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7. PERFORMING ORGANIZATION NAMES AND ADDRESSES

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14. ABSTRACT

15. SUBJECT TERMS

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 15. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
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| UU | UU | UU | UU | | 19b. TELEPHONE NUMBER<br>515-294-9691 |

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# RPPR Final Report
as of 31-Jul-2019

Agency Code:

Proposal Number: 70059MSRIP **Agreement Number: W911NF-17-1-0196**

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DUNS Number: 005309844 EIN: 426004224
**Report Date:** 14-Apr-2019 Date Received: 31-May-2019
**Final Report** for Period Beginning 15-Apr-2017 and Ending 14-Jan-2019
**Title:** High Pressure and Large Shear Deformation System for Materials Research
**Begin Performance Period:** 15-Apr-2017 **End Performance Period:** 14-Jan-2019
**Report Term:** 0-Other
Submitted By: Valery Levitas Email: vlevitas@iastate.edu
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**Distribution Statement:** 1-Approved for public release; distribution is unlimited.

**STEM Degrees:** **STEM Participants:**

**Major Goals:** The goal of this project is to initiate experimental rotational diamond anvil cell (RDAC) research at Iowa State University (ISU) and couple it with our theoretical and computational efforts. Experimental RDAC research will be performed with emphasis on mechanical characterization, effects, and phenomena. In particular, we intend to measure complete stress/strain tensor fields within a RDAC, determine the mechanical and physical properties of phases under high pressure and plastic shear, and quantitatively study the effect of stress and plastic strain tensors on various phase transformations (PTs).
The current project will therefore involve the purchase and installation of a complete RDAC system including optical components for pressure measurement and Raman spectroscopy at ISU. This new system will first be employed in routine RDAC experiments at ISU while offering invaluable training to students and post docs. It will be adapted for in-situ XRD studies (mainly for PT investigations) using existing XRD system. Next, the system will also permit preliminary experiments at ISU in preparation for more extensive work at synchrotron facilities. Since the main component of the system, the RDAC, is portable it can easily be adapted for use at major national facilities with expertise in high pressure research (e.g., Beamlines X17C and X17B3 at the National Synchrotron Light Source (NSLS) - Brookhaven National Laboratory; and Sectors 13 - GSECARS and 16 - HPCAT at the Advanced Photon Source (APS) - Argonne National Laboratory). This way, RDAC research will become more wide- spread nationwide. Until the recent development of a RDAC at the Army Research Laboratory our group was alone in the USA in doing experimental RDAC work. Dr. Levitas and co-workers, however, continue to maintain their uniqueness worldwide in theoretical RDAC work.

**Accomplishments:** 1. Rotational diamond anvil cell

New automated rotational cell with diamond anvils for in-situ x-ray diffraction and Raman scattering studies, with a pressure range up to 100 GPa and unlimited torsion, has been designed, developed, and manufactured. The cylinder of this RDAC has a large conical opening angle of 60^o for XRD studies using Boehler type anvils allowing XRD images up to large Q range and better structural analysis. For in-situ thickness measurements, annular metallic disks are mounted around both the diamond anvils and sample thickness is estimated through capacitance changes due to change in gap between these under load/shear. This RDAC is equipped with motorized mechanism making it remotely controllable and suitable for both laboratory-based and synchrotron-based facilities. The XRD measurements are performed at high brightness synchrotron facilities such as Advanced Photon Source (APS), Argonne, whereas spectroscopic measurements are done at in house lab. This cell will be used to perform experimental investigations on materials under controlled stress environment utilizing plastic strain tensors and plastic strain-induced defect structure as new thermodynamic and kinetic parameters to induce phase transformations and to utilize this information for developing material synthesis approaches under such conditions.

## 2. RDAC laboratory

For in house laboratory-based measurements, a Raman spectroscopy laboratory (RDAC laboratory) has been developed at Department of Aerospace Engineering. This laboratory is equipped with Confocal Micro-Raman setup along with all required paraphernalia necessary for carrying out high pressure experiments viz. electric and mechanical drill machine, stereo zoom microscope, sample preparation tools and accessories, etc.

The Raman system is equipped with 532 nm, 300 mW diode pumped solid state laser (as excitation source) and Andor 500i spectrometer with Andor iDUS CCD detector for recording Raman spectra (both Stokes and anti-Stokes) starting from 5 cm-1 onwards with a resolution of ~ 2-3 cm-1 . This system is capable of recording Raman signal from sample size as small as 1 micron and with 2 axis motorized stages at sample position, it can be used for 2D Raman imaging with a resolution of 1 micron. This system is also equipped with magnified viewing arrangement with 10X magnification to precisely align sample position with respect to excitation laser spot. The laser beam is first cleaned using narrow band OptiGrate reflecting band pass filter. It is then directed to sample through 1:4 beam expander, mirror, BragGrate filter and Mitutoyo 10X objective. The focused laser spot size at sample is ~ 1 μm. The Raman signal is then collected at the spectrometer through a confocal arrangement (providing depth resolution of ~4-5 μm) and BragGrate notch filters (blocking the Rayleigh line in a narrow range of ± 5 cm-1).

