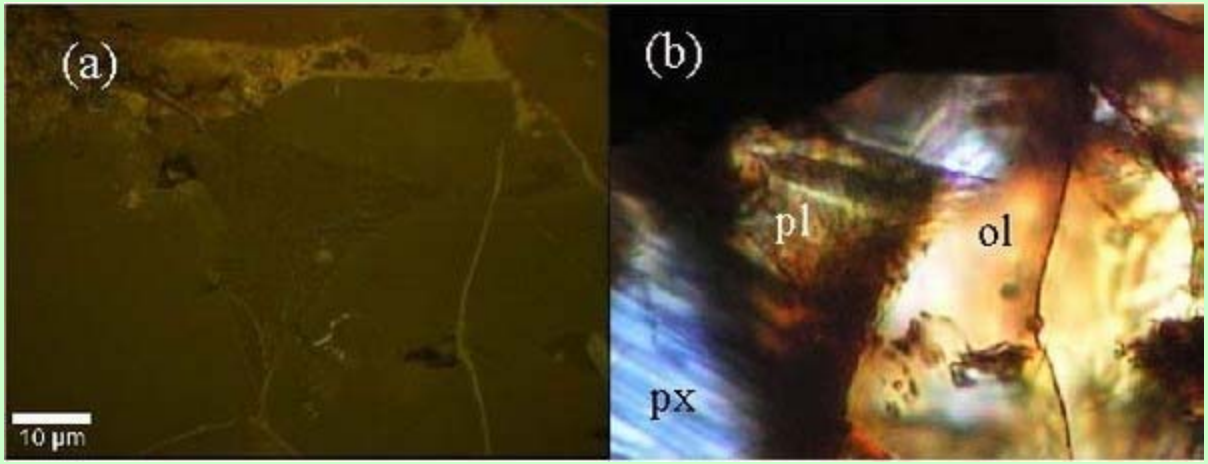
GG 711: Advanced Techniques in Geophysics and Materials Science

Lecture 19

Advanced Techniques at the University of Hawaii

Pavel Zinin

HIGP, University of Hawaii, Honolulu, USA



www.soest.hawaii.edu\~zinin

Sample Characterization at UH

1. Studying of a specimen by optical microscopy
2. of a specimen by SEM and determination of the elemental composition by EDS
3. Identification of the chemical bonds of the specimen by Raman spectroscopy
4. Unit cell determination by x-ray diffraction
5. Accurate measurement of the elemental composition of specimen by EMP
6. Determination of the elemental composition of specimen at nano-level by TEM with EELS
7. Measurements of different properties of a specimen using different including atomic force microscopy, Brillouin scattering etc.
8. Writing a paper or PhD thesis

Raman Spectroscopy at UH

There are three modern Raman confocal microscope at SOEST:

(a) ***Renishaw inVia Raman*** (Renishaw, Gloucestershire GL12 7DW, United Kingdom). In the *inVia Raman* system, the Raman spectra are excited by an Invictus 830 nm NIR laser (Kaiser Optical Systems, Inc., Arbor, MI, USA) with Leica x50/0.75 (x50 is the magnification, 0.75 the value of the numerical aperture) N Plan objective and by a frequency-doubled argon-ion laser at 244 nm (Lexel Laser Inc., Fremont, CA, USA) with LMU-40x-UVB Microspot focusing objective (40x/0.50). Contact *Shiv Sharma*, HIGP.

(b) ***Kaiser RXN system*** (Kaiser Optical Systems, Inc., Arbor, MI, USA) confocal Raman system (WiTec *alpha300*), In the micro-*Raman RXN system*, the Raman spectra are excited by an Invictus 785-nm NIR laser (Kaiser Optical Systems, Inc., Arbor, MI, USA) with Leica x50/0.75 N Plan objective. Contact *Shiv Sharma*, HIGP.

(c) **WiTec *alpha300*** confocal Raman system. In WiTec *alpha300* confocal microscope, the Raman spectra were excited by a Nd-YAG green (532-nm) laser (Coherent Compass, Dieburg, Germany) with Nikon 50x/0.75 E Plan objective. Contact *Gary Huss*, HIGP.

Electron Microprobe, SEM and EDS

Hyperprobe JXA-8500F at UH, POST Building Room 621
Contact: Dr. Eric Hellebrand: (808) 956-6193;
e-mail: ericwgh@hawaii.edu;

Dr. Michael Garcia: (808) 956-6641;
e-mail: mogarcia@hawaii.edu;
Probelab (808) 956-9406.

Department of Oceanography, Marine Sciences Building: Zeiss DSM 962 SEM with backcattered electron detector and an Oxford Instruments, Links energy dispersive X-ray fluroescnece spectrometer.

UH contact: Prof. James Cowen.

E-mail: jcowen@iniki.soest.hawaii.edu.

W. M. Keck Cosmochemistry Laboratory at HIGP, The JEOL JSM-5900 scanning electron microscope equipped with EDS detector
UH contact: *Gary Huss, Kazuhide Nagashima or Sasha Krot*.

The Biological Electron Microscope Facility (BEMF)

Hitachi S-4800 Field Emission Scanning Electron Microscope with Oxford INCA X-Ray Microanalysis system

The Biological Electron Microscope Facility (BEMF) at the University of Hawai'i is a multi-user/service facility, administered by the Pacific Biosciences Research Center (PBRC). The mission of the BEMF is to provide biological-biomedical researchers with state-of-the-art instrumentation, training and services for high-resolution scanning electron microscopy, conventional and energy-filtering transmission electron microscopy, optical, fluorescence, and laser scanning confocal microscopy, and image analysis on a recharge basis

LEO 912 Energy-Filtering Transmission Electron Microscope (Zeiss)

Director/Manager: *Marilyn F. Dunlap, Ph.D.;*
Supervisor: *Tina M. (Weatherby) Carvalho, M.S.*

Other Techniques

•Laser Heating in Diamond Anvil Cell. Pressure inside the cell can reach 100 GPa and the temperature can be up to 3000. Contact Dr. *Li Chun Ming* (HIGP).

•The Atomic Force Microscope. Digital Nanoscope III. Contact *Pavel Zinin*, HIGP.

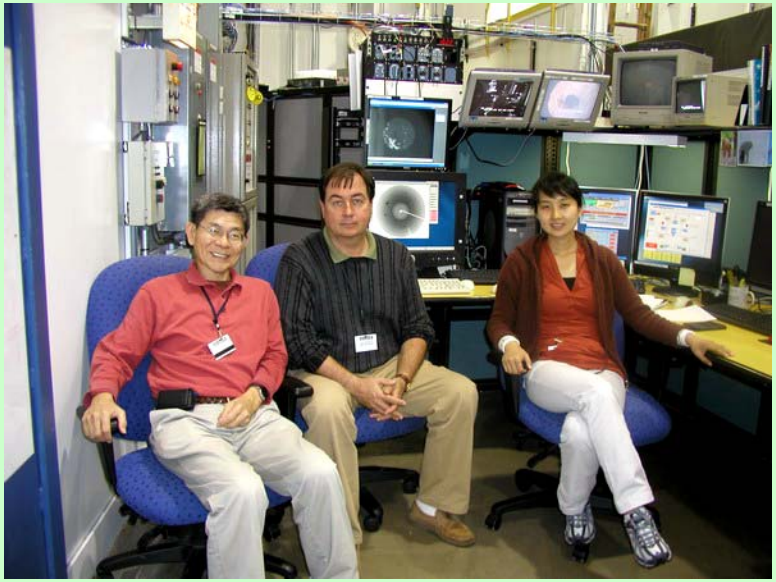
•Brillouin Spectrometer. Contact *Pavel Zinin*, HIGP.

X-ray Data Collection at Synchrotron

Contact *Li Chun Ming* (HIGP).

A very powerful X-ray source

- Thousands or millions of times more powerful than laboratory sources
- Higher Resolution
- Sometimes proton positions can be resolved
- Works with smaller crystals
- Argonne National Laboratory: $\lambda \sim 0.5$ Å

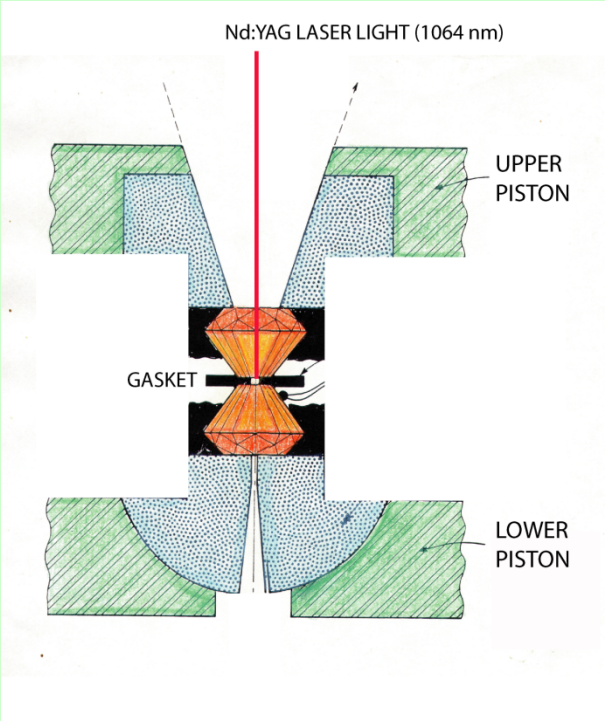


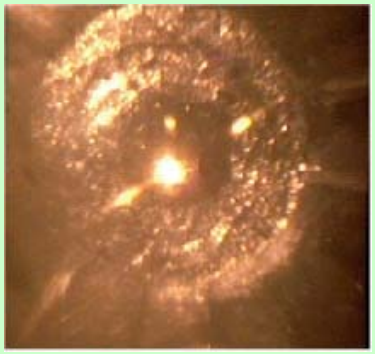
Example: Synthesis and Characterization
of novel Heterediamonds from B-C-N triangle

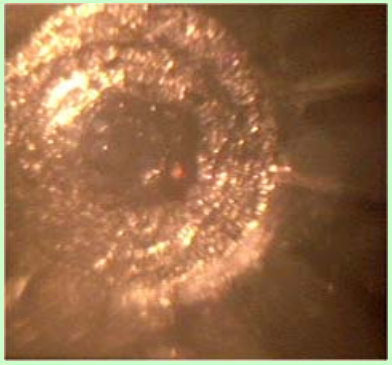
Synthesis of Novel Materials under High Pressure and High Temperaure

