Environment and Natural Resources Trust Fund

M.L. 2022 Approved Work Plan

General Information

ID Number: 2022-180

Staff Lead: Becca Nash

Date this document submitted to LCCMR: June 9, 2022

Project Title: Green Solar Cells from a Minnesota Natural Resource

Project Budget: $673,000

Project Manager Information

Name: Chris Leighton

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Project Reporting

Date Work Plan Approved by LCCMR: June 27, 2022

Reporting Schedule: March 1 / September 1 of each year.

Project Completion: June 30, 2025

Final Report Due Date: August 14, 2025

Legal Information

Legal Citation: M.L. 2022, Chp. 94, Art. , Sec. 2, Subd. 07a

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.

Appropriation End Date: June 30, 2025

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
B. Exploration of ultralow-sulfur-vacancy-density pyrite	June 30, 2023
C. Photophysics studies of n- and p-type pyrite	June 30, 2023
D. Control of the S vacancy energy level in pyrite	December 31, 2023
E. Photophysics studies of pyrite p-n homojunctions	December 31, 2023

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)	June 30, 2023

B. Electrical testing of p-n homojunctions	June 30, 2024
C. Solar cell testing of p-n homojunctions	June 30, 2025
D. Translation from single-crystal to thin-film devices	June 30, 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	December 31, 2024
D. Geologic/materials/natural-resource-science-based assessment of feasibility	June 30, 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

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
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		$151,764
Co-Investigator		George Hudak, co-Investigator			26.7%	0.27		$49,874
							Sub Total	**$574,060**
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
							Sub Total	**$49,470**
Equipment, Tools, and Supplies								
	Tools and Supplies	Lab materials and supplies	Purchase of standard lab materials and supplies (chemicals, gases, glassware, etc.)					$49,470
							Sub Total	**$49,470**

Capital Expenditures								
							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**

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
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)....

Optional Attachments

Support Letter or 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

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 agree travel expenses must 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, or sale of products and assets?

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

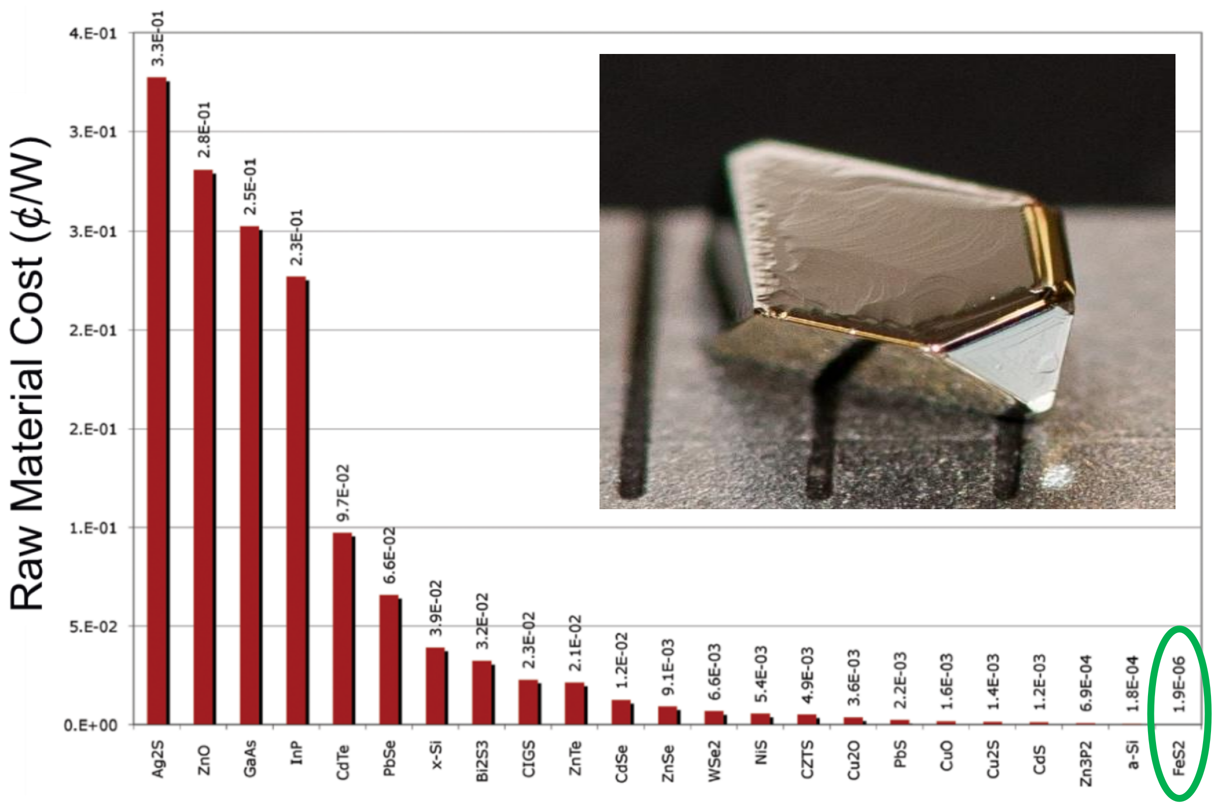

Figure 1: Estimated materials costs (¢ per Watt of power) to produce solar cells at large scale from various photovoltaics. Note iron disulfide (circled green) with 100-times lower cost than its nearest competitor and 10,000-times lower cost than crystalline silicon (from Wadia *et al*., *Environ. Sci. Technol*. **43**, 2072 (2009)). Crystalline Si, the type used in commercial solar cells, is shown here as "x-Si". **Inset:** Synthetic University of Minnesota photovoltaic pyrite crystal.

Figure 2: Left: Sulfur stockpile in Vancouver harbor, Canada. Sulfur is a waste by-product of oil refinement, is thus stockpiled in vast quantities worldwide, and has very low value. **Right:** The MN Mesabi Iron Range. Augmented with capacity from MI, this resource produces approximately 98% of the iron ore used in US steel production.