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14. ABSTRACT
The goal of this proposal was to acquire upgrades such as ultrafast Raman spectrometer (ANDOR Newton EMCCD from Raman inVia®) with polarization and UV Raman spectroscopic capabilities for characterizing the deformation behavior of ultrahard ceramics (e.g., SiC, B4C, and B6O) used for body- and vehicular-armor. In particular, the system is used for mapping the amorphization zones and residual stresses within boron-rich solids as well as to analyze the compositional variations in ceramic composites. The PI has upgraded the current Raman

15. SUBJECT TERMS
DURIP, Raman spectroscopy, EMCCD, UV, Polarization

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Report Title

Final Report: Acquisition of Upgrades for Raman Spectroscope for Enhanced Speed, UV and Polarization Capabilities

ABSTRACT

The goal of this proposal was to acquire upgrades such as ultrafast Raman spectrometer (ANDOR Newton EMCCD from Raman inVia®) with polarization and UV Raman spectroscopic capabilities for characterizing the deformation behavior of ultrahard ceramics (e.g., SiC, B4C, and B6O) used for body- and vehicular-armor. In particular, the system is used for mapping the amorphization zones and residual stresses within boron-rich solids as well as to analyze the compositional variations in ceramic composites. The PI has upgraded the current Raman microscope system with a high-speed encoded stage (HSES), polarization optics and lenses for an ultraviolet laser, an Andor EMCCD camera, a dual-wavelength 325 nm (UV) and 442 nm He-Cd laser, a dual-wavelength laser power supply, an upgraded video camera for optical microscopy, and an enclosure for safety purposes. Several graduate and undergraduate students who are currently working on Army-funded projects have been trained in the proper use of this instrument. Preliminary results on B6O have demonstrated an improved spectral signature in response to excitation from the new UV laser as opposed to its response to the 532 nm visible laser. The total cost of the equipment was $184,184.00.

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

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

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

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

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

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

Received Paper

TOTAL:

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

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

Received Paper

TOTAL:

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

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Ghatu Subhash (PI)
- National Academies Panel member for 'Ballistic Science and Engineering' at the Army Research Laboratories, National Research Council, 2015-2017
- Orr 'Best Paper' Award, ASME-Journal of Engineering Materials and Technology, 2016
- 'Technology Innovator Award', University of Florida, 2016
- 'College of Engineering Doctoral Dissertation Advisor/Mentoring Award', University of Florida, 2015-2016
- Associate Editor, Experimental Mechanics journal, 2014-present
- Associate Editor, ASME Journal of Engineering Materials and Technology, 2014-present
- Associate Editor, Mechanics of Materials, an International Journal, 2008-present
- Associate Editor, Journal of the American Ceramic Society, 2006-present

Gregory Parsard (Ph.D., graduated)
- NSF Graduate Research Fellowship Program (NSF GRFP), 2011-2016

Alison Trachet (Ph.D., graduated)
- Fulbright Scholarship, 2015-2016

Cody Kunka (Graduate Student)
- NSF Graduate Research Fellowship Program (NSF GRFP), 2015-present
- Finalist in Florida Statewide Graduate Student Research Symposium, 2016
- Honorable Mention in the Elegance of Science Art Competition, 2017
- Mechanical & Aerospace Engineering Graduate Student Research Award, 2017

Matthew DeVries (Graduate student)
- NSF Graduate Research Fellowship Program (NSF GRFP), 2016-present
- DoD-NDSEG Fellowship offered (declined in order to accept NSF GRFP), 2016
- Sung and Yvonne Lu Graduate Fellowship Award, 2017

Secretary, Mechanical & Aerospace Engineering Graduate Student Council, 2016-present

Graduate Students

NAME	PERCENT_SUPPORTED	DISCIPLINE
Alison Trachet	0	Materials Science and Engineering, PhD
Gregory Parsard	0	Mechanical Engineering, PhD
Cody Kunka	0	Mechanical Engineering, PhD
Matthew DeVries	0	Mechanical Engineering, PhD
Kshitiz Upadhyay	0	Mechanical Engineering, PhD
FTE Equivalent:	**0.00**	
Total Number:	**5**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Ghatu Subhash	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	DISCIPLINE
Molly Coovert	0	Mechanical and Aerospace Engineering
Matthew Banks	0	Mechanical and Aerospace Engineering
Douglas Steinbach	0	Mechanical and Aerospace Engineering
Susan Stanfill	0	Mechanical and Aerospace Engineering
Santiago Salinas	0	Mechanical and Aerospace Engineering
Pedro Cruz	0	Mechanical and Aerospace Engineering
FTE Equivalent:	**0.00**	
Total Number:	**6**	

