Solid State Chemistry - Materials Science

High Pressures - High Temperatures

In Situ : Synthesis, Structure, Properties

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University College London

Davy-Faraday Lab., Royal Institution

Materials Chemistry Centre

Chemistry-Chemical Engineering

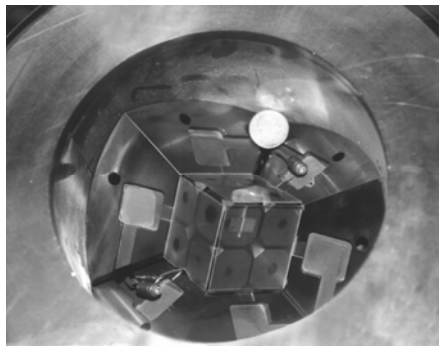
Catalysis ; Magnetics ; Ceramics ; Thin Films, Nanoparticles

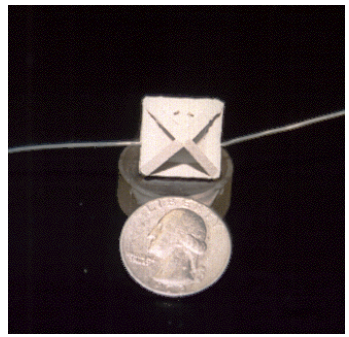
EPRSC Portfolio : RI-Birkbeck-UCL : CRA Catlow, P Barnes, PFM

"Functional Materials" : Laboratory + Synchrotron + Theory

High P-T Solid State Chemistry

Synthesis, In Situ Studies

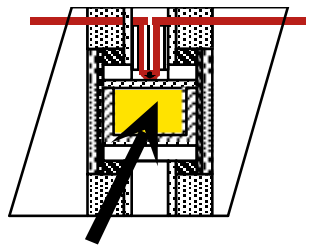


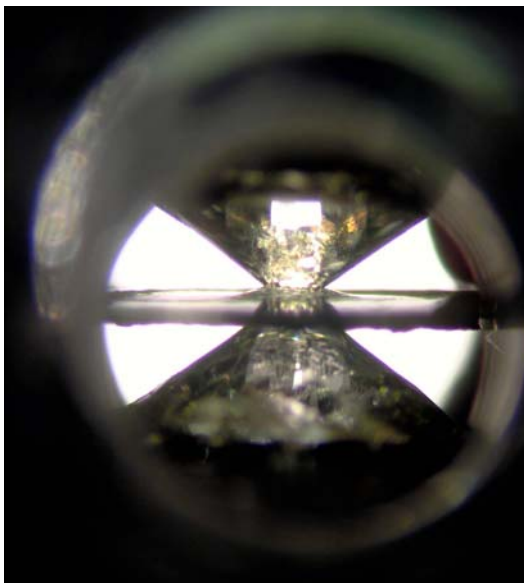


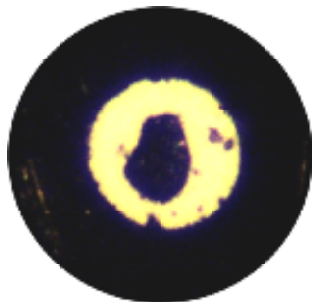
Multi-anvil

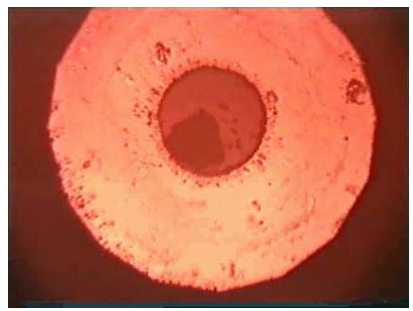
Piston cylinder

Diamond anvil cell ; laser heat







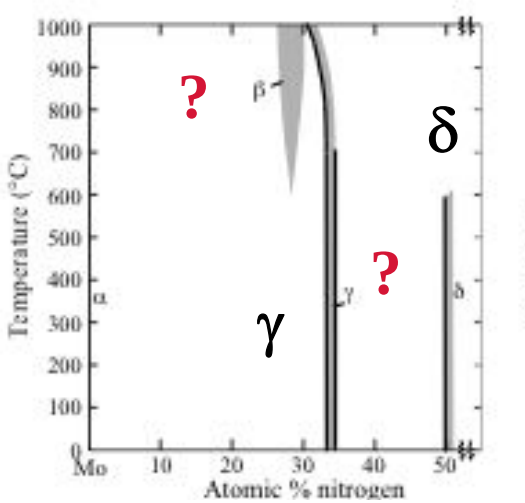


Focusing ; high penetration (to 100 keV)

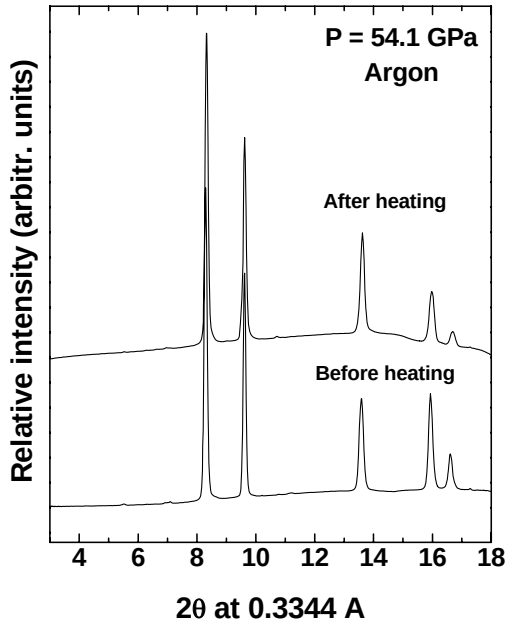
diffraction, imaging, spectroscopy : 3-G

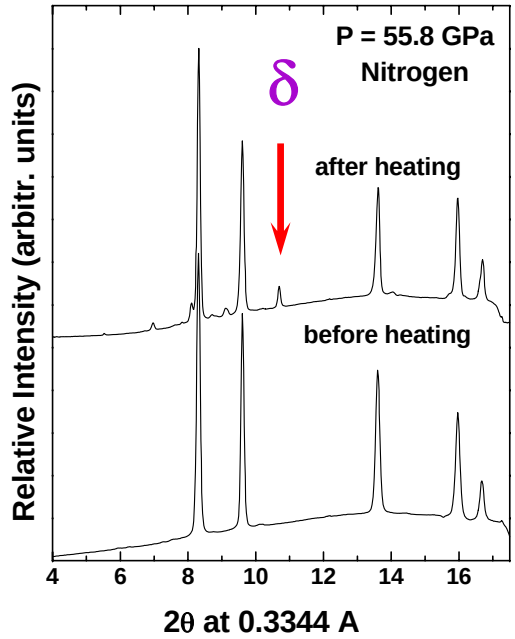
Transition metal nitrides, carbides

High hardness : high T_c : δ MoN-γ Mo_2N : NbN-MoN ?



