# REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggesstions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any oenalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.
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| | | |
|---|---|---|
| 1. REPORT DATE (DD-MM-YYYY)<br>28-02-2023 | 2. REPORT TYPE<br>Final Report | 3. DATES COVERED (From - To)<br>15-Oct-2018 - 14-Oct-2022 |

4. TITLE AND SUBTITLE
Final Report: Optical and Optoelectrical Properties of Franckeite: A Naturally Occurring Van Der Waals Heterostructure

5a. CONTRACT NUMBER
W911NF-19-1-0007

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
106012

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHORS

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
72495-RT-REP.21

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 15. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| a. REPORT | b. ABSTRACT | c. THIS PAGE | | | AKM Newaz |
| UU | UU | UU | UU | | 19b. TELEPHONE NUMBER<br>415-338-2944 |

# RPPR Final Report
as of 27-Mar-2023

Agency Code: 21XD

Proposal Number: 72495RTREP **Agreement Number: W911NF-19-1-0007**

**INVESTIGATOR(S):**

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**Phone Number:** 4153382944
**Principal:** Y

Organization: **San Francisco State University**
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DUNS Number: 942514985 EIN: 931137247
**Report Date:** 14-Jan-2023 Date Received: 28-Feb-2023
**Final Report** for Period Beginning 15-Oct-2018 and Ending 14-Oct-2022
**Title:** Optical and Optoelectrical Properties of Franckeite: A Naturally Occurring Van Der Waals Heterostructure
**Begin Performance Period:** 15-Oct-2018 **End Performance Period:** 14-Oct-2022
**Report Term:** 0-Other
Submitted By: AKM Newaz Email: akmnewaz@sfsu.edu
Phone: (415) 338-2944
**Distribution Statement:** 1-Approved for public release; distribution is unlimited.

**STEM Degrees:** 7 **STEM Participants:** 10

**Major Goals:** The goal of this proposal was to study excitons and explore their physical properties in atomically thin van der Waals heterostructures (vdWHs) fabricated from a naturally occurring vdWH Franckeite with the long-term goal to explore new emergent physical phenomena and determine their suitability for quantum nanophotonic applications.
Newly developed atomically thin van der Waals crystals, including graphene, hexagonal boron-nitride, and the dichalcogenide MoS2, reveal remarkable electrical, optical, and optoelectrical properties and show great promise for the development of novel nanoscale optoelectronic devices for the use in both civil and military applications. They offer a platform for tailoring the properties of materials by stacking different two-dimensional (2D) crystals to form vdWHs. These vdWHs are ideally suited to design functionalities at the atomically thin limit. Currently, vdWHs are fabricated synthetically by stacking different 2D van der Waals crystals vertically. This methodology is cumbersome as it relies on deterministic layer placement methods that have two major drawbacks: First, there is poor control over the crystal lattice orientation. Second, the presence of undesired adsorbates or air bubbles between the stacked layers damages the sample.

These limitations are removed and new functionality is created, when nature is involved in stacking two different semiconducting layered materials, as is the case in Franckeite (Fr, Pb5Sn3Sb2S14). Although Fr provides a unique platform to study exciton behavior in a naturally occurring vdWH, to date little is known about the optoelectronic properties and excitons in Fr. This research will increase the understanding of the optical, optoelectrical and exciton behavior in Fr, which promises to opens new avenues for preparing designer materials. The proposed research builds on the preliminary work of the PI, in which he and his students probed many-body states in Fr and other van der Waals crystals through the use of photocurrent spectroscopy (PCS) and photoluminescence spectroscopy (PL).

The PI and his students proposed to accomplish four specific objectives:

1) Prepare and characterize monolayers SnS2 (1L- SnS2), PbS (1L-PbS), and Fr (1L-Fr) through the use of Raman spectroscopy, optical microscopy, and atomic force microscopy.

2) Investigate intralayer excitons in 1L-SnS2 and 1L-PbS, and interlayer excitons in 1L-Fr by photoluminescence (PLS) spectroscopy.

3) Probe exciton dissociation in 1L-SnS2, 1L-PbS and 1L-Fr by photocurrent spectroscopy (PCS).

4) Probe exciton behavior in Fr quantum dots (QDs) and compare their optical properties to colloidal QDs

comprised of SnS2 and PbS.

Techniques: We employed several microscopy and spectroscopy techniques: (i) optical microscopy; (ii) atomic force microscopy; (iii) scanning electron microscopy; (iv) energy-dispersive X-ray spectroscopy; (v) Raman spectroscopy; (iv) photoluminescence spectroscopy; and (vii) photocurrent spectroscopy.

**Accomplishments:** Please see the pdf file in the upload section.

**Training Opportunities:** 1) Three graduate students (Ms. Viviane Costa, Mr. Bryce Baker, and Zhuowa Wu) obtained training on attocube attodry 2100 cryogen-free cryostat. Both obtained training on operating several component of the equipment; (i) confocal microscope at the base temperature, (ii) variable temperature insert, (iii) superconducting magnetic field (0 T -12 T), and (iv) micro-photoluminescence and micro-Raman measurement.

2) Two graduate students (Ms. Viviane Costa, and Zhuowa Wu) and one post doctoral fellow (Dr. Shirin jamali) obtained training on preparing atomically thin samples.

3) Two graduate students (Ms. Viviane Costa, and Zhuowa Wu) and one post doctoral fellow (Dr. Shirin jamali) obtained training on micro photoluminescence and microphototurrent measurement techniques.

4) One undergradutae student obtained training onb programin in LabView.

5) One undergradute student obtained training on micro photoluminescence and microphototurrent measurement techniques.

# RPPR Final Report
as of 27-Mar-2023

**Results Dissemination:** Peer Reviewed Manuscript:

1) Semimetal–Monolayer Transition Metal Dichalcogenides Photodetectors for Wafer-Scale Broadband Photonics-Advanced Photonics Research, (Accepted) DOI: 10.1002/adpr.202300029

2) Observation of Photoluminescence from a Natural van der Waals Heterostructure- Viviane Z. Costa, Bryce Baker, Hon-Loen Sinn, Addison Miller, K. Watanabe, T. Taniguchi, Akm Newaz-Appl. Phys. Lett. 120, 253101 (2022); https://doi.org/10.1063/5.0089439

3) Strong Effects of Interlayer Interaction on Valence-Band Splitting in Transition Metal Dichalcogenides-Garrett Benson, Viviane Zurdo Costa, Neal Border, Kentaro Yumigeta, Mark Blei, Sefaattin Tongay, K. Watanabe, T. Taniguchi, Andrew Ichimura, Santosh KC, Taha Salavati-fard, Bin Wang, Akm Newaz- J. Phys. Chem. C 2022, 126, 20, 8667–8675m (2022)
https://doi.org/10.1021/acs.jpcc.1c10631

4) V. Z. Costa†, Liangbo Liang, Sam Vaziri, Addison Miller, Eric Pop, A. K. M. Newaz- Vibrational Properties of a Naturally Occurring Semiconducting van der Waals heterostructure- ACS Journal of Physical Chemistry C, 125, 39, 21607–21613 (2021) https://doi.org/10.1021/acs.jpcc.1c05241
5) A. Seredinski, E. G. Arnault, V. Z. Costa, L. Zhao, T. F. Q. Larson, K. Watanabe, T. Taniguchi, F. Amet, A. K. M. Newaz, and G. Finkelstein-One-dimensional edge contact to encapsulated MoS2 with a superconductor, AIP Advances 11, 045312 (2021); https://doi.org/10.1063/5.0045009

6) Hao Lee†, S. Deshmukh, Jing Wen, V.Z. Costa†, J. S. Schuder†, M. Sanchez‡, A. Ichimura, Eric Pop, Bin Wang, and A. K. M. Newaz, Layer dependent Interfacial Transport and Optoelectrical properties of MoS2 on Ultra-flat metals- ACS Applied Materials and Interfaces, 11, 31543-31550 (2019); DOI: 10.1021/acsami.9b09868.

