Final Abstract

Final Report Approved on October 20, 2026

M.L. 2022 Project Abstract

For the Period Ending June 30, 2026

Project Title: Green Solar Cells from a Minnesota Natural Resource

Project Manager: Chris Leighton

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Funding Source:

Fiscal Year:

Legal Citation: M.L. 2022, Chp. 94, Sec. 2, Subd. 07a , as extended by laws 2025, First Special Session, Art. 2, Sec. 2, Subd. 17

Appropriation Amount: $673,000

Amount Spent: $672,978

Amount Remaining: $22

Sound bite of Project Outcomes and Results

This project at the University of Minnesota developed the material pyrite iron disulfide as a semiconductor for electronic and clean energy applications. In particular, the project demonstrated that Minnesota iron ore, a key and existing state resource, can be used to synthesize semiconductor-quality pyrite, potentially unlocking new clean energy applications.

Summary of Project and Outcomes

In addition to being an important mineral, pyrite iron disulfide, or fool's gold, is also a semiconductor (much like silicon) with substantial unrealized potential in electronic devices, solar cells, batteries, and other energy applications. The goals of this project were to develop iron pyrite for these applications by understanding its electronic properties, its optical properties, and how to synthesize the material, at semiconductor-quality, from Minnesota natural resources. Successful outcomes were achieved in all main directions. The electronic properties of pyrite, for example, were advanced through the demonstration of controllable n-type and p-type doping, an essential step in the development of any semiconductor, opening up the first route to a form of pyrite solar cell known as a homojunction cell. These devices have the potential to outperform prior pyrite heterojunction solar cells, making this an important scientific and engineering development.

The physics of pyrite under illumination was also advanced, in particular the understanding of how photoexcited electrons couple to the pyrite atomic lattice, providing yet further insight into optimal design principles for opto-electronic devices. As required for large-scale applications, the synthesis of semiconductor-quality pyrite crystals from abundant natural resources was also explored. It was demonstrated that existing Minnesota iron ores such as taconite can be chemically converted into pyrite through relatively simple materials processing steps, resulting in surprisingly high electronic quality semiconducting material, despite the very high initial impurity content in taconite. The mechanisms by which this is possible were clarified in detail, the implication being that an additional revenue stream for an existing and abundant Minnesota resource could potentially be developed, for applications in electronic devices and clean energy technologies.

Project Results Use and Dissemination

The results from this project have been widely disseminated, in scientific publications in established journals, through conference and meeting presentations, and in popular-press news articles on the publications. There are currently five publications from the project, with a further one expected by the end of 2026. One of the more recent publications, on the synthesis of semiconductor-quality pyrite from Minnesota iron ore (https://journals.aps.org/prapplied/abstract/10.1103/6twd-lvvg), attracted substantial news attention, a few examples being:
https://phys.org/news/2026-08-minnesota-iron-ore-key-sustainable.html
https://interestingengineering.com/innovation/iron-ore-semiconductor-pyrite
https://www.miragenews.com/minnesota-iron-ore-key-to-cheaper-sustainable-1727466/
https://xenospectrum.com/en/iron-ore-pyrite-semiconductor-minnesota/

Environment and Natural Resources Trust Fund

M.L. 2022 Approved Final Report

General Information

Date: October 28, 2026

ID Number: 2022-180

Staff Lead: Lisa Bigaouette

Project Title: Green Solar Cells from a Minnesota Natural Resource

Project Budget: $673,000

Project Manager Information

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Project Reporting

Final Report Approved: October 20, 2026

Reporting Status: Project Completed

Date of Last Action: October 20, 2026

Project Completion: June 30, 2026

Legal Information

Legal Citation: M.L. 2022, Chp. 94, Sec. 2, Subd. 07a , as extended by laws 2025, First Special Session, Art. 2, Sec. 2, Subd. 17

Appropriation Language: $673,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota to develop an efficient, low cost, and nontoxic pyrite solar cell and conduct a feasibility study for using Iron Range resources to manufacture this product. This appropriation is subject to Minnesota Statutes, section 116P.10. Carryforward; extensions (a) The availability of the appropriations for the following projects is extended to June 30, 2026: (9) Laws 2022, chapter 94, section 2, subdivision 7, paragraph (a), Green Solar Cells from a Minnesota Natural Resource.

Appropriation End Date: June 30, 2026

Narrative

Project Summary: Recent U of M breakthroughs will be built upon to realize the first truly environmentally friendly solar cells, simultaneously unlocking exciting new renewable energy opportunities for the MN Iron Range.

Describe the opportunity or problem your proposal seeks to address. Include any relevant background information.

It is now widely accepted that climate change is underway, that it results from human activity, and that it will soon induce global changes of enormous concern. The development of renewable energy sources to mitigate climate change thus may be the defining challenge of our time. Due to the abundance of sunlight, solar power will undoubtedly form part of the solution. In the context of the environment, however, it is imperative that materials used in solar cells (photovoltaics) be fundamentally "green", i.e., non-toxic, earth-abundant, low-carbon-cost, etc. Strikingly, this is not true of current photovoltaics. Silicon, for example, requires so much electricity for its production that the time to "net neutral carbon" is years. Competitors like cadmium telluride and copper indium gallium selenide are yet worse, being based on toxic (e.g., cadmium), rare (e.g., tellurium), or sensitive elements (e.g., indium), for which reliance on foreign resources is up to 100%. Materials called perovskites are rapidly emerging as alternatives, but are typically based on highly toxic lead. We thus lie on the verge of solving one environmental problem only to create numerous others. Developing fundamentally "green" solar cell materials is thus a grand scientific challenge, directly addressed here.

What is your proposed solution to the problem or opportunity discussed above? Introduce us to the work you are seeking funding to do. You will be asked to expand on this proposed solution in Activities & Milestones.

We propose an innovative solution, not only developing a fundamentally "green" solar cell material, but doing so with MN natural resources. This emerges from a decade-long effort by Leighton and collaborators at the U, focusing on the extraordinary material iron disulfide, otherwise known as pyrite or fool's gold (Figure 1). This photovoltaic is not only based on low-toxicity, earth-abundant elements but is also estimated to be 100 times cheaper than its nearest competitor and 10,000 times cheaper than silicon (Figure 1). This is due to the negligible cost of sulfur (a globally-stockpiled waste product (Figure 2)) and the massive abundance of iron. The semiconducting properties of pyrite, essential for photovoltaics, are also near-ideal. Despite this promise, the efficiency of pyrite solar cells has barely exceeded 3%, ten times below its potential. Motivated by this, Leighton and collaborators invested a decade of research into understanding and eliminating roadblocks to pyrite photovoltaics. This has been highly productive, culminating in 2020 in the identification of the origin of poor solar cell efficiency, and the first viable route to circumvent it (using "homojunction" solar cells). Here, we propose to translate these breakthroughs into real applications, realizing the first efficient pyrite solar cells.

What are the specific project outcomes as they relate to the public purpose of protection, conservation, preservation, and enhancement of the state's natural resources?

Vitally, our proposed work could not only realize the first truly "green" solar cell technology, but could do so with MN natural resources. Specifically, pyrite solar cells would need to be based on precisely-engineered synthetic pyrite formed from sulfur and iron. Efficient pyrite solar cells thus create the possibility of using MN Iron Range resources (Figure 2) in a fundamentally renewable energy technology, in stark contrast to their current use in carbon-costly steel production. To this end, we will thus also make a materials/geology/natural-resource-science-based evaluation of the feasibility of using Iron Range resources to manufacture this "green" photovoltaic.

Project Location

What is the best scale for describing where your work will take place?

Statewide

What is the best scale to describe the area impacted by your work?

Statewide

When will the work impact occur?

During the Project and In the Future

Activities and Milestones

Activity 1: 1. Completing the understanding of pyrite electronic and opto-electronic properties

Activity Budget: $201,900

Activity Description:
The prior work of Leighton essentially identified three possible origins of poor efficiency in pyrite solar cells: (i) unwanted secondary phases (e.g., FeS in FeS2); (ii) difficulties with “doping” (the process used to control properties of photovoltaics); and (iii) irregularities with pyrite surfaces. Possibility (i) was comprehensively eliminated. Significant advances were then made with (ii), resolving a problem known as the “pyrite doping puzzle”, and proving that typical pyrite doping occurs due to defects called sulfur vacancies (missing sulfur atoms). Control was then demonstrated, leading to tunable “n-type” doping, i.e., controlled concentrations of electrons. The most significant advance, however, came in (iii), through the discovery that anomalous electronic properties of pyrite surfaces are the specific origin of poor solar cell performance. Vitally, these advances point to the first viable route to circumvent the problems with existing pyrite solar cells. This route is a “homojunction” cell, essentially a junction between two differently-doped pyrite regions (called "n-type" and "p-type"). Activity 1 will thus address the final barriers to the first efficient pyrite homojunction solar cells: improved control of n-type doping, development of an effective p-type dopant, and improved understanding of pyrite optoelectronics, i.e., its conversion of light to electricity.

Activity Milestones:

Description	Approximate Completion Date
A. Development of phosphorous as a p-type dopant in pyrite	December 31, 2022
C. Photophysics studies of n- and p-type pyrite	September 30, 2025
B. Exploration of ultralow-sulfur-vacancy-density pyrite	December 31, 2025
D. Control of the S vacancy energy level in pyrite	December 31, 2025
E. Photophysics studies of pyrite p-n homojunctions	December 31, 2025

Activity 2: 2. Developing efficient pyrite homojunction solar cells

Activity Budget: $336,500

Activity Description:
The goal of Activity 2 is to build on recent breakthroughs in the understanding of pyrite, in addition to knowledge from Activity 1, to drive this technology from science to applications. The essential concept is that prior pyrite solar cells were based on “heterojunctions” i.e., interfaces between other materials and pyrite surfaces. Armed with the new understanding that these surfaces behave anomalously, limiting performance, pyrite homojunction cells become the central goal. Our first goal in Activity 2 will therefore be to develop strategies to eliminate parasitic surface effects in homojunctions. Treatments using ion beams will be tested, eliminating surface conduction, and enabling us to properly test homojunctions. Following this, we will explore two routes to p-n homojunction solar cells: naturally-formed internal p-n junctions due to p-type surfaces on n-type crystals, and artificially-fabricated p-n junctions using approaches known as “contact doping” and “ion implantation”. We will then perform extensive electrical characterization, culminating in solar cell testing, i.e., under solar illumination. Finally, to exploit pyrite's extraordinarily high light absorption, pyrite solar cells should ultimately be based on very thin films of the material (to minimize materials costs); we will thus also explore translation of this research towards thin film devices.

Activity Milestones:

Description	Approximate Completion Date
A. Development and testing of device isolation strategies (controlling surface conduction)	August 31, 2025

B. Electrical testing of p-n homojunctions	December 31, 2025
C. Solar cell testing of p-n homojunctions	December 31, 2025
D. Translation from single-crystal to thin-film devices	December 31, 2025

Activity 3: 3. Assessing the feasibility of MN Iron Range iron for the manufacture of pyrite-based "green" solar cells.

Activity Budget: $134,600

Activity Description:

An important feature of pyrite solar cells is that they would be fabricated from earth-abundant sulfur and iron (mineral pyrite cannot be used due to uncontrolled electronic properties), thus creating a potential renewable energy application for a key MN resource. Activity 3 will combine the Twin Cities faculty expertise (materials science, electrical engineering, chemistry), with the expertise of Hudak (geology, natural resources), to make the first assessment of the feasibility of using Iron Range resources for synthesis of this photovoltaic. Iron Range hematite samples from both the taconite process and an emerging ilmenite process will be converted to iron, then used to synthesize pyrite crystals and films. We will then conduct extensive testing, assessing purity, structural quality, electronic/optical properties, etc. Direct conversion of hematite to pyrite will also be explored, potentially streamlining the process. Importantly, all of these approaches should induce substantial purification during synthesis, as required for photovoltaics. Finally, Hudak will also perform an analysis of the economics of utilizing Iron Range resources for photovoltaic pyrite synthesis. Critical factors such as the availability of appropriately-pure MN iron, production costs, and environmental impacts will be considered, providing the first assessment of the feasibility of this emerging renewable energy application.

Activity Milestones:

Description	Approximate Completion Date
A. Conversion of Iron Range hematite to iron	December 31, 2022
B. Fabrication and testing of pyrite crystals and thin films from Iron Range iron	June 30, 2024
C. Direct conversion of Iron Range hematite to pyrite	August 31, 2025
D. Geologic/materials/natural-resource-science-based assessment of feasibility	December 31, 2025

Project Partners and Collaborators

Name	Organization	Role	Receiving Funds
Prof. Renee Frontiera	Department of Chemistry, University of Minnesota (Twin Cities)	Prof. Frontiera, collaborating with Leighton, will lead aspects of the proposed work related to pyrite photophysics/opto-electronics, i.e., how pyrite absorbs light, creates carriers of electricity (electrons), and how these carriers move. She is a renowned expert on the study of these processes at high time and spatial resolution.	Yes
Dr. George Hudak	Natural Resources Research Institute, University of Minnesota (Duluth)	Dr. Hudak, collaborating with Leighton, will lead aspects of the proposed work related to assessing the geologic/natural resource science feasibility of using MN Iron Range iron to manufacture pyrite solar cells. He is a renowned expert on economic geology, actively working on issues related to the MN Iron Range.	Yes
Prof. Steve Koester	Department of Electrical and Computer Engineering, University of Minnesota (Twin Cities)	Prof. Koester, collaborating with Leighton, will lead aspects of the proposed work related to solar cell device design, fabrication, and testing. He is a renowned expert on semiconductor opto-electronic devices with expertise both in academia and industry (including 14 years at IBM).	Yes
Shashi Rao	Natural Resources Research Institute, University of Minnesota (Duluth)	Replacement on this project for George Hudak (retired)	Yes
Saleh Mamun	Natural Resources Research Institute, University of Minnesota (Duluth)	Replacement on this project for George Hudak (retired)	Yes

Dissemination

Describe your plans for dissemination, presentation, documentation, or sharing of data, results, samples, physical collections, and other products and how they will follow ENRTF Acknowledgement Requirements and Guidelines.
The research performed with this ENRTF funding will be published in high-quality, high-visibility, peer-reviewed journals in science and engineering. We will favor scientific-society-based journals for this, keeping page charges for publication to an absolute minimum. All data from these publications will be made available to any interested party upon any reasonable request for information, following best practices in the field. The investigators will additionally follow best practices for storage and archiving of data, for which the U of M has state-of-the-art tools such as DRUM (Data Repository for the University of Minnesota). Prior to archiving, all data will be stored on shared servers with 24-hour automatic back-up. Physical samples produced as part of the work will be stored in the Project Manager's lab; this lab has a dry storage area for this purpose.

In terms of dissemination, in addition to the publications mentioned above, the investigators working on this project will additionally disseminate this work via their regular seminars and conference presentations. In-state possibilities to share

this research in this mode will be actively sought out, in order to enhance the profile and visibility of this research in MN. Travel to these conferences will be supported from the investigators' discretionary funds.

Long-Term Implementation and Funding

Describe how the results will be implemented and how any ongoing effort will be funded. If not already addressed as part of the project, how will findings, results, and products developed be implemented after project completion? If additional work is needed, how will this work be funded?

This proposed work builds on substantial prior research, funded primarily by federal and state sources. We will now leverage this to translate these scientific breakthroughs towards a real technology, via the demonstration of the first efficient pyrite-based solar cells. Such a demonstration is highly likely to enable subsequent fundraising from more applied/technological programs (both government (e.g., Department of Energy) and industrial), to move beyond demonstration solar cells. In essence, what is needed now is the support of a program willing to back an emerging technology with extraordinary renewable energy potential, specifically tied to Minnesota natural resources.

Budget Summary

Category / Name	Subcategory or Type	Description	Purpose	Gen. Ineligible	% Benefits	# FTE	Classified Staff?	$ Amount	$ Amount Spent	$ Amount Remaining
Personnel										
Principal Investigator		Chris Leighton, principal Investigator			26.7%	0.09		$27,846	-	-
Co-Investigator		Renee Frontiera, co-Investigator			26.7%	0.09		$19,473	-	-
Co-Investigator		Steve Koester, co-Investigator			26.7%	0.09		$29,469	-	-
Postdoctoral Research Associate		Postdoctoral Research Associate, Chemical Engineering and Materials Science			20.25%	3		$189,536	-	-
Graduate Research Assistant		Graduate Research Assistant, Chemistry			22.74%	1.5		$106,098	-	-
Graduate Research Assistant		Graduate Research Assistant, Electrical and Computer Engineering			43.7%	1.5		$146,565	-	-
Co-Investigator		George Hudak, co-Investigator			26.7%	0.01		$515	-	-
Co-investigator		Shashi Rao, NRRI, co-investigator			27%	0.23		$24,680	-	-
Postdoctoral Research Associate		Saleh Mamun, NRRI, postdoc			27%	0.32		$24,679	-	-
							Sub Total	**$568,861**	**$568,861**	**-**
Contracts and Services										
University of Minnesota shared facility usage (Characterization Facility and Minnesota Nano Center)	Internal services or fees (uncommon)	These two University of Minnesota shared facilities (the Characterization Facility and Minnesota Nano Center) are essential to perform this research. They house many of the laboratory instruments required for the work, which are accessed on an hourly-charge basis by student and post-doctoral researchers.				0		$49,470	$49,470	-
							Sub Total	**$49,470**	**$49,470**	**-**
Equipment, Tools, and Supplies										

	Tools and Supplies	Lab materials and supplies	Purchase of standard lab materials and supplies (chemicals, gases, glassware, etc.)					$54,669	$54,647	$22
							Sub Total	**$54,669**	**$54,647**	**$22**
Capital Equipment										
							Sub Total	**-**	**-**	**-**
Acquisitions and Stewardship										
							Sub Total	**-**	**-**	**-**
Travel In Minnesota										
							Sub Total	**-**	**-**	**-**
Travel Outside Minnesota										
							Sub Total	**-**	**-**	**-**
Printing and Publication										
	Publication	Publication of scientific/engineering papers resulting from the research. This will be done in society-based journals that have no page charges. Thus there are no costs in this category.	Publication of the key research results will be a vital product of the proposed work.					-	-	-
							Sub Total	**-**	**-**	**-**
Other Expenses										
							Sub Total	**-**	**-**	**-**
							Grand Total	**$673,000**	**$672,978**	**$22**

Classified Staff or Generally Ineligible Expenses

Category/Name	Subcategory or Type	Description	Justification Ineligible Expense or Classified Staff Request

Non ENRTF Funds

Category	Specific Source	Use	Status	$ Amount	$ Amount Spent	$ Amount Remaining
State						
			State Sub Total	-	-	-
Non-State						
			Non State Sub Total	-	-	-
			Funds Total	-	-	-

Attachments

Required Attachments

Visual Component

File: b058d99e-3d5.pdf

Alternate Text for Visual Component

Proposal figures (reattached per comments)....

Supplemental Attachments

Capital Project Questionnaire, Budget Supplements, Support Letter, Photos, Media, Other

Title	File
Proposal figures	a68e4fc5-c3a.pdf
Submission letter from the University of Minnesota Sponsored Projects Administration	e0063d1e-8e5.pdf
Background Check Form	38f0d0f4-b0f.pdf
Controlled p-Type Doping of Pyrite FeS2 (ACS Applied Materials and Interfaces)	ca5328ab-34f.pdf
Electronic transport across the insulator-metal transition in Co-doped pyrite FeS2 single crystals	7b5fa6d0-6e3.pdf
Excited-state electron-phonon coupling in pristine and doped iron pyrite	edaac1cb-f06.pdf
Semiconductor-quality pyrite FeS2 from iron ore	f801cbe9-c7b.pdf
Electronic transport properties of single-crystal pyrite FeS2	b3b50c8f-973.pdf

Media Links

Title	Link
First paper: Controlled p-type doping of pyrite FeS2	https://pubs.acs.org/doi/full/10.1021/acsami.3c04662

Difference between Proposal and Work Plan

Describe changes from Proposal to Work Plan Stage

The budget has been trimmed in the following ways. Support for each of the U of M Twin Cities faculty has been reduced by 25%. Support for the NRRI staff member has been reduced by 10%. The ineligible $15,803 for out-of-state travel has been removed. Any required travel will need to be supported from the investigators' discretionary funds. Support for lab services and materials and supplies has been trimmed to reach the $673,000 appropriation. By these means, we are able to keep the student and post-doc support at the full level.

In response to the comments, please note: (1) the out-of-state travel has been removed, (2), there are no costs for publications as we plan to publish in society journals, (3) I tried to reattach the figures, although the system shows them as already there?

Additional Acknowledgements and Conditions:

The following are acknowledgements and conditions beyond those already included in the above workplan:

Do you understand and acknowledge the ENRTF repayment requirements if the use of capital equipment changes?

N/A

Do you understand that travel expenses are only approved if they follow the "Commissioner's Plan" promulgated by the Commissioner of Management of Budget or, for University of Minnesota projects, the University of Minnesota plan?

N/A

Does your project have potential for royalties, copyrights, patents, sale of products and assets, or revenue generation?

Yes

Do you understand and acknowledge IP and revenue-return and sharing requirements in 116P.10?

Yes

Do you wish to request reinvestment of any revenues into your project instead of returning revenue to the ENRTF?

No

Does your project include original, hypothesis-driven research?

Yes

Does the organization have a fiscal agent for this project?

Yes, Sponsored Projects Administration

Do you understand that a named service contract does not constitute a funder-designated subrecipient or approval of a sole-source contract? In other words, a service contract entity is only approved if it has been selected according to the contracting rules identified in state law and policy for organizations that receive ENRTF funds through direct appropriations, or in the DNR's reimbursement manual for non-state organizations. These rules may include competitive bidding and prevailing wage requirements

N/A

Work Plan Amendments

Amendment ID	Request Type	Changes made on the following pages	Justification For Amendment Request (word limit 75)	Date Submitted	Approved	Date of LCCMR Action
1	Amendment Request	• Project Collaborators - Project Partner Info • Budget - Personnel	George Hudak (NRRI, Duluth) has decided to retire shortly. His tasks on this project will now be performed by Shashi Rao (NRRI) and Saleh Mamun (NRRI), who are well qualified for the geological and economic aspects of this work, respectively. This amendment is to make this change, and assign some budgeted dollars to the two new people involved.	October 11, 2023	Yes	October 12, 2023
2	Completion Date	Previous Completion Date: 06/30/2025 New Completion Date: 12/31/2025; Governor Approved on 06/14/2025	Two outcomes may not be met by the scheduled project end. The first is the economic geological analysis of using Iron Range resources to manufacture solar cells. This is due to unforeseen circumstances, precipitated by the retirement of an NRRI staff member. Second, one of the scientific aspects of device development has progressed slower than hoped. We now have a remedy to this problem and have increased resource allocation in this direction.	December 7, 2024	Yes	June 25, 2025
3	Amendment Request	• Budget • Other • Activities and Milestones • Budget - Professional / Technical Contracts • Budget - Capital, Equipment, Tools, and Supplies	I was requested to amend dates for milestones in light of the recent approval of the extension of this project. I have now done so for all the milestones that are not yet complete.	July 16, 2025	Yes	July 17, 2025
4	Completion Date	Previous Completion Date: 12/31/2025 New Completion Date: 06/30/2026	As requested by Lisa Bigaouette to align completion and appropriation dates.	December 3, 2025	Yes	December 5, 2025
5	Amendment Request	• Budget • Other • Attachments	Our expenses on materials and supplies slightly exceeded the original budget. This was balanced by a reduction in personnel	September 11, 2026	Yes	September 14, 2026

		• Budget - Personnel • Budget - Capital, Equipment, Tools, and Supplies	spending, specifically on a researcher in ECE. As requested, specific materials/supplies costs: Chemicals: $687 Used for synthesis of FeS2 samples. Liquid nitrogen: $2443 Used for cooling for electronic transport measurements and certain synthetic needs. Gases: $1836 Nitrogen, argon, forming gas, etc., for synthesis of FeS2 Gas cylinder fees: $210 As required for the above gases			

Status Update Reporting

Final Status Update August 14, 2026

Date Submitted: September 21, 2026

Date Approved: September 22, 2026

Overall Update

The overall goals of this project are to: (i) develop the science to realize pyrite-based solar cells, (ii) demonstrate a pyrite-based homojunction solar cell, and (iii) achieve the synthesis of semiconductor-quality pyrite from Iron Range resources, thus unlocking a new revenue stream for this abundant MN resource. Activity 1 deals with pyrite electronic and optoelectronic properties, Activity 2 deals with solar cells, and Activity 3 deals with using Iron Range resources to manufacture pyrite.

At the close of this project, Milestones A, B, C, and D of Activity 1 are entirely complete. Only Milestone E was not completed, due to aspects of Activity 2 not reaching completion. In Activity 2, Milestones A, B, and C were completed, but we were not able to complete Milestone D before the end of the project. Finally, Activity 3 was the major success of this project. All milestones were completed by the end of the award, including D, which was just recently completed by NRRI researchers. The scientific publication on Activity 3 was just published this week, and is currently being publicized by the U of M.

In summary, major breakthroughs were made across all activities, but a pyrite solar cell was not achieved.

Activity 1

Activity 1 was almost entirely completed by the end date of this project. Milestone A was completed some time ago and was published as item 1 in the list shown in the Dissemination Update below. Milestones B and D were completed in the Leighton Lab by graduate student Yeon Lee, who will graduate with a Ph.D. around the new end date of the project and has recently accepted an offer of employment in the semiconductor industry in the US. These Milestones are the basis for publication 6 in the list below. Milestone C was also completed recently. Graduate student Shahzad Alam in the Frontiera Group, working with the Leighton Group, generated publication 3 in the list below, which was published earlier this year. Alam has since graduated and is now employed in a post-doctoral position in the US. Milestone E was the only one not completed in Activity 1, the stumbling block being slower than anticipated progress with Activity 2, specifically Milestone C, as discussed below.

Activity 2

In Activity 2, Milestones A and B were completed some time ago. The device isolation strategies described in prior progress reports eventually worked, allowing us to move from Milestone A to Milestone B. Significant progress was also made with a part of Milestone D, although this was not entirely completed. Specifically, thin films of FeS_2 were made from Iron Range resources, but with mixed results. We were not able to optimize this process by the end of the award.

Milestone C was by far the most challenging aspect of this project. We were able to test some devices, but none had the photoactivity or efficiency that we were aiming for. While the project was ultimately able to clearly define the best path forward in this direction, we were not able to complete this research prior to the end of the award. However, in publication 5 in the list below, which is a review of the electronic properties of pyrite, we were able to explicitly elaborate the most likely strategies to improve on pyrite solar cell performance in the future. This publication was accepted in this reporting period and is in-press at the journal Physical Review Materials.

Activity 3

Activity 3 was extremely successful. Milestones A and B were completed in full and written up as paper number 4 in the

list below (Dissemination Update), which just appeared in print. As alluded to in prior reports, we believe this to be a significant advance. We demonstrated successful fabrication of semiconductor-quality pyrite crystals from Iron Range resources, with no additional purification, potentially unlocking a new revenue stream for an important MN resource. We engaged with public relations teams at the University, College, and LCCMR, and are currently publicizing this work widely (more details below). In performing the later parts of this work, we also realized that Milestone C, which we thought at some point may not even be needed, was also within reach. This was in fact completed recently, and is described in publication 4 in the list below. In the current reporting period, Milestone D was also completed. Our colleagues and collaborators at the NRRI in Duluth completed an initial techno-economic assessment of the feasibility of using Iron Range resources as a means to manufacture semiconducting pyrite, which will soon be published as an NRRI Technical Report, and shared with the LCCMR.
(This activity marked as complete as of this status update)

Dissemination
Scientific publications generated:

1. “Controlled p-type doping of Pyrite FeS2”, Voigt, Stolik Valor, Moore, Jeremiason, Kakalios, Leighton and Aydil, ACS Appl. Mater. Interfaces 15, 28258 (2023).

2. “Electronic transport across the insulator-metal transition in Co-doped pyrite FeS2 single crystals”, Das, Voigt, Moore, Maiti, Lee, Chaturvedi, Haugstad, Manno, Aydil, and Leighton, Phys. Rev. Mater. 9, 054601 (2025).

3. “Excited-state electron-phonon coupling in pristine and doped iron pyrite”, Alam, Lee, Voigt, Moore, Das, Maiti, Leighton, and Frontiera, J. Phys. Chem. Lett. 17, 3580 (2026).

4. “Semiconductor-quality pyrite FeS2 from iron ore”, Lee, Mitchell, Komar, Mlinar, Taguta, Hudak, and Leighton, Phys. Rev. Appl. 26, 024033 (2026).

5. “Electronic transport properties of single-crystal pyrite FeS2”, Leighton and Lee, Phys. Rev. Mater. 10, 080301 (2026).

6. "Controlling pyrite crystal growth and doping through cooling rate", Lee and Leighton, in preparation for ACS Cryst. Growth Design (2026).

These acknowledge ENRTF funding as the primary source. Several oral and poster presentations have also been made at local and national conferences.

The most recent versions of all papers have been uploaded; only 6 is not yet available.

The first news article on 4 (there are now about a dozen):
https://cse.umn.edu/college/news/minnesota-iron-ore-could-be-key-sustainable-and-lower-cost-semiconductor

Status Update Reporting

Status Update March 1, 2026

Date Submitted: March 20, 2026

Date Approved: March 24, 2026

Overall Update
Activity 1 deals with pyrite electronic and optoelectronic properties, Activity 2 deals with developing solar cells, and Activity 3 deals with using Iron Range resources to manufacture pyrite.

Currently, Milestones A, B, C, and D of Activity 1 are completed. Milestone E is posing challenges, related to slower progress with certain aspects of Activity 2. Milestones A and B of Activity 2 are now completed, and C and D are underway. Milestones A, B, and C are all complete in Activity 3, and Milestone D is on-track for completion by the new end date.

In summary, almost all of Activity 1 will be completed by the new end date, there are challenges to completing parts of Activity 2 (they are being worked on), but Activity 3 has been such a success that progress beyond original Milestones has been achieved.

In response to the request for revisions:
> It is uncertain if Milestone E, Activity 1 will be completed.
> It is uncertain if Milestone C, Activity 2 will be completed.
> We do not have any funding to complete this work after the end of this project. We are currently working to secure additional funding. We thus cannot provide an expected completion date.

Activity 1
Activity 1 is near-complete. Milestone A was completed some time ago and was published as item 1 in the list shown in the Dissemination Update below. Milestones B and D were recently completed in the Leighton Lab by graduate student Yeon Lee, who will graduate with a Ph.D. around the new end date of the project. These Milestones are the basis for publication 6 in the list below. Milestone C was also completed in this reporting period. Graduate student Shahzad Alam in the Frontiera Group, working with the Leighton Group, generated publication 3 in the list below, which was accepted for publication juts a few days ago. Alam has since graduated and is now employed in a post-doctoral position in the US. Milestone E is the only remaining challenge in Activity 1, the stumbling block being slower than anticipated progress with Activity 2, specifically Milestone C.

Activity 2
In Activity 2, Milestones A and B are now complete. The device isolation strategies described in prior progress reports eventually worked, allowing us to move from Milestone A to Milestone B, in which we have now put substantial effort. Significant progress has also been made with a part of Milestone D, as the work in Activity 3 was found to impinge on this. Specifically, as part of publication 4 in the list below, Yeon Lee in the Leighton Lab was able to demonstrate successful growth of pyrite thin films from Iron Range resources. While aspects of Activity 2, Milestone D thus remain to be completed, some parts have been done. Finally, Milestone C continues to be challenging, thus impacting Milestone E of Activity 1. These two Milestones are the ones that are now the primary focus of this project until it ends.

Activity 3
Activity 3 has been extremely successful. Milestones A and B are now complete in full and written up as paper number 4 in the list below (Dissemination Update). As alluded to in prior reports, we believe this to be a significant advance. We have demonstrated successful fabrication of semiconductor-quality pyrite crystals from Iron Range resources, with no

additional purification, potentially unlocking a new revenue stream for an important MN resource. We have engaged with public relations teams at the University, College, and LCCMR, and are hoping to publicize this work widely when it is published. In performing the later parts of this work, we also realized that Milestone C, which we thought at some point may not even be needed, was also within reach. This was in fact completed in the most recent reporting period, and is described in publication 4 in the list below.

Milestone D is also now close to completion. Our colleagues and collaborators at the NRRI in Duluth are working on this actively and remain confident that it can be completed by the new (extended) end date of this project. We thus anticipate that this Activity will be entirely complete by the end of the project.

Dissemination
Multiple scientific publications that have been generated:

1. “Controlled p-type doping of Pyrite FeS2”, Voigt, Stolik Valor, Moore, Jeremiason, Kakalios, Leighton and Aydil, ACS Appl. Mater. Interfaces 15, 28258 (2023).

2. “Electronic transport across the insulator-metal transition in Co-doped pyrite FeS2 single crystals”, Das, Voigt, Moore, Maiti, Lee, Chaturvedi, Haugstad, Manno, Aydil, and Leighton, Phys. Rev. Mater. 9, 054601 (2025).

3. “Excited-state electron-phonon coupling in pristine and doped iron pyrite”, Alam, Lee, Voigt, Moore, Das, Maiti, Leighton, and Frontiera, in press, J. Phys. Chem. Lett. (2025).

4. “Semiconductor-quality pyrite FeS2 from iron ore”, Lee, Mitchell, Komar, Mlinar, Taguta, Hudak, and Leighton, submitted, Phys. Rev. Appl. (2025).

5. “Electronic transport properties of single-crystal pyrite FeS2”, Leighton and Lee, in preparation for Phys. Rev. Mater. (2026).

6. "Controlling pyrite crystal growth and doping through cooling rate", Lee and Leighton, in preparation for ACS Cryst. Growth Design (2026).

These acknowledge primary ENRTF funding as the primary source. Several oral and poster presentations have also been made at local and national conferences and meetings. For publication 4 above, both U of M and LCCMR have been engaged for publicity efforts.

Per your revision request, 1-4 have now been uploaded. 5,6 are in preparation.

Additional Status Update Reporting

Additional Status Update February 14, 2026

Date Submitted: March 20, 2026

Date Approved: March 24, 2026

Overall Update
In this project, Activity 1 deals with understanding pyrite electronic and optoelectronic properties, Activity 2 deals with developing efficient pyrite solar cells, and Activity 3 deals with the feasibility of using Iron Range resources to manufacture pyrite for energy applications.

At the current time, Milestones A, B, C, and D of Activity 1 are essentially all completed. Milestone E poses some problems, related to slower progress than anticipated with certain aspects of Activity 2. Milestones A and B of Activity 2 are now completed, and C and D are underway. Milestones A, B, and C are all complete in Activity 3, and Milestone D is on-track for completion by the new project end date.

In summary, almost all of Activity 1 will be completed by the new end date, there are challenges to completing parts of Activity 2 (they are being worked on), but Activity 3 has been such a success that progress beyond the original Milestones has been achieved, as described below.

Activity 1
Activity 1 is near-complete. Milestone A was completed some time ago and was published as item 1 in the list shown in the Dissemination Update below. Milestones B and D were recently completed in the Leighton Lab by graduate student Yeon Lee, who will graduate with a Ph.D. around the new end date of the project. These Milestones are the basis for publication 6 in the list below. Milestone C was also completed in this reporting period. Graduate student Shahzad Alam in the Frontiera Group, working with the Leighton Group, generated publication 3 in the list below, which was accepted for publication juts a few days ago. Alam has since graduated and is now employed in a post-doctoral position in the US. Milestone E is the only remaining challenge in Activity 1, the stumbling block being slower than anticipated progress with Activity 2, specifically Milestone C.

Activity 2
In Activity 2, Milestones A and B are now complete. The device isolation strategies described in prior progress reports eventually worked, allowing us to move from Milestone A to Milestone B, in which we have now put substantial effort. Significant progress has also been made with a part of Milestone D, as the work in Activity 3 was found to impinge on this. Specifically, as part of publication 4 in the list below, Yeon Lee in the Leighton Lab was able to demonstrate successful growth of pyrite thin films from Iron Range resources. While aspects of Activity 2, Milestone D thus remain to be completed, some parts have been done. Finally, Milestone C continues to be challenging, thus impacting Milestone E of Activity 1. These two Milestones are the ones that are now the primary focus of this project until it ends.

Activity 3
Activity 3 has been extremely successful. Milestones A and B are now complete in full and written up as paper number 4 in the list below (Dissemination Update). As alluded to in prior reports, we believe this to be a significant advance. We have demonstrated successful fabrication of semiconductor-quality pyrite crystals from Iron Range resources, with no additional purification, potentially unlocking a new revenue stream for an important MN resource. We have engaged with public relations teams at the University, College, and LCCMR, and are hoping to publicize this work widely when it is published. In performing the later parts of this work, we also realized that Milestone C, which we thought at some point may not even be needed, was also within reach. This was in fact completed in the most recent reporting period, and is described in publication 4 in the list below.

Milestone D is also now close to completion. Our colleagues at the NRRI in Duluth are working on this actively and remain confident that it can be completed by the new (extended) end date of this project. We thus anticipate that this Activity will be entirely complete by the end of the project.

Dissemination

There are now multiple scientific publications that have been generated through this project:

1. “Controlled p-type doping of Pyrite FeS2”, Voigt, Stolik Valor, Moore, Jeremiason, Kakalios, Leighton and Aydil, ACS Appl. Mater. Interfaces 15, 28258 (2023).

2. “Electronic transport across the insulator-metal transition in Co-doped pyrite FeS2 single crystals”, Das, Voigt, Moore, Maiti, Lee, Chaturvedi, Haugstad, Manno, Aydil, and Leighton, Phys. Rev. Mater. 9, 054601 (2025).

3. “Excited-state electron-phonon coupling in pristine and doped iron pyrite”, Alam, Lee, Voigt, Moore, Das, Maiti, Leighton, and Frontiera, in press, J. Phys. Chem. Lett. (2025).

4. “Semiconductor-quality pyrite FeS2 from iron ore”, Lee, Mitchell, Komar, Mlinar, Taguta, Hudak, and Leighton, submitted, Phys. Rev. Appl. (2025).

5. “Electronic transport properties of single-crystal pyrite FeS2”, Leighton and Lee, in preparation for Phys. Rev. Mater. (2026).

6. "Controlling pyrite crystal growth and doping through cooling rate", Lee and Leighton, in preparation for ACS Cryst. Growth Design (2026).

All of these acknowledge ENRTF funding as the primary source. In addition, several oral and poster presentations have been made on this project, at a range of local and national conferences and meetings. For publication (4) above, both U of M and LCCMR have been engaged for publicity efforts.

Status Update Reporting

Status Update September 1, 2025

Date Submitted: September 4, 2025

Date Approved: November 10, 2025

Overall Update

Due to the additional status report in July 2025 (triggered by the no-cost extension of the project), only about 6 weeks have passed since the last report. With respect to Activity 1, Milestones A and C are essentially now complete, and Milestones B and D are also nearing completion. Adding to the two scientific publications already generated, a third publication is now nearing completion and readiness for submission to a journal. In Activity 2, Milestones A and B are progressing well, as detailed below (Milestone A is very close). With regard to Activity 3, Milestones A and B are complete, C is essentially no longer necessary given the nature of the progress with A and B, and Milestone D is well underway. In this Activity, progress has in fact been made beyond any of the stated Milestones and a fourth publication is now in preparation, as detailed further below. Significant progress is thus being made in all project directions, as discussed below. Of particular note is the progress in Activity 3, which has realized a very significant advance (the subject of one of the manuscripts under preparation).

Activity 1

As noted in prior reports, Milestone A in Activity 1 is already complete and published. Milestone B has also almost been reached, as work in Leighton's lab has successfully demonstrated low sulfur vacancy densities in pyrite single crystals through control of post-growth cooling rate. A publication on this topic is taking shape and should be submitted in the 2025 calendar year, prior to completion of the project (this will be the 5th publication from this project). A Leighton/Frontiera collaboration has also led to noteworthy results on pyrite photophysics, going a long way toward achieving Milestone C. The results (from resonance Raman experiments) are currently being written up for submission to a journal, the manuscript now reaching a stage where submission is imminent (this will be the 3rd publication from this project). Research in the Leighton lab has also made great progress towards Milestone D, using methods that overlap with those employed in Milestone B. Activity 1 has thus seen excellent progress, with only Milestone E requiring attention, as further progress is made in Activity 2.

Activity 2

In Activity 2, substantial progress towards Milestones A and B has been achieved. As noted previously, device fabrication on pyrite single crystals grown in Leighton's lab is now routine, using facilities in the Leighton Lab and Minnesota Nano Center. Several of the essential device isolation strategies have been tested, with ionic gating using printed ion gels being the most effective. This essentially completes Milestone A, while B and C remain underway. In the last few weeks, Milestone B has yielded to significant progress. Milestone D has also yielded to recent progress, as pyrite thin films are now being routinely deposited in Leighton's group and the Minnesota Nano Center. While activity 2 has proven challenging, this is more than offset by the progress in Activity 3, which is extremely encouraging and significant.

Activity 3

In Activity 3, the most important thing to report is that Leighton and the NRRI have now achieved convincing and reproducible synthesis of semiconductor-quality pyrite FeS_2 single crystals from multiple Iron Range resources. As noted in our last report, the ilmenite-derived hematite samples from Mlinar and Taguta can be reduced to iron and used to grow synthetic pyrite crystals with sufficiently low carrier density and high enough mobility to function as quality semiconductors. This is a noteworthy advance, which we plan to publish soon, as publication number 4 from this project. As mentioned in the last report, this not only means that Milestone C is no longer really necessary, but also that it may even be possible to generate semiconductor-quality pyrite from taconite resources, and we now have promising preliminary data in that regard. Notably, this was all achieved in the last few months, going a long way to establishing a

new revenue stream for a clean energy material from an Iron Range resource that is already in production. We expect these results to attract significant attention and we are targeting publications and associated news releases in 2025. Accompanying economic geological analysis is underway at NRRI, with promising progress.

Dissemination

With respect to dissemination, there are now two published papers from this project:

1. “Controlled p-type doping of Pyrite FeS2”, B. Voigt, L. Stolik Valor, W. Moore, J.D. Jeremiason, J. Kakalios, C. Leighton and E.S. Aydil, ACS Appl. Mater. Interfaces 15, 28258 (2023).
2. “Electronic transport across the insulator-metal transition in Co-doped pyrite FeS2 single crystals”, B. Das, B. Voigt, W. Moore, M. Maiti, Y. Lee, V. Chaturvedi, G. Haugstad, M. Manno, E. Aydil, and C. Leighton, Phys. Rev. Mater. 9, 054601 (2025).

As noted above, a third is now in preparation and will be submitted shortly:

3. “Excited-state electron-phonon coupling in pure and doped iron pyrite”, S. Alam, Y. Lee, B. Voigt, W. Moore, B. Das, C. Leighton, and R.R. Frontiera, in preparation (2025).

As also noted above, fourth and fifth publications are now taking shape, the most significant being the Twin-Cities/NRRI collaboration on the synthesis of semiconducting pyrite FeS2 from MN Iron Range resources. The end of 2025 is being targeted as a submission date for these final two publications.

The above publications have been accompanied by several oral and presentations by the graduate students and U of M faculty involved in the project.

Additional Status Update Reporting

Additional Status Update July 12, 2025

Date Submitted: July 16, 2025

Date Approved: July 17, 2025

Overall Update
As noted in prior reports, the project continues to progress at full speed. Leighton, Koester, and Frontiera (the primary U of M - Twin Cities investigators) all have graduate research assistants appointed on the project, and collaborators Taguta and Mlinar at NRRI are actively involved. With respect to Activity 1, Milestone A is complete, Milestone C is very close, and Milestones B and D are also nearing completion. Adding to the scientific publication already generated, in this period a second paper was published in a highly regarded scientific journal. In Activity 2, Milestones A and B are progressing well, as detailed below (Milestone A is very close). With regard to Activity 3, Milestones A and B are complete, C is essentially no longer necessary given the nature of the progress with A and B, and Milestone D is well underway. In this Activity, progress has in fact been made beyond any of the stated Milestones. Significant progress is thus being made in all project directions, as discussed in further detail below. Of particular note is the progress in Activity 3, which has realized a very significant advance.

Activity 1
Milestone A is complete and has been documented in a publication some time ago.

Milestones B and D are also now essentially completed and are the subject of a publication that is in preparation in the Leighton Group. Submission by the end of the extended award is our target. The graduate student leading this, Yeon Lee, is expected to graduate with a Ph.D. at the end of this project. The project will describe a study of the electronic properties of single crystals of pyrite grown under different sulfur vapor pressures to control the sulfur vacancy density.

Milestone C is also now complete and was written up and submitted for publication as a joint work between the Frontiera and Leighton Groups. The paper is under final review and is very close to publication in the American Chemical Society's Journal of Physical Chemistry Letters.

Milestone E is under active study now and is posing some challenges, mostly related to delays in Activity 2.

Activity 2
Milestones A and B are essentially now complete. Surface isolation strategies were ultimately successful and led to multiple test on internal p-n junctions in pyrite single crystals in the Leighton Group. We have now progressed to Milestone C. While full success with Milestone D is likely out of reach by the end of the project, graduate student Yeon Lee did demonstrate successful growth of thin-film pyrite from Iron Range resources, essentially completing a "hybrid" of Milestone D from Activity 2 and Milestones A and B from Activity 3.

Activity 3
Activity 3 has been a major success of this project. Milestones A through C are now all complete. A comprehensive publication on this work, coauthored by Leighton and the two current NRRI collaborators, was submitted a few weeks ago and is now under review and expected to be published by the end of the extended award. Project Manager Leighton has been working with the U of M, College of Science Engineering, and LCCMR public relations teams to generate press releases and other publicity relating to this work, which we believe to be particularly significant. The work essentially demonstrates successful synthesis of semiconductor-quality pyrite FeS_2 single crystals from MN Iron Range resources through surprisingly simple approaches, and is likely to generate substantial attention.

Dissemination

With respect to dissemination, the previously reported publication on p-type pyrite in ACS Applied Materials and Interfaces is now joined by a second paper published in the journal Physical Review Materials of the American Physical Society. This paper reports on controlled n-type doping across the FeS2 insulator-metal transition. As noted above, by the end of the project, we expect to add a publication on low-sulfur-vacancy density pyrite by post-growth cooling control, a paper on resonance Raman analysis of the photophysics of pyrite, and the important publication on establishing semiconductor pyrite from Iron Range ilmenite and taconite. This will be accompanied by several presentations by the graduate students and U of M faculty involved in the project.

Status Update Reporting

Status Update March 1, 2025

Date Submitted: April 3, 2025

Date Approved: April 15, 2025

Overall Update

As noted in prior reports, the project continues to progress at full speed. Leighton, Koester, and Frontiera (the primary U of M - Twin Cities investigators) all have graduate research assistants appointed on the project, and collaborators Taguta and Mlinar at NRRI are actively involved. With respect to Activity 1, Milestone A is complete and Milestones B, C, and D are nearing completion. Adding to the scientific publication already generated, in this period a second paper was submitted for publication in a highly regarded scientific journal. In Activity 2, Milestones A and B are progressing well, as detailed below. With regard to Activity 3, Milestones A and B are complete, C is essentially no longer necessary given the nature and extent of the progress with A and B, and Milestone D is well underway. Significant progress is thus being made in all project directions, as discussed in further detail below. Of particular note is the progress in Activity 3, which is poised to soon realize a very significant advance.

Activity 1

As noted in prior reports, Milestone A in Activity 1 is already complete and published. In the current period, great progress has been achieved toward Milestones B, C, and D. Milestone B has essentially been reached, as work in Leighton's lab has successfully demonstrated low sulfur vacancy densities in pyrite single crystals through control of post-growth cooling rate. A publication on this topic is taking shape and should be submitted in the 2025 calendar year, prior to completion of the project. A Leighton/Frontiera collaboration has also led to noteworthy results on pyrite photophysics, going a long way toward achieving Milestone C. The results (from resonance Raman experiments) remain under analysis, but should be brought to a conclusion in another publication by the end of the project. Research in the Leighton lab has also made great progress towards Milestone D, using methods that overlap with those employed in Milestone B. Activity 1 has thus seen excellent progress, with only Milestone E requiring attention, as further progress is made in Activity 2.

Activity 2

In Activity 2, led by Koester, substantial progress towards Milestones A and B has been achieved. As noted previously, device fabrication on pyrite single crystals grown in Leighton's lab is now routine, using facilities in the Koester Lab and the Minnesota Nano Center. Several of the essential device isolation strategies have been tested now, with ionic gating using printed ion gels now appearing the most promising. Important progress has thus been made, to the point that Milestones A-C remain achievable by the conclusion of the project at the end of the 2025 calendar year. Milestone D is also being actively worked on, and we are striving to make as much progress as possible by the end of the 2025 calendar year. An important step was recently made by a graduate student in the Leighton Lab, who is now synthesizing high-quality polycrystalline thin films of FeS_2, suitable for fabricating thin-film solar cells. While activity 2 has certainly proven challenging, this is more than offset by the progress in Activity 3, which is extremely encouraging and significant, as described below.

Activity 3

In Activity 3, the most important thing to report is that Leighton and the NRRI have now achieved convincing and reproducible synthesis of semiconductor-quality pyrite FeS_2 single crystals from a Minnesota Iron Range resource. The ilmenite-derived hematite samples from Mlinar and Taguta can now be reduced to iron and used to grow synthetic pyrite crystals, with sufficiently low carrier density and high enough electron mobility to function as quality semiconductors. This is a noteworthy advance, which we plan to publish soon. Remarkably, this progress not only means that Milestone C is no longer really necessary (we have achieved the overall goal without it), but also that it may even be

possible to generate semiconductor-quality pyrite from taconite resources. This would not only establish a new revenue stream for a clean energy material from an Iron Range resource, but also do so with an established resource that is already in mass production. We expect these results to attract significant attention and we are targeting publications and associated news releases in 2025. Accompanying economic geological analysis is also underway at NRRI, with promising progress.

Dissemination

With respect to dissemination, the previously reported publication on p-type pyrite in the journal ACS Applied Materials and Interfaces is now joined by a second paper submitted to the journal Physical Review Materials of the American Physical Society. This paper reports on controlled n-type doping across the FeS2 insulator-metal transition. As noted above, by the end of the project, we expect to add at least a publication on low-sulfur-vacancy density pyrite by post-growth cooling control, a publication on pyrite photophysics, and the important publication on establishing semiconductor-quality pyrite from Iron Range ilmenite. This will be accompanied by several presentations by the graduate students and U of M faculty involved in the project.

Status Update Reporting

Status Update September 1, 2024

Date Submitted: September 5, 2024

Date Approved: October 8, 2024

Overall Update

As noted in prior reports, this LCCMR/ENRTF project is in full flow; Leighton, Koester, and Frontiera (the primary U of M investigators) all have graduate research assistants appointed. In addition, Rao and Taguta at Duluth (who replaced Hudak due to retirement - see Project Amendment) have part of their time committed. With respect to Activity 1, as noted previously, Milestone A was comprehensively completed, resulting in a publication in the journal ACS Applied Materials and Interfaces of the American Chemical Society. Work on Milestones B, C, and D is now underway and substantial progress has been made with all three, as described below. In Activity 2, Milestone A is now close to completion and Milestone B is underway. Again, more details are provided below. Finally, with respect to Activity 3, we can now report that both Milestones A and B are complete. Milestone C may or may not be required, given how well the first two milestones progressed. Finally, Milestone D is now underway. Significant progress is thus being made in all project directions. While work towards a small number of milestones is behind, we are substantially ahead of the proposed timeline in other respects, especially Activity 3.

Activity 1

Milestone A on p-type pyrite is complete and published. Work in Leighton's lab is now focusing on Milestones B and D. Both of these are challenging and have moved into 2024. There are two very positive developments, however. First, a full study of control of electronic properties of pyrite with the n-type dopant cobalt is complete, and the corresponding publication should be submitted by the end of 2024. Second, Leighton's group have now successfully controlled the cooling rate after crystal growth to tune the sulfur vacancy density (and thus doping) in pyrite. This is another first, and it is likely that another paper can be generated in 2025. In Frontiera's lab, in parallel with this, work is progressing with Milestone C. They have used powerful resonance Raman methods to examine changes in the photovoltaic performance of pyrite across the solar spectrum. The results indicate that doping significantly alters Raman intensities, influencing the electron-phonon coupling and energetic dissipation within solar cells. Current efforts are focused on obtaining complementary absorption spectra and optical constants. These studies are breaking new ground in the understanding of how light absorption affects pyrite, and a significant scientific publication is likely to emerge.

Activity 2

In Activity 2, led by Koester, the focus thus far has been on Milestones A and B. Progress with A is very promising and encouraging. Lithographic processes to pattern electrical test structures are now well refined in both Koester's lab and at the Minnesota Nano Center, and device isolation strategies using both argon ion implantation and ionic gating are well underway. Ionic gating now appears easily the most promising route and is our primary focus. Essentially, we can use it to generate an isolation ring on the surface with near zero doping. This is an important step towards Milestone B, in which vertical electronic transport measurements through the depth of naturally formed pyrite p-n junctions are the focus. While the work in Activity 2 has proven challenging, we believe that by spring/summer 2025 Milestones A-C should have yielded to appropriate progress.

Activity 3

With Leighton, Rao and Taguta have identified the key factors for the economic/geological assessment of the potential of MN resources for the synthesis of semiconducting pyrite for energy applications. These include: Quantifying iron ore resources; assessing quality/purity for synthesis; determining associated mining and processing costs; accounting for purification costs; analyzing solar panel costs and market prices; comprehensive economic analysis; and sensitivity analyses. This work towards Milestone D is now underway, in parallel with Leighton's efforts with the scientific aspects

in Milestones A and B, both of which are now completed. Leighton's team now routinely reduces taconite- and ilmenite-derived hematite to iron and then use the product for single-crystal and thin-film pyrite production. Electron densities are as low 10 to the power 18 per centimeter cubed, easily low enough to obtain semiconducting behavior, constituting the first demonstration of the power of Iron Range resources for semiconducting applications. If the time scales match, we will combine this result with the economic geological assessment to write a paper on the whole issue, which will break entirely new ground in terms of resource usage in MN. Work in Activity 3 is thus progressing extremely well, ahead of schedule in several aspects.

Dissemination

The most significant item to report to date in terms of dissemination is the publication "Controlled p-type doping of Pyrite FeS2", B. Voigt, L. Stolik Valor, W. Moore, J.D. Jeremiason, J. Kakalios, E.S. Aydil, and C. Leighton, ACS Appl. Mater. Interfaces 15, 28258 (2023). This journal is a highly visible publication of the well-respected American Chemical Society. ENRTF and LCCMR are acknowledged as the primary funders of this work. See: https://pubs.acs.org/doi/10.1021/acsami.3c04662. This article has now been downloaded 778 times since publication, attracting four scientific citations already. The next publications likely to emerge from this work (in order) are on n-type doping of pyrite with cobalt (see Activity 1 above), synthesis of electronic-quality pyrite from Iron Range resources (see Activity 3 above), and control of sulfur vacancy doping by crystal growth cooling rate (see Activity 1 above).

Status Update Reporting

Status Update March 1, 2024

Date Submitted: March 1, 2024

Date Approved: April 2, 2024

Overall Update

As noted in the last progress reports, this project is in full flow; Leighton, Koester, and Frontiera (the primary U of M investigators) all have graduate research assistants appointed on the project. In addition, Rao and Mamun at Duluth (who replaced Hudak due to retirement - see recent Project Amendment) have time committed. With respect to our Activity 1, as noted in our last report, Milestone A was comprehensively completed, resulting in a publication in the journal ACS Applied Materials and Interfaces of the American Chemical Society. Work on Milestones B, C, and D is now underway simultaneously and substantial progress has been made with all three, as described later in this report. In Activity 2, Milestone A is now close to completion and Milestone B is underway. Again, more details are provided below. Finally, with respect to Activity 3, Milestone A is complete, Milestone B is progressing well ahead of the proposed timeline, and even Milestone D is now underway. Significant progress is thus being made in all main project directions. While work towards a small number of milestones is slightly behind, we are substantially ahead of the proposed timeline in other respects, especially in Activity 3.

Activity 1

With respect to Activity 1, as noted above, Milestone A on p-type pyrite is complete and published. Work in Leighton's lab is now focusing on Milestones B and D. As anticipated, both of these directions are challenging, and both have moved into the 2024 calendar year. In a very positive development, however, a full study of control of the electronic properties of pyrite with the n-type dopant cobalt is now nearing completion. It is likely that this could be the next publication to emerge from this work and we will update on this in the next report. In Frontiera's lab, in parallel with the above, work is progressing with Milestone C. In single-crystal pyrite with various precisely controlled doping levels, resonance Raman spectroscopy measurements have been performed and analysis of the excited state dynamics is underway. These studies are breaking entirely new ground in the understanding of how light absorption affects pyrite, and a scientific publication is likely to emerge in the longer term. In general, while the completion dates for the Milestones in Activity 1 were likely aggressive, the work itself is nevertheless progressing. Moreover, as detailed below, faster progress than expected is occurring in Activity 3, offsetting this.

Activity 2

In Activity 2, led by Koester, the focus thus far has been on Milestones A and B. Progress with A is very promising and encouraging. Lithographic processes to pattern electrical test structures are now well refined, and device isolation strategies using both argon ion implantation and ionic gating are well underway. We anticipate having important results in hand on both approaches within a matter of weeks. These are the first steps towards Milestone B, in which vertical electronic transport measurements of naturally formed p-n junctions will be performed. Plans for these are all well underway, involving the groups of both Koester and Leighton. It therefore remains possible that Milestone B will be at or near completion by the initially projected date of Summer 2024.

Activity 3

In Activity 3, Rao and Mamun (who replaced Hudak – see recent Project Amendment) are now fully engaged and have met with the team several times. Importantly, they have identified the key factors that need to be part of the economic/geological assessment of the potential of MN resources for the synthesis of semiconducting pyrite for energy applications. Specific steps they will take include: Quantifying iron ore resources; assessing quality and purity for pyrite synthesis; determining associated mining and processing costs; accounting for purification costs; analyzing solar panel costs and market prices; comprehensive economic analysis; and sensitivity analyses to key parameters. This work

towards Milestone D is thus now underway, in parallel with Leighton's efforts with the corresponding science in Milestones A and B. As described in our last report, Milestone A is completed; our team can now routinely reduce Iron Range samples to relatively high-purity iron. More excitingly, Milestone B is now well underway; both single crystals and thin films are being synthesized in the Leighton Lab, and we will be testing structural, chemical, and electronic properties in a matter of weeks. In totality, the work in Activity 3 is thus progressing extremely well, ahead of schedule in several aspects.

Dissemination

The most significant item to report to date in terms of dissemination is the publication "Controlled p-type doping of Pyrite FeS2", B. Voigt, L. Stolik Valor, W. Moore, J.D. Jeremiason, J. Kakalios, E.S. Aydil, and C. Leighton, ACS Appl. Mater. Interfaces 15, 28258 (2023). This journal is a highly visible publication of the well-respected American Chemical Society. ENRTF and LCCMR are acknowledged as the primary funders of this work. See: https://pubs.acs.org/doi/10.1021/acsami.3c04662. This article has now been downloaded 530 times since publication, attracting two scientific citations already. The next publications likely to emerge from this work are on n-type doping of pyrite with cobalt (see Activity 1 above) and the work on synthesis of electronic-quality pyrite from Iron Range resources (see Activity 3 above). The latter may or may not combine scientific/engineering research with economic/geological aspects, depending on how the two related threads progress over the coming months.

Status Update Reporting

Status Update September 1, 2023

Date Submitted: August 22, 2023

Date Approved: September 27, 2023

Overall Update

As noted in the last report, the project is in full flow; Leighton, Koester, and Frontiera all have graduate research assistants appointed on the project (Koester and Leighton are coadvising one, providing additional cohesion), and Hudak has part of his time committed. Since the last report, we are happy to update that Activity 1, Milestone A has been comprehensively completed, resulting in the submission, peer review, and publication of a paper in the high quality journal ACS Applied Materials and Interfaces (American Chemical Society). As noted below, activities in Milestones B and C are well underway. In Activity 2, Milestone A has yielded to progress, and we are optimistic that Milestone B will soon become a secondary focus. In Activity 3, Milestone A is now completed and we are well into Milestone B, with the first key results likely to be obtained in the next few months. We believe that completion of Milestone B would result in a second scientific publication from this project, likely to generate broad interest in terms of utilization of Iron Range resources in green energy technologies. Significant progress is thus being made in all main project directions.

Activity 1

Most significantly, Milestone A, driven by Leighton, has been achieved. Our last report mentioned the goal of submission of this work for publication by the current time, but in fact things moved ahead of schedule and the paper is now published. The paper reports detailed structural/chemical characterization of phosphorous-doped pyrite single crystals, along with the electronic transport and thermopower data needed to comprehensively prove p-type doping. This is the first demonstration of successful and controlled p-type doping of pyrite, opening up the possibility of homojunction solar cells in pyrite, which is key to our overall strategy. Leighton's team, working with Koester, have now moved on to Milestone B; the first experiments are underway, have already revealed some surprises, and should yield to major results in the coming weeks. In terms of Milestone C, Frontiera's group have performed resonance Raman intensity analysis of pyrite single crystals at various wavelengths. Rigorous quantitative analysis is underway to understand excited state energy surfaces, a key issue in the photophysics of pyrite for solar applications. Femtosecond stimulated Raman spectroscopy has also been done, but will likely require thin films rather than crystals; these can be provided by Leighton and the requisite work is underway.

Activity 2

Work on this Activity in this period again focused on Milestone A, seeking to isolate pyrite crystals electrically so that surface conduction can be negated and the true electronic properties of pyrite crystal homojunctions can be characterized. A student coadvised by Koester and Leighton has made significant progress with this. The initial attempts using beams of argon ions to bombard the surface are now understood to actually increase the n-type doping by forming sulfur vacancies. While this is not what we hoped to achieve, it is potentially a publishable result in its own right that this approach can be used to control sulfur vacancy doping; this was not previously known. Moving on, the student has developed all the lithography processes needed to fabricate devices and is now working on the alternative strategy of ion implantation. A detailed plan is in place to explore this strategy. We expect to have substantial results for the next progress report.

Activity 3

As noted in the last report, progress with Activity 3 has been highly encouraging. At this stage, Milestone A is now complete. The graduate student working with Leighton and Hudak has achieved reduction to high purity iron from both taconite and ilmenite processes, using samples direct from the MN Iron Range. The critical question now is whether pyrite crystals grown from these iron starting materials are pure enough to have workable electronic properties. Not all

impurities have deleterious effects on semiconducting behavior in pyrite, so this is an interesting science question. The first step in this work is single crystal pyrite growth from these iron samples, which is already underway. After that, we will perform characterization, impurity analyses, and the all-important electronic measurements. We expect to have significant data on this in the coming months, meaning that we are on track to complete Milestone B by the anticipated summer 2024 target date. Success in this endeavor would generate the important and generally interesting result that a new revenue stream for Iron Range resources exists, in green energy technologies.

Dissemination

The most significant item to report in terms of dissemination is the publication discussed above, which is: “Controlled p-type doping of Pyrite FeS2”, B. Voigt, L. Stolik Valor, W. Moore, J.D. Jeremiason, J. Kakalios, E.S. Aydil, and C. Leighton, ACS Appl. Mater. Interfaces 15 28258 (2023). This journal is a highly visible publication of the well-respected American Chemical Society. ENRTF and LCCMR are acknowledged as the primary funders of this work. See: https://pubs.acs.org/doi/10.1021/acsami.3c04662. Beyond this, in addition to the two presentations reported in our last update (by Leighton and Hudak), graduate student Shahzad Alam, from Frontiera's group, received a notable award for his work in this reporting period, at the U of M's Chemistry Graduate Student Research Symposium. As alluded to above, the next publications likely to emerge from this project are on pyrite crystals from Iron Range resources, control of surface electronic properties in FeS2, and photophysics in FeS2, driven by Leighton, Koester, and Frontiera, respectively, but performed collaboratively in each case.

Status Update Reporting

Status Update March 1, 2023

Date Submitted: February 27, 2023

Date Approved: March 24, 2023

Overall Update

The project is now in full flow. Leighton, Koester, and Frontiera now all have graduate research assistants appointed on the project (Koester and Leighton are also coadvising one, providing additional cohesion in the project), and Hudak has part of his time committed. Progress has been made with all three activities. Particular progress has been made with: Activity 1, Milestones A and C; Activity 2, Milestone A; and Activity 3, Milestones A and B. Significantly, the progress with Activity 1, Milestone A has been so substantial that a scientific publication is already being written. We expect that this should have been submitted by the next report (September 2023). In addition, Activity 3, Milestone A needs some amount of further refinement, but is now essentially complete. The work in that Activity has moved on to Milestone B; success in that direction would result in additional publications and presentations. Significant progress is thus being made in all main directions, working towards a demonstration homojunction solar cell made from pyrite FeS2.

Activity 1

As noted above, the focus in the initial stages of the project has been on Milestones A and C. In Milestone A, Leighton's work to establish phosphorous as a working p-type dopant in pyrite FeS2 has been fruitful. Phosphorous doping works well in single crystals and we now have structural characterization, a large quantity of electronic transport data, and thermopower data to support this. The entire story is very complete and is currently in the early stages of preparation for publication. This publication will be significant; this is the first demonstration of successful and controlled p-type doping of pyrite, which opens up the possibility of homojunction solar cells in pyrite, which are key to our overall strategy. By the next report, we hope to have this work submitted for publication in a high-quality refereed journal. In terms of Milestone, C, Frontiera has now performed resonance Raman measurements and femtosecond stimulated Raman on a variety of pyrite crystals with varying doping. These experiments are designed to understand the photophysics and energy dissipation on ultrafast timescales, with the goal of determining how structure impacts function in pyrite solar cells.

Activity 2

In this period, the work on this Activity has focused on Milestone A, seeking to isolate pyrite crystals electrically so that surface conduction can be negated and the true electronic properties of pyrite crystal homojunctions can be characterized. A student coadvised by Koester and Leighton is attempting this by using argon ion beams to modify the surface. The argon ion etch rate has been determined, and the temperature dependence of the resistance has been studied before and after argon ion exposure. Highly encouragingly, after ion milling, a significant change is observed in resistance vs. temperature. Specifically, the surface barrier effect usually observed in the pyrite crystals is absent after ion etching, which is the desired effect, showing that device isolation should be possible. Several other interesting changes in electronic properties are also observed, and are under current study. The significance of these advances is that they open a path to measuring the electrical properties of pyrite homojunctions, an essential step towards solar cells.

Activity 3

Progress with Activity 3 has been highly encouraging. Working towards Milestone A, Leighton and Hudak have collaborated to first characterize the crystal structure and purity of a variety of hematite samples from not only the established taconite process but also the emerging ilmenite process. These samples were taken directly from the MN Iron Range. Encouragingly, Leighton has established that: (a) the phase purity of these samples is really quite high, especially from the ilmenite process, and (b) that reduction to iron metal is relatively facile in safe (low-hydrogen-

content) “forming gas”. The student working on this project needs to establish some final details, but Milestone A is now more or less complete. We have thus moved on to Milestone B. We are confident that pyrite crystals can be grown from these materials but the central question is the purity level and electronic doping of these crystals. Success with this Milestone would be a truly notable achievement: Establishment of a route to a high-quality semiconductor from MN Iron Range resources.

Dissemination

As noted above, the most significant thing to report in this category is the preparation of the first paper from this award, which we hope to have submitted by the next report. In addition, Leighton gave a presentation on this project to a large group of faculty and administrators in the College of Science and Engineering at the University of Minnesota earlier this month. This meeting was focused on “Sustainability”. Additionally, Hudak delivered a presentation covering this work recently: G. Hudak, J.Chen, M. Mlinar, A. Halim, S. Rao, V. Lakshmanan, S. Monson Geerts, R. Sridhar and E. Gluck, “Recent Results of Hydrometallurgical Processing of an Oxide-Bearing Critical Mineral Deposit in NE Minnesota”, Southern Minnesota Subsection of the Society for Mining, Metallurgy, and Exploration, November 2022.