P = 1 atm phase diagram

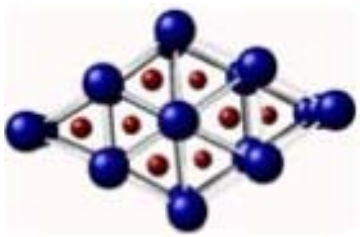


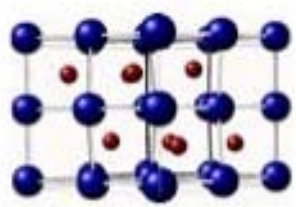


γ-Mo_2N + Ar
No transition

γ-Mo_2N + N_2
growth of δ-MoN

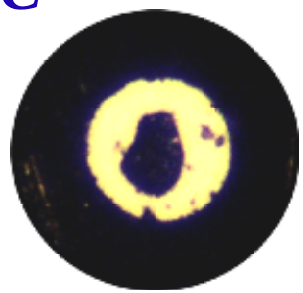
Laser-heated DAC





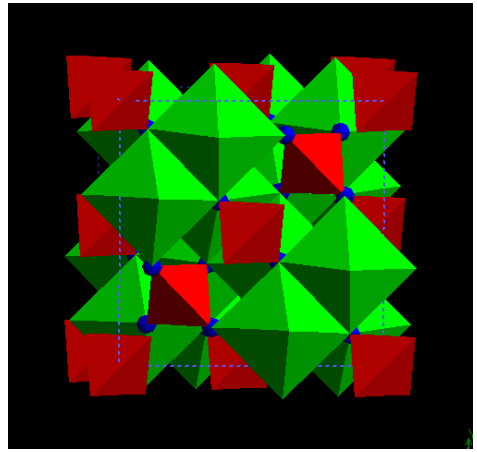
Hexagonal δ-MoN

Cubic γ-MoN_{1-x}



D. Machon phys stat sol (b) 2006

Nitride Spinels P ~10-12 GPa ; T ~1200-1500°C



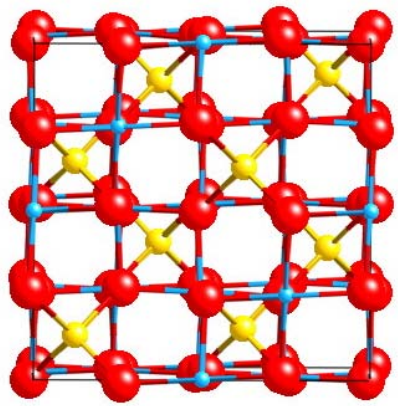
γ-Ge_3N_4, γ-Si_3N_4, Sn_3N_4

Zerr *et al Nature* **1999,** *400*, 340
Leinenweber *et al Chem. Eur. J.* **1999,** *5*, 3076

Incompressible : high-hardness
high-T stability (in N_2, air ?)

K_o = 290 GPa
H_V : 30-43 GPa

α-Al_2O_3 : H_V = 32 GPa
α-, β-Si_3N_4 : H_V = 20 GPa



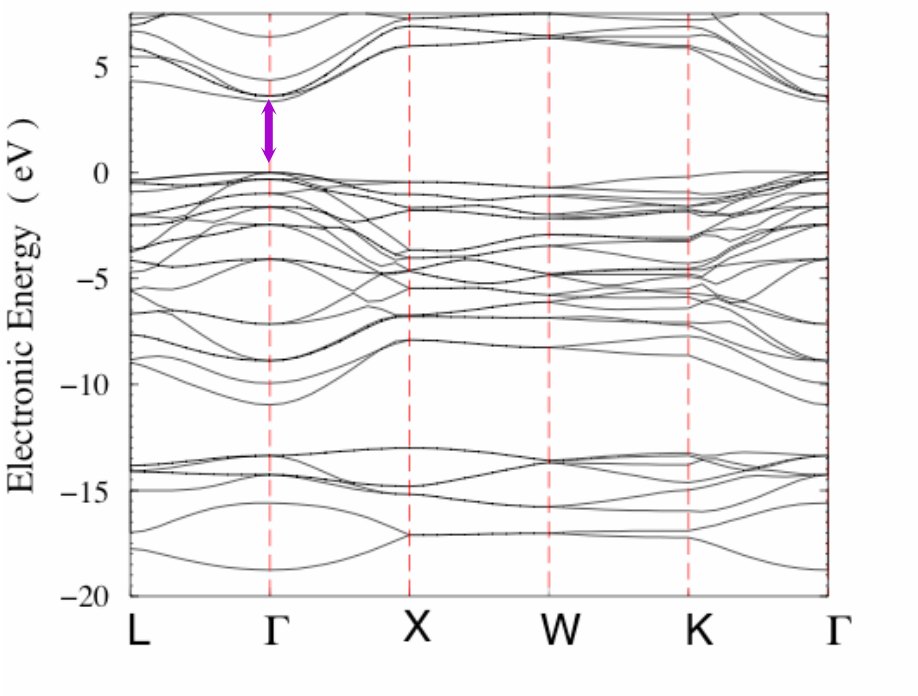
Synchrotron : Synthesis, K_o

Wide direct-gap : 2-4 eV ?

