

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 18-05-2015		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 1-Feb-2014 - 31-Jan-2015	
4. TITLE AND SUBTITLE Final Report: Acquisition of an X-Ray Scattering System with Solid-Gas Reactor Chamber and Ultrafast Detection Capabilities for Research and Instruction in Science and Engineering			5a. CONTRACT NUMBER W911NF-14-1-0055		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 206022		
6. AUTHORS Cristian E. Botez			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Texas at El Paso 500 W. University Ave. Admin Bldg, room 209 El Paso, TX 79968 -0697			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 64705-CH-REP.1		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT This project was aimed at the acquisition of an x-ray scattering system for research and student instruction. We purchased a Panalytical Empyrean with unique sample-environment-control capabilities that enable studies of functional materials under their actual operating conditions. The system has been installed, commissioned and is fully functional. Moreover, the system became the centerpiece of a new x-ray core facility that now includes three diffractometers (two powder and one single crystal). Following the DoD-HBCU sponsorship of this project, UTEP provided internal funding for the single crystal system, a Bruker D8 Quest (December 2014), for the renovation of					
15. SUBJECT TERMS x-ray diffraction instrumentation, fuel cell electrolytes, research and student instruction					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Christian Botez
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 915-747-8869

Report Title

Final Report: Acquisition of an X-Ray Scattering System with Solid-Gas Reactor Chamber and Ultrafast Detection Capabilities for Research and Instruction in Science and Engineering

ABSTRACT

This project was aimed at the acquisition of an x-ray scattering system for research and student instruction. We purchased a Panalytical Empyrean with unique sample-environment-control capabilities that enable studies of functional materials under their actual operating conditions. The system has been installed, commissioned and is fully functional. Moreover, the system became the centerpiece of a new x-ray core facility that now includes three diffractometers (two powder and one single crystal). Following the DoD-HBCU sponsorship of this project, UTEP provided internal funding for the single crystal system – a Bruker D8 Quest (December 2014), for the renovation of two rooms to house the facility (February 2015), and for the hiring of a postdoctoral researcher to oversee its day-to-day operations (January 2015). The internal funding amount was \$390,000. The facility is now operational and has begun serving its main two objectives: 1) research aimed at investigating the atomic level structures and dynamics that govern the enhanced proton conductivity in compounds that can function as fuel cell electrolytes at intermediate temperatures (e.g. doped Sn-pyrophosphates and phosphate-solid-acid/silica composites), and 2) instruction of student-faculty teams in acquiring skills and experiences necessary to actively participate in a UTEP – National Laboratory collaborative program.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
-----------------	--------------

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
-----------------	--------------

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

- 2014 Award for Outstanding Efforts in Securing External Funding from The University of Texas at El Paso Office of Research and Sponsored Projects (awarded specifically for securing this grant, which is the first DoD instrumentation grant in the College of Science)

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Mustafa Golam	0.00	
Heber Martinez	0.00	
Israel Martinez	0.00	
Joshua Morris	0.00	
Alex Price	0.00	
Andres Encerrado	0.00	
FTE Equivalent:	0.00	
Total Number:	6	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Alan Goos	0.00
FTE Equivalent:	0.00
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	<u>Discipline</u>
Victor Gonzalez	0.00	Biology, B.S.
Adan Anchondo	0.00	Physics, B.S.
Jacob Fong	0.00	Physics, B.S.
FTE Equivalent:	0.00	
Total Number:	3	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

- Synchrotron x-ray diffraction experiments on $\text{In}_x\text{Sn}_{1-x}\text{P}_2\text{O}_7$ carried out at the National Synchrotron Light Source (Brookhaven National Laboratory)
- High-pressure x-ray diffraction on CsH_2PO_4 and RbH_2PO_4 carried out at the National Synchrotron Light Source (Brookhaven National Laboratory)
- High-pressure neutron diffraction work on CsH_2PO_4 and RbH_2PO_4 carried out at the Manuel Lujan Neutron Scattering Center (Los Alamos National Laboratory)
- Neutron vibrational spectroscopy carried out on CsH_2PO_4 at the Manuel Lujan Neutron Scattering Center (Los Alamos National Laboratory)
- Met with Dr. Andrew Dattelbaum, MPA-11 Group Leader at Los Alamos National Laboratory, discussed the possibility of joint research projects involving UTEP students and faculty and MPA-11 researchers. Dr. Dattelbaum visited UTEP, met with the Dean of the College of Science. We wrote a grant proposal to initiate a UTEP – LANL partnership to the Nuclear Regulatory Commission in 2014 – proposal was recommended funding, but funding decision was postponed due to limited budget.
- Communicated with Dr. Chi-Chang Kao, director of SLAC National Laboratory. PI will visit SLAC in the Spring of 2015 to discuss potential collaborations with scientists at the SSRL synchrotron and write joint grant proposal aimed at funding research and student instruction partnership.

