High pressure x-ray diffraction studies at synchrotrons

Nandini Garg

Outline

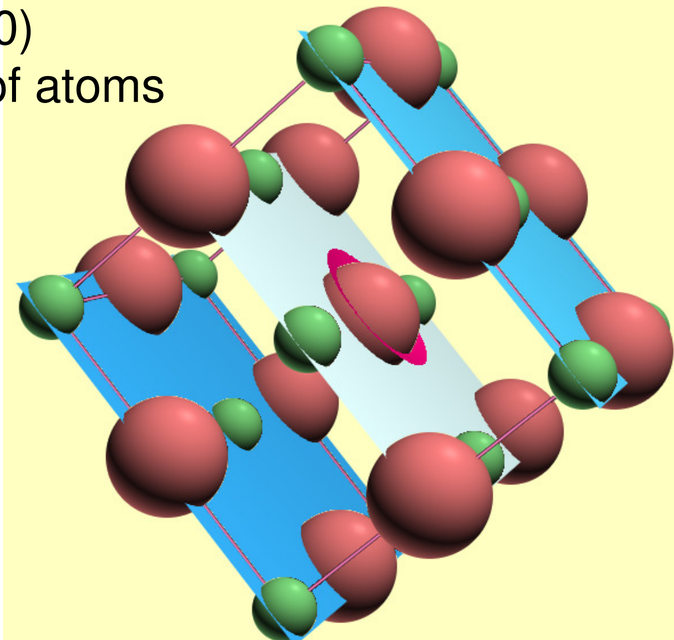
- Developments related to high pressure research at INDUS II
- XRD beamline, IR beamline, EXAFS beamline,
- Interpretation of x-ray diffraction data collected at high pressures with different examples
- Silicon, Nano Yttrium chromate, porous silicon, Bis glycinium oxide

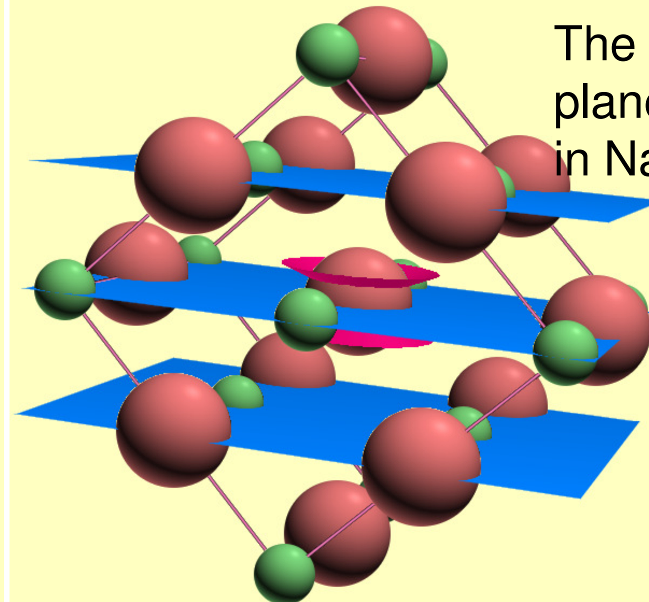
Part 1

- Developments related to high pressure research at INDUS II ----EDXRD-BL11

- Brief introduction to x-ray diffraction and different measurement techniques
- Adaptation of the diamond anvil cell for these studies
- EDXRD beamline BL11
- Different experiments feasible at this beamline
- Understanding the data collected by HPGe detector
- Typical example
- GIXRD

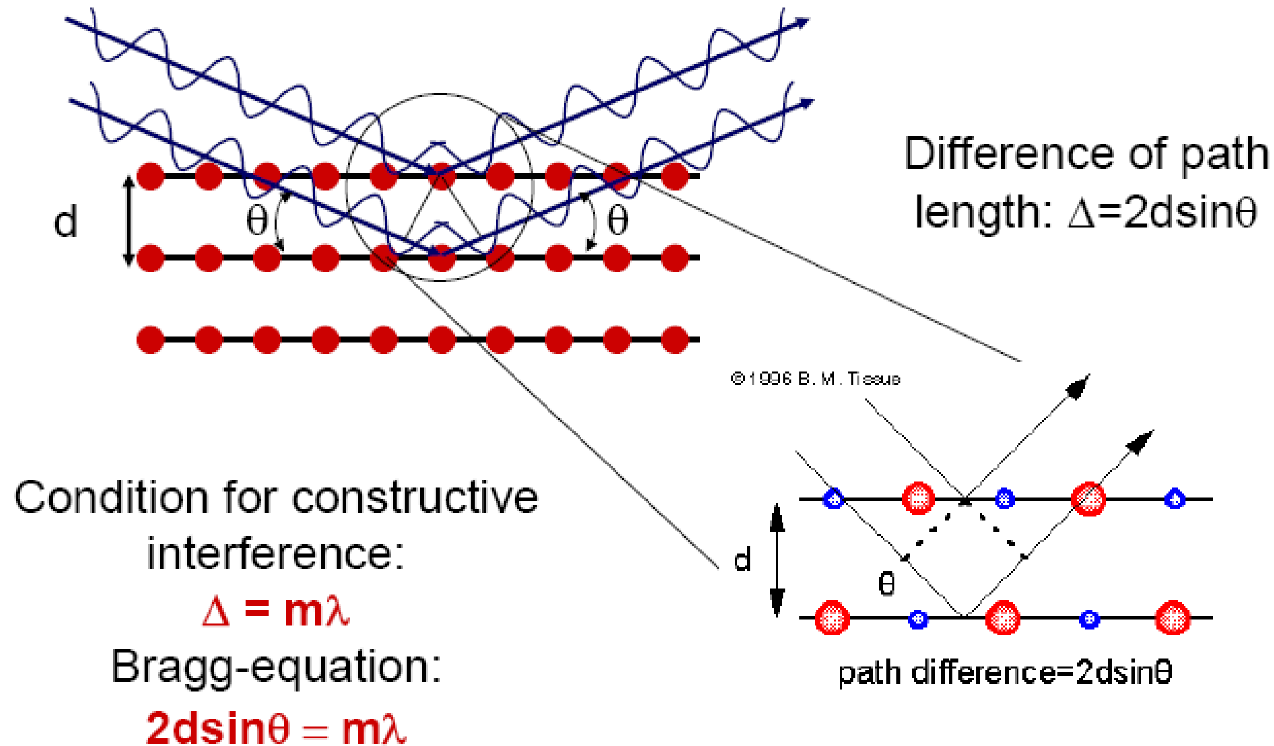
Crystalline materials are characterized by the orderly periodic arrangements of atoms.





- The unit cell is the basic repeating unit that defines a crystal.
- Parallel **planes of atoms** intersecting the unit cell are used to define directions and distances in the crystal.
  - These crystallographic planes are identified by **Miller indices**.

Real space interference condition



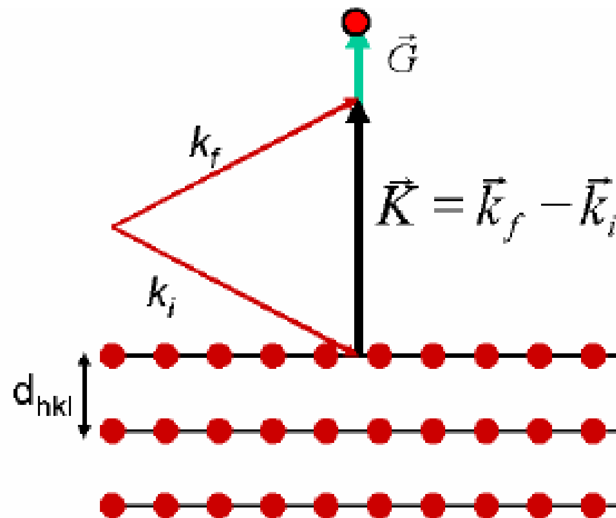
Diffraction occurs when each object in a periodic array scatters radiation coherently, producing concerted constructive interference at specific angles.

