Bulk crystal growth I

Stephen D. Wilson
Professor
Materials Department
University of California,
Santa Barbara
Overview

- Why crystals?
- Floating Zone Technique
  - Quick Overview
  - Parameters
  - Traveling Solvent, Flux additives
- Floating zone furnaces
  - Types
  - Advantages
- High Pressure Floating Zone
- Flux Growth Technique
- Vapor Transport Technique
Crystal growth

From “Introduction to the synthesis of Quantum Materials”

• Why study crystals versus powders?
• Traditional frontier for new state discovery
• Diversity of techniques
  • Targeted for different purities/volumes/composition types
• Different communities study crystal growth process itself vs use it to make new materials
  • Technological relevance vs fundamental research
Crystals allow for new insights

- Signatures of structural/electronic symmetry breaking can often be missed in powders

Ortiz et al., PRL (2020)

M. K. Crawford et al., PRB (1994)

C. Dhital et al., PRB (2013)
Science driven by crystal purity

**Observation of itinerant ferromagnetism in layered Sr₃Ru₂O₇ single crystals**

- G. Cao, S. McCall, and J. E. Crow
- National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32306
- (Received 23 August 1996; revised manuscript received 1 October 1996)

**Ground state in Sr₃Ru₂O₇: Fermi liquid close to a ferromagnetic instability**

- Sanei Ishida,1,2, and Yoshiteru Morosin1
- 1Department of Physics, Kyushu University, Fukuoka, Japan
- 2Department of Physics, Osaka University, Osaka, Japan

**Sensitivity to Disorder of the Metallic State in the Ruthenates**

- L. Capogna,1, A. P. Mackenzie,1,2, R. S. Perry,1, S. A. Grigera,1,2, L. M. Galvin,1, P. Raychaudhuri,1, and A. J. Schofield1
- 1School of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom
- 2School of Physics and Astronomy, University of St. Andrews, North Haugh, St. Andrews, Fife KY16 9SS, Scotland

**Formation of a Nematic Fluid at High Fields in Sr₃Ru₂O₇**

- R. A. Borzi,1,2,3, R. S. Perry,1, S. J. Lister,1, S. L. Lee,1, D. A. Tennant,1, Y. Maeno,6, and A. P. Mackenzie1

**Field-tunable spin-density-wave phases in Sr₃Ru₂O₇**


**Weak FM metal**

**Nonmagnetic Fermi Liquid**

**Quantum critical metal**

**Electronic nematic state**

**Spin density wave metal**

Increasing Purity
General considerations

- Technique for melting/dissolving a material and then resolidifying it in a controlled way
- Goal is to promote grain growth to achieve single domain crystals that can be studied with your desired technique(s)
  - Different bars for different techniques
  - 10’s of microns OK for x-ray structural studies, cm³ needed for inelastic neutron scattering
- Thermal melting/resolidification, wet chemistry growth from saturated solution, sublimation/vapor transport, etc...

1 kg Si crystal sphere at NIST

Si powder comprised of many small crystallites
Unidirectional solidification
Crucible-based growth

From “Introduction to the synthesis of Quantum Materials”

- For congruently melting materials (e.g. PtSn)
  - Find a crucible that doesn’t react with your material
  - Find a furnace that can get you above the melting point
  - Create a thermal gradient and slowly cool down
Bridgman growth

Molten charge

Grown crystal/seed
Floating Zone Growth
Floating Zone Crystal Growth

- William Pfann and Henry Theurer (Bell Laboratories) & Paul Keck (Army Signal Lab)
  - Inductive means of *remotely* melting and recrystallizing materials
  - Seminal in advancing semiconductor purity <1ppb (Si/Ge)

