Non-ambient Diffraction in the Laboratory Environment

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Overview

• Why work in the lab when synchrotron data is better?
  • ‘A bird in the hand….’ (i.e. access!)

• Commercial stages
  • Some example developments
  • Sample displacement – the old irritant…

• DIY setups
  • Considerations and ‘mind-set’
  • Low temperature capillary – high speed data with mirror optics & PSD
  • High gas pressure – a special case and big headache?
  • Iron ore sintering - high speed data collection using curved PSD
Commercial vendors…

- Some developments…
  - Tensile test stage
  - Dome stages for 2D detectors
  - Extremely-low temperature
  - Close-cycle coolers → cryogen-free cold stream
  - Combined XRD-DSC (Rigaku)

Anton-Paar TS 600

Oxford Cryosystems Phenix

mri BTS-BASIC

Cryo Industries close cycle cooler
Sample displacement – different approaches

- Z-stepper motor on HTK1200 oven

Triclinic-hexagonal phase transition of $\text{Ca}_{10}(\text{AsO}_4)_6\text{F}_2$ apatite in HTK1200 equipped with z-stepper motor

- Has to be properly calibrated

Parallel-beam geometry

- No sample displacement peak shifts

Can have confidence that these shifts are real...

\( \alpha \rightarrow \beta \)-quartz transition

shift in \( \alpha \)-quartz lattice expansion only

\( \text{Al}_2\text{O}_3 \) 104 reflection with displacement (twin mirrors)
Parallel-beam: the down-side

- Lower peak resolution
- Choice of Soller slits a factor….

Comparison of the main quartz reflection from different optics
No-one sells what you want? now the fun starts…

• Mind set – it’s a complete system, not just a stage

• Some engineering restrictions
  • Size
  • Stage weight (vertical goniometers)
  • Access to pass-throughs
  • $\theta-\theta$ (don’t foul arms!)
  • Door closure

Example where engineering restrictions complicate things:

Bulk (clearance+heat)
Heavy – 10kg
High pressure line pass-through transducer, thermocouples & heaters
Low temperature capillary work

• System specced and built specifically for rapid low T non-ambient phase studies with large capillaries
  (before Oxford Cryo Compact was available!)

• Laminar flow along capillary axis minimizes LN2 usage without icing (goniometer heat shield needed)

• Vertical goniometer
  • Limited space for nozzle

• Long transfer line not good (if you can get it inside)
  • Put dewar inside the cabinet?
Look familiar?

Figure 1. Experimental Diagram

Figure 2. Experimental Mess
NH$_4$NO$_3$ phase transitions

- Focussing mirror optics, cryoflow with linear PSD
- Snapshots, 8° window, 2 second datasets every 2°C
- Continuous temperature ramp (0.1°C/s)

Proof of concept. Phase transitions of NH$_4$NO$_3$
Something more practical….

- Ability to automate complex ramp-soak programs
- 4 minute datasets - shorter than ramp/dwell times
- 48 datasets in ~7 hours

Phase behaviour of the Li-battery electrolyte solvent dimethyl carbonate
Beyond CuK$_\alpha$ ...

- Engineering for high pressures often dictates use of higher energies for optimal usage..

- 1$^{\text{st}}$ mainstream company to venture down this route.....?

- Anton-Paar HPC-900
  - 100 bar pressure for H$_2$, etc
  - Requires MoK$_\alpha$
    - Not a simple add-on
DIY under pressure?

• Home-designed and built pressure vessels?
• Space for sample stage and ancillary stuff limited
• The elephant in the cupboard
  • The pressure codes (ASME in North America) 😞
  • Restricts the materials you can use
  • What conditions you can use them under (max stress, temp)
  • Design concepts and validation
  • QC and manufacture

Just one of the ASME pressure codes…
DIY thought process... 300bar, 300°C

- 3 years from concept to delivery
- No modifications – have to think of everything 1st time!