For mounting loaded RDAC at the micro-Raman system, XYZ stages have been assembled near the focal plane of excitation laser. The X stage is manual and is used to bring the sample loaded between the diamond anvils at focal plane using 10X magnified viewing arrangement. Y and Z stages are motorized and are used to scan the sample to facilitate 1D or 2D Raman imaging. For pressure distribution measurements, ruby powder is loaded along with sample and pressure at each scanning point across anvil diameter is estimated from shift in ruby fluorescence peaks. Besides, pressure is also estimated using shift in Raman peak from diamond anvil. A Python General graphical User (GUI) based automation software has been developed to control both Raman spectrometer and motorized stages to perform 1D and 2D Raman scanning measurements. To measure displacement field under load / torsion condition, a digital image correlation (DIC) based method has been developed. For this, fine ruby powder is spread over sample and 2D ruby fluorescence images are acquired. Two methods have been implemented: 1) by performing 2D scan of entire culet and recording ruby fluorescence spectra at each scanning point; 2) by recording magnified optical image of entire culet, spectrally filters in the wavelength range from 650nm to 750nm using a set of high pass and low pass filter in the optical path of viewing arrangement. Method #2 is advantageous for fast acquisition whereas method#1 also provide pressure field besides displacement field but is little more time taking.

## 3. Investigations on ultra-pure zirconium sample

First in situ quantitative X-ray diffraction (XRD) study of plastic strain-induced phase transformation under compression in diamond anvil cell and shear under fixed force in RDAC was performed. Alpha-omega PT in ultrapure Zr was considered. Radial distributions of pressure in each phase and in mixture, and concentration of omega-Zr, all averaged over the sample thickness, as well as thickness were measured using synchrotron X-ray source. Ultrapure Zr sample was purchased from Ames Laboratory with Hf content <55 ppm. The compression and/or shear experiments were performed both using steel gasket and without gasket. Samples were pre-deformed plastically through cold rolling from initial thickness of 1.25 mm down to 140 μm or 90 μm. Without gasket, 140 μm thick and 3 mm diameter punch-cut discs were loaded in RDAC whereas with gasket, 90 μm thick and 300 μm diameter discs, cut using laser cutting facility at HPCAT at Advanced Photon Sources (APS) were loaded in pre-indented steel gasket of same thickness. In situ XRD measurements were carried out at 16-BM-D beamline at APS using x-rays of wavelength 0.3108 A. At each load/shear condition, the sample was radially scanned over entire culet diameter (500 μm ) with steps of 10 μm. 2D XRD images were recorded at each scanning point using Perkin Elmer flat panel detector using focused X-ray beam of spot size 5 μm. Radial distribution of lattice parameters of both alpha and omega phases, and their concentrations, averaged over the sample thickness were obtained using Rietveld refinement of XRD patterns. Pressure distribution was determined using thus obtained lattice parameters of Zr phases and their equations of state determined through hydrostatic compression experiments with helium as pressure-transmitting medium. Radial distribution of the total pressure was defined based on mixture theory.

X- ray absorption measurements along the radius were used to determine the sample thickness profile. The minimum pressure for the strain-induced alpha-omega PT is found to be 1.2 GPa which is 4.5 times smaller than under hydrostatic loading. Also, it is found to be independent of the loading path.
Obtained results open new opportunity for quantitative study of strain-induced PTs and reactions with applications to mechanical characterization, material synthesis and processing, mechanochemistry, and geophysics.

# RPPR Final Report
as of 31-Jul-2019

**Training Opportunities:** Nothing to Report

**Results Dissemination:** Nothing to Report

**Honors and Awards:** Nothing to Report

**Protocol Activity Status:**

**Technology Transfer:** Nothing to Report

**PARTICIPANTS:**

**Participant Type:** Postdoctoral (scholar, fellow or other postdoctoral position)
**Participant:** Krishan Kumar Pandey
**Person Months Worked:** 8.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

# Final Report

**Project title:** High Pressure and Large Shear Deformation System for Materials Research

**PI: Valery Levitas**

**Agreement No. : W911NF1710196**

**Proposal No. : 70059**

**List of items acquired:**

| S. No. | Item details | Manufacturer / Supplier | Cost ($) |
|---|---|---|---|
| 1. | Rotational diamond anvil cell | Science & Tech. Center Ukraine | 40,713.00 |
| 2. | Diamond anvils | Almax Easylab Inc. | 5,555.00 |
| 3. | Optical table | Newport Corp. | 9,032.70 |
| 4. | Spectrometer | Andor Technology Ltd. | 28,504.91 |
| 5. | Optical and opto-mechanical components for micro-Raman and ruby fluorescence spectroscopy | Thorlabs. Inc. | 15,718.03 |
| 6. | 532 nm Raman excitation laser | Laser Quantum Inc. | 8,960.00 |
| 7. | Laser power meter | Coherent Inc. | 460.04 |
| 8. | Laser beam expander | Edmund Optics | 107.99 |
| 9. | Brag Grate Raman filter set | OptiGrate Corporation | 5,048.00 |
| 10. | Motorized stages | Daniel F Crews, LLC | 5,907.00 |
| 11. | Stereo zoom microscope | NCI Inc. | 17,123.45 |
| 12. | Mini pellet press | Specac | 1,357.50 |
| 13. | Rolling mill | Rio Grande Inc. | 734.75 |
| 14. | Mechanical micro-drill press | Cameron Micro drill presses | 3,833.62 |
| 15. | Monocular microscope | Titan tool supply | 883.45 |
| 16. | Other miscellaneous items | Digi Key Corp. /WW Grainger/ Fishersci Ecom. | 1,272.26 |
|  | **Total** |  | **145,211.70*** |

*Grant funding is $144,295. The difference was paid from the PI’s endowment.