"floating" via surface tension
Zone refining

- William Pfann @ Bell Telephone Laboratories

\[ C = kC_0(1 - g)^{k-1} \]

\[ r = kC_0 \]

\[ K = kC_0 \]

\[ C_0 \]

\[ 0 \]

\[ 1 \]

\[ x \]

\[ l \]

\[ \]
Advantages of Floating Zone

- Crucible-free
  - Removes impurities born from molten zone attacking container
- High purity
  - Zone refining active during growth
- Active technique
  - Growth can/must be monitored and adjusted
- Large volume, seeded technique
- Works for low $T_M$ and high $T_M$ materials
- Works with fluxes and incongruently melting materials
Limitations of Floating Zone

• Zone stability is paramount
  • Volatile species are problematic
  • Low viscosity melts are difficult
• Remote coupling to feed material can be challenging
  • Reflectivity of melt/material is a factor
  • Conduction of heat away from zone
• Sharp thermal gradients can degrade microstructure
  • Thermal cracking of crystals
• Processing gas environments are constrained in standard systems
  • Typically 1 atm
  • Recent advances have shown $<10^{-7}$ Pa to $10^8$ Pa possible
Growth parameters for congruently melting system

- Growth atmosphere
- Heating power
- Feed rate
- Growth (seed translation) rate
- Feed/seed rotation
  - Mixing in melt
- Thermal gradient
  - Afterheater
  - High angle light shielding
  - Tailored optics
  - Field concentrators
Feed/Seed pull parameters

- Variable feed/seed growth rates
  - Control of volume of crystal/zone shape
  - Necking
  - Grain selection
Starting without a seed
Feed rod preparation

• Rod preparation is important!
  • High density \( \rho > 90\% \)
  • Uniform radius/density (constant volume of feed)
  • Straight helps...

• Typical preparation routes:
  • Cold isostatic press + sinter
  • Hot press
  • Spark plasma sintering + surface polish

• Floating zone furnace often leveraged
  • Rod quickly “premelted” via fast pass through hot zone
Bulk crystal growth II

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What about incongruently melting systems?

- Traveling-solvent floating zone
- Self-adjusted flux
- Flux-feed technique
Types of floating zone furnaces

- Induction (commercial)
- Optical (research grade): mirror furnace and laser furnace
Mirror furnace designs

Mirror furnace light sources

Halogen light bulbs: 100 W to 1,500 W typical
2100 °C obtainable with good low-T control
High power = Large filament = Poor focus

Xenon lamps: 5 to 15 kW typical
~2800 °C obtainable with low-T threshold
(mitigated in new furnace designs)
Common mirror furnace vendors

SciDres
Vertical geometry

Crystal Systems
Horizontal geometry
(4 mirrors)

QDUSA
Horizontal geometry
(2 and 4 mirrors)

Cyberstar
Horizontal geometry
(2 mirrors)
Laser-based floating zone (early)

High melting point oxides grown via CO$_2$-lasers

$\text{Al}_2\text{O}_3$, $\text{CaZrO}_3$, $\text{Y}_2\text{O}_3$

(CO$_2$ laser invented in 1964)

2 x 400W lasers
+ Resistance furnace
Laser-based floating zone (later)


7 x 50 W diode lasers
975 nm light channeled into light pipes

Multiple commercial systems now available
High-Pressure Floating Zone
What is *high* pressure?

• Typical commercial systems are constrained to $P=0.001$ GPa (10 atm) gas environments (historically the “high pressure” option)

• High pressure multianvil furnaces can reach 20 GPa

• Diamond anvil cells can reach 100’s of GPa

• High-Pressure floating zone now typically $P > 0.01$ GPa (100 atm)

• Why? Grow ultrahigh purity crystals of previously inaccessible materials
  • Volatile
  • Metastable
  • Modified phase diagrams for incongruently melting materials
  • Control of chemical potential, oxidation state, phase formation
Frontiers opened in HP Floating zone