FINAL REPORT - Grant # 64705CHREP

(Reporting Period: February 2014 – January 2015)

**Acquisition of an X-ray Scattering System for Research and
Instruction in Science and Engineering**

PI Name: Cristian E. Botez

Department: Physics

The University of Texas at El Paso, El Paso, TX 79968

TABLE OF CONTENTS

List of appendixes, illustrations and tables	3
1. Statement of the problem	4
1.1. Objective	4
1.2. Approach	4
1.3. Relevance to the Army	6
2. Summary of the most important results	7
2.1. Accomplishments for reporting period	7
2.2. Collaborations and technology transfer	8
3. Appendixes	9
A. Examples of research projects	9
B. Student instruction / X-ray Scattering Facility	12
4. Bibliography	14

LIST OF APPENDIXES, ILLUSTRATIONS AND TABLES

Illustrations

<i>Rietveld refinement of the crystal structure of $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ from x-ray diffraction data</i>	9
<i>Lattice parameter dependence on the In doping level x in $\text{Sn}_{1-x}\text{In}_x\text{P}_2\text{O}_7$ obtained from LeBail fits against x-ray diffraction data</i>	9
<i>Schematic representation of a working perovskite solar cell based on the PEDOT: PSS hole transport layer and PCBM electron transport layer</i>	10
<i>XRD pattern recorded at the UTEP x-ray facility on the active $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer of a solar cell</i>	10
<i>X-ray diffraction patterns collected in the UTEP facility on hybrid samples of CeO_2/porous carbon, and TiO_2/microwave reduced graphene nanowires</i>	11
<i>Panoramic view of the x-ray scattering facility</i>	12
<i>Students working on the Panalytical Empyrean and Bruker D8 Advance diffraction systems in the new x-ray scattering facility at The University of Texas at El Paso</i>	12
<i>Flowchart of the UTEP – National Laboratory Partnership Program operation</i>	13

Appendixes

<i><u>Appendix A: Examples of Research Projects</u></i>	9
<i><u>Appendix B: Student Instruction / X-ray Scattering Facility</u></i>	12

1 STATEMENT OF THE PROBLEM

1.1. Objective

The project consists of the acquisition, installation, commissioning and operation of a Panalytical Empyrean powder X-ray diffractometer equipped with an Anton Paar XRK 900 solid-gas reaction chamber and an ultrafast PIXcell^{3D} detector. The instrument enables studies of functional materials under their actual operating conditions and is used by faculty members in Physics, as well as in other departments in the Colleges of Science and Engineering. The main research objective of the project is to uncover the atomic level structures and dynamics that govern the enhanced proton conductivity in compounds that can function as fuel cell electrolytes at intermediate temperatures (e.g. doped Sn-pyrophosphates and phosphate-solid-acid/silica composites). The main instruction objective is to build an x-ray facility (including both powder and single crystal instruments), where our students will acquire skills and experiences necessary to actively participate in a UTEP – National Laboratory research and instruction program.

1.2. Approach

There are three specific research goals related to the above-mentioned main research objective:

- 1) To identify the pathways and transport mechanisms that govern the enhanced proton conductivity in doped Sn-based pyrophosphates. The approach to achieve this goal will include:
 - Accurately determining the crystal structure and its temperature evolution for $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$, the compound that has the highest proton conductivity among doped pyrophosphates. Modern x-ray powder diffraction techniques will allow atomic positions to be determined with sub-Ångstrom resolution.
 - Quantitatively determining salient features of the proton dynamics in the above-mentioned compound, such as the probability of proton jumps between sites where protons (once incorporated) can temporarily reside, and the length of such jumps.