High Pressure Minerals Physics and Materials Science Laboratory

Contact: *Li Chung Ming and Pavel Zinin*



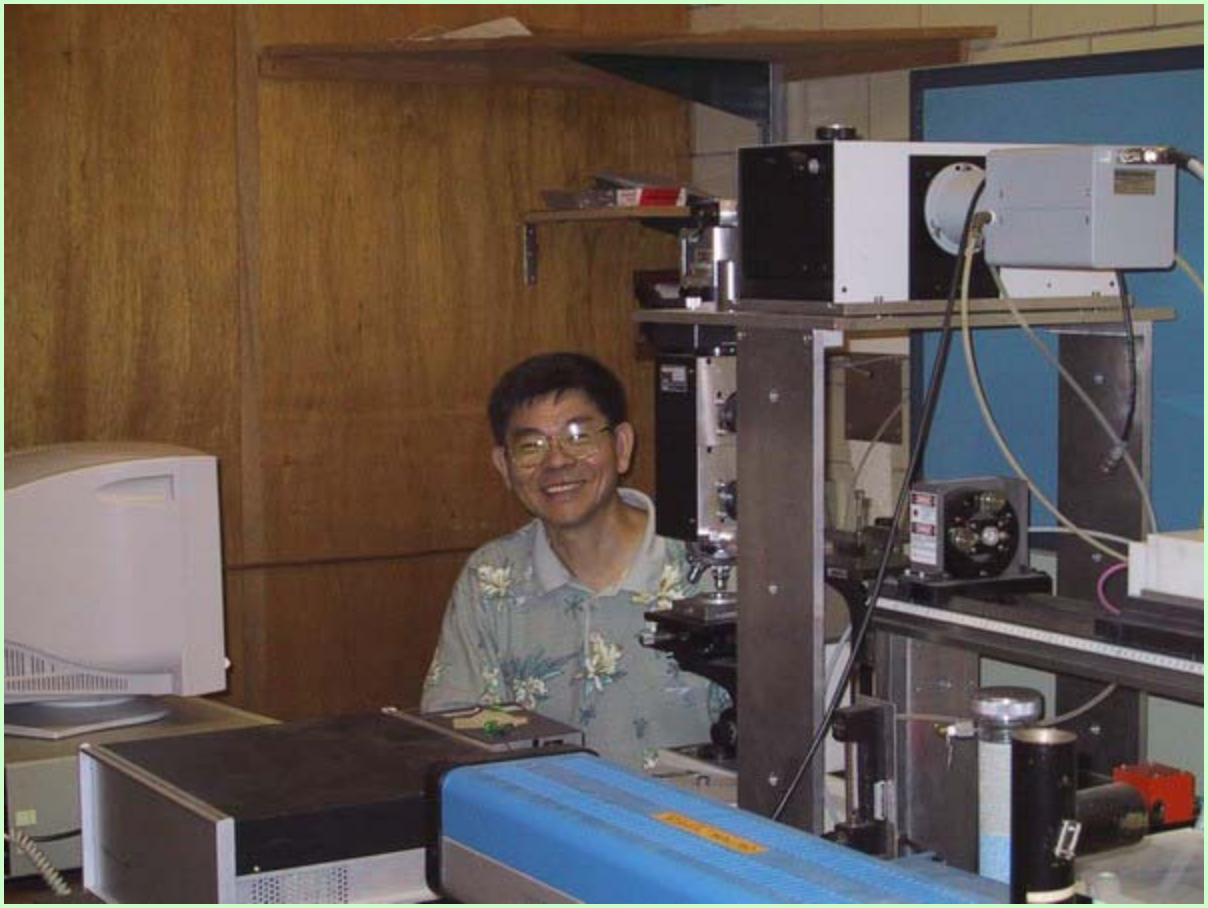




Laser Heating in DAC (Pressure up to 100 GPa, Temperature up to 3000 K)

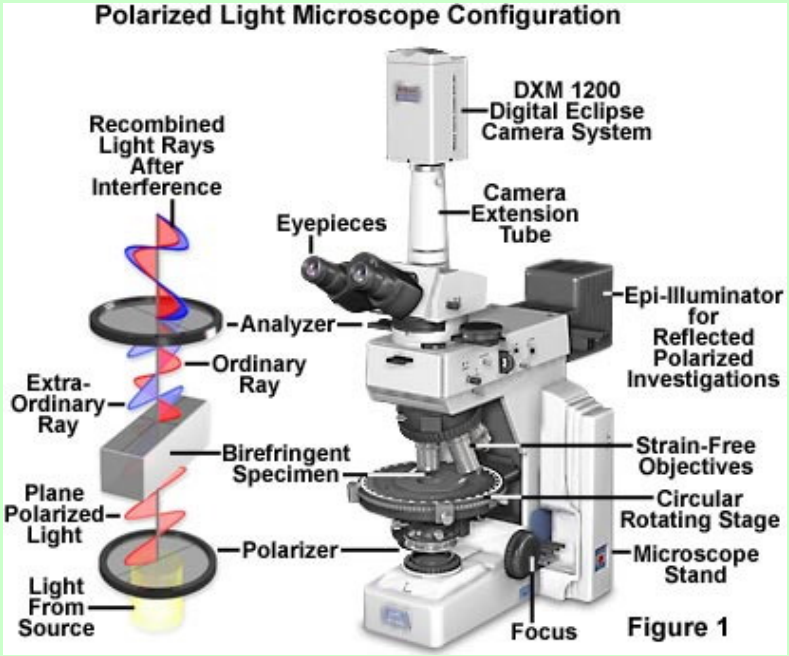
Laser-heating facilities at the University of Hawaii: The laser-heating system with a Nd-doped YAG laser (wavelength = 1064 nm, power = 90W) makes it possible to heat samples up to 3000 K. A laser with a heated spot of 10-20 m scanned the central area of both samples. The temperatures of both samples were determined from thermal radiation. Duration time of laser heating at each point in the DAC was more than 10 sec for all samples.

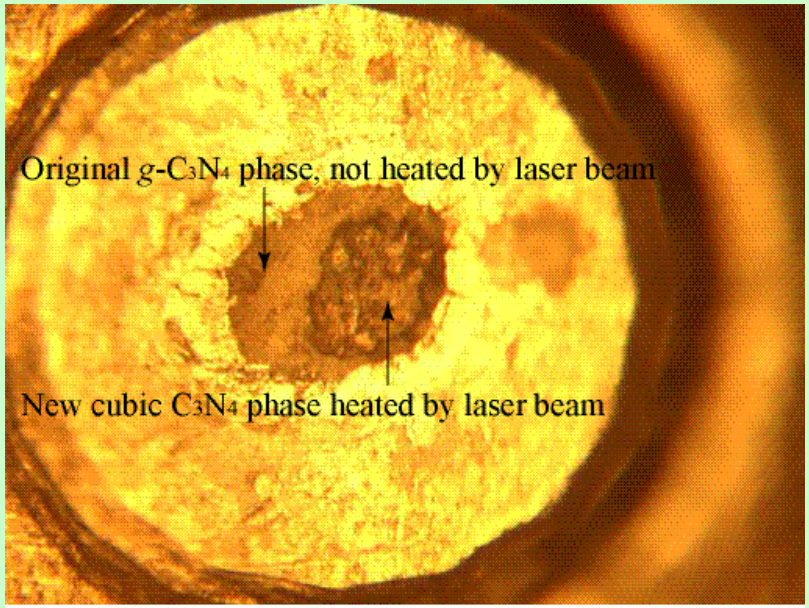
Laser Heating Facilities at UH



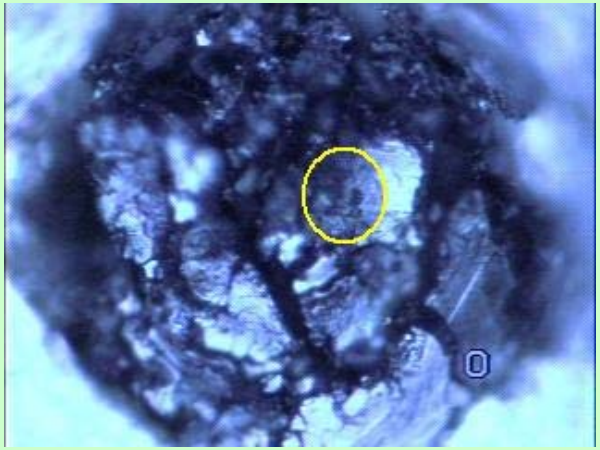
Laser Heating in Diamond Anvil Cell. Pressure inside the cell can reach 100 GPa and the temperature can be up to 3000. Contact Dr. *Li Chun Ming* (HIGP).

Optical Microscopy





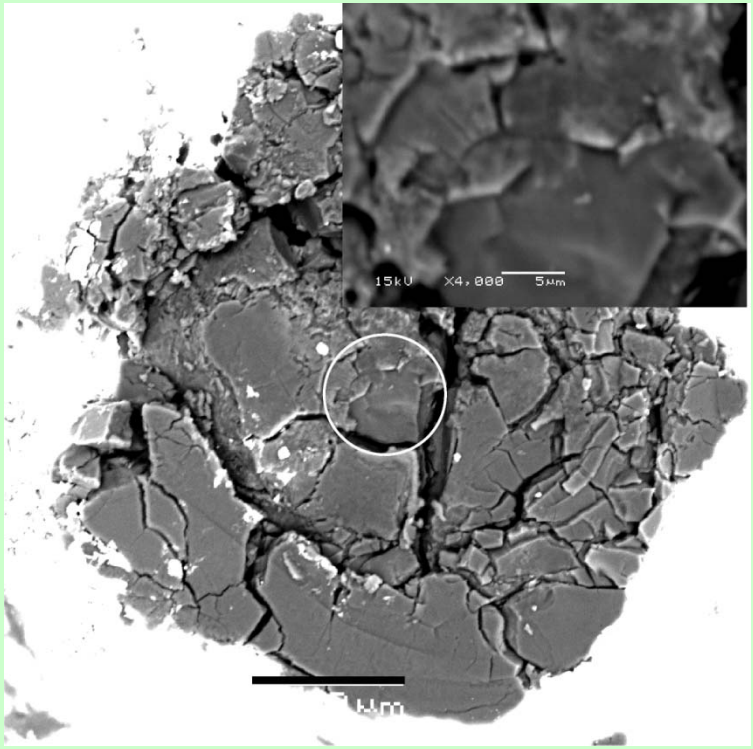
Optical image of the C_3N_4 specimen after heating in DAC



Optical image of the BC_3 sample inside gasket after laser heating. Field of view is 100 x 75 μm.

