Bulk Crystal Growth of Chalcogenides
at the NSF Materials Innovation Platform 2DCC

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Outline

- Overview of 2DCC scientific goals for the bulk growth effort
- Chalcogenides: what are the materials of interest and why?
- Bulk growth processes, equipment and capabilities
- Transition metal dichalcogenide (TMD) bulk growth
- Bi- and Sb-chalcogenide topological insulators (TIs), topological crystalline insulators (TCIs), and new topological materials.
- Bulk Growth RFI and Bulk Growth Research Proposal Solicitation
2DCC Personnel: Bulk Growth

Tom Mallouk
Chemistry
Bulk Synthesis and Exfoliation

David Snyder
ARL/MatSE/ChemE
Bulk Synthesis

Joan Redwing
MatSE/EE
Platform Director and Synthesis Lead

Joshua Robinson
MatSE
Director of User Programs, MOCVD Growth

Part-time staff:
• Randal Cavalero (ARL)
• Robert Lavelle (ARL)
• Ron Redwing (MatSE)
• Post-doctoral researcher
• Research technologist
Overview of 2DCC Platform

Develop custom deposition tools with *in situ* and real time characterization of monolayer and few layer films.

Unique capabilities in simulation of reaction kinetics through first principles + reactive potential approach

Todays presentation will provide an update on the *Bulk Crystal Growth component of the Synthesis task*
Scientific Goals – Bulk Growth

- Develop capabilities to prepare high quality bulk crystals of a range of chalcogenides
- Investigate equilibrium growth of alloys and doped crystals
- Benchmark and compare the properties of exfoliated bulk crystals and MOCVD/MBE films
- Explore the synthesis and properties of new phases/compositions of 2D crystals
- Develop large bulk crystals and fabrication methods for substrate preparation

Bulk growth provides opportunities for 2D materials discovery and benchmarking.
There Are Many 2D Chalcogenides to Study…

<table>
<thead>
<tr>
<th>Dichalcogenides</th>
<th>2D Alloys</th>
<th>Monochalcogenides</th>
<th>2D Superconductors</th>
</tr>
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<tbody>
<tr>
<td>CoSe₂</td>
<td>TiGaSe₂</td>
<td>CuS</td>
<td>VSe₂</td>
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<tr>
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<td>TiInS₂</td>
<td>GeS</td>
<td>PtSe₂</td>
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<td>CuFeTe</td>
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<td>GePbSe</td>
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<td>MoReS₂</td>
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<td>ReNbS₂</td>
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<td>SbAsS₂</td>
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<td>CuFeTe</td>
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<tr>
<td>TaS₂</td>
<td>WSSe</td>
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<td>FeTeSe</td>
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Materials of immediate interest

- Chalcogenide ‘topological insulators’: Bi$_2$Se$_3$, Bi$_2$Te$_3$, Sb$_2$Te$_3$, PbSnTeSe
- Transition metal dichalcogenides (TMDs): WTe$_2$, MoTe$_2$, WSe$_2$, MoSe$_2$, NbSe$_2$
- Transition metal monochalcogenide superconductors: FeSe, FeTe
- Magnetic doping of host Bi- and Sb-chalcogenides

Focus on 2D chalcogenides in a broad sense.
Tailored Synthetic Bulk Crystals

Metal Transformation

"Soft Chalcogenization"

\[ M(s) + X_{2(g)} \rightarrow MX_2 \]

Solid State Reactions

\[ M(s) + X_{2(s)} \rightarrow MX_2 \]

Chemical Vapor Transport

Bulk Crystal Formation

\[ M_{(s)} + 2X_{(s)} + \text{Transport Agent} \rightarrow MX_2 + \text{TA}_{(s)} \]

Chemical Vapor Deposition

Molecular Beam Epitaxy
Electrochemical Synthesis
Pulsed Laser Deposition
Spray Pyrolysis

Other

1) Load and seal source materials in evacuated ampoule. Heat to react and compound material. Heat entire ampoule above melting point, equilibrate.

2) Translate ampoule from hot zone into cold zone to directionally crystallize.

3) Stop translation, equilibrate furnace, anneal fully solid crystal in-situ.

- Growth can be seeded or self-seeded
- Typical growth time is 3-10 days for total process
New Mellen Vertical Bridgman system for melt growth

- Ampoules up to 50 mm dia.
- Three zone furnace
- Max Temperature up to 1250°C
- Crucible rotation
- Programmable linear translation and data logging

Expected delivery: March 2017
Existing bulk crystal growth equipment at Penn State – High Temperature VB Growth Systems

Mellen Vertical Bridgman Furnace Systems (3)
- Four zone configuration.
- High Temperature ~1500ºC
- 50mm diameter,
- 200mm length
- Fully automated process control and data acquisition.