Neutron vibrational spectroscopy and neutron quasielastic scattering will be used to accomplish this objective.

- Generating scenarios for the proton transport, and test them against the above-described structural and dynamics information, as well as against previous knowledge from macroscopic-property measurements.
- 2) To reveal how certain doping-induced microscopic features (structural and dynamic) influence the efficiency of the proton conduction. The approach to achieve this goal will include:
- Identifying subtle doping-induced structural features such as tetrahedral distortions, bond-length variations, etc. in the crystal structures of $\text{Sn}_{1-x}\text{M}_x\text{P}_2\text{O}_7$ ($\text{M}=\text{In}, \text{Sc}, \text{Al}$).
 - Determining, for each of the investigated doped pyrophosphate, proton-dynamics related quantities such as the proton jump probability and jump length.
 - Establishing connections, and possibly a pattern, between these doping-induced structural and dynamics features and the macroscopic proton conductivity.
- 3) To understand the effect of mixing solid acids CsH_2PO_4 and RbH_2PO_4 with dispersed silica (SiO_2) on the properties of their superprotonic phases. The approach to achieve this goal will include:
- Determining the relationship between the composition and microstructure of the $(1-x)\text{CsH}_2\text{PO}_4/x\text{SiO}_2$ and $(1-x)\text{RbH}_2\text{PO}_4/x\text{SiO}_2$ composites and the proton conductivity of their high temperature phases.
 - Determining the thermal behavior of the solid-acid component upon heating under ambient and high-pressure, as a function of the silica content and average grain size.

There are also two specific instruction goals related to the above-mentioned main instruction objective:

- 1) To establish a core x-ray facility at UTEP, where both graduate and undergraduate students will receive hands-on training in scattering methods and techniques commonly used at national synchrotron x-ray and neutron facilities. The approach to achieve this goal will include:

- Securing internal matching funds from UTEP to purchase a single-crystal x-ray diffraction instrument (Bruker D8 Quest) that complements the one acquired from this DoD grant. Securing internal funds to renovate the x-ray facility room. Hiring a Ph.D. scientist to operate the facility and provide instruction to graduate/undergraduate students.
 - Implementing protocols for facility operation and procedures for student instruction.
- 2) To involve students in sustainable research and instruction based on a UTEP – National Laboratory Partnership Program. The approach to achieve this goal will include:
- Initiate discussions with group leaders and managers at National Facilities, design and present plan for partnership aimed at student participation in experimental work carried out at National Laboratories
 - Secure external funding to implement the UTEP – National Laboratory Partnership Program.

1.3. Relevance to the Army

Fuel cell technology offers unique advantages for both military and civil applications such as: low/zero emissions, few moving parts, portability, quietness, etc. The main potential applications for defense purposes (soldier power) are communications, sensors, battery chargers for caravans, special purpose vehicles (e.g. unmanned aerial and ground vehicles), and silent camp/watch capabilities. There are also multiple civil applications from appliances to the automotive industry. Many of the applications would tremendously benefit from fuel cell functionality at intermediate temperatures (between 150 and 300°C). Unfortunately, however, stable electrolytes that allow an efficient ion conduction within this temperature range are not as well developed or understood from the structural, physical and electrochemical perspectives as their low- and high-temperature counterparts. Our work is aimed at uncovering the microstructural and ion dynamics details that enable certain compounds to function as intermediate temperature fuel cell electrolytes. We believe that understanding and ultimately controlling these microscopic features will allow the rational design of high performance electrolytes through chemical manipulation.

2 SUMMARY OF THE MOST IMPORTANT RESULTS

2.1. Accomplishments for Reporting Period

Accomplishments related to research goals:

- Synthesized powders of $\text{In}_x\text{Sn}_{1-x}\text{P}_2\text{O}_7$ of different doping levels $0 < x < 0.2$, carried out temperature-resolved x-ray diffraction under different sample environments as a function of x , and performed LeBail and Rietveld refinements of the crystal structures
- Observed, for the first time, a salient structural feature (increase in the lattice parameter) that is specific for $\text{In}_{0.1}\text{Sn}_{0.9}\text{P}_2\text{O}_7$ ($x=0.1$ doping level), which is the sample that exhibits the highest proton conductivity
- Showed that the lattice parameter increase is not observed if the x-ray measurements are carried out on samples contained under vacuum; this is important because it can be corroborated with proton conductivity measurements carried out under vacuum to assess if the above-mentioned structural modification is related to the enhanced proton conductivity of $\text{In}_{0.1}\text{Sn}_{0.9}\text{P}_2\text{O}_7$
- Demonstrated the isomorphism between the superprotonic phases of CsH_2PO_4 and RbH_2PO_4 through structural refinements based on high-pressure, high-temperature x-ray diffraction data