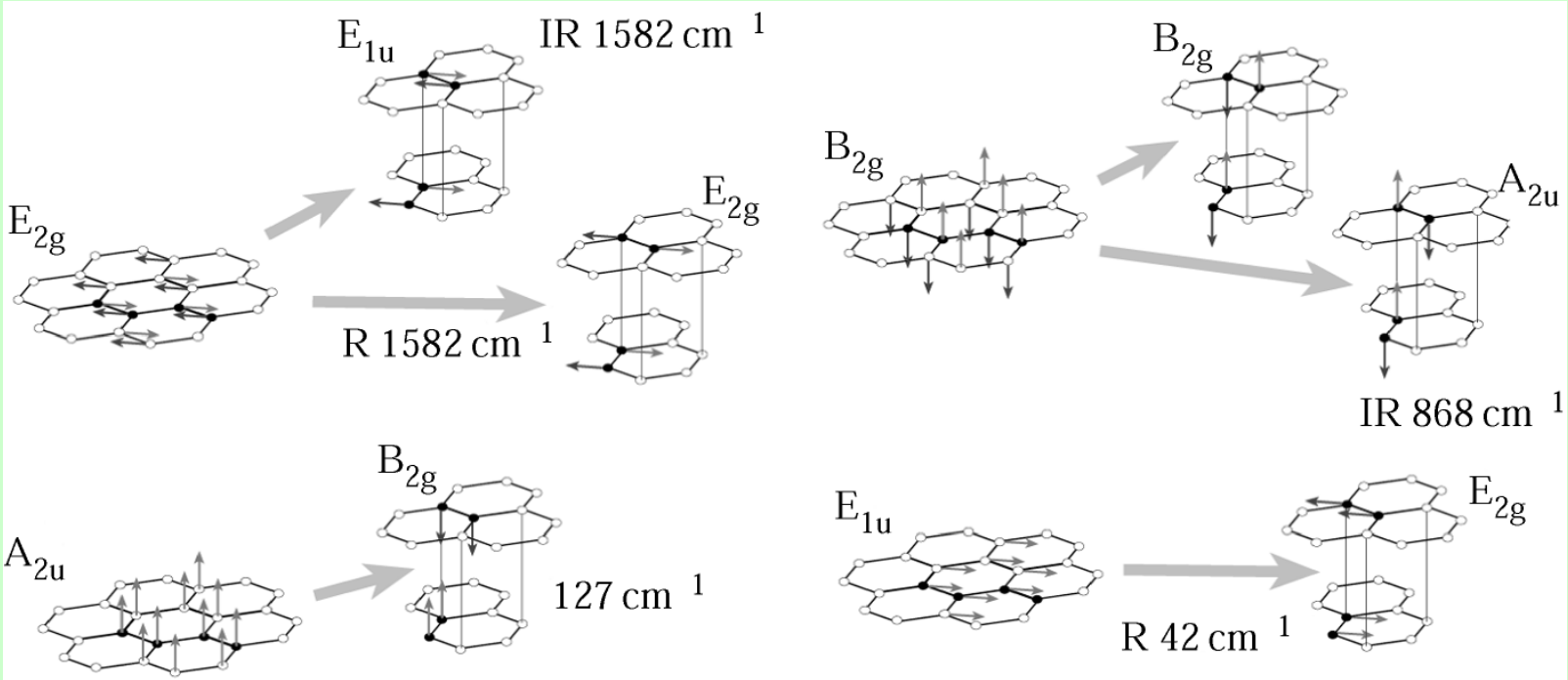
SEM and EDS

The JEOL JSM-5900 scanning electron microscope equipped with EDS detector



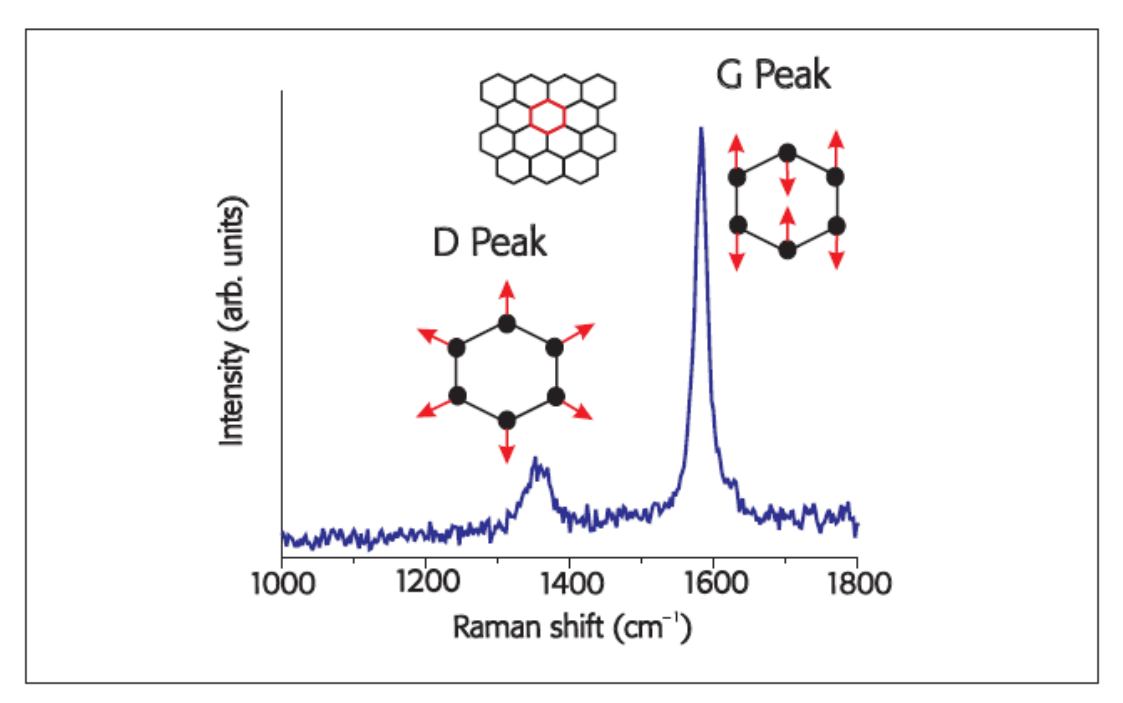
SEM image of the post-heated BC1.6 sample recovered from 45 GPa and 2230 K and with the NaCl layer being removed. Marker is 50 μm. The SEM system (JEOL JSM-5900) equipped with an energy-dispersive detector was used for quantitative chemical analysis of B-C phase. EDS measurements of the post-laser heated sample conducted at several points inside the circle area in Fig. 1 provide an average value for C/B ratio: C/B = 1.55 ± 0.14 (Zinin e*t al*., JAP, 2006).

Raman spectroscopy of graphite



Phonon eigenvectors of graphene and graphite. Every phonon eigenvector of graphene gives rise to two vibrations of graphite. For example, the in-phase combination of the two layers for the E2g optical mode of graphene yields E2g ⊗ A1g =E2g and the out-of-phase combination E2g ⊗ B1u =E1u. Next to the graphite modes we indicate whether they are Raman (R) or infrared (IR) active and the experimentally observed phonon frequencies. The translations of graphite were omitted from the figure (From By Stephanie Reich1 and Christian Thomsen *Phil. Trans. R. Soc. Lond.* A (2004) **362**, 2271–2288.

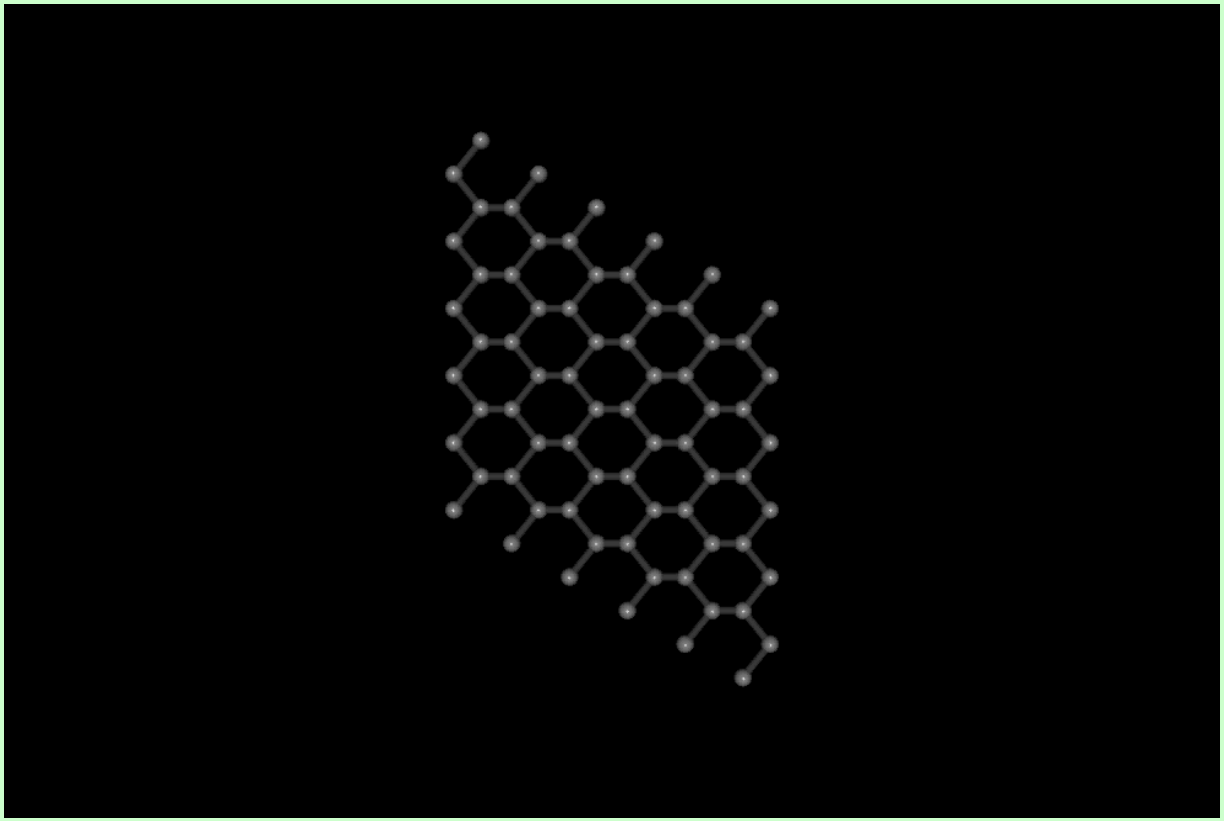
Raman spectroscopy of the graphite

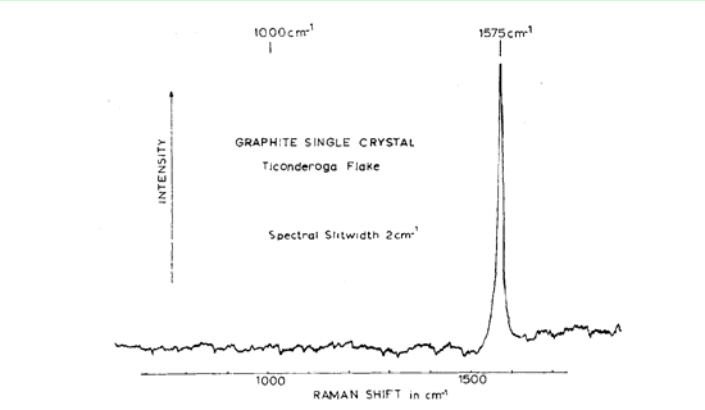


Raman spectrum (514 nm) of highly orientated pyrolitic graphite (J. Filik, *Spectrosc. Europe*, 2005)

The 1575 cm $^{-1}$ peak (called the "G" peak, after crystalline graphite) is the only Raman active mode of the infinite lattice. The other peak (the "D" peak from disordered graphite) is caused by breakdown of the solid-state Raman selection rules.