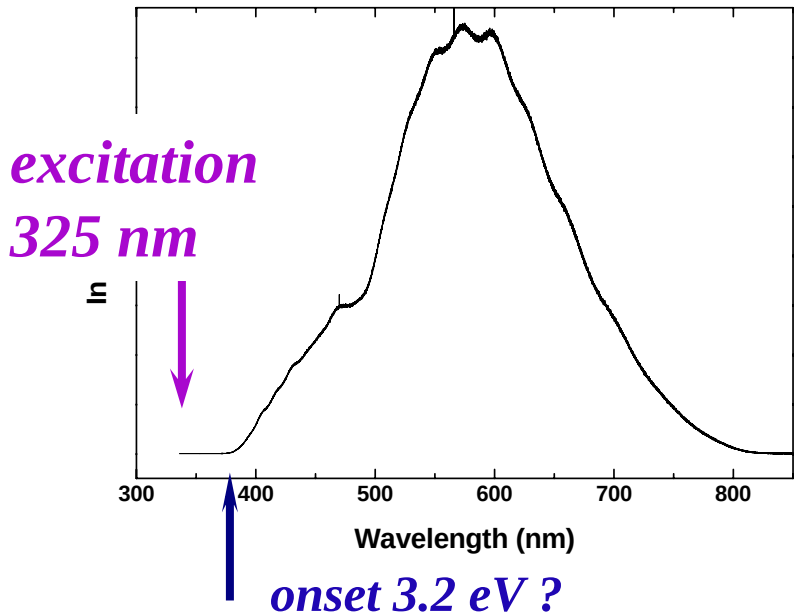
Soignard *et al J. Phys. C* **2001,** *13*, 555
Zerr *et al J Am Ceram Soc* **2002,** *85*, 86

***Shock wave** : large-scale powder synthesis :*
Sekine et al Appl. Phys. Lett. ***2000****, 76, 3706*

Mo, Ching et al, PRL ***1999***
J. Dong et al, PRB ***2000, 2004***
Leitch et al J Phys Cond Mat 2004
XAS, XES : ALS



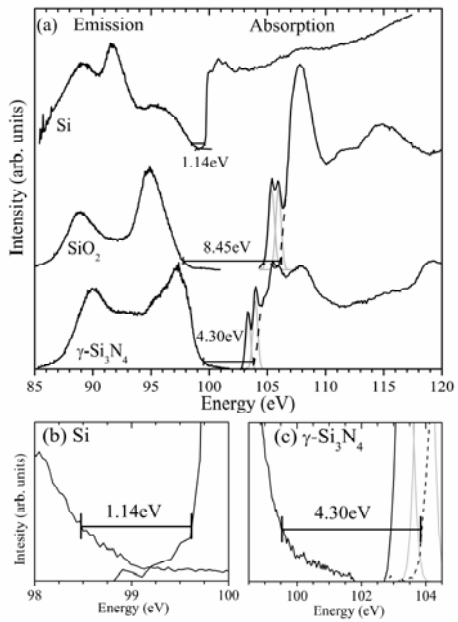
laboratory PL ; CL



γ-Ge_3N_4; γ-Si_3N_4

Defects (N^{3-} vacancies ?) : Raman :

XRD : ***Chem. Mat. 16 (2004) 3533***



ALS : ***synchrotron X-ray absorption, XES***

Alex Moewes : Leitch et al J Phys Cond Mat (2004)

γ-Si_3N_4 : E_g = 4.3 eV

probe excited electronic states

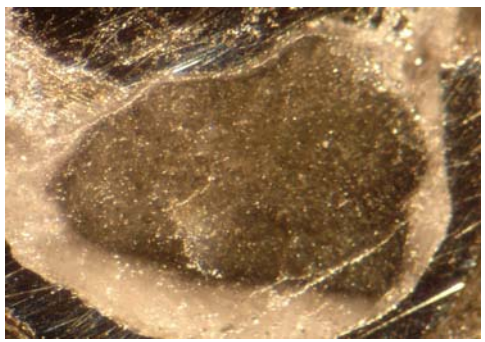
Ga-O-N spinels : Ga_3O_3N (cf : γ- , δ-Al_2O_3 ; AlO_xN_y)

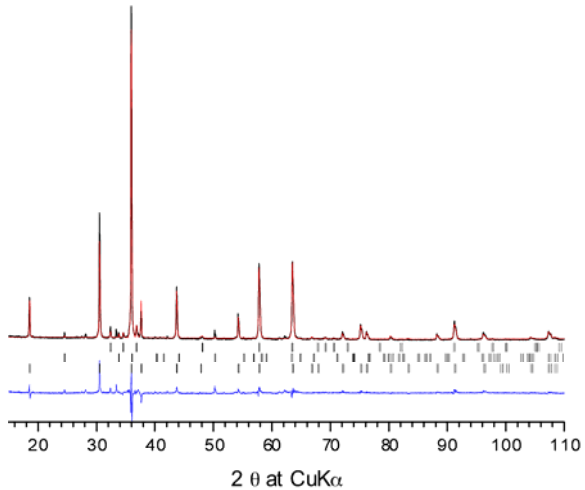
Chemical precursors + high-P,T synthesis : I. Kinski et al. :
$Ga_{2.81}O_{3.57}N_{0.43}$ *Z Naturforsch. (2005)*

GaN/Ga_2O_3 mixtures : E Soignard et al Chem Mat 17 (2005) 5465

$GaN + Ga_2O_3 = Ga_{2.8}O_{3.24}N_{0.64}$

Ga^{3+} vacancies - octahedral sites





DAC + Multi-anvil syntheses : P ~ 5 GPa ; 1200-1700°C

Wide-gap : luminescent; catalysis

GaN ; Ga_2O_3 phase transitions : D. Machon et al PRB 2006

Ti_3N_4?

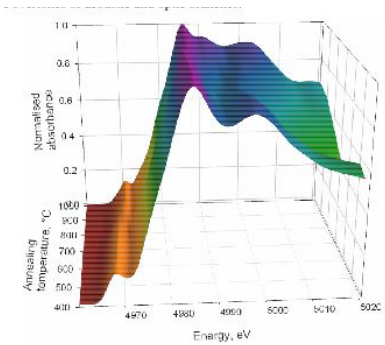
- *Predicted stable : spinel structure :* ***Ching et al PRB (2000)***
- **But : Ti + N_2 ; highly refractory, high density ; usually non-stoichiometric TiN_x**
- **However : X-ray amorphous "Ti_3N_4" : from precursors :** ***Baxter et al (1996)***

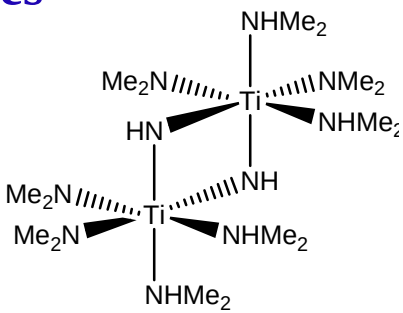
A. Hector, A. Jackson (Southampton) : O. Shebanova (UCL/RI) : characterise "amorphous" products : high-P,T treatment of precursors : JSSC 2006

