M.L. 2014 Project Abstract
For the Period Ending June 30, 2017

PROJECT TITLE: Solar Cell Materials from Sulfur and Common Metals
PROJECT MANAGER: Lee Penn and Eray Aydil
AFFILIATION: University of MN – Twin Cities ; Department of Chemistry
Mailing Address: 207 Pleasant St. SE
City/State/Zip Code: Minneapolis, MN 55455
Telephone Number: 612 626 4680
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FUNDING SOURCE: Environment and Natural Resources Trust Fund
LEGAL CITATION: M.L. 2014, Chp. 226, Sec. 2, Subd. 08a

APPROPRIATION AMOUNT: $494,000
AMOUNT SPENT: $476,496
AMOUNT REMAINING: $17,504

Overall Project Outcomes and Results

We successfully synthesized the proposed transition metal sulfide materials with controlled composition. Preparing materials without impurities, which essential for success since impurities in the thin film of light absorbing material will cause solar cells to fail, was particularly challenging. We identified which synthetic variables are most important for preventing impurities. In addition, we can successfully control particle size, which is important for making high quality thin films of these materials. We developed a reproducible protocol for preparing thin films of the particles. We examined effects of annealing conditions (sulfur partial pressure, heating rate, heating time, pre-annealing compaction, the nature of the molybdenum layer beneath the CZTS particles, and more) on the CZTS films and were able to identify ideal conditions for the necessary annealing step.

A particularly exciting outcome was the development of a protocol for removing impurities from the thin films. During the annealing step, impurities often form even when the thin films are prepared using pure material. To solve this problem, we developed a selective etching method that effectively removes those impurities ("Selective Etching of Light Absorber Substrates", Application No. 62/328,851, which was filed April 28, 2016 but did not proceed to patent status).

Our biggest outcome expected was a fundamental advance in our ability to make high quality thin films of photovoltaic quality CZTS, and we did succeed in that regard. High quality thin films are required for the fabrication of high performing solar cells. In addition, we developed a green synthetic method for the controlled production of CZTS nanoparticles and can prepare high quality, microcrystalline thin films on conductive substrates using the microwave synthesis method. Unfortunately, we did not realize our final goal, which was to make a prototype solar cell fabricated using the aforementioned materials.

Project Results Use and Dissemination

We have published three papers in the peer-reviewed literature describing our results and two additional papers that are currently in review with scientific journals.

Unfortunately, Application No. 62/328,851, which was filed April 28, 2016, did not proceed to patent status. Our technology would have been used in the production of both copper indium gallium disulfide

(CIGS) and copper zinc tin sulfide (CZTS) thin film solar cells. The changing solar cell market landscape and continued significant dominance of silicon solar cells over CIGS and CZTS devalued our technology despite its green advantages. Silicon solar cells now dominate over 90% of the solar cell market. Moreover, the provisional patent application was returned with objections and to narrow the claims. Continuing the patent application for these reasons did not make economic sense.

Environment and Natural Resources Trust Fund (ENRTF) M.L. 2014 Work Plan

Date of Report: 30 January 2019

Date of Next Status Update Report: final report

Date of Work Plan Approval: 4 June 2014

Project Completion Date: 30 June 2017

Does this submission include an amendment request? no

PROJECT TITLE: Solar Cell Materials from Sulfur and Common Metals

Project Manager: Lee Penn and Eray Aydil

Organization: Univerisity of MN – Twin Cities ; Department of Chemistry

Mailing Address: 207 Pleasant St. SE

City/State/Zip Code: Minneapolis, MN 55455

Telephone Number: 612 626 4680

Email Address: rleepenn@umn.edu

Web Address: http://www.chem.umn.edu/groups/penn/

Location: Hennepin County (Univerisity of MN – Twin Cities ; Department of Chemistry and Department of Chemical Engineering and Materials Science); anticipated impact is expected to be at the statewide level.

Total ENRTF Project Budget:	**ENRTF Appropriation:**	**$494,000**
	Amount Spent:	**$476,496**
	Balance:	**$ 17,504**

Legal Citation: M.L. 2014, Chp. 226, Sec. 2, Subd. 08a

Appropriation Language:
$494,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota to develop solar cell materials using nontoxic and common metals combined with sulfur. This appropriation is subject to Minnesota Statutes, section 116P.10. This appropriation is available until June 30, 2017, by which time the project must be completed and final products delivered.

I. PROJECT TITLE: Solar Cell Materials from Sulfur and Common Metals

II. PROJECT STATEMENT:

Safe and clean energy production is a grand challenge facing our society. The development of sustainable electrical energy sources is an urgent need in the state of Minnesota and in the United States. Solar energy is renewable and is a viable and attractive option. To become commonplace, solar cells must be inexpensive and robust, and they must be comprised of abundant, cheap, nontoxic materials. We propose to develop innovative methodology for producing thin films of metal sulfides for use in solar cells. Instead of using toxic elements like cadmium, we propose to use iron, copper, and other far less toxic metals combined with sulfide. By targeting sulfides for use in solar cells, sulfur waste from mining and other industrial operations could become a viable resource in the production of robust and inexpensive solar cells. Finally, we propose to exploit microwave energy so as to reduce the energy required to produce photovoltaic quality materials.