Student Metrics

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

The number of undergraduates funded by this agreement who graduated during this period: 3.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 3.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 1.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 2.00

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

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

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

Names of Personnel receiving masters degrees

NAME	
Matthew DeVries	
Total Number:	**1**

Names of personnel receiving PHDs

NAME	
Alison Trachet	
Gregory Parsard	
Total Number:	**2**

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachment

Technology Transfer

Boron carbide disks were subjected to impact testing with spherical projectiles by researchers at Aberdeen Proving Grounds, Army Research Laboratory (Dr. Phillip Jannotti, Dr. Jerry LaSalvia, and Dr. Timothy Walter) and were shipped to the PI in order to map and analyze impact-induced amorphization using Raman spectroscopy. The Streamline HR Rapide® upgrade facilitates the analysis by enabling the Raman microscope to scan large damaged regions at much higher rates than previously possible. This work is currently in progress.

Project Summary - Grant # W911NF-16-1-0180
(Reporting Period: 04/11/2016-04/10/2017)

DURIP-2016: Acquisition of Upgrades for Raman Spectroscope for Enhanced Speed, UV and Polarization Capabilities

Ghatu Subhash, Ph.D.
Department of Mechanical and Aerospace Engineering
University of Florida, Gainesville, FL, 32611

Abstract

The goal of this proposal was to acquire upgrades such as ultrafast Raman spectrometer (ANDOR Newton EMCCD from Raman inVia®) with polarization and UV Raman spectroscopic capabilities for characterizing the deformation behavior of ultrahard ceramics (e.g., SiC, B_4C, and B_6O) used for body- and vehicular-armor. In particular, the system is used for mapping the amorphization zones and residual stresses within boron-rich solids as well as to analyze the compositional variations in ceramic composites. The PI has upgraded the current Raman microscope system with a high-speed encoded stage (HSES), polarization optics and lenses for an ultraviolet laser, an Andor EMCCD camera, a dual-wavelength 325 nm (UV) and 442 nm He-Cd laser, a dual-wavelength laser power supply, an upgraded video camera for optical microscopy, and an enclosure for safety purposes. Several graduate and undergraduate students who are currently working on Army-funded projects have been trained in the proper use of this instrument. Preliminary results on B_6O have demonstrated an improved spectral signature in response to excitation from the new UV laser as opposed to its response to the 532 nm visible laser. The total cost of the equipment was $184,184.00.

Objective

Raman spectroscopy, a nondestructive material characterization technique which relies upon the inelastic scattering of laser light to glean information about materials, has long been established as a versatile tool for material characterization. The PI has used this technique to map variations in both the composition and stress state of ceramics at the microscopic scale, successfully creating volumetric maps of the regions affected by the amorphization phase transformation beneath Vickers indentations in boron carbide as well as maps of ceramic composites showing the distribution of their constituents and process-induced residual stresses. The primary goal of this effort is to extend these analytical capabilities in (a) scope (analysis of new materials, such as polymers, biological materials, and thin films / coatings), (b) scale (analysis of larger regions of interest, such as the damage zones beneath ballistic impact sites on armor ceramics), (c) specificity (e.g., mapping individual components of stress along particular directions, rather than just its overall magnitude), and (d) speed (days vs months).

Approach

The current DURIP grant allowed for the enhancement of the existing Renishaw inVia® Raman microscope by incorporating the following features:

- A dual-wavelength He-Cd laser was added to supplement the existing 532 nm Si laser with a
    - 442 nm (visible) laser and
    - 325 nm (ultraviolet, UV) laser.

  The 442 nm laser provides increased sensitivity because the Raman scattering intensity is proportional to $1/\lambda^4$ where λ is the laser wavelength. Decreasing the wavelength from 532 nm to 442 nm more than doubles the scattering efficiency.