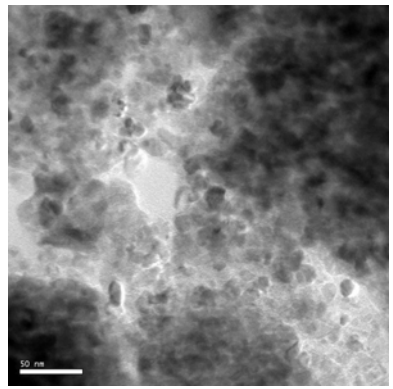
- **High T annealing :** ***microcrystalline TiN in "amorphous" matrix***
- **Low T (<450°C) : $TiC_{0.22}N_{1.01}H_{0.07}$: ~ $Ti_3(N,C)_4$**
- ***Amorphous matrix + nc-TiN (superhard nanocomposites ?)***
- **XAS/EXAFS - amorphous matrix : octahedral Ti :**

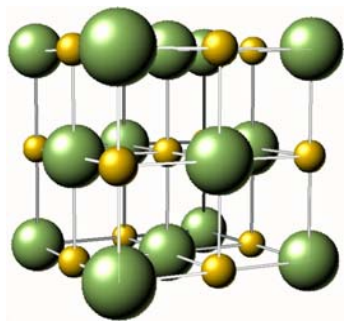
50-60% vacancies on cation and anion sites

"ladder" structures

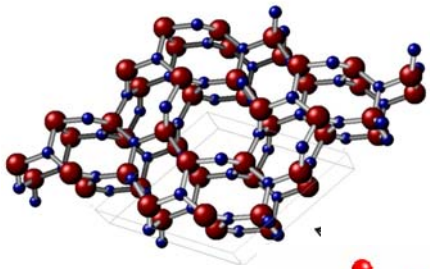






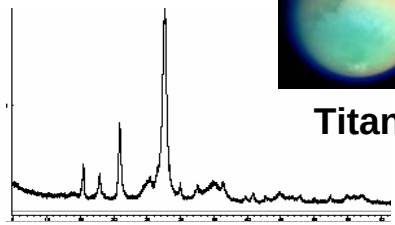


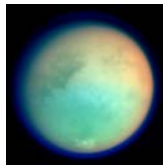
Light-element solids : C-O-N chemistry at high P,T



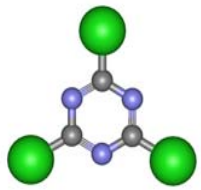
β-C_3N : *superhard ?*

M. Cohen, PRB 1985





Titan



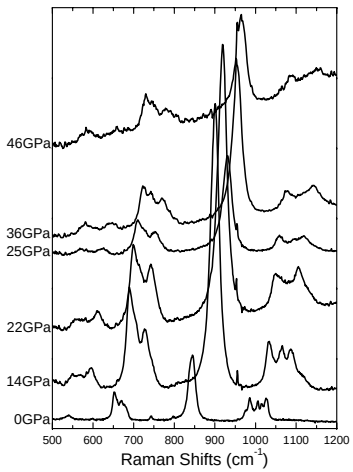
$C_3N_3Cl_3$ **$C_3N_6H_6$**

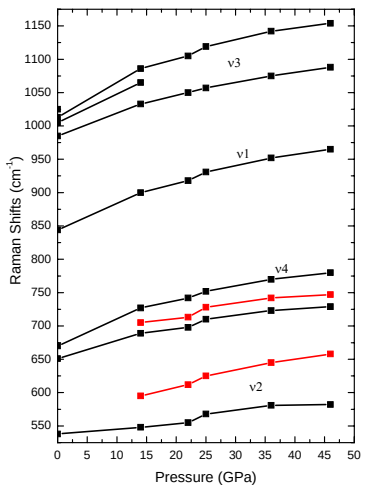
JACS

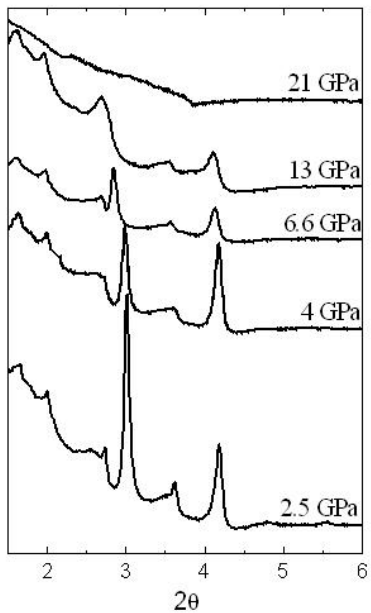
<u>123</u> (2001) 7788

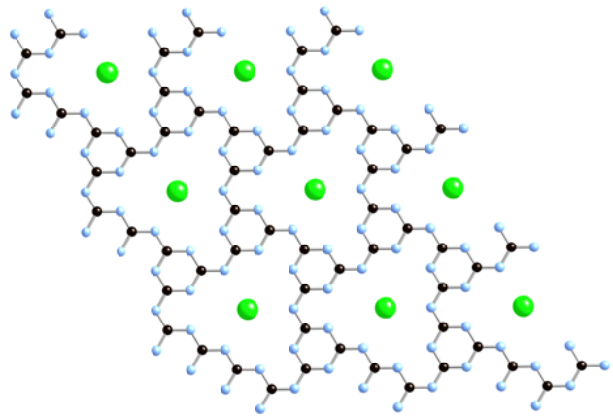
CO_2-V : C-S Yoo, V Iota (1999)