Accomplishments related to instruction goals:

- Secured internal funds for the new UTEP research and student instruction x-ray facility to: acquire a new single-crystal Bruker D8 Quest diffractometer (\$270,000), hire a Ph.D. scientist/ postdoctoral to operate the facility and provide instruction to students (\$90,000 / 2 years), and renovate Rms. 134 and 132 in the Physical Sciences Building to house the facility (\$30,000)
- Established protocols for the use of the x-ray facility by other UTEP researchers and for student instruction; since the the facility became fully operational (Feb. 2015), more than 10 students of all levels – from Ph.D. to undergraduate – received instruction and actively participated in experiments, and 5 research groups from

Physics, Chemistry, and Mechanical Engineering performed experimental work in the facility.

- Established contacts and collaborations with administrators and scientists at National Laboratories and wrote ~\$500,000 grant proposal to the Nuclear Regulatory Commission for joint research and student instruction projects between UTEP and Los Alamos National Laboratory.

2.2. Collaborations and Technology Transfer

- Synchrotron x-ray diffraction experiments on $\text{In}_x\text{Sn}_{1-x}\text{P}_2\text{O}_7$ carried out at the National Synchrotron Light Source (Brookhaven National Laboratory)
- High-pressure x-ray diffraction on CsH_2PO_4 and RbH_2PO_4 carried out at the National Synchrotron Light Source (Brookhaven National Laboratory)
- High-pressure neutron diffraction work on CsH_2PO_4 and RbH_2PO_4 carried out at the Manuel Lujan Neutron Scattering Center (Los Alamos National Laboratory)
- Neutron vibrational spectroscopy carried out on CsH_2PO_4 at the Manuel Lujan Neutron Scattering Center (Los Alamos National Laboratory)
- Met with Dr. Andrew Dattelbaum, MPA-11 Group Leader at Los Alamos National Laboratory, discussed the possibility of joint research projects involving UTEP students and faculty and MPA-11 researchers. Dr. Dattelbaum visited UTEP, met with the Dean of the College of Science. We wrote a grant proposal to initiate a UTEP – LANL partnership to the Nuclear Regulatory Commission in 2014 – proposal was recommended funding, but funding decision was postponed due to limited budget.
- Communicated with Dr. Chi-Chang Kao, director of SLAC National Laboratory. PI will visit SLAC in the Spring of 2015 to discuss potential collaborations with scientists at the SSRL synchrotron and write joint grant proposal aimed at funding research and student instruction partnership.

3. APPENDIXES

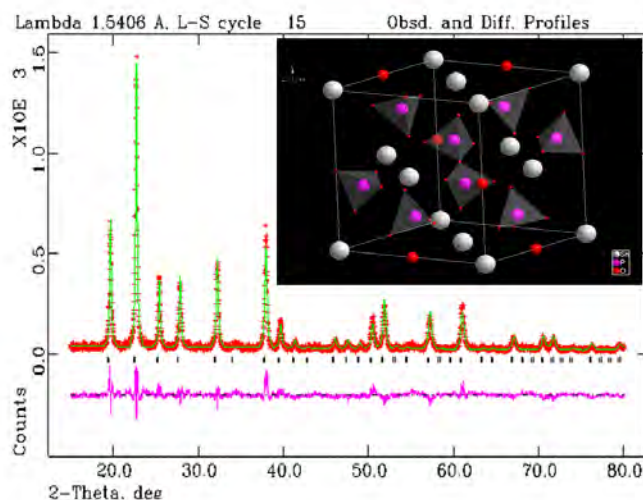
A. EXAMPLES OF RESEARCH PROJECTS

1) Cristian Botez – Physics

Crystal structures and proton conduction mechanisms in $\text{Sn}_{1-x}\text{In}_x\text{P}_2\text{O}_7$ pyrophosphates

The main goal of this research is to uncover the atomic-level structures and microdynamics responsible for the high proton conductivity of In-doped tin pyrophosphates. X-ray diffraction, enhanced by the use of modern in-house instrumentation and synchrotron radiation, is the first analytical technique we used in this project.