We aim to develop a method for producing CZTS, for example, with the high efficiencies required for realistic implementation of the affordable photovoltaic devices but without the hazards associated with using rare and/or toxic elements and other source materials.

The biggest outcome expected is a fundamental advance in our ability to make high quality thin films of photovoltaic quality CZTS.

Major Results Expected:

1. Generalized, green synthetic methods for the controlled production of kesterite nanoparticles.
2. Successful methods for preparation of high quality, microcrystalline thin films directly onto conductive substrates using the microwave synthesis method.
3. Prototype solar cell fabricated using promising candidate materials.

Deliverables: Open scientific presentations and papers addressing the above objectives; patents for methods to produce photovoltaic quality thin films of CZTS using our new method.

III. PROJECT STATUS UPDATES:

Project Status as of January 1, 2015: Two researchers are working on the project: Dr. Seung Wook Shin and Mr. Alex Pinto. The research-grade microwave has been purchased and installed, and the instrument is performing well. We have successfully synthesized transition metal sulfide materials, but a particular challenge is preparing materials without impurities. Impurities will cause solar cells to fail. We have determined which synthetic variables are most important for preventing the formation of impurities. We have also made progress in controlling particle size as well as controlling the stoichiometry of the resultant materials, with the ideal stoichiometry somewhat copper deficient. Both researchers have received the necessary training to effectively synthesize and characterize materials.

Amendment Request (December 29, 2014):

Due to accounting office schedules, the winter project report due dates are requested to occur on January 15, 2016 and January 15, 2017.

Approved by the LCCMR January 7, 2015.

Amendment Request (January 5, 2015):

Request transfer of $466 from Equipment/Tools/Supplies to Capital Expenditures.

Approved by the LCCMR January 7, 2015.

Project Status as of July 1, 2015: Two researchers continue on the project: Dr. Seung Wook Shin and Mr. Alex Pinto. We have successfully synthesized transition metal sulfide materials, and we can control the mixture of phases produced. However, a continuing challenge is preparing materials without impurities, which will cause solar cells to fail. We have further refined the synthetic conditions so as to prevent the formation of impurities and eliminate the need for surfactants. Even more importantly, we have developed a selective etching method that removes key impurities. We have achieved substantial control over the stoichiometry of the transition metal sulfides, with preparation of phase-pure materials containing differing amounts of copper, zinc, cobalt, tin, iron, sulfur, and selenium. Preparation of thin films of the transition metal sulfides has begun, with careful characterization before and after annealing.

Amendment Request (January 14, 2016):

We request a retroactive transfer of $3,462 from Repairs and Maintenance ($1,864 from activity 1 and $1,568 from activity 2) and moving forward a transfer of $22,000 from personnel into User Fees for instrumentation. Materials characterization is essential to the success of our proposed work. We have had excellent success producing materials with controlled stoichiometry and the work involving the preparation of thin films is also proceeding with great success. Our productivity has lead to a higher than expected number of samples requiring materials characterization for progress on this project. The user fees pay for the use of techniques such as transmission electron microscopy and Raman spectroscopy.

Amendment approved by LCCMR 1-25-2016

Project Status as of January 15, 2016: Two researchers continue on the project: Dr. Seung Wook Shin and Mr. Alex Pinto. We have successfully synthesized transition metal sulfide materials, and we can control the mixture of phases produced. We have addressed the challenge of preparing materials without impurities, which cause solar cells to fail. We have refined the synthetic conditions so as to prevent the formation of impurities and eliminate the need for surfactants. We have achieved substantial control over the stoichiometry of the transition metal sulfides, with successful preparation of phase-pure materials containing differing amounts of copper, zinc, cobalt, tin, iron, sulfur, and selenium. Preparation of thin films of the transition metal sulfides is in full swing, with careful characterization before and after annealing. During annealing, impurities sometimes form. Importantly, we have refined the selective etching method developed in the previous cycle. The method effectively removes those key impurities while leaving the mixed transition metal sulfide intact, and we are in the process of filing a patent on the process.

Project Status as of July 1, 2016: Two researchers continue on the project: Dr. Seung Wook Shin and Mr. Alex Pinto. Our synthetic conditions enable us to avoid the use of surfactants, which results in higher quality thin films of the transition metal sulfides. We have achieved substantial control over the stoichiometry of the transition metal sulfides, with successful preparation of phase-pure materials containing differing amounts of copper, zinc, cobalt, tin, iron, sulfur, and selenium. Our methods for preparing thin films of the transition metal sulfides are improving, and results from careful characterization before and after annealing demonstrate that the quality of the thin films is sensitive to sodium ion concentration as well as the temperature at which the films are annealed. During annealing, impurities sometimes form, and the selective etching method effectively removes those impurities ("Selective Etching of Light Absorber Substrates", Application No. 62/328,851. Filed April 28, 2016). In addition, a research article was submitted to *Green Chemistry*, and the paper is currently in revision. This paper reports on the experimental results demonstrating the efficacy of the selective etching process. Finally, a research article describing synthetic results is currently in review with *Inorganic Chemistry*.

