

## Optics and Photonics Research for Montana Economic Development - MREDI Project Quarter 6 - February 6, 2017

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### Introduction

This project is on schedule and within budget, and is continuing to enable important collaboration between the optics and photonics research and business communities. The status of technology transfer for commercialization is as follows.

Subproject 1: Ultra-compact spectral imagers for precision agriculture and mapping of wildfires and natural resources (Joseph Shaw with NWB Sensors, Inc.) – negotiations for a “know how” license on weed mapping during harvest are in progress.

Subproject 5: Microcavity sensors for hyperspectral imaging (Zeb Barber with Advanced Microcavity Sensors LLC) – the PCT patent application is being nationalized in the US, Europe, and Canada. Advanced Microcavity Sensors is exercising its option to convert it into a license.

Subproject 7: Translational research to commercialize micro-mirror technology (Arrasmith at Revibro Optics) – MSU now has an exclusive licensing agreement with Revibro.

Subproject 8: Active waveguides and integrated optical circuits (Rufus Cone collaborating with Babbitt, Nakagawa, Barber, Himmer, Avci, and Thiel with S2 Corp., AdvR, FLIR/Scientific Materials, and Montana Instruments) – provisional patent related to crystal cooling is in process, expected to be filed by March.

The other subprojects all have promise for commercialization, but without specific commercialization activities yet. Finally, an additional \$6.339M of related funding has been received as of the time of this report. In the following pages we report specific progress toward meeting the milestones for each subproject.

**Subproject 1: Ultra-compact spectral imagers for precision agriculture and mapping of wildfires and natural resources** (Joseph Shaw, [joseph.shaw@montana.edu](mailto:joseph.shaw@montana.edu), with NWB Sensors, Inc.). Development of ultra-compact imaging systems for weed mapping in precision agriculture, UAV mapping of wildfires, and a wide variety of ground-based and airborne remote sensing.

Milestones

- a) September 30, 2015: Initial agricultural data collection completed
- b) December 31, 2015: Initial weed maps complete
- c) June 30, 2016: Prepare a refined imaging system and application-specific algorithm
- d) December 31, 2016: Complete results of summer 2016 harvest experiment
- e) June 30, 2017: Finish imaging system and algorithms and transfer to private partner

Introduction

During this quarter we performed a quantitative analysis of the weed detection algorithm’s performance and began finalizing the weed detection and mapping documentation. We also worked on preparing publications and on arranging for transfer of the technology to a commercial partner.

Weed detection accuracy

This quarter our work focused on quantifying the accuracy of the weed mapping results reported previously. We processed image data from 2015 and 2016 with weed detection software, and then compiled the output images into time-lapse videos. A group of participants and experts observed these videos to evaluate the machine learning software’s performance. The observer and camera results were quantified using the statistical metrics listed in Table 1-1 (TP = true positive, TN = true negative, FP = false positive, and FN = false negative). The true and false states were determined by expert observers, who viewed the time-lapse videos repeatedly, and all outcomes are described relative to their determinations. In the table, “true fraction” is the fraction of correct answers, “false fraction” is the fraction of incorrect decisions, “precision” (*p*) is the number of correct positive results over the number of all detected positive results, “recall” (*r*) is the number of correct positive results over the total number of weeds that either were or should have been detected. The overall accuracy of the binary weed/no-weed decision is represented by the *F*<sub>1</sub> score computed as shown below, with a maximum value of 1 for a perfect classifier.

Table 1-1. Statistical metrics used to quantify weed-detection performance

Metric	Function
True Fraction	$\frac{TP+TN}{TP+TN+FP+FN}$
False Fraction	$\frac{FP+FN}{TP+TN+FP+FN}$
Precision ( <i>p</i> )	$\frac{TP}{TP+FP}$
Recall ( <i>r</i> )	$\frac{TP}{TP+FN}$
<i>F</i> <sub>1</sub> Score	$2 \frac{p \times r}{p+r}$

The machine learning algorithm was a Support Vector Machine (SVM) learning model, trained with an independent subset of 75 images selected from the 2015 GoPro data (and then excluded from the subsequent analysis). Table 1-2 shows the statistical parameters that resulted from using the SVM machine learning algorithm to process the 2015 GoPro data (top two rows) and the 2016 Garmin data (bottom two rows). The “Participant” row gives results of comparing the SVM classifications to the participant classifications, while the “Expert” row gives results of comparing the SVM classifications to the expert classifications. Each column gives a number for the different parameters discussed earlier, but the  $F_1$  score expresses the overall statistical accuracy without being biased by the large number of true negatives (i.e., by not being biased by the field being mostly free of weeds). An example interpretation of several of the numbers for the August 2015 data would be that the SVM algorithm detected weeds or lack weeds 92.86% of the time compared with the experts (and 94.31% of the time compared with the non-expert participants). However, many of those detections were true positives (detecting the absence of weeds), so the  $F_1$  score removes that bias to give a more statistically rigorous estimate of the accuracy with which the SVM algorithm detected weeds.

The bottom rows in Table 1-2 show results of processing the 2016 data with the SVM that was trained with 2015 data. The accuracy is generally lower in this case, and could be a result of using different cameras, encountering different lighting conditions, or even possibly encountering very different field conditions. Further controlled studies would be required to identify which of these (or other) potential causes are most significant. Nevertheless, the SVM was successful at detecting patches of perennial quack grass (*E. repens*) and milkweed (*Asclepias*) in time-lapse videos from both years (the 2016 time-lapse video did not contain as many quack grass patches as the 2015 video).

Table 1-2. Weed-detection algorithm performance statistics

User	True Fraction	False Fraction	Precision	Recall	$F_1$ Score
<b>August 2015, GoPro Hero IV</b>					
Participant	0.9431	0.0569	0.7254	0.8978	0.8024
Expert	0.9286	0.0714	0.7390	0.8000	0.7683
<b>August 2016, Garmin VIRB</b>					
Participant	0.9665	0.0136	0.9845	0.4342	0.5659
Expert	0.9722	0.0278	0.8863	0.3269	0.4593

The 2015 GoPro data contained a large number of weeds in its imagery and provided a platform for further understanding of the machine learning software’s performance. Table 1-3 compares the results from the 2015 GoPro imagery made by the machine vs. expert, machine vs. non-expert participant, and participant vs expert. In an attempt to see how much certain features in the images influenced the overall accuracy, this table lists  $F_1$  scores calculated for weed detections made by the human eye and by the machine with different subsets of data removed. Specifically, results are shown for the full data set, the data set after removal of images containing dirt tracks (which tend to accumulate weeds), the data set without images from the outer field edges (which contain grasses and weeds that are outside of the field), the data set after removal of images containing single, isolated weeds (which are difficult to detect), and the data set after removal of both field edges and single weeds. Probably the most meaningful of these estimates is the center column, representing all the images in the interior of the field. This is a very reasonable subset because the SVM was not trained to detect the grasses and weeds that lay outside of the field. The machine detected weeds that surrounded the dirt tracks made by irrigation equipment most of the time.

The human participants and experts also agreed with the true detections of the machine. Consequently, excluding the images with dirt tracks caused the  $F_1$  scores to decrease.

Table 1-3.  $F_1$  Scores for data exclusions of the GoPro image data set from 2015.

	All Images	Images with no Dirt Tracks	Images with no Field Edges	Images with no Single Weeds	Images with no Single Weeds or Field Edges
Machine vs. Expert	0.7683	0.6548	0.8190	0.7899	0.8415
Machine vs. Participants	0.8024	0.6991	0.8466	0.8102	0.8539
Participants vs. Expert	0.8741	0.8100	0.8914	0.8942	0.9081

Single perennial plants of milkweed were found in both the 2015 and 2016 image data sets. The single plants were not detrimental to crop efficiency during that year; however, if not eliminated the single plants would eventually turn into a patch. Single plants similar to the one seen in Figure 1-1 were included in the training of our SVM, but the weed detection software missed many of these images. Training additional images and evenly weighing the quantity of image data selected from quack grass patches and the single milkweed plants could possibly prevent missed detections by the software.



Figure 1-1. Missed detection of a single plant of milkweed in a GoPro image.

The majority of the 2015 data were collected under clear skies, and therefore the SVM was trained for detecting weeds in clear-sky conditions. Therefore, lighting changes caused by clouds and low sun angles resulted in higher rates of false detections by the machine learning software. The image brightness normalization discussed in the fifth quarterly report may prevent these false detections, but further work is needed to provide a reliable implementation of this solution.



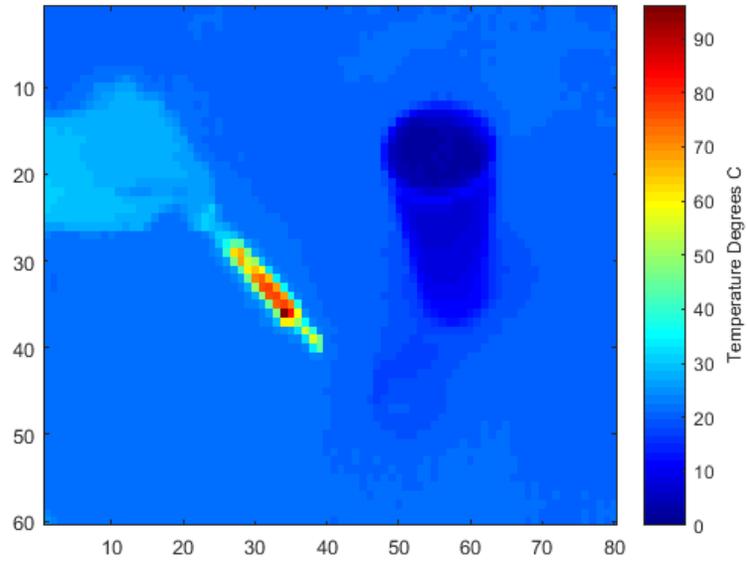
Figure 1-2. False detection of weeds in a GoPro image due to lighting change.

The weed detection methodology and results are being prepared for publication. One paper discusses the use of low-cost visible imagers to map weeds in fields. The second discusses the use of low-cost multi-spectral imagers (including near-infrared channels) to map weeds in fields.

We will continue our publications throughout the next quarter. We will also finalize transfer of the technology to a local company for commercialization. If resources become available, future research will be directed at implementing brightness corrections on image data and creating a broader training set for the SVM to improve the weed detection software's performance.

#### Ultra-compact IR Camera Calibration

We also recently finalized radiometric calibration and characterization of an ultra-compact, low-cost, thermal imaging module (FLIR Lepton). The results were part of a master's degree thesis for David Riesland (M.S. Optics and Photonics, Dec. 2016) and will be submitted for publication in the coming quarter. This thesis quantified the uncertainties that arise when thermal imagers are calibrated without accurate knowledge of the camera's spectral response function. This is important for applications such as imaging in agriculture, ecology or environmental science, and wildfire mapping. It is of growing importance because low-cost infrared imaging modules are rapidly becoming widely available at low cost, but largely without any (or good) radiometric calibration. This means that the images are merely "pretty pictures" and do not provide the quantitative information about scene temperature that many users require. An example of a calibrated thermal image is shown in Figure 1-3, in which the colors represent the temperature in degrees C. The reasonable accuracy of this image can be inferred by looking at the region of the image showing the hand that is holding a soldering iron next to a cold cup of water. The hand temperature is within the range of expected human skin temperatures (~30-34 °C).



*Figure 1-3. Calibrated Lepton image showing a hand holding a soldering iron and a glass of ice water.*

**Expenditures to date** (Grant 41W410) Personnel \$141,273.38. Benefits \$36,861.75. Operations \$36,462.04. Sub Award \$134,778.67, total Expenditures **\$394,375.84.**

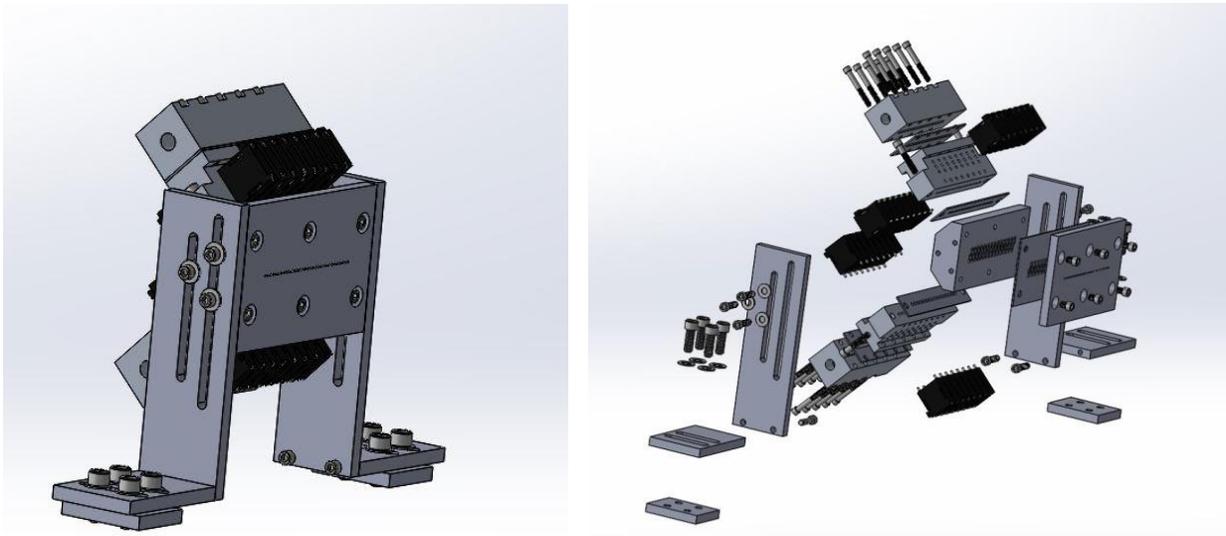
**Subproject 2: High-performance, real-time image processing for hyperspectral imaging** (Ross Snider with Resonon, Inc.) Design a high-speed hyperspectral waterfall sorting system to fuse object edge information with hyperspectral data to sort agricultural products quickly and efficiently using Resonon's Hyperspectral Imagers and remove rejected items via air jets. The goal is to perform the data fusion, accept/reject decision, and removal all in real-time using FPGA technology.

#### Milestones

- a) February 1, 2016: Determination of center of mass of each food item in image/line scan
- b) September 1, 2016: Determine trajectory of food item for precise timing removal
- c) February 1, 2017: Integrate hyperspectral data within food item edge boundaries
- d) June 31, 2017: Use hyperspectral data within food item edges to classify food item as accept/reject
- e) June 31, 2017: Time air jets to remove rejected food items
- f) June 31, 2017: Final report emphasizing commercial products and potential

#### Activities to date

1. The airjet manifold for the hyperspectral waterfall sorting has been design with 32 air jets and 32 associated air valves. Figure 2-1 shows the SolidWorks design of the airjet manifold.