  The 325 nm UV laser excitation allows for interaction with specimen surfaces over a depth of only a few nanometers, which allows for the characterization of thin films used in the semiconductor industry and ceramic surface coatings used for thermal protection and wear resistance. UV excitation also allows for increased sensitivity because the Raman scattering intensity is proportional to $1/\lambda^4$ where λ is the laser wavelength. Scanning with UV light yields more than 7 times the scattering efficiency of a typical visible (532 nm) laser. UV Raman spectroscopy is more powerful for some specific applications. UV Raman spectroscopy is also ideally suited to investigate gels because of its high sensitivity to extremely low-density biological species such as DNA, viruses, and bacteria as well as water molecules.
- The Raman microscope has also been upgraded to support Streamline HR Rapide®, an option offered by the manufacturer which enables the instrument to scan materials at speeds hundreds of times faster than was possible in its previous configuration. At such speeds, the stress distribution and chemical composition of significantly larger regions can be scanned within a much shorter timeframe than previously possible.
- In addition to being able to determine the magnitude of stresses within materials, the directionality of stresses can now be determined due to the addition of polarization optics for the 532 nm laser of the Raman microscope. This is relevant to a variety of materials with military applications, including single-crystal boron carbide, transparent single-crystal silicon carbide, sapphire, quartz.
- A Raman enclosure assembly was purchased for the Raman microscope. An unenclosed Raman system presents three main issues: (1) laser light scattered away from the specimen can be harmful to the human eye, (2) the system's detector is exposed to ambient light, which can have an adverse effect upon measurements recorded by the system, potentially obscuring important information about scanned specimens, and (3) the specimen is exposed to the ambient environment. The microscope enclosure assembly addresses all three of these issues by shielding users from the laser and shielding the specimen from ambient light while isolating the specimen from the ambient environment.
- An interlock override was also purchased for the Raman microscope. An interlock override allows the system to be operated while the optics enclosure is open, which is necessary for service visits and troubleshooting by technicians who need to be able to see what is taking place inside the system while it is in operation.

Relevance to Army

Boron carbide is a prime candidate for lightweight ceramic armor due to its high strength, high hardness, and low density. These factors also contribute to its use in civilian and industrial settings in automotive brake pads and in grinding operations as a hard abrasive. Despite its exceptional material properties, ballistic impacts at sufficiently high velocities have been observed to trigger a phase transformation in boron carbide which weakens the material and results in severe fragmentation. The structural changes caused by this transformation (amorphization) can be detected with Raman spectroscopy. A fundamental understanding of the initiation and growth of amorphization is crucial to the development of amorphization-resistant boron carbide ceramics as effective armor materials for ballistic applications.

The increased speed of the Streamline HR Rapide® upgrade enables Raman spectroscopy to investigate the extent of amorphization beneath impact sites up to length scales on the order of centimeters. Tiles of ceramic composites, which are also used in armor systems, can be mapped at high rates to evaluate how fabrication techniques affect the magnitude and distribution of process-induced residual stresses in the interest of manufacturing better armor materials. The directionality of stress within those ceramics can also be determined using the new polarization optics for the Raman microscope. For anisotropic, single-crystal transparent armor materials (e.g., sapphire), the direction of strain can impact the material behavior. The various strain components can be evaluated and the optimum crystal orientation can be determined for better performance.

The addition of an ultraviolet laser enables the instrument to collect Raman spectra from biological species, such as DNA, as well as polymeric gels, biological surrogates (e.g., ballistic gels), and water molecules. With this expanded range of materials that can be examined, studies can be performed to better understand blast-induced fluid exchange across various organs, traumatic brain injury (TBI), and post-traumatic stress disorder (PTSD). Ultraviolet lasers also collect information over a much smaller interaction volume than visible lasers, thus enabling the analysis of thin ceramic films and coatings, which are used in the semiconductor industry and in surface coatings used for thermal protection and wear resistance. Understanding the residual stress evolution and its influence on mechanical properties of thin ceramic films is crucial to developing constitutive models for evaluating the performance potential of these materials.

Accomplishments for Reporting Period

- An engineer from Renishaw visited the University of Florida to upgrade the inVia® Raman Microscope and conducted a training session for the research team of graduate and undergraduate students with regard to the new capabilities of the Raman microscope.
- The Raman microscope has been upgraded to support Streamline HR Rapide®, which enables scans to be performed many times faster than the maximum speed of the previous configuration.
- A dual-wavelength He-Cd laser (325 nm and 442 nm) has been added to the Raman microscope (see Figure 1), expanding the range of materials that can be scanned to include gels and biological surrogates, which react more favorably to ultraviolet light (i.e., the 325 nm laser), and thin ceramic films, which can now be inspected due to the nanometer-scale interaction volume of ultraviolet light. A set of specialized optics were also purchased for use with the UV laser (see Figure 2). The 325 nm UV laser has a better signal-to-noise ratio and has provided better Raman scans of some materials, such as B_6O. Figure 3 shows Raman spectra collected from a specimen of B6O using both the 532 nm laser and 325 nm laser. The

Raman peaks produced by scanning B_6O with a 325 nm UV laser are much more prominent than those obtained with a 532 nm laser.