Na_3NO_4



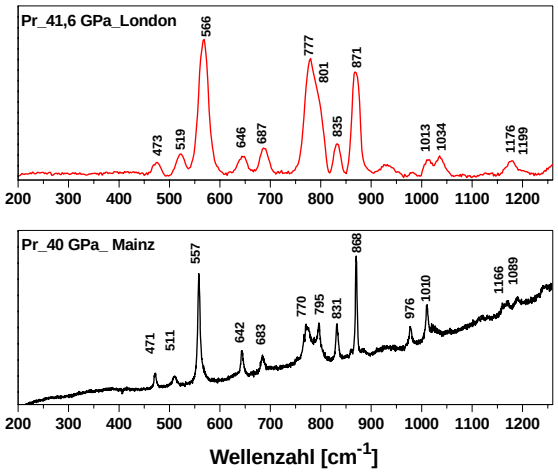


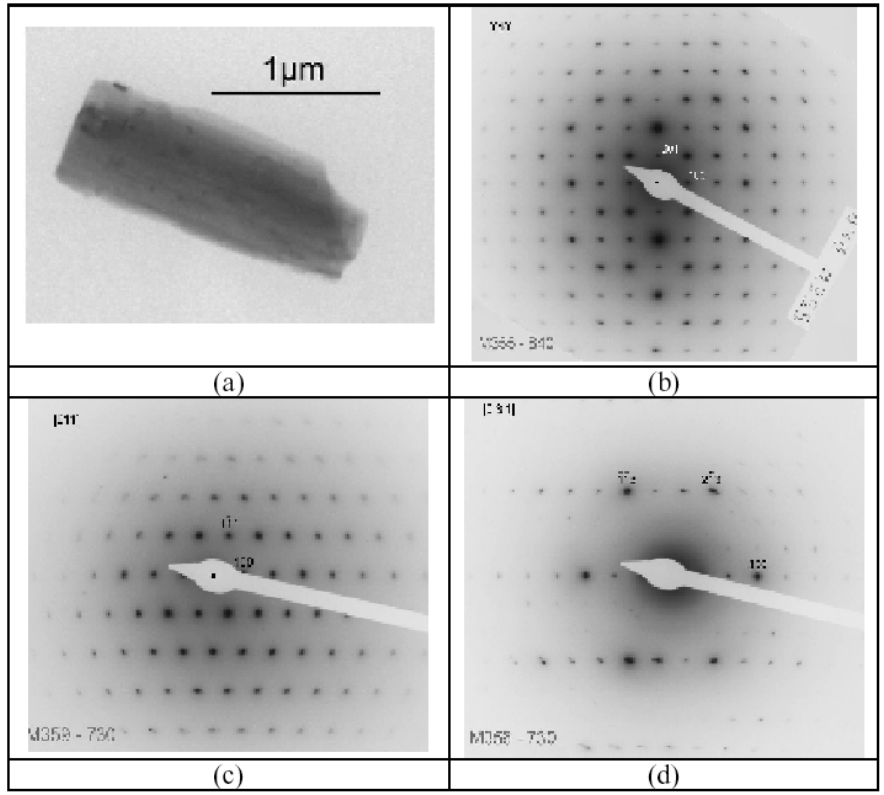


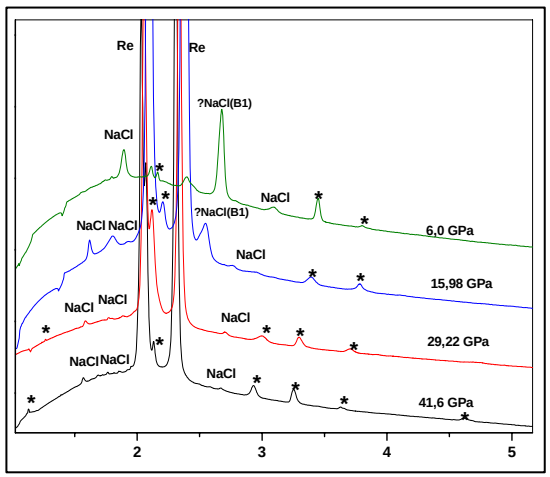


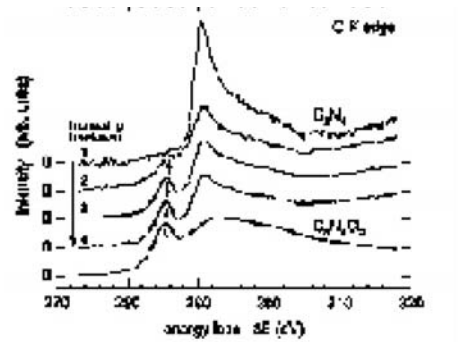
Pressure-induced amorphisation

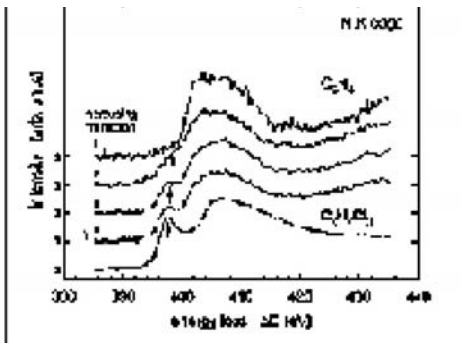
$H_4C_2N_2$ at 40 GPa : laser heat











E. Horvath-Bordon, R. Riedel, A. Zerr, O. Shebanova, D. Machon, G. Miehe, P. v. Achen, P. Kroll, E. Lowther : Darmstadt-London

Diamond anvil : *megabar, high-T : laser heat*

- **tight focus / collimation to 1-5 μm**
  (heat load on optics : focusing : <u>access</u>)
- **mono ADXRD *(+ white beam ED : imaging)***
  multi-wavelength : scattering, spectroscopy
- **high flux *(low-Z materials) : 3-G +***

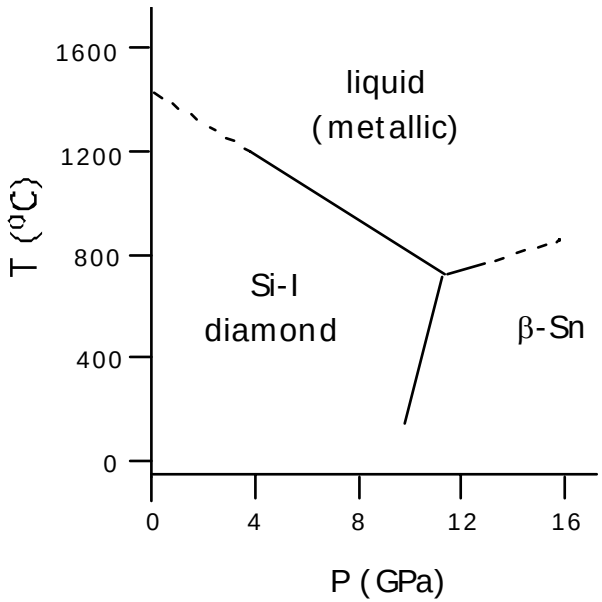
Multi-anvil (*toroidal)* cells - *large volume*