*Figure 2-1. Mechanical drawings of the airjet manifold used for waterfall sorting.*

Figure 2-2 shows the machined aluminum parts of the manifold with the 32 airjet valves attached (assembled for the picture, but gaskets still need to be made for the part interfaces so this is not the final assembly).

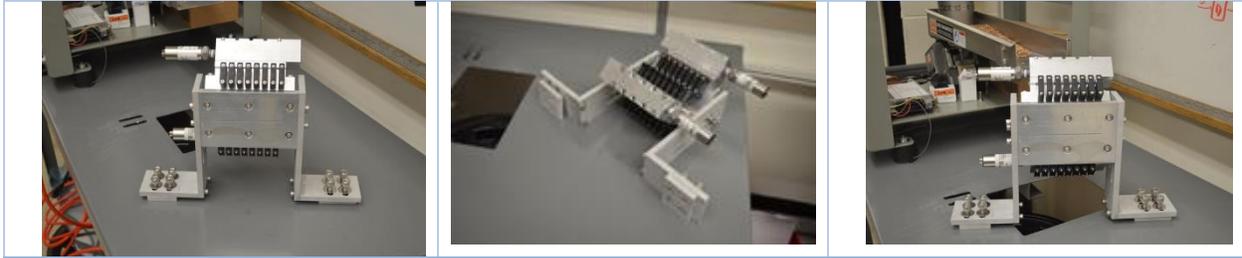


Figure 2-2. Machined aluminum parts of the manifold with 32 airjet valves attached.

Undergraduate student Sam Kysar is shown in Figure 2-3. Sam designed the airjet manifold in SolidWorks and machined all the parts.

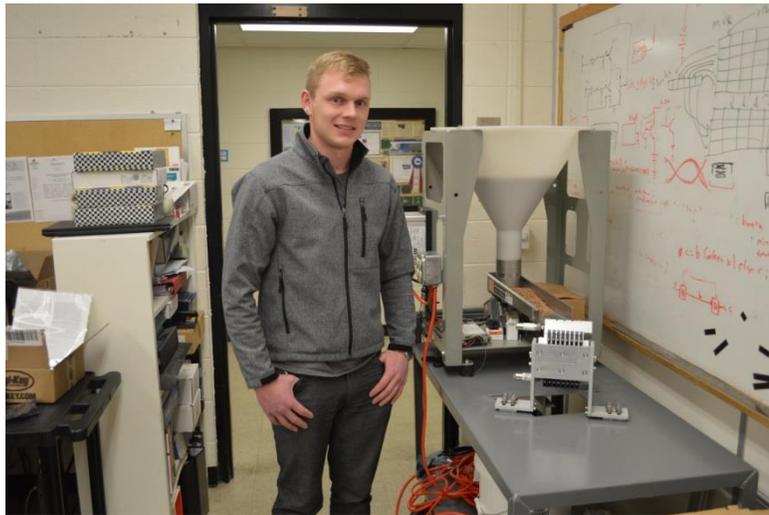


Figure 2-3. Undergraduate student Sam Kysar, who designed and built the airjet manifold.

- Now that the high speed (6 Gbps) serial links are functional, a senior design team composed of Nick Lapp, Hendrick Haataja, and Hannah Mohr have started working on a mSATA interface that will allow high speed video to be stored to an mSATA solid state drive (SSD). A block diagram of their project can be seen in Figure 2.4.

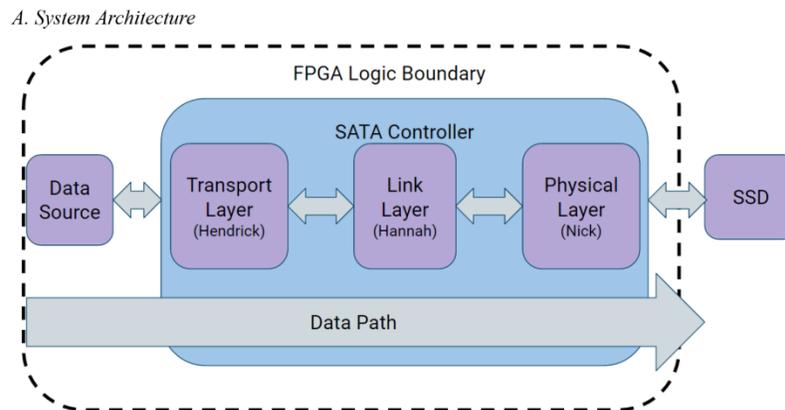


Figure 2.4. High-level block diagram of mSATA interface for storing high-speed video data.

## Activities with Hyperspectral imaging for monitoring metabolic state of live cells (subproject 6).

Work has been done to control the CellASIC microfluidics platform from Matlab. The built in potential to control with ActiveX was used. ActiveX control is used to control an open ONIX2 Software application through an OCX (ActiveX server). Once an object has been created through the Matlab command 'actxserver', the supported commands can be run. These commands are cumbersome, if intuitive for the CellASIC, and require strings as the parameters that would normally be thought of as a numerical value. Thus Matlab wrapper functions have been written to make the scripting less cumbersome, and more intuitive with respect to parameters. All of the conversion of numbers to strings are handled within the functions. The names and length of the function names are intuitive for the operation to be performed. Some usability was also added. For instance the ActiveX command to open well groups on the CellASIC is `onix.OpenWellGroups("00X00X00")`. Where `onix` is the object created by the `actxserver` command, and "00X00X00" corresponds to well groups 1 through 8 from left to right. This is a cumbersome way of telling the CellASIC to open wells 3 and 6 to pressure X. It also doesn't provide an easy way to set the pressure. Using the Matlab command for this same action is done by: `OpenWells([3 6], 2)`. Here '[3 6]' are the well groups to open, and '2' is the pressure in kPa at which to open them. Two separate ActiveX commands are needed to do this, the one above and `onix.SetPressureX('2')`. Both of these are handled within the Matlab function `OpenWells`. A command to close the wells, `CloseWells`, has been created as well, which operates similar to the `OpenWells`, but without the pressure argument. Other functions set the temperature and add time between commands providing the ability to perform most CellASIC experiments through a Matlab script file. Future work will allow for as much control as the ONIX2 software provides, including the ability to have dual pressures, and sending emails if an error occurs. Below is an example Matlab script that controls the CellASIC platform.

```
global onix;
onix = actxserver('ONIXCOMServer.OnixHandler');

Temperature(37.5)      %set temp to 37.5C

OpenWells([6],1.8)    %open well 6 and load cells
WaitTime(0,0,6)       %0hours 0mins 6sec

OpenWells([2],4)      %open well 2 with 4kPa and close
well 6
WaitTime(8,0,0)       %8hours, 0mins, 0sec

OpenWells([3],4)      %open well 3 with 4kPa and close
well 2
WaitTime(8,0,0)       %8hours, 0mins, 0sec
```

### Expenditures to date (41W411)

Personnel to date \$45,441.30. Benefits \$1,069.27, Operations \$73,246.95, Capital equipment \$4845.00.  
Total Expenditures **\$124,602.52.**

**Subproject 3: Remote Sensing Algorithms for Precision Agriculture** (Rick Lawrence with Resonon, Inc.)  
Develop and apply a methodology using hyperspectral imagery for determining optimal narrow spectral band combinations for identifying targeted invasive weeds in specific crops.

#### Milestones

- a) July 31, 2016: Collect invasive weed field data
- b) August 31, 2016: Collect hyperspectral image data
- c) October 31, 2016: Complete image preprocessing
- d) January 31, 2017: Complete analysis of spectral band optimization and weed species mapping
- e) June 30, 2017: Final report, including applications for commercial site-specific agriculture

#### Activities to date:

- Use different random samples of training and validation data, holding all else constant, to show no accuracy dependence on samples.
- Comparison of different combinations of classification methods and optimal 3 and 2 band sets in R program.

Using three combinations of the training and validation data the same classification and optimization techniques were used to test for effects of different data sets on classification accuracy. It was shown that no statistical difference existed between the three data sets. Different 3 band combinations provided from 4 optimization techniques were run through 7 classifications. Some 2 band combinations have been run and show low accuracies compared to the 3 band combinations. Most classifications resulted in overall accuracies below an acceptable level of 70 percent. Classification using all bands and a support vector machine classification attained an overall accuracy of 72.6 percent. This accuracy was closely matched by 3 different optimal band combination classifications. A map using a set of optimal bands resulting from transformed divergence optimization and random forest classification can be seen in Figure 3-1 in red. Spatial patterns of the likely weed patches are similar in this map compared with the other map, in yellow, which used all 80 bands. In both maps the outside edges show the densest weed patches. The outside edges are more susceptible to weed invasion as weed seeds can migrate from neighboring areas. Distinct line feature can be seen in both maps as well where equipment may have transported seed along crop rows. Based on my firsthand knowledge this map seems to match what was seen in the field. Further statistical analysis will indicate if these and the other maps differ on a significant level.



*Figure 3-1: Weed maps using hyperspectral data. Red using only 3 optimal bands. Yellow using all available bands.*

**Expenditures to date** (Grant 41W417) Personnel \$36,428.55, Benefits \$2,518.50, Operations \$11,459.39; total Expenditures **\$50,406.44**

**Subproject 4: Machine Vision Algorithms for Precision Agriculture** (Neda Nategh with Resonon and NWB Sensors, Inc.) Develop machine vision algorithms for weed detection and food sorting using spectral imaging data.

#### Milestones

- a. Sep. 30, 2016 Initial testing of machine vision algorithms complete.
- b. May 31, 2017 Final testing and development complete.
- c. June 30, 2017 Final report completed.

#### Progress toward objectives

- Students were advised on the analysis of hyperspectral image data and statistical modeling
- A new grant proposal is planned for submission based on a similar idea in the MREDI Optics project.
  - “Developing a computational framework for vision-based detection and tracking of small space debris” – NASA – Early Career Faculty– \$100,000.

**Expenditures to date** (Grant 41W413) Personnel \$74,009.29. Benefits \$5,651.91. Operations \$10,802.90., total Expenditures **\$90,464.10**.

**Subproject 5: Microcavity sensors for hyperspectral imaging** (Zeb Barber with Advanced Microcavity Sensors LLC). Advance MSU/Advanced Microcavity Sensors LLC (AMS) technology on microcavity hyperspectral imaging sensors toward commercial applications in agriculture and engineering tests to determine feasibility of mounting sensor technology on UAV; secondary objective solving MT problems in agriculture and biomedical (skin cancer). The primary objective focused on MREDI goal #2: creating private sector jobs.

#### Milestones

- a) June 1, 2016: Investigate non-circular symmetric micro-cavity mirrors for transverse mode manipulation
- b) September 1, 2016: Evaluate Microcavity Hyperspectral Imaging prototype system for early crop disease/weed detection
- c) December 30, 2016: Determine engineering specifications for use of Hyperspectral Sensor on UAV
- d) June 30, 2017: Submit final report specifying technical accomplishments and outlining commercial potential.

#### Related Funding Summary

This microcavity technology and project has attracted significant other funding mainly for commercialization through the SBIR and STTR programs and support from the Montana Board of Research and Commercialization Technology. Almost \$900K has been invested in the technology in MT from other sources during the MREDI project. A list of additional funding for MSU Spectrum Lab and Advanced Microcavity Sensors (AMS) includes:

- \$77,682 for (8/15 – 3/16) from a Phase 1 STTR contract with the Air Force. The prime on this contract is Spectral Molecular Imaging Inc. (SMI) of Beverly Hills, CA.
- \$59,482 for (8/15 – 10/16) from an AMS research contract with the Montana Board of Commercialization and Technology (MBRCT). The total project was funded at \$209,015 between AMS and MSU. The AF STTR project above also represents matching funds for the MBRCT effort.

- \$24,960 for (1/16 – 6/16) from Advanced Microcavity Sensors (AMS) on an NSF \$150,000 SBIR Phase I to develop the microcavity hyperspectral imaging technology for biomedical applications.
- \$230,540 for (8/16 – 7/18) from a Phase 2 STTR contract with SMI and AMS as a continuation of the Phase 1. The total contract value is \$750K with another ~\$100K as a subcontract to AMS.
- \$65,495 for (10/16 – 10/17) from AMS under another Montana Board of Research and Commercialization Technology (MBRCT) grant entitled, “Light Emitting Diode Pumped Laser Array for Ultra-Spectral Imaging”. The total funding between AMS and MSU is \$129,168.

In addition, AMS is in the process of applying to the NSF Phase 2 SBIR program which could represent an additional \$750K investment in the microcavity technology.

### Personnel Summary

The MREDI and additional funding on this microcavity project has enabled significant contribution to jobs at MSU and in the Bozeman area. In the first place, Dr. Russell Barbour who is the co-inventor of the technology at MSU, has through the MBRCT and NSF funding been able to form his company AMS, where he works full time on commercializing the microcavity technology. In addition, two PhD hires, Dr. David Atherton and Dr. Caleb Stoltzfus, were made at MSU Spectrum Lab due to the strength of the funding on this project. Dr. Atherton received his degree in Physics from MSU and a PhD and MBA from the University of Nevada-Reno. Dr. Atherton is continuing to work the MREDI project and additionally is pursuing a new technology based on laser particle levitation for high performance accelerometry and force sensing that should have markets in the energy sector. Dr. Stoltzfus is a Montana native and received both his undergraduate degree and PhD in Physics from MSU. His PhD emphasis in biophotonics under Prof. Alex Rebane is an asset to the project. At AMS, in addition to Dr. Barbour, the NSF funding provide employment for Mr. Austin Beard, a Montana native and graduate of the Electrical Engineering program at MSU.

### Additional Highlights Summary

- Caleb Stoltzfus presented a poster entitled “Liquid Crystal Arrayed Microcavities (LCAM)” at the annual OpTec meeting on October 4<sup>th</sup>, 2016 in Bozeman, MT.
- Dr. Daniel Farkas collaborator from Spectral Molecular Imaging Inc. gave an OpTec colloquium on Sept. 29<sup>th</sup> 2016.

### Technical Progress toward Objectives

a) MSU Spectrum Lab continued work on characterizing the crater and cavity profiles constructed by Advanced Microcavity Sensors. One issue that we have been dealing with is the presence of debris in the craters that form the curved mirror substrates. This debris could be from the laser ablation process, or could be from environmental dust in AMS’s facility where they performed the laser ablation. To test this theory we moved the laser ablation setup temporarily into a cleaner lab environment at Spectrum Lab and also ran test with different ablation setup including adding a fan to blow away laser ablation debris so it cannot resettle on the surface and/or orienting the ablated surface downward so the debris falls away from surface. These improvements greatly reduced the debris on the craters (see Figure 5-2).