Amendment Request (January 13, 2017):

We request a retroactive transfer of $13,774 from Personnel and moving forward an additional transfer of $20,000 from personnel into User Fees for instrumentation. Materials characterization is essential to the success of our proposed work. We have had excellent success producing materials and thin films but require additional materials characterization in order to obtain data to facilitate further refinement of the thin film methods. The user fees pay for the use of techniques such as transmission electron microscopy and Raman spectroscopy at the University of Minnesota Characterization Facility. Our higher-than-anticipated productivity means that we can decrease funds in the personnel category without compromising project aims.

Amendment Approved by LCCMR 1/30/2017

Project Status as of January 15, 2017: Two researchers continue on the project: Dr. Seung Wook Shin and Mr. Alex Pinto. We have spent substantial effort examining the effects of annealing conditions (sulfur partial pressure, heating rate, heating time, pre-annealing compaction, the nature of the molybdenum layer beneath the CZTS particles, and more) on the CZTS films. During annealing, impurities sometimes form, and the selective etching method effectively removes those impurities ("Selective Etching of Light Absorber Substrates", Application No. 62/328,851, which was filed April 28, 2016). An important result of ongoing research has been refining the etching process so that we can remove the impurity phases. In addition, a research article was submitted to *Green Chemistry*, and the paper is currently in revision. Finally, the research article submitted to *Inorganic Chemistry* that describes synthetic results is currently in revision.

Amendment Request (January 13, 2018):

We request a retroactive transfer of $2,450 from User Fees for instrumentation into personnel. We spent $2,450 more than anticipated with our amendment of January 2017 and substantially less than the $20,000 that had been transferred into the area of User Fees for instrumentation.

Overall Project Outcomes and Results: We successfully synthesized transition metal sulfide materials with controlled composition. A particular challenge was preparing materials without impurities, which essential for success since impurities in the thin film of light absorbing material will cause solar cells to fail. We determined which synthetic variables are most important for preventing the formation of impurities. We can successfully control particle size and composition of the resultant materials. We have established a reproducible protocol for preparing thin films of the CZTS particles. We examined effects of annealing conditions (sulfur partial pressure, heating rate, heating time, pre-annealing compaction, the nature of the molybdenum layer beneath the CZTS particles, and more) on the CZTS films and were able to identify ideal conditions for the necessary annealing step. During annealing, impurities sometimes form, and the selective etching method effectively removes those impurities ("Selective Etching of Light Absorber Substrates", Application No. 62/328,851, which was filed April 28, 2016 but did not proceed to patent status). Our biggest outcome expected was a fundamental advance in our ability to make high quality thin films of photovoltaic quality CZTS, and we did succeed in that regard. High quality thin films are required for the fabrication of high performing solar cells. We developed a green synthetic method for the controlled production of CZTS nanoparticles and can prepare high quality, microcrystalline thin films on conductive substrates using the microwave synthesis method. Unfortunately, we did not realize our final goal, which was to make a prototype solar cell fabricated using the aforementioned materials.

We have published three papers in the peer-reviewed literature describing our results.

Pinto, A.H., S.W. Shin, E.S. Aydil, and R.L. Penn, "Selective removal of Cu2-x(S,Se) phases from Cu2ZnSn(S,Se)(4) thin films," Green Chemistry, 18, 5814-5821 (2016).

Pinto, A.H., S.W. Shin, E. Isaac, T. R. Knutson, E.S. Aydil, and R.L. Penn, “Controlling Cu2ZnSnS4 (CZTS) phase in microwave solvothermal synthesis” Journal of Materials Chemistry A, 5, 23179-23189 (2017).

Pinto, A.H., S.W. Shin, A. Sharma, R.L. Penn, and E.S. Aydil, "Synthesis of Cu2(Zn1-xCox)SnS4 Nanocrystals and Formation of Polycrystalline Thin Films from Their Aqueous Dispersions" Journal of Materials Chemistry A (Manuscript ID: TA-ART-07-2017-006295.R1) Status – In Press.

In addition, we have two additional papers that are currently in review with scientific journals.

Unfortunately, Application No. 62/328,851, which was filed April 28, 2016, did not proceed to patent status. Our technology would have been used in the production of both copper indium gallium disulfide (CIGS) and copper zinc tin sulfide (CZTS) thin film solar cells. The changing solar cell market landscape and continued significant dominance of silicon solar cells over CIGS and CZTS devalued our technology despite its green advantages. Silicon solar cells now dominate over 90% of the solar cell market. Moreover, the provisional patent application was returned with objections and to narrow the claims. Continuing the patent application for these reasons did not make economic sense.

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: *Develop synthetic process using sulfur, common metals, and a microwave-based method for producing mixed metal sulfides*

Description: Using Nature as a guide and applying eight of the twelve principles of Green Chemistry, we will develop a rational approach to the green synthesis of CZTS thin films with properties ideal for incorporation into advanced technologies. Critical control parameters include the degree to which the material is nonstoiciometric (e.g., some degree of Cu deficiency is good from the perspective of electrical and optical properties), crystal size (i.e., hundreds of nanometers for the best photovoltaic properties), and defects (concentration, type, and distribution).