- Polarization optics for the 532 nm laser have been added to the Raman microscope, granting the ability to discern the direction of residual stresses in specimens compatible with the 532 nm laser (primarily ceramics).
- An enclosure assembly (see Figure 4) has been purchased to improve the safety and reliability of the instrument. Our system focuses a Class 3B laser through a set of optics onto specimens in order to obtain information about their composition, stress state, etc. The enclosure assembly allows the microscope to be sealed during operation, which presents multiple benefits in that it
  - protects operators and observers from potentially harmful laser light which may be scattered away from the specimen,
  - eliminates interference from ambient light that could otherwise enter the detector and potentially obscure important spectral features of the specimen,
  - isolates the specimen from the ambient environment than when the specimen is exposed to the ambient atmosphere, and
  - includes an enclosure interlock override, which allows the laser to be operated while the optics chamber is open, which is necessary during service visits and troubleshooting sessions so that technicians can inspect the optics during operation.
- Laser safety eyewear (see Figure 5) was purchased to protect operators from exposure to laser wavelengths from 190 nm - 560 nm

Collaborations and Technology Transfer

- Boron carbide disks were subjected to impact testing with spherical projectiles by researchers at Aberdeen Proving Grounds, Army Research Laboratory (Dr. Phillip Jannotti, Dr. Jerry LaSalvia, and Dr. Timothy Walter) and were shipped to the PI in order to map and analyze impact-induced amorphization using Raman spectroscopy. The Streamline HR Rapide® upgrade facilitates the analysis by enabling the Raman microscope to scan large damaged regions at much higher rates than previously possible. This work is currently in progress.

Resulting Journal Publications during Reporting Period

- n/a

Graduate Students Involved During Reporting Period

- Alison Trachet (Ph.D., graduated, Materials Science and Engineering)
- Matthew DeVries (Ph.D., current, Mechanical and Aerospace Engineering)
- Cody Kunka (Ph.D., current, Mechanical and Aerospace Engineering)
- Gregory Parsard (Ph.D., graduated, Mechanical and Aerospace Engineering)
- Kshitiz Upadhyay (Ph.D., current, Mechanical and Aerospace Engineering)
- Matthew Banks (Undergraduate, Mechanical and Aerospace Engineering)
- Molly Coovert (Undergraduate, Mechanical and Aerospace Engineering)
- Douglas Steinbach (Undergraduate, Mechanical and Aerospace Engineering)
- Susan Stanfill (Undergraduate, Materials Science and Engineering)
- Santiago Salinas (Undergraduate, Mechanical and Aerospace Engineering)

- Pedro Cruz (Undergraduate, Mechanical and Aerospace Engineering)

Awards, Honors and Appointments

Ghatu Subhash (PI)

- National Academies Panel member for 'Ballistic Science and Engineering' at the Army Research Laboratories, National Research Council 2015-2017
- Orr 'Best Paper' Award, ASME-Journal of Engineering Materials and Technology 2016
- 'Technology Innovator Award', University of Florida 2016
- 'College of Engineering Doctoral Dissertation Advisor/Mentoring Award', University of Florida 2015-2016
- Associate Editor, *Experimental Mechanics* journal 2014-present
- Associate Editor, *ASME Journal of Engineering Materials and Technology* 2014-present
- Associate Editor, *Mechanics of Materials, an International Journal* 2008-present
- Associate Editor, *Journal of the American Ceramic Society* 2006-present

Gregory Parsard (Ph.D., graduated)

- NSF Graduate Research Fellowship Program (NSF GRFP) 2011-2016

Alison Trachet (Ph.D., graduated)
Fulbright Scholarship 2015-2016

Cody Kunka (Graduate Student)

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- DoD-NDSEG Fellowship offered (declined in order to accept NSF GRFP) 2016
- Sung and Yvonne Lu Graduate Fellowship Award 2017
- Secretary, Mechanical & Aerospace Engineering Graduate Student Council 2016-present

