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RPPR Final Report
as of 02-Dec-2019

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Major Goals: Optical spectroscopy is a very powerful tool for materials research that employs a wide range of frequencies in the electromagnetic spectrum to probe structural, electronic and magnetic properties of materials. Optical spectroscopy is a broadly defined term that includes spectroscopic techniques that involve use of electromagnetic spectrum in the energy range from far-infrared (FIR)/THz to ultravoilet (UV). This energy scale carries the fingerprints of various physical phenomena that determine fundamental characteristics of material. Henceforth, optical spectroscopy remains as the best non-destructive characterization method for scientists across various disciplines such as physics, chemistry, life sciences and engineering.

Investigations on materials properties require not only an accurate probing tool but also controlled external environments that tune the properties of materials. The response of materials to these external parameters unravels the microscopic phenomena responsible for their properties. The most common external control parameter is temperature and mechanisms involving very small energy scale are best analyzed at temperatures as low as possible. Therefore, spectroscopic studies are performed on materials at low temperatures. In addition to very low temperature, high magnetic fields and high pressures also act as excellent extreme conditions for manipulating material properties. Combining one or more of low temperature, high magnetic fields and high pressures with spectroscopic techniques requires superior experimental skills due to the difficulty level involved. Therefore, experiments employing all three extreme conditions are less common even though the yielded information is usually groundbreaking and extremely beneficial in understanding the nature of materials. It is also worth noting that spectroscopy in general is quite difficult to accomplish depending on the frequency range of the electromagnetic spectrum. Some frequencies are more difficult to access than others due to strict laws of nature.

The expertise of the PI is to combine the spectroscopy with one or more of extreme conditions to investigate functional materials. EPR, THz and infrared spectroscopy, Raman scattering and photoluminescence spectroscopy will be employed in combination with low temperatures, high magnetic fields and/or high pressures.

Most of the research work especially those requiring high magnetic fields will be accomplished as an external user at the National High Magnetic Field Laboratory (Maglab). Maglab is an unique world-class user facility that offers excellent resources for conducting experiments at magnetic fields up to 45 T. However optical spectroscopy at high pressures, which is a powerful yet an uncommon technique, is currently not available. Moreover, an efficient research and education environment can not be offered to FAMU students, both at undergraduate and graduate levels, by solely relying on a user facility where a typical instrument time of about 6 weeks/year may be allotted to each user. Furthermore, a Broadband Fourier Transform Infrared (FTIR) spectrometer that offers the requested frequency ranges is currently unavailable to any of the researchers at FAMU.

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The major goal of this project is to procure a FTIR spectrometer coupled to an infrared microscope covering a frequency range from far-infrared to UV. This instrument combined with cryostats will allow broadband spectroscopy at high pressures and/or low temperatures.

Henceforth, a FTIR spectrometer and an infrared microscope that can cover a broad frequency range from 1 meV up to 3.5 eV is requested within this proposal, for research and education purposes in the College of Science and Technology (CST), FAMU. This equipment will be installed in the laboratory of the PI and will be made available for use to all faculties in CST-FAMU. The usage may also be extended to other colleges such as the College of Pharmacy and Pharmaceutical Sciences.

The preferred spectrometer (Bruker vertex 70v) consists of a wear-free interferrometer with a warranty of 10 years.

Accomplishments: The equipment grant was acquired to set up a broadband optical spectroscopic capabilities in PI's laboratory. The PI had acquired a very basic version of the spectrometer even before the equipment grant was awarded using the start-up funds provided by the university. Although the bare bones of the facility was procured, the facilities was limited to a narrow frequency range (mid-infrared frequency range).

With the award of this grant, the PI was able to expand the facilities to a fully-functional broadband optical spectroscopy lab. The following items have been added to the facility:

1. Broadband FTIR spectrometer with infrared microscope:

The FTIR spectrometer of our choice is Bruker vertex 70v coupled to Hyperion IR microscope. The layout of the spectrometer is shown in Figure 1. The spectrometer is the state-of-the-art research grade instrument that overs high resolution optical spectroscopic measurements on nearly any material of interest. Although, there are several FTIR spectrometers available in the market, the requested equipment is a unique evacuated optics spectrometer. It facilitates spectroscopy over a very wide frequency range in a single instrument with in a reasonable time while keeping the high resolution and stability. Furthermore, it is the only known spectrometer that can be readily coupled to an IR microscope without reduction in the covered frequency range. The microscope enables spectroscopic study of materials of very small dimensions. Therefore, it is an essential equipment for performing IR measurements at high pressures using diamond anvil cells (DACs) where the studied samples do not exceed micrometer dimensions.