Using less toxic metals in combination with sulfur, we will develop methods for producing nanoparticles composed of common and less toxic elements. Systematic experiments will use metal salts in combination with sulfur sources in order to determine the best synthetic conditions for phase pure product. These experiments will enable development of a general synthetic procedure for producing pure materials that will have excellent performance in solar cells. Using microwaves will enable both faster production and dramatically reduced energy requirements.

The products of the above syntheses will be characterized using four primary methods: X-ray diffraction (XRD), Raman Spectroscopy, Scanning Transmission Electron Microscopy (STEM) with Electron Energy Loss Spectroscopy (EELS) and Energy Dispersive Spectroscopy (EDS), and UV-Vis Spectroscopy. XRD will enable quick determination if the material synthesized has a structure that is consistent with the kesterite structure and whether impurities of quite different structures (e.g., oxides or other sulfide structures) are present. In kesterites, it has been found that the S sublattice determines the unit cell dimensions. Consequently, it is difficult to identify and distinguish different kesterites based on XRD alone. Raman spectra are sensitive to the metal cations, making Raman spectroscopy a sensitive characterization method for kesterites. Thus, Raman spectroscopy will be the second technique employed. For materials that look promising by XRD and Raman spectroscopic characterization, UV-Vis spectroscopy will be used to determine the band gap of the material using methods well established in our laboratories. Finally, STEM with EELS and/or EDS will be employed to determine whether the elements are distributed homogeneously or heterogeneously.

Materials will be tested using established methods in order to predict performance in solar cell applications.

Summary Budget Information for Activity 1:	**ENRTF Budget:**	$ **241,568**
	Amount Spent:	**$ 241,568**
	Balance:	**0**

Completion Date: *Spring 2016*

Outcome	**Completion Date**	**Budget**
1. . Develop effective synthetic methods for pure transition metal sulfides	Summer 2015	$140,000
2. Preparation of photovoltaic quality materials and extensive testing	Spring 2016	$ 101,568

Activity Status as of January 1, 2015: We have made solid progress towards developing a green synthesis of metal sulfides with controlled particle size and stoichiometry. We have successfully synthesized phase-pure transition metal sulfide materials. A particular challenge is preparing materials without impurities. We have determined which synthetic variables are most important for preventing the formation of impurities since impurities will catastrophically impact the solar cells fabricated. We have also made progress in controlling particle size as well as controlling the stoichiometry of the resultant materials. Both researchers have received the necessary training to effectively synthesize and characterize materials.Several phase-pure transition metal sulfides have been successfully synthesized. Results demonstrate that the oft added ethylenediamine, which is a hazardous chemical, is not a necessary additive to produce phase-pure materials. Rather, pH is the important control parameter. A combination of hydrothermal, which avoids the use of toxic solvents, and microwave processing has been employed. Microwave processing results in high quality materials in minutes rather than hours.

Products of syntheses have been characterized using X-ray diffraction (XRD), Raman Spectroscopy, Transmission and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (EDS), and UV-Vis Spectroscopy. XRD results demonstrate phase pure material in the case of the cobalt iron sulfides. In the case of CZTS, a combination of results obtained using Raman spectroscopy and XRD demonstrate that we can prepare CZTS in both the wurtzite structure and in the kesterite structure. This is important because the preparation of thin films from wurtzite CZTS may enable the production of better thin films. EDS, which enables quantitatation of the composition of the produced materials demonstrates that we are improving our control over stoichiometry, with experiments aimed at producing copper deficient CZTS currently in progress.

The two researchers on the project have received training in standard operating procedures, safety protocols, and the synthesis and characterization methods to undertake the project. The tools required for annealing samples in the presence of sulfur vapor are now in place and have been tested using CZTS nanoparticles. The research-grade microwave has been purchased and installed, and the instrument is performing well.

Activity Status as of July 1, 2015: We are refining our green synthesis of metal sulfides with controlled particle size and stoichiometry. We have successfully synthesized phase-pure transition metal sulfide materials with controlled stoichiometry. We have achieved substantially improved control over the stoichiometry of the resultant materials. EDS enables quantitatation of the composition of the produced materials, and results demonstrate improved control over stoichiometry, with experiments aimed at producing copper deficient CZTS currently in progress. Microwave processing continues to produce superior materials in minutes rather than hours.

During the previous period, a combination of results obtained using Raman spectroscopy and XRD demonstrated that we can prepare CZTS in both the wurtzite structure and in the kesterite structure. This is important because the preparation of thin films from wurtzite CZTS may enable the production of better thin films. Now, we have learned how to control the phase composition of the CZTS produced from the reaction mixture. Key control parameters are the molar ratio of the sulfur source to the total metal cations added as well as the oxidation state of the tin ions.

A particular challenge is preparing materials without impurities. We have determined which synthetic variables are most important for preventing the formation of impurities since impurities will catastrophically impact the solar cells fabricated. However, we have developed a procedure for selective removal of key impurities – most notably – copper sulfide. A combination of mercapto ethanol and ethylenediamine results in the selective dissolution of the copper sulfide, which is one of the most problematic impurities, but leaves the CZTS intact. This is a major step forward and will enable preparation of improved thin films.

Activity Status as of January 15, 2016: We have further improved our control over the stoichiometry of materials produced using the microwave method. Microwave processing continues to produce superior materials in minutes rather than hours. During the previous period, we demonstrated control over the phase of the product material, and we have successfully used those results to produce materials in larger quantities for use in preparing thin films.