- Notable examples in oxides
  - RNiO$_3$ (R=rare earth)
    - J. Zhang et al., Cryst. Growth and Des. (2017) and others...
  - Li$_2$CuO$_2$
  - R$_4$Ni$_3$O$_{10}$
    - J. Zhang et al., arxiv 1904.10048
  - BaFe$_{12}$O$_{19}$
  - + many others

- Little explored regime
- Rapidly developing
- Instrument-limited

Systems in US
- ANL (150 atm)
- ORNL (150 atm)
- NSF PARADIGM Facility @ JHU (300 atm)
- UCSB (1000 atm)
Large solid angle of optical access mandates transparent growth chambers

Pressure limitation imposed (10 atm for most commercial systems)

High-pressure floating zone furnaces


100 atm environment  150 atm environment (SciDres)  300 atm environment (SciDres)
Vertical mirror design

- Balbashov mirror design allows for small aspect ratio chamber to be utilized
- Increases pressure stability
- Scale to thicker sapphire chambers

Remains a design inherited from the late 1960’s
Alternatives to cylindrical sapphire/silica

Moving to high pressure windows/discrete points of optical access

Implement high strength steel chamber
1000 atm easily attainable

Requires high power laser heating sources

Wavelengths must be compatible with high-strength window materials
Focal array

Furnace assembly

FZ growth at 1000 atm
Growth of $\text{Al}_2\text{O}_3$

Interesting melt dynamics with large bandgap materials
High purity crystals not meltable, high purity powder is doable
GdTiO$_3$ example

- High molecular weight, low viscosity makes zone unstable
- Unreacted rods, no rotation in conventional 4-mirror furnace in atm of Ar

Holger Roth dissertation (2008)

- 35 bar Ar overpressure
- Sintered rods with rotation
- Highest $T_c=36$ K reported

Decomposition of flux, target materials under low pressures of $O_2$

- High $O_2$ pressures required to stabilize 5d precious metal oxides
  - $IrO_2$ at 2000 K decomposes near $\sim 1000$ atm
- Balance vs volatility of higher oxidation state gaseous species
Effects on volatility in precious metal oxides

Flux feeding technique:

Sr$_3$Ru$_2$O$_7$ provides an established metric:


Growth rate: 15 mm/hr

Growth atmosphere: 80:20 (Ar:O$_2$)

<table>
<thead>
<tr>
<th>Precursor stoichiometry</th>
<th>SrRuO$_3$ Content [ppm]</th>
<th>Pressure (Psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$<em>3$Ru$</em>{2.52}$O$_7$</td>
<td>100,000</td>
<td>200 psi (80:20) + 800 psi Ar</td>
</tr>
<tr>
<td>Sr$<em>3$Ru$</em>{2.27}$O$_7$</td>
<td>45</td>
<td>200 psi (80:20) + 800 psi Ar</td>
</tr>
<tr>
<td>Sr$<em>3$Ru$</em>{2.57}$O$_7$</td>
<td>40</td>
<td>200 psi (80:20)</td>
</tr>
</tbody>
</table>
Collisional suppression of volatility

- Example: \( \text{Nd}_2\text{Zr}_2\text{O}_7 \)

### Table

<table>
<thead>
<tr>
<th>Source</th>
<th>Sample</th>
<th>Atmosphere</th>
<th>( a ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference 20</td>
<td>P</td>
<td>Air</td>
<td>10.678</td>
</tr>
<tr>
<td>Reference 21</td>
<td>SC</td>
<td>Air</td>
<td>10.62652(9)</td>
</tr>
<tr>
<td>This work</td>
<td>SC</td>
<td>Air</td>
<td>10.6240(1)</td>
</tr>
<tr>
<td>This work</td>
<td>SC</td>
<td>35 bar Ar</td>
<td>10.66387(4)</td>
</tr>
<tr>
<td>This work</td>
<td>SC</td>
<td>70 bar Ar</td>
<td>10.67171(5)</td>
</tr>
</tbody>
</table>
Nd$_2$Zr$_2$O$_7$ with mitigated defects
Nd$_2$Zr$_2$O$_7$
Spin chain system $\text{Li}_2\text{CuO}_2$