## Goal:

The goal of this project is to initiate experimental rotational diamond anvil cell (RDAC) research at Iowa State University (ISU) and couple it with our theoretical and computational efforts. Experimental RDAC research will be performed with emphasis on mechanical characterization, effects, and phenomena. In particular, we intend to measure complete stress/strain tensor fields within a RDAC, determine the mechanical and physical properties of phases under high pressure and plastic shear, and quantitatively study the effect of stress and plastic strain tensors on various phase transformations (PTs).

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**Accomplishments:**

### 1) Rotational diamond anvil cell

New automated rotational cell with diamond anvils for in-situ x-ray diffraction and Raman scattering studies, with a pressure range up to 100 GPa and unlimited torsion, has been designed, developed, and manufactured. The RDAC has a piston-cylinder assembly where load is applied through lever mechanism (Fig. 1 and 2).

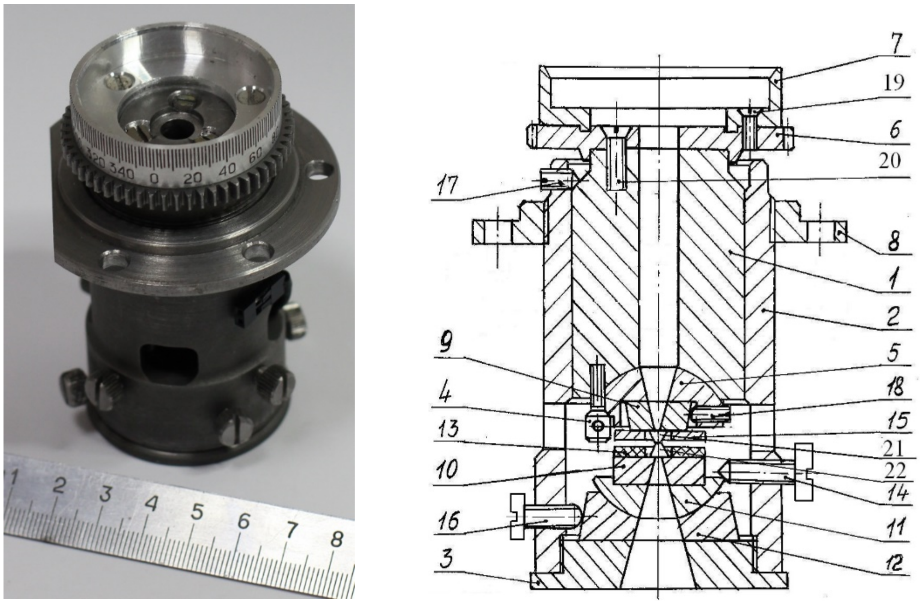


Fig. 1. Rotational diamond anvil cell (RDAC). 1 – moving piston; 2 – frame; 3 – bottom; 4 – screw; 5 – upper half-spherical seat; 6 – gear; 7 – limb; 8 – flange; 9 – upper seat; 10 – lower seat; 11 – lower half-spherical seat; 12 - half-spherical seat; 13 – foil-coated textolite plate; 14 – screw; 15 – metal plate; 16 – 20 - screws; 21 – moving diamond anvil; 2 – diamond anvil.

Both piston and cylinder are equipped with hemispherical rockers and base plates facilitating easy alignment of anvils. The cylinder of this RDAC has a large conical opening angle of 60° (4θ) for XRD studies using Boehler type anvils allowing XRD images up to large Q range and better structural analysis. For in-situ thickness measurements, annular metallic disks are mounted around both the diamond anvils and sample thickness is estimated through capacitance changes due to change in gap between these under load/shear. This RDAC is equipped with motorized mechanism making it remotely controllable and suitable for both laboratory-based and synchrotron-based facilities. The XRD measurements are performed at high brightness synchrotron facilities such as Advanced Photon Source (APS), Argonne, whereas spectroscopic measurements are done at in house lab. This cell will be used to perform experimental investigations on materials under controlled stress environment utilizing plastic strain tensors and plastic strain-induced defect structure as new thermodynamic and kinetic parameters to induce phase transformations and to utilize this information for developing material synthesis approaches under such conditions.