The selective etching method has been put to the test, and we have demonstrated that the method effectively removes binary compounds (e.g., copper sulfide or tin sulfide) from the product material without significant loss of the desired mixed metal sulfide. Detailed characterization using EDS demonstrates that the method leaves the desired mixed metal sulfide intact.

A manuscript describing the etching process is currently in preparation. A manuscript describing our improved control over the stoichiometry of materials produced using the microwave method is currently in preparation. Both will be submitted to peer-reivewed scientific journals. Finally, a patent describing the selective etching of Cu sulfide and selenide impurities from CZTSSe thin films is currently in progress (Provisional Patent Application - OTC Case 20160046).

Activity Status as of July 1, 2016: Results from activity 1 are being applied to work in activity 2. The synthetic methods enable production of materials for the preparation of thin films, which is the focus of activity 2. The patent application describing the selective etching of Cu sulfide and selenide impurities from the thin films has been filed ("Selective Etching of Light Absorber Substrates", Application No. 62/328,851. Filed April 28, 2016). In addition, a research article was submitted to *Green Chemistry*, and the paper is currently in revision. This paper reports on the experimental results demonstrating the efficacy of the selective etching process. Finally, a research article describing synthetic results is currently in review with *Inorganic Chemistry*.

Activity Status as of January 15, 2017: Results from activity 1 are being applied to work in activity 2. The synthetic methods enable production of materials for the preparation of thin films, which is the focus of activity 2.

Final Report Summary: Results from activity 1 were successfully applied to work in activity 2. The synthetic methods enabled production of materials for the preparation of thin films, which was the focus of activity 2.

ACTIVITY 2: *Preparation of Thin films*
In order to prepare solar cells, the material must be made into a high quality thin film. The above methods will be adapted to enable production of thin films of metal sulfides on both rigid and flexible materials. Using the synthetic conditions determined from the above work, thin films will be synthesized directly onto conductive substrates. Important properties include an ideal thickness of on the order of 2 microns, a grain size in the range of hundreds of nanometers, and phase purity. Synthetic conditions may have to be modified in order to achieve these goals with a thin film. A major goal is to retain the low energy requirements and directly synthesize thin films that are pure, have excellent particle size, and optimal properties for use in solar cells.

Microwave heating of a conductive material submerged in a solution results in preferential heating of the conductive material while leaving the surrounding solution comparatively cool. We will exploit this effect in order to directly coat substrates with CZTS. Results from the work described above, in which CZTS is synthesized by precipitation from the solution phase, will inform the experimental design for the controlled synthesis of CZTS onto conductive substrates. In fact, we have successfully prepared CZTS thin films by submerging substrates coated with conductive material into metal precursor solutions. When the microwave energy is absorbed strongly by the thin conductive coating, its temperature increases enough to deposit films exclusively onto the conductive layer, leaving the uncoated portions of the substrate CZTS-free and the surrounding solution free of precipitates. To date, resulting films are approximately 1-3 microns thick, which is a suitable thickness for use as a photovoltaic material. However, the crystal size is ca. ten nanometers in diameter, which is not large enough.

In addition, the ideal crystal size is hundreds of nanometers for the best photovoltaic properties. Post-deposition microwave annealing in neat solvent increased crystallite volume by eightfold, but this has only resulted in increasing the average crystal size to a few tens of nanometers. When nanocrystalline CZTS films are annealed in sulfur gas at high temperature (ca. 500 °C), substantial grain growth is achieved (results in the Aydil lab). At typical annealing temperatures, the S exists as vapor, and we have developed strategies to avoid S condensation on the films. Sintering and Ostwald ripening occur simultaneously, which results in substantial grain growth to sizes in the 0.5-2 µm size range. Here, we propose to tuning solution conditions during the microwave anneal step (see below) in order to achieve the larger size needed for the best photovoltaic properties. Experimental variables include the solvent properties and the solubility of S-bearing species in that solvent. Employing microwaves will enable drastic reduction in the energy required to anneal the films and may enable the use of flexible substrates.

The CZTS films will be annealed using the microwave approach, in which the sample is placed in a solution prepared using the target solvent and elemental sulfur or sulfur-containing molecules and exposed to microwaves so as to preferentially heat the underlying conductive layer and the CZTS film. In addition, CZTS films will be annealed using the more conventional high temperature approach, in which the sample is sealed into an ampule containing elemental sulfur or H2S gas and heated to high temperature, for comparison. Films will be characterized using the techniques described below. We hypothesize that employing a solvent in which CZTS is sparingly soluble but sulfur is moderately soluble will enable improved annealing so as to achieve the necessary crystal size (i.e., hundreds of nanometers).

The thin films produced will be characterized using four primary methods: X-ray diffraction (XRD), Raman Spectroscopy, Scanning Transmission Electron Microscopy (STEM) with Electron Energy Loss Spectroscopy (EELS) and Energy Dispersive Spectroscopy (EDS), and UV-Vis Spectroscopy.