Atoms in a crystal form a periodic array of coherent scatterers.
Diffraction from different planes of atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal

Bragg equation

Scattering vector: $\vec{K} = (\frac{4\pi}{\lambda}\sin\theta)\hat{n}$

Reciprocal lattice vector: $\vec{G} = \frac{2\pi}{d_{hkl}}\hat{n}$



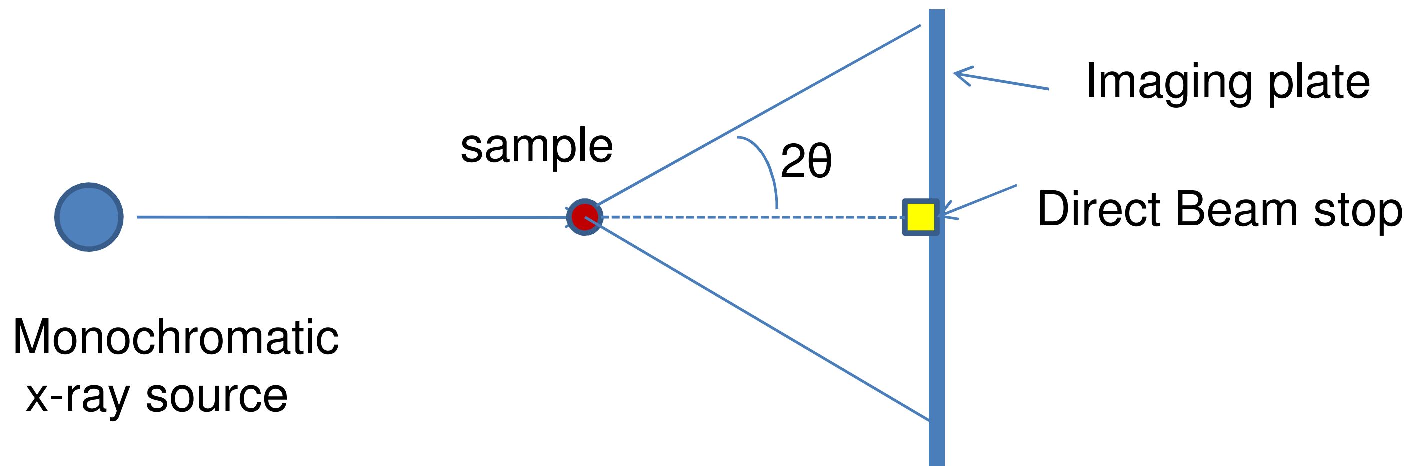
Bragg condition:

$$\vec{K} = \vec{G}$$

The space between diffracting planes of atoms determines peak positions.

The peak intensity is determined by what atoms are in the diffracting plane.

Angle dispersive measurements

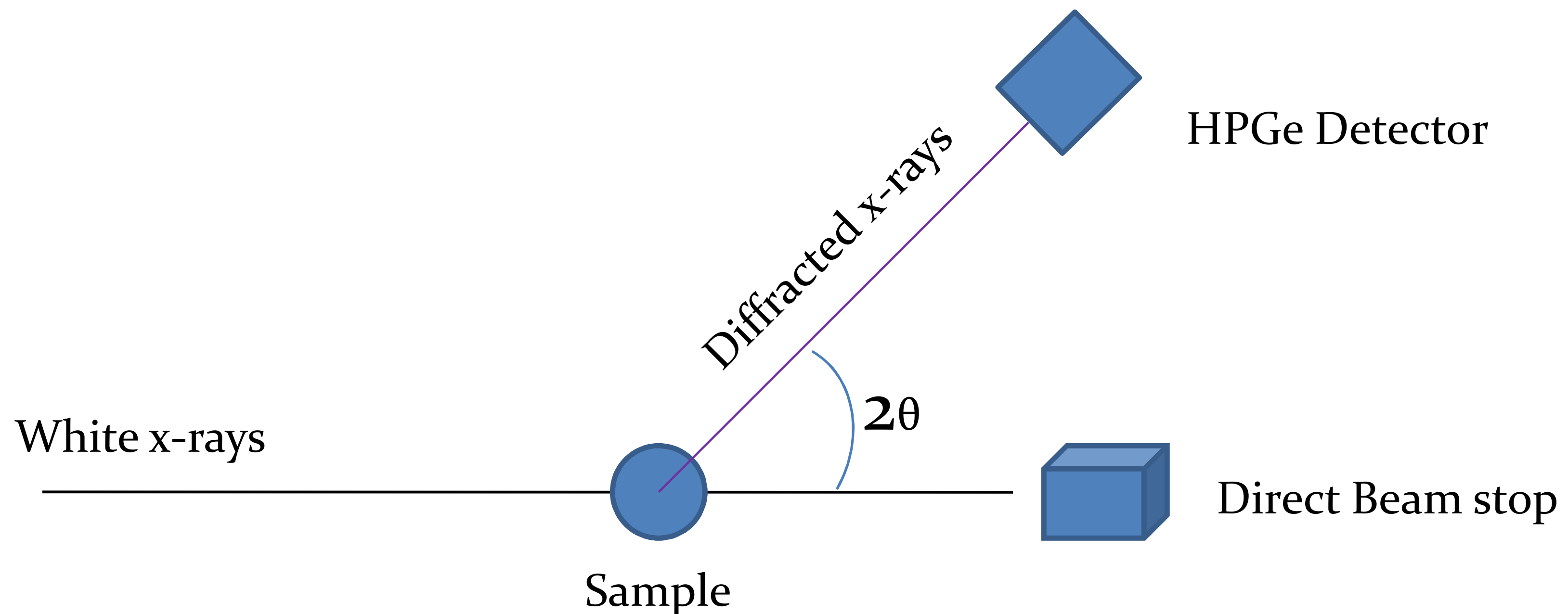


$$2d_{hkl} \sin\theta_{hkl} = n\lambda$$

Lambda is fixed

Energy dispersive measurements

$$E\, d_{hkl} \,\mathrm{Sin}\, \theta = 6.19926$$



Once we know the value of 'd' we can calculate the cell constants

The 'd' spacing formula for

Cubic, a=b=c, $\alpha=\beta=\gamma$

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

tetragonal, a=b ≠ c, $\alpha=\beta=\gamma$

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

(100) Diffraction peak **$d_{100} = a$**

(110) Diffraction peak **$d_{110} = a/2^{1/2}$**

So if ratio between the first two diffraction peaks is $2^{1/2}$ we can infer that it is either a cubic system or a tetragonal system

In a tetragonal system a=b ≠ c

So d_{110} and d_{011} will not be the same

Look at the ratio of d_{100} and d_{011}

If this is not equal to $2^{1/2}$ we can infer that the system is not cubic

Energy Resolution in EDXRD

Total beam divergence $\Delta\theta = (\alpha_i^2 + \alpha_{di}^2)^{1/2}$

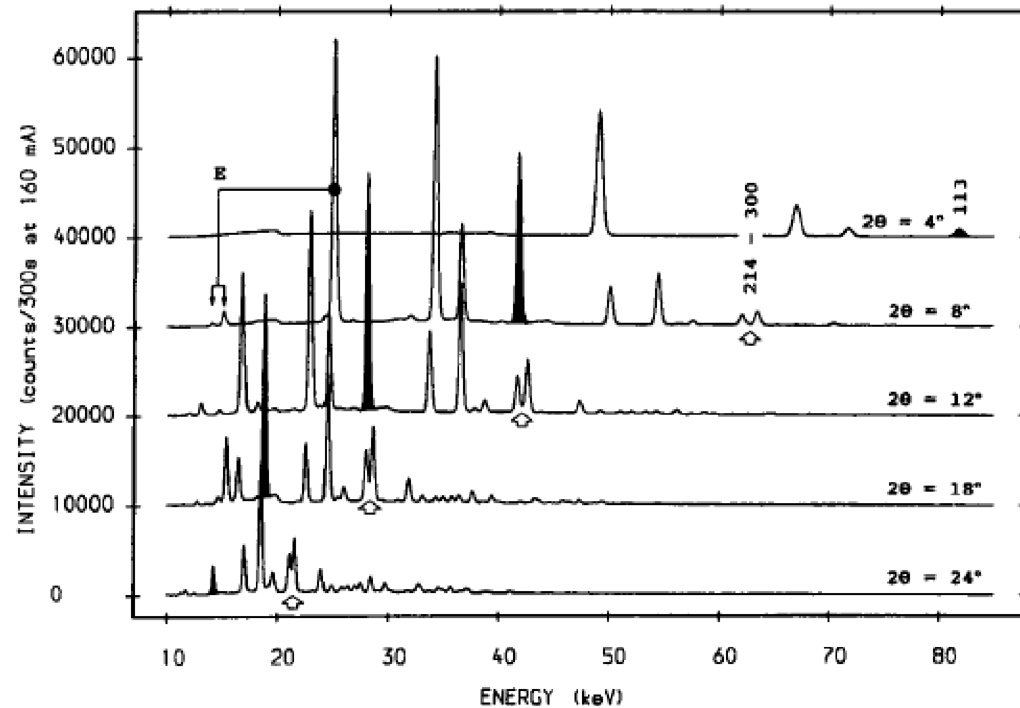
Energy resolution due to total beam divergence $\Delta E_\theta / E = \cot\theta \cdot \Delta\theta$