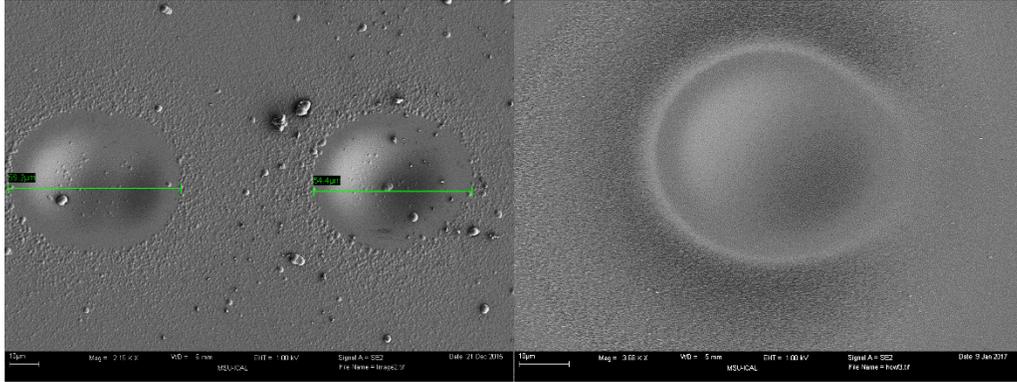


Figure 5-2 (Left) Scanning electron microscope (SEM) image of older set of craters that were ablated for the microcavities showing significant debris in the craters that will cause reduced transmission and resolution performance. (Right) Newer SEM image showing no debris in the craters. We think the reduction in debris is due to improved laser ablation process leaves less debris on the wafer, moving the ablation setup into a cleaner lab environment, and more attention to cleanliness in the whole process.

b) As discussed previous quarterly reports, we came to the conclusion that most agricultural applications are ill-suited to the high spectral resolution provided by the LCAM. For this reason we have re-evaluated application areas more suited to the LCAM. Two areas stand out: passive optical sensing of atmospheric gases and the microcavity based dye laser application that will be funded by the MBRCT. For the last part of the MREDI project, we are going to demonstrate the use of the LCAM to measure an atmospheric gas optical absorption using the sun as a light source and the LCAM as a spectral sensing element. The reason why the LCAM is ideal for this sort of sensing is the high spectral resolution, which can resolve the narrow absorption lines in a cheap compact size. Candidates for the gas sensing include water vapor, O<sub>2</sub>, CO<sub>2</sub>, and Methane. CO<sub>2</sub> and Methane sensors would utilize absorptions in the 1.5  $\mu\text{m}$  – 2  $\mu\text{m}$  region.

The microcavity-based laser application is now being pursued on the MBRCT funding. However, before this project started some initial work was performed on the MREDI funding. Below shows the enhanced emission from a microcavity filled with Rhodamine 6G dye mixture pumped with a diode laser at 450 nm. The emission is enhanced by the cavity modes giving the multiple peak structure shown in Figure 5-3. By tuning the liquid crystal the position of the emission peaks can be tuned. However, measurements designed to show coherent lasing by observing the characteristic threshold behavior of a laser have so far failed to show lasing. Optical emission dynamics with the very small mode volume used in the microcavity can be unusual, which means that the emission may be dominated by enhanced spontaneous emission rather than stimulated emission which leads to lasing.

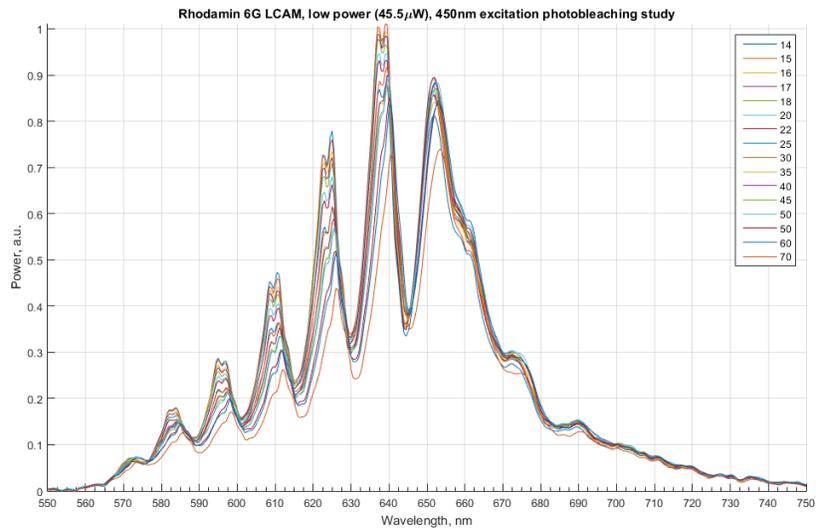


Figure 5-3 Enhanced fluorescence emission from Rhodamine 6G mixture in LCAM cavity.

c) On this task we have made progress in the manufacturability and compactness of the LCAM (see Figure 5-4). This new design allows the LCAM to fit in a standard 1" optic holder and easily make electrical contacts using spring loaded contacts. This combined with more compact input and output coupling optics makes for a compact and robust system.



Figure 5-4 (Left) Compact holder for the LCAM with spring loaded electric contacts. (Right) Characterization setup for the LCAM.

In addition, this quarter we have determined that the liquid crystal tuning approach is much superior to piezo-electric tuning for long term and short term stability and robustness to vibrations. The piezo-electric tuning requires a mount that allows the two sides of the microcavity to move relative to one another, this makes for a more complex mounting system that becomes susceptible to thermal drifts and vibrations. With the liquid crystal tuned LCAM the two sides of the cavity are glued together with only 2  $\mu\text{m}$  thick layer of epoxy which makes the dimensional stability and stiffness very good. With the liquid crystal tuned design, the main stability issues come from the input and output coupling optics, which could be made more robust using permanently mounted optics like microlenses.

**Expenditures to date** (Grant 41W418) Personnel \$47,242.54, Benefits \$16,852.35, Operation \$2,148.47;  
Total Expenditures **\$66,243.36**

**Subproject 6: Hyperspectral imaging for monitoring cell growth** (Ed Dratz with Resonon, Inc.). Design a hyperspectral imaging system for monitoring the metabolic state of live cells in culture. Applications to stem cells for understanding disease mechanisms in individuals, drug testing in cells from individuals, potentially optimize personal nutrition, and solve Montanan's health problems.

#### Milestones

- a) February 1, 2016: Complete design and testing of proof-of-principle prototype hyperspectral imager with improved cost/benefit, prototype interface for cell hyperspectral analysis, and development of stem cell labeling.
- b) May 1, 2016: Integrate the prototype systems for advanced analysis of stem cell metabolism with hardware and software control. Test for evaluation of optimization of selected nutrients.
- c) October 1, 2016: Refine and improve software and operating conditions of real time hardware and software for variations of metabolic state for culture optimization.
- d) February 1, 2017: Enhance user interface to control system and software to control and optimize nutrient composition; evaluate possible changes in microscope system for improved performance.
- e) June 30, 2017: Proof of principle for feedback control of nutrient optimization with nutrient dosing control system. Investigate biochemical individuality in pilot experiment.
- f) June 30, 2017: Submit grant proposals to leverage additional support. Final report to MUS that summarizes accomplishments and commercial potential.

#### Activities to date

There are six components that need to be integrated to complete this project. The hyperspectral microscope system, the high-speed and high-accuracy sample stage, the microfluidic nutrient dosing and cell growth chamber system, the control and analysis software, and the integration and testing of the fluorescent sensors of the metabolic state of the human adult stem cells. Progress has been made on all of these components.

The inverted epifluorescence microscope optical system has been designed, delivered and installed at Resonon for further system integration and refinement as shown in Figure 6-1. A single microscope vendor, Applied Scientific Instrumentation (ASI), was able to provide an integrated, high-performance inverted microscope solution, which has a very open design for optical access and is also extremely stable. The inverted microscope configuration is essential for viewing live cells and monitoring their metabolic state. This vendor is the only US manufacturer of integrated microscope systems and will provide the best possible price on the complete optical systems needed for development of a commercial product. This excellent price for the optical components will facilitate the commercialization of the complete hyperspectral microscope with the integrated microfluidic cell culture system and complete, powerful computer control and software system that is under development at MSU. The final system will be much more compact, but the open configuration on the optical table shown is the best approach for optimizing the system. It is possible from Figure 6-1 to get an impression of the strength, stability, and openness of the microscope system. The Resonon camera is just above edge of computer Microfluidic, environmentally controlled cell growth master on the right. Software has been written at MSU to command the addition of nutrients to observe metabolic changes in the live cells being monitored.

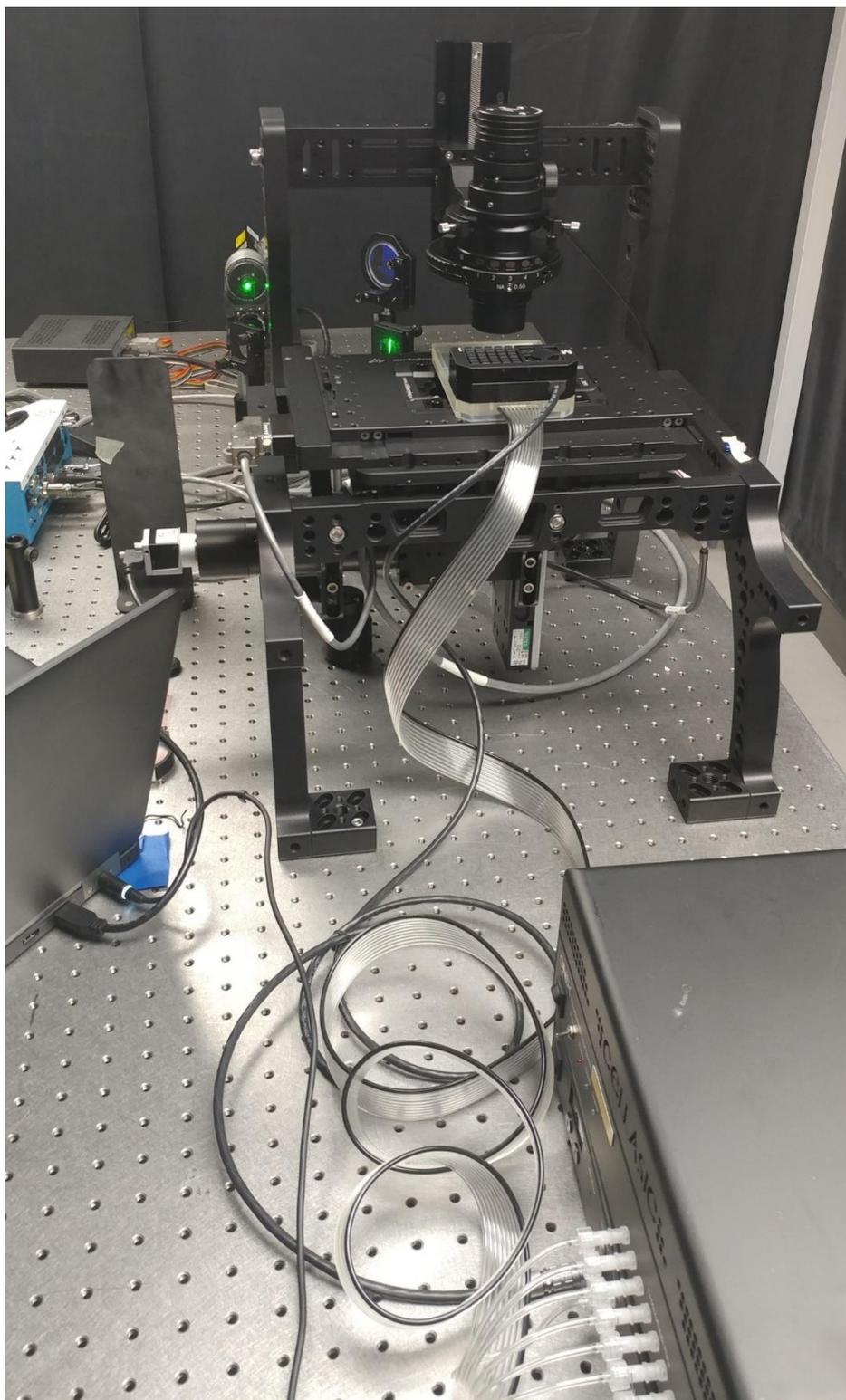


Figure 6-1. Hyperspectral components being integrated with the modular inverted microscope.

Prof. Snider's team has completed the software to integrate the Onix CellAsic microfluidic culture control system as described below. They have also made progress with the software hyperspectral data acquisition and processing software and have started on integrating the software to control the automated XY sample stage, which has to be able to scan in small, very high resolution steps for maximum hyperspectral resolution, along with rapid movement speed (7mm/sec in this case), so we can rapidly revisit cells in the field for repeated spectral measurements after modifying the nutritional state. The software developed by Prof. Snider's team is described at the end of the Subproject 2 section.

Figure 6-2 shows laser excitation of the Onix cell growth chamber mounted on the microscope with initial laser line illumination. The line excitation here is saturating the detector and thus appears broader than the true intensity profile. The Resonon camera, mounted on the output channel of the fluorescent inverted microscope, sees about 12 micrometers at half height, which is within a factor of three of the desired excitation width. A tighter focus will be attained with the addition of a couple of optics to the sample excitation train and with a better sample holder that will allow sharper focus in the image plane.