Summary Budget Information for Activity 2: **ENRTF Budget:** $ **252,432**
Amount Spent: **$ 177,867**
Balance: **$ 17,504**

Completion Date: *Summer 2017*

Outcome	Completion Date	Budget
1. Photovolatic quality thin films combined with extensive testing	Summer 2017	$ 154,000
2. Data synthesis, reporting, and recommendations	Summer 2017	$ 98,432

Activity Status as of January 1, 2015: None to date.

Activity Status as of July 1, 2015: None to date.

Activity Status as of January 15, 2016: We have begun to prepare thin films using product materials. An important step in preparing high quality films is annealing in order to produce films suitable for use in a photovoltaic device. Thus far, the microwave annealing approach has not produced satisfactory results. However, annealing the thin films in sealed ampules containing elemental sulfur has proven very successful. Unfortunately, impurities such as copper sulfide sometimes form. We have applied the selective etching method to thin films with good success. The method is similar to what is described in Activity 1 except that the thin film is dipped directly into the etching solution. Characterization demonstrates that the thin film remains intact as the copper sulfide impurity is removed. We are currently preparing a manuscript describing the results for publication, and a patent describing the selective etching of Cu sulfide and selenide impurities from CZTSSe thin films is currently in progress (Provisional Patent Application - OTC Case 20160046).

Activity Status as of July 15, 2016: Work refining our methods for preparing thin films continues. Work from activity 1 means that we have good materials to use in the preparation of the thin films. Critical variables include how films are compressed prior to annealing, the amount of sodium added, and annealing temperature. The best films will have crystallites with sizes in the micron range and no cracks. In addition, the molybdenum layer onto which the film is deposited must be preserved, and we have made progress in finding conditions that minimize the formation of a thick MoS_2 layer. The etching method is effective in removing copper sulfide impurities from thin films, and work continues to refine the method for further improvement. In addition, films subjected to the etching process will be tested for impact on properties related to solar cell performance.

Activity Status as of January 1, 2017: We have spent substantial effort examining the effects of annealing conditions (sulfur partial pressure, heating rate, heating time, pre-annealing compaction, the nature of the molybdenum layer beneath the CZTS particles, and more) on the CZTS films. During annealing, impurities sometimes form, and the selective etching method effectively removes those impurities ("Selective Etching of Light Absorber Substrates", Application No. 62/328,851, which was filed April 28, 2016). An important result of ongoing research has been refining the etching process so that we can remove the impurity phases. An additional challenge is that some conditions result in the CZTS thin film peeling away from the underlying substrate, which makes the thin film unsuitable for use in a solar cell. We continue experiments to attempt to solve this problem. Finally, we are completing the preparation of scientific reports for submission to the peer-reviewed scientific literature.

Final Report Summary: We established a reproducible protocol for preparing thin films of the CZTS particles. We examined effects of annealing conditions (sulfur partial pressure, heating rate, heating time, pre-annealing compaction, the nature of the molybdenum layer beneath the CZTS particles, and more) on the CZTS films and were able to identify ideal conditions for the necessary annealing step. During annealing, impurities sometimes form, and the selective etching method effectively removes those impurities ("Selective Etching of Light Absorber Substrates", Application No. 62/328,851, which was filed April 28, 2016 but has not proceeded to patent status). Our biggest outcome expected was a fundamental advance in our ability to make high quality thin films of photovoltaic quality CZTS, and we did succeed in that regard. We developed a green synthetic method for the controlled production of CZTS nanoparticles and can prepare high quality, microcrystalline thin films on conductive substrates using the microwave synthesis method. Unfortunately, we did not realize our final goal, which was to make a prototype solar cell fabricated using the aforementioned materials.

V. DISSEMINATION:

Description: Open scientific presentations and papers addressing the above objectives; patents for methods to produce photovoltaic quality thin films of CZTS using our new method; incorporation of solar cell in outreach activities.

Status as of January 1, 2015: None to date.

Status as of July 1, 2015: One manuscript is currently under preparation. It describes control over the phase composition of CZTS prepared using our microwave synthesis method. In addition, we are initiating the process for filing a patent for the selective dissolution of impurities from product materials.

Status as of January 1, 2016: Two manuscripts are currently under preparation, including the one started in the previous period. The first describes control over the phase composition of CZTS prepared using the microwave synthesis method and will be submitted within the next six weeks. The second describes the selective etching method. Finally, the process for filing a patent describing the selective etching method is underway.

A patent describing the selective etching of Cu sulfide and selenide impurities from CZTSSe thin films is currently in progress (Provisional Patent Application - OTC Case 20160046).

Status as of July 1, 2016: Provisional Application (UMN 20160046) has been filed. "Purification of Thin Film Solar Cell Absorber Materials" was recognized as a 2016 TechConnect National Innovation Awardee at the May 2016 TechConnect-National Innovation Summit, Washington, D.C. In addition, a research article was submitted to *Green Chemistry*, and the paper is currently in revision. This paper reports on the experimental results demonstrating the efficacy of the selective etching process. Finally, a research article describing synthetic results is currently in review with *Inorganic Chemistry*. Two new manuscripts are also under preparation.

Status as of January 1, 2017: The research article submitted to *Green Chemistry* has been published. Finally, the research article submitted to *Inorganic Chemistry* that describes synthetic results is currently in revision. Two new manuscripts are nearing submission to journals, and one additional manuscript is in preparation.