Expenditures

Equipment upgrades (UV and polarizer optics, lasers, EMCCD camera, enclosure)	$173,787.30
Installation and Training	$10,000.00
Shiping and Handling	$396.70

Total	$184,184.00

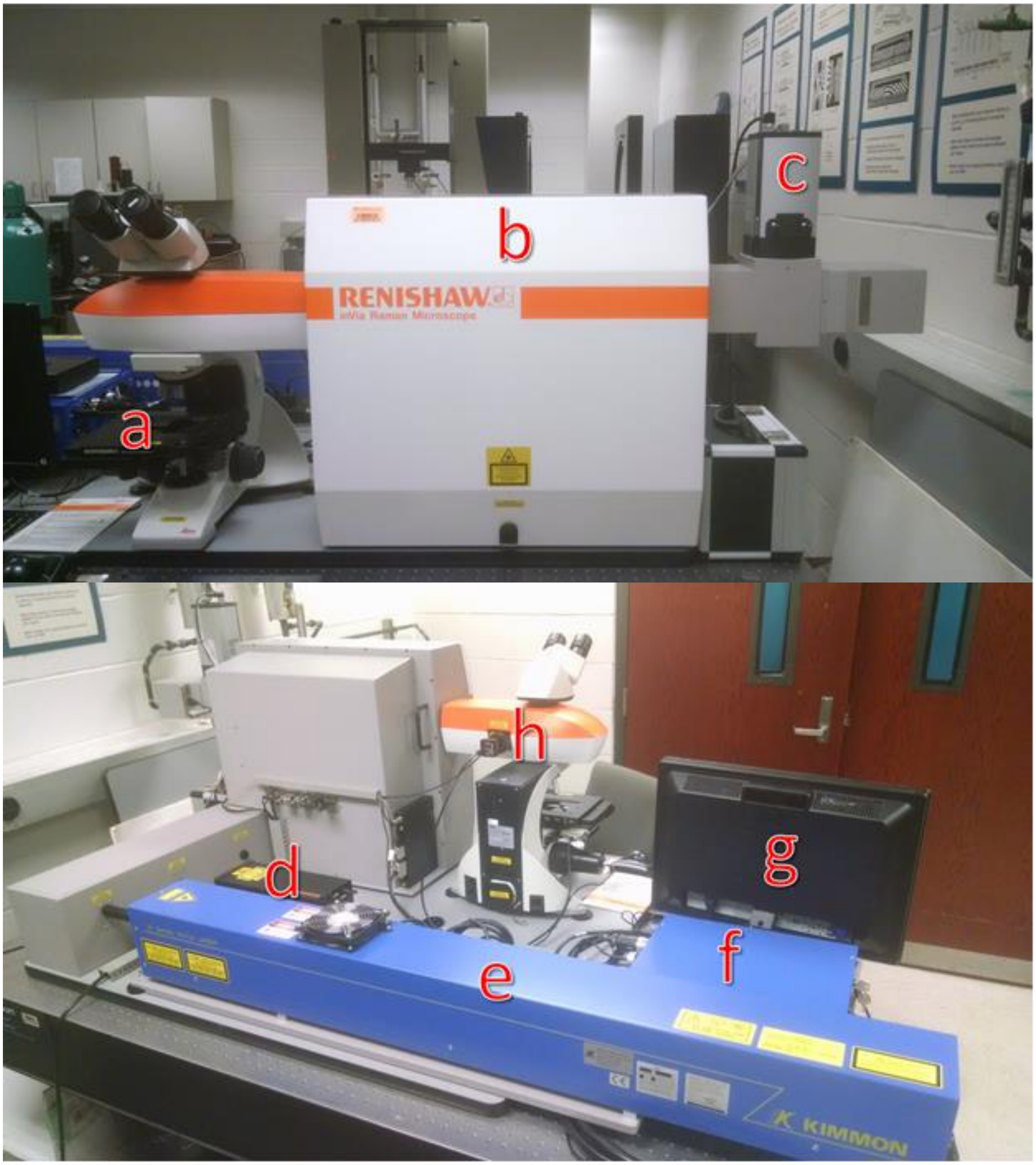

Figure 1. (Top) (a) Raman microscope high-speed encoded stage (HSES), (b) optics chamber (contains polarization optics and lenses for ultraviolet laser), (c) Andor EMCCD camera, **(bottom)**, (d) 532 nm Si laser and power supply, (e) dual-wavelength 325 nm (UV) and 442 nm He-Cd laser, (f) dual-wavelength laser power supply, (g) monitor, (h) upgraded video camera for optical microscopy.

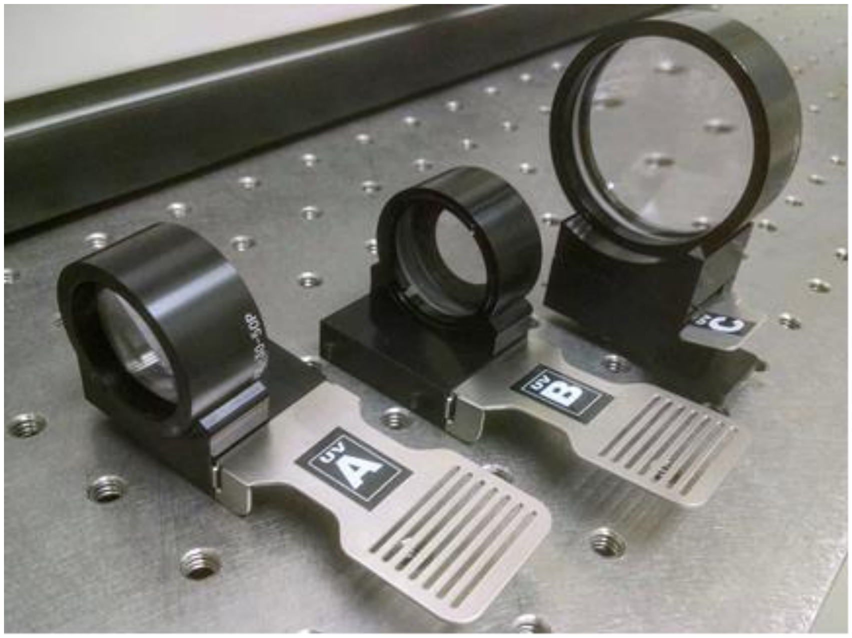

Figure 2. Specialized lenses for ultraviolet Raman spectroscopy.

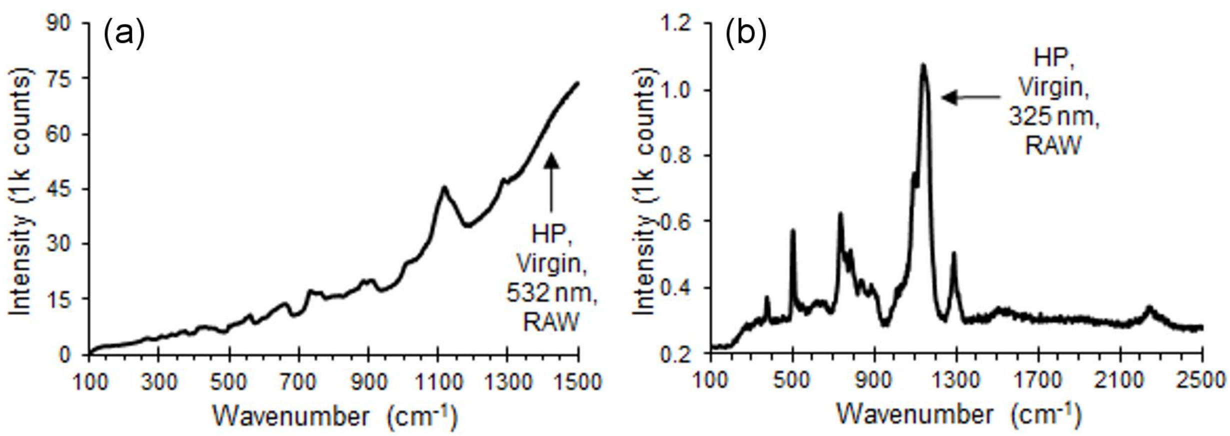

Figure 3. Typical Raman spectra from B_6O resulting from the use of (a) 532 nm visible laser and (b) 325 nm ultraviolet laser. Note the increase in signal-to-noise ratio in response to the 325 nm UV laser.

Figure 4. Enclosure assembly surrounding the Raman microscope stage. An enclosure rated for Class 1 lasers is shown for illustration purposes, but the enclosure assembly purchased as part of this grant is suitable for use with the Class 3B laser in our system. Source: http://www.renishaw.com/en/invia-safety--25907

Figure 5. Laser safety eyewear used to protect against lasers of wavelength 190 nm - 560 nm.