We have synthesized high-quality, impurity free samples of $\text{Sn}_{1-x}\text{In}_x\text{P}_2\text{O}_7$ ($0 < x < 0.2$), and used temperature-resolved x-ray diffraction data to structurally characterize them via LeBail (full profile) and Rietveld refinements (Figure 1).

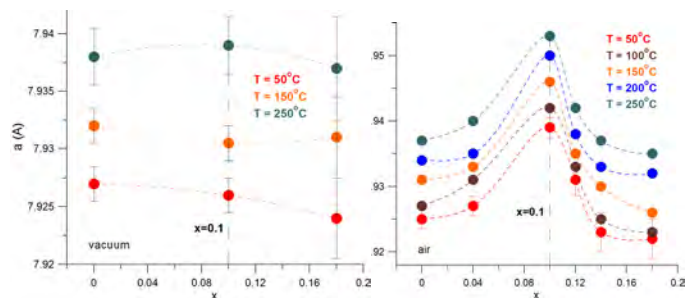


Rietveld refinement of the crystal structure of $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ from x-ray diffraction data (red crosses). The green line is the calculated intensity, the lower trace is the difference between observed and calculated x-ray profiles, and the vertical bars are the Bragg reflection markers.

We first observed that the indium ion solubility limit of is ~ 0.12 . We then found that the tetrahedral distortions (at different x values) are minimal, and consequently are not likely to play a key role in the proton conductivity enhancement observed for $x=0.1$. Instead,

analysis of the x dependence of the lattice constant of $\text{Sn}_{1-x}\text{In}_x\text{P}_2\text{O}_7$, obtained from LeBail refinements of temperature-resolved x-ray data collected in air (Figure 2, left panel), demonstrate that the lattice

constant exhibits a robust peak at $x=0.1$. This occurs at all temperatures used in our investigation, and suggests that the unit cell volume increase might facilitate the proton transport in this material. Interestingly, we found no lattice parameter increase at $x=0.1$ upon carrying out the same experiment



Lattice parameter dependence on the In doping level x in $\text{Sn}_{1-x}\text{In}_x\text{P}_2\text{O}_7$ obtained from LeBail fits against x-ray diffraction data collected at different temperatures in air (left panel) and in vacuum (right panel)

on $\text{Sn}_{1-x}\text{In}_x\text{P}_2\text{O}_7$ samples kept under vacuum during data collection (Figure 2, right panel). This observation is significant in view of recent proton conductivity results¹, and given the fact that these pyrophosphates do not nominally contain protons in the bulk. It also provides the first experimental evidence of a structural feature directly associated with the high proton conductivity of $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$.

2) Luis Echegoyen – Chemistry

Perovskites as active layers in solar cells

Photovoltaics is a constantly changing and evolving field that involves the collection of light energy from the sun and its subsequent transformation into electrical energy. Specifically, our goal is to utilize a perovskite material (methylammonium lead iodide perovskite, $\text{CH}_3\text{NH}_3\text{PbI}_3$) as the active layer of a solar cell. Recently, this has been the main focus of photovoltaic research with efficiencies starting at a mere 3.8% in 2009 and has already reached an astonishing 20.1% as of 2015 by the Korean Research Institute of Chemical Technology (KRICT).^{2,3} Shown in Figure 1 is our specific cell architecture involving $\text{CH}_3\text{NH}_3\text{PbI}_3$ as the light harvester. With this architecture we have been able to reach efficiencies of 11%, close to the reported efficiencies for similar architectures. The use of x-ray diffraction (XRD) is vitally important for the characterization of our perovskite layer, and data collected for our materials matches published results as shown in Figure 2.⁴ We have future plans to use XRD as a primary method of characterization through varied angle and temperature studies of our samples.