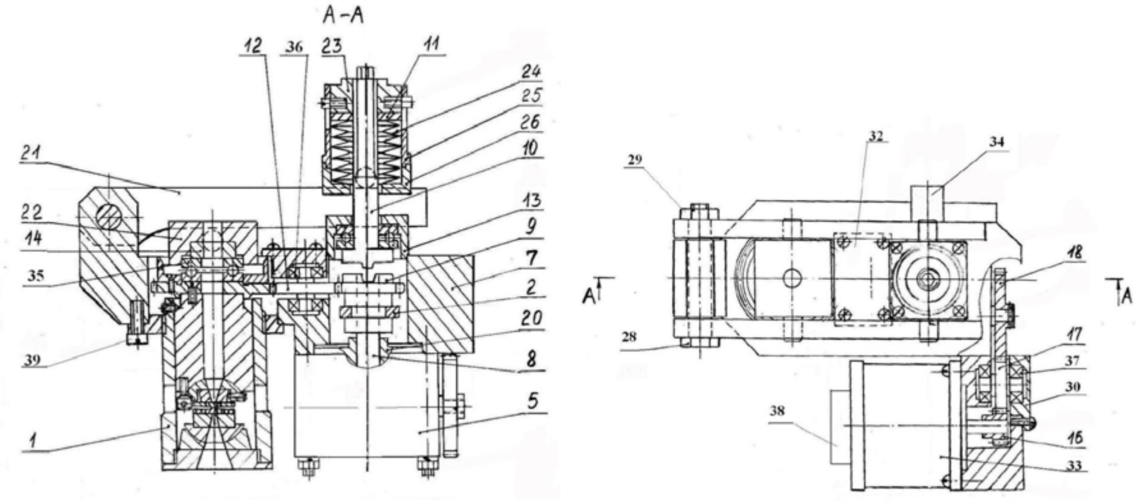


Fig. 2. The RDAC with the automatic loading device. 1 – RDAC; 2 – elevator; 5 – reducer; 7 – frame; 8 – screw; 9 – moving half-coupling; 10 – half-coupling; 11 – washer; 12 – gear; 13 – becket; 14 – support; 16 – 18 - gear; 20 – bushing; 21 – second class arm; 22 – washer; 23 – nut; 24 – flat springs; 25 – cylinder; 26 – cartridge; 28 – spindle; 52 – step motor; 53 – servo; 56 – axial bearing; 57 – rotating angle optical sensor.

## 2. RDAC laboratory

For in house laboratory-based measurements, a Raman spectroscopy laboratory (RDAC laboratory) has been developed at Department of Aerospace Engineering. This laboratory is equipped with Confocal Micro-Raman setup (Figs. 3 and 4) along with all required paraphernalia necessary for carrying out high pressure experiments viz. electric and mechanical drill machine, stereo zoom microscope, sample preparation tools and accessories, etc. (Fig. 5).

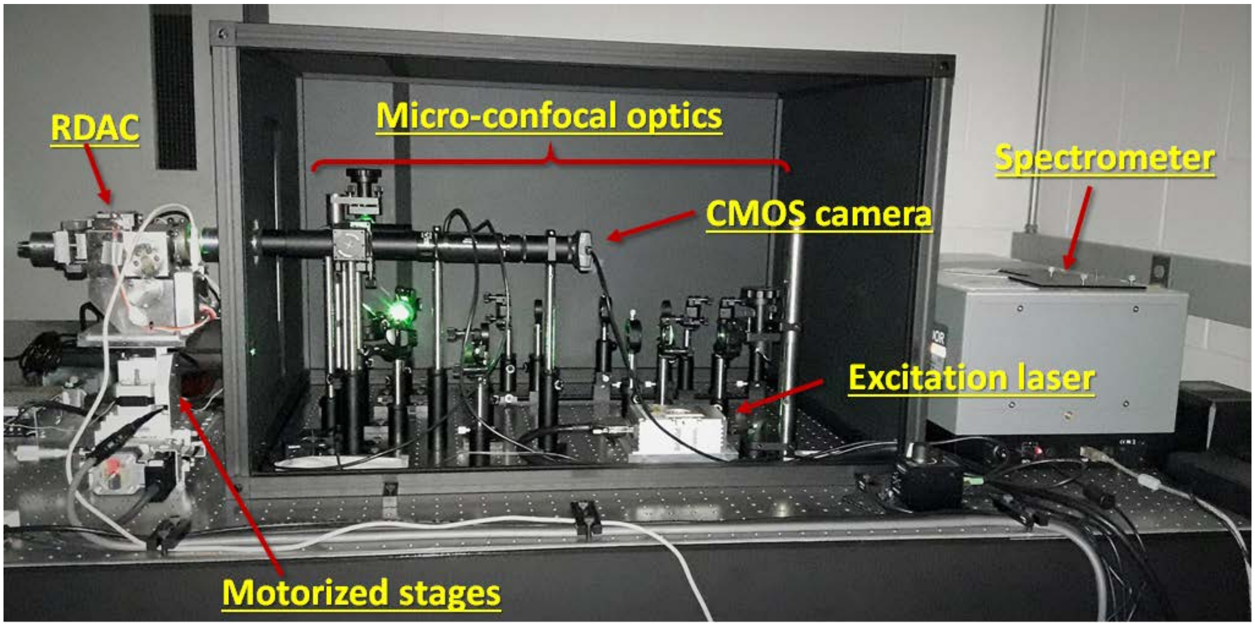


Fig. 3. Confocal micro-Raman system at RDAC laboratory.