Energy resolution due to detector and beam divergence $\Delta E = ((\Delta E_D)^2 + (\Delta E_\theta)^2)^{1/2}$

$$\frac{\Delta d}{d} = \frac{\Delta E}{E} + \cot\theta\Delta\theta$$

Choice of Two theta

Absorption in sample
d-spacing range of interest
Resolution

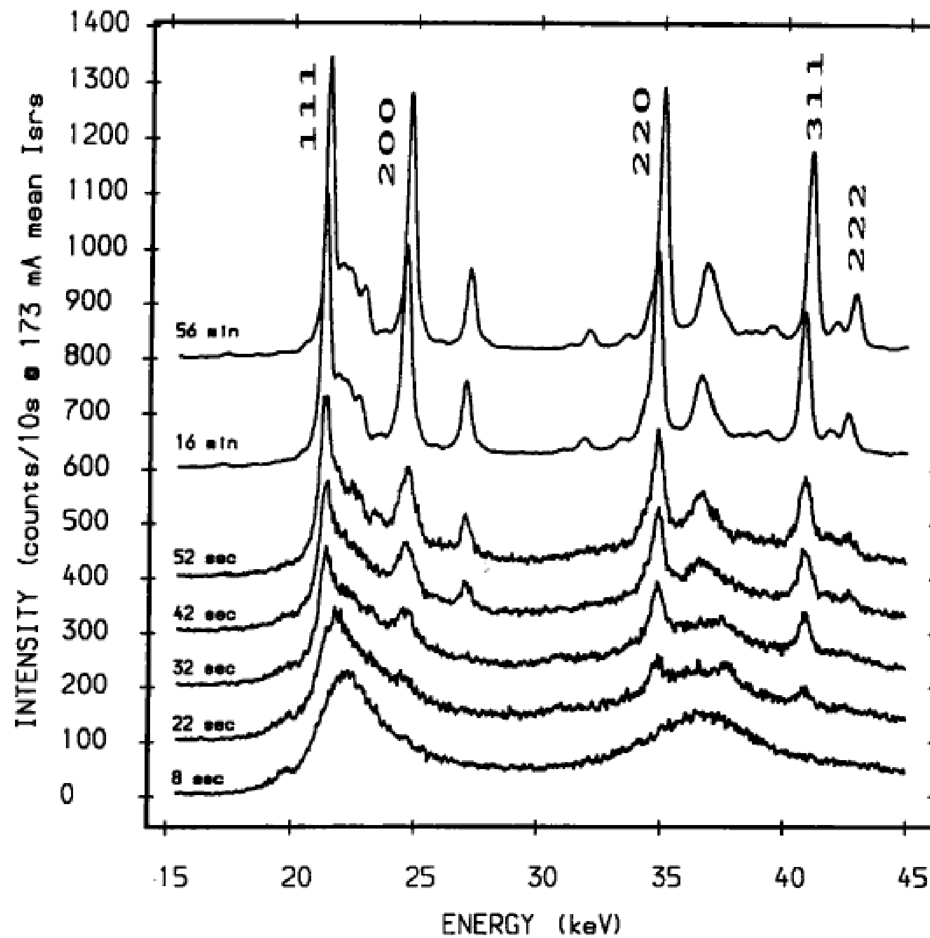


BL-11 Indus 2

Al_2O_3 Hausermann et al
Phase transitions, 1992

Metal absorber to enhance high energy peaks

Crystallization of 100 micron amorphous metal at 525˚ C
50 micron Cu absorber is used to enhance the high energy peaks



Hausermann et al
Phase transitions, 1992

INDUS II

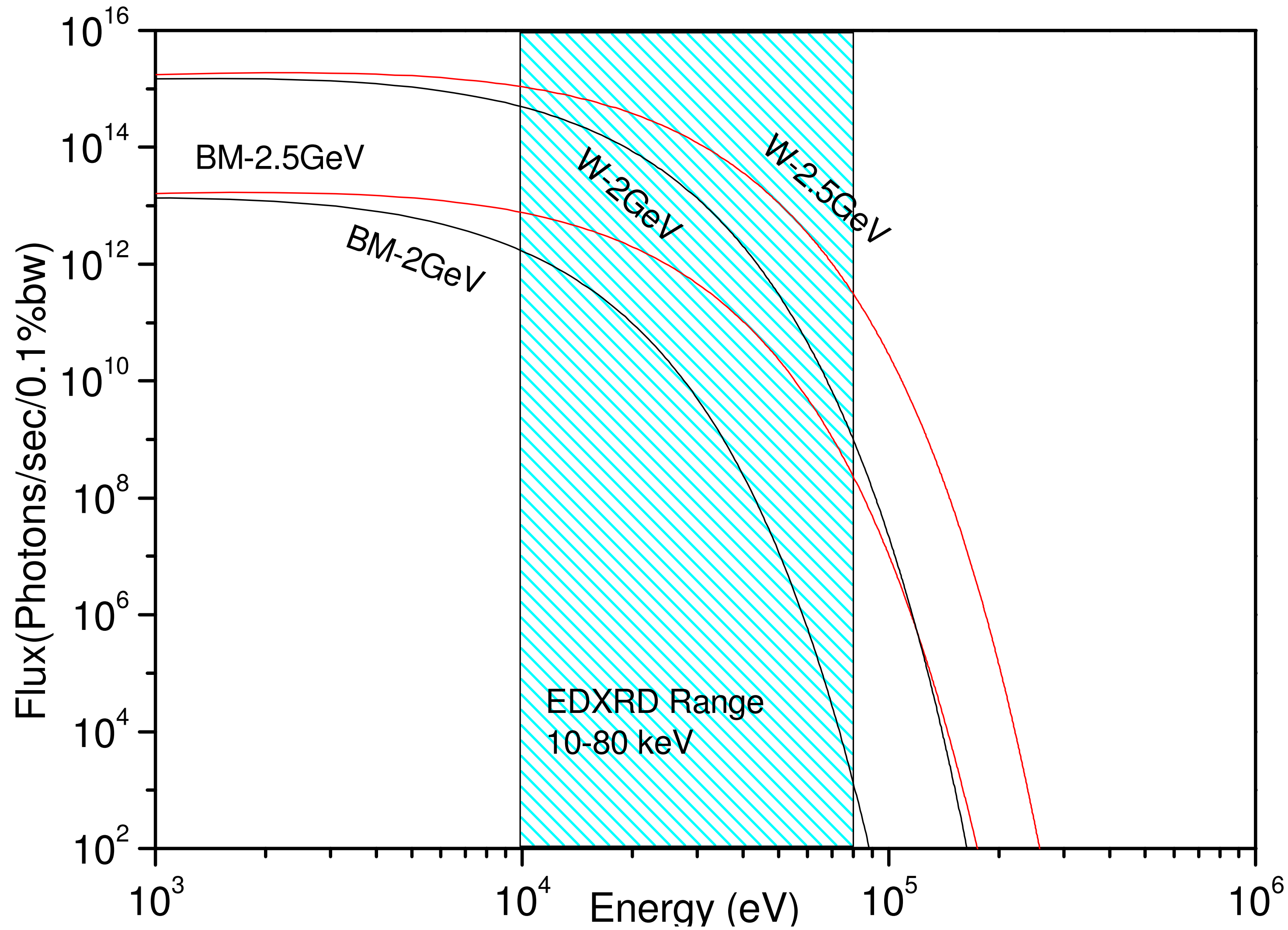
MODE 1

- Energy – 2.5 GeV
- Current – 300 mA
- Critical wavelength – 2Å

MODE 2

- Energy – 2 GeV
- Current – 300 mA
- Critical wavelength – 3.88Å

Flux at different energies



Specifications of EDXRD beamline

Source : White beam from bending magnet

Energy range : 5 KeV to 45 KeV @2.5 GeV / 25 mA
5 KeV to 35KeV @2 GeV/ 60 mA

Q range : 1.3 to 9.2 $Å^{-1}$(for 2θ =15°)

Beam acceptance : 1 mrad x 0.4 mrad

Spot size at sample: 8mm X 8mm (max), 100μm X 100μm(min)

