Dynamic studies of film nanostructure by Grazing Incidence X-ray Scattering

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Yttria-stabilised zirconia films

- Coatings

- ZrO_2 films:

- good chemical and dimensional stability
- high melting point
- low thermal conductivity
- high wear resistance

WF Li, XY Liu, AP Huang, PX Chu, *J. Phys. D.* 40 (2007) 2293 – 2299

- Yttria doping

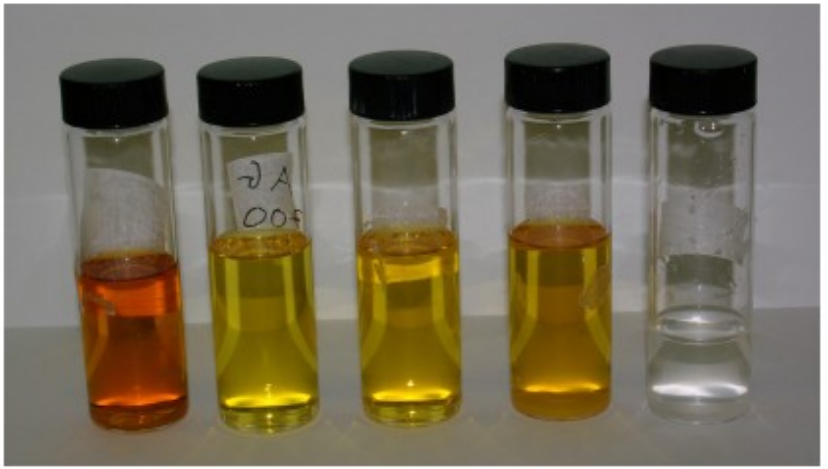
  - ZnO films: solar cell applications

  •*L. Bahadur, M. Hamdani, J.F. Koenig, P. Chartier, Solar Energy Mater. 14 (1986) 107-120*

  - SiO_2 films: strengthening of glass

  •B.D. Fabes, W.F. Doyle, B.J.J. Zelinski, L.A. Silverman, D.R. Uhlmann, *J. Non-Cryst. Solids* 82 (1986) 349-355

YSZ sols

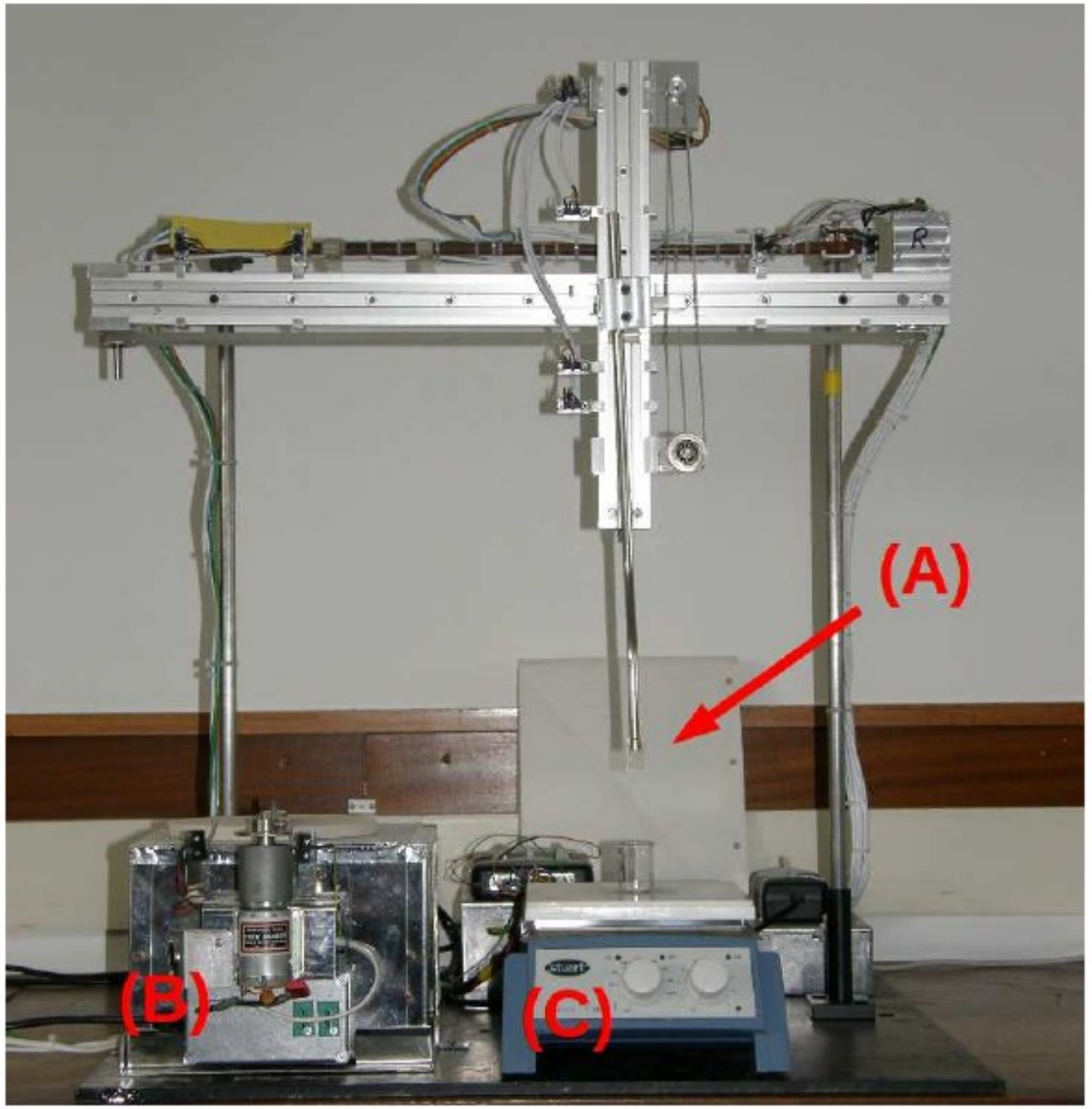


- Zr precursor: Zr(nPrO)4
- chelating agent: acetyl acetone
- buffer: acetic acid
- solvent: iso-propanol

- reaction starter: water
- Y source: Y(NO3)3

- **Bespoke sample environments**
- **Dynamic GISAXS**
- **Combined in-situ techniques**
- **Chemical contrast**

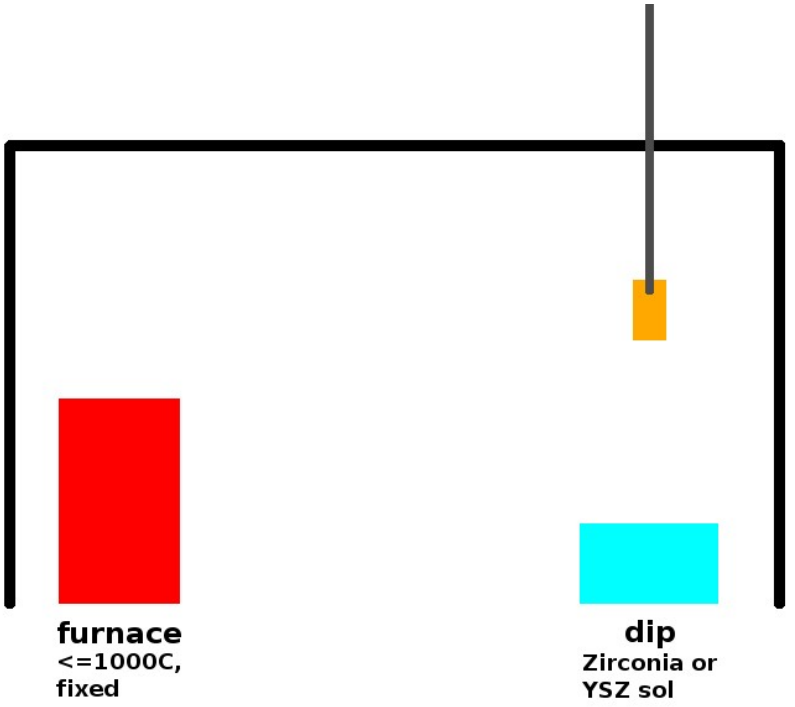
The Ystwyth Dipper



A - sample at beam position

B - furnace

C - hotplate



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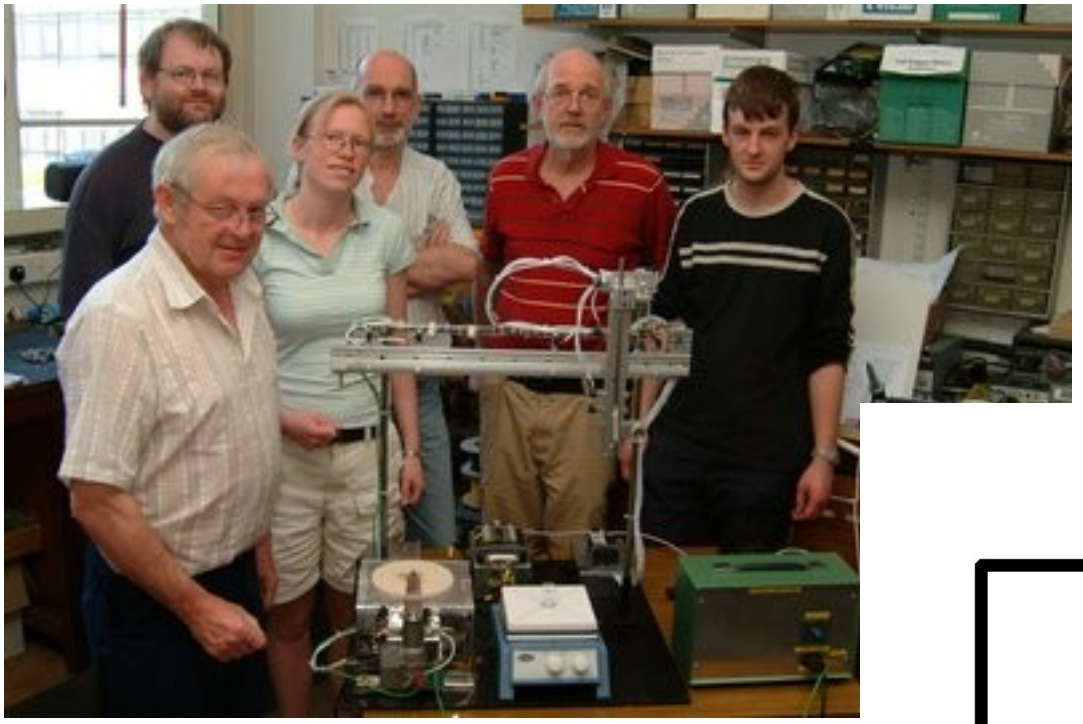

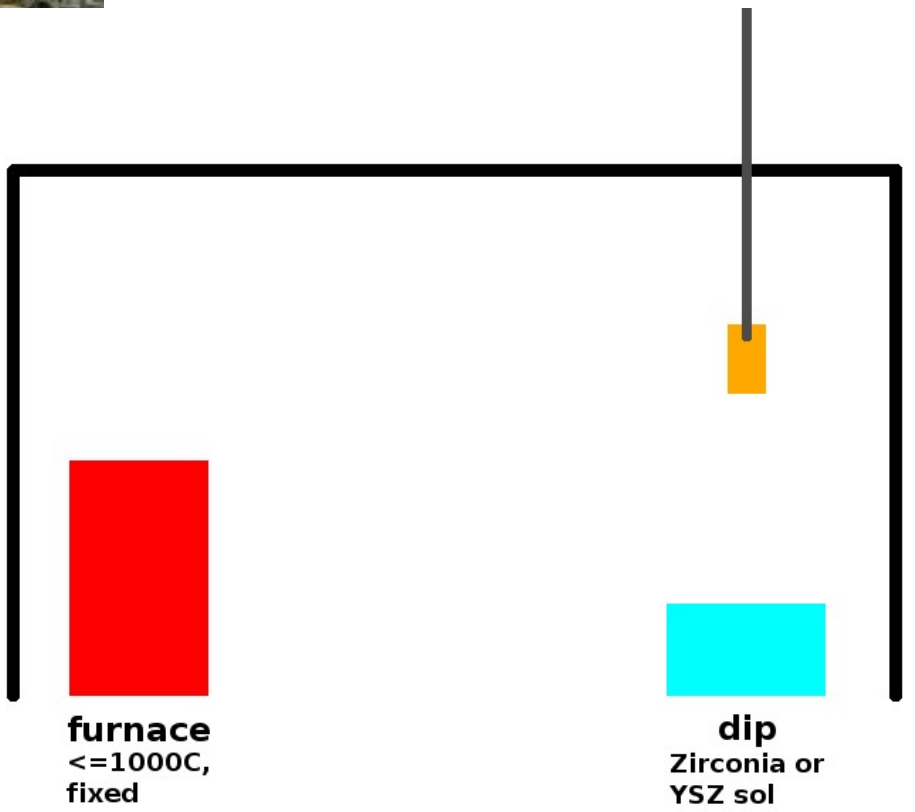

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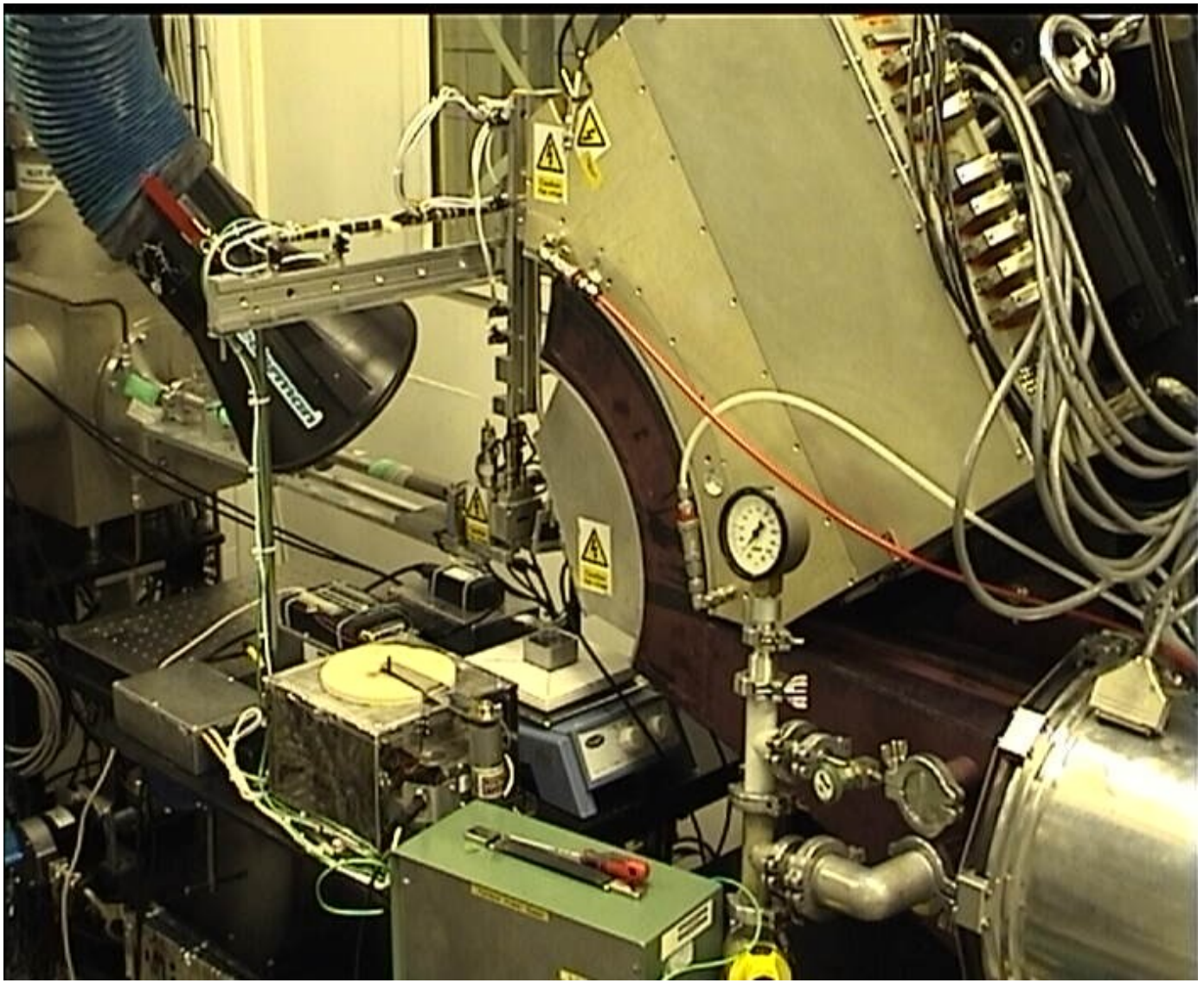
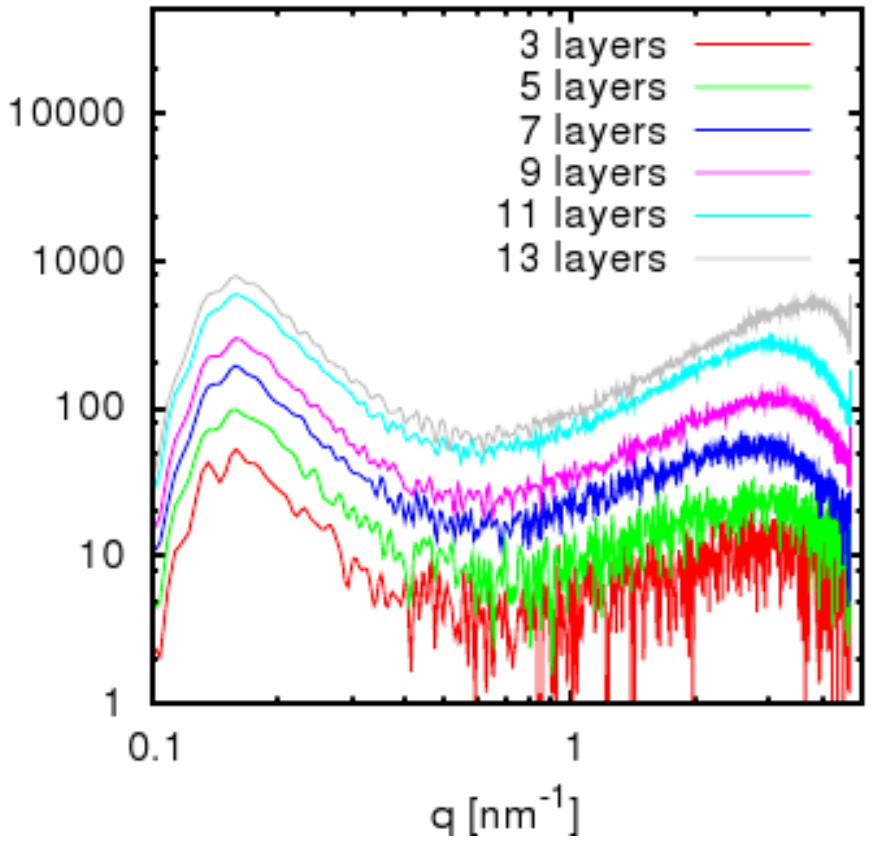
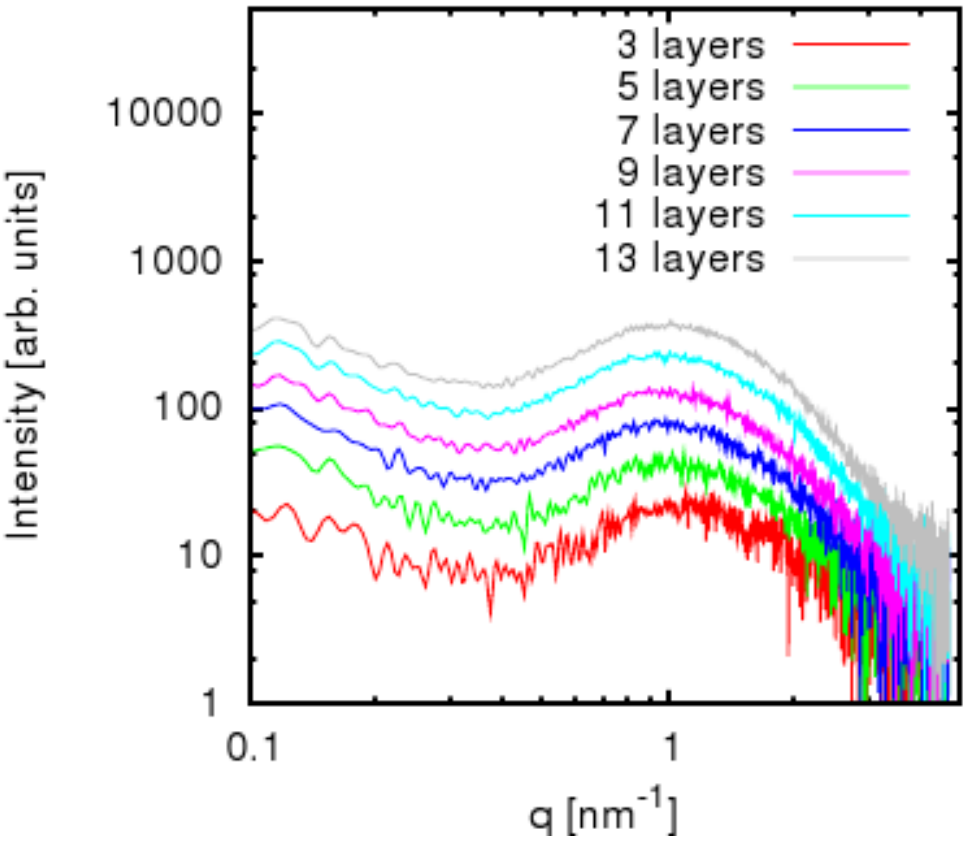


In-situ dip-coating experiment

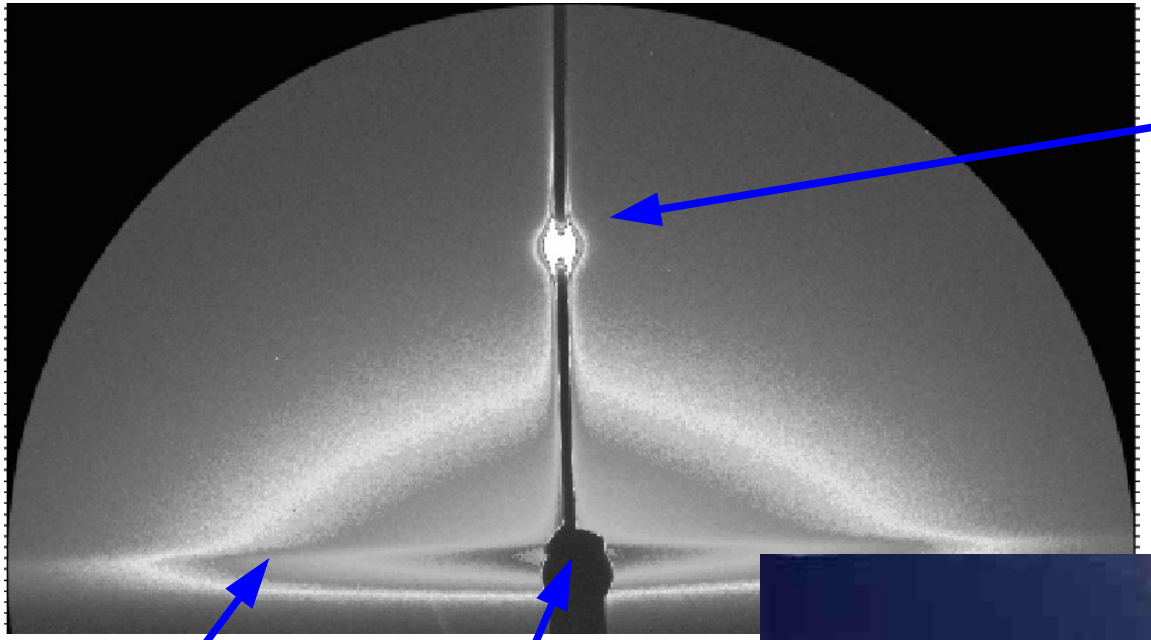
500°C



700°C



- Bespoke sample environments
- **Dynamic GISAXS**
- Combined in-situ techniques
- Chemical contrast

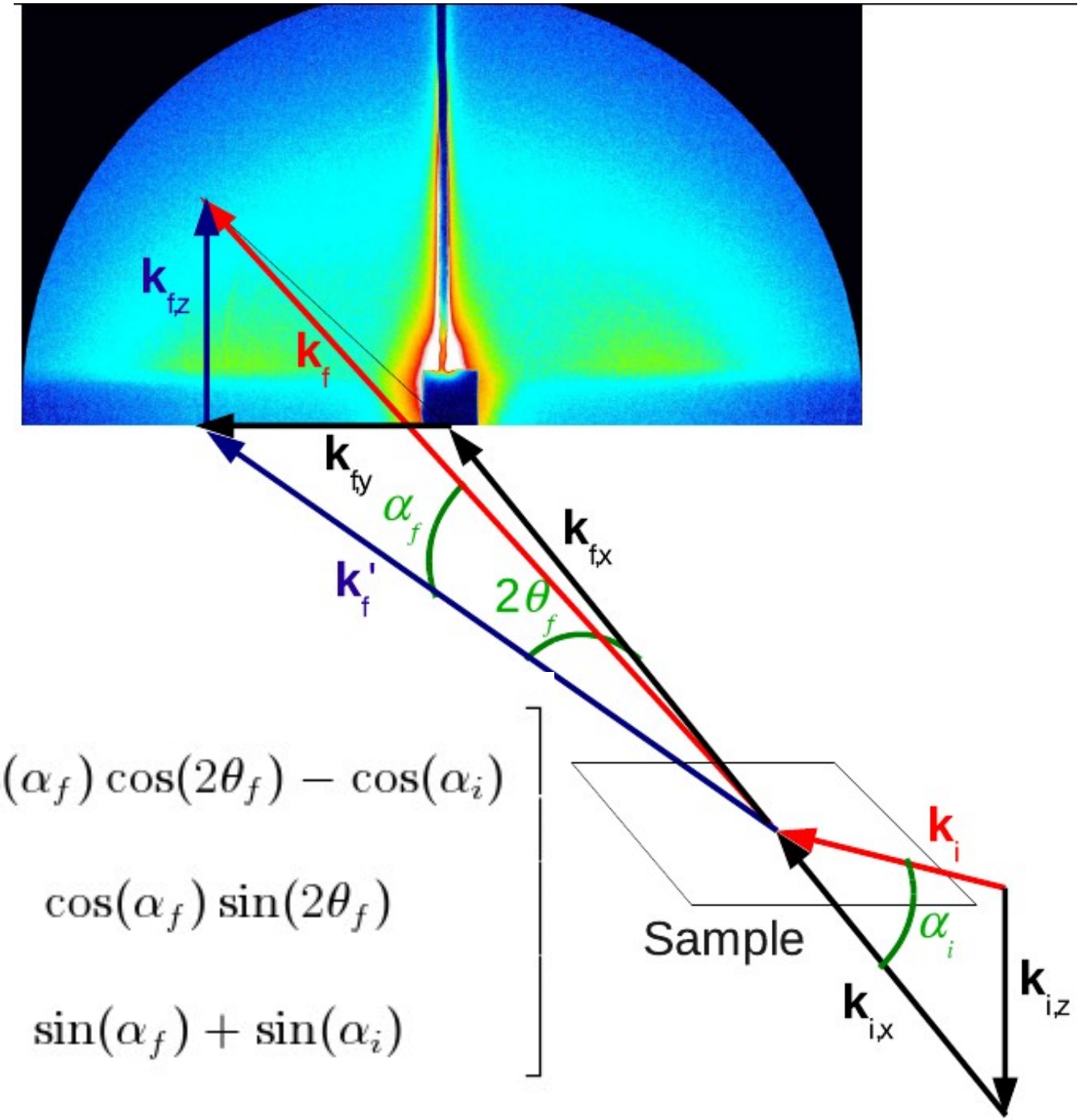


reflected beam

'horizon'