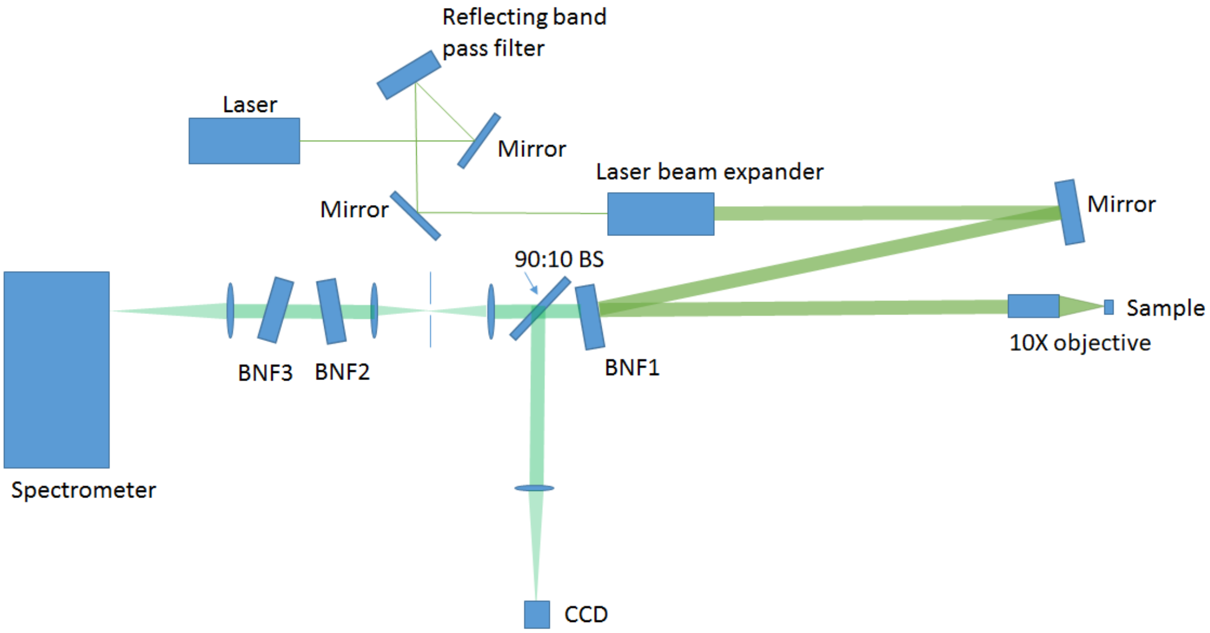


Fig. 4. Optical layout of micro-confocal Raman system.

The Raman system is equipped with 532 nm, 300 mW diode pumped solid state laser (as excitation source) and Andor 500i spectrometer with Andor iDUS CCD detector for recording Raman spectra (both Stokes and anti-Stokes) starting from 5 $cm^{-1}$ onwards with a resolution of ~ 2-3 $cm^{-1}$ . This system is capable of recording Raman signal from sample size as small as 1 micron and with 2 axis motorized stages at sample position, it can be used for 2D Raman imaging with a resolution of 1 micron. This system is also equipped with magnified viewing arrangement with 10X magnification to precisely align sample position with respect to excitation laser spot. Optical layout of the confocal Raman system is shown in Fig. 4. The laser beam is first cleaned using narrow band OptiGrate reflecting band pass filter. It is then directed to sample through 1:4 beam expander, mirror, BragGrate filter and Mitutoyo 10X objective. The focused laser spot size at sample is ~ 1 µm. The Raman signal is then collected at the spectrometer through a confocal arrangement (providing depth resolution of ~4-5 µm) and  BragGrate notch filters (blocking the Rayleigh line in a narrow range of ± 5 cm$^{-1}$).

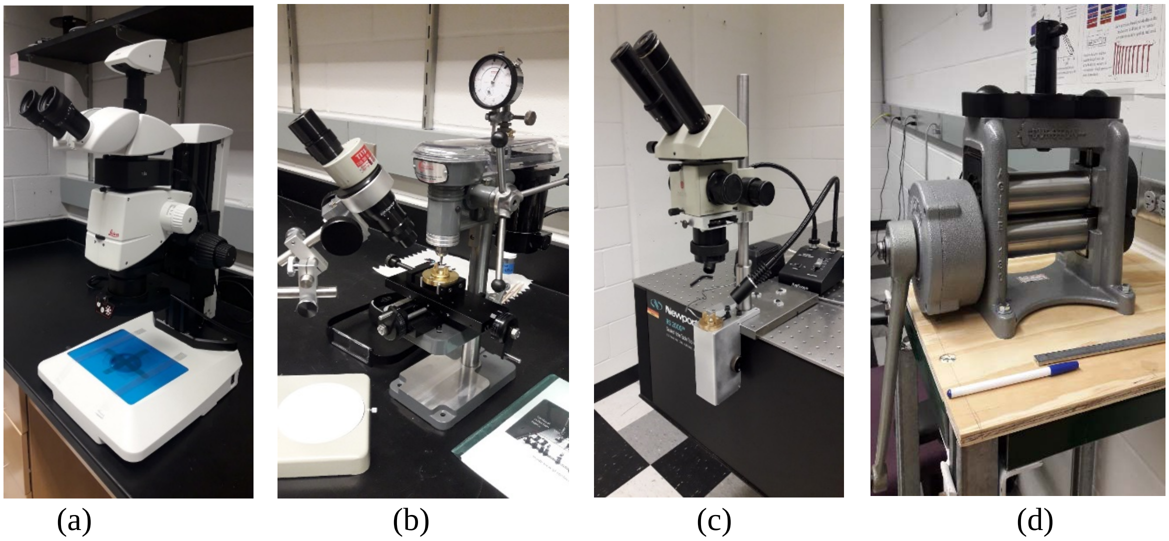
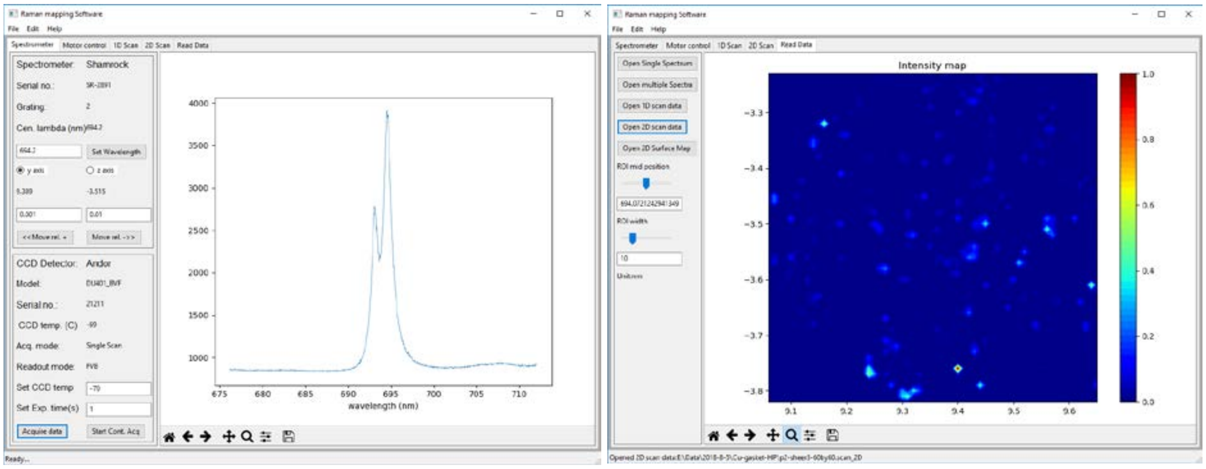


