaime, Fedor and Ross (NHFL, Los Alamos); Graf, Yan and Irinel (NHMFL, Tallahassee)

Scanning tunneling microscopy
Diebold (Tech Univ. Vienna); Plummer (LSU); Hasan (Princeton); Yan (UIUC)

Optical spectroscopy
Basov (Columbia); Talbayev (Tulane)

High pressure study
Shiyan Li (Fudan Univ.); Higashi-Hiroshima (Hiroshima Univ., Japan); Hamlin (UF)

Theory
Dobrosavljevic (NHMFL); Fang and Weng (Institute of Physics, Beijing); Liu (Chinese Academy of Sciences)

Other collaborations on ruthenates and iron-based superconductors
Liu (PSU); Gopalan (PSU); Wu ((Rutgers); Freeland (Argonne); Prozorov and Tanatar (AMES); Piamonteza (Swiss Light Source),