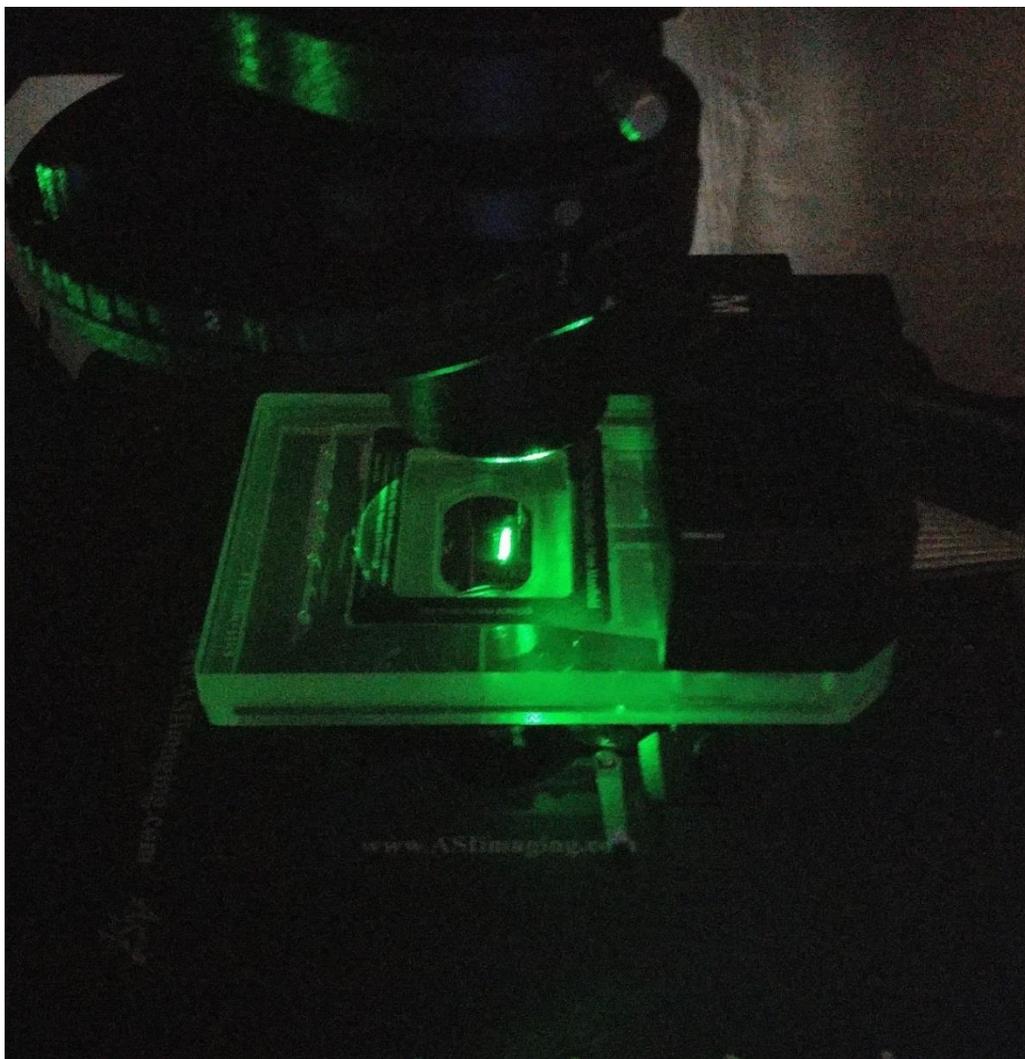


Figure 6-2. Laser excitation of the Onix cell growth chamber mounted on the microscope with initial laser line illumination

The ASI Company, in Portland, has also expressed interest in teaming with us to refine the development of our planned commercial product. The microscope will do an initial rapid scan of the image field, the software will locate cells, and the cells will then be scanned at high resolution repeatedly during the course of the experiments. Thus, the stage has to be able to scan rapidly between cells and then switch to much slower, small step sizes for high- resolution imaging. The software control for the XY stage and Z automatic focusing with programmable nose piece for changing objectives for different magnifications is in prototype and will be tested as soon as the stage arrives. The upright epifluorescence microscope test system from the Dratz Lab that was moved to the new Resonon facility is being used for initial testing of the excitation laser system for hyperspectral imaging.

Continuing progress has been made in the Dratz lab on introducing optogenetic probes of the oxidation/reduction state into human adult stem cells and other useful cells in culture. The probes have been transferred to efficient carrier vectors that are providing improved, more facile optical probe introduction. We have also introduced the optogenetic probes in to Murine smooth muscle cells to begin to demonstrate the wide applicability of our systems for metabolic monitoring of live cells. There is a great deal of local experience with these smooth muscle cells and monitoring the control of the metabolic state if these cell lines. A graduate student in the Dratz lab is devoting full effort to working with the optogenetic probes, assisted by a research undergraduate, two postdoctoral researchers in the Reijo Pera lab, and Robert Usselman, a Research Assistant Professor in the Singel lab, all in the MSU Chemistry and Biochemistry Department. An advanced undergraduate Electrical and Computer Engineering (ECE) Design Team in the Snider lab in Electrical and Computer Engineering has completed the controller for the cell culture environmental control system, as noted above and is continuing to design the microscope stage controller system, which can make much faster progress now that the fast and accurate stage is installed. A graduate student in the Snider lab is devoting full effort to the high-speed hyperspectral imaging analysis software and will be working on this crucial aspect of this project into the next year. The personnel include two graduate students devoting full effort to the project, two advanced undergraduates on an ECE Design team.

**Expenditures to date** (Grant 41W414) Personnel \$49,792.95. Benefits \$9,000.17. Operations \$33,719.79. Capital Equipment \$74,502.70; total Expenditures **\$167,015.61.**

**Subproject 7: Translational research to commercialize micro-mirror** technology (Arrasmith at Revibro Optics). Translate MSU-developed deformable mirror technology to a commercially sustainable product.

#### Milestones

- a) June 30, 2016: Refine production to achieve a repeatable fabrication process. This milestone will involve a redesign of fabrication masks, purchase of new wafer bonding equipment, and refinement of wafer bonding process
- b) Obtain funding from another source. Revibro will pursue funding through commercial sales and commercial R&D efforts (June 2016), and through SBIR/STTR or similar government funding (June 2017)
- c) Create 2 full time Montana jobs: One job will be created immediately to sustain the founder of Revibro – August 2015; Technical and/or sales and marketing hire – December 2015

#### Activities during Q6

- Completed our first two orders for mirror prototypes
- Hired our first full time employee, Drew Moen, in October
- Received a Phase I SBIR award from the National Science Foundation
- Began optical design for new bonding apparatus

We are excited to report that during Q6 we shipped out our first two prototype orders to US customers. One order was for our standard 4-mm diameter mirror, and the second was a more involved development effort resulting in functional 2-mm diameter mirrors. We are continuing to work with these “early adopter” customers to ensure successful integration of our mirrors into their optical designs. Also, we were awarded an SBIR Phase I award from the National Science Foundation and are excited to begin a new R&D effort to improve the reflectivity of our mirrors by adding gold and silver mirror surface options. This Phase I award will span the 2017 year, and provides substantial help to improve our technology and bring it to market. We have successfully completed Milestone B by obtaining both commercial and government funding, and will continue to pursue additional sources for funding during 2017.

As reported previously, Revibro hired its first employee in October 2016. Drew Moen is an MSU electrical engineering master’s graduate. He has been critical to keeping our fabrication process going to fill early orders, and is also working to improve our mirror yield through fabrication refinements. Revibro now has two full-time employees, fulfilling the requirement for Milestone C from this project.

We continue to improve our fabrication yield as described in Milestone A. We recently purchased components for a new alignment system to improve our wafer bonding process, and are working to complete the system design and assembly in the next month. This new alignment system will greatly improve alignment between the top wafer and bottom wafer in our fabrication process, and improve bonding repeatability. Also, we will undertake a redesign of the bonding apparatus we currently use to improve bond quality and mirror flatness. The improvements to bond alignment optics and bonding apparatus will take place during the next 2 quarters to achieve a more repeatable fabrication process and higher fabrication yields. So, Milestone A is currently a full-time effort, and we will provide updates on success related to it in the next two reports.

**Total Expenditures:** (Grant 41W410 Sub-Award) Personnel & Benefits \$134,778.67, Total Expenditures **\$134,778.67.**

### **Subproject 8: Active waveguides and integrated optical circuits**

(Rufus Cone, collaborating with Babbitt, Nakagawa, Barber, Himmer, Avci, and Thiel with S2 Corp., AdvR, FLIR/Scientific Materials, and Montana Instruments. Our goal is to advance and integrate unique Montana technologies, expertise, and capabilities to improve marketability, performance, and enable additional Montana photonic products. These optical, or “photonic,” devices can provide performance far beyond the capabilities of modern electronics. Our MREDI work develops new capabilities and technologies at MSU directly targeted at increasing Montana participation in international markets that use light “guided” through crystals to process information. These integrated photonic “waveguide” devices have many more functionalities than the more familiar optical fibers and are the essential next generation of product applications.



*Figure 8-5. Example of optical fiber coupling of an AdvR Inc. waveguide within a Montana Instruments Corp. cryostat system.*

The word “integrated” here implies subminiaturized packaging of the type familiar from modern electronics. Indeed, we are making “circuits for light.”

Our vision is to employ special rare-earth-activated crystals produced by Scientific Materials-FLIR with the waveguide design and the miniature packaging capabilities of AdvR Inc., all integrated with Montana Instruments Corp. low temperature systems to enable photonic signal processing systems produced by S2 Corp., leading to new products for each company. This project involves broad interdisciplinary collaborations between six different research groups at MSU from several departments and centers, all working with the four local Montana companies above, providing unique synergy that establishes a long-term program of sustainable collaboration in this field, with short-term development focused on immediate return for Montana businesses and current research programs at MSU. *This collaborative, Montana-focused effort is only made possible by the MREDI program, opening completely new opportunities to leverage unique Montana technologies towards research and development efforts that are beyond the capabilities of individual research groups or companies.*

#### **Milestones**

- a) Fall 2015: Fabrication of rare earth doped optical waveguide suitable for optical signal processing applications (SUCCESS)
- b) Summer 2016: Integration of an optical waveguide into a cryostat (SUCCESS)
- c) Spring 2017: Demonstration of SSH processing in a cryogenic waveguide (In Progress)
- d) June 2017: Final report summarizing technical results and emphasizing commercial potential

#### **Activities to date**

During this sixth reporting period, progress continued on all project activities. A wide range of coordinated research and development activities are advancing rapidly at this stage of our effort, most of which are in close collaboration with our Montana industrial partners.

Work is progressing on schedule for demonstrations of photonic signal processing in cryogenic waveguide packages (see Figure 8-5 and Figure 8-6, for example). This effort will be greatly enhanced by \$500k of new federal funding from the NSF SBIR program that has been awarded to S2 Corp. in January 2017 that will involve implementing and expanding on our MREDI waveguide integration for their photonic signal

processing technology, with \$148k of these new funds sub-contracted from S2 Corp. to MSU Spectrum Lab.

Another key outcome of this quarter's efforts was the development of a new technology for providing enhanced thermal contact with insulating optical materials to increase maximum system operating powers in the cryogenic environment. We are currently working with Montana State University TechLink to prepare a provisional patent application for this invention that has been developed as part of our MREDI project. We expect this technology to directly impact local Montana companies S2 Corp, Montana Instruments Corp., and Scientific Materials Corp., each for a different potential market segment (photonic signal processing, cryogenic systems, and high-power lasers, respectively) and licensing of the intellectual property to these companies will be pursued once the patent is filed.

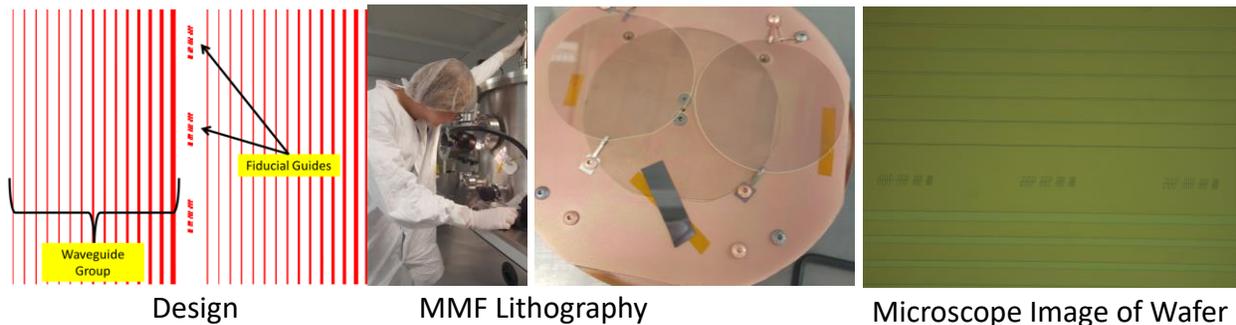


Figure 8-6. Illustration of the optical waveguide fabrication process.

In addition to these selected highlights from this quarter, below we also outline a number of key results and metrics that demonstrate the economic, scientific, and educational successes and impacts of our MREDI supported efforts.

#### Impact on New University Research Funding:

This MREDI project has already had a significant impact on new research funding at Montana State University by nurturing new ideas in their early stages, providing new experimental and computational capabilities, generating new ideas from the interdisciplinary collaborations, and illuminating opportunities for new technologies from interactions with the local Montana optics industry. While we expect the impact of our MREDI efforts on academic and industrial research and development to continue to increase over time, there have already been a significant number of new research projects funded at the university over the course of the project that are briefly outlined below. **MREDI provides key support, capabilities, and technologies for these projects totaling \$1,446,000 of new research funding brought into the state for MSU.**

- **\$60,000** awarded to MSU from S2 Corporation for extending the project “Efficient Photonic Computational Engine for Selection and Filtering” (PI: Barber) for the period 12/2015 to 3/2016.
- **\$763,000** awarded to MSU over three years (11/2015 – 11/2018) as part of a >\$11 million contract with the Office of Naval Research in the area of Electronic Warfare for the project “Full-Spectrum Staring Receiver (FSSR)” (PI: Barber). This project is led by BAE Systems or Nashua, NH. The core of the system is based on the S2-SA technology that was developed at MSU and S2 Corporation. In total, \$4.5 M of this contract is for Montana-based entities. The MSU press release can be found at

<http://www.montana.edu/news/16038/s2-corporation-and-msu-jointly-announce-contract-to-provide-wideband-sensor-capability-to-u-s-navy> and a TV segment filmed and produced by KXLF-TV in Bozeman, MT on this award can be viewed at:

<https://www.youtube.com/watch?v=k9TnY49tvyc&feature=youtu.be>

- **\$181,000** awarded to MSU over 1 year (8/2016 – 6/2017) as a subcontract from S2 Corporation on a SBIR project from Air Force Research Labs (AFRL) called “Instantaneous Wideband 10 GHz Time Difference of Arrival” (PI: Barber).
- **\$50,000** awarded to MSU over 4/1/16 to 12/31/16 for the project "Nanoscale Poling and Structuring in Nonlinear Optical Materials," (PI: Himmer and Nakagawa) funded by the NASA Montana Space Grant Consortium.

Spectrum Lab will also receive two additional subcontracts from S2 Corporation that begin in the next quarter:

- **\$148,000** awarded to MSU over two years (Q1 2017 – Q1 2019) as part of a NSF Phase IIB SBIR project "Photonics Enabled Extreme Bandwidth Wireless Communications Receiver" (PI: Barber). The goal of this project is to implement the waveguide integration techniques developed on MREDI into S2-SA and S2 processor applications at S2 Corp.
- **\$244,000** awarded to MSU over one year (Q1 2017 – Q1 2018) as part of a joint S2 Corporation/Spectrum lab IARPA effort on “Efficient, High-data rate Photonic Computational Engine for 2-D Image Processing” (PI: Babbitt) to apply the S2 processing to 2D image analysis.