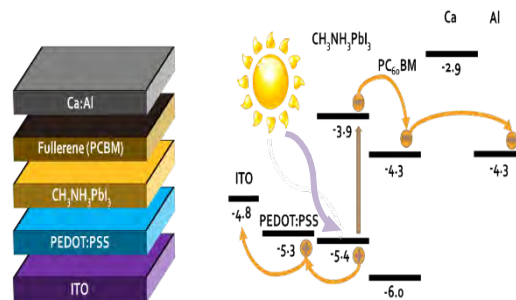


Figure 1 - Schematic representation of a working perovskite solar cell based on the PEDOT: PSS hole transport layer and PCBM electron transport layer.

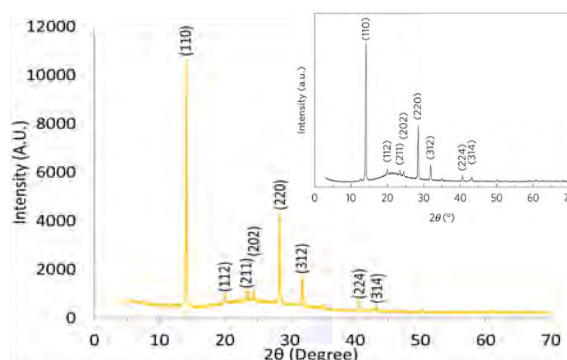


Figure 2 - XRD pattern recorded at the UTEP x-ray facility on the active $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer of a solar cell (yellow line) compared to XRD pattern from Ref [3] (inset).

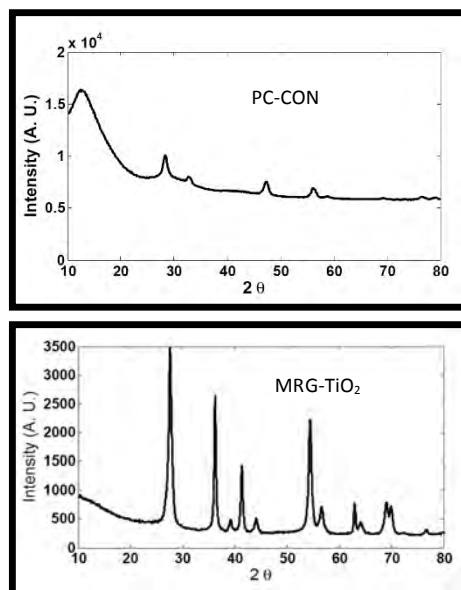
3) Yirong Lin - Mechanical Engineering

Synthesis of nanoparticles and nanowire hybrids

Synthesis of nano-hybrids is a complex process, where the proper crystallization of the active phase is paramount for the operation of these functional materials. From this point of view, x-ray diffraction (XRD) is a key technique that can accurately assess the quality of the synthesis of hybrid nano-systems. Below, we present two examples of such syntheses and corresponding XRD characterization

Porous Carbon/Cerium oxide nanoparticle (PC-CON) hybrids

The PC-CON hybrid synthesis is a one-step hydrothermal method. At first 100mg porous carbon (ACS Material, LLC) was dispersed in 200mL of deionized water (DI) water. Then 150mL of 0.02M Ammonium Cerium Nitrate $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ was added to the solution and the solution was sonicated for 45 minutes. The mixture was then separated by centrifugation. At this stage $\text{Ce}(\text{OH})_4$ was formed on the pores and surfaces of the porous carbon. Then product was mixed with 100mL 5M NaOH solution and transferred into a Teflon lined autoclave. After heating the mixture for 45 hours at 180°C , the solution was separated by centrifugation, washed with DI water for three times. Then the remnant was dried at 70°C . At last the product was heated at 450°C in Argon for 2 hours.^{5,6}



The crystal structures of the PC-CON hybrid were determined utilizing a PANalytical Empyrean XRD using Cu K α radiation (Figure 1). The peak at $\sim 13^\circ$ represents porous carbon and rest of the XRD peaks indicate that the products were well crystallized and have a cubic fluorite structure of CeO_2 (space group: Fm3m) with lattice constant $a=5.411\text{\AA}$, which is in agreement with the JCPDS file for CeO_2 (JCPDS 34-0394). No extra peaks corresponding to any other secondary phases were observed.

X-ray diffraction patterns collected in the UTEP facility on hybrid samples of CeO_2 /porous carbon (upper panel), and TiO_2 /microwave reduced graphene nanowires (lower panel). The data demonstrate that the desired active phases are presents in the nano-composites.