Fig. 5. Laboratory items for sample preparation: a) Stereo zoom microscope; b) Mechanical micro-drill machine; c) Electric discharge drill machine; d) Rolling mill.

For mounting loaded RDAC at the micro-Raman system,  XYZ stages have been  assembled near the focal plane of excitation laser. The X stage is manual and is used to bring the sample loaded between the diamond anvils at focal plane using 10X magnified viewing arrangement. Y and Z stages are motorized and are used to scan the sample to facilitate 1D or 2D Raman imaging. For pressure distribution measurements, ruby powder is loaded along with sample and pressure at each scanning point across anvil diameter is estimated from shift in ruby fluorescence peaks. Besides, pressure is also estimated using shift in Raman peak from diamond anvil. A Python General Graphical User based automation software has been developed to control both Raman spectrometer and motorized stages to perform 1D and 2D Raman scanning measurements. Fig. 6 shows screen shots of this automation software. To measure displacement field under load / torsion condition, a digital image correlation based method has been developed. For this, fine ruby powder is spread over sample and 2D ruby fluorescence images are acquired. Two methods have been implemented: 1) by performing 2D scan of entire culet and recording ruby fluorescence spectra at each scanning point; 2) by recording magnified optical image of entire culet, spectrally filters in the wavelength range from 650nm to 750nm using a set of high pass and low pass filter in the optical path of viewing arrangement. Method #2 is advantageous for fast acquisition whereas method#1 also provide pressure field besides displacement field but is little more time taking. Fig.

7 and 8 show representative pressure and displacement field measurements carried out at RDAC lab.



Spectrometer: Shamrock
Serial no.: SR-2891
Grating: 2
Cen. lambda (nm) 694.2
694.2
9.389 -3.515
0.001 0.01
CCD Detector: Andor
Model: DU401_BVF
Serial no.: 21211
CCD temp. (C) -99
Acq. mode: Single Scan
Readout mode: FVB
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Set Exp. time(s) 1
Ready...

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ROI width 10
Unit:nm
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Fig. 6. Screen shots of Python GUI based Raman mapping software.