A number of other funding proposals have been submitted and more are being prepared based on the results of our MREDI efforts.

#### *Impact on Montana Industry Funding:*

While the technologies and new products being developed in our MREDI effort have broad economic impact on the Montana optics and photonics industry, one of the more easily quantifiable measures of economic impact is new federal contracts and research funding brought into the state. While MREDI is supporting the university research and development efforts and does not directly support new projects at the commercial businesses, our work provides the foundation for the continued growth of the state industries through the early-stage technologies and expertise being advanced to the point where transfer to Montana companies is practical.

In particular, our MREDI efforts on developing cryogenic optical waveguide technology are crucial for the next level of integration and miniaturization of the photonic signal processing devices being developed at S2 Corporation. Just over the course of our MREDI effort, S2 Corporation has secured significant federal funding in the amount of **\$8,608,000** to develop the S2 technology, as outlined by the table in Figure 8-7 that was provided by S2 Corporation. While this funding is not a direct result of the MREDI project, it shows the significant continued interest and development of the S2 technology, with our MREDI effort providing the seed technologies required to develop the next generation of S2 technology.

<b>Funding Agency</b>		<b>S2 prime</b>	<b>Start date</b>
Office of Naval Research (ONR) - Electronic Warfare (BAE Systems prime contractor)	ONR base Y1	\$ 1,870,000	
	ONR adds	\$ 600,000	Jun-15
Air Force Research Labs Sensors Division Phase III SBIR and DARPA - S2 System Build and Delivery	AF Sys bld	\$ 1,604,000	Oct-15
Air Force Research Labs Sensors Division Phase III SBIR and ONR - Field Testing	VH2	\$ 800,000	Jan-16
National Science Foundation Phase 2B SBIR	NSF Ph2B	\$ 500,000	Jan-17
Air Force Research Labs Sensors Division Phase III SBIR and ONR - Time Difference of Arrival Demo	TDOA	\$ 920,000	Jun-16
Army Rapid Innovation Fund - S2 System Improvements and Tests	Army RIF	\$ 1,300,000	Jun-16
IARPA High Throughput 2D Image Correlation	IARPA 2-D	\$ 1,014,000	Feb-17
	SUM	\$ 8,608,000	

*Figure 8-7. Recent Federal funding secured by S2 Corporation to develop the S2 technology for defense applications. (Courtesy of Dr. Kris Merkel, CEO and President of S2 Corporation).*

*Impact on Montana Student Education and Training:*

The MREDI effort has provided a unique educational opportunity for Montanans at all levels of education. In addition to the senior university personnel, we have had **3 research scientists, 2 postdoctoral students, 6 graduate students, and 6 undergraduate students** all working on this MREDI sub-project, with 2 students receiving BS degrees and 1 student receiving an MS degree. As part of the MREDI group effort, there have been **more than 10 public presentations and colloquia** where students working on MREDI have presented their research. In addition to these presentations, a seminar series for students involved in the MREDI project has been offered as a class through the Physics Department where the students learn about the physics of optical coherent transient phenomena, including those used in the coherence testing of Montana Instrument’s cryostat; the physics and chemistry of the spectral hole burning crystals produced by Scientific Materials; the physics and engineering involved in the spectral hole burning based spectrum analyzer produced by S2 Corporation; and the design and commercial technology of optical components and laser systems, including those produced by AdvR and Bridger Photonics.

The particular and unusual focus of MREDI on developing new technologies with direct economic impact has exposed the students to ideas and practical issues critical for entrepreneurial careers. Undergraduate and graduate students are working in close collaboration with professionals in the local optics industry with benefits for all involved. Students regularly visit the local companies to use their specialized equipment, such as the M-lines waveguide characterization system and wafer dicing saw at AdvR Inc. and the crystal X-ray diffraction system at Scientific Materials Corp. During these exchanges, the students gain remarkable insight into industry and business while the companies also learn more about capabilities and expertise available at the university. *These valuable relationships lead to career opportunities for the students and encourage them to remain in Montana and contribute their skills to the development of the local community.*

These researchers and students also have had a broader impact on the community through their outreach and volunteer activities. Specifically, over the course of the MREDI effort, students have provided Science, Technology, Engineering, and Mathematics (STEM) outreach by volunteering at local schools and non-profit charities (example shown in Figure 8-8), including at Mindbenders Preschool, Morning Star Elementary School, Hawthorne



*Figure 8-8. STEM outreach at Montana schools.*

Elementary School, and Eagle Mount in Bozeman. Researchers have also helped encourage diversity in STEM fields while working on this MREDI effort, such as graduate student Aislinn Daniels helping to organize the Conference for Undergraduate Women in Physics at MSU on January 13-15, 2017 (see Figure 8-9).



*Figure 8-9. Group Photo of attendees and organizers of the Conference for Undergraduate Women in Physics hosted by Montana State University on January 13-15, 2017. MREDI-supported graduate student Aislinn Daniels acted as a member of the organization committee. Professor Babbitt also contributed to a round table event.*

#### Impact on Montana University Competitiveness:

MREDI continues to have a significant positive impact on the educational and scientific competitiveness of the Montana University System. This project has engendered a range of new collaborations between groups and departments within the university as well as between the university and Montana industry. This has led to innovative research and development as well as enhanced student involvement in interdisciplinary investigations. As part of MREDI and the unique optics and photonics community in Montana, we can provide unparalleled educational training involving close collaboration with both academic and industrial researchers in the field. Furthermore, the new cutting-edge technologies being studied as part of MREDI also provide a rich research environment for students at all stages of their education.

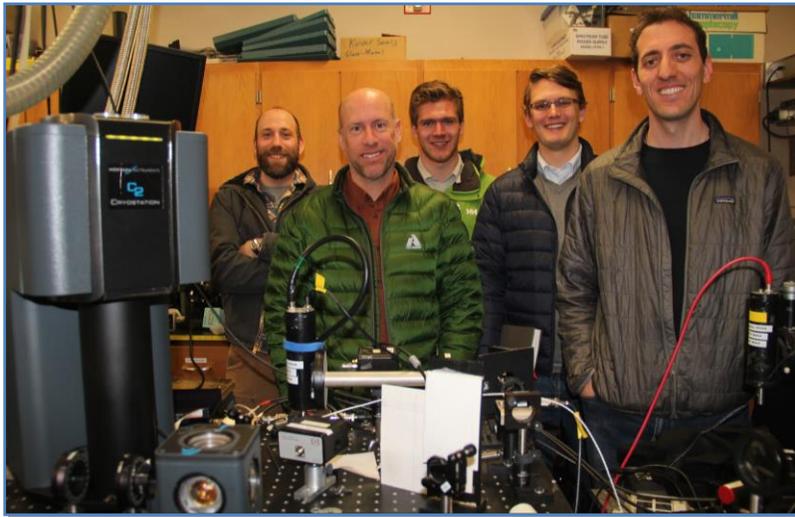
In addition to the impact on students, our MREDI research has also increased the profile of the already excellent fundamental scientific research carried out at MSU. By seeking to combine basic science with practical photonic device integration, our MREDI effort provides an important element in the university research program that attracts new international collaborations and allows more ambitious funding proposals to be submitted to funding agencies.

Our MREDI efforts have also made significant contributions to the university research infrastructure. For example, integration of waveguide devices with cryogenic technology allows new properties of optical materials to be studied that previously could not be accessed. Advanced computational software that has been acquired as part of MREDI (such as Comsol Multiphysics) allows a wide range of photonic and nonlinear optical devices to be designed and simulated, enabling new research proposals that have been submitted. New capabilities for cutting very thin crystalline samples has allowed new optical materials to be studied and also enable new collaborative projects with local companies. A range of optical crystal growth and processing capabilities have been developed at MSU as part of MREDI, allowing us to produce entirely new samples of optical materials that are of both commercial and scientific interest. New laser systems have been built and new interferometric characterization systems have been built to study their properties. Entirely new technologies for characterizing performance of optical waveguides and

variations of the speed of light in crystals have been developed, impacting university research and the local industry as well.

### Impact on Montana Industry Competitiveness

In addition to developing new technologies that will lead to new products for Montana companies, our MREDI efforts have a range of broader impacts on the local optics industry. For example, we have been working with Montana Instruments Corp. to evaluate the performance of their systems in a range of laboratory environments, providing essential feedback (see Figure 8-10). We have also been in discussion to test new prototype systems being developed by Montana Instruments, helping them to refine their product while also providing the university with a new cutting-edge technology beyond the capabilities of systems at other universities. The international exposure that we help provide for their products has also helped to increase sales of their systems, with many researchers working in fields related to current MSU research programs now using Montana Instruments cryocoolers (for example, see work highlighted on the Montana Instruments web site at <http://montanainstruments.com/low-temperature-physics-research/spotlight-on-researchers/1200/Spectral-hole-memory-for-light-at-the-single-photon-level/>).



*Figure 8-10. Engineers and scientists from Montana Instruments visiting MSU to discuss our MREDI efforts and how their instruments are used in practical operation.*

We have also been working closely with Scientific Materials Corp. to develop specialized crystal growth capabilities that will allow some optoelectronic materials to be produced more efficiently. We are also working with Scientific Materials to study optical crystal quality, new materials of commercial interest, and new methods to fabricate very thin, low strain samples of crystals.

As part of MREDI we have also begun studies of how different spectroscopic properties of materials may be used to characterize the chemical and structural properties of optical waveguides produced by AdvR Inc. In addition to being an essential tool for our university research, these studies may also lead to improved performance of their waveguide devices in some applications. We have also adapted the advanced remote sensing and ranging technologies used by the local companies Bridger Photonics and Blackmore Sensors and Analytics (Bozeman) to study the quality of optical waveguides and lithography of AdvR, Inc. products, potentially providing them with an improved non-destructive method for product quality control and optimization that could lead to greater product yields and lower costs. Furthermore,

we expect that our work on developing sub-micron periodically-poled nano-photonic devices will directly lead to an entirely new class of products for AdvR, Inc.

Tying everything together, our innovations and studies all directly impact the photonic signal processing devices under development at S2 Corporation. Each technology developed or improved as part of our MREDI work can be incorporated into the integrated signal processing devices, potentially improving system performance or providing alternative design options. As such, this work supplies key seedling technologies that lead to continued product development, new federal funding, and increased revenue.

#### Impact on Student Employment in Montana Industries:

Employment in the optics and photonics industry has continued to expand at a rapid pace, with new personnel recently being hired at all of our partner companies. In particular, management at both S2 Corporation and Montana Instruments Corporation have said that their needs for employees is far surpassing the supply of workers being produced in the state. MREDI provides a key service in helping to make students aware of these career opportunities and encouraging them to enter these fields where the Montana economy is rapidly growing. This strong collaborative and invigorating environment also encourages more senior professionals to remain in the state. In one case, a senior researcher turned down a lucrative job offer to move to CA to work on lighting system development in order to remain in Montana and work with MSU and local industry on this MREDI effort. In addition, the students that have graduated while working on this MREDI effort have all either found immediate employment in their chosen field or continued with their higher education in Montana.

Undergraduate student Kaitlin Poole completed her Bachelor's degree in Physics at MSU while working on this MREDI effort, and after graduating from MSU, she received a commission as an active duty second lieutenant and was deployed to the Information Directorate of the Air Force Research Lab (AFRL) in Rome, NY, where her title is Physicist. Kaitlin achieved her immediate career goals as a result of this MREDI work and her Air Force ROTC training, and she plans to continue with her professional career in lasers and photonics development. Kaitlin and her family are residents of Bozeman, where her father works in health care.

Undergraduate student Brett Wilkins, shown in Fig. 8-11, also completed his Bachelor's degree in Physics at MSU while working on this MREDI effort. After graduating from MSU, as a direct result of this MREDI effort Brett applied for a job at AdvR, Inc. in Bozeman, MT and was subsequently hired for a position to help with producing and characterizing their waveguide products. Brett has recently entered the physics graduate program at MSU and is continuing to work part time at AdvR Inc. while pursuing his MS degree.



*Figure 8-11. Brett Wilkins completed his MSU Physics B.S. degree and was employed by AdvR Inc. to help develop optical waveguide products.*

#### Impact on New Technology Patents:

During our MREDI effort, a promising new technology was developed for providing enhanced thermal contact with insulating optical materials, allowing increased maximum system operating powers in the cryogenic environment. We are working with MSU TechLink to prepare a provisional patent application for this invention. We expect that this technology will directly impact several local Montana companies, including S2 Corp., Montana Instruments Corp., and Scientific Materials Corp., each for a different

potential market segment (photonic signal processing, cryogenic systems, and high-power lasers, respectively).

Impact on International Scientific Collaborations:

The results and technologies resulting from our MREDI effort have greatly enhanced our international scientific collaborations. Many aspects of our MREDI work are more broadly relevant to emerging fields such as secure quantum communications, leading to new interactions with other research groups and institutes. During MREDI, we have hosted **12 international visitors** as part of collaborations with groups at California Institute of Technology, University of San Francisco, University of South Dakota, University of Calgary (Alberta, Canada), Australian National University (Australia), Chimie Paristech (France), AlphaNov (France), and University of Otago (New Zealand), some of which are shown in Figure 8-12. No MREDI funds were used for any visits and all expenses were covered either by the visiting researchers or other sources.

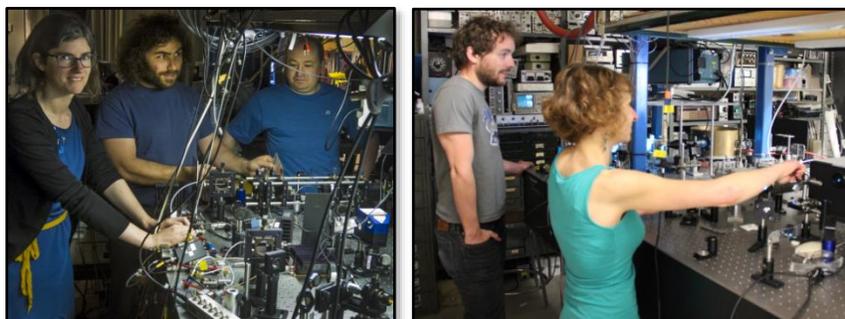


Figure 8-12. (left) Researchers and students working on MREDI efforts in the MSU Physics Department. (right) A visiting scientist and graduate student from University of Calgary working in the MSU Physics Department on characterizing new rare-earth materials for signal processing applications related to the MREDI effort.