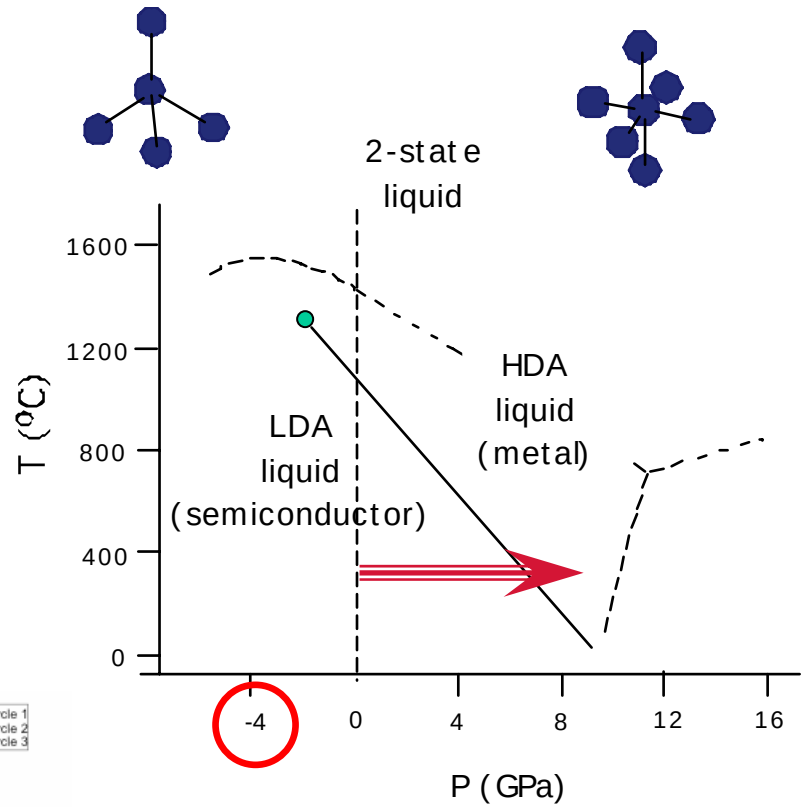
- **highly penetrating X-rays : capsule assemblies ;**
  high-Z samples : >80-100 keV
- **white beam *(ED; transmission/fluorescence imaging)* ;**
  monochromatic ADXRD
- **high intensity : rapid data collection : *reaction***
  ***kinetics*, mapping inside reaction chambers**

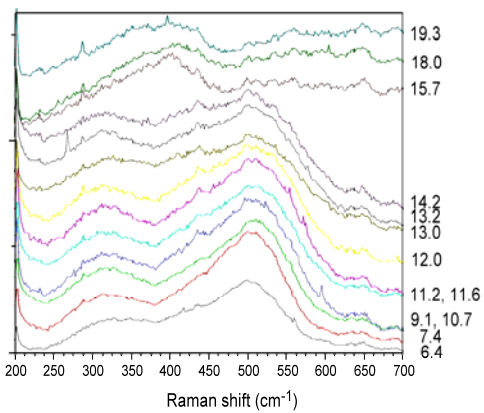
Liquids, Glasses, Amorphous Solids at High-P,T :

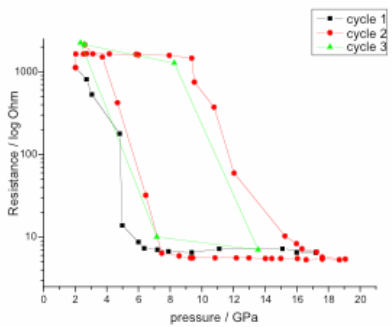
"Polyamorphism" : Liquid-Liquid Phase Transitions

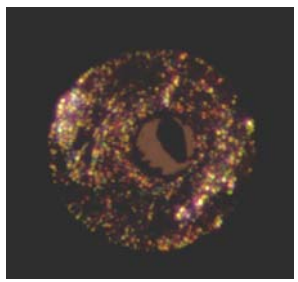
Amorphous Si : PIA : semiconductor LDA - metallic HDA