Microwave Reduced Graphene/Titanium dioxide nanowire (MRG-TiO₂) hybrids

The MRG-TiO₂ was synthesized following a simple hydrothermal method. 150mg microwave reduced graphene were transferred to a 250mL Pyrex glass bottle and mixed with a 50mL solution containing DI water and concentrated (37.3% Assay, Fischer Scientific) hydrochloric acid (HCl) with a 1:1 ratio. Subsequently, 2.5mL of the titanium tetrachloride (99.0% purity, Sigma Aldrich) was added dropwise to this solution. The glass bottle was then placed inside and aluminum cylinder and transferred into an oven at 160°C for 4 hours. After that, the resulting materials were rinsed several times with DI water and dried at 90°C for 30 minutes.

XRD data on the MRG-TiO₂ is shown in Figure 2. All the peaks matched with the standard diffraction data of TiO₂ (JCPDS, No. 76-1940). The XRD pattern exhibited strong diffraction peaks at 27° , 36° and 55° indicating that TiO₂ is in the rutile phase.⁷ No extra peaks corresponding to any other secondary phases were observed.

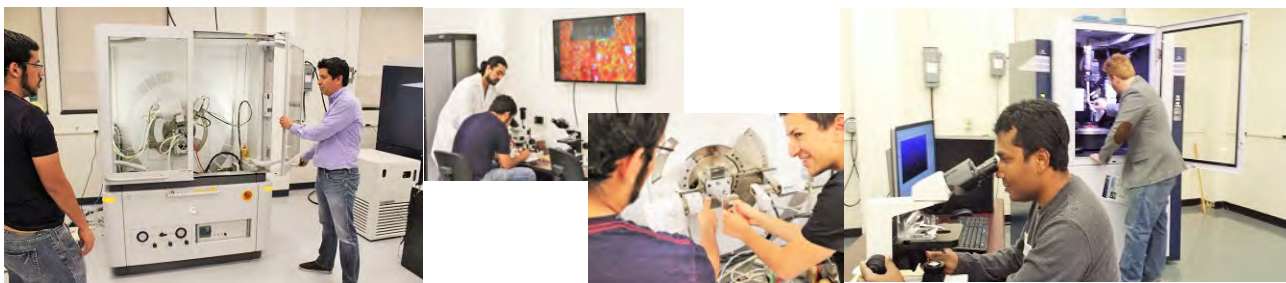
B. STUDENT INSTRUCTION / X-RAY SCATTERING FACILITY

The **X-ray Scattering Facility at The University of Texas at El Paso** is located in Rooms 134 and 132, Physical Science Building. The facility includes two powder and one single-crystal diffractometers:



Panoramic view of the new UTEP x-ray scattering facility

- A new PANalytical Empyrean powder x-ray scattering system equipped with an Anton Paar XRK 900 solid-gas reaction chamber and an ultrafast PIXcel^{3D} detector (sponsored by this DoD grant). The system has unique characteristics. The XRK 900 is the only chamber on the market that allows reactive gas flow through a polycrystalline sample (at different temperatures, pressures and flow rates), enabling it to replicate conditions under which functional materials actually operate. Structural and/or chemical modifications induced by variable sample environments that occur on time scales from a few seconds to tens of hours can be tracked in real time by the PIXcel^{3D} detector. The system includes state-of-the-art software that allows chemical change/phase transition identification and ultra-precise ($\pm 0.01\text{\AA}$) quantitative determinations of lattice parameters, atomic positions, and bond lengths.
- A Siemens D5000 powder x-ray diffractometer equipped with an MBraun position sensitive detector for rapid data collection and a Paar TTK chamber for temperature control. The instrument allows Rietveld-refinement-quality powder diffraction patterns corresponding to a 20° - 60° 2θ range ($\chi=1.5406\text{\AA}$) collected in the reflectivity geometry in about 90 min. at temperatures between 25 and 500°C . Within this range the temperature is stable to 0.1°C .
- A new Bruker D8 single-crystal diffractometer equipped with a Photon 100 large area detector and low temperature (80 K) capabilities (sponsored by UTEP). The system allows rapid data collection for crystal structure determination. Powder samples can also be run in the in the transmission (capillary mode) mode