The FTIR spectrometer (Bruker Vertex 70v) can cover a broad frequency range from 10 cm-1 to 30000 cm-1 i.e., far-infrared (FIR) to UV frequencies. It employs three different light sources for the different ranges in the infrared frequencies. Depending on the frequency required for the measurement, different combinations of source, beamsplitter and the detector are chosen. The size of the beam spot can be chosen using apertures of size 0.25 mm -12 mm with the remotely-controlled aperture wheel. The wide range beamsplitter and the KBr beamsplitter will allow measurements in low frequencies while quartz beamsplitter is needed for accessing frequencies in the visble and UV range. The silicon-based bolometer used in the FIR frequency range is a cryogenic detector operated at liquid helium temperature, while mercury cadmium telluride (MCT) and InGaAs detectors used at mid-infrared (MIR) and near-infrared (NIR) frequencies, respectively, are operated at liquid nitrogen temperature. Deuterated triglycine sulfate (DTGS) detectors that are used optionally in FIR and MIR ranges are operable at room temperature. A silicon diode and a GaP diode detector can be used for the measurements in the visible/UV range.

The optical layout of the infrared microscope is shown in Figure 1. The main parts of the infrared microscope are two identical Schwarzschild (or cassegrain) objectives. One objective is used for focusing the light on the sample and the second one serves as condenser for transmission measurements. Each objective consists of a concave and a convex mirror; the chosen objective has a magnification of 15x and a working distance of 24 mm. Field apertures in the focal plane of the objective, of sizes in the range of 0.3-3.75 mm, are used to define the sample area to be analyzed. Through a system of remotely-controlled mirrors, it is possible to guide the incident light in the optical path of the microscope for the view mode, the reflection mode and the transmission mode. The optical path for both the reflection and transmission modes are highlighted in Figure 1.

The picture of the FTIR instrument showing both the spectrometer and the microscope is shown in the Figure 2. The picture was taken during the installation and testing of the equipment.

2. Micro-manipulator:

The Micro-support micromanipulator that includes a microscope with two micromanipulator arms for micro-sample manipulator, and a manually-controlled sample stage [Figure 3]. The motion of the two arms is controlled through software that the user controls. Motion on the arms is effected through a software interface that allows for motion to be specified by selected different directional arrows in the software or through an interface on the video image that is shown. Micromanipulator arms has 3D motorized motion where the X and Y directions have a 20 mm range of motion while the Z direction has a 30 mm. Motion in the micromanipulator arms is effected through stepper motors with a stepping resolution of 100 nm per step and the microscope has the option of being supplied with 1.5X, 3X, and 5X objectives. These specifications allows us to use samples of all shapes and sizes especially while loading high pressure cells.

3. Glovebox with integrated microscope for handling micron-sized samples:
This single workstation system is a super glove box from Vacuum Technology Inc. It is equipped with an integrated gas purification system (one column), PLC controller (with a touchscreen HMI), electronics enclosure, large and small antechambers, replaceable sight glass, and vacuum pump. Attainable purity of this system is $H_2O < 1$ppm, $O_2 < 1$ppm. The system was customized to house a high resolution Leica microscope to handle small samples of dimensions less than 500 microns.

4. Optical microscope cryostat with cryogen-free cooling capability [Figure 4]:
CRYO Industries Universal Cryocoolers provide cryogen free, closed cycle flow cooling of various cryostats to <5 K (depending upon model selected). The Universal Crycooler provides a continuous cold helium gas stream without the use of liquid helium. Helium gas is cooled by the refrigerator and the cold gas transverses the transfer line and exits at the nozzle. The transfer line exit nozzle (downstream leg) inserts into the continuous flow cryostat, making a truly universal cooler for multiple experiments.

The glovebox and cryocooler have been delivered in full. However, the installation of this system is still pending due to requirement of cooling water system. The work order for the cooking water system is currently being processed by the NHMFL facilities team.

The construction of this optical spectroscopic facility has allowed PI to establish collaboration between FAMU and other research universities. One such collaboration is with Prof. David Mandrus at University of Tennessee and Oak Ridge National Laboratory. This creates more opportunities for FAMU students to gain scientific training and exposure in national level. The PI was also offered affiliation to chemical engineering department in FAMU broadening the participation of more STEM students. Furthermore, the PI has been able to participate in several new collaborative proposals that has been submitted to multiple federal funding agencies. These developments clearly indicates that this grant has opened a door for FAMU (which is a minority institution) to participate in world-class research projects.

In conclusion, the PI was able to setup a functional laboratory with state-of-the-art optical spectroscopy lab including facilities required for handling very small (micron-sized) as well as air-sensitive samples. The PI was also able to acquire a cryogen-free cooling optical cryostat. This piece of the equipment is extremely crucial for a university such as FAMU since the institution do have capabilities to ensure steady supply of cryogens such as liquid nitrogen and helium. PI laboratory will now be able to support competent research which is required for producing excellent physics PhDs from FAMU. Also, other faculties from departments such as chemistry and pharmacy will be able to use this facility. Therefore, this grant award and subsequently PI's laboratory is a significant leap forward in developing an excellent materials research program in FAMU.

Training Opportunities: The two graduate students, Gary Knight and Rachael Richardson, were trained on the technical aspects of spectroscopy such as the instrument operation, maintenance as well as cryogen handling.