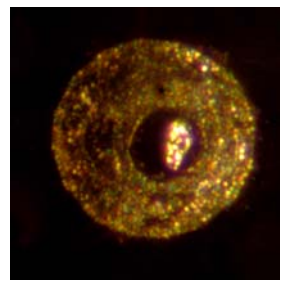


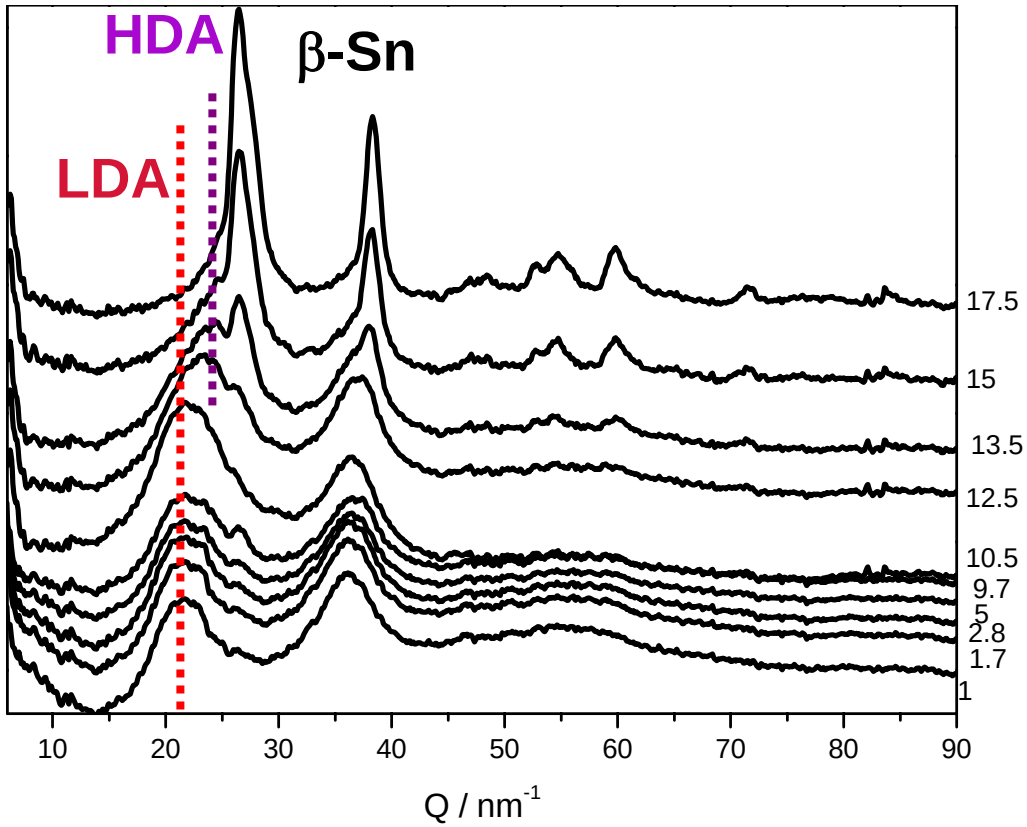


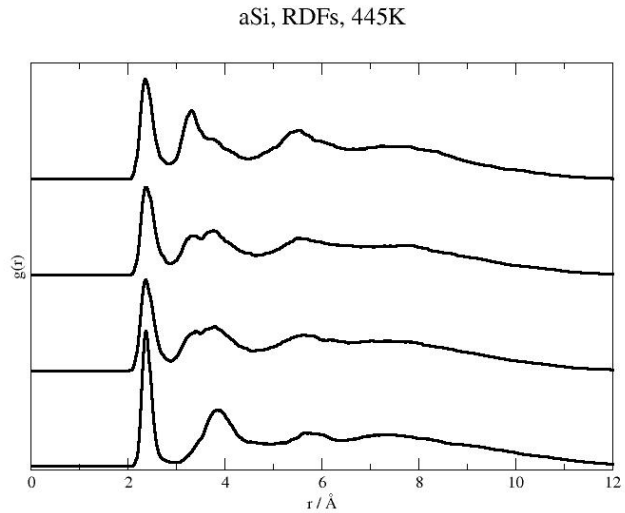


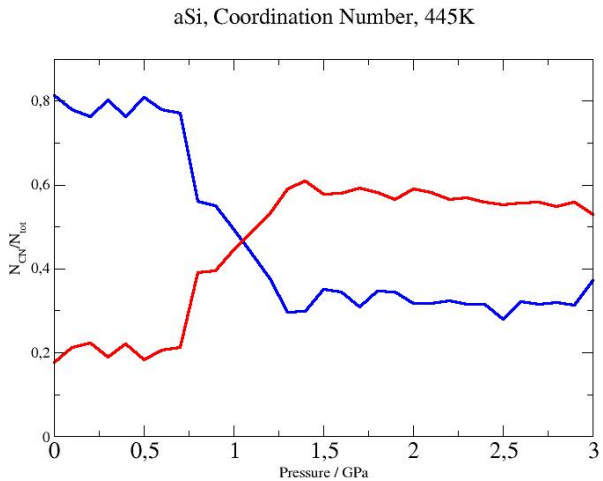












S(Q) : ESRF ID-15A (Dec 2005)

D. Daisenberger, D. Machon, M. Wilson, PFM

MD : Stillinger-Weber

Amorphous/liquid state studies: high-Q : high flux : time domain ?

In Situ Studies of Functional Materials

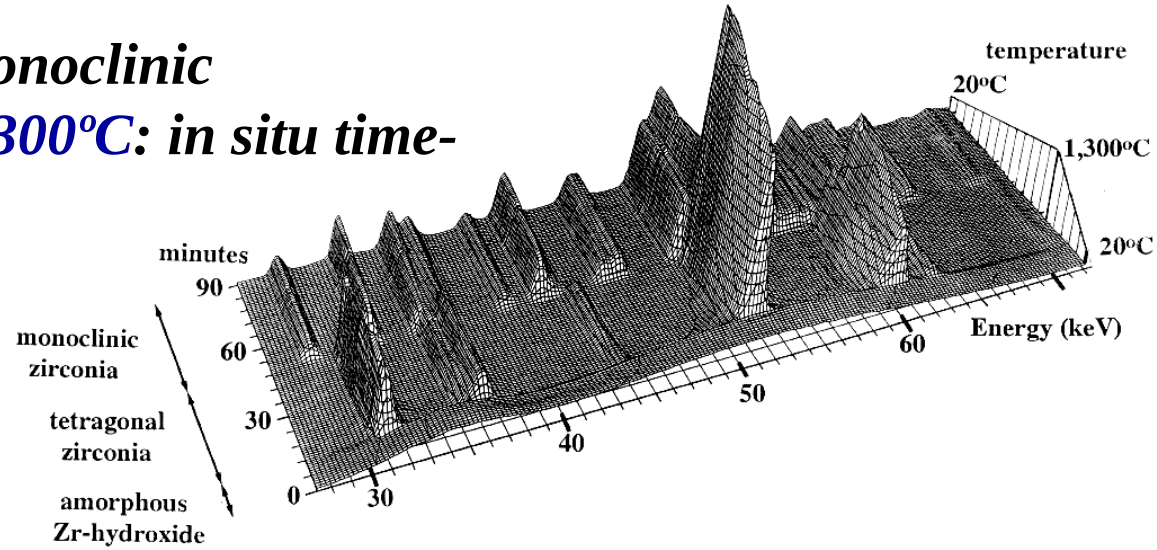
EPSRC Portfolio P
Barnes, PFM,
CRA Catlow

Catalysts ; Ceramics : Synthesis : In Situ Studies

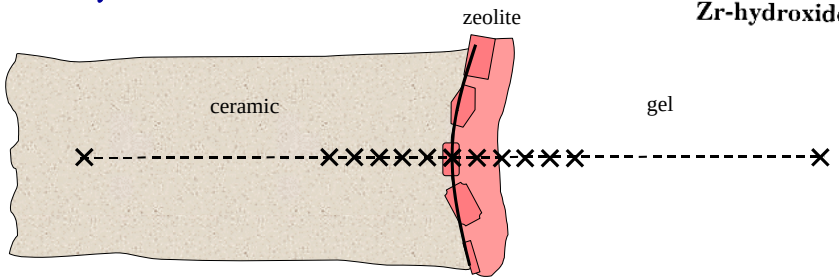
P. Barnes, S. Jacques, O. Leynaud, P. Hutchins, R. Cernik, M. Vickers, M. Sheehey

- ***highly penetrating beam : furnace/autoclave; high-Z samples***
- ***white beam - energy dispersive - TEDDI***
- ***time-resolved - 3-D imaging : reactor profiles :***
  diffraction, spectroscopy, transmission imaging

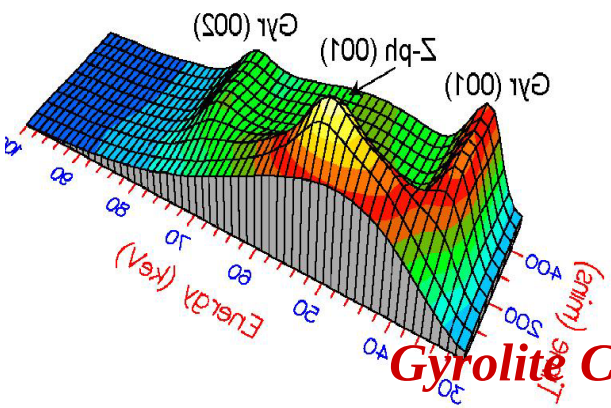
Amorphous-Tetragonal-Monoclinic crystallisation in ZrO_2 to 1300°C: in situ time-resolved ED-XRD