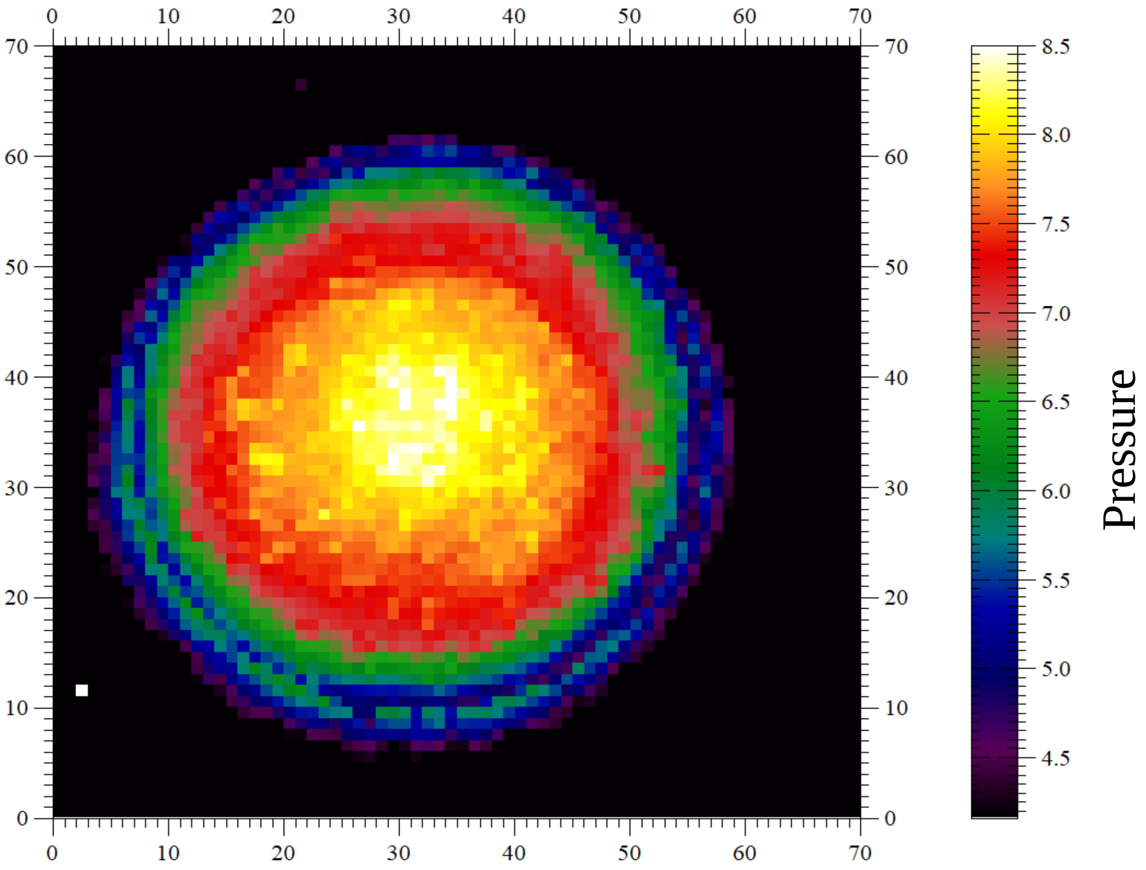


Fig. 7. 2D map of pressure field in tungsten gasket at 105 kgf load. Each pixel corresponds to 10 µm step.

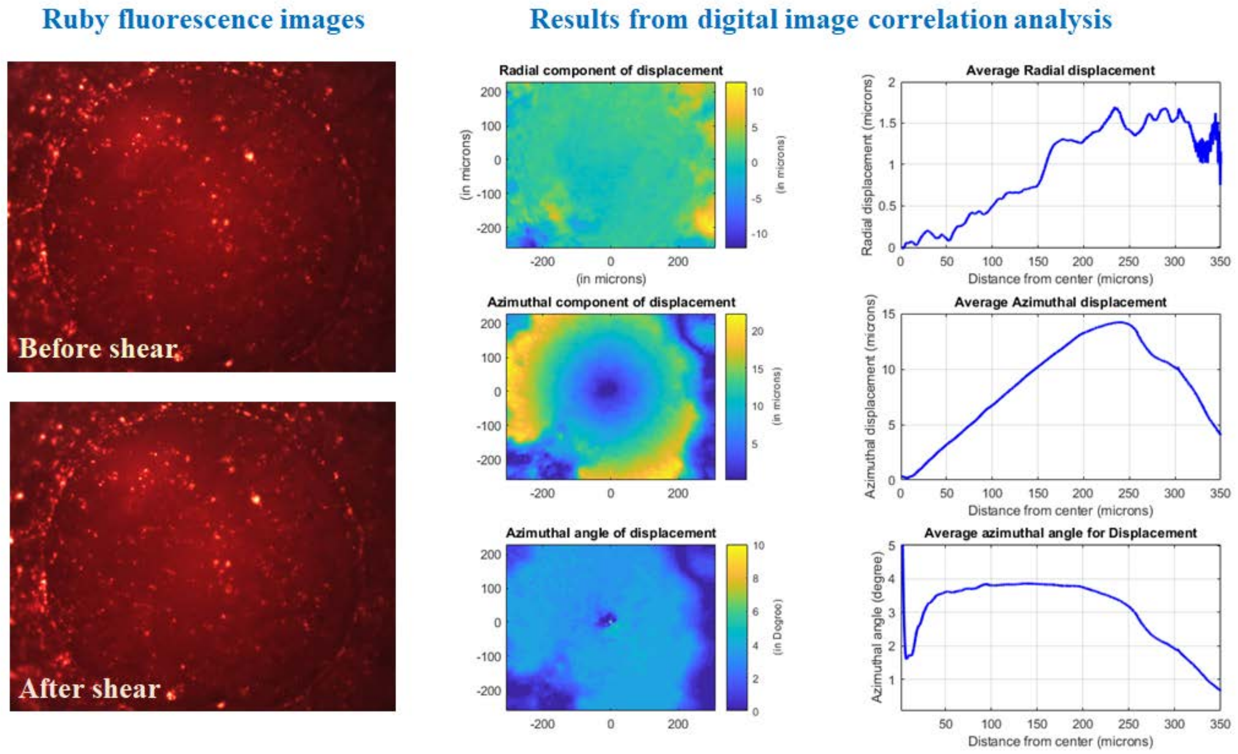


Fig. 8. Displacement field measurements in RDAC using digital image correlation analysis of ruby florescence images before and after shear.

## 3. Investigations on ultra-pure zirconium sample

First in situ quantitative X-ray diffraction (XRD) study of plastic strain-induced phase transformation under compression in diamond anvil cell and shear under fixed force in RDAC was performed. α - ω PT in ultrapure Zr was considered. Radial distributions of pressure in each phase and in mixture, and concentration of ω-Zr, all averaged over the sample thickness, as well as thickness were measured using synchrotron X-ray source. Ultrapure Zr sample was purchased from Ames Laboratory with Hf content <55 ppm. The compression and/or shear experiments were performed both using steel gasket and without gasket. Samples were pre-deformed plastically through cold rolling from initial thickness of 1.25 mm down to 140 µm or 90 µm. Without gasket, 140 µm thick and 3 mm diameter punch-cut discs were loaded in RDAC whereas with gasket, 90 µm thick and 300 µm diameter discs, cut using laser cutting facility at HPCAT at Advanced Photon Sources (APS) were loaded in pre-indented steel gasket of same thickness. In situ XRD measurements were carried out at 16-BM-D beamline (Fig. 9) at APS using x-rays of wavelength 0.3108 A°. At each load/shear condition, the sample was radially scanned over entire culet diameter (500 µm) with steps of 10 µm. 2D XRD images were recorded at each scanning point using Perkin Elmer flat panel detector using focused X-ray beam of spot size 5 µm. Radial distribution of lattice parameters of both α, ω phases, and their concentrations, averaged over the sample thickness were obtained using Rietveld refinement of XRD patterns. Pressure distribution was determined using thus obtained lattice parameters of Zr phases and their equations of state determined through hydrostatic compression experiments with helium as pressure-transmitting medium. Radial distribution of the total pressure was defined based on mixture theory.