Cover retention. Strong enough but removable using 12 tapered pins

Holes for tapered pins

Heavy-duty! Strong enough at temp with ASME allowables + a bit

Corrosion-resistant C22 Ni superalloy. Adjustable Ta knife-edge

Fittings also need to be corrosion-resistant
300bar NRC pressure vessel

- Window is the weak-spot
  - Swagelok-type seal (regulator comfort!)
  - Be window material for transmission
  - Be corrosion protection?
  - Strength? (structural grade SR200)
- Windows 6¼ mm thick Be
  - 2μm Ta coating
- Interior flooded with water/steam
- Interior beampath ca. 15 mm
- Penetration is key…..
The exception rather than the rule…

- In this case AgK\(\alpha\) (22 keV) needed for increased transmission
- Has consequences….
  - Getting hold of a tube
  - 1.5kW versus 3kW (LFF)
  - Require new PSD optimized for higher energies
  - Pd \(\beta\)-filter effects even worse
- Difference between no signal and some signal
  - Increase in accuracy = \(\infty\) 😊

Calculated transmission through the GEN1 pressure stage at different energies
Can you actually see anything?

- Worst case - fully flooded with cold water
- Total beampath
  - 12.5mm Be, 8µm Ta, 15mm water

View through dummy windows

SRM1976 plate
20 minute scan
AgKα
500µm Lynxeye (no monochromator/mirror – budget cut!)
Anything else easy in comparison...

- Autoclave conditions \(~190^\circ C\)
- \(161\text{psi steam} + 100\text{psi CO}_2\)
Iron Ore Sintering - *In Situ* X-ray Diffraction

Industrial sinter machine

Heating Regime 25-1350-25°C
pO₂ = 5 x 10⁻³ atm

High-temperature chamber
Detector
X-rays
Gas inlet

Australian Synchrotron
Introduction – Industrial Context

- Iron ore sintering = important stage of the steelmaking process
- SFCA is the ‘glue’ phase for sinter

**SFCA and SFCA-I bonding matrix**

- **Iron ore fines**
  - < 6.3 mm Fe₂O₃, FeOOH

- **CaCO₃ flux**
- **~1300°C**

- **SFCA** = Silico-Ferrite of Calcium and Aluminium
  - SFCA = $M_{14}O_{20}$, SFCA-I = $M_{20}O_{28}$, $M$ = Fe, Ca, Si, Al

Results – Heating, 25-1350°C

Fe$_3$O$_4$ + melt

SFCA
SFCA-I

CaFe$_2$O$_4$

Ca$_2$Fe$_{2-x}$Al$_x$O$_5$

*New phase

Iron Ore Sinter Studies
Laboratory Based *in situ* Data Collection

- Beamtime hard to get
  - Waiting time ~ 6 months
- Once phases known from synchrotron experiments – use lab instrumentation
- INEL CPS120
  - Incident beam, multilayer mirror for high intensity
- CoK$_\alpha$

![Image of lab diffractometer setup]

- High temperature chamber to 1500°C
- X-ray optics
- Gas inlet
- Gas outlet
- Detector
- Strip heater
- Lab diffractometer setup
Iron Ore Sinter Studies

Laboratory Based *in situ* Data Collection

- Heating rate
  - 20°C min⁻¹, 25 → 600°C
  - 10°C min⁻¹, 600 → 1350°C

- Data collection time
  - 30 sec for 120° 2θ

- Resolution not as good as synchrotron but most information still visible

- Problem
  - Industry not so interested if conditions not close to real processing conditions
Actual Industrial Heating Rates? Attempt to Emulate in Laboratory

- Heating rate
  - 200°C min⁻¹, 25 → 1350°C

- Data collection time
  - 6 sec for 120° 2θ

- Major and some minor phases still apparent

Typical industrial time-temperature profile
Conclusions

• Lab studies still have a role to play
  • Easy access and the freedom to ‘play’

• Think holistically!
  • In-situ stages don’t work in isolation
  • Source, optics and detector can be changed/tweaked
  • Integration with diffractometer systems desirable but not vital

• Think beyond CuKα

• High gas pressure is a real pain (or the regulations are)
  • “abandon hope all ye who pass here!”
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Questions?

"If I have 3 bones and Mr. Jones takes away 2, how many fingers will he have left?"