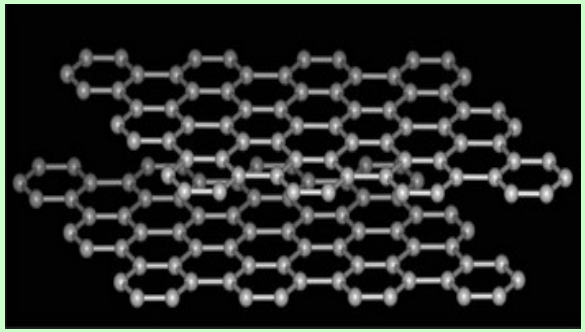
Raman spectroscopy of the graphite

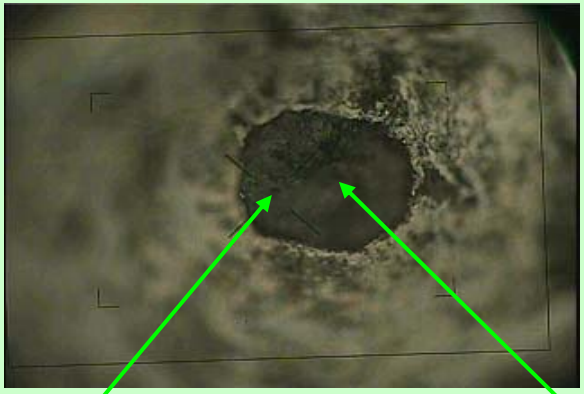


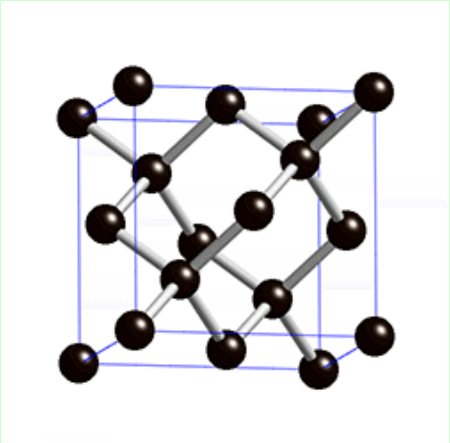


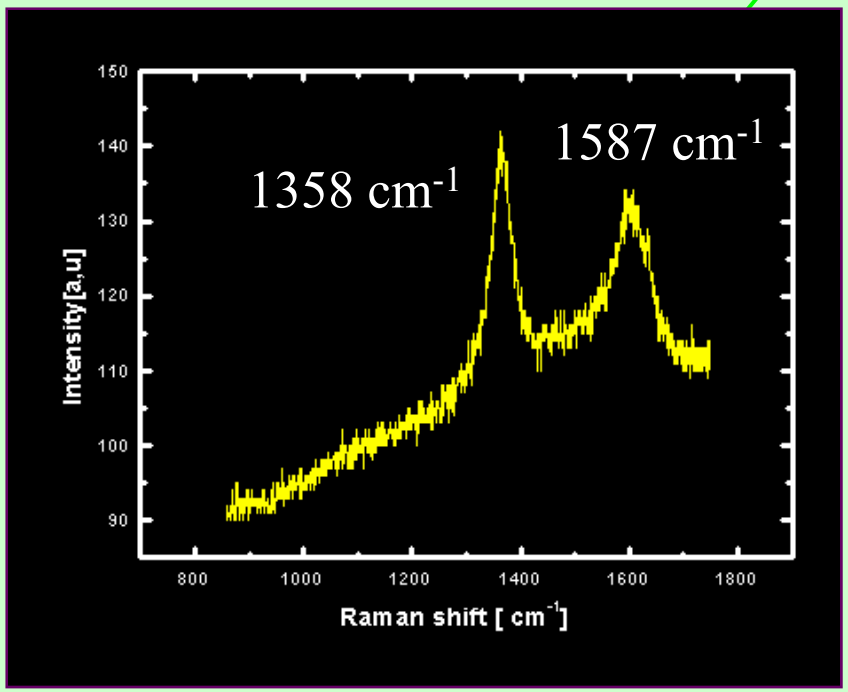
Courtesy to Ted Lowther

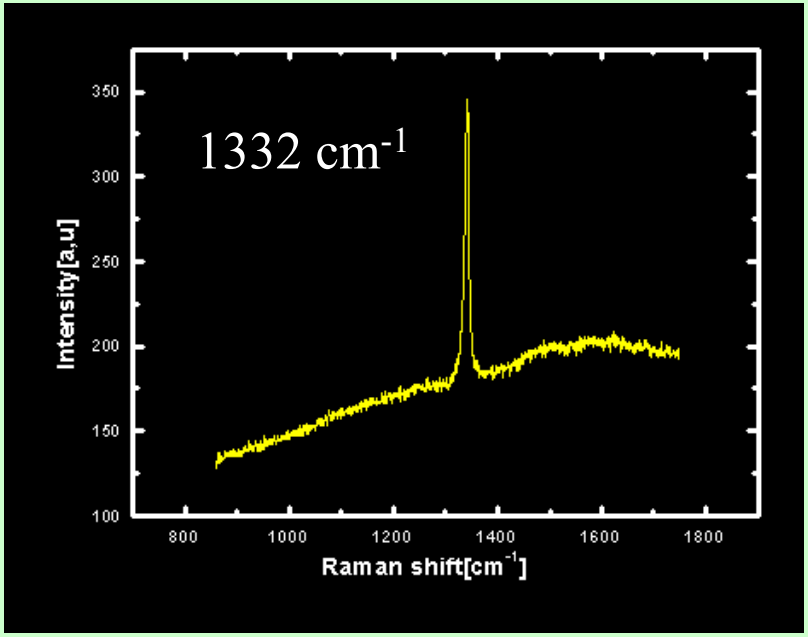
Laser Heating in DAC of graphite, 50 GPa, 1500 K)



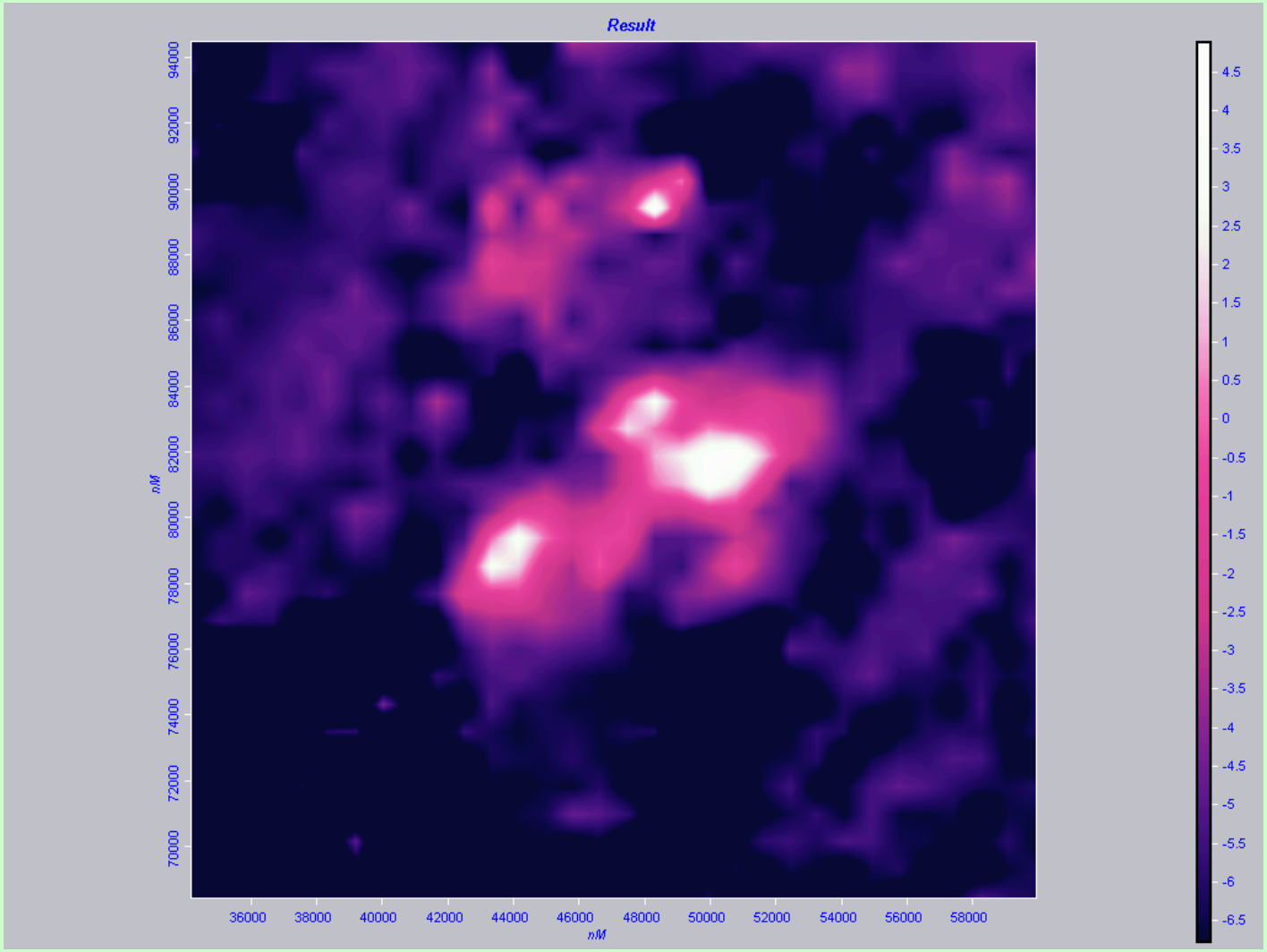






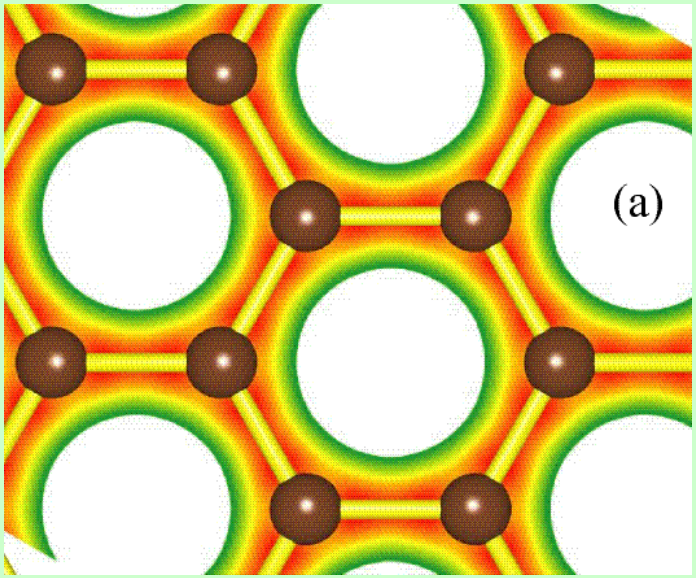


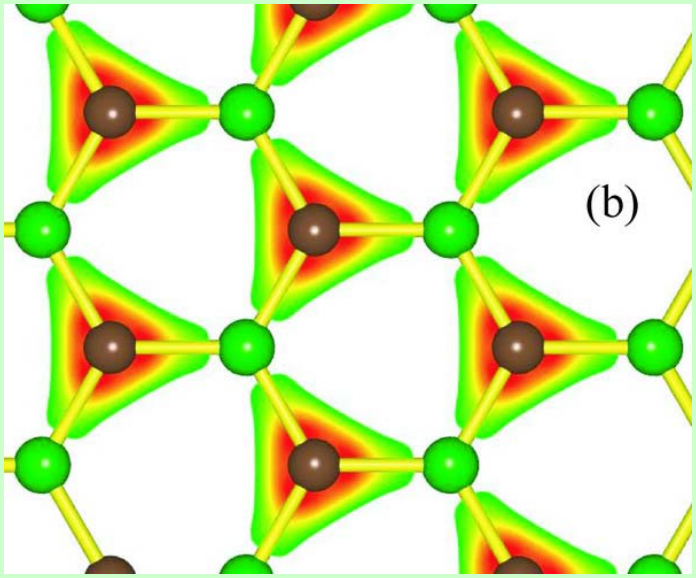
Graphite after laser heating at 50 GPa and 1500 K



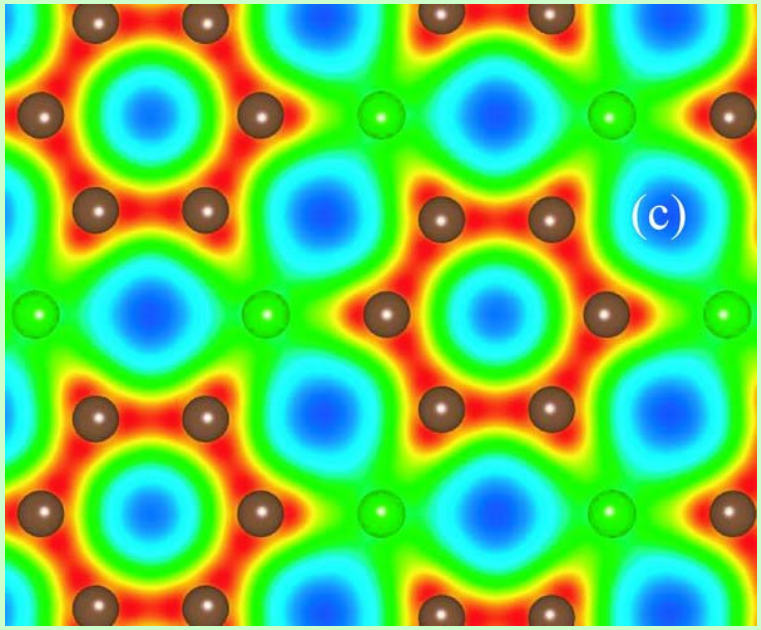
Intensity XY mapping (16 x 16 μm) of peak 1332 cm^{-1}