$\text{Cu}^{2+} : d^9$

$\text{O}^{2-}$

$\text{Li}^{1+}$

Space group = Immm (#71)
Chain direction along $K$
Moment direction along $H$

- High pressure $O_2$ required to stabilize growth and heal vacancies


Li$_2$CuO$_2$ without vacancies

- New magnetic bound states (quasiparticles) resolved in ultrapure samples
Other complexities to consider

- High-pressure O$_2$/Reactive gas environments may act like a liquid solvent
  - Transport material
  - Convective transport

Convective cells inside and outside molten zone

Flow can be engineered; Modeling is difficult

Outlook and future (my opinion)

• High pressure OFZ techniques are rapidly evolving
  • New materials being stabilized
• Higher pressures are certainly feasible
• Many designs based on legacy ideas
  • 1 cm diameter crystals not really needed in research anymore
  • Diameter can be scaled down
• Combination of laser heating + high-pressure is very powerful
  • Sharp thermal gradient
  • Stabilizing overpressure
  • New processing regimes accessible (high-T high-P)


2 GPa windows are possible
Crucible-based flux growth

For incongruently melting materials (e.g. PtSn$_2$)
- Directly melting and cooling leads to a multiphase system
- One needs to choose a “flux” to direct the solidification process to the desired material
  - Add excess Sn to PtSn$_2$ to reach the right peritectic line in binary phase diagram
- This is often challenging because phase diagrams are often wrong/incomplete/unknown
Crucible-based flux growth

From “Introduction to the synthesis of Quantum Materials”

- What actually goes on?
- Load starting stoichiometry into appropriate crucible
- Run target thermal profile
- Remove excess flux
  - Centrifuge at temperature
  - Postgrowth chemical etching
- Evaluate crystals grown

High throughput, low-cost means of discovering new phases and generating crystals
Vapor Transport
PVT and CVT methods

- Sometimes melting a system directly is problematic due to volatility, chemical compatibility issues.
- Using a thermal gradient and sublimation (PVT) or gaseous chemical agent (CVT) can be effective.
The advantages of vapor transport

• Crystals are grown below melting/decomposition temperature
• Leverages volatility of constituents (esp. chalcogenides)
• High quality crystals depending on optimization
• Different environments → Different crystal morphologies

The disadvantages of vapor transport

• It can be somewhat of a black box
• Kinetics are hard to predict and model
• It can be slower than most methods
• Systemic optimization studies are necessary info, but hard to come by.
The anatomy of a VT reaction

- A temperature gradient plus a transport agent facilitates transport of a powder from one end of a tube to another

\[ \text{GaB}_4\text{Q}_8 \text{ (s) + Cl} \rightleftharpoons \text{GaCl}_3 \text{ (g) + BCl}_x \text{ (g) + S (g)} \]

- Different transport gasses \( \rightarrow \) Reaction enthalpy changes \( \rightarrow \) Temperature dependence, growth stability
Example of transport tube

- Typical multizone furnaces have a zone widths of 6-8 inches
- Tube needs to span multiple zones for precise control of thermal gradient
Three zone furnace for vapor transport
VT growth of GaV$_4$S$_8$

- 14mm ID quartz tube with ~8mg/cm$^3$ of iodine
  - Transport kept intentionally slow for high quality
- Tube extends into hot 3$^{rd}$ zone to prevent crystals from growing on the end
- Crystals pictured were grown for 2 months
VT growth of GaNb$_4$Se$_8$

- In literature: Nb and Se tend to react with I to form ternary crystals
- 7mm ID quartz tube with ~2.5mg/cm$^3$ of PtCl$_2$
- Tubes that did not extend into the third zone grew faster and did not decompose
- Crystals pictured were grown for 1 month