Results Dissemination: Nothing to Report

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

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Participant Type: PD/PI
Participant: Komalavalli Thirunavukkuarasu
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

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Person Months Worked: 4.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
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Participant Type: Graduate Student (research assistant)
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Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
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Other Collaborators:

BROADBAND OPTICAL SPECTROSCOPY FOR INTERDISCIPLINARY MATERIALS RESEARCH

FINAL REPORT ATTACHMENTS

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Attachments for accomplishments section of the ARO Final report:

1. The layout of the spectrometer in combination with infrared microscope.
2. The Bruker vertex 70v together with Hyperion 2000 microscope installed in the lab.
3. The picture of microsupport micromanipulator installed in the lab.
4. The configuration of cryocooler with the optical microscope cryostat.

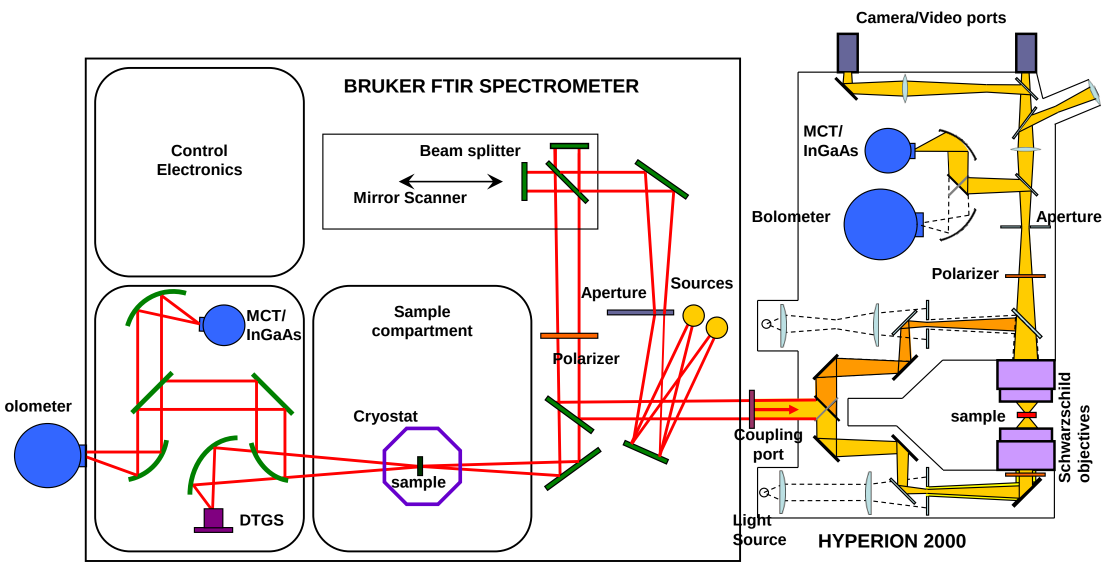

Figure 1: *Optical layout of Bruker Fourier transform infrared spectrometer coupled to IR microscope illustrating the their coupling and the entire optical configuration.*

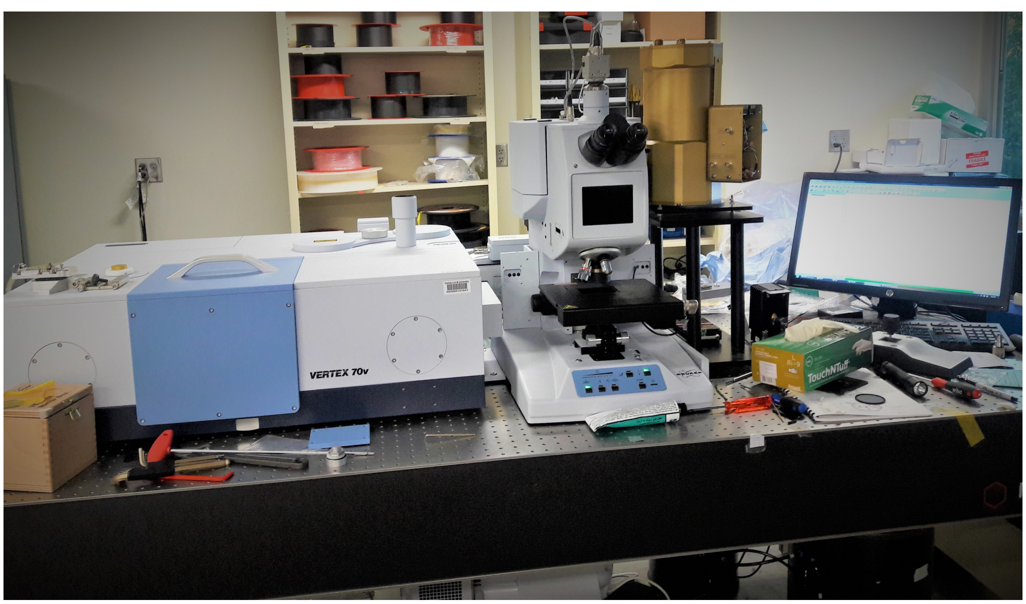

Figure 2: *A photograph of the Bruker Fourier transform infrared spectrometer Vertex 70v coupled to IR microscope Hyperion 2000 taken during the installation.*

Figure 3: *A photograph of the microsupport micromanipulator in PI's Laboratory.*

Figure 4: *A picture that illustrates the configuration of cryocooler in combination with microscope cryostat.*