Raman active modes of *g*-BC_3



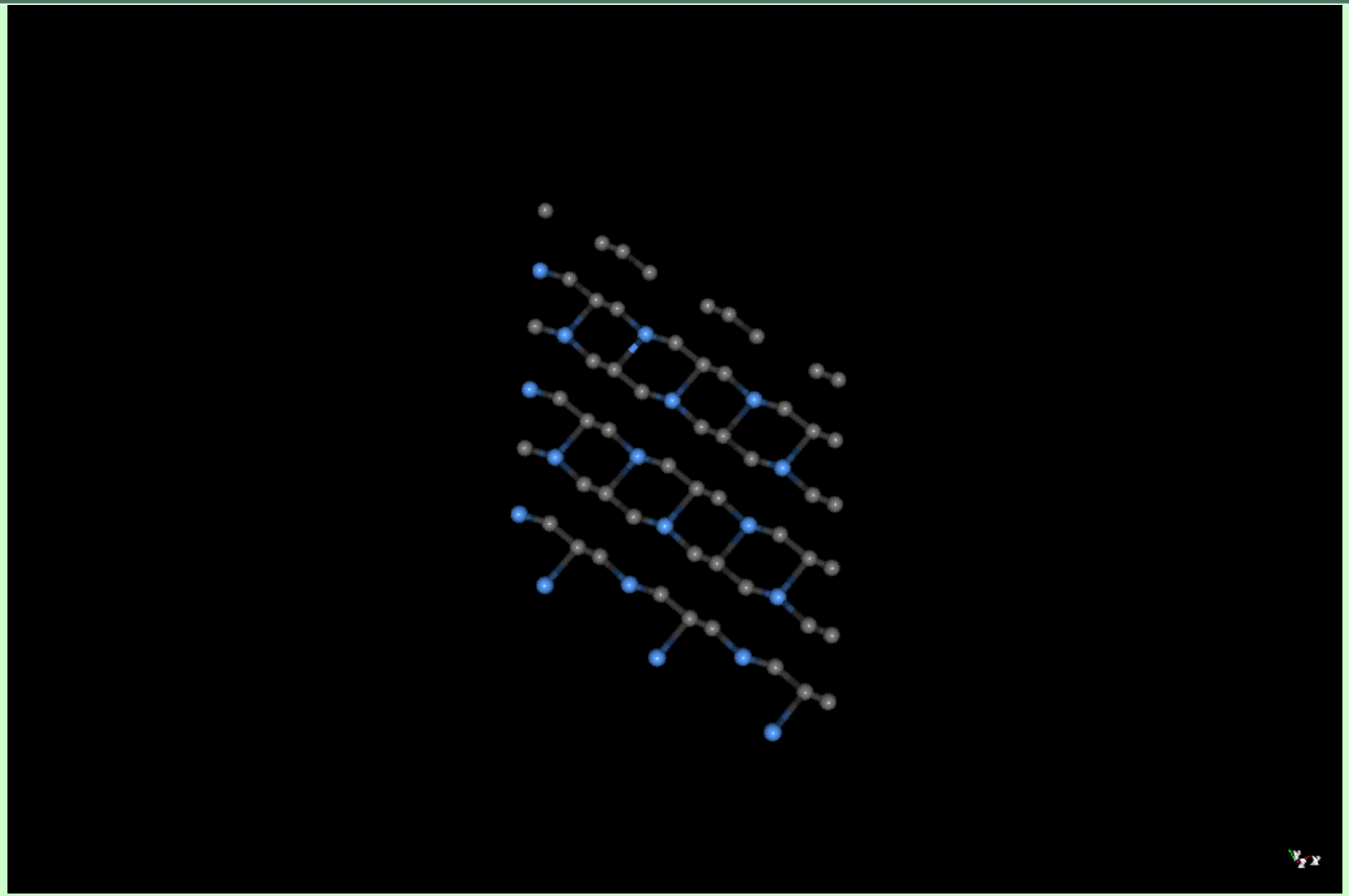


Electronic charge distribution (a) in graphene sheet, (b) in graphitic BC, and (c) in graphitic BC3.



Images of the electronic structures were simulated by Prof. *Ted Lowther*, University of the Witwatersrand, Johannesburg, South Africa

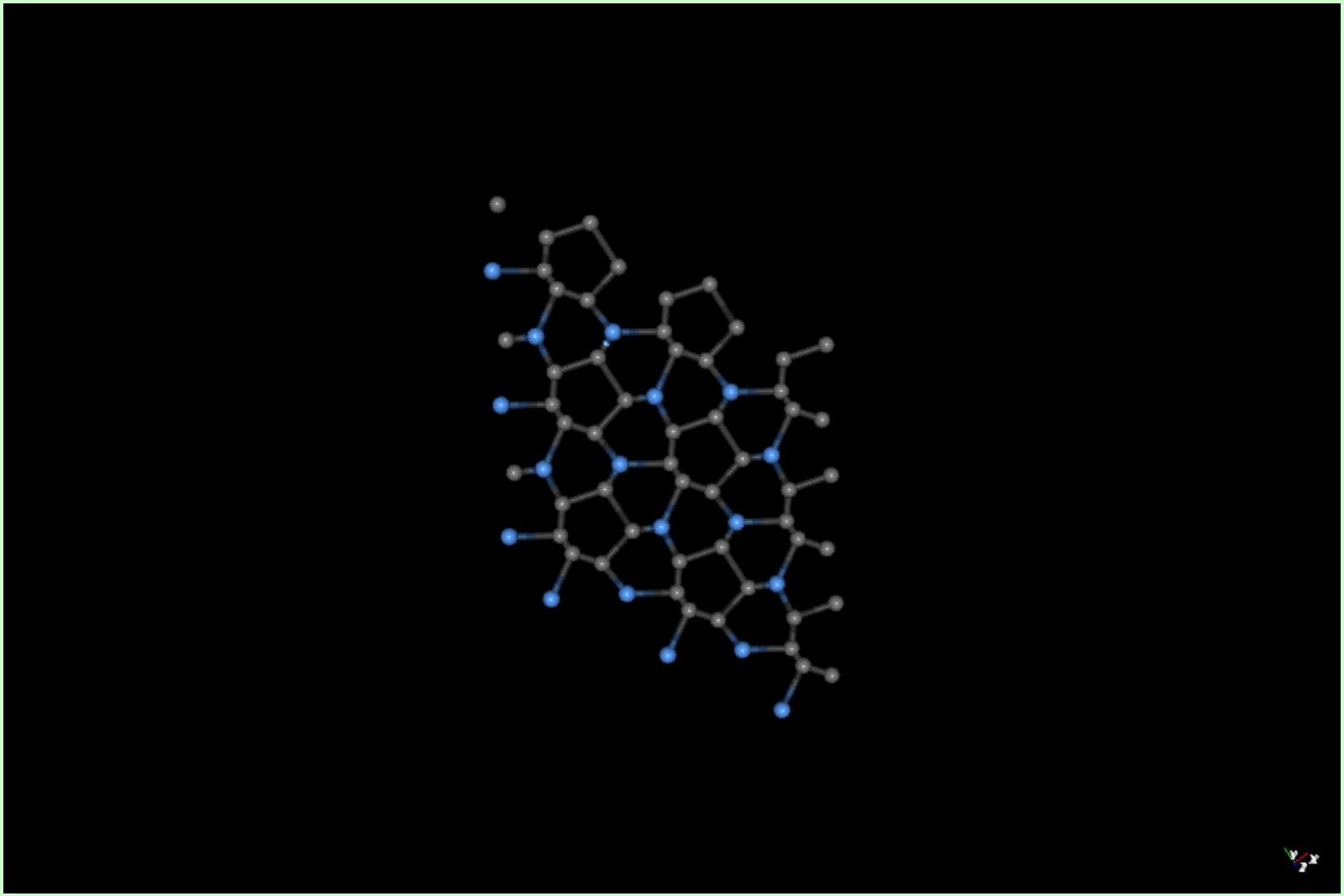
Raman active modes of g-BC_3



High energy vibration of g-BC_3 calculated at 1550 cm^{-1}. Atomic displacements are slightly away from the interatomic bond unlike graphene

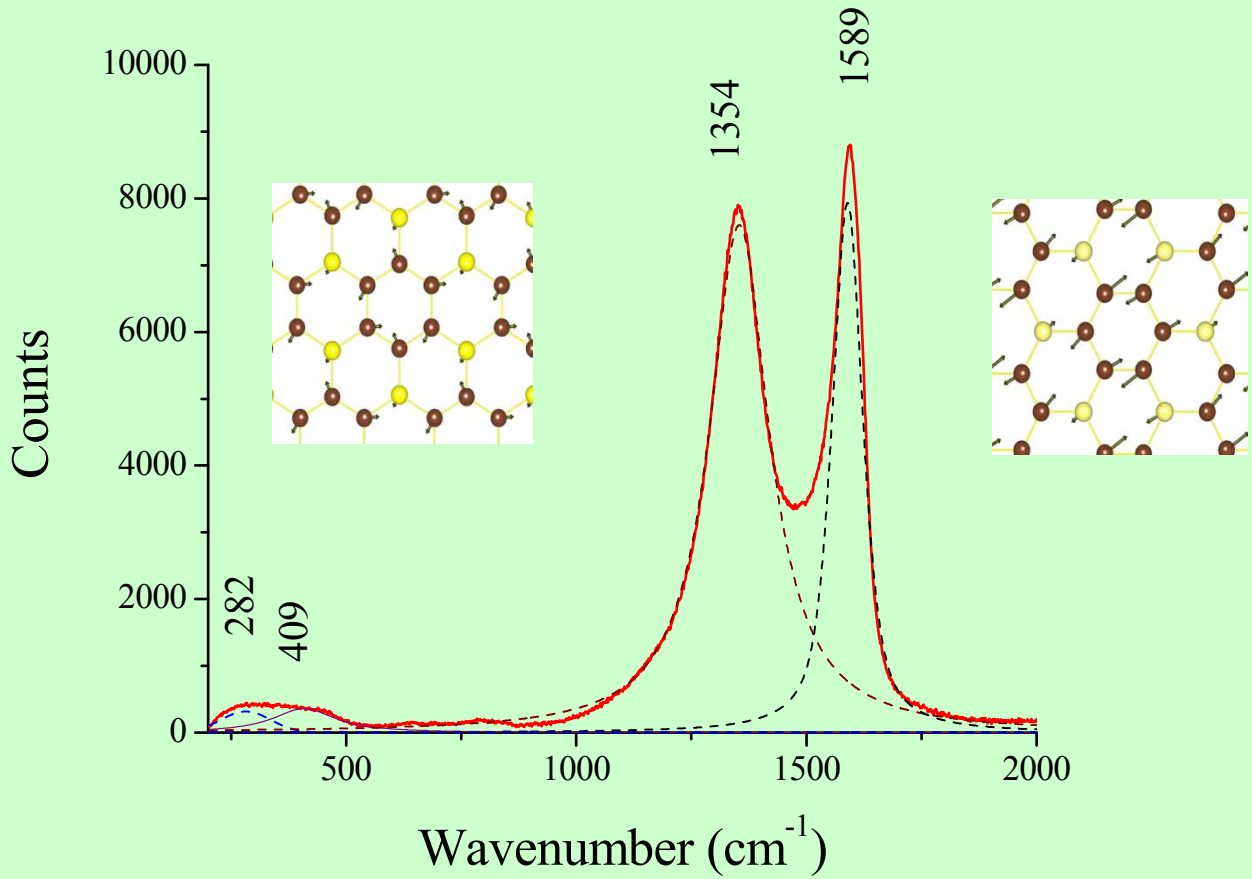
(Simulations by Prof. *Ted Lowther*, University of the Witwatersrand, Johannesburg, South Africa).

Raman active modes of g-BC_3



Second highest energy vibration of the g-BC_3 vibration structure calculated at 1347 cm^{-1} (Lowther *et al.*, *PRB*, 2009).