Available for 2DCC use...
Existing bulk crystal growth equipment at Penn State – Large Diameter, High-Temperature VB Growth Systems

Mellen Vertical Bridgman Furnace Systems (2)
- Currently used to grow topological insulators
- Four zone configuration
- 75mm diameter, 150mm length
- Fully automated process control and data acquisition.
- Capable of multi-boule growth experiments for compositional and doping studies
Ampoule and support configurations for:

- Single-boule
- 3-boule simultaneous
- 6-boule simultaneous

Allows for a wide range of compositions, dopants and doping levels to be explored with fewer growth runs...
2) Bulk crystal growth – CVT Process

Chemical Vapor Transport (CVT)

For CVT growth:

A polycrystalline sample and a transporting species are loaded in a sealed ampoule, typically quartz.

When heated, the transporting species reacts with the sample to produce a gaseous species.

The gaseous species is transported, typically from the hot zone to the cold zone (for endothermic reactions), and redeposits the sample material and releases the transport agent.

The ampoule loading system at 2DCC will be capable of wide range of transport agents including I₂, Br₂, Cl₂…

The CVT method is good for growing high quality crystals, however, the transport rate and crystal growth rate tend to be very low…
Chemical vapor transport (CVT) (2) systems are being procured for transport-assisted growth.

The initial system will be an MTI four zone furnace to allow for full control of the axial gradient.

Temperature up to 1100°C

Ampoule diameters up to 2 inches

Fully automated temperature programming and data logging

Ampoule loading system capable of iodine, bromine and chlorine transport agents

Initial system delivery expected March 2017
Second system expected June 2017
3) Physical Vapor Transport (PVT) Process

- Sublimation from source material
- Vapor transport down temperature gradient
- Condensation on seed crystal
- Surface diffusion
- Incorporation and growth of crystal at step edges

*Useful approach for growth of a wide range of II-VI compounds*
Additional Bulk Crystal Growth Capabilities at Penn State – Physical Vapor Transport (PVT)

Induction Heated Physical Vapor Transport Systems (4)

- Capable of wide range of temperatures and axial gradients
- Susceptor shape, coil position, radiation window control axial gradient.
- 100mm diameter,
- 200mm length
- Temperatures up to 2500ºC
- Turbo pumped, cold walled configuration
- Fully automated process control and data acquisition.
- Have been used to growth SiC, ZnS, PbTe…
4) Large Area 2D Substrates – Epitaxial & CVD Graphene

Induction Heated PVT Systems Can Be Used to Synthesize and Hydrogenate Epitaxial Graphene up to 100mm diameter

Large Diameter CVD System Can Be Used To Grow/Transfer CVD Graphene to a Range of Substrates up to 100 diameter
5) Large Area Substrates – Hexagonal Boron Nitride

1) Direct Growth of BN on Si(111) and Al₂O₃
   - CVD deposition of polyborazylene (B₃N₃Hₓ) at 250°C or 400°C on insulating or conductive substrates
   - Conversion to BN via a 1000°C anneal.

2) h-BN Growth on Cu Substrates
   - h-BN grown via a catalytic CVD process on copper substrates.
   - Sublimation of Ammonia Borane to the precursor borazine at 135°C → decomposes into h-BN at 1000°C on a 99.98% purity copper foil substrate.
6) Additional bulk crystal growth equipment at Penn State – Cz Growth

- Thermal Technology, Inc. Model 7004CI System
  - 25 KW Induction power supply
  - Capable of 50 mm dia. x 150 mm length
  - Chamber capable of inert, oxidizing or vacuum
  - Water cooled load cell (2 kg range, 0.01 g resolution)
  - Dedicated closed loop cooling system (+/- 0.5C)
  - LabVIEW Automatic Diameter Control (Bruni Algorithm)

High temperature growth system
Configured for up to 2100ºC operation.
Translation and rotation
Vacuum, atmosphere control

Hot zone insulation
And coil assembly
Water cooled load cell and pull rod mechanism
Bulk Crystal Growth – Equipment

Support Equipment Being Upgraded for Ampoule Preparation

**Quartz Sealing Station**
- system for ampoule sealing
  - Torch sealing of ¼” to 2” dia. quartz tubes

**Compounding Furnace**
- system for source preparation
  - Single zone (1250°C) rocking furnace for powder melting and mixing

**Ampoule Loading Station**
- system for ampoule loading, transport agent introduction
  - New system designed to be capable of a wide variety of transport agents.
Timeline: Setup, Ramp-up & Operation

Bridgman

- System #1 ordered: 03/16
- System #1 arrives at PSU: 09/16
- System #2 ordered: 03/17
- System #2 arrives at PSU: 09/17

CVT Furnaces

- Furnace #1 online for external users: March 2017
- Furnace #2 online for external users: July 2017