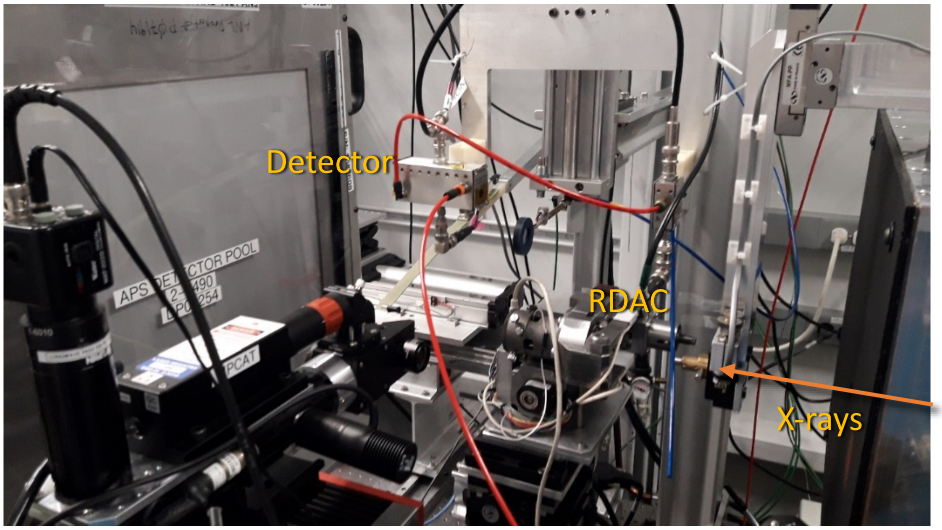
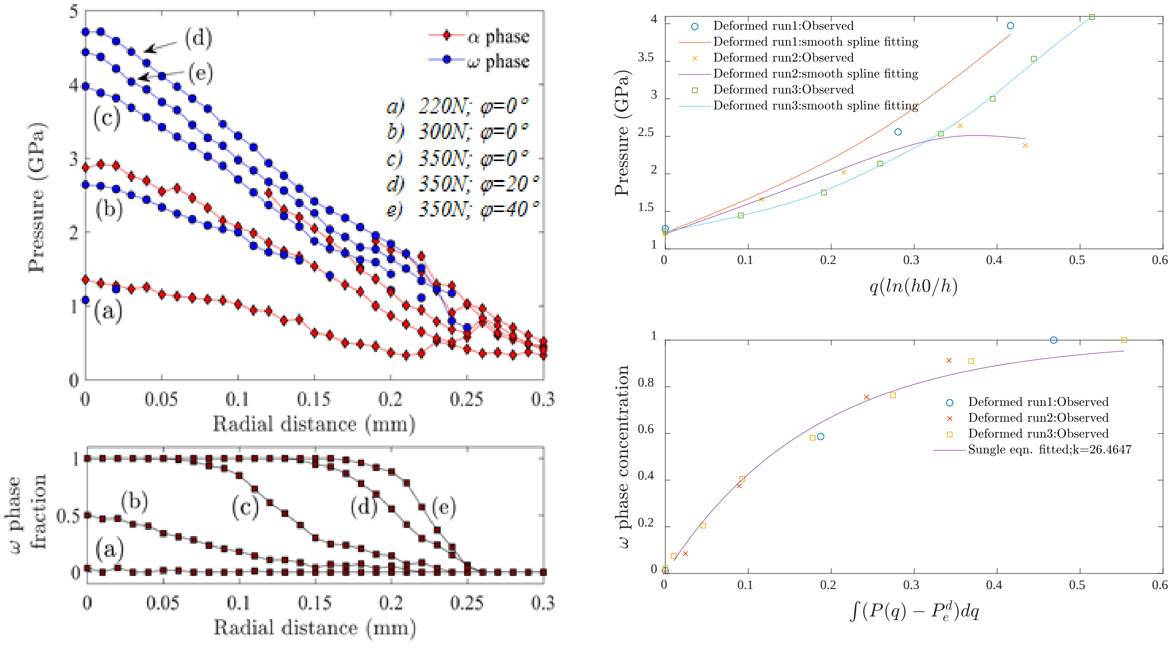


Fig. 9. Experimental station at 16-BM-D beamline at Advanced Photon Source, Argonne.



(a) (b)

Fig. 10. a) Radial profile of pressure in α and ω phases and phase fraction of ω phase at different load /shear condition; b) Kinetics of strain-induced α→ω phase transition.

X- ray absorption measurements along the radius were used to determine the sample thickness profile. The minimum pressure for the strain-induced α→ω PT is found to be 1.2 GPa which is 4.5

times smaller than under hydrostatic loading. Also, it is found to be independent of the loading path. Fig. 10 (a) shows radial pressure profiles in α and ω phases and ω phase concentration profile at different loading / shear conditions. Fig. 10 (b) shows kinetics of strain induced α→ω PT studied in different loading paths. Obtained results open new opportunity for quantitative study of strain-induced PTs and reactions with applications to mechanical characterization, material synthesis and processing, mechanochemistry, and geophysics.