Visible (514 nm) Raman spectra of the g-BC_5

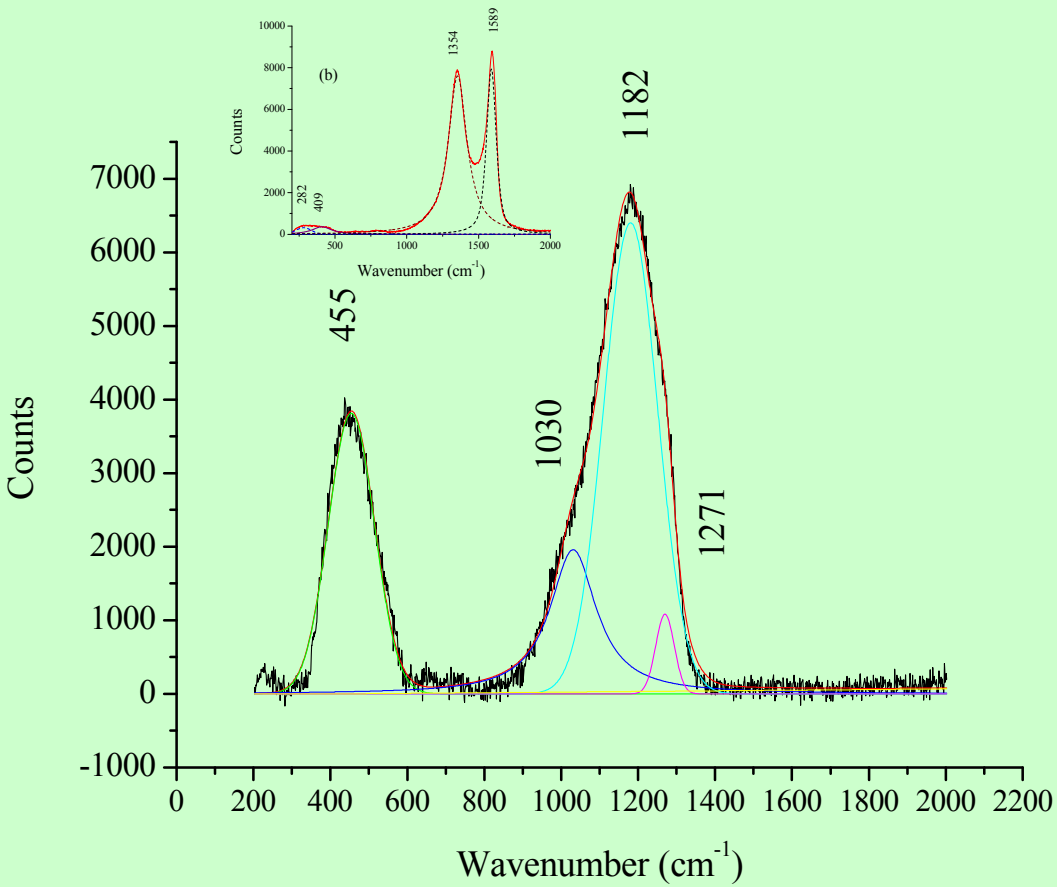


Visible Raman spectrum taken with ×20 objective; integration time was 1 min.; laser power on sample was 2 mW (Zinin *et al*. Diamond Related Mater. 2009).

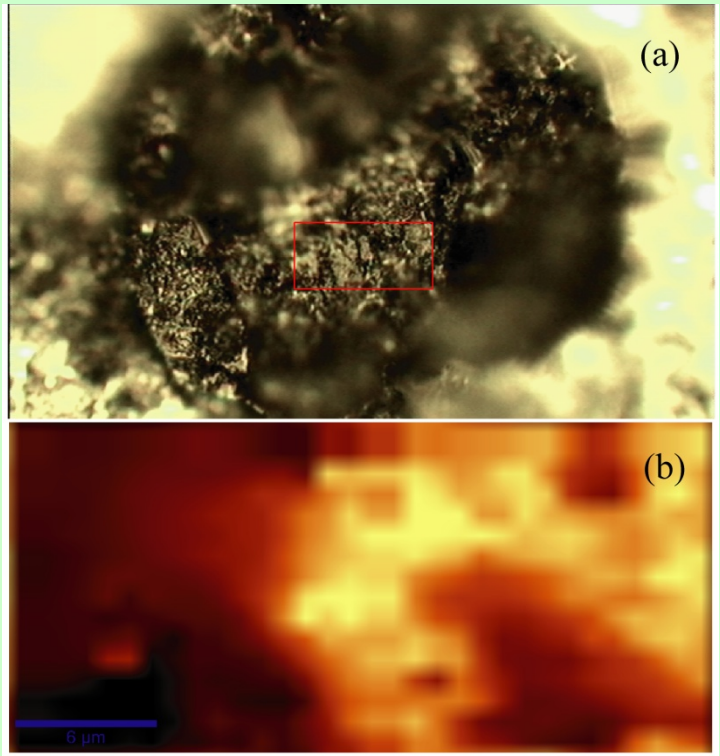
Renishaw *InVia* Micro-Raman system

•Laser Excitation Wavelengths Available: 244 nm (UV), 514.5 nm (Green) & 830 nm (NIR)

Raman Spectroscopy of cubic BC_4

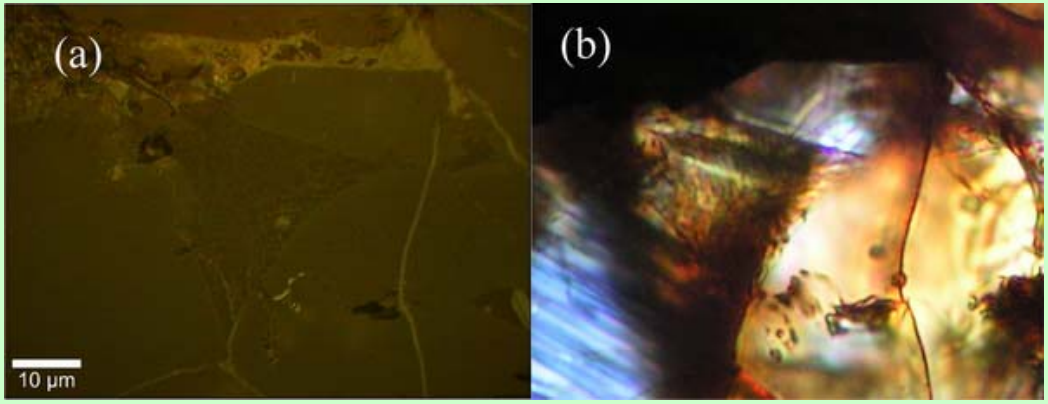


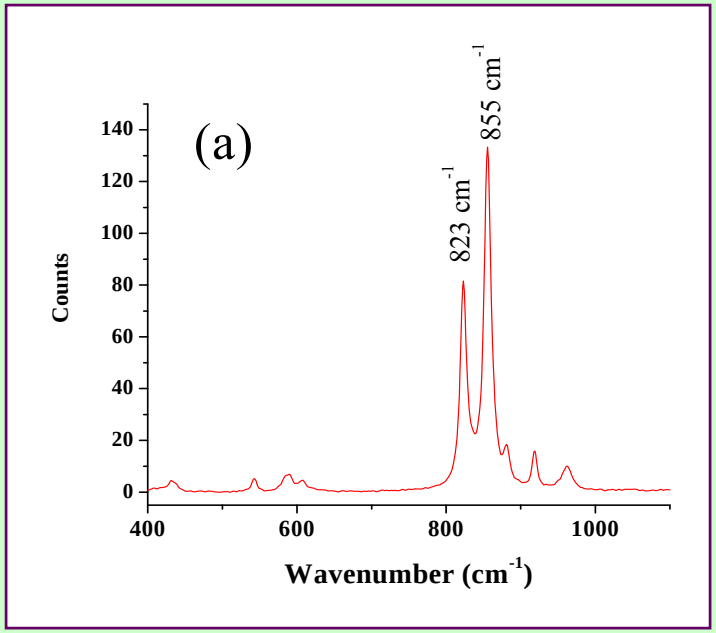
Raman spectrum (532 nm) of *c*-BC_4 phase: integration time was 4 min, laser power was 2 mW.



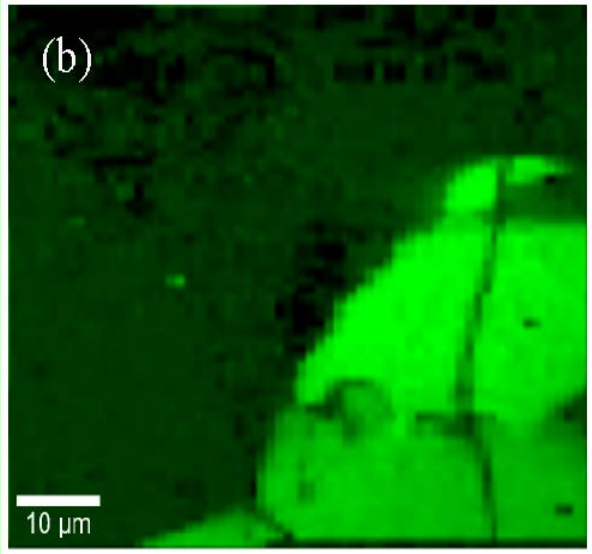
(a) Optical image of the *c*-BC_4 phase and (b) a map of the Raman peak intensity at 1193 cm^{-1} shown in a yellow colour scale.

Raman Spectroscopic Study of Roosevelt County (RC) 075 Chondrite



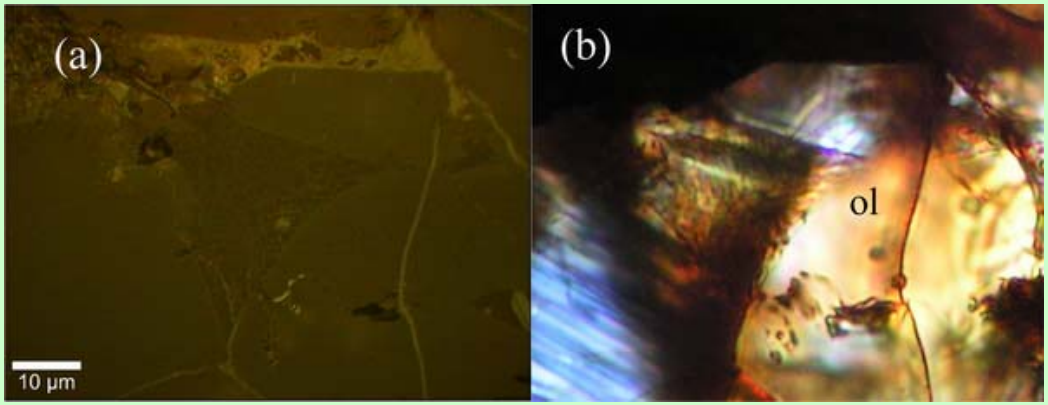


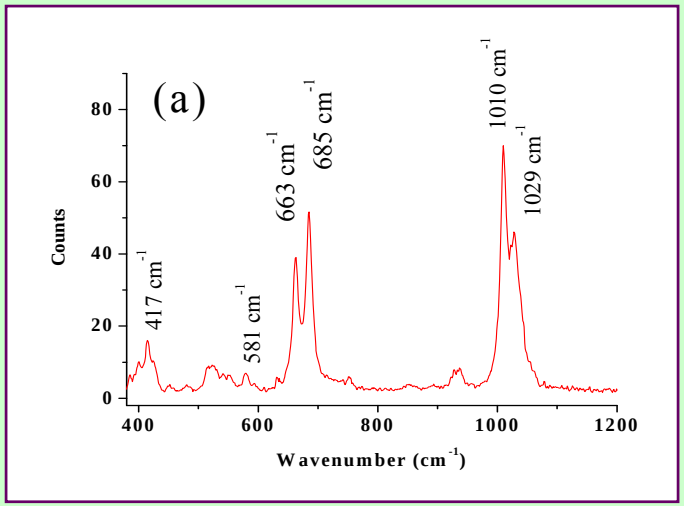
Reflected (a) and cross polarized transmitted (b) light images of RC 05.