New VB furnace online for external user: May 2017

Bulk Growth Webinar 2/23/17
Bulk Growth Solicitation ~3/17
Bulk Crystal Fabrication Support
Equipment Available at Penn State

- **Slicing**
  - Diamond wire Technology single wire saw
  - Diamond wire Technology multi wire saw
  - Multiple ID/OD slicing saws
  - X-ray orientation: Alvord system for rapid, in-house orientation; Phillips, Rigaku, PANalytical, Multiwire Laue for specialized X-ray analysis)

- **Dicing**
  - Micro Automation dicing saws
  - K&S dicing saws
  - Surface finish assessment
  - Subsurface damage assessment

- **Mechanical Polishing/ CMP**
  - Full range of Engis Polishing equipment

- **CNC Machining**
  - Optipro eSX150 machining system
  - HAAS Super Mini Mill machining system

- **Metrology**
  - Zygo white light interferometer
  - Zygo optical interferometer
  - Optical dimensional analysis
CVT Bulk Crystal Growth

Transition Metal Dichalcogenides (TMDs)

Short term goals:

• Establish baseline synthesis capabilities for chemical vapor transport (CVT) of binary TMDs (MoS$_2$, WSe$_2$, WS$_2$, NbSe$_2$, etc.)

• Expand range of materials to include alloy TMDs and dopants.

• Develop processes and provide samples with unique compositions and doping for both internal research efforts and external user research projects.

• Develop standard characterization protocols for these samples.

Phase change materials

$\text{(Mo,W)Te}_2$

$\text{(Mo,W)S}_2$


Longer term goals:

• Compare properties of bulk and thin film TMDs to understand impact of thermodynamics vs. kinetics on material properties.

• Investigate properties of TMD alloys and doped crystals.
Bulk crystal growth

Topological Insulators

Short term goals

- Develop synthesis capabilities for Bridgman growth of common TIs including $\text{Bi}_2\text{Se}_3$, $\text{Bi}_2\text{Te}_3$, related alloys, and various dopants.
New Topological Materials

Longer term goals:
• Investigate the synthesis and properties of new topological phases
• Topological semimetals
• Topological crystalline insulators.

Interested in using the 2DCC-MIP Bulk Crystal Growth Facility?

The 2DCC-MIP is expecting to release a call for user proposals focusing on the Bulk Crystal Growth of chalcogenides in mid-to-late March 2017.

Let the 2DCC-MIP Leadership know about the chalcogenide bulk crystals of interest in your research.

All responses are confidential and will be used to better tailor the call to community needs.

Linked on the 2DCC Homepage: www.mip.psu.edu

Direct Link at: https://www.mri.psu.edu/materials-innovation-platform/become-user/user-resources/interested-using-2dcc-mip-bulk-crystal
INTERESTED IN USING 2DCC-MIP BULK CRYSTAL GROWTH FACILITY

First Name *

Last Name *

Institute *

Position *

Email Address *

Chalcogenide Bulk Crystals of Interest *

(e.g., chemistry and stoichiometry, crystal diameter, length, orientation, dopants, doping levels)

Send My Response
Bulk Crystal Growth Call for Proposals

Expected Release: March 17, 2017
Expected Due Date: May 12, 2017
Will be Released on the 2DCC Website in the Proposal Submission Portal

**Proposals for this call should be submitted as a research project proposal in the portal. The details of the call will be posted next to the submission area.**

Content of a Research Project Proposal Submission
- PI and Project User Information
- 3 Page Project Description (plus references)
- NSF-format bios of the named personnel (not required for students)

Next Steps
**Regardless of whether a response to the RFI is submitted, you are encouraged to contact any of the following 2DCC personnel to discuss proposed research prior to submission of a user proposal to the future topical solicitation.**

Contacts
Joan Redwing – Platform Director & Synthesis Lead; jmr31@psu.edu
Thomas Mallouk – Bulk Synthesis and Exfoliation; tem5@psu.edu
David Snyder – Bulk Synthesis; dws13@psu.edu
Joshua Robinson – Director of User Programs; jar403@psu.edu
Summary

- Bulk growth of chalcogenides offers the opportunity to investigate equilibrium growth of alloys and doped crystals, provide material for exfoliation to compare properties to films and to explore the synthesis and properties of new phases and compositions of 2D materials.
- The 2DCC is establishing a bulk growth facility with emphasis on CVT and VB growth and the capability and capacity to grow a wide range of unique materials, compositions and doping.
- An additional outcome of the bulk growth effort will be the ability to provide tailored substrates for thin film growth.
- The large range of potential chalcogenide compositions and doping along with relatively lengthy growth times necessitate close ties with theory and characterization for efficient experimental studies.
- The current RFI will be used to formulate a Bulk Crystal Growth Call for Proposals with an expected release date of March 17, 2017.