Detector: High purity Germanium detector

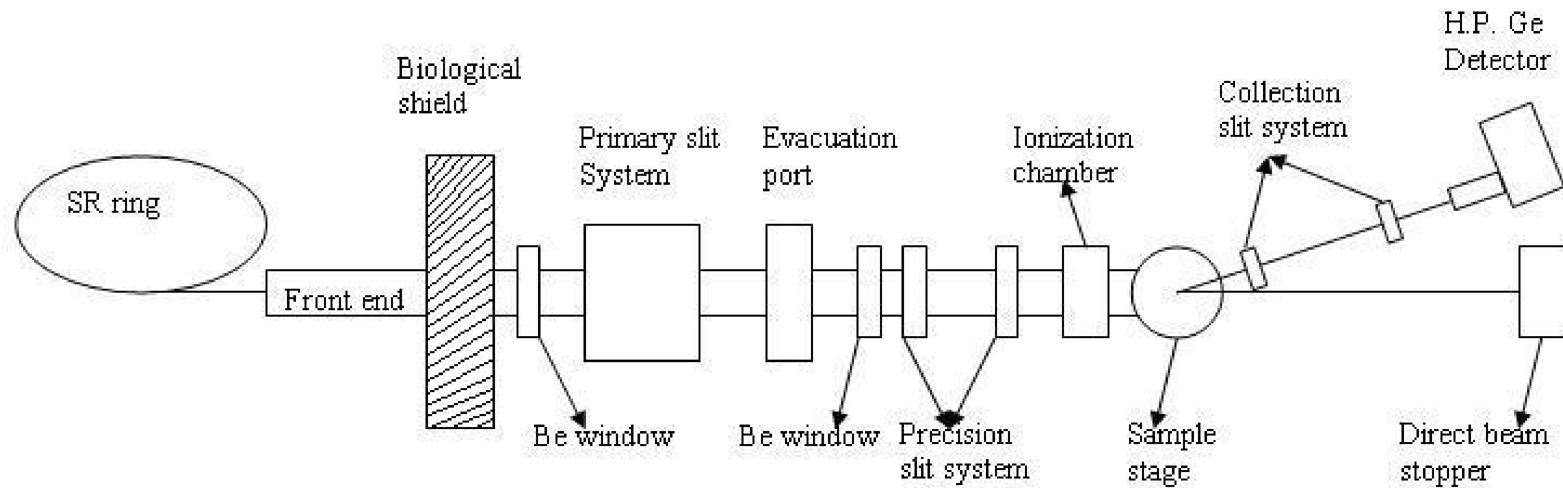
Detector resolution: 140 eV @5.9 KeV; 475 eV @ 122 KeV

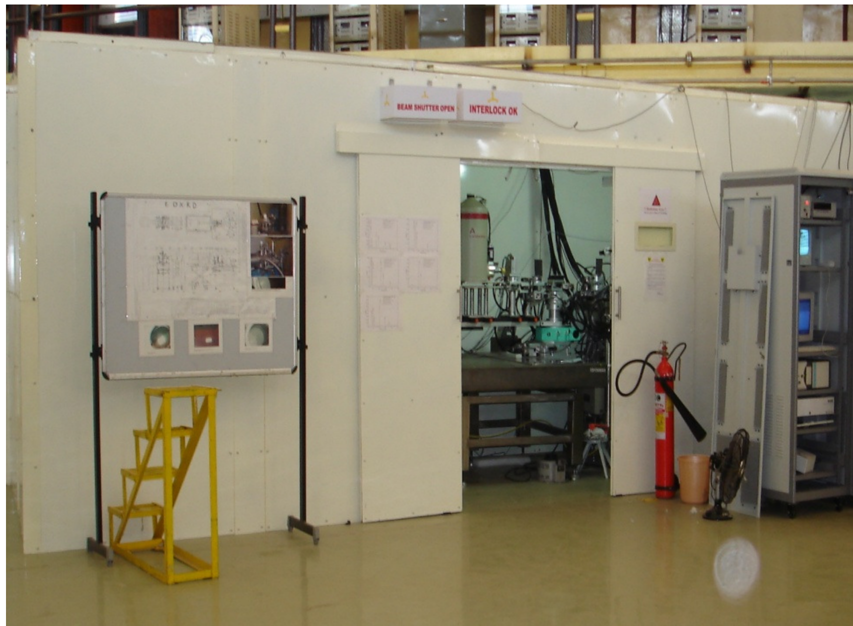
Typical resolution : 10^{-2} (ΔE/E)

Diffraction angle range: ± 25°

Total flux at sample : 10^{11} photons/s (for 300 mA @ 2.5 GeV ,100x100 μm)

EDXRD BL-11



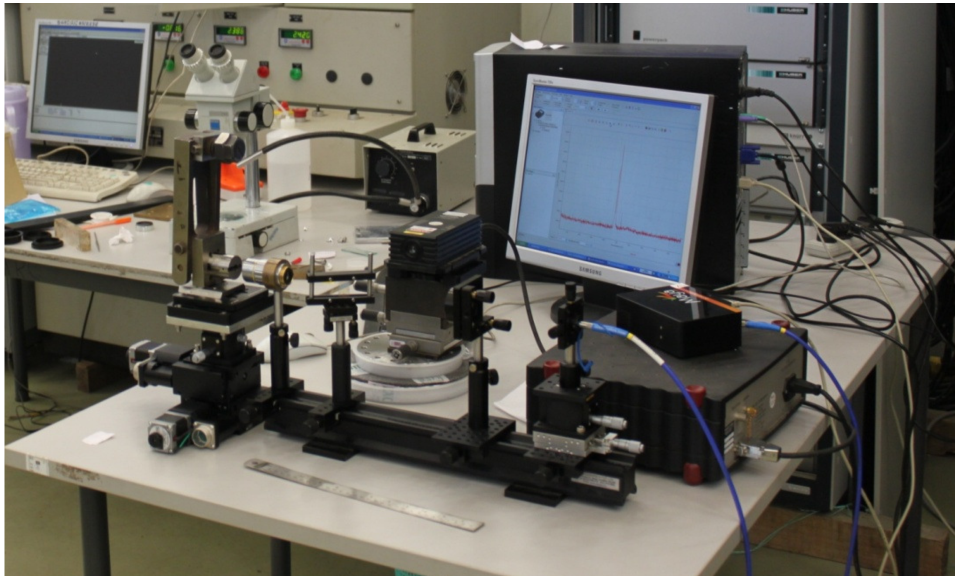


Immediate Experiments

- XRD of powder and single crystal samples for characterization
- Fluorescence studies
- Studies at extreme conditions (high pressure, high temperature)
- Determination of equation of state
- Study of phase diagrams
- Kinetics studies
- Thin film grazing incidence XRD
- Study of disordered systems

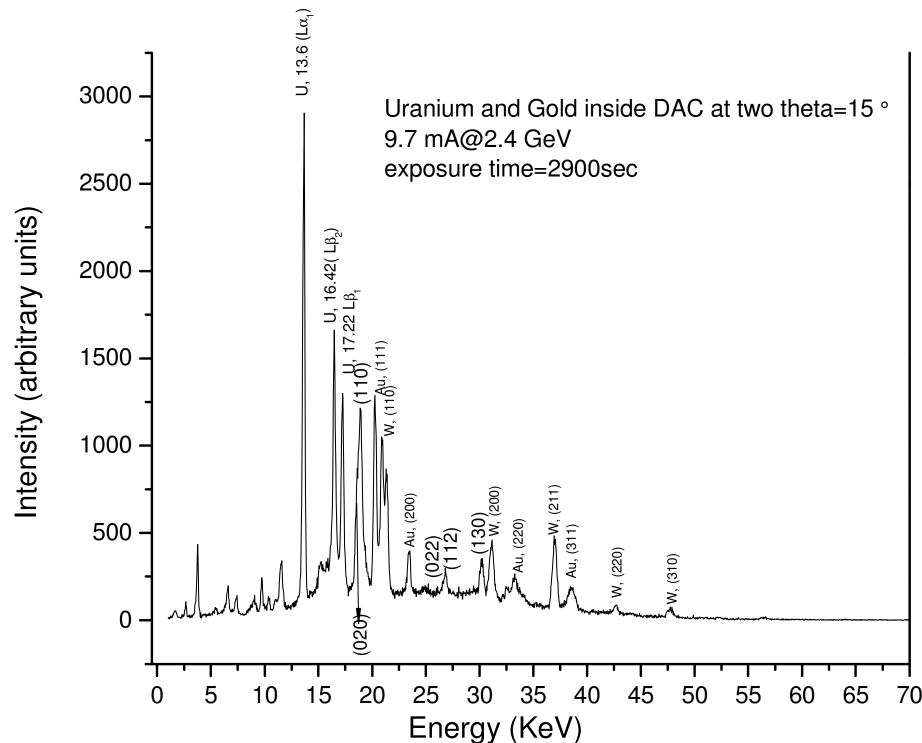
Facilities for high pressure experiments

