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RPPR Final Report
as of 28-Oct-2022

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Final Report for Period Beginning 17-May-2019 and Ending 16-Aug-2022
Title: Coupling Magnetic and Ferroelectric Phenomena in Designed 2D Thio- and Selenophosphate Crystals
Begin Performance Period: 17-May-2019
End Performance Period: 16-Aug-2022
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STEM Degrees: 6
STEM Participants:

Major Goals: The focus of this project was to develop and explore metal chalcophosphates (thiophosphates and selenophosphates) as a new class of materials that exhibit both magnetic and ferroelectric order with a coupling of the two order parameters at the atomic level, leading to a new class of magnetoferroelectric materials with potential topological properties. Another goal was to see if this unique combination of non-linear ferromagnetic and ferroelectric phenomena in the thiophosphates and selenophosphates coupled with topological phase behavior could provide unique and unexpected findings.

Accomplishments: 1) Developed A P2S5 Reactive Flux Method for Rapid Synthesis of Mono- and Bimetallic 2D Thiophosphates M2-xM?xP2S6

2) Developed A P2Se5 Reactive Flux Method for the Rapid Synthesis of Mono- and Bimetallic 2D Selenophosphates M2-xM'xP2Se6

3) Studied the Mixed Metal Thiophosphate Fe2-xCoxP2S6: Role of Structural Evolution and Anisotropy

4) Investigated the tuning of the structural and magnetic properties in mixed cation MnxCo2-xP2S6

5) Investigated the cation segregation in exfoliated Fe2-xCoxP2S6

6) Investigated the thiophosphate Heterostructure Assembly and Transport

For a detailed report, please see the uploaded pdf file.

Training Opportunities: The project provided many important training opportunities for graduate and undergraduate students. They learned the investigative skills needed for successful modern scientific research, which positively impacts our national competitiveness. Students are exposed to a broad battery of chemical synthesis techniques and sophisticated physical and chemical property characterization tools. They also benefit from high impact interdisciplinary collaborations within and beyond Northwestern. Finally, the broad dissemination of our scientific results and gained knowledge through peer-reviewed publications and conference events positively impact broad scientific awareness and stimulate new research activities in our lab and elsewhere. This research experience produced highly versatile, broadly educated and well-trained students,

This research project provides a significant training ground for graduate students' education and intellectual growth in solid state and materials chemistry, synthesis, design, discovery and property characterization. This type of fundamental science deriving from the sustained NSF support of solid state chemistry in academia, ultimately affects the strength of industry and therefore the US economy. Students' intellectual growth is also augmented by our regular interactions with the three groups of the co-PIs in this project at Northwestern, exposing them to multiple scientific perspectives. Interactions among students and the co-PI faculty across three academic departments were very strong, and this is a hallmark at Northwestern University that is interwoven into the cultural fabric of the institution.

Results Dissemination: Conferences and Presentations

1. "Probing Optical Phenomena of Si@MoS2 Core-Shell Architectures at Nanoscale by Valence EELS," 2022 Microscopy & Microanalysis Conference, Portland, (July 21-August 4, 2022)
2. "Heterogeneous Integration of 2D MoS2 on Silicon Nanoparticle in a Core-Shell Architecture for Photonic Applications," 2021 Materials Research Society Fall Conference, Boston, (November 29-December 2, 2021)
3. "Structural and chemical analysis of mixed cation antiferromagnetic layered metal chalcophosphates Fe2-xCoxP2S6" Microscopy and Microanalysis 2021.
4. "Si@MoS2 Core-Shell Architecture: Characterizations and Implications for Nanophotonic Applications," 2021 Microscopy & Microanalysis Conference, Virtual, (August 1-5, 2021)
5. "Structural and chemical analysis of mixed cation antiferromagnetic layered metal chalcophosphates Fe2-xCoxP2S6" Materials Research Society Fall Meeting 2021.
6. "Structural, Chemical, and Local Properties of Layered Metal Chalcophosphate Systems". Microscopy and Microanalysis 2020.

Publications

1. Matthew Cheng, Abishek K. Iyer, Xiuquan Zhou, Alexander Tyner, Yukun Liu, M. Arslan Shehzad, Pallab Goswami, Duck Young Chung, Mercouri G. Kanatzidis, and Vinayak P. Dravid. "Tuning the Structural and Magnetic Properties in Mixed Cation MnxCo2–xP2S6". Inorg. Chem. 2022, 61, 35, 13719–13727. https://doi.org/10.1021/acs.inorgchem.2c01116.

2. M Arslan Shehzad, Yea-Shine Lee, Matthew Cheng, Dmitry Lebedev, Alexander C Tyner, Paul Masih Das, Zhangyuan Gao, Pallab Goswami, Roberto dos Reis, Mark C Hersam, Xinqi Chen, Vinayak P Dravid. "Vapor-Liquid Assisted Chemical Vapor Deposition of Cu2X Materials", IOP Science, IOP Publishing Ltd, 2D Mater. 2022, 9 (4), 045013. https://doi.org/10.1088/2053-1583/ac8435

3. Alexander, Grant C. B ; Krantz, Patrick W ; Jung, Hee Joon ; Davis, Samuel Kenneth ; Xu, Yaobin ; Dravid, Vinayak P ; Chandrasekhar, Venkat ; Kanatzidis, Mercouri G.; "Controllable Nonclassical Conductance Switching in Nanoscale Phase?Separated (PbI2)1?x(BiI3)x Layered Crystals". Advanced materials (Weinheim), Vol.33 (51), p. e2103098-n/a. DOI:10.1002/adma.202103098 (October 02, 2022). https://doi.org/10.1002/adma.202103098

4. Yea-Shine Lee, Tatsuki Hinamoto, Sina Abedini Dereshgi, Shiqiang Hao, Matthew Cheng, Hiroshi Sugimoto, Minoru Fujii, Christopher Wolverton, Koray Aydin, Roberto dos Reis, Vinayak P Dravid. "Probing the Optical Responses and Local Dielectric Functions of an Unconventional Si@MoS2 Core-Shell Architecture". Microscopy and Microanalysis, Vol. 28, S1, August 2022, pp. 2016 – 2018. DOI:10.1017/S1431927622007838, https://doi.org/10.1017/S1431927622007838

5. Cheng, Matthew ; Lee, Yea-Shine ; Iyer, Abishek K. ; Chica, Daniel G. ; Qian, Eric K. ; Shehzad, Muhammad Arslan ; dos Reis, Roberto ; Kanatzidis, Mercouri G. ; Dravid, Vinayak P. "Mixed Metal Thiophosphate Fe2–xCoxP2S6: Role of Structural Evolution and Anisotropy". Inorganic Chemistry, 2021, Vol.60 (22), p.17268-17275 https://doi.org/10.1021/acs.inorgchem.1c02635

6. Matthew Cheng, Yea-Shine Lee, Roberto dos Reis, Abishek Iyer, Daniel Chica, Mercouri Kanatzidis and Vinayak Dravid (2021). "Structural and Chemical Analysis of Mixed Cation Antiferromagnetic Layered Metal Chalcophosphate FeCoP2S6". Microscopy and Microanalysis, 27(S1), 140-143. https://doi.org/10.1017/S1431927621001112

7. Chica, Daniel G.; Iyer, Abishek K.; Cheng, Matthew; Ryan, Kevin M.; Krantz, Patrick; Laing, Craig; Dos Reis, Roberto; Chandrasekhar, Venkat; Dravid, Vinayak P.; Kanatzidis, Mercouri G. (2021). "P2S5 Reactive Flux Method for the Rapid Synthesis of Mono- and Bimetallic 2D Thiophosphates M2xM?xP2S6". Chem. (2021), 60, 6, 3502-3513. https://doi.org/10.1021/acs.inorgchem.0c03577

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Article Title: P2S5 Reactive Flux Method for the Rapid Synthesis of Mono- and Bimetallic 2D Thiophosphates M2?xM? xP2S6
Authors: Daniel G. Chica, Abishek K. Iyer, Matthew Cheng, Kevin M. Ryan, Patrick Krantz, Craig Laing, Roberto
Keywords: two-dimensional materials, thiophosphate materials
Abstract: We report a reactive flux technique using the common reagent P2S5 and metal precursors developed to circumvent the synthetic bottleneck for producing high-quality single- and mixed-metal two-dimensional (2D) thiophosphate materials. For the monometallic compound, M2P2S6 (M = Ni, Fe, and Mn), phase-pure materials were quickly synthesized and annealed at 650 °C for 1 h. Crystals of dimensions of several millimeters were grown for some of the metal thiophosphates using optimized heating profiles. The homogeneity of the bimetallic thiophosphates MM?P2S6 (M, M? = Ni, Fe, and Mn) was elucidated using energy-dispersive X-ray spectroscopy and Rietveld refinement. The quality of the selected materials was characterized by transmission electron microscopy and atomic force microscopy measurements. We report two novel bimetallic thiophosphates, MnCoP2S6 and FeCoP2S6. The Ni2P2S6 and MnNiP2S6 flux reactions were monitored in situ using variable-temperature powder X-ray diffraction to understand the
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Authors: Grant C. B. Alexander, Patrick W. Krantz, Hee Joon Jung, Sam Davis, Yaobin Xu, Vinayak P. Dravid, V
Keywords: Conductance Switching, Nanoscale, Phase Separation, Non-linear Charge Transport
Abstract: Transition metal dichalcogenides (TMDs) are known for their layered structure and tunable functional properties. However, a unified understanding on other transition metal chalcogenides (i.e. M2X) is still lacking. Here, the relatively new class of copper-based chalcogenides Cu2X (X = Te, Se, S) is thoroughly reported. Cu2X are synthesized by an unusual vapor-liquid assisted growth on a Al2O3/Cu/W stack. Liquid copper plays a significant role in synthesizing these layered systems, and sapphire assists with lateral growth and exfoliation. Similar to traditional TMDs, thickness dependent phonon signatures are observed, and high-resolution atomic images reveal the single phase Cu2Te that prefers to grow in lattice-matched layers. Charge transport measurements indicate a metallic nature at room temperature with a transition to a semiconducting nature at low temperatures accompanied by a phase transition, in agreement with band structure calculations. These findings establish a fundamental
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Authors: Matthew Cheng, Yea-Shine Lee, Abishek K. Iyer, Daniel G. Chica, Eric K. Qian, M. Arslan Shehzad, Ro
Keywords: 2D materials, metal thiophosphates, transmission electron microscopy
Abstract: Transition metal dichalcogenides (TMDs) are known for their layered structure and tunable functional properties. However, a unified understanding on other transition metal chalcogenides (i.e. M2X) is still lacking. Here, the relatively new class of copper-based chalcogenides Cu2X (X = Te, Se, S) is thoroughly reported. Cu2X are synthesized by an unusual vapor-liquid assisted growth on a Al2O3/Cu/W stack. Liquid copper plays a significant role in synthesizing these layered systems, and sapphire assists with lateral growth and exfoliation. Similar to traditional TMDs, thickness dependent phonon signatures are observed, and high-resolution atomic images reveal the single phase Cu2Te that prefers to grow in lattice-matched layers. Charge transport measurements indicate a metallic nature at room temperature with a transition to a semiconducting nature at low temperatures accompanied by a phase transition, in agreement with band structure calculations. These findings establish a fundamental
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Authors: Matthew Cheng, Yea-Shine Lee, Roberto dos Reis, Abishek Iyer, Daniel Chica, Mercouri Kanatzidis, Vir
Keywords: 2D thiophosphate materials, magnetism
Abstract: In this study, we report on the structural characterization of mixed metal cation FeCoP2S6 prepared through a novel flux method. The data reveal, in depth, the nature of the cation distribution in bimetallic FeCoP2S6 and the resulting impact on its electronic structure and magnetic properties in comparison with that of monometallic Fe2P2S6 and Co2P2S6. We believe that these metal chalcophosphates will prove to be an interesting addition to the 2D library of materials due to their intrinsic ferroic properties that warrant further study and exploration.
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Article Title: Tuning the Structural and Magnetic Properties in Mixed Cation Mn
Authors: Matthew Cheng, Abishek K. Iyer, Xiuquan Zhou, Alexander Tyner, Yukun Liu, M. Arslan Shehzad, Palla
Keywords: OXIDATIONMODESMN
Abstract: Transition metal dichalcogenides (TMDs) are known for their layered structure and tunable functional properties. However, a unified understanding on other transition metal chalcogenides (i.e. M2X) is still lacking. Here, the relatively new class of copper-based chalcogenides Cu2X (X = Te, Se, S) is thoroughly reported. Cu2X are synthesized by an unusual vapor-liquid assisted growth on a Al2O3/Cu/W stack. Liquid copper plays a significant role in synthesizing these layered systems, and sapphire assists with lateral growth and exfoliation. Similar to traditional TMDs, thickness dependent phonon signatures are observed, and high-resolution atomic images reveal the single phase Cu2Te that prefers to grow in lattice-matched layers. Charge transport measurements indicate a metallic nature at room temperature with a transition to a semiconducting nature at low temperatures accompanied by a phase transition, in agreement with band structure calculations. These findings establish a fundamental
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Article Title: Vapor–liquid assisted chemical vapor deposition of Cu
Authors: M Arslan Shehzad, Yea-Shine Lee, Matthew Cheng, Dmitry Lebedev, Alexander C Tyner, Paul Masih D
Keywords: vapor-liquid CVDCu2XCu2Temetal-semiconductor transition
Abstract: Transition metal dichalcogenides (TMDs) are known for their layered structure and tunable functional properties. However, a unified understanding on other transition metal chalcogenides (i.e. M2X) is still lacking. Here, the relatively new class of copper-based chalcogenides Cu2X (X = Te, Se, S) is thoroughly reported. Cu2X are synthesized by an unusual vapor-liquid assisted growth on a Al2O3/Cu/W stack. Liquid copper plays a significant role in synthesizing these layered systems, and sapphire assists with lateral growth and exfoliation. Similar to traditional TMDs, thickness dependent phonon signatures are observed, and high-resolution atomic images reveal the single phase Cu2Te that prefers to grow in lattice-matched layers. Charge transport measurements indicate a metallic nature at room temperature with a transition to a semiconducting nature at low temperatures accompanied by a phase transition, in agreement with band structure calculations. These findings establish a fundamental
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Article Title: Structural defects in transition metal dichalcogenide core-shell architectures
Authors: Jennifer G. DiStefano, Akshay A. Murthy, Hee Joon Jung, Roberto dos Reis, Vinayak P. Dravid
Keywords: INORGANIC NANOTUBESMOS2TOPOLOGYHYBRIDSSITESJANUSATOM
Abstract: Curvature presents a powerful approach to design atomic structure and tailor material properties in atomically thin transition metal dichalcogenides (TMDs). The emerging TMD core-shell architecture, in which a multilayer TMD shell encapsulates a curved nanoparticle core, presents the opportunity to controllably induce defects into a TMD crystal by strategically constructing the shape of the underlying core. However, harnessing this potential platform first requires robust characterization of the unique structural features present in the core-shell architecture. To this end, transmission electron microscopy (TEM) and scanning TEM (STEM) are particularly powerful tools for direct structural characterization of 2D materials with a high spatial resolution and precision. Here, we reveal and describe defects inherently present in the TMD core-shell architecture. We develop a comprehensive framework to classify the observed defects and discuss potential origins and implications of structural
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Article Title: Probing the Optical Response and Local Dielectric Function of an Unconventional Si@MoS
Authors: Yea-Shine Lee, Sina Abedini Dereshgi, Shiqiang Hao, Matthew Cheng, Muhammad Arslan Shehzad, Cl
Keywords: MONOLAYER MOS2PHOTOLUMINESCENCEEMISSION
Abstract: Heterostructures of optical cavities and quantum emitters have been highlighted for enhanced light-matter interactions. A silicon nanosphere, core, and MoS2, shell, structure is one such heterostructure referred to as the core@shell architecture. However, the complexity of the synthesis and inherent difficulties to locally probe this architecture have resulted in a lack of information about its localized features limiting its advances. Here, we utilize valence electron energy loss spectros-copy (VEELS) to extract spatially resolved dielectric functions of Si@MoS2 with nanoscale spatial resolution corroborated with simulations. A hybrid electronic critical point is identified similar to 3.8 eV for Si@MoS2. The dielectric functions at the Si/MoS2 interface is further probed with a cross-sectioned core-shell to assess the contribution of each component. Various optical parameters can be defined via the dielectric function. Hence, the methodology and evolution of the dielectric function h
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Title: Synthesis and Crystal Growth of Layered Chalcophosphate and Framework Chalcoborate Compounds Using Reactive Flux and Chemical Vapor Transport Methods
Authors: Daniel Chica
Acknowledged Federal Support: **Y**

Partners

,

I certify that the information in the report is complete and accurate:
Signature: Mercouri Kanatzidis
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Introduction

Two-dimensional (2D) materials like graphene and transition metal dichalcogenides (TMD) have seen a surge in interest over the past decade from a fundamental science perspective. However, these materials have low functional tunability thereby limiting their development. Metal chalcophosphates (MCP) are a family of 2D materials that have been shown to have a high degree of tunability via chemical manipulation. **Figure 1** shows the crystal structure observed: $M_2P_2Q_6$, $MM'P_2Q_6$ (M and M' = divalent or trivalent metals; Q = S, Se), AMP_2Q_6 (A = monovalent metals; M = divalent or trivalent metals; Q = S, Se). MCP's have found wide ranging applications from ferroelectricity ($CuInP_2S_6$) to anisotropic magnetic insulators ($Fe_2P_2S_6$) and catalysis ($Ni_2P_2S_6$).[1]

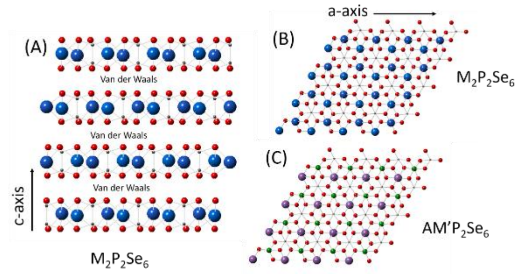

Figure 1. Crystal structure of (a) $M_2P_2Se_6$, viewed along c-axis, (b) along *a* axis and (c) $AM'P_2Se_6$ along the *a* axis.

The key challenge until now has been the synthesis of these materials which can take up to 3 months to obtain phase pure materials. This report summarizes our efforts to reduce reaction times by using flux (P_2S_5 and P_2Se_5) and the characterization of new bimetallic chalcophosphates using transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy (EDS), Raman spectroscopy and Mossbauer spectroscopy. Magnetic studies were performed on the $Mn_{2-x}Co_xP_2S_6$ family of compounds and heterostructure of some MCPs were made with MoS_2.

A P_2S_5 Reactive Flux Method for Rapid Synthesis of Mono- and Bimetallic 2D Thiophosphates $M_{2-x}M'_xP_2S_6$

Here, we introduced the P_2S_5 flux method for synthesizing and crystal-growth of mono- and bimetallic thiophosphates in greatly reduced synthesis times. The excess P_2S_5 serves as a reactive flux that oxidizes the metal of interest and increases solubility to reduce reaction times and increase crystallite size. As several systems were explored, the metal to P_2S_5 ratio was kept constant at 2:3. The remaining P_2S_5 flux was easily removed with a 1:1 mixture of EtOH and water, allowing for the facile isolation of the product of interest. Multiple different heating profiles were investigated with these systems; relevant profiles for this summary are referred to here as **Heating 1**, **2**, **3**, and are shown in **Table 1**.

Table 1. Tabulated heating profiles for the synthesis of mono- and bimetallic thiophosphates compounds.

Heating profile abbreviation	Heating profile steps
Heating 1	$RT \xrightarrow{10\,h} 650°C$ $\xrightarrow{36\,h} 650°C \xrightarrow{12\,h} 250°C \xrightarrow{step} RT$
Heating 2	$RT \xrightarrow{10\,h} 650°C$ $\xrightarrow{72\,h} 650°C \xrightarrow{24\,h} 250°C \xrightarrow{step} RT$
Heating 3	$650°C \xrightarrow{96\,h} 650°C \xrightarrow{quench} RT$

The reaction pathway for the formation of layered thiophosphate phases in the P_2S_5 flux was elucidated through variable temperature (VT) powder X-ray diffraction (PXRD) *in situ* measurements. Upon cooling, P_2S_5 recrystallized at 250°C. These results demonstrate the one-step formation of the compound with no competing undesirable nickel sulfide/phosphide phases. This highlights the effectiveness of the P_2S_5 flux in targeting the layered phases at a relatively low temperature. The direct formation of the layered $M_2P_2S_6$ phases from the reaction of the metal with the P_2S_5 flux is, therefore, a redox reaction in which P^{5+} oxidizes the metal to the M^{2+} state, forming the P^{4+} species of $[P_2S_6]^{4-}$ *in situ*, which then coordinates to the metal cation. The compositions of the $MM'P_2S_6$ products were probed using EDS analysis.

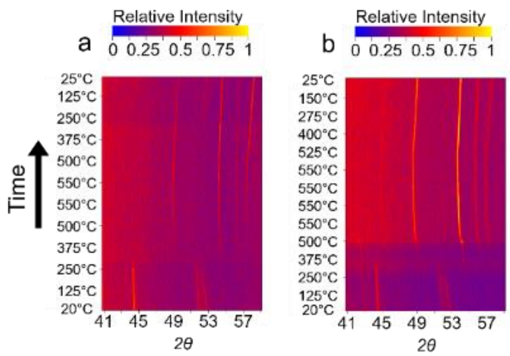

Figure 2. Variable temperature PXRD of (a) Ni/P_2S_5 and (b) $Mn/Ni/P_2S_5$ reactions.

Two reactions were used to elucidate the crystal growth of $Ni_2P_2S_6$, **Heating 3**, annealing at 650°C, and slow cooling from 650°C. The largest crystals of $Ni_2P_2S_6$ (~7 mm^2 in areal dimensions) and $CuInP_2S_6$ (4 × 3 mm^2 in dimensions) were formed from day 4 annealing process as seen in **Figure 3**.

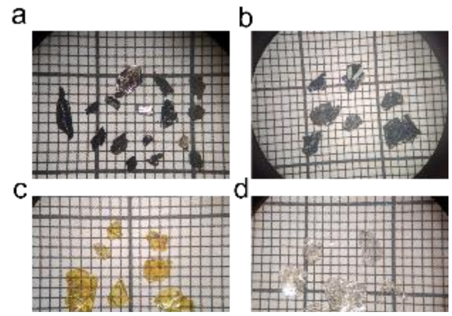

Figure 3. Optical images of (a) $Ni_2P_2S_6$, (b) $Co_2P_2S_6$, (c) $CuInP_2S_6$, (d) and $Zn_2P_2S_6$ single crystals. Each square is 1×1 mm^2.

The reactive flux method employing molten P_2S_5 is effective for synthesizing various layered metal thiophosphates, including two novel bimetallics, $MnCoP_2S_6$ and $FeCoP_2S_6$. Additionally, this method synthesizes materials of interest more rapidlu than other methods. The size of the crystals ranged from a few microns to an areal dimension of several mm^2, which can be mechanically separated. This variety of sizes will prove useful for applications that require a specific size distribution, e.g., catalysis and intercalation studies.

P_2Se_5 Reactive Flux Method for the Rapid Synthesis of Mono- and Bimetallic 2D Selenophosphates $M_{2-x}M'_xP_2Se_6$

Compared to the sulfides, the selenides have been underexplored due to the long reaction times up to 3 months. Success with using a P_2S_5 flux to synthesize $M_{2-x}M'_xP_2S_6$ materials,[2] naturally led to an analogous investigation into $M_{2-x}M'_xP_2Se_6$ synthesis by P_2Se_5 flux. Multiple metal to P_2Se_5 ratio and heating profile combinations were investigated, tabulated in **Table 2**. Using a ratio of 2:15 with **Heating 4** produced large (>1 mm^2) crystalline flakes. A ratio of 2:3 with **Heating 5** was sufficient to obtain phase pure powders. Further experiments with a pre-heated furnace revealed that powdered $Mn_2P_2Se_6$ could be synthesized as quickly as 30 minutes at 650 °C in a 2:3 flux ratio. Excess P_2Se_5 was successfully removed in a temperature gradient between 350 °C and 20 °C to volatize and dry distill remaining unreacted P_2Se_5 (**Heating 6**).

Table 2. Tabulated heating profiles for the synthesis of mono- and bimetallic thiophosphates compounds.

Heating profile abbreviation	Heating profile steps
Heating 4	$RT \xrightarrow{12\ h} 800°C \xrightarrow{24\ h} 800°C \xrightarrow{24\ h} 200°C \xrightarrow{step} RT$
Heating 5	$RT \xrightarrow{12\ h} 650°C \xrightarrow{24\ h} 650°C \xrightarrow{24\ h} 200°C \xrightarrow{step} RT$
Heating 6	$RT \xrightarrow{6\ h} 350°C \xrightarrow{24\ h} 350°C \xrightarrow{step} RT$

The reaction pathway for the formation of layered selenophosphate phases in the P_2Se_5 flux was elucidated in variable-temperature (VT) powder X-ray diffraction (PXRD) *in situ* measurements on Mn/P_2Se_5 and Cr/P_2Se_5 systems, as shown in **Figure 4**. Between 475 °C and 525 °C, Mn was consumed to form $Mn_2P_2Se_6$ with MnSe as a minor parasitic phase. The MnSe peak weakened in intensity by 625 °C and doesn't reappear on cooling, suggesting that both Mn and MnSe can be consumed in P_2Se_5 flux to form $Mn_2P_2Se_6$. The $Mn_2P_2Se_6$ then remained stable in the flux as the reaction cooled to room temperature. As for the Cr/P_2Se_5 system, Cr was consumed between 675 °C and 775 °C during the heating cycle to form $Cr_2P_2Se_6$, bypassing the formation of any parasitic or intermediary binary products. $Cr_2P_2Se_6$ also remained stable in the flux during cooling. We developed a generalizable method for synthesis of metal selenophosphate flakes (**Figure 5**) and powders. Single crystals up to 5 mm^2 could be obtained for $Fe_2P_2Se_6$ and $CuInP_2Se_6$.The P_2Se_5 flux also encourages concurrent dissolution and crystallization of multiple metals in the flux. The implications of this are extraordinary – not only could new combinations of $M^{1+}M^{3+}P_2Se_6$ be devised for further discovery of new ferro-/ferri-/antiferro-/antiferri- electric systems, such as $LiCrP_2Se_6$ or $LiBiP_2Se_6$, but use of a P_2Se_5 flux could be the gateway to exploring crystals of mixed $M^{2+}M'^{2+}P_2Se_6$ systems, like how P_2S_5 flux techniques allowed exploration into the mixed $FeCoP_2S_6$ and $MnCoP_2S_6$ systems

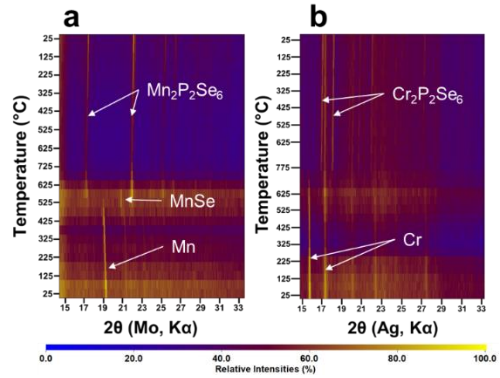

Figure 4. Variable temperature PXRD patterns for (a) Mn/P_2Se_5 and (b) Cr/P_2Se_5 reactions.

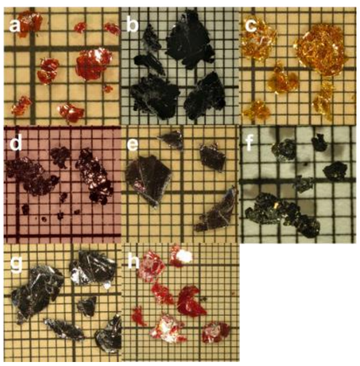

Figure 5. Optical images of (a) $Mn_2P_2Se_6$, (b) $Fe_2P_2Se_6$, (c) $Cd_2P_2Se_6$, (d) $CuCrP_2Se_6$, (e) $CuInP_2Se_6$, (f) $AgCrP_2Se_6$, (g) $AgInP_2Se_6$, and (h) $LiInP_2Se_6$ flakes on square mm grid

Mixed Metal Thiophosphate $Fe_{2-x}Co_xP_2S_6$: Role of Structural Evolution and Anisotropy

The P_2S_5 flux-mediated synthesis produced two novel bimetallics $MnCoP_2S_6$ and $FeCoP_2S_6$ with potential to exhibit novel magnetic properties. For example, $Fe_2P_2S_6$ and $Co_2P_2S_6$ are antiferromagnetic systems, as are all the thiophosphates, however the magnetic moments in $Fe_2P_2S_6$ will order in the out of plane direction while the magnetic moments in $Co_2P_2S_6$ will align in the in-plane direction.[1] Thus, it is of interest to alloy the two systems together as they have the potential to exhibit novel magnetic properties. Using the P_2S_5 method that was detailed in our previous study, a series of novel alloyed $Fe_{2-x}Co_xP_2S_6$ (x = 0, 0.25, 1, 1.75, 2.0) was synthesized and a

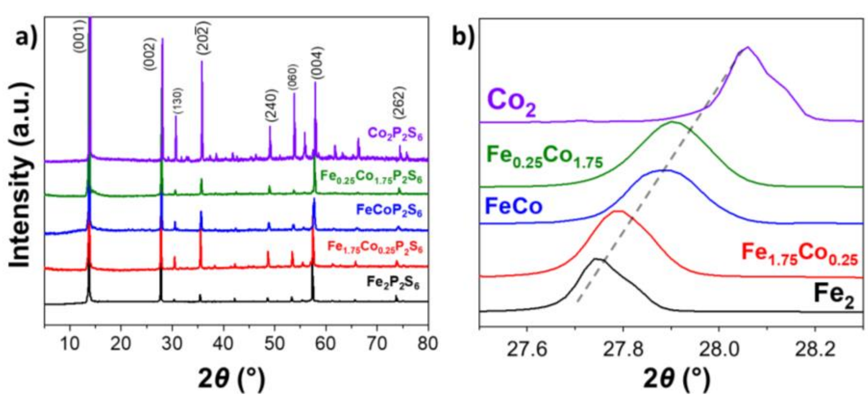

Figure 6. a) Powder X-ray diffraction (pXRD) of alloyed $Fe_{2-x}Co_xP_2S_6$. Due to the 2D nature of the thiophosphates the (*00l*) peaks are the most intense. **b)** Zoomed in region of spectra at (002)-peak.

thorough characterization study of the alloyed systems using powder pXRD, TEM, Raman spectroscopy, and XPS.[3]

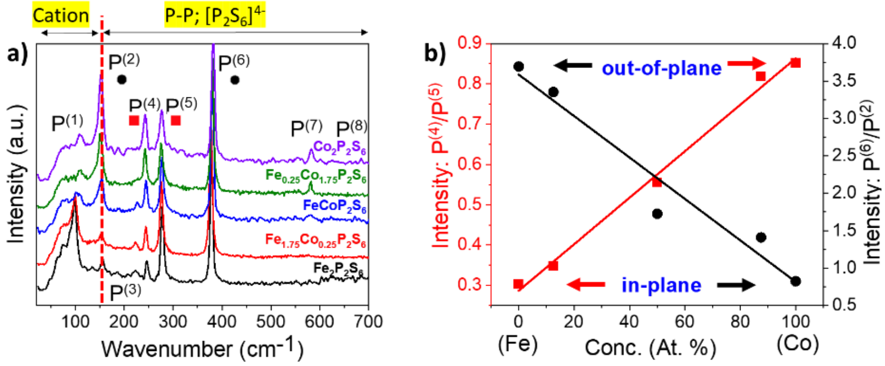

Figure 7.a) Raman spectra for $Fe_{2-x}Co_xP_2S_6$. **b)** Intensity ratio of $P^{(4)}/P^{(5)}$ and $P^{(6)}/P^{(2)}$ as a function of Co atomic%.

From the pXRD, it was observed that the diffraction patterns shift to higher 2θ with increasing Co concentration as show in **Figure 6(a, b)**. TEM measurements determined that twin planes along the out-of-plane direction is present but all samples are of highly crystalline nature with expected stoichiometry as determined by STEM-EDS. Most intriguing is the evolution of the Raman spectra as the Fe:Co ratio is varied as shown in **Figure 7(a)**. Eight Raman modes (A_g and B_g) corresponding to a C_{2h} symmetry are apparent but a distinct change in the relative intensities of the pairs of peaks $P^{(6)}/P^{(2)}$ and $P^{(4)}/P^{(5)}$ provide a rapid fingerprinting method to evaluate the composition of bimetallic thiophosphate systems where a nearly linear trend in the composition and the respective intensity ratios is observed in **Figure 7(b)**. The Raman modes at $P^{(2)}$ and $P^{(6)}$ correspond to $[P_2S_6]^{4-}$ vibrational modes while $P^{(4)}$ and $P^{(5)}$ correspond to P-P vibrational modes. This initial study is intended to provide motivation for additional studies.

Tuning the structural and magnetic properties in mixed cation $Mn_xCo_{2-x}P_2S_6$

Continuing from our study of the alloyed $Fe_{2-x}Co_xP_2S_6$ system we determined to explore the potential to alloy other transition metal thiophosphates with $Co_2P_2S_6$. In this study, we synthesized a series of alloyed $Mn_2P_2S_6$ with $Co_2P_2S_6$ and conducted a thorough top-down characterization of the evolution of the structure and magnetic properties as the composition of Mn and Co is varied.

Starting with pXRD the expected diffraction pattern for both $Mn_2P_2S_6$ and $Co_2P_2S_6$ is obtained. A distinct shift of the diffraction patterns to higher 2θ as Co concentration is increased in line with Vegard's law.[4]

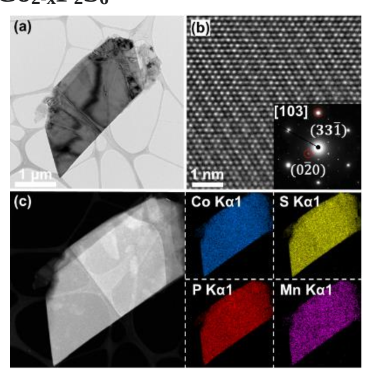

Figure 8. a) Representative bright field TEM image of $Mn_{0.5}Co_{1.5}P_2S_6$. **b)** HRTEM image of $Mn_{0.5}Co_{1.5}P_2S_6$ with inset diffraction pattern along [103]-axis (c*-axis). **c)** HAADF-STEM of same flake with accompanying EDS maps of Mn, Co, P, and S at given length scales.

The most intense peaks correspond with the (00*l*) planes due to the preferred orientation of the two-dimensional layers. TEM and STEM-EDS is used to evaluate the crystallinity and homogeneity of exfoliated flakes of alloyed $Mn_{2-x}Co_xP_2S_6$. A representative TEM image of $Mn_{0.5}Co_{1.5}P_2S_6$ shown in **Figure 8(a)** shows the typical layered structure of the exfoliated flakes. From the HRTEM image of $Mn_{0.5}Co_{1.5}P_2S_6$ and inset diffraction pattern in **Figure** 8**(b)** it can be determined that the $Mn_{2-x}Co_xP_2S_6$ samples are of highly crystalline character and that twin planes along the c*-axis are present. Furthermore, STEM-EDS maps indicate that Mn, Co, P, and S maps indicate a homogeneous distribution of all elements within the flake at given length scales in **Figure 8(c)**. A similar Raman peak intensity behavior is observed in $Mn_{2-x}Co_xP_2S_6$ as is seen in $Fe_{2-x}Co_xP_2S_6$ where the

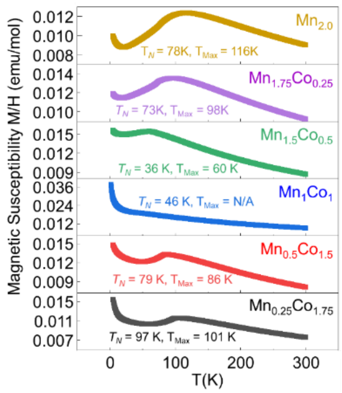

Figure 9. Magnetic susceptibility measurements for $Mn_{2-x}Co_xP_2S_6$.

change in the relative Raman intensities can provide a fingerprint of Mn and Co concentration.[4] The alloying composition of Mn:Co also has a direct effect on the magnetic properties of the alloyed $Mn_{2-x}Co_xP_2S_6$. Magnetic susceptibility curves (**Figure 9**) of all $Mn_{2-x}Co_xP_2S_6$ systems show an AFM behavior with the ordering temperature, $T_{Néel}$, determined by the maximum $d\chi/dT$ value, where χ is the magnetic susceptibility.[4] From this, it is observed that the ordering temperature is reduced with increasing Co concentration until a minimum $T_{Néel}$ measured from $Mn_{1.5}Co_{0.5}P_2S_6$ which increases with further Co alloying. A broad transition region is seen in nearly all alloyed systems, marked as T_{max}, which is due to local low-dimensional spin-ordering that is typically seen in layered chalcogen systems. The observations and conclusions in this work shed further light on the engineering of metal chalcophosphates for useful applications such as next generation nanodevices and catalytic materials.

Cation segregation in exfoliated $Fe_{2-x}Co_xP_2S_6$

Due to increasing interest in high entropy alloy (HEA) metal chalcophosphate systems (MCPs) it is of intellectual merit to determine the homogeneity of the metal cation species within the $[P_2S_6]^{4-}$ lattice for potential applications within nanodevices due to the different material properties, such as magnetism, that is affected by the stoichiometry of exfoliated flakes.[5] To that end, our current studies return to the $Fe_{2-x}Co_xP_2S_6$ system to determine if potential phase segregation may occur with simply two cation species present.

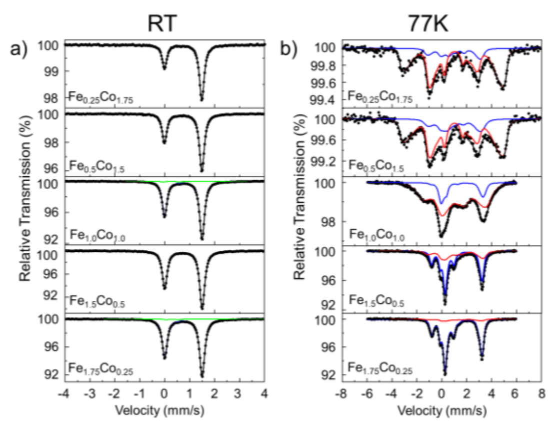

Figure 10. a) Room temperature Mössbauer spectra for alloyed $Fe_{2-x}Co_xP_2S_6$. **b)** Mössbauer spectra for alloyed $Fe_{2-x}Co_xP_2S_6$ when cooled to 77K.

As was previously reported, pXRD measurements show an expected shift to higher 2θ as Co concentration is increased while all expected diffraction planes are present. No peak splitting was apparent that will be a strong indicator of phase segregation. Further analysis with Mössbauer spectroscopy with a ^{57}Fe source RT (**Figure** 10 **(a)**) indicates that all Fe cations are consistently in a 2+ state and no broadening of the two resonant lines as the stoichiometry is changed indicates no distortions on the local or global level. Thus, negligible cation vacancies will present in all the alloyed $Fe_{2-x}Co_xP_2S_6$ and indicates both Fe and Co will be in a 2+ state to retain charge neutrality. When cooled to 77K (**Figure 10 (b)**) the resulting resonant lines are affected by the local magnetic ordering due to nearest neighbor cation occupations. From these spectra, two separate components represented by the blue and red curves indicates the presence of Fe-rich and Co-rich regions, where the Co-rich regions become more dominant with increasing Co-composition. To determine the extent of this phase segregation, flakes were exfoliated onto Si substrates for Raman analysis and on to TEM grids for STEM-EELS analysis. From **Figure 11(a)** the Raman spectra for 5 randomly selected flakes exfoliated from $FeCoP_2S_6$ shows Flakes 1 and 5 with a different relative Raman peak intensities as compared with Flakes 2, 3, and 4. By plotting the

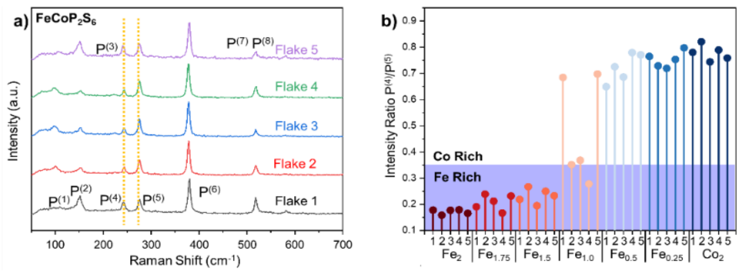

Figure 11. a) Raman spectra of 5 flakes exfoliated from $FeCoP_2S_6$ bulk sample. **b)** Intensity ratio $P^{(4)}$(~240cm^{-1}) / $P^{(5)}$(~275cm^{-1}) for 5 randomly selected flakes for all exfoliated

intensity ratio $P^{(4)}/P^{(5)}$ and using the finger printing method developed in our earlier publication the relative Fe and Co compositions can be observed in **Figure 11(b)** for 5 randomly selected flakes from all the alloyed $Fe_{2-x}Co_xP_2S_6$ which indicates that the largest composition variation is present in $FeCoP_2S_6$. The exfoliated flakes were also on the order of ~200 nm in thickness as determined by atomic force microscopy (AFM). The STEM-EELS analysis also shows evidence of segregation in the lateral directions within thin flakes on the order of ~10nm in thickness. This study emphasizes the importance of confirming the stoichiometry of alloyed MCP systems, depending on the desired applications, as small compositional variations at small length scales can also have a large effect on the desired properties of the exfoliated crystal. This work also hopes to motivate future work on developing methodologies to control the distribution of metal cations within the metal chalcophosphates.

Thiophosphate Heterostructure Assembly and Transport

There has been substantial interest in exploring the properties of van der Waals compounds by the construction of heterostructures consisting of two or more such 2D materials. Alongside efforts to synthesize and characterize MCPs, we have developed tools to manipulate and combine exfoliated bulk crystals via a recently reported strongly adhesive dry transfer method for these materials.[6] Due to the unusual adhesive strength of few layer chalcophosphate crystals, and the rich physical properties they exhibit, their use in heterostructure assembly may enable novel functionality.

Notably, we have demonstrated compatibility of magnetic and ferroelectric chalcophosphates $Mn_2P_2S_6$ and $CuInP_2S_6$ with the transition metal dichalcogenide MoS_2 as an encapsulated interlayer. This was chosen in order to facilitate potential transport studies utilizing the highly insulating chalcophosphates as proximate ferroic materials, which could potentially couple indirectly by interactions with the semiconducting MoS_2. This was performed using a purpose-built transfer stage to selectively "stack" mechanically exfoliated flakes of the three materials one by one, with interlayer alignment performed at each step to ensure a consistent crystallographic orientation is maintained throughout the structure. Subsequently, the samples were annealed in an inert Ar atmosphere to remove trapped gas, adsorbates or dislocations between layers. The resulting heterostructure is shown in **Figure 12**, alongside cross-sectional TEM analysis performed on the same sample, which indicates that direct atomic interfaces are obtained through this

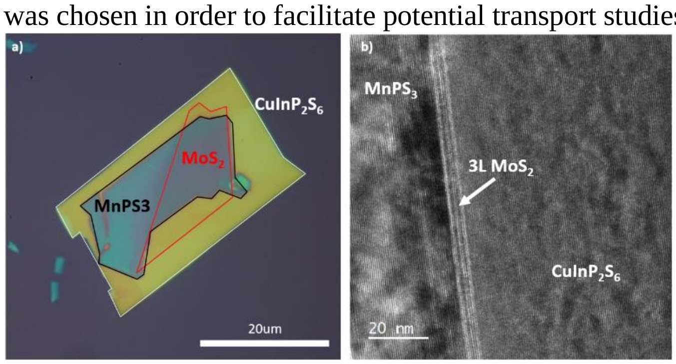

Figure 12. a) Optical image of a heterostructure of $Mn_2P_2S_3$ (top layer, black outline), MoS_2 (tiddle layer, red outline), and $CuInP_2S_6$ (bottom layer, white outline) **b)** Cross sectional TEM of the same device, showing atomic interfaces between MoS_2 and the chalcophosphates.

procedure. This is essential to demonstrating potential coupling of the ferroic order of these compounds through heterostructure assembly, as disorder at the interface will strongly suppress such interactions.

To study the behavior of these layered pairing individually, we have made transport measurements of heterostructures consisting of MoS_2 and $Mn_2P_2S_6$ alone. Two-terminal transfer curves of bare and $Mn_2P_2S_6$ encapsulated MoS_2 taken at room temperature show a strong modification of the doping towards p-type behavior, as is show in **Figure 13**. These results indicate a suppression of the intrinsic conductivity in such devices, potentially due to charges or polarization at the interface of the heterostructure. Further work is required to explore the origin of this effect and impact of chalcophosphate encapsulation on transition metal dichalcogenides.

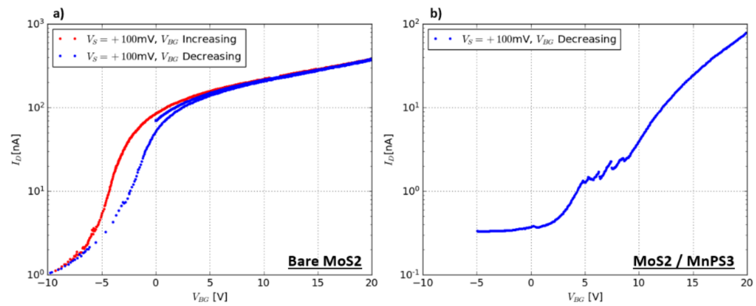

Figure 13. a) Characteristic transfer curve of few layer MoS_2, gated through a 300nm SiO_x substrate back gate. **b)** Transfer curve obtained for a region of MoS_2 encapsulated by $MnPS_3$.

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