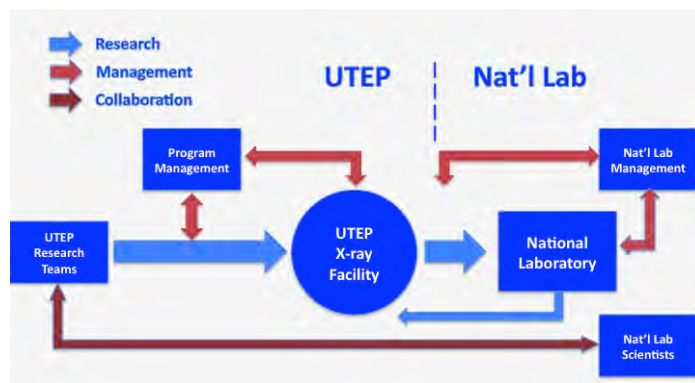


Students working on the Panalytical Empyrean and Bruker D8 Advance diffraction systems in the new X-ray Scattering Facility at The University of Texas at El Paso

Student instruction in modern x-ray scattering techniques and student participation in research projects relevant to the DoD mission is a priority within our x-ray scattering facility. Since the facility became fully operational in February 2015, more the 10 undergraduate and graduate students have

received such instruction, became able to operate the instruments independently, and actively participated in research. Collaborations with other groups at UTEP are also important; we have developed protocols for facility access by researchers within the Colleges of Science and Engineering, and so far 5 such groups have used our instrumentation and collected x-ray data important for their research projects.

Our next goal is to use the x-ray facility as a key component of a **UTEP – National Laboratory Partnership Program** that, we believe, will afford unique, career-defining opportunities to our minority students. We will engage our faculty and students in multidisciplinary research projects that are initiated and carried out primarily at UTEP but have a well-defined component to be performed at a partner synchrotron and neutron laboratory. We have already established contacts and collaborations with administrators and scientists at National Laboratories and wrote a grant proposal to the Nuclear Regulatory Commission to fund the program's implementation.



Flowchart of the UTEP – National Laboratory Partnership Program operation

Our program will function as follows:

- Multidisciplinary teams of faculty and students from the Colleges of Science and Engineering will design projects aimed at investigating functional materials and propose experiments that are initiated in our newly developed x-ray facility, but have a component that requires the use of synchrotron x-rays and/or neutrons.
- UTEP program management will assess the feasibility and prospects for success of the proposed work, and selected teams will receive theoretical and hands-on instruction before starting their work.
- Teams will carry out experiments in the UTEP x-ray facility aimed at confirming the quality of their samples, collecting preliminary data, and familiarizing themselves with techniques and experimental setups they will encounter at National Laboratories.
- Teams will travel to national synchrotron and neutron laboratories, perform experiments, and interact with members of the “user” community and National Laboratory scientists, setting the basis for long term collaborations and joint grant proposals.
- Teams will return to UTEP, continue working on their projects in the UTEP x-ray facility, and prepare for the next set of experiments at the National Laboratories

The program, whose proper implementation and sustainability critically depends on the UTEP x-ray facility, would tremendously benefit our minority and underprivileged students. They will do research at some of the best facilities in the world, and demonstrate that once offered the same sustained level of instruction and access, they can perform as well as any of their peers.

4. BIBLIOGRAPHY

1. Nagao et al., J. of Electrochem. Soc. **153** (8), A1604 (2006).
2. A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, J. Am. Chem. Soc., **2009**, 131, 6050.
3. Best Research-Cell Efficiencies. Digital image. National Center for Photovoltaics. National Renewable Energy Lab, 5 Feb. **2015**.
4. N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu, and S. Seok, Nat. Mater., **2014**, 13, 897
5. Padmanathan, N., and S. Selladurai. "Shape controlled synthesis of CeO₂ nanostructures for high performance supercapacitor electrodes." RSC Adv.4.13 (**2014**): 6527-6534.
6. Li, Changqing, et al. "Controllable preparation and properties of composite materials based on ceria nanoparticles and carbon nanotubes." Journal of Solid State Chemistry 181.10 (**2008**): 2620-2625.
7. Hu, Wanbiao, et al. "Tailoring the nanoscale boundary cavities in rutile TiO₂ hierarchical microspheres or giant dielectric performance." Journal of Materials Chemistry 20.39 (**2010**): 8659-8667.