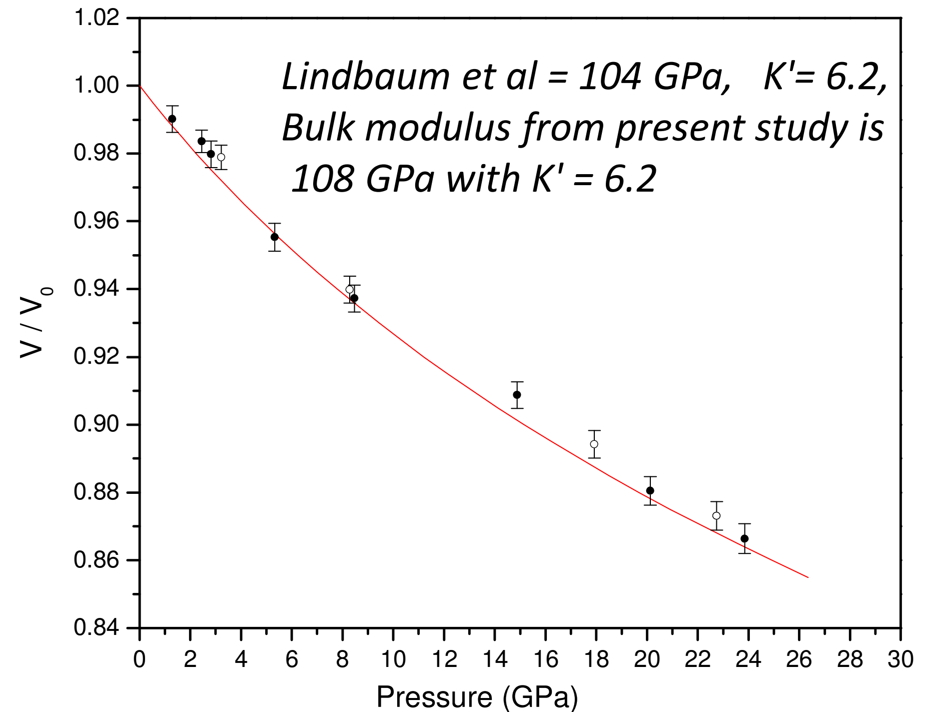
- Off line Ruby fluorescence setup for pressure measurement



- Hole drilling facility for preparing sample chamber

High Pressure studies at BL-11





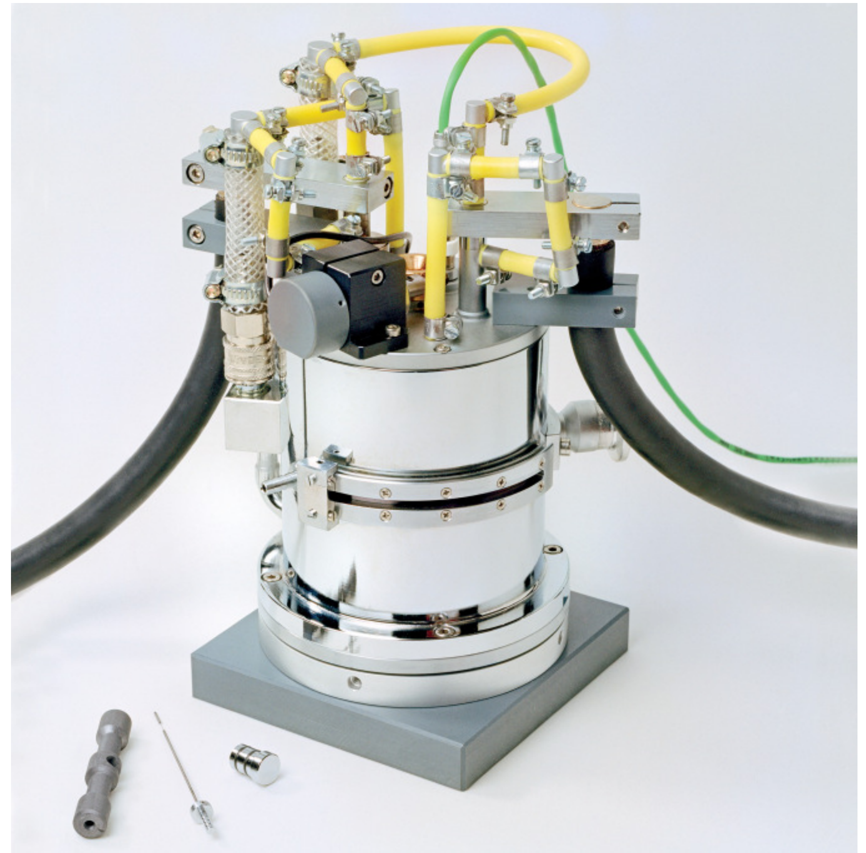
Birch Murnaghan equation of state

$$P = 1.5\mathbf{K}[(V_o/V)^{7/3}-(V_o/V)^{5/3}]\{1-0.75(4-\mathbf{K'})[(V_o/V)^{2/3}-1]\}$$

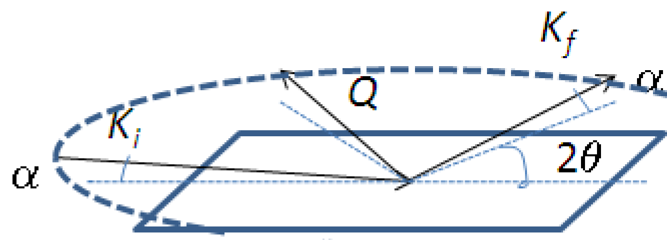
High temperature studies

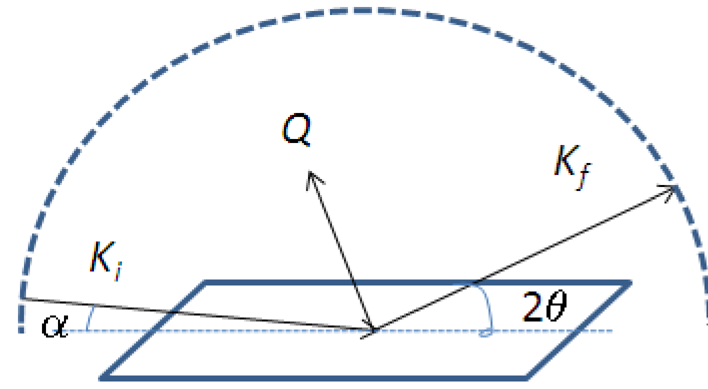
1. EDXRD studies at high temperatures up to 1500°C