Final Report Summary:
A Provisional Application (UMN 20160046) was filed. "Purification of Thin Film Solar Cell Absorber Materials" was recognized as a 2016 TechConnect National Innovation Awardee at the May 2016 TechConnect-National Innovation Summit, Washington, D.C.

We published three papers in the peer-reviewed literature describing our results.

Pinto, A.H., S.W. Shin, E.S. Aydil, and R.L. Penn, "Selective removal of Cu2-x(S,Se) phases from Cu2ZnSn(S,Se)(4) thin films," Green Chemistry, 18, 5814-5821 (2016).

Pinto, A.H., S.W. Shin, E. Isaac, T. R. Knutson, E.S. Aydil, and R.L. Penn, "Controlling Cu2ZnSnS4 (CZTS) phase in microwave solvothermal synthesis" Journal of Materials Chemistry A, 5, 23179-23189 (2017).

Pinto, A.H., S.W. Shin, A. Sharma, R.L. Penn, and E.S. Aydil, "Synthesis of Cu2(Zn1-xCox)SnS4 Nanocrystals and Formation of Polycrystalline Thin Films from Their Aqueous Dispersions" Journal of Materials Chemistry A (Manuscript ID: TA-ART-07-2017-006295.R1) Status – In Press.

In addition, we have two additional papers that are currently in review with peer-reviewed scientific journals.

VI. PROJECT BUDGET SUMMARY:

A. ENRTF Budget Overview:

Budget Category	$ Amount	Explanation
Personnel:	$104,250	Support for graduate student (3 years funding plus fringe); co-advised and working in close collaboration with the post-doctoral researcher; Design and execute synthetic methods for preparation of thin films using green methods. Characterize materials and films for suitability as photovoltaics. Prepare the prototype solar

		cell(s) in direct collaboration with the post-doctoral researcher.
Personnel:	$166,635	Support for Post-doctoral researcher (; 3 years funding plus fringe); co-advised; Design and execute synthetic methods for preparation of thin films using green methods. Characterize materials and films for suitability as photovoltaics. Provide some supervision and mentoring towards the graduate student. Prepare the prototype solar cell(s) in direct collaboration with the graduate student.
Personnel:	$60,841	Support for R. Lee Penn, project manager. 1.5 months summer salary per year (plus fringe). Supervise post-doc and graduate student; perform electron micrscopy on samples; evaluate data and design experiments.
Personnel:	$55,366	Support for Eray Aydil (co-project manager; 1 months summer salary per year + fringe); supervise post-doc and graduate student; design characterization experiments; evaluate data and design experiments.
Equipment/Tools/Supplies:	$36,000	User fees for instrumentation (electron microscopes, X-ray scattering equipment, spectroscopic methods) at the University of Minnestoa - College of Science and Engineering's Characterization Facility ($12k/yr)
Equipment/Tools/Supplies:	$35,908	Chemicals (metal precursors, elemental sulfur and other sulfur containing precursors, solvents), standards, conductive glasses as well as polymers for thin film support, lab supplies including reactors for microwave system, and supplies for materials testing
Equipment/Tools/Supplies:	$10,000	Repairs and maintenance
Capital Expenditures over $5,000:	$25,000	Research-grade microwave system.
TOTAL ENRTF BUDGET:	**$494,000**	

Details are provided in the accompanying excel file.

Explanation of Use of Classified Staff:

Explanation of Capital Expenditures Greater Than $5,000: Research-grade microwave system optimized for thin film production (based on quote from one of the major equipment producers). This equipment is substantially more specialized than a conventional microwave oven. The system enables use of flow-through cells (fresh reagents can flow into the cell and concentrations of ingredients varied as a function of time) as well as enable monitoring of temperature and pressure during synthesis. Finally, the microwave enables very fine tuning of power output. This equipment will be used for its full useful life and made available to other researchers at no charge.

Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation: 6.62

Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation:

B. Other Funds:

Source of Funds	$ Amount Proposed	$ Amount Spent	Use of Other Funds
Non-state			
	$232,722	$	**In-kind Services During Project Period:** *During Project Period: Dr. Penn and Dr. Aydil will also devote 1% time per year in kind ($2900). Because the project is overhead free, laboratory space, electricty, and other facilities/adminstrative costs (52% of direct costs excluding permanent equipment and graduate student academic year fringe benefits) are provided in-kind ($229,822)*
State			
	$	$	
TOTAL OTHER FUNDS:	**$232,722**	**$**	

Add or remove rows as needed

VII. PROJECT STRATEGY:

A. Project Partners: Project Managers Lee Penn and Eray Aydil are the supervising partners on this project. The graduate student and post-doc will be recruited and hired once funding is in place. We do not have additional partners involved.

B. Project Impact and Long-term Strategy: Safe and clean energy production is a grand challenge facing our society. The development of sustainable electrical energy sources is an urgent need in the state of Minnesota and in the United States. Solar energy is renewable and is a viable and attractive option. To become commonplace, solar cells must be inexpensive and robust, and they must be comprised of abundant, cheap, nontoxic materials. Innovative methodology for producing thin films of metal sulfides for use in solar cells resulting from the proposed work will move us closer to commonplace installation of solar cells. Solar cells produced in the proposed work will be composed of less toxic elements like iron, copper, and other far less toxic metals, combined with sulfide. By targeting sulfides for use in solar cells, sulfur waste from mining and other industrial operations could become a viable resource in the production of robust and inexpensive solar cells. Finally, we propose to exploit microwave energy so as to reduce the energy required to produce photovoltaic quality materials.