In addition to these visits, our MREDI efforts have allowed us to initiate new collaborations with groups at the University of Ghent (Belgium) and the Wigner Research Centre for Physics (Hungary) that have provided us with new specialized optical materials that open new avenues for research and potential photonic applications.

Impact on International Promotion of Montana Science and Industry

The extensive international collaborations involved in parts of our MREDI research have led to increased exposure of the local optics industry to international markets. We routinely arrange for visiting researchers to tour several of the local companies whenever they visit Bozeman, increasing awareness of the impressive technological products produced here in Montana. Furthermore, presentations by MSU personnel at international professional conferences highlight the interaction with the local industry and the unique products available from them. During the course of this project, personnel working on MREDI have presented **10 invited talks, seminars, and colloquia**, with all travel expenses paid for with other funding sources. At many of these meetings, substantial excitement and interest was expressed by the audience regarding the Montana photonics industry and the products that they offer.

## Impact on Scientific Research Publications

Our MREDI-supported research has already led to **10 publications in peer-reviewed scientific journals**. These publications increase the international prestige and profile of the university research programs as well as the state of Montana more broadly. These publications are listed below.

- “Enhanced properties of a rare-earth-ion-doped waveguide at sub-Kelvin temperatures for quantum signal processing,” N. Sinclair, D. Oblak, C. W. Thiel, R. L. Cone, and W. Tittel, *Physical Review Letters*, accepted (2017).
- “Effects of mechanical processing and annealing on optical coherence properties of  $\text{Er}^{3+}:\text{LiNbO}_3$  powders,” T. Lutz, L. Veissier, C. W. Thiel, P. J. T. Woodburn, R. L. Cone, P. E. Barclay, and W. Tittel, *Journal of Luminescence*, accepted (2017).
- “Effects of disorder on optical and electron spin linewidths in  $\text{Er}^{3+}, \text{Sc}^{3+}:\text{Y}_2\text{SiO}_5$ ,” S. Welinski, C. W. Thiel, J. Dajczgewand, A. Ferrier, R. L. Cone, R. M. Macfarlane, T. Chanelière, A. Louchet-Chauvet, and P. Goldner, *Optical Materials* 63 (2017) 69.
- “Quadratic Zeeman effect and spin-lattice relaxation of  $\text{Tm}^{3+}:\text{YAG}$  at high magnetic fields,” L. Veissier, C. W. Thiel, T. Lutz, P. E. Barclay, W. Tittel, and R. L. Cone, *Physical Review B* 94 (2016) 205133.
- “Effects of fabrication methods on spin relaxation and crystallite quality in Tm-doped  $\text{Y}_3\text{Al}_5\text{O}_{12}$  powders studied using spectral hole burning,” T. Lutz, L. Veissier, C. W. Thiel, P. J. T. Woodburn, R. L. Cone, P. E. Barclay, and W. Tittel, *Science and Technology of Advanced Materials* 17 (2016) 63.
- “Optical spectroscopy and decoherence studies of  $\text{Yb}^{3+}:\text{YAG}$  at 968 nm,” T. Böttger, C. W. Thiel, R. L. Cone, Y. Sun, and A. Faraon, *Physical Review B* 94 (2016) 045134.
- “Modification of phonon processes in nanostructured rare-earth-ion-doped crystals,” T. Lutz, L. Veissier, C. W. Thiel, R. L. Cone, P. E. Barclay, and W. Tittel, *Physical Review A* 94 (2016) 013801.
- “Optical decoherence and spectral diffusion in an erbium-doped silica glass fiber featuring long-lived spin sublevels,” L. Veissier, M. Falamarzi, T. Lutz, E. Saglamyurek, C. W. Thiel, R. L. Cone, and W. Tittel, *Physical Review B* 94 (2016) 195138.
- “Rare-earth doped transparent ceramics for spectral filtering and quantum information processing,” N. Kunkel, A. Ferrier, C. W. Thiel, M. O. Ramírez, L. E. Bausá, R. L. Cone, A. Ikesue, and P. Goldner, *APL Materials* 3 (2015) 096103.
- “Efficient and long-lived Zeeman-sublevel atomic population storage in an erbium-doped glass fiber,” E. Saglamyurek, T. Lutz, L. Veissier, M. P. Hedges, C. W. Thiel, R. L. Cone, and W. Tittel, *Physical Review B* 92 (2015) 241111(R).

## Highlights of Technical Achievements

Over the course of the MREDI project, many technical goals and new innovations have been achieved. Some of these successes and developments have been summarized in earlier project reports, with several of the more significant accomplishments briefly highlighted in the following list.

- Optical coupling of waveguides held at 4K in mechanical cryocoolers
- Testing of Montana Instruments and S2 Corporation mechanical cryocoolers
- Spectroscopic testing of new laser materials produced by Scientific Materials Corp
- Development of a new technology for nondestructive characterization of optical waveguides
- Optical study of optical waveguide properties at cryogenic temperatures
- Numerical simulations of rare-earth-ion resonance lineshapes in crystals

- Investigation of deuterium-exchanged optical waveguides
- Development of sub-micron periodically-poled nano-photonic devices
- Testing vibrationally induced coherence loss in closed-cycle optical cryostats
- Development of improved laser characterization capabilities at new wavelengths
- Study of the effects of chemical processing on optical spectra of crystals
- Development of fluorescence and Raman microscopy waveguide characterization techniques
- Optical lithography and waveguide fabrication in lithium niobate crystal wafers
- Lithium niobate opto-electronic crystal growth
- Diffusion doping of rare earth ions into lithium niobate crystals
- Fabrication of proton exchanged waveguides in rare-earth-activated crystals at MSU
- Theoretical analysis of the effects of spectral hole burning on optical waveguides
- Material and waveguide chemical composition characterization at MSU physics and ICAL
- Design of lithography masks for testing rare-earth-activated waveguide devices
- Development of new cryogenic sample mounting hardware
- Optical waveguide theoretical modeling and computer simulations using COMSOL Multiphysics

### Highlights of Recent Project Activities (Q6)

- While working on this MREDI effort, undergraduate student Riley Nerem (Physics), wrote and submitted a successful research proposal “Development of Low-Cost Scanning Fabry-Perot Interferometers to Characterize High-resolution Laser Systems” for the Spring 2017 semester that was funded by the MSU Undergraduate Scholars Program. Riley’s project is directly related to our MREDI goals.
- S2 Corporation in consultation with Spectrum Lab contracted the growth of a Tm:LiNbO<sub>3</sub> crystal from United Crystals with S2 internal funds. Samples were provided to S2 Corp., scattering analysis performed by Spectrum Lab showed a couple small defects in one sample. However, the defects were small enough to allow a clear path for further laser testing of the material. S2 Corp. has ordered additional samples from United Crystals out of this boule. In addition, S2 Corp. has contracted the growth of a Tm:LiNbO<sub>3</sub> crystal from Gooch & Housego with S2 funds. Sample crystals from this boule are being delivered and will be characterized for absorption and coherence as in Figure 8-13.

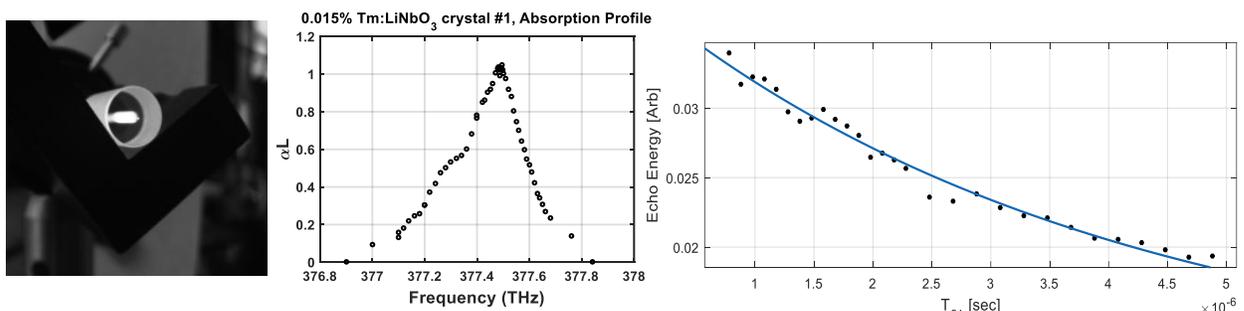


Figure 8-13. (Left) Picture of Tm:LiNbO<sub>3</sub> crystal with laser beam shined through crystal to look for defects. (Middle) Absorption spectrum of the United Crystals Tm:LiNbO<sub>3</sub> sample measured using the Rabi edge technique. The 3 dB absorption bandwidth is over 180 GHz wide. (Right) A fit to the two pulse echo measurement gives a coherence time ( $T_2$ ) of 16  $\mu$ s which is similar to prior Tm:LiNbO<sub>3</sub> samples used by Spectrum Lab.

- Work continued on fabrication and modeling of nano-scale periodically poled non-linear crystals (see Figure 8-14). The COMSOL simulation software was employed to model the electric field distributions present during these poling experiments. Preliminary models of the nano-scale electrode's poling field have been investigated. Further work to incorporate the field's time dependence and evolution of the flipping ferroelectric domains is underway. Based on the potential for this technology to provide strong non-linear optical response that would be of benefit for remote sensing applications, a proposal for further funding was submitted in October 2016. The proposal stresses the important collaboration between MSU's various laboratories and local companies including MMF, ICAL, AdvR Inc., and Spectrum Lab.

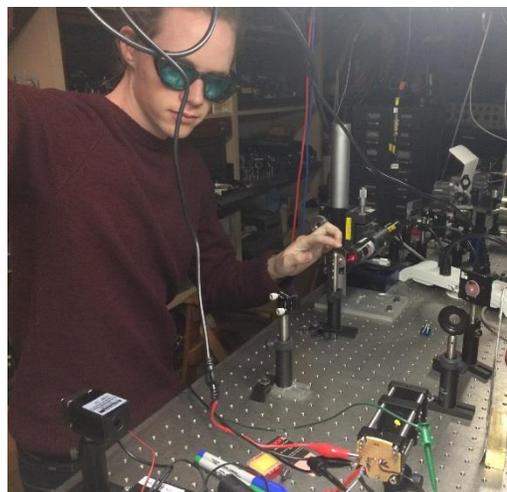


*Figure 8-14. Resolution marks showing 2,5, and 10 micron scale lithographic patterning of chrome on a fused quartz substrate. Successful UV lithographically patterned electrodes will be the basis for electron beam lithography nano-patterning.*

- MSU graduate students worked with Scientific Materials Corp. to help optimize crystal growth of rare-earth-doped lithium niobate with feedback from optical spectroscopy performed at MSU.
- The Cone-Thiel Research group has worked with a recently hired product manager at Scientific Materials Corp to provide them with a new technique developed at MSU for optically orienting biaxial crystals.
- New cryogenic sample mounts for the Montana Instrument C2 Cryostation system were designed that can mask and hold multiple samples. This design was shown to Montana Instruments engineers who will work on implementing these types of sample holders for new and existing customers (see Figure 8-10).
- Undergraduate Kyle Olson with graduate students Tino Woodburn and Aaron Marsh worked with AdvR to use their M-Line system to characterize waveguide samples fabricated at MSU.
- Postdoctoral researcher Dr. Caroline Richard joined the Cone research group to work on the MREDI effort.
- Undergraduate student Brock Pommer, majoring in Physics and Mechanical Engineering, has joined the Cone research group to work on the MREDI research efforts.
- During Fall semester 2016, undergraduate and graduate students enrolled for class credit in a weekly seminar series focused on MREDI and Spectrum Lab related research efforts.
- Dr. Charles Thiel presented an invited talk "Design and Characterization of Materials for Rare-earth Quantum Memories" at the 47th Winter Colloquium on the Physics of Quantum Electronics in Snowbird Utah, January 8-13, 2017 that described our MREDI research and related work. All travel expenses were paid by the National Science Foundation.

- Dr. Jevon Longdell from University of Otago, New Zealand visited MSU January 14-17, 2017 to discuss ideas for new potential applications of rare-earth-activated materials and collaborative research plans. Dr. Longdell also presented a seminar "Toward quantum state conversion between microwave and optical photons' information using rare earth ions in solids" at MSU during his visit.
- Dr. Paul Barclay from University of Calgary, Canada will visit MSU February 9-11, 2017 to discuss collaborative research projects and present a colloquium on "Nanophotonic optomechanical devices: towards coupling photons, phonons and spins".
- MREDI-supported graduate student Aislinn Daniels acted as a member of the organization committee for the Conference for Undergraduate Women in Physics hosted by Montana State University on January 13-15, 2017. Specific roles included campaigning for funding for the conference from local optics businesses, organizing and running the undergraduate poster session during the conference itself, and serving as organizational support during the conference.
- Graduate Student Aislinn Daniels helped write sample questions for the Optics portion of the Montana Science Olympiad on November 22, 2016.
- Professor Babbitt participated in a round table event at the Conference for Undergraduate Women in Physics hosted by Montana State University on January 13-15, 2017. He discussed with interested physics students about his experiences working in research and answered their many questions.
- Graduate student Tino Woodburn had an outreach presentation at the Hawthorne Elementary School January 26 describing his scientific research on MREDI and encouraging STEM careers.
- Professor Babbitt did an outreach presentation for the 5th Grade Class at Morning Star Elementary School in Bozeman (December 2015), encouraging young students to pursue a career in science.
- Graduate student Aaron Marsh developed and implemented a new interferometric measurement technique for measuring changes in refractive indices in bulk media. Extending the process to measuring optical waveguides within the Montana Instruments cryocooler is currently underway.

- Undergraduate Riley Nerem, with guidance from Aaron Marsh and Tino Woodburn constructed a low-cost Scanning Fabry perot interferometer (SFPI) for use with lasers at the common 632 nm He-Ne wavelength (Figure 8-15). Testing of the SFPI has shown that its free spectral range is slightly unstable. Future options for improvement in this area include increasing the mass of the SFPI and better isolating the SFPI in a light tight enclosure. Information gained from building and testing this SFPI will be used to create similar SFPIs at the variety of wavelengths required in the lab.
- A new collaboration has begun with a student in the MFA in Science & Natural History Filmmaking (SNHF) program to make short videos about the research we are pursuing.



*Figure 8-15. Undergraduate Riley Nerem working on development of a Scanning Confocal Fabry-Perot Interferometer to characterize new laser sources being developed as part of MREDI.*

**Expenditures to date** (Grant 41W416) Personnel \$274,084.60, Benefits \$67,207.15, Operations \$150,017.44, Capital Equipment \$127,240.00; Total Expenditures **\$618,549.19**.

**Subproject 9: Optical Parametric Oscillator for Tunable Lasers** (Kevin Repasky, repasky@ece.montana.edu, with AdvR, Inc.). Investigate optical parametric oscillator performance in support of characterizing large aperture periodically poled non-linear optical crystals and in support of continued development of large area methane detection.