Vacuum environment,
Purge with a desired gas
Rotating Capillary



GIXRD





a

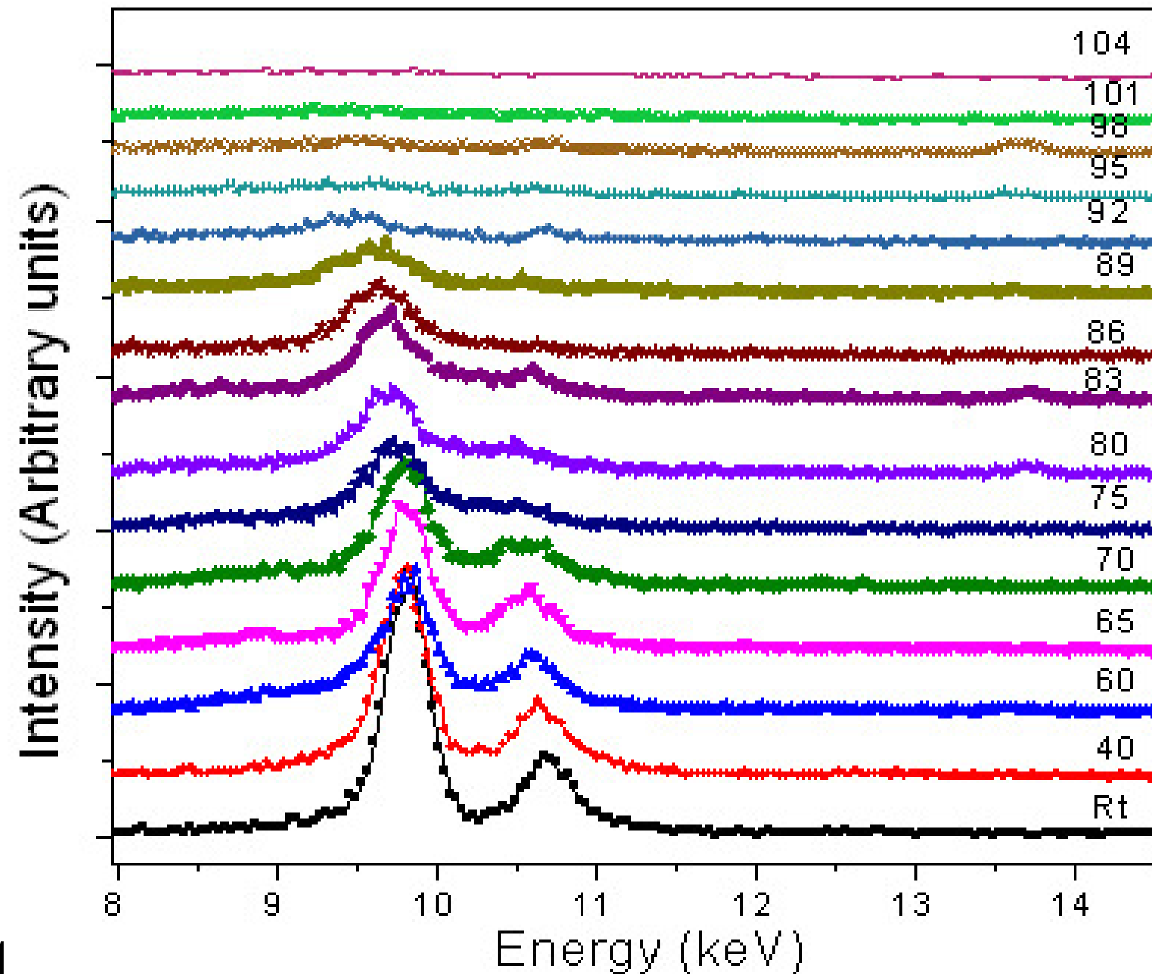
b

In Plane geometry

Out of Plane geometry

GIXRD

In-situ GIXRD measurement on Cd- arachitate LB film at different temperature (Degree Celsius)



K.K. Pandey etal 2011

Reaction Kinetics

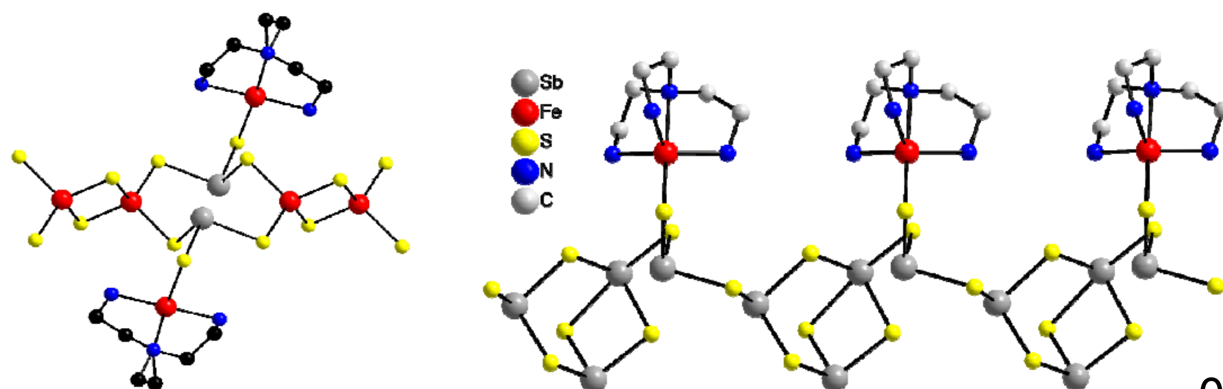


Figure 1: Structures of [Fe(tren)]FeSbS$_4$ (left) and [Fe(tren)]Sb$_4$S$_7$ (right).

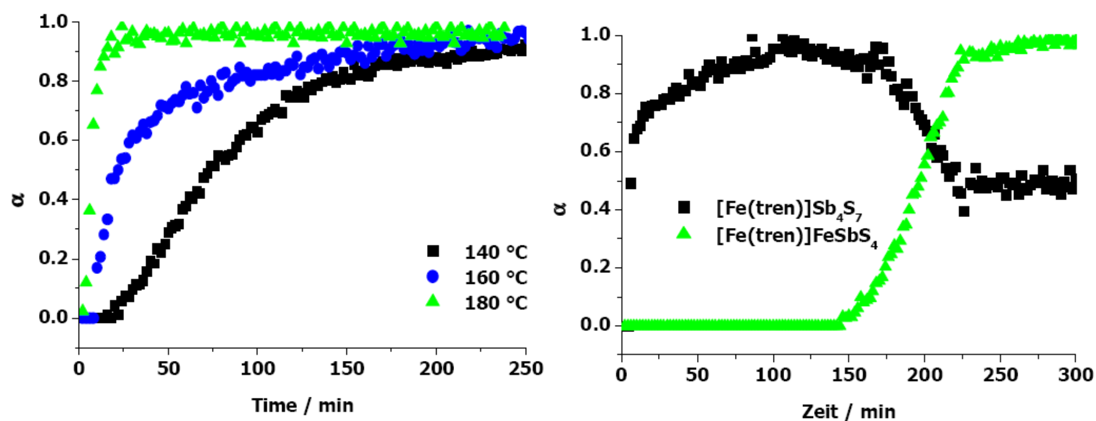
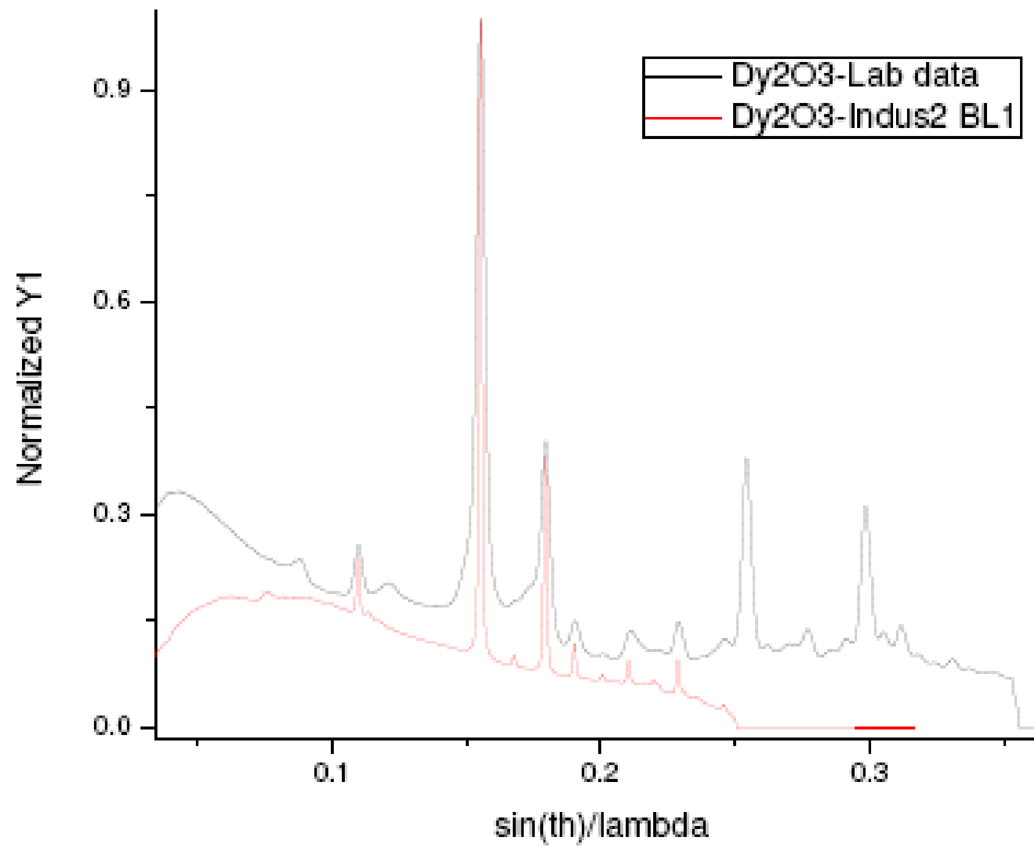


Figure 2: Evolution of the normalized area of the (002) reflection of **I** depending on T (left) and evolution of the normalized areas of the (002) reflections of **I** and **II** (concentration of tren = 80 %, T = 160 °C) (right).