Growth of zeolite A 10 μm membrane



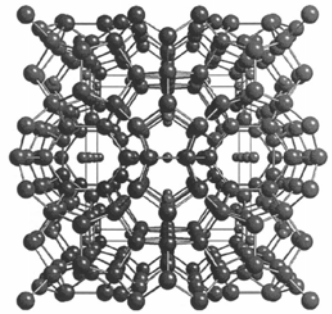
catalysis; hydrothermal processing; environmental geochemistry

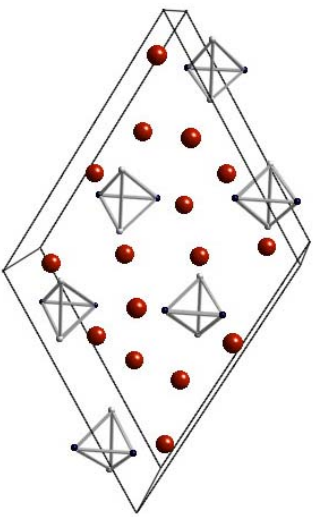


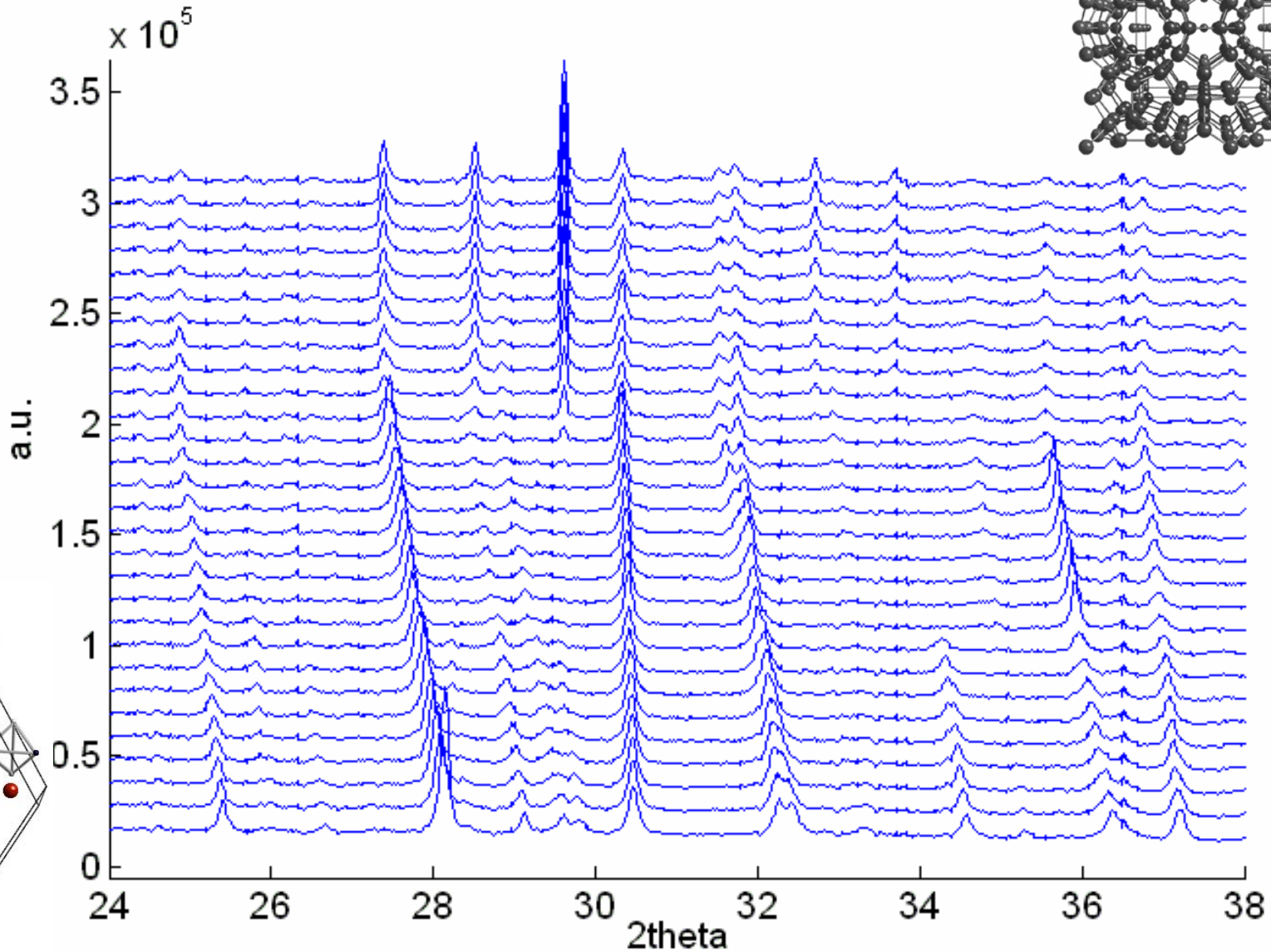
pilot station : ESRF

Gyrolite $Ca_{16}Si_{24}O_{60}(OH)_8.14H_2O$
cement mineral : radwaste

NaSi --> Na_8Si_{46} : high T (ramp); high vac







RAPID2 detector: SRS 6.2

P Hutchins, O Leynaud, P Barnes, PFM et al

Studies at CHESS/ERL :

- ***In situ*** **high-P,T chemistry : DACs :** ***tight*** **focus**
- **High flux : low-Z materials : *time-resolved reaction chemistry ? ; amorphous diffraction***
- **Use X-ray beam to initiate reactions ? (*SHS* : *one pulse to initiate, one pulse to study: shock studies ?*)**
- ***Investigate excited states of solids ?***
- **Large volume cells (multi-anvil, toroidal) : high penetration (<80-100 keV : sample assemblies; high-Z materials) : autoclaves, reaction chambers, catalytic reactors ..... *XRD, imaging, tomography***
- **Time resolution *(detectors)* : map reaction profiles (kinetics), mixing inside reactors**