Milestones

- a) December 2016: Model optical parametric oscillator performance using SNLO modeling tools
- b) June 30, 2017: Demonstrate singly resonant optical parametric oscillator pumped at 1064 nm and seeded at 1571 nm
- c) June 30, 2017: Final report including scientific merit and commercial products or potential

Progress toward objectives

A dither locking system was added to the optical cavity as shown in the block diagram in Figure 9-1. In this process, a sinusoidal signal with a frequency of 5000 Hz from a function generator is fed into an acousto-optic modulator (AOM) that modulates the input seed laser with a Doppler shift. The first order beam is then fiber coupled into the optical amplifier while the rest of the seed laser path remains unchanged. For locking the cavity, the output signal transmitted through the cavity at the seed wavelength of 1571 nm is measured on an InGaAs detector. This information is next sent to the hold circuit and then to the lock-in amplifier. Here, the amplitude of signals oscillating at the dither frequency is extracted to create the error signal which is proportional to the change of cavity length required to keep the cavity in resonant at 1571 nm. This error signal is then used as an input and a reference for a ramp generator when controlling a piezo-electric transducer (PZT) that is attached to the flat mirror for locking the cavity.

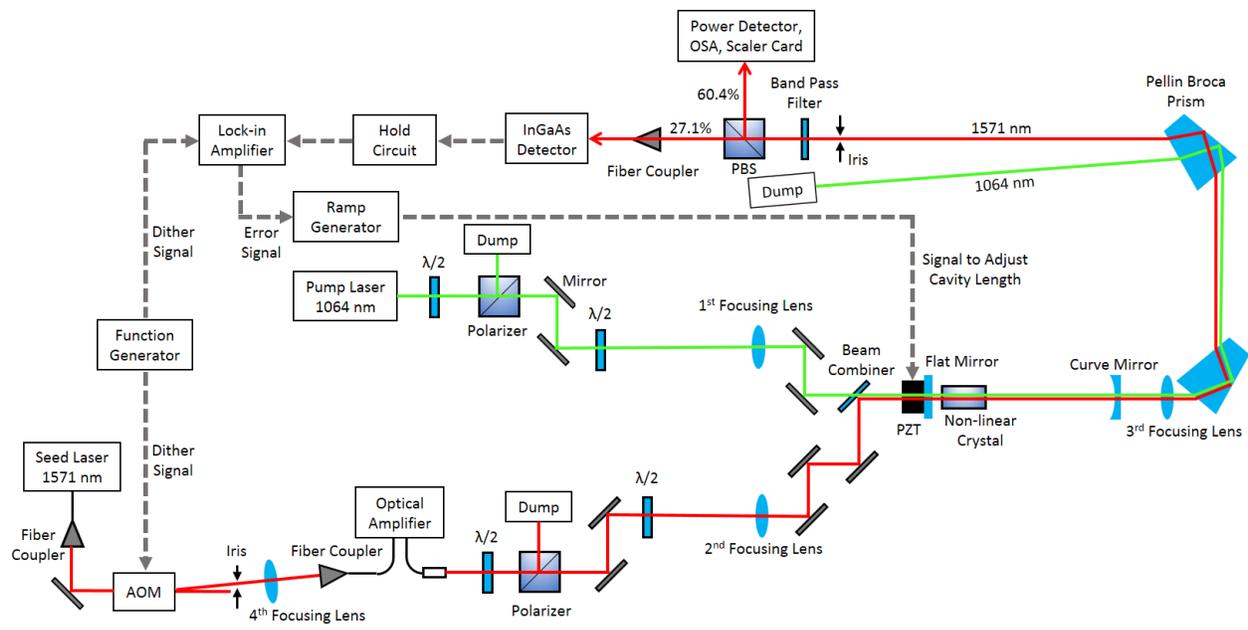


Figure 9-1. Schematic of the setup for the locked OPO

Figure 9-2 shows the results of the output signal energy measurement for OPG, OPA, unseeded-unlocked OPO, seeded-unlocked OPO, and seeded-locked OPO cases. As expected, the output energy from the seeded-locked OPO is the highest among the five, followed by the seeded-unlocked OPO, unseeded-unlocked OPO, OPA, and OPG. At the input pump energy above 8 mJ, all three OPO output energies drops down and becomes lower than that of OPG and OPA. This is likely due to the broadening of the spectra at higher pump energies, which may be corrected with a higher power seed laser. The conversion efficiency for each case is calculated and plotted in Figure 9-3.

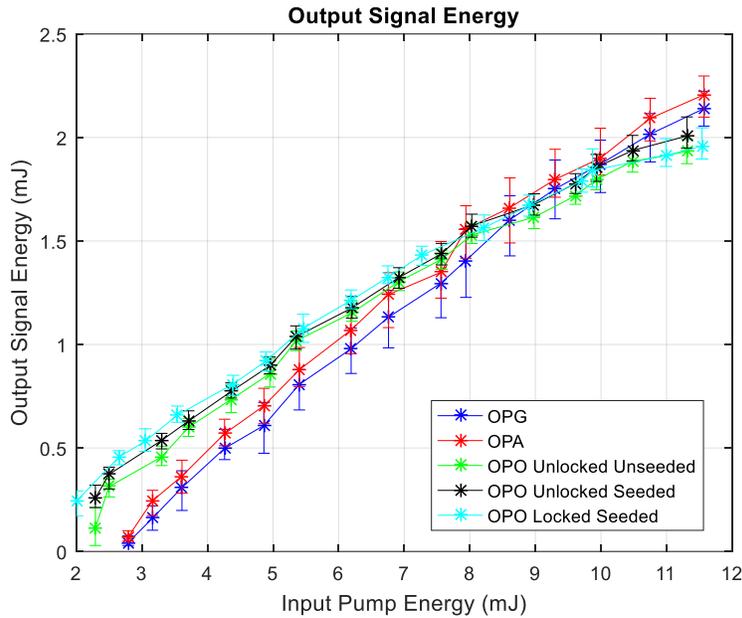


Figure 9-2. Output signal energy for OPG/OPA/OPO cases.

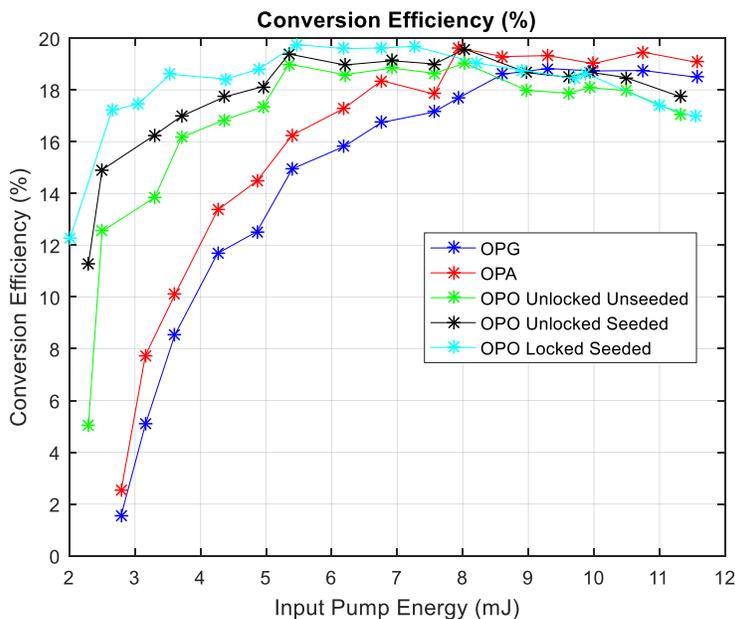


Figure 9-3. Conversion efficiency correspond to figure 9-2.

SNLO program developed at Sandia National Laboratory is used to calculate and predict the performance of the OPA process. The program input values involved specifically in this experiment including the information about nonlinear crystal such as type, dimensions, location, and index of refraction at operating wavelengths, as well as the information about the pump and seed laser's Gaussian properties are shown in figure 9-4. The program runs separately for each case of the pump input power ranged from 0.5-12 mJ, the nonlinear coefficient  $d_{\text{eff}}$  ranged from 12-16 pm/V, and  $\Delta k$  value ranges from 0-0.3  $\text{mm}^{-1}$ .

	Red1	Red2	Blue
Wavelengths (nm)	1571	3297	1064
Indexes of refraction	2.207493	2.078871	2.147591
Phases at input (rad)	0	0	0
ar coated (1=yes 0=no)	1	1	1
Crystal loss (1/mm)	0	0	0
Energy/power (J or W)	0.160	0.00E0	0.012
Pulse duration (fwhm ns)	0	10	10
Beam diam. (fwhm mm)	0.22091	0.40358	0.40358
Supergaussian coeff.	1	1	1
n2 red1 (sq cm/W)	0.00E0	0.00E0	0.00E0
n2 red2 (sq cm/W)	0.00E0	0.00E0	0.00E0
n2 blue (sq cm/W)	0.00E0	0.00E0	0.00E0
beta red1 (cm/W)	0.00E0	0.00E0	0.00E0
beta red2 (cm/W)	0.00E0	0.00E0	0.00E0
beta blue (cm/W)	0.00E0	0.00E0	0.00E0
Walkoff angles (mrad)	0	0	0
Offset in wo dir. (mm)	0	0	0
Rad. curv. (mm/air)	-420.548	-121.7259	-121.7259
# of integ/grid points	500	256	256
Crystal/grid sizes (mm)	32	0	0
Deff (pm/V)	15		
Delta k (1/mm)	0		
Dist. to image (mm)	0		
# time steps	20		

Suggested value = 20. Increase for greater time resolution.  
(irrelevant for all cw beams).

Figure 9-4. SNLO program inputs for OPA using 1571 nm seed laser.

Plots of OPA output energy and conversion efficiency both from the experiment and SNLO are shown in figure 5 and 6 respectively. The most agreeable result between the experiment and SNLO is when  $d_{\text{eff}} = 13 \text{ pm/V}$  and  $\Delta k = 300 \text{ m}^{-1}$ . It should be noted that the experimental results at high input pump energies tends to disagree with that from SNLO. This is likely due to more broadening of the spectra at higher pump energies, which may be corrected with a higher power seed laser.

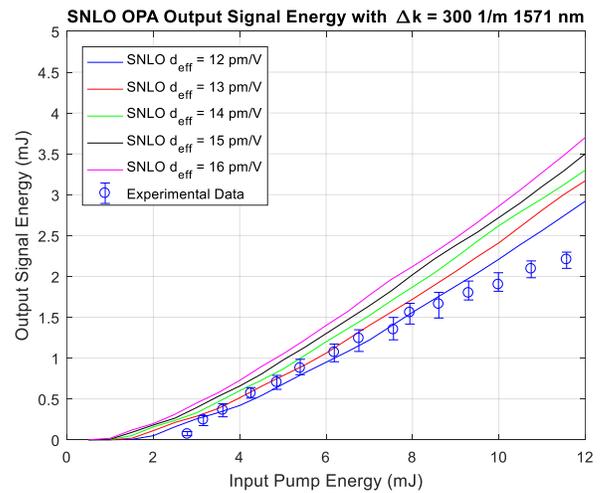
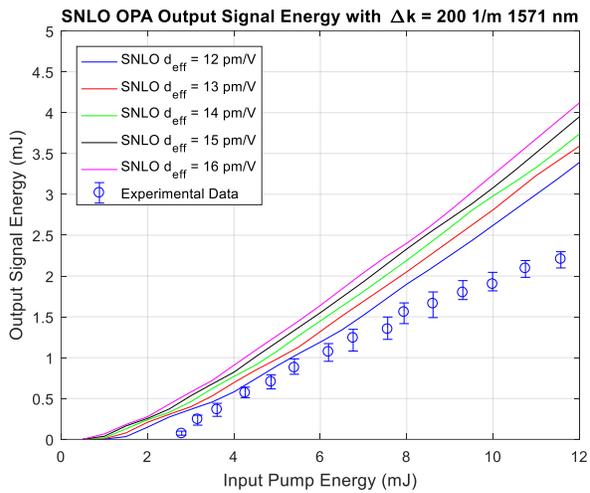
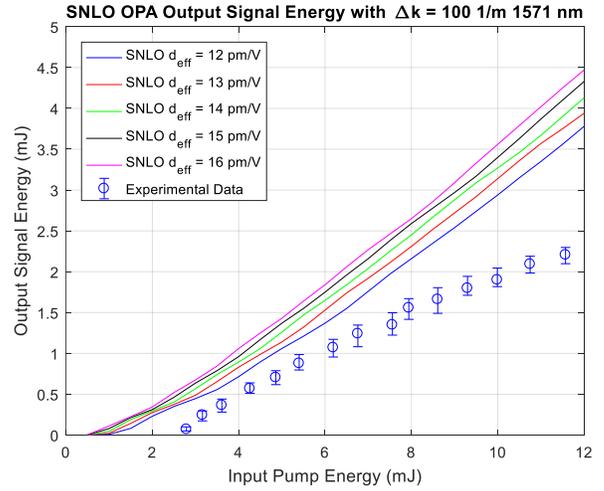
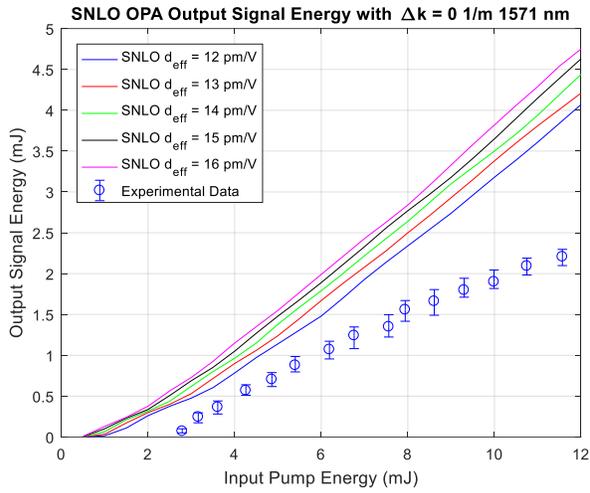


Figure 9-5. Plots of OPA output energy from the experiment and SNLO predictions with different values of  $d_{\text{eff}}$  and  $\Delta k$ .