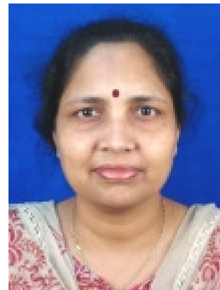
0.3 mmol FeCl3
0.3 mmol Sb
0.9 mmol S
2 ml of 50% - 100% tren
Tris-(2-aminoethyl)amine

B Seidlhofer etal 2011

Angle dispersive using silicon crystal 111 plane ~ 12 KeV



BL-11 Team



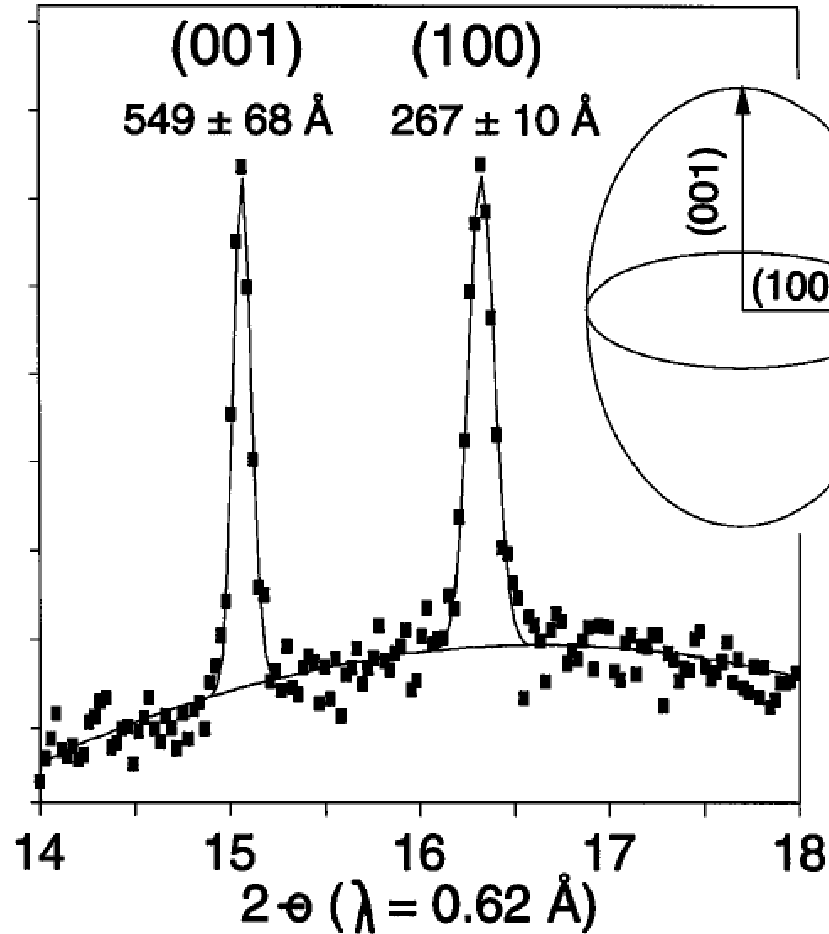
Part 2

- Interpretation of x-ray diffraction data collected at high pressures with different examples
- Silicon, Nano Yttrium chromate, porous silicon, Bis glycinium oxide

Interpretation of data at high pressures

- Shape change of crystallite from x-ray diffraction
- Anomalous change in FWHM of some diffraction peaks – indication of a new phase
- Subtle change in slope of EOS can also indicate a phase transformation
- Rietveld analysis may not necessarily give you the true high pressure phase----- One needs to be careful
- Interpretation of high pressure data using only one technique may not give you the true picture.

FWHM- Crystallite shape change



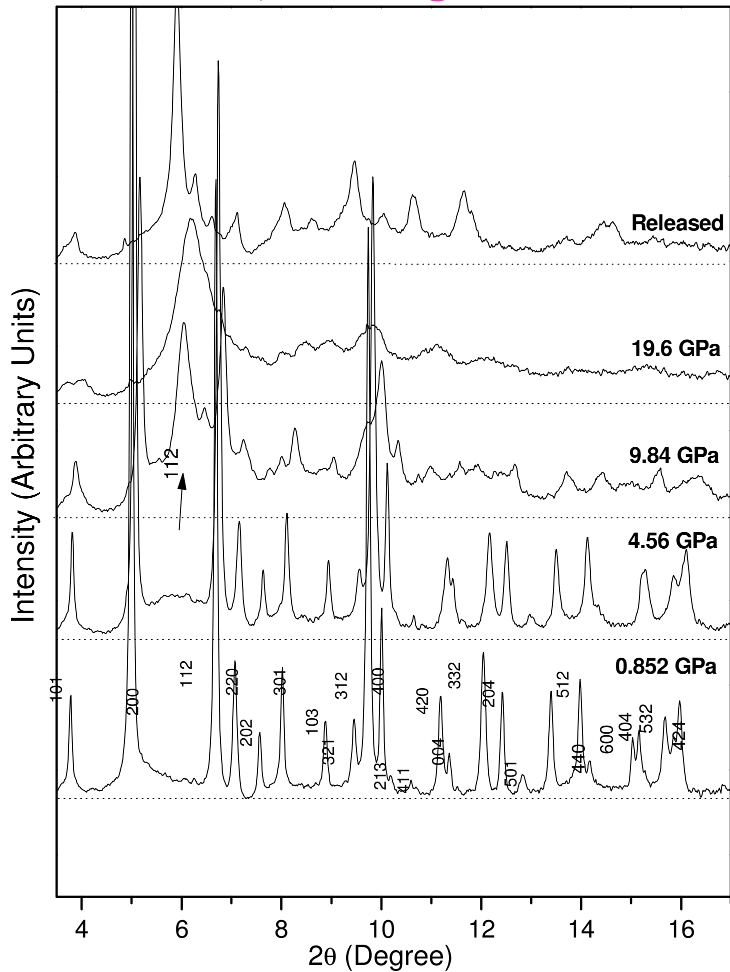
Nano silicon

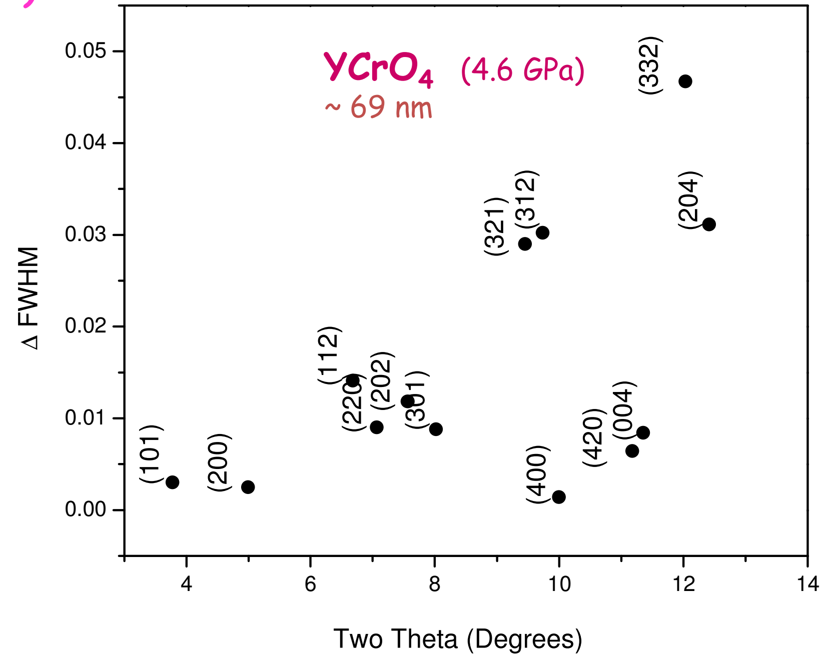
(Tolbert et al, PRL 1996)

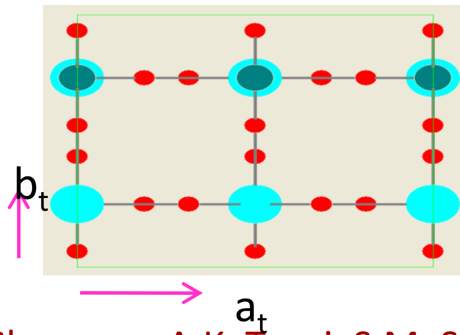
$$B(2\theta) = \frac{0.94\lambda}{(Size)\cos\theta}$$

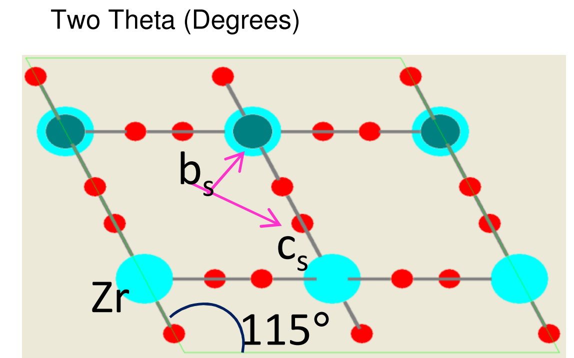
FWHM – Phase transition

(Bulk) $YCrO_4$ Long et al PRB 2007 (3 GPa)