Raman spectrum of olivine (a) and map of the Raman peak centered at 855 cm-1 (b). The intensity of the 855 cm-1 peak is shown in a green color scale

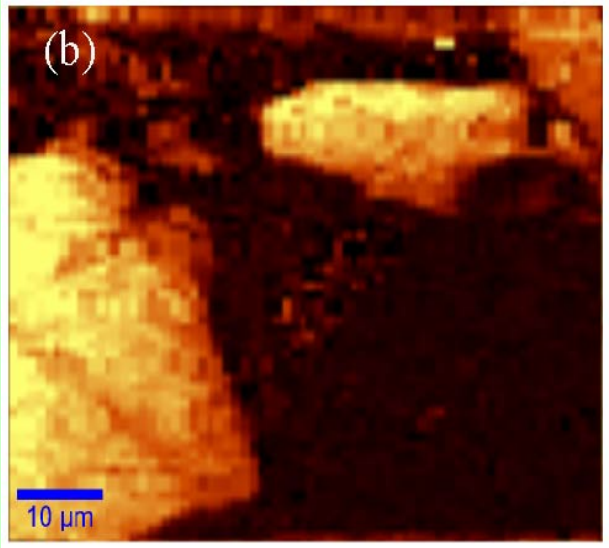
Raman Spectroscopic Study of Roosevelt County (RC) 075 Chondrite



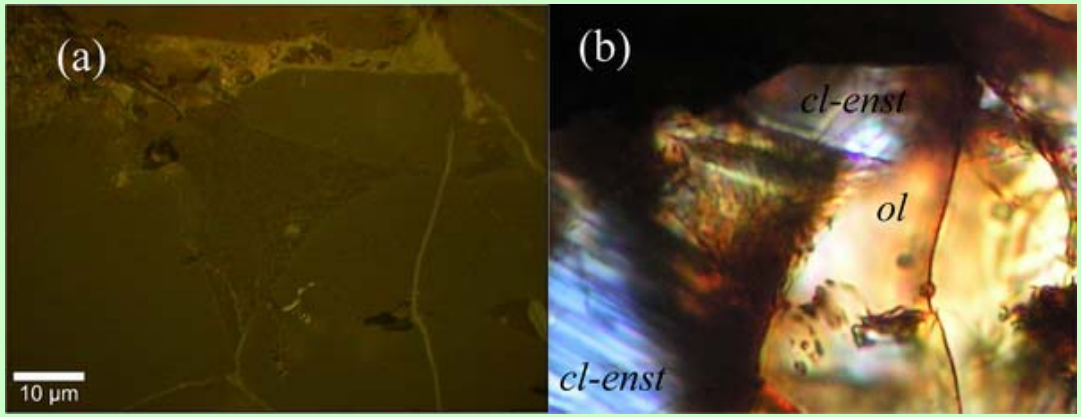


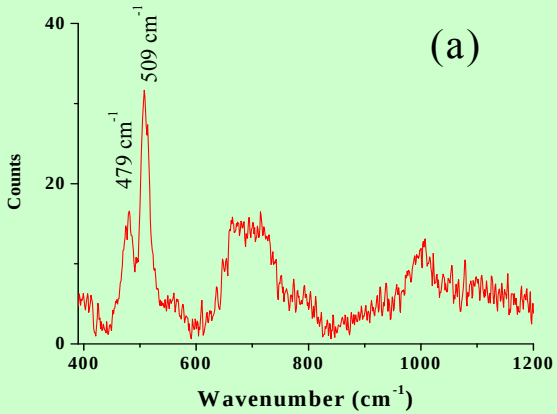
Reflected (a) and cross polarized transmitted (b) light images of RC 05: *ol* = olivine;.

Raman spectrum of the clinoenstatite (a) and map of the Raman peak centered at 1010 cm-1 (b). The intensity of the 1010 cm-1 peak is shown in a yellow color scale

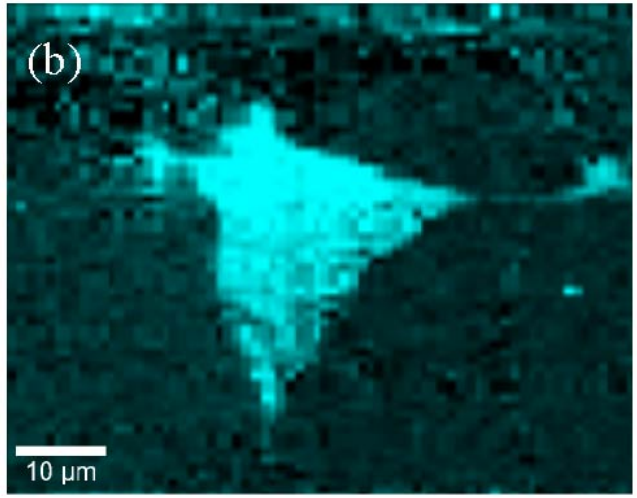


Raman Spectroscopic Study of Roosevelt County (RC) 075 Chondrite



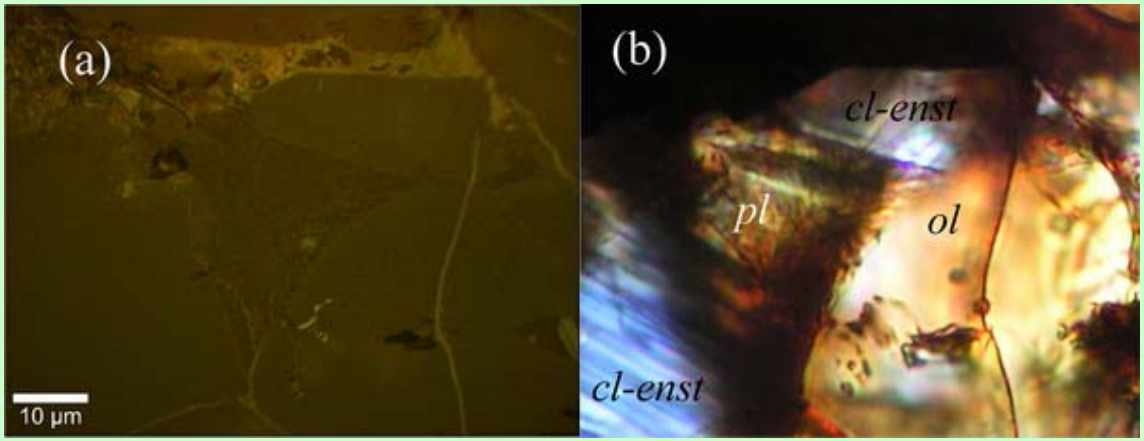


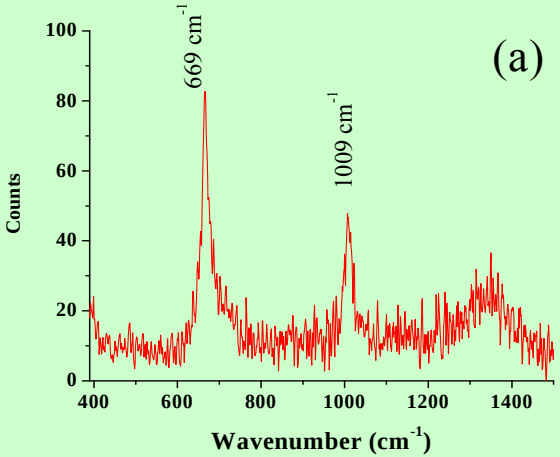
Reflected (a) and cross polarized transmitted (b) light images of RC 05: *ol* = olivine; *cl-enst* = clinoenstatite.



Raman spectrum of the plagioclase (a) and map of the Raman peak centered at 509 cm-1 (b). The intensity of the 509 cm-1 peak is shown in a blue color scale.

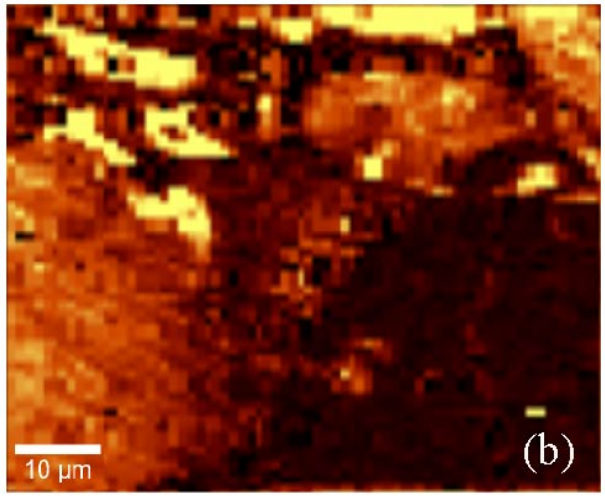
Raman Spectroscopic Study of Roosevelt County (RC) 075 Chondrite



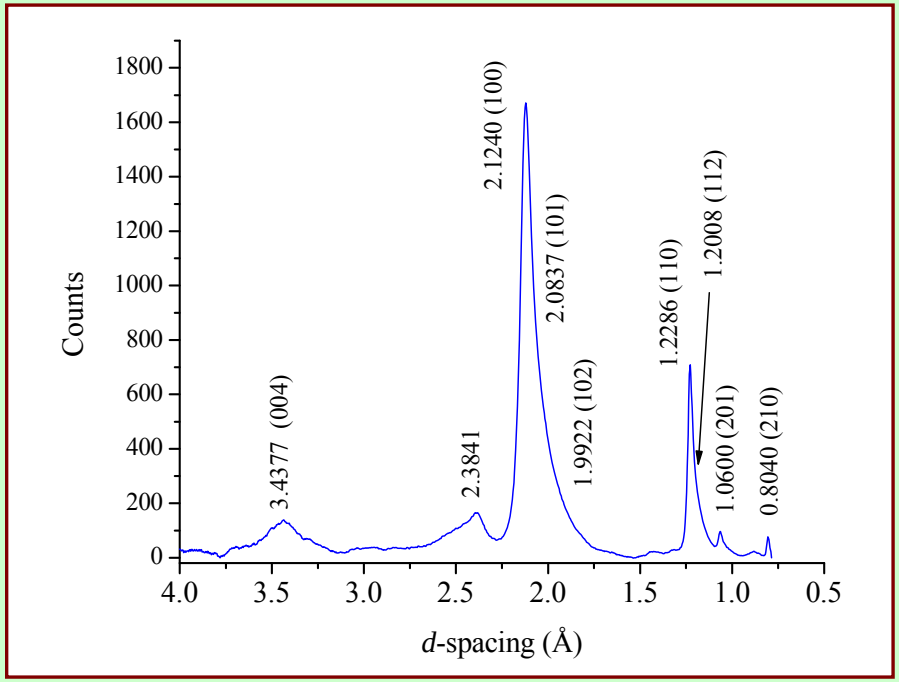


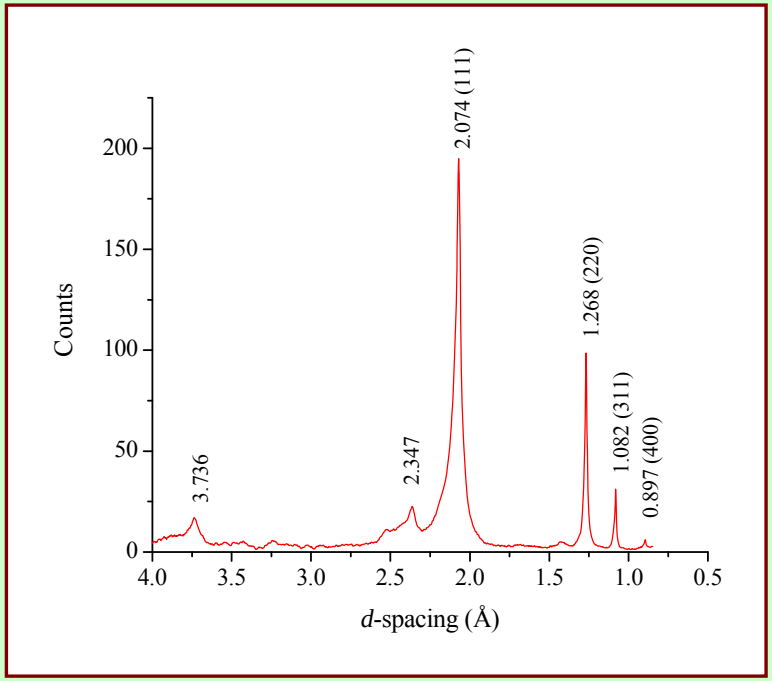
Reflected (a) and cross polarized transmitted (b) light images of RC 05: *ol* = olivine; *pl* = plagioclase; *cl-enst* = clinoenstatite.

Raman spectrum of the clinopyroxene (a) and map of the Raman peak centered at 1009 cm-1 (b). The intensity of the 1009 cm-1 peak is shown in a yellow color scale



Synthesis of cubic-BC_4 phase at 37 GPa





X-ray diffraction of the graphitic BC_4 (*g*-BC_4(I)) as the starting material, where the broad peak around 2.384 Å is from the B_4C.