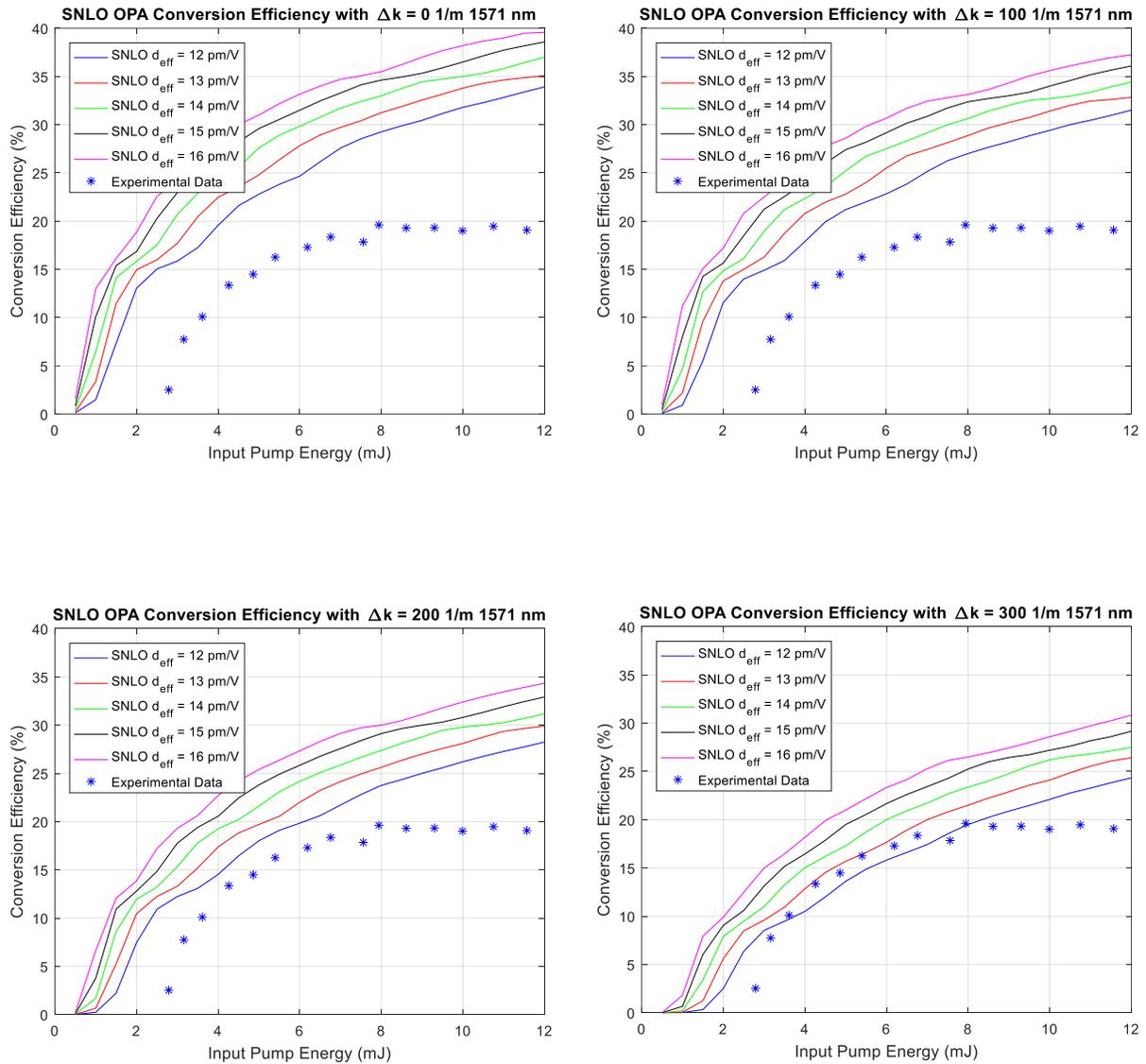


Figure 9-6. Plots of the corresponding OPA output conversion efficiency for figure 9-5.

The SNLO program was also used to predict the output energies for the OPA case with the 1654 nm seed laser. The SNLO input for the 1654 nm case is shown in figure 9-7. SNLO results for  $d_{\text{eff}}$  ranging from 12-16 pm/V and  $\Delta k = 0$  and  $0.3 \text{ mm}^{-1}$  are shown in figure 9-8.

2 dimensional long-pulse mixing

	Red1	Red2	Blue
Wavelengths (nm)	1654	2983	1064
Indexes of refraction	2.204883	2.159973	2.228959
Phases at input (rad)	0	0	0
ar coated (1=yes 0=no)	1	1	1
Crystal loss (1/mm)	0	0	0
Energy/power (J or W)	0.180	0	0.012
Pulse duration (fwhm ns)	0	10	10
Beam diam. (fwhm mm)	0.22091	0.40358	0.40358
Supergaussian coeff.	1	1	1
n2 red1 (sq cm/W)	0.00E0	0.00E0	0.00E0
n2 red2 (sq cm/W)	0.00E0	0.00E0	0.00E0
n2 blue (sq cm/W)	0.00E0	0.00E0	0.00E0
beta red1 (cm/W)	0.00E0	0.00E0	0.00E0
beta red2 (cm/W)	0.00E0	0.00E0	0.00E0
beta blue (cm/W)	0.00E0	0.00E0	0.00E0
Walkoff angles (mrad)	0	0	0
Offset in wo dir. (mm)	0	0	0
Rad. curv. (mm/air)	-420.548	-121.7259	-121.7259
# of integ/grid points	300	256	256
Crystal/grid sizes (mm)	32	0	0
Deff (pm/V)	16		
Delta k (1/mm)	0.3		
Dist. to image (mm)	0		
# time steps	20		

Accept

Phase velocity mismatch  $\Delta k = k_{\text{blue}} - (k_{\text{red1}} + k_{\text{red2}})$ .  
This is not automatically calculated from the refractive indices input on line 2.

Figure 9-7. SNLO program inputs for OPA using 1654 nm seed laser.

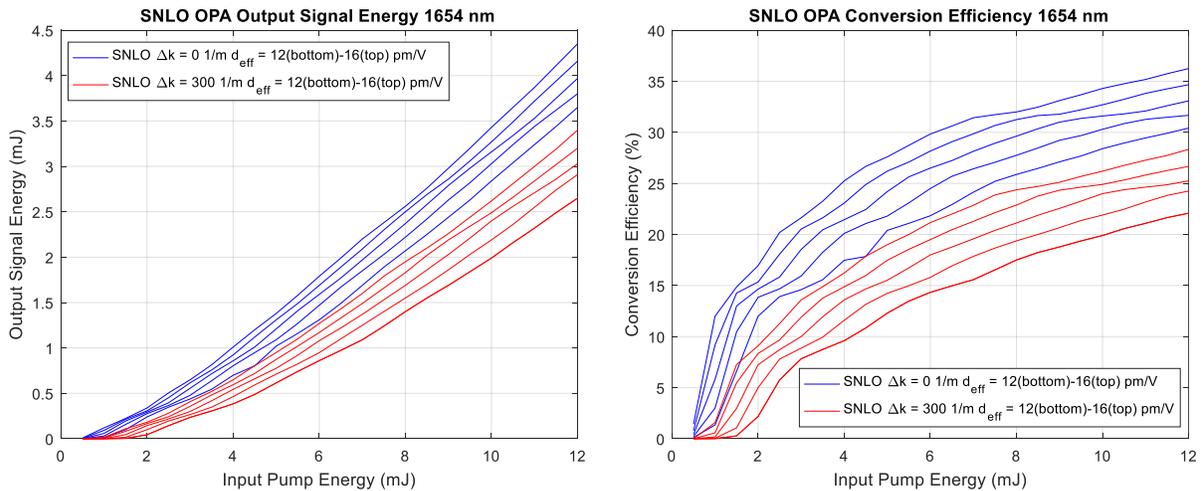


Figure 9-8. SNLO program output energy and conversion efficiency for OPA using 1654 nm seed laser.

**Expenditures to date** (Grant 41W412) Personnel \$45,415.55. Benefits \$3,297.47, Operations \$27,210.90; total Expenditures **\$75,920.92**.

**Subproject 10: Nonlinear Optical Detection of Surface Contaminants** (Rob Walker, rawalker@chemistry.montana.edu, with Altos Photonics). Develop a new method for detecting organic contaminants that accumulate on the surface of water based on nonlinear vibrational overtone spectroscopy (NVOS).

#### Milestones

- a) December 2015: Demonstrate feasibility of using new spectroscopic method for surface detection of adsorbed species
- b) June 2016: Submit SBIR application with Altos to develop detection and monitoring instrument based on NVOS
- c) December 2016: Successful application of NVOS to environmentally relevant systems including contaminants on water surfaces and solid substrates

#### Progress toward objectives

This project's goal is to develop new surface specific, optical methods capable of detecting adsorbed molecules. Specifically, our efforts are focused on exploiting the advantages of nonlinear optical spectroscopy to create a simple, sensitive technique that can identify the presence of organic contaminants at water/air and solid/liquid interfaces. Our ultimate objective is to use discoveries from our seminal studies to guide the development of portable devices capable of being used for field measurements.

The fourth quarter of 2016 saw significant disruption and a lack of productivity on project-specific activity due to construction for the new dining hall on the north end of CBB and an unexpected, building-wide power outage in December. The original service visit in late-October brought the Ti:sapphire laser back up to specifications but those advances were short lived. Dust and other residue resulting from construction coupled with improved laser powers resulted in damage to optics and NLO crystals in the optical parametric amplifier. We continue to repair damage wrought by the construction activity (and its ripple effects) and will have the final installation of new nonlinear optical crystals in the OPA in early February 2017. These repairs are being covered, by agreement, with the state insurance claims department.

During this time, we performed a number of thermodynamic, surface tension measurements on systems that we will use to test ideas about NLO overtone vibrational spectroscopy. These surface tension measurements characterized the effects of solutes on insoluble lipid monolayers and data are being used to calculate energies of adsorption. While this work is not directly related to the 'optical' mission of the project, it does serve a valuable purpose by characterizing surface coverage, phase behavior and (inferred) molecular organization at environmentally relevant aqueous-air interfaces.

While students continued to work on making our experimental assembly functional again, I submitted one proposal to continue the work initiated with MREDI funding. The proposal was submitted to the National Science Foundation's Chemistry Division, with the title, NONLINEAR OPTICAL STUDIES OF HIGH TEMPERATURE SURFACE CHEMISTRY IN ENERGY CONVERSION SYSTEMS. The proposal's project summary appears on the next page. The proposal requests \$417K (\$320K direct) over 3 years with a requested start date of May 1, 2017. If awarded, this proposal will support two graduate students, one of whom will continue to develop new NLO methods for studying interfaces.

Another new proposal to be submitted to the DOE was begun in December and will be submitted January 31. This proposal will be described in the next quarterly report.

Finally, a manuscript was submitted to the Journal of Physical Chemistry B describing the properties a solute experiences adjacent to environmentally relevant lipid membranes. MREDI funding provided partial support for these studies. Reviews have been returned and are generally favorable. I expect that the manuscript will be accepted for publication in February, 2017. The title of the manuscript is "Temperature Dependent Partitioning of Coumarin 152 in Phosphatidylcholine Lipid Bilayers" with a lead author of Christine Gobrogge (MSU graduate student) and Heather Blanchard (MSU undergraduate alumna).

The following page contains the project summary of the grant proposal submitted to the National Science Foundation in October, 2016.

### **Project Summary**

**Overview.** Directly observing chemical changes on high temperature surfaces of functional materials is difficult. Materials need to be integrated into devices at room temperature and then heated to operational conditions. All components of a high temperature sample cell must have thermal expansion coefficients suitably matched to avoid mechanical stresses that can develop as the assembly is heated. Furthermore, the need for optical access at high temperatures imposes significant challenges for managing thermal loads. Maintaining dual atmosphere and electrochemical polarization control adds an additional level of complexity to apparatus design. Difficulties notwithstanding, however, quantitative information about phase stability, catalytic activity, and material migration (mass transfer) are necessary for either validating proposed high temperature surface chemistry mechanisms or spurring the development of new models.

Research described in this proposal will develop approaches that use second order nonlinear optical (NLO) spectroscopy to study chemical changes occurring on high temperature materials commonly used in energy conversion applications. In this context, 'high temperature' refers  $T \geq 600^\circ\text{C}$ . Relevant energy conversion applications include electrochemical oxidation and electrolysis in solid oxide fuel cells (SOFCs) and hydrogen generation in concentrated solar thermal reactors where a material's catalytic activity is tuned by controlling temperature,  $\text{P}_{\text{O}_2}$ , composition, and applied electrochemical bias. Particular attention will focus on performing measurements *in operando*. The primary NLO method developed in this work will be resonance enhanced second harmonic generation (SHG). SHG is a well suited for stand-off, noninvasive studies of materials in chemically aggressive environments. In instances where a material's bulk structure is centrosymmetric, the SHG response is necessarily localized to the anisotropic surface region. SH signal *can* arise from bulk materials that lack inversion symmetry but the surface contribution can still be extracted through analysis of the signal's phase and wavelength dependent resonance behavior. Resonance enhancement ensures the chemical (or material) selectivity necessary for answering specific questions about oxidation states, phase formation, and mass transfer.

**Intellectual Merit.** Very few methods have proven capable of measuring high temperature surface chemistry *in operando* with the chemical specificity needed to validate proposed mechanisms describing chemical and electrochemical oxidation and reduction. The proposed research goals are as follows:

- Developing and applying 2<sup>nd</sup> order NLO techniques to study high temperature surface chemistry in functioning energy conversion devices.

- Testing proposed mechanisms that describe material segregation and new phase formation in ceramic electrodes with a particular emphasis on reversible and irreversible electrochemically driven changes in material structure and chemical oxidation state.

Collectively, these goals represent an ambitious push of 2<sup>nd</sup> order NLO spectroscopy into new areas that have remained off limits to material specific, *operando* investigation.

**Broader Impact.** Addressing the goals presented in the Intellectual Merit will significantly expand the capability of 2<sup>nd</sup> order NLO spectroscopy and open up new areas of materials chemistry for surface and species specific optical investigation. The proposed research program will provide a deep and broad multi-disciplinary platform to train graduate students and prepare them to become leaders in the general fields of surface and materials science, chemical analysis and physical chemistry. Outreach is structured to provide a platform that develops strong communication skills and mentoring abilities. Additionally, mentoring efforts also serve underrepresented populations through MSU's Montana Apprenticeship Program (MAP) run by MSU's American Indian Research Opportunities (AIRO) Office. Participants in this program learn about the opportunities, challenges and rewards of scientific research and, depending on the duration of their stay, assist in performing experiments. The experience has been successful for the PI in the past 7 years and led to strong relationships with AIRO director and staff. Finally, students supported by this program will participate in community engagement and education activities by volunteering to help organize and judge elementary school science fairs throughout the Bozeman Public School District.

**Expenditures to date** (Grant 41W415) Personnel \$39,219.51. Benefits \$1,852.09, Operations \$19,397.24; total Expenditures **\$60,468.84**