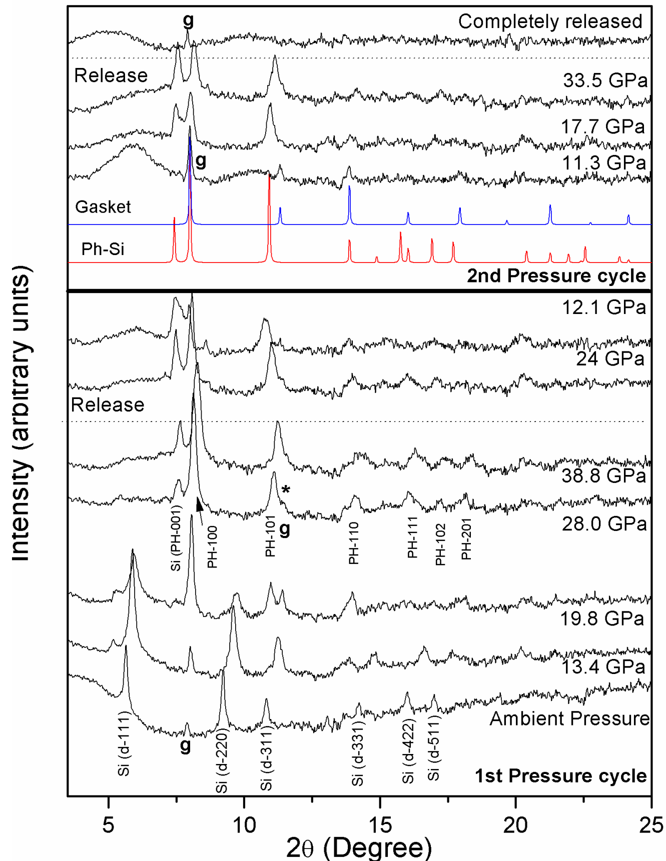


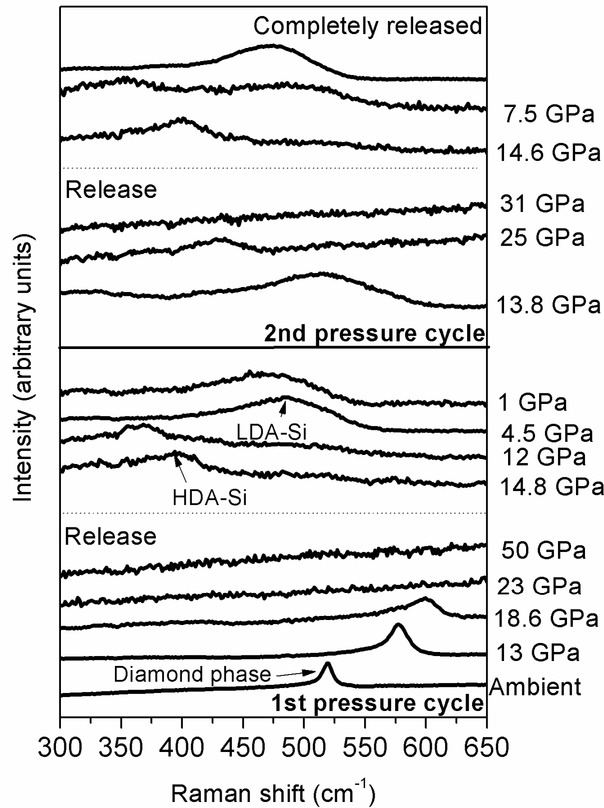


A.K. Mishra, Nandini Garg, K.K. Pandey, K.V. Shanavas, A.K. Tyagi, S.M. Sharma

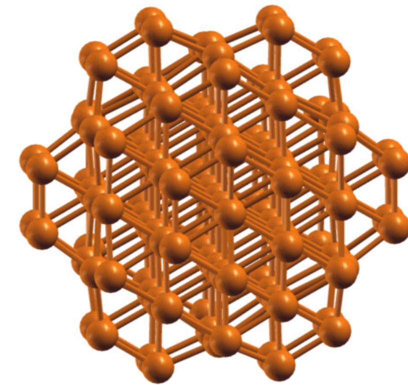
Phys. Rev. B, 81, 104109, 2010

Nano porous silicon

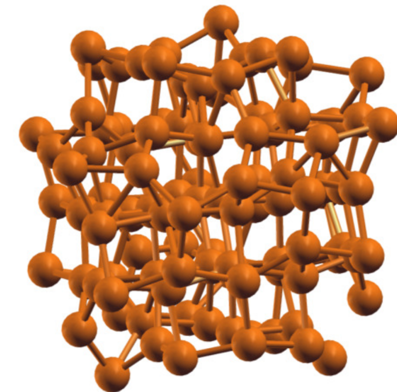




Ph-Si cluster



Beta tin cluster



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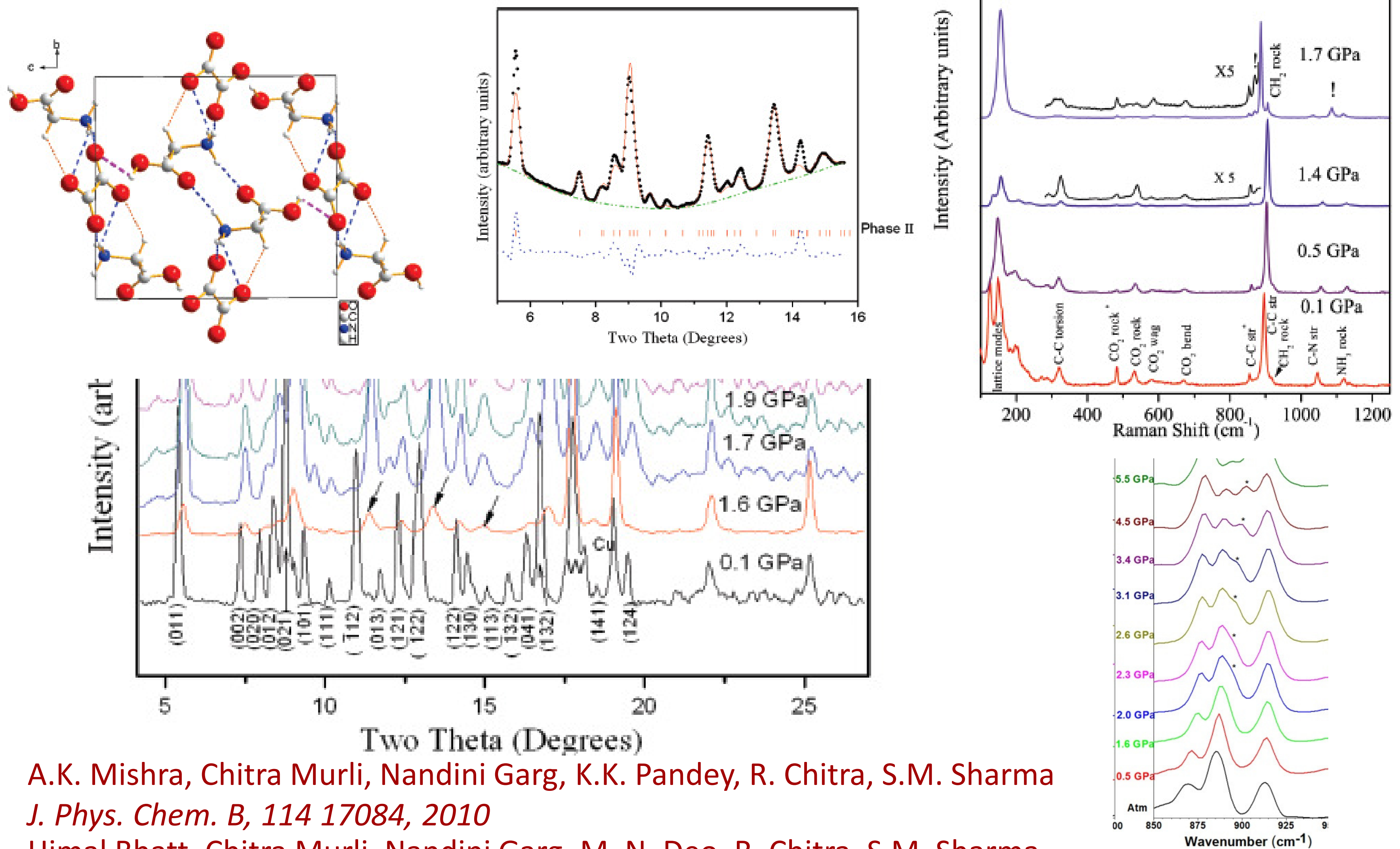
K.K. Pandey, Nandini Garg, K.V. Shanavas, S.M. Sharma, ***J. App. Phys.,109, 113511, 2011***

Bis Glycinium oxalate



A.K. Mishra, Chitra Murli, Nandini Garg, K.K. Pandey, R. Chitra, S.M. Sharma
J. Phys. Chem. B, 114 17084, 2010

Himal Bhatt, Chitra Murli, Nandini Garg, M. N. Deo, R. Chitra, S.M. Sharma submitted

Thanks for your attention