The ambient x-ray diffraction pattern of a post-lasered BC_4 (*c*-BC_4(II)) phase recovered from 37 GPa. Two weak and broad peaks at 3.736 and 2.347 are from the B_4C in the starting material.

L. C. Ming, P. V. Zinin,*et al.*, *J. Phys.*: *Conf. Ser.*. In press (2009).

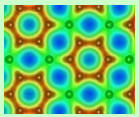
Elemental composition of the new cubic phase

•Electron microprobe analysis of the recovered BCx sample was performed using JEOL *Hyperprobe* JXA-8500F

•In order to ensure a reliable result, a pure B_4C powder was used as the standard for calibration of boron and carbon in the sample, and the rinsed BCx sample in the gasket was first fixed with an epoxy resin and then polished until an optically flat surface from the sample was fully exposed. The result obtained from EMP measurements gives a C/B ratio of around 4 (*C/B = 3.91 ± 0.26*).

•Two samples were loaded to 24 and *44 GPa*, and laser-heated to 2020 and *1984 K*, respectively. It was found that the sample pressure remained the same for the first sample at 24 GPa, while the pressure dropped *from 44 GPa to 37 GPa* in the second sample. The large pressure drop in the second sample is most likely related to volume change as a result of the transition to a denser phase in the sample.

Phase Transitions in BC_4

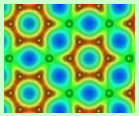


g-BC_4 (I) – hexagonal
(graphite-related phase)

24 GPa, 2020 K

44 GPa, 1984 K

(a)

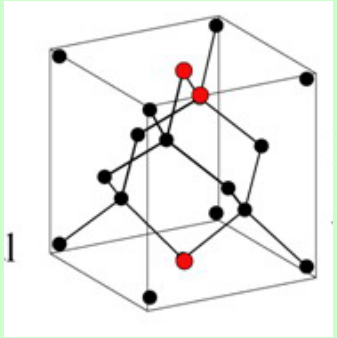


g-BC_4 (II) – hexagonal
(graphite-related phase)

c-BC_4 – cubic
(diamond-like phase)

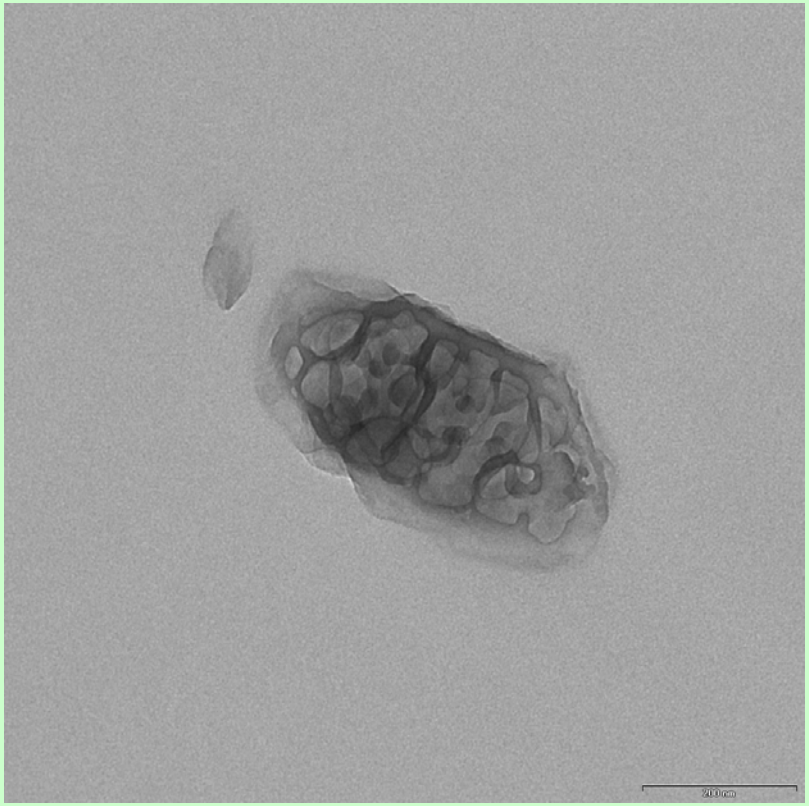
Factors that could effect the lattice parameter of the diamond-like BCx phases

- Structure defect – Higher the vacancy, larger the lattice parameter
- Synthesis pressure: Higher the synthesis P, Smaller the lattice parameter



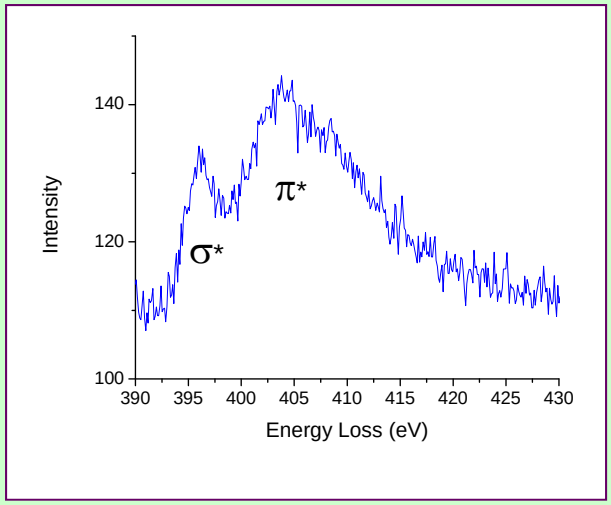
BC_4 diamond-like phases should have 3 vacancy defect in the structure.

TEM and EELS at UH

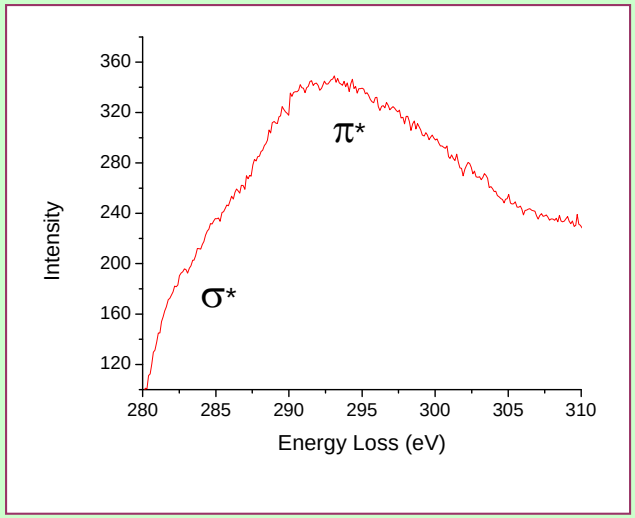


TEM image of the starting graphitic-C_3N_4 phase. Marker is 200 nm

EELS spectra of carbon, C-K in the graphitic C_3N_4

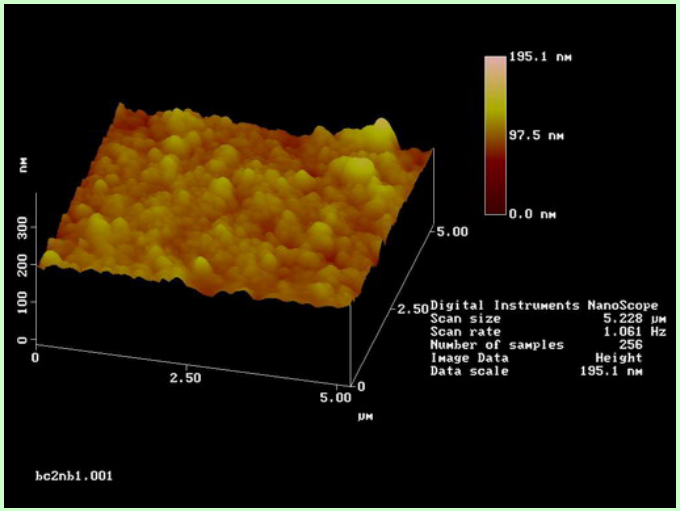


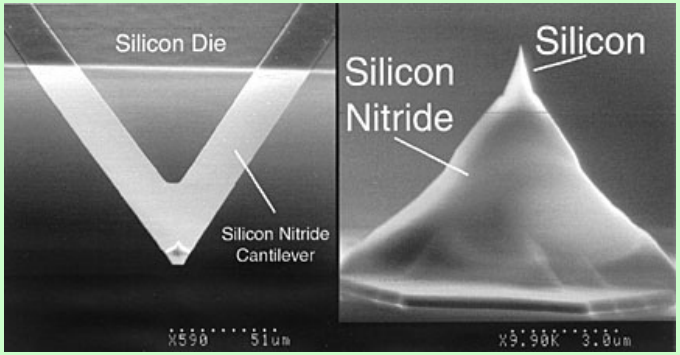
EELS spectra of nitrogen, N-K in the graphitic C_3N_4



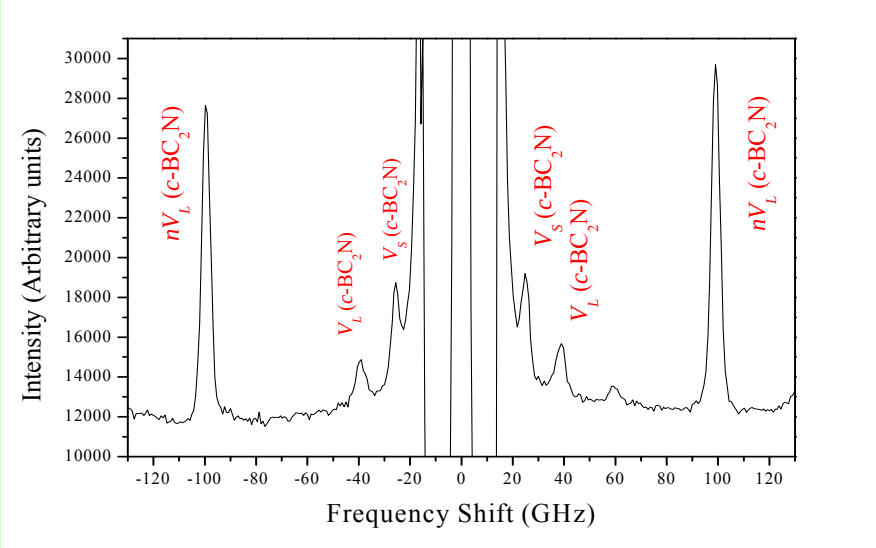
Atomic (Scanning) Force Microscopy

The Atomic Force Microscope. Digital Nanoscope III. Contact *Pavel Zinin*, HIGP.

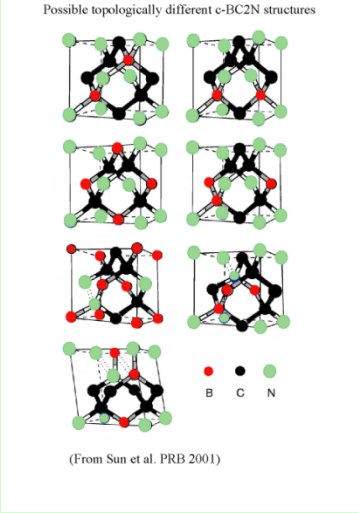




Experimental BS spectrum (θ =50°) of Nanocrystalline c-BC_2N



S. Tkachev, V. Solozhenko, P. Zinin, *et al.*, *Phys. Rev. B.* **68** 052104 (2003).



Contact *Pavel Zinin*, HIGP.

Sample Characterization at UH

1. Studying of a specimen by optical microscopy
2. SEM and determination of the elemental composition by EDS
3. Identification of the chemical bonds of the specimen by Raman spectroscopy
4. Unit cell determination by x-ray diffraction
5. Accurate measurement of the elemental composition of specimen by EMP
6. Determination of the elemental composition of specimen at nano-level by TEM with EELS
7. Measurements of different properties of a specimen using different including atomic force microscopy, Brillouin scattering etc.
8. Writing a paper or PhD thesis