Conference Presentations:

1) Semimetal-Monolayer Transition Metal Dichalcogenides Photodetectors for Wafer-Scale Ultraviolet Photonics-Akm S Newaz, Hon-Loen Sinn, Aravindh Kumar, and Eric Pop, APS March Meeting 2023 (Las vegas)
2) Semimetal-Monolayer Transition Metal Dichalcogenides Photodetectors for Wafer-Scale Ultraviolet Photonics-Hon-Loen Sinn, Aravindh Kumar, Eric Pop, and Akm S Newaz, MRS Spring Meeting 2023 (San Francisco)
3) In-Plane Thermal Conductivity of Twisted 2D Materials-Sorren Warkander, Zhuowa Wu,AKM Newaz,Junqiao Wu (MRS Fall Meeting, Boston, 2022)
4) Observation of photoluminescence from Franckeite, a natural van der Waals heterostructure-, Akm S Newaz, Bryce Baker, Viviane Z. Costa, Addison Miller, (APS March Meeting 2022, Chicago)
5) Shirin Jamali, Viviane Z. Costa, Garrett Benson, Andrew Ichimura, Akm Newaz -Tunneling Mechanism in Ultimate Thin Vertical Au/MoS2/Au Tunnel Junction-APS March Meeting 2021 (Virtual Meeting)
6) Andrew Seredinski, Ethan Arnault, Viviane Z. Costa, Lingfei Zhao, Trevyn Larson, Kenji Watanabe, Takashi Taniguchi, Francois Amet, Akm Newaz, and Gleb Finkelstein- One-Dimensional Edge Contact to Encapsulated MoS2 with a Superconductor- APS March Meeting 2021 (Virtual Meeting)
7) Akm Newaz, Garrett Benson, Viviane Z. Costa, Shirin Jamali, Kentaro Yumigeta, Mark Blei Blei, Sefaattin Tongay, Bin Wang, Santosh KC, Andrew Ichimura-Temperature- and layer- dependent spin-orbit coupling APS March Meeting 2021 (Virtual Meeting)
8) Viviane Z. Costa, Liangbo Liang, Addison Miller, Sam Vaziri, Shirin Jamil, Andrew Ichimura, Eric Pop, Akm Newaz-Raman studies of a natural van der Waals heterostructure- APS March Meeting 2021 (Virtual Meeting)
7) V. Z. Costa*, A. Miller, S. Vaziri, S. Jamil, A. Ichimura, E. Pop, AKM Newaz, “Raman studies of a natural van der Waals heterostructure,” Virtual MRS Fall Meeting, Nov 2020 (Poster)
9) Viviane Zurdo Costa†, Sam Vaziri, Shirin Jamali, Addison Miller, Andrew Ichimura, Eric Pop, Akm Newaz - Temperature-dependent Raman studies of a natural van der Waals heterostructure, ICFO-MIT SCHOOLS ON THE FRONTIERS OF LIGHT, The Institute of Photonic Sciences (ICFO), Barcelona, Spain, July, 2020.
10) Garrett Benson†, Viviane Zurdo Costa†, Neal Border‡, Shirin Jamali, Kentaro Yumigeta, Mark Blei, Sefaattin Tongay, Andrew Ichimura, Akm Shah Newaz -Temperature dependence of van Hove singularity excitons in atom thick semiconductors, APS March Meeting, Denver 2020 (Canceled due to COVID-19 pandemic).
11) Viviane Zurdo Costa†, Sam Vaziri, Shirin Jamali, Addison Miller, Andrew Ichimura, Eric Pop, Akm Shah Newaz -Temperature-dependent Raman studies of a natural van der Waals heterostructure, APS March Meeting, Denver 2020 (Canceled due to COVID-19 pandemic)
12) Viviane Zurdo Costa†, Sam Vaziri, Shirin Jamali, Addison Miller, Andrew Ichimura, Eric Pop, Akm Shah Newaz

-Temperature-dependent Raman studies of a natural van der Waals heterostructure, International Winterschool on Electronic Properties of Novel Materials - IWEPNM, Kirchberg in Tirol, Austria, March 7 - March 14, 2020.
13) Hao Lee†, Sanchit Deshmukh, Jing Wen, Viviane Costa‡, Eric Pop, Bin Wang, Akm Newaz- Layer number dependent barrier height of MoS2 on ultra-flat conducting surfaces- Material Research Society (MRS) Spring Meeting, Phoenix, Arizona, 2020
14) Hao Lee†, Sanchit Deshmukh, Jing Wen, Viviane Costa‡, Eric Pop, Bin Wang, Akm Newaz- Layer number dependent barrier height of MoS2 on ultra-flat conducting surfaces- American Physical Society (APS) March Meeting, Boston, March, 2019

Thesis:
1) Bryce Baker (05/13/2022)
Thesis Title: Temperature and Magnetic Field Dependent Raman Spectroscopy of Graphene
2) Viviane Zudro Costa (06/03/2021)
Thesis Title: Vibrational Properties of Franckeite
3) Garrett Benson (10/16/2020),
Thesis Title: Temperature and Layer Dependent Spin-Orbit Coupling in Atomically Thin Semiconductors.
4) Hao Lee (4/25/2019) (Current Position: Linguist Specialist, Apple Inc., Cupertino, CA)
Thesis Title: Conductive and photoconductive AFM on exfoliated MoS2

Graduate Student Showcase:
A total of six posters were presented over the period of funding

**Honors and Awards:** Nothing to Report

**Protocol Activity Status:**

**Technology Transfer:** Provisional Patent applicaiton has been submitted:
Semimetal-monolayer transition metal dichalcogenides photodetector for wafer-scale photonics (Application number: 63/368,923)

**PARTICIPANTS:**

**Participant Type:** PD/PI
**Participant:** AKm Newaz
**Person Months Worked:** 5.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Graduate Student (research assistant)
**Participant:** Bryce Russell Baker
**Person Months Worked:** 4.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Undergraduate Student
**Participant:** Faiyaz Rayhan Chaudhury
**Person Months Worked:** 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Postdoctoral (scholar, fellow or other postdoctoral position)

**Participant:** Shirin Jamali
**Person Months Worked:** 15.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Graduate Student (research assistant)
**Participant:** Viviane Costa
**Person Months Worked:** 15.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Graduate Student (research assistant)
**Participant:** Zhuowa Wu
**Person Months Worked:** 2.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**ARTICLES:**

**Publication Type:** Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
**Journal:** ACS Applied Materials & Interfaces
Publication Identifier Type: DOI Publication Identifier: 10.1021/acsami.9b09868
Volume: 11 Issue: 34 First Page #: 31543
Date Submitted: 9/10/19 12:00AM Date Published: 7/1/19 7:00AM
Publication Location:
**Article Title:** Layer-Dependent Interfacial Transport and Optoelectrical Properties of MoS
**Authors:** Hao Lee, Sanchit Deshmukh, Jing Wen, Viviane Z. Costa, Joachim S. Schuder, Michael Sanchez, Andr
**Keywords:** MoS2 layer dependence electronic transport photoconductivity photoconductive AFM metal?MoS2 junction Schottky barriers
**Abstract:** Layered materials based on transition-metal dichalcogenides (TMDs) are promising for a wide range of electronic and optoelectronic devices. Realizing such practical applications often requires metal–TMD connections or contacts. Hence, a complete understanding of electronic band alignments and potential barrier heights governing the transport through metal–TMD junctions is critical. However, it is presently unclear how the energy bands of a TMD align while in contact with a metal as a function of the number of layers. In pursuit of removing this knowledge gap, we have performed conductive atomic force microscopy (CAFM) of few-layered (1 to 5 layers) MoS2 immobilized on ultraflat conducting Au surfaces [root-mean-square (rms) surface roughness < 0.2 nm] and indium–tin oxide (ITO) substrates (rms surface roughness < 0.7 nm) forming a vertical metal (CAFM tip)–semiconductor–metal device. We have observed that the current increases with the number of layers up to five layers.
**Distribution Statement:** 2-Distribution Limited to U.S. Government agencies only; report contains proprietary info
Acknowledged Federal Support: **Y**

**Publication Type:** Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
**Journal:** AIP Advances
Publication Identifier Type: DOI Publication Identifier: 10.1063/5.0045009
Volume: 11 Issue: First Page #: 045312
Date Submitted: 11/12/21 12:00AM Date Published: 4/7/21 7:00AM
Publication Location:
**Article Title:** One-dimensional edge contact to encapsulated MoS2 with a superconductor
**Authors:** A. Seredinski, E. G. Arnault, V. Z. Costa, L. Zhao, T. F. Q. Larson, K. Watanabe, T. Taniguchi, F. Am
**Keywords:** 2D semiconductots, superconductor-semiconductor contact, transport
**Abstract:** Establishing ohmic contact to van der Waals semiconductors such as MoS2 is crucial to unlocking their full potential in next-generation electronic devices. Encapsulation of few layer MoS2 with hBN preserves the material’s electronic properties but makes electrical contacts more challenging. Progress toward high quality edge contact to encapsulated MoS2 has been recently reported. Here, we evaluate a contact methodology using sputtered MoRe, a type II superconductor with a relatively high critical field and temperature commonly used to induce superconductivity in graphene. We find that the contact transparency is poor and that the devices do not support a measurable supercurrent down to 3 K, which has ramifications for future fabrication recipes.
**Distribution Statement:** 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

**Publication Type:** Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
**Journal:** J. Phys. Chem. C
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpcc.1c05241
Volume: 125 Issue: 39 First Page #: 21607
Date Submitted: 11/12/21 12:00AM Date Published: 9/23/21 2:00PM
Publication Location:
**Article Title:** Vibrational Properties of a Naturally Occurring Semiconducting van der Waals Heterostructure
**Authors:** V. Z. Costa, Liangbo Liang, Sam Vaziri, Addison Miller, Eric Pop, A. K. M. Newaz
**Keywords:** Natural van der Waals heterostructure, Franckeite, Raman spectroscopy, DFT, thermal properties
**Abstract:** We present vibrational properties of Franckeite, which is a naturally occurring van der Waals heterostructure consisting of two different semiconducting layers. Franckeite is a complex layered crystal composed of alternating SnS2-like pseudohexagonal and PbS-like pseudotetragonal layers stacked on top of each other, providing a unique platform to study vibrational properties and thermal transport across layers with mass density and phonon mismatches. Using micro-Raman spectroscopy and first-principles Raman simulations, we found that the PbS-like pseudotetragonal structure is mostly composed of Pb3SbS4. We also discovered several low-frequency Raman modes that originate from the intralayer vibrations of the pseudotetragonal layer. Using density functional theory, we determined all vibrational patterns of Franckeite, whose signatures are observed in the Raman spectrum.
**Distribution Statement:** 2-Distribution Limited to U.S. Government agencies only; report contains proprietary info
Acknowledged Federal Support: **Y**

**CONFERENCE PAPERS:**

**Publication Type:** Conference Paper or Presentation **Publication Status:** 0-Other
**Conference Name:** APS March Meeting
Date Received: 12-Nov-2021 Conference Date: 02-Mar-2020 Date Published: 06-Mar-2020
Conference Location: Denver Colorado
**Paper Title:** Temperature dependence of van Hove singularity excitons in atom thick semiconductors
**Authors:** Viviane Costa, Sam Vaziri, Shirin Jamali, Addison Miller, Andrew Ichimura, Eric Pop, And Akm Newaz
Acknowledged Federal Support: **Y**

**Publication Type:** Conference Paper or Presentation **Publication Status:** 0-Other
**Conference Name:** APS March Meeting
Date Received: 12-Nov-2021 Conference Date: 03-Mar-2020 Date Published: 07-Mar-2020
Conference Location: Denver CO
**Paper Title:** Temperature-dependent Raman studies of a natural van der Waals heterostructure
**Authors:** Garrett Benson, Viviane Zurdo Costa, Neal Border, Shirin Jamali, Kentaro Yumigeta, Mark Blei, Sefaatti
Acknowledged Federal Support: **Y**

**Publication Type:** Conference Paper or Presentation **Publication Status:** 0-Other
**Conference Name:** Material Research Society (MRS) Spring Meeting
Date Received: Conference Date: 13-Apr-2020 Date Published: 17-Apr-2020
Conference Location: Phoenix, AZ
**Paper Title:** Layer number dependent barrier height of MoS2 on ultra-flat conducting surfaces
**Authors:** Hao Lee, Sanchit Deshmukh, Jing Wen, Viviane Costa, Eric Pop, Bin Wang, Akm Newaz
Acknowledged Federal Support: **Y**

**Publication Type:** Conference Paper or Presentation **Publication Status:** 0-Other
**Conference Name:** APS March Meeting 2021
Date Received: 12-Nov-2021 Conference Date: 15-Mar-2021 Date Published: 15-Mar-2021
Conference Location: Nashville, TN (Virtual)
**Paper Title:** Tunneling Mechanism in Ultimate Thin Vertical Au/MoS2/Au Tunnel Junction
**Authors:** Shirin Jamali, Viviane Z. Costa, Garrett Benson, Andrew Ichimura, Akm Newaz
Acknowledged Federal Support: **Y**

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published
**Conference Name:** APS March Meeting 2021
Date Received: 12-Nov-2021 Conference Date: 15-Mar-2021 Date Published: 15-Mar-2021
Conference Location: Nashville, TN, USA (virtual)
**Paper Title:** One-Dimensional Edge Contact to Encapsulated MoS2 with a Superconductor
**Authors:** Andrew Seredinski, Ethan Arnault, Viviane Z. Costa, Lingfei Zhao, Trevyn Larson, Kenji Watanabe, Tak
Acknowledged Federal Support: **Y**

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published
**Conference Name:** APS March Meeting 2021
Date Received: 12-Nov-2021 Conference Date: 15-Mar-2021 Date Published: 15-Mar-2021
Conference Location: Nashville, TN, USA (virtual)
**Paper Title:** Temperature- and layer- dependent spin-orbit coupling in atom-thick transition metal dichalcogenides
**Authors:** Akm Newaz, Garrett Benson, Viviane Z. Costa, Shirin Jamali, Kentaro Yumigeta, Mark Blei Blei, Sefaatt
Acknowledged Federal Support: **Y**

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published
**Conference Name:** APS March Meeting 2021
Date Received: 12-Nov-2021 Conference Date: 15-Apr-2021 Date Published: 15-Apr-2021
Conference Location: Nashville, TN, USA (virtual)
**Paper Title:** Raman studies of a natural van der Waals heterostructure
**Authors:** Viviane Z. Costa, Liangbo Liang, Addison Miller, Sam Vaziri, Shirin Jamil, Andrew Ichimura, Eric Pop, A
Acknowledged Federal Support: **Y**

**DISSERTATIONS:**

**Publication Type:** Thesis or Dissertation
**Institution:** San Francisco State University
Date Received: 10-Sep-2019 Completion Date: 5/24/19 6:21PM
**Title:** Conductive and photoconductive AFM on exfoliated MoS2
**Authors:** Lee, Hao
Acknowledged Federal Support: **N**

**Publication Type:** Thesis or Dissertation
**Institution:** San Francisco State University
Date Received: 12-Nov-2021 Completion Date: 8/16/21 7:00AM
**Title:** VIBRATIONAL MODES AND THERMAL CONDUCTIVITY OF A NATURAL VAN DER WAALS HETEROSTRUCTURE
**Authors:** Viviane Zurdo Costa
Acknowledged Federal Support: **N**

**Publication Type:** Thesis or Dissertation
**Institution:** San Francisco State University
Date Received: 17-Feb-2023 Completion Date: 12/20/22 7:20PM
**Title:** Vibrational properties of atomically thin semiconductors on ultra-flat metals
**Authors:** Daniel C. Touzeau
Acknowledged Federal Support: **Y**

**Publication Type:** Thesis or Dissertation
**Institution:** San Francisco State University
Date Received: 17-Feb-2023 Completion Date: 5/17/21 8:07PM
**Title:** Temperature and Magnetic Field Dependent Raman Spectroscopy of Graphene
**Authors:** Bryce Baker
Acknowledged Federal Support: **N**

**WEBSITES:**

**URL:** https://news.sfsu.edu/news-story/sf-state-researchers-use-lasers-gold-test-super-thin-materials
Date Received:
**Title:** SF State researchers use lasers, gold to test super-thin materials
**Description:**

**Partners**

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# RPPR Final Report

as of 27-Mar-2023

I certify that the information in the report is complete and accurate:
Signature: Akm Newaz
Signature Date: 2/28/23 2:26PM

# Optical and optoelectrical properties of Franckeite: A naturally occurring van der Waals Heterostructure

**PI: AKM Newaz, Institution: San Francisco State University**

## PROJECT ABSTRACT

In response to the mission of the Optoelectronics and Photonics Division of the Air Force, we proposed to investigate the intriguing optical and optoelectrical properties of the naturally occurring van der Waals heterostructure (vdWH) Franckeite (Fr). We probed functionalities at the atomically thin limit and potential use in novel nanoelectronics and nanophotonics applications. Van der Waals heterostructures (vdWHs) belong to the group of two-dimensional (2D) atomic crystals, in which layered van der Waals crystal (e.g., graphene, hexagonal boron-nitride, and transition metal dichalcogenides) are stacked in a predefined sequence to prepare designer heterostructures. Due to their intriguing properties, these atomically thin vdWHs are currently at the frontier of condensed matter physics and materials science research. They show great promise for the development of novel nanoscale electronic, optical and optoelectronic devices and for the fabrication of designer materials at the atomically thin limit. Currently, 2D vdWHs are fabricated synthetically in the laboratory by stacking 2D van der Waals crystals. This methodology relies on cumbersome placement methods of different atom layers, which is prone to unrepairable damages. These limitations are removed and new functionality is created, when nature is involved in creating the vdWH.

We investigated the optical and optoelectronic properties of Fr that is comprised of alternating, weakly bonded, stacked pseudotetragonal lead sulfide (PbS) and pseudohexagonal tin sulfide ($SnS_2$) layers. Unlike vdWHs prepared in the laboratory, the crystal orientation of the two neighboring layers in Fr are preserved across the sample and, simultaneously, the samples are free from fabrication related spurious interlayer adsorbates. The optical and optoelectronic properties of Fr originate from excitons, i.e., the bound state of an electron and a hole that form in a semiconductor when photons are absorbed. Two types of excitons in Franckeite were studied: interlayer excitons formed in the same layer and intralayer excitons formed in neighboring layers. We investigate the exciton formation in Fr and the effect of dimensional confinement on exciton behavior. The research goals were accomplished by using microscopy and spectroscopy techniques: (i) optical microscopy; (ii) atomic force microscopy; (iii) Raman spectroscopy; (iv) photoluminescence spectroscopy; and (v) photocurrent spectroscopy.

The conducted research on Fr has advanced the knowledge of preparing novel vdWHs with designer functionalities and vdWH-based optoelectronic devices for a wide range of scientific and consumer applications. The project has enhanced STEM education at the Department of Physics & Astronomy at San Francisco State University (SFSU), a Hispanic Serving Institution, by engaging undergraduate and Master's students in nanophotonic research focusing on students from underrepresented groups. It has engaged diverse students, mainly the physics and engineering majors, in stimulating research at the forefront of nanoelectronics and nanophotonic device physics- one of the areas of scientific interest to Air Force Office of Scientific Research (AFOSR) and Army Research Office (ARO).

## Specific Objectives

The PI and his students proposed to accomplish four specific objectives:

1) Prepare and characterize monolayers $SnS_2$ (1L- $SnS_2$), PbS (1L-PbS), and Fr (1L-Fr) through the use of Raman spectroscopy, optical microscopy, and atomic force microscopy.

2) Investigate intralayer excitons in 1L-$SnS_2$ and 1L-$Pb_S$, and interlayer excitons in 1L-Fr by photoluminescence (PLS) spectroscopy.

3) Probe exciton dissociation in 1L-$SnS_2$, 1L-PbS and 1L-Fr by photocurrent spectroscopy (PCS).

4) Probe exciton behavior in Fr quantum dots (QDs) and compare their optical properties to colloidal QDs comprised of SnS2 and PbS.

***Objective 1: Prepare and characterize monolayers SnS2 (1L- SnS2), PbS (1L-PbS), and Fr (1L-Fr) through the use of Raman spectroscopy, optical microscopy, and atomic force microscopy.***

1) ***Improving sample quality and towards preparing atomically thin Franckeite:*** We prepared many samples using mechanical micro-exfoliation. We optimized our exfoliation to obtain high quality Franckeite sample on $SiO_2$, an important substrate to probe optical and optoelectrical properties. The developed technique significantly improved the quality of exfoliated flakes, increasing their size and, most significantly, their surface area. Figure 1 presents the optical and AFM images of two exfoliated samples.

   ***Optimized exfoliation techniques:*** Franckeite samples were exfoliated using adhesive-type micromechanical cleavage technique (a.k.a. adhesive tape method). It is important that the flake in which one starts the exfoliation, or starting flake, is prepared carefully to assure a high-quality sample. Franckeite is a very brittle material. While a good starting flake for most of 2D materials can be easily found to be large (around 1 cm of length) and flat, Franckeite flakes are much smaller and grainy (sizes < 1 mm).

   We found that there are many parameters in the exfoliation process that can determine the quality of the resulting flakes: exfoliation speed and speed consistency, type of tape, hydrophilicity of the substrate, and so forth. However, the quality of the starting flake is a parameter that has one of the

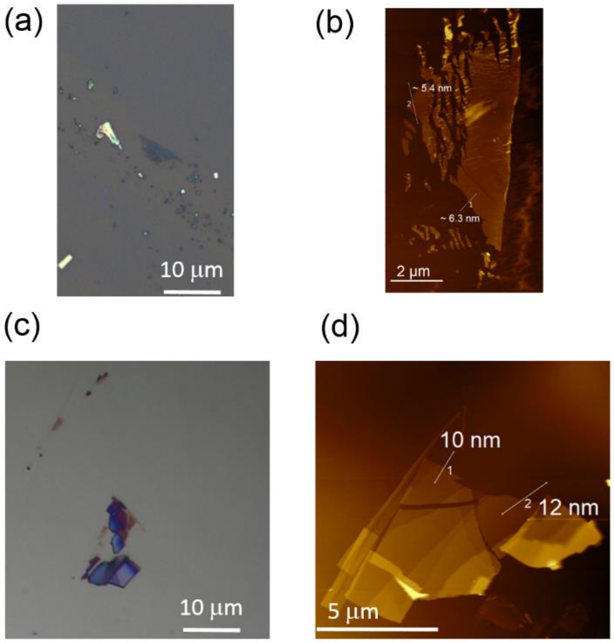

**Figure 1:** Physical characterization of atomically thin Franckeite. (a) Optical microscope image of an exfoliated Franckeite sample $SiO_2$. (b) AFM image of a sample. The thickness of the sample is shown along the white lines. (c)Optical microscope image of another exfoliated Franckeite sample. (c) AFM image of the sample. The thickness of the sample is shown along the white lines. Inset: height profile along the drawn line. The length of the scale bar is also shown in each image.

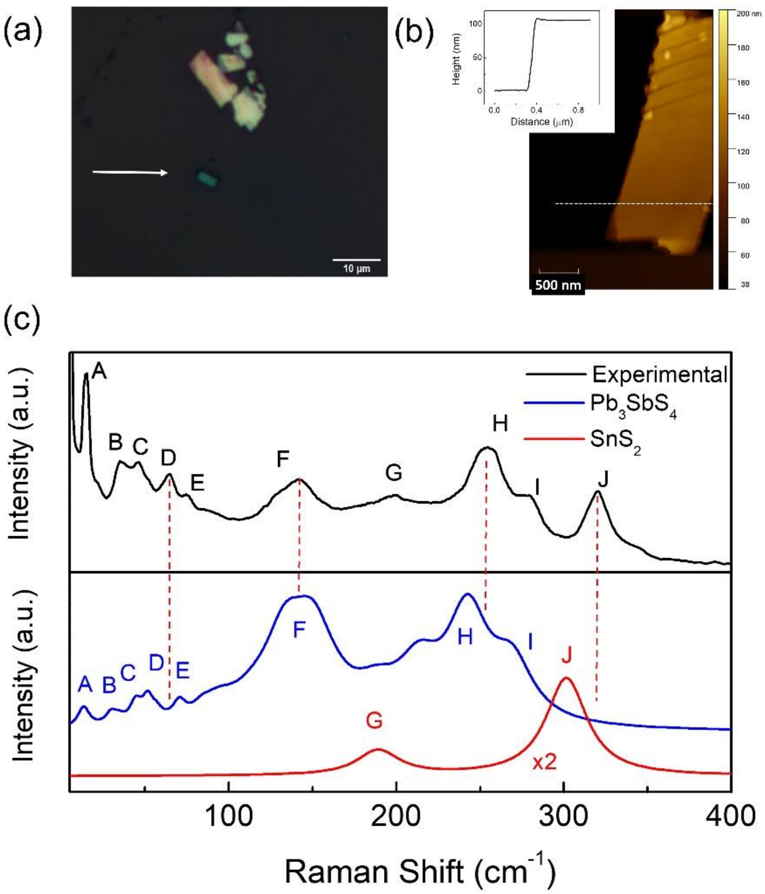

**Figure 2:** Optical and atomic force microscope image of a Franckeite sample. (a) The optical image of the sample used in the study (marked by an arrow). The sample is immobilized on a $SiO_2$ (90 nm)/$p^+$Si substrate (b) The AFM image of the same sample shown in (a). The sample thickness is ~100 nm. The inset is showing the height profile along the dashed line mark in the main panel. Raman spectroscopy of many-layer Franckeite. (a) Experimentally measured Raman spectroscopy at room temperature. The excitation laser wavelength is 633 nm. The Raman modes are marked alphabetically as A (15 $cm^{-1}$), B(35 $cm^{-1}$), C(45 $cm^{-1}$), D(64 $cm^{-1}$), E(75 $cm^{-1}$), F(140 $cm^{-1}$), G(195 $cm^{-1}$), H(256 $cm^{-1}$), I(276 $cm^{-1}$) and J(321 $cm^{-1}$). (b) Calculated Raman spectra of Franckeite are shown here. The blue line presents the Raman modes for $Pb_3SbS_4$ and the red line for $SnS_2$.

highest impacts in how many thin and large flakes yield on the sample. Because Franckeite is so brittle and grainy, it is even more crucial to have starting flakes that are large and flat. Note that Franckeite, unlike the other 2D materials that are soft and a starting flake can be peeled with tweezers, is also a hard material. One must delicately carve Franckeite using a sharp razor blade or a scalpel in order to obtain a flat large flake. The selected starting flakes were carefully placed on a piece of adhesive-tape. To assure the flakes are firmly in contact with the adhesive-layer of the tape, it is necessary to rubdown the flake onto the tape. Because touching the flake would introduce contaminants, it is useful to use a piece of clean PDMS (polydimethylsiloxane) as a support. The tape is placed on the PDMS with the flakes facing down and the back of the flakes are gently rubbed with the tip of Teflon tweezers. After that, another piece of tape is placed on top of the flakes (the same method of using PDMS as support can be used to make sure the entire surface area of the flake is in contact with the adhesive layer of the tape), and the two pieces of tape are then peeled apart very slowly. In this last step, the flakes get divided between the two pieces of tape, reducing its thickness and layer number. After a few times that this process has been repeated, the final piece of tape is then placed on top of a clean substrate. The substrate with the tape on top is placed on a hot-plate at 130 °C for approximately 5 minutes before peeling the tape off the substrate.

2) ***Vibration properties of Franckeite:*** Vibrational properties of layered materials is crucial to understand the electron−phonon interaction, which determines the transport properties. Moreover, vibrational properties are also of fundamental importance to understand anharmonicity in the lattice potential energy. Though Fr provides a fascinating 2D crystal heterostructure with possibilities of exploring new physics and developing many attractive applications, some of its fundamental properties remain unknown. First, though the crystal structure of H-layer is known ($SnS_2$), the composition crystal structure of Q-layer is highly debated. It is also unclear whether pseudotetragonal (*Q*) layer is predominantly made of $Pb_3SbS_4$ or it is Sn based $PbSnS_2$. Second, the Raman spectroscopy of Fr is not understood. Because Fr contains two different layered semiconducting materials, it may provide unique vibrational behavior because of mass density and phonon mismatches. We answered these fundamental questions by performing micro-Raman spectroscopy, and first-principles density functional theory (DFT) studies.

We studied room temperature Raman spectroscopy of different thickness Franckeite as well as the temperature dependence of several Raman peaks. Room temperature Raman spectrum of a Franckeite sample is shown in Fig.2 along with DFT based simulations. Confocal micro-Raman measurements were performed using commercial equipment (Horiba LabRAM Evolution). A 100× objective lens with a numerical aperture of 0.9 was used. The excitation source was a 532 nm laser (2.33 eV) with an optical power of ∼170 μW. The Raman modes are marked alphabetically as A (15 $cm^{-1}$), B(35 $cm^{-1}$), C(45 $cm^{-1}$), D(64 $cm^{-1}$), E(75 $cm^{-1}$), F(140 $cm^{-1}$), G(195 $cm^{-1}$), H(256 $cm^{-1}$), I(276 $cm^{-1}$) and J(321 $cm^{-1}$). We employed DFT based simulation to determine the Raman modes for $Pb_3SbS_4$ and for $SnS_2$ and the results are presented in Fig.2c. We found that the experimentally measured Raman peaks are in good agreement with the calculated ones from $Pb_3SbS_4$ and $SnS_2$ layers (see Fig. 2 for comparison).

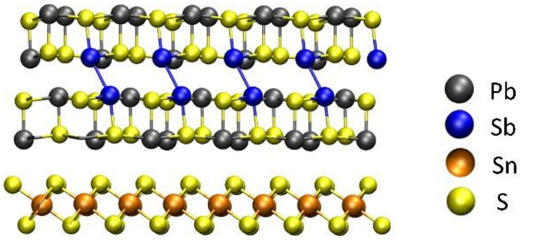

Figure 3: The crystal structure of Franckeite used for calculating the Raman spectra. The top is the Q-layer ($Pb_3SbS_4$) and the bottom is the H-layer ($SnS_2$). The colors assigned to different atoms are shown on the right.

Our simulation results suggest that Q layer is mostly like composed of $Pb_3SbS_4$ (Fig.3) instead of $PbSnS_2$. Furthermore, in the low frequency region, our calculations also show that Raman peaks of $Pb_3SbS_4$ layer match better with experimental ones than those of $PbSnS_2$ layer. With the crystal structure of Q layer in Franckeite determined, we then computed the atomic vibrational patterns of all Raman peaks, including the low frequency and high frequency ones, and illustrate them in Fig.4.

The results have been published in an ACS journal the Journal of Physical Chemistry C (Vibrational Properties of a Naturally Occurring Semiconducting van der Waals heterostructure-Authors: V. Z. Costa, Liangbo Liang, Sam Vaziri, Addison Miller, Eric Pop, A. K. M. Newaz ACS Journal of Physical Chemistry C, 125, 39, 21607–21613 (2021))

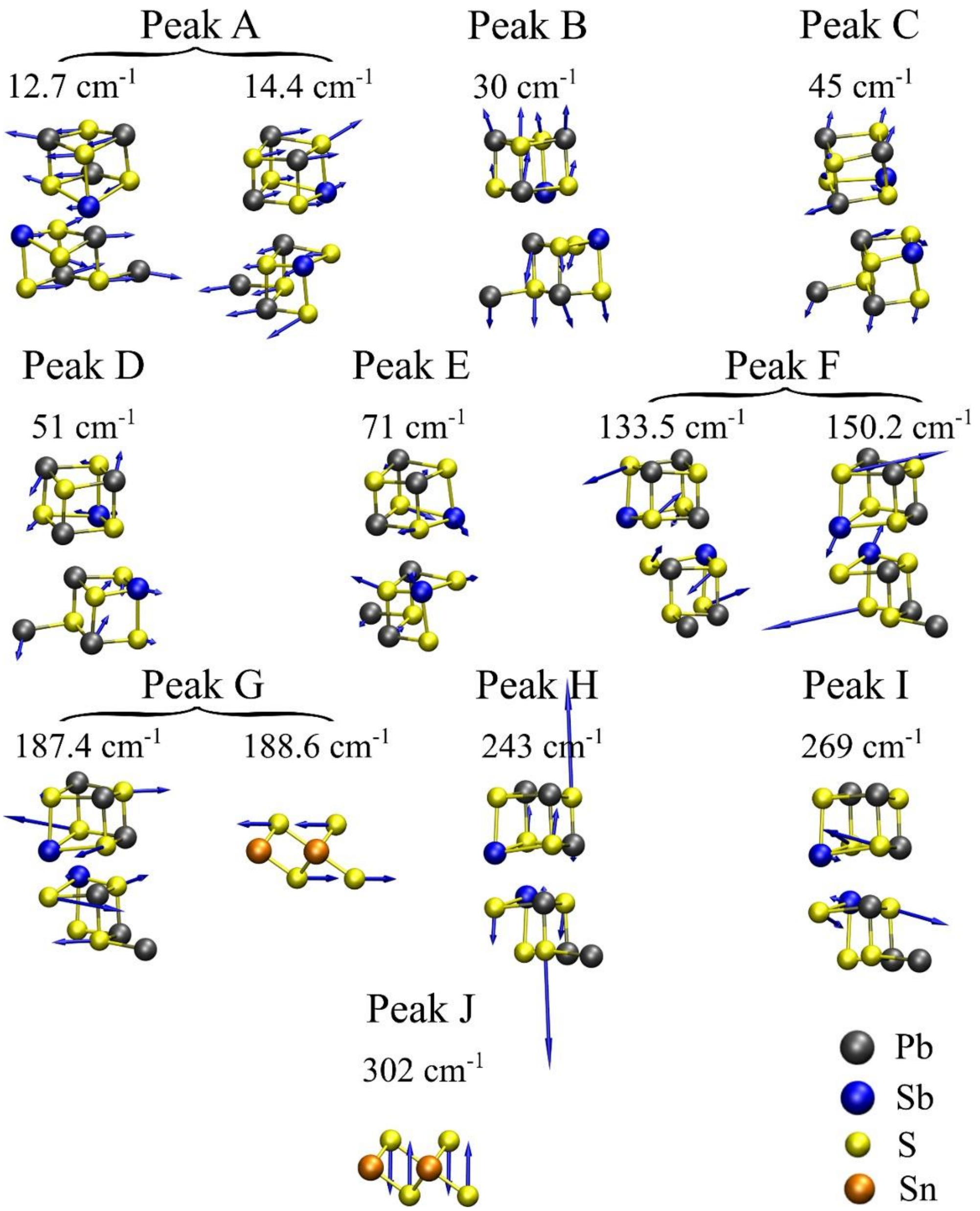

**Figure 4:** Calculated atomic vibrational patterns of experimental Raman peaks A-J in Franckeite. Raman modes from Q layer ($Pb_3SbS_4$) and H layer ($SnS_2$) are shown separately. The calculated phonon frequencies are shown for each mode. The symbols for different atoms are shown in the bottom right. Since $Pb_3SbS_4$ layer has no symmetry, every phonon mode is Raman active in principle, and thus there are many Raman peaks showing up in the experimental Raman spectra. Furthermore, some Raman peaks are contributed by multiple phonon modes close to each other (e.g., peak A, peak F, peak G, etc), which contributes to the large widths of Raman peaks in the experimental data. The $SnS_2$ layer has high symmetry and it only has two distinctive Raman modes: one around 188.6 cm$^{-1}$ (contributing to peak G), and the other one around 302 cm$^{-1}$ (corresponding to peak J). Other Raman peaks primarily originate from vibrations of $Pb_3SbS_4$ layer.

***Objective 2: Investigate intralayer excitons in 1L-SnS2 and 1L-PbS, and interlayer excitons in 1L-Fr by photoluminescence (PLS) spectroscopy.***

3) ***Photoluminescence property of Franckeite:*** Van der Waals heterostructures comprised of two-dimensional (2D) materials offer a platform to obtain materials by design with unique electronic properties. Franckeite (Fr) is a naturally occurring van der Waals heterostructure comprised of two distinct alternately stacked semiconducting layers; (i) $SnS_2$ layer and (ii) $Pb_3SbS_4$. Though both layers in the heterostructure are semiconductors, the photoluminescence from Franckeite remains elusive. We observed photoluminescence (PL) from Franckeite. We observed two PL peaks at ~ 1.97 eV and ~ 2.12 eV at 1.5 K. By varying the temperature from 1.5 K to 280 K, we found that the PL peak position blueshifts and the integrated intensity decreases slowly as we increase the temperature. We observed linear dependence of photoluminescence integrated intensity on excitation laser power indicating that the photoluminescence is originating from free excitons in the $SnS_2$ layer of Fr. By comparing the PL from Fr with the PL from a monolayer $MoS_2$, we determined that the PL quantum efficiency from Fr is an order of magnitude lower than that of a monolayer $MoS_2$. Our study provides a fundamental understanding of the optical behavior in a complex naturally occurring van der Waals heterostructure, and may pave an avenue toward developing nanoscale optical and optoelectronic devices with tailored properties.

   The results have been published in the Applied Physics Journal, Viviane Z. Costa†, Bryce Baker†, Hon-Loen Sinn†, Addison Miller, K. Watanabe, T. Taniguchi, **Akm Newaz**- Observation of Photoluminescence from a Natural van der Waals Heterostructure -Appl. Phys. Lett. 120, 253101 (2022); https://doi.org/10.1063/5.0089439

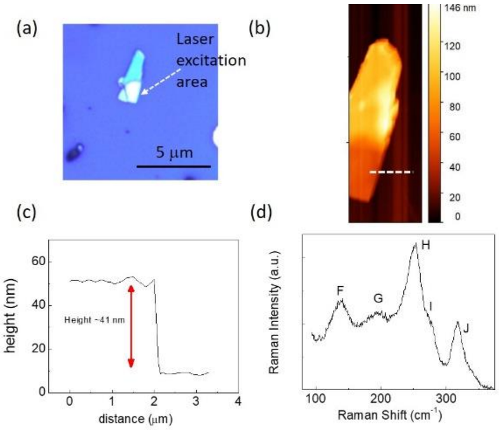

**Figure 5:** (a) The optical image of a Franckeite sample immobilized on a $SiO_2/Si$ substrate. The white arrow marks the region where the laser hit the sample for PL measurements. (b) The AFM image of the Fr flake in Fig.(a). (c) the height profile of the AFM image along the dashed white line in Fig.(b). The thickness of the Fr flake is ~ 41 nm. (d) Raman spectrum of the sample recorded at room temperature. The laser excitation wavelength was 633 nm with power ~200 μW.

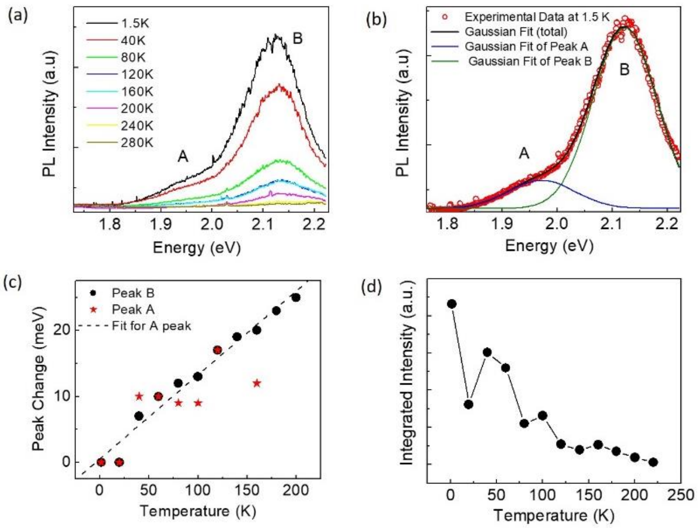

**Figure 6:** (a) Photoluminescence intensity from the Fr flake at varying temperature from 1.5 K to 280K. The laser excitation wavelength is 532 nm. (b) The PL spectrum of Fr measured at ~1.5 K (red circles). The two peaks are marked by A- and B-peak. The data are fitted by two gaussian peaks (blue and green lines for A- and B-peak, respectively). The resultant fit line is shown by a black line. (c) The plot presents the shift ($\Delta = E_{1.5} - E_T$) of the temperature-dependent peak positions of A- (red star) and B-peaks (black circles) measured by the Gaussian fitting shown in Fig.(b). The dash-line is a linear fit to the change of the B-peak energy. The slope of the fit is - 0.12 meV/K. The PL intensity becomes too low for temperatures above 200 K (160 K) to measure the B-(A-) peak energy. (d) Integrated photoluminescence intensity from Fr at varying temperature.

### ***Objective 3: Probe exciton dissociation in 1L-SnS2, 1L-PbS and 1L-Fr by photocurrent spectroscopy (PCS).***

We attempted hundreds of time to fabricate Fr devices using isolated 1L-SnS2, 1L-PbS and 1L-Fr. Unfortunately, we were not successful in making those devices. Instead, we were successful in making devices based on transition metal dichalcogenides. Using the fabricated devices, we have studied exciton dissociation and valence band splitting.

4) ***Valence band splitting Intralayer excitons in 2D (Objective 2):*** We didn't observe any splitting in the exciton peaks from Franckeite due to spin orbit coupling. We attributed this to two major issues: (i) the crystal defects, and (ii) impurity atoms in Franckeite. To obtain the research goals of understanding the excitons dissociation in atomically thin semiconductors, we studied high-quality transition metal dichalcogenide samples.

   We have fabricated the sample using standard microexfoliation techniques and measured photocurrent spectroscopy at different temperatures. We studied of valence band splitting (VBM) splitting ($\Delta$) in atomically thin $MoS_2$ and $WS_2$ by employing photocurrent spectroscopy. We found

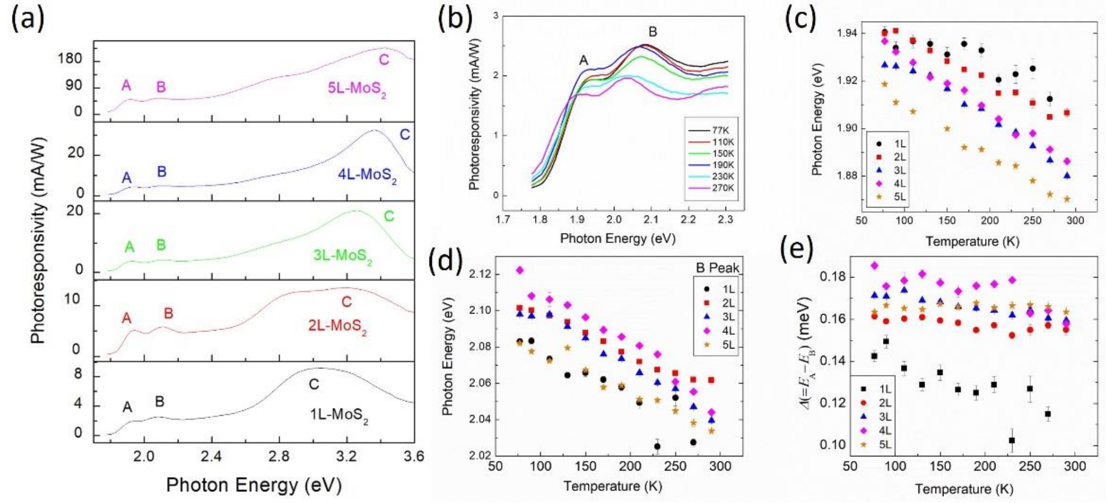

Figure 7: VBM splitting of MoS2. (a) Photocurrent spectra of different layered $MoS_2$ (1L to 5L). The left axis is presenting the photoresponsivity. (b) Photoresponsivity of a 1L-$MoS_2$ sample at different temperatures. (c) The plot is showing the A-peak position at different temperatures for different layered thicknesses. (d) The plot is showing the B-peak position at different temperatures for different layered thicknesses. (e) The difference between the energy of the A and B peaks or VBM splitting Δ at different temperatures.

that VBM splitting in monolayer $MoS_2$ and $WS_2$ depends strongly on temperature, which contradicts the theory that spin–orbit coupling solely determines the VBM splitting in a monolayer TMD. We also found that the rate of change of VBM splitting with respect to temperature ($m = \frac{\partial \Delta}{\partial T}$) is the highest for monolayer (−0.14 meV/K for $MoS_2$) and the rate decreases as the layer number increases (m ≈ 0 meV/K for 5 layers $MOS_2$). Our density functional theory (DFT) and the GW with Bethe–Salpeter Equation (GW-BSE) simulations agree with the experimental observations and demonstrate that the temperature dependence of VBM splitting in monolayer and multilayer TMDs originates from the changes in the interlayer coupling strength between the neighboring layers and substrates. We also found that VBM splitting depends on the layer numbers and the type of transition metals. We present the VBM splitting results in Figure 7 for $MoS_2$ sample. Similar results were observed for $WS_2$ samples.

The results have been published in a ACS journal the Journal of Physical Chemistry C. Garrett Benson†, Viviane Zurdo Costa, Neal Border, Kentaro Yumigeta, Mark Blei, Sefaattin Tongay, K. Watanabe, T. Taniguchi, Andrew Ichimura, Santosh KC, Taha Salavati-fard, Bin Wang, Akm Newaz- Giant Effects of Interlayer Interaction on Valence-Band Splitting in Transition Metal Dichalcogenides, J. Phys. Chem. C, 126, 20, 8667–8675 (2022),

https://doi.org/10.1021/acs.jpcc.1c10631

***Objective 4: Probe exciton behavior in Fr quantum dots (QDs) and compare their optical properties to colloidal QDs comprised of $SnS_2$ and PbS***

5) ***Fabrication of 2D-quantum using Helium beam:*** To achieve specific objective 4 or goal 4, we worked on fabricating 2D-QDs by using helium beam using a helium microscope. To optimize the fabrication method to prepare QDs based on 2D materials, we started with a well-known material, such as $MoS_2$. We completed the dose test to determine the impact of the dose on its optical properties. The photoluminescence data for different dose is shown in Fig.8. After completing the effect of the dose applying uniformly, we have studied a new batch monolayer $MoS_2$ samples residing on ultra-flat hBN substrate, where the dose where applied as an array of points. We have acquired extensive data at wide range of temperature (1.5 K – 300 K) and currently analyzing the data to understand the impact of doses.

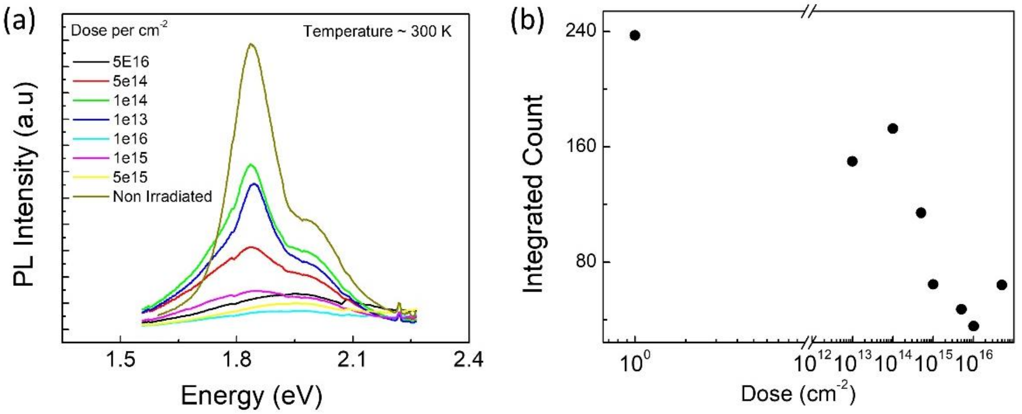

Figure 8: (a) The impact of Helium does on the photoluminescence from a monolayer $MoS_2$ residing on $SiO_2$/Si substrate. The dose rate per cm$^{-2}$ is shown on the left. (b) The integrated PL count for different dose.

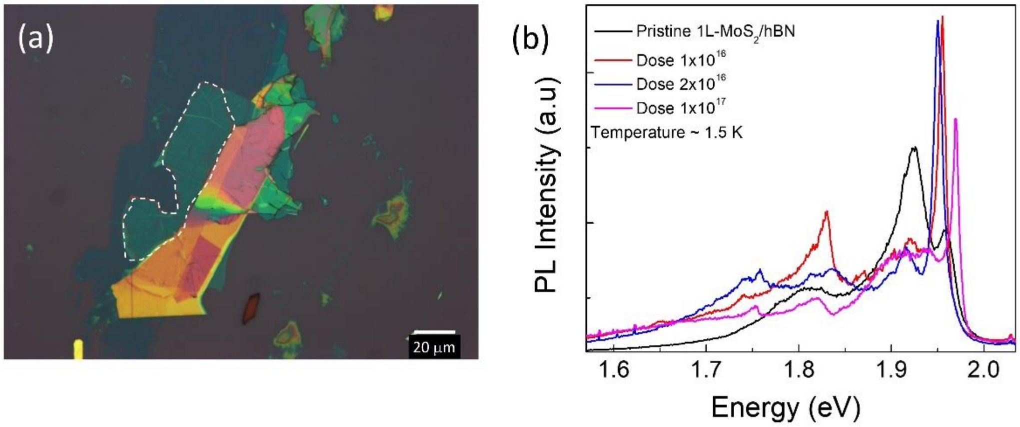

Figure 9: (a) The optical image of a monolayer $MoS_2$ sample. The dashed white line is showing the boundary of the sample residing on hBN. (b) The photoluminescence from the sample measured at 1.5 K using the attoDRY2100 confocal microscope.

***Work due to a change in objectives:*** One of the overarching goals of the project was to demonstrate that 2D materials are attractive for next-generation nanoscale optoelectronics devices. Despite numerous attempts, we were not successful in fabricating optoelectronic devices based on high-quality monolayer Franckeite. We have changed the objective and developed wafer-scale ultraviolet (UV) and broadband photonics devices based on monolayer $MoS_2$. We believe that this work will be very useful in covert communication for Air Force and DoD.

6) **Semimetal-Monolayer Transition Metal Dichalcogenides Photodetectors for Wafer-Scale Broadband Photonics:**

Broadband photodetectors (BPD) with spectral coverage ranging from ultraviolet (UV) to near-infrared (NIR) range are at the heart of many applications ranging from high-capacity optical communication, night vision, biological analysis, environmental sensors, wide spectral switches, fire monitoring, and space exploration to radiation detection. For example, near-infrared light detection capabilities enable image sensors fused with night vision systems. Another important application is in the UV covert communication as Ultraviolet (UV) wireless is very suitable for local area Non-line of sight (NLOS) dedicated covert communication.

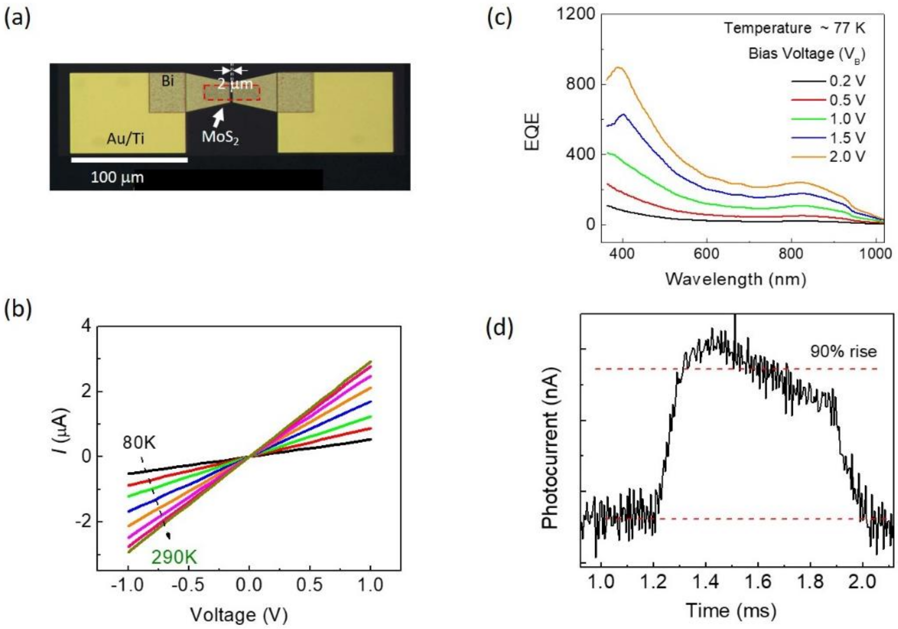

**Figure 10:** (a) The image of a single device. First, a full-area coverage monolayer $MoS_2$ was grown by solid source chemical vapor deposition (CVD). The sample strips were prepared by optical lithography followed by oxygen plasma etching (red-dashed line rectangle). (b) (a) Current-voltage (I-V) curve of a device at different temperatures from 80 K to 290 K at every 30 K steps. The I-V curves were measured in the dark. The IV curve shows excellent linear behavior. (c) External quantum efficiency (EQE), which is defined as the number of electrons for one photon, of a sample measured at different wavelengths. We have observed very high EQE. The highest efficiency was observed for UV photons (~ 400 nm). (a) The time response of the device for a single laser pulse was measured at 77 K. We used a 405 nm laser modulated by a mechanical chopper ($f$ ~ 700 Hz). We observed that a 90% rise time is 0.1 ms.

Atomically thin two-dimensional (2D) transition metal dichalcogenides (TMDs), such as $MoS_2$, are promising candidates for nanoscale photonics because of strong-light matter interactions. However, Fermi level pinning due to metal-induced gap (MIGS) states at the metals-monolayer (1L) $MoS_2$ interface limits the application of optoelectronic devices based on conventional metals because of the high contact resistance of the Schottky contacts. On the other hand, a semimetal-TMD-semimetal device can overcome this limitation, where the MIGS are sufficiently suppressed and can result in ohmic contacts. We demonstrate the optoelectronic performance of a bismuth-1L $MoS_2$-bismuth device with ohmic electrical contacts and extraordinary optoelectronic properties. To address the wafer-scale production, we grew full coverage 1L $MoS_2$ by using chemical vapor deposition method. We measured high photoresponsivity of 300 A/W at wavelength 400 nm measured at 77 K, which translates into an external quantum efficiency (EQE) ~ 1000 or $10^5$%. We found that the 90% rise time of our devices at 77 K is 0.1 ms, which suggests that the current devices can operate at the speed of ~ 10 kHz. We demonstrate high-performance broadband photodetector with spectral coverage ranging from 380 nm to 1000 nm. The combination of large-array device fabrication, high sensitivity, and high-speed response offers great potential for applications in photonics that includes integrated optoelectronic circuits.

The results have been accepted for publication in Advanced Photonics Research journals. (Semimetal-Monolayer Transition Metal Dichalcogenides Photodetectors for Wafer-Scale Broadband Photonics- Hon-Loen Sinn, Aravindh Kumar, Eric Pop, and Akm Newaz, Advanced Photonics Research (2023)-(Accepted) (arXiv:2301.12635). Also, a provisional patent application has been submitted (Semimetal-monolayer transition metal dichalcogenides photodetector for wafer-scale photonics (4878.004PRV)).

## Conclusions:

We investigated fundamental physical properties of a natural van der Waals heterostructure and advanced knowledge of van der Waals heterostructure.

Accomplishments:

1) We developed a sample preparation technique to obtain large Franckeite samples and studied fundamental physical properties.
2) By measuring Raman spectroscopy, we determined the crystal structure of Franckeite. More specifically, we found that PbS-like pseudotetragonal structure is mostly composed of $Pb_3SbS_4$.
3) We demonstrated the photoluminescence from Franckeite for the first time. Our study provides a fundamental understanding of the optical behavior in a complex naturally occurring van der Waals heterostructure.
4) We investigate spin-orbit-induced valence band splitting (VBM) in atomically thin semiconductors ($MoS_2$ and $WS_2$). We observed that the VBM splitting in monolayer transition metal dichalcogenides (TMDs) depends on the temperature, which contradicts the theory that VBM splitting in 1L-TMDs originates solely from the SOC. We explain the observations using the density functional theory.
5) We developed efficient UV and broadband wafer-scale photonics devices based on atomically thin semiconductors, which are electrically connected by a semimetal. We found that the presence of semimetal (Bi) reduces the metal-induced gap states. This device may find applications in many applications ranging from high-capacity optical communication, covert communications, night vision, biological analysis, environmental sensors, wide spectral switches, fire monitoring, and space exploration to radiation detection.
6) A total of six peer-reviewed manuscripts and 4 M.Sc. theses have been published.

7) One provisional application for patent has been submitted.
*8)* We gave a total of 14 (both Oral and poster) research presentations in domestic and international conference presentations.

Challenges:

1) Even though we were able to prepare large many layer flakes, we couldn't find any monolayer after exfoliation. We found that Franckeite is very brittle compared to other 2D materials such as $MoS_2$ and $WS_2$.
2) Since we could not isolate a monolayer Franckeite sample, we couldn't fabricate optoelectrical devices based on Franckeite.
3) One of the major limitations of naturally occurring van der Waals is the purity of the natural van der Waals mineral as compared to the synthetic or lab-grown counterpart. For example, our Energy Dispersive Spectroscopy (EDX) measurements showed that Franckeite has significant Fe, Al, and Ag impurities, which affects the electrical, optical, and optoelectrical properties. For example, we observed that the PL signals from Franckeite are an order of magnitude lower than a monolayer $MoS_2$. We attributed this to the presence of crystal structural defects and impurities.

Future:

1) Surprisingly, plenty of naturally occurring van der Waals minerals can be found with a wide range of chemical compositions and crystal structures whose properties are mostly unexplored.[1] Studying electrical, optical, and optoelectrical properties of other natural van der Waals Heterostructure will advance our understanding of complex materials.
2) We plan to study naturally occurring magnetic van der Waals heterostructure (e.g. Cylindrite).[2] This type of 2D material can be an alternative to other 2D magnetic materials and an ideal platform for studying the quantum anomalous Hall effect, axion insulator states, and the topological magnetoelectric effect.
3) Currently, only naturally grown Franckeite is available and is very brittle. One future research direction can be developing a procedure to grow large-scale or wafer-scale natural van der Waals complex materials by employing different deposition growth techniques (e.g., solid-state chemical vapor deposition and molecular beam epitaxy).
4) Franckeite is a naturally grown van der Waals heterostructure, which maintains the crystals orders between neighboring layers. It is an attractive material to study coupled quantum dots prepared in the vertical direction. Coupled vertical quantum dots can be prepared by using a Helium focused ion beam direct milling. We plan to fabricate and investigate coupled quantum dot systems based on naturally occurring van der Waals Heterostructure. This type of coupled quantum dots may find applications in photonic quantum computation.[3]

References:

1 Frisenda, R., Niu, Y., Gant, P., Muñoz, M. & Castellanos-Gomez, A. Naturally occurring van der Waals materials. *npj 2D Materials and Applications* **4**, 38 (2020). https://doi.org:10.1038/s41699-020-00172-2

2 Niu, Y. *et al.* Mechanical and liquid phase exfoliation of cylindrite: a natural van der Waals superlattice with intrinsic magnetic interactions. *2D Materials* **6**, 035023 (2019). https://doi.org:10.1088/2053-1583/ab1a4c

3 Ren, B.-C. & Deng, F.-G. Hyper-parallel photonic quantum computation with coupled quantum dots. *Scientific Reports* **4**, 4623 (2014). https://doi.org:10.1038/srep04623