C. Spending History: *Related to this project*

Funding Source	M.L. 2008 or FY09	M.L. 2009 or FY10	M.L. 2010 or FY11	M.L. 2011 or FY12-13	M.L. 2013 or FY14
NSF grant for previous data analysis and testing					$42,000

VIII. ACQUISITION/RESTORATION LIST:

IX. VISUAL ELEMENT or MAP(S):

X. ACQUISITION/RESTORATION REQUIREMENTS WORKSHEET:

XI. RESEARCH ADDENDUM: We have prepared a research addendum, which has been submitted to the LCCMR office separately. It is being kept confidential to protect against potential unintended release of information that could compromise patents that might result from the research.

XII. REPORTING REQUIREMENTS:
Periodic work plan status update reports will be submitted not later than January 1, 2015; July 1, 2015; January 15, 2016; July 1, 2016, and January 15, 2017. A final report and associated products will be submitted between June 30 and August 15, 2017.

Environment and Natural Resources Trust Fund

M.L. 2014 Project Budget

Project Title: Solar Cell Materials from Sulfur and Common Metals

Legal Citation: *M.L. 2014, Chp. 226, Sec. 2, Subd. 08a*

Project Manager: *R Lee Penn*

Organization: University of Minnesota

M.L. 2014 ENRTF Appropriation: *$494,000*

Project Length and Completion Date: *3 Years, June 30, 2017*

Date of Report: *12 Janaury 2018*

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Activity 1 Budget Revised 1/15/2016	Amount Spent	Activity 1 Balance	Activity 2 Budget Revised 1/13/2018	Amount Spent	Activity 2 Balance	TOTAL BUDGET	TOTAL BALANCE
BUDGET ITEM								
Personnel (Wages and Benefits): overall	$171,613	$171,613	$0	$162,155	$162,155	$0	$333,768	$0
Support for graduate student (3 years funding plus fringe); co-advised and working in close collaboration with the post-doctoral researcher; Design and execute synthetic methods for preparation of thin films using green methods. Characterize materials and films for suitability as photovoltaics. Prepare the prototype solar cell(s) in direct collaboration with the post-doctoral researcher. [Estimated total $104,250]								
Support for Post-doctoral researcher (; 3 years funding plus fringe); co-advised; Design and execute synthetic methods for preparation of thin films using green methods. Characterize materials and films for suitability as photovoltaics. Provide some supervision and mentoring towards the graduate student. Prepare the prototype solar cell(s) in direct collaboration with the graduate student. [Estimate $166,635]								
Support for R. Lee Penn, project manager. 1.5 months summer salary per year (plus fringe). Supervise post-doc and graduate student; perform electron micrscopy on samples; evaluate data and design experiments. [Estimated $60841]								
Support for Eray Aydil (co-project manager; 1 months summer salary per year + fringe); supervise post-doc and graduate student; design characterization experiments; evaluate data and design experiments. [Estimated $55,366]								
Equipment/Tools/Supplies								
User fees for instrumentation	$21,462	$21,462	$0	$71,324	$58,576	$12,748	$92,786	$12,748
These are the instruments, and their hourly rates, we intend to use. The budget is based on rough estimates of time required for materials characterization. We will report on the actual hours used for each piece of equipment. TEM $44.00, SEM $44.00, SAXS $25.00, Raman $25.00, XRD $20.00, XPS $40.00, Elliposmetry $20.00, Maskmaking $360.00, Metal Evap $60.00, Sputtering $40.25								
Equipment/Tools/Supplies	$19,921	$19,921	$0	$15,521	$12,188	$3,334	$35,442	$3,334

Chemicals (metal salts, sulfur sources, nitrogen gas, solvents) [Estimated $9,303]								
Vials and caps for microwave systems [Estimated $4,500]								
Lab equipment (pH probe, balance, XRD sample holders, stir plate, UV-Vis flow cell, centrifuge) [Estimated $3,900]								
Grids and stubs for electron microscopy [Estimated $1,600]								
Lab supplies (safety supplies like gloves, pipets and pipet tips, vials, weigh boats, lab tape, centrifuge tubes, quartz cuvettes) [Estimated $7,800]								
Glove box (for preparation of precursors in controlled atmosphere) [Estimated $2,500]								
Substrates and materials for thin film preparation (e.g., conductive film (indium tin oxide) coated glass, flexible substrates, glass for use with molybdenum conductive films, silicon substrates) [Estimated $6,305]								
Equipment/Tools/Supplies: Repairs and maintenance	$3,106	$3,106	$0	$3,432	$2,010	$1,422	$6,538	$1,423
Capital Expenditures Over $5,000. ***Research-grade microwave system [$25,466].***	$25,466	$25,466	$0	$0	$0	$0	$25,466	$0
COLUMN TOTAL	**$241,568**	**$241,568**	**$0**	**$252,432**	**$234,928**	**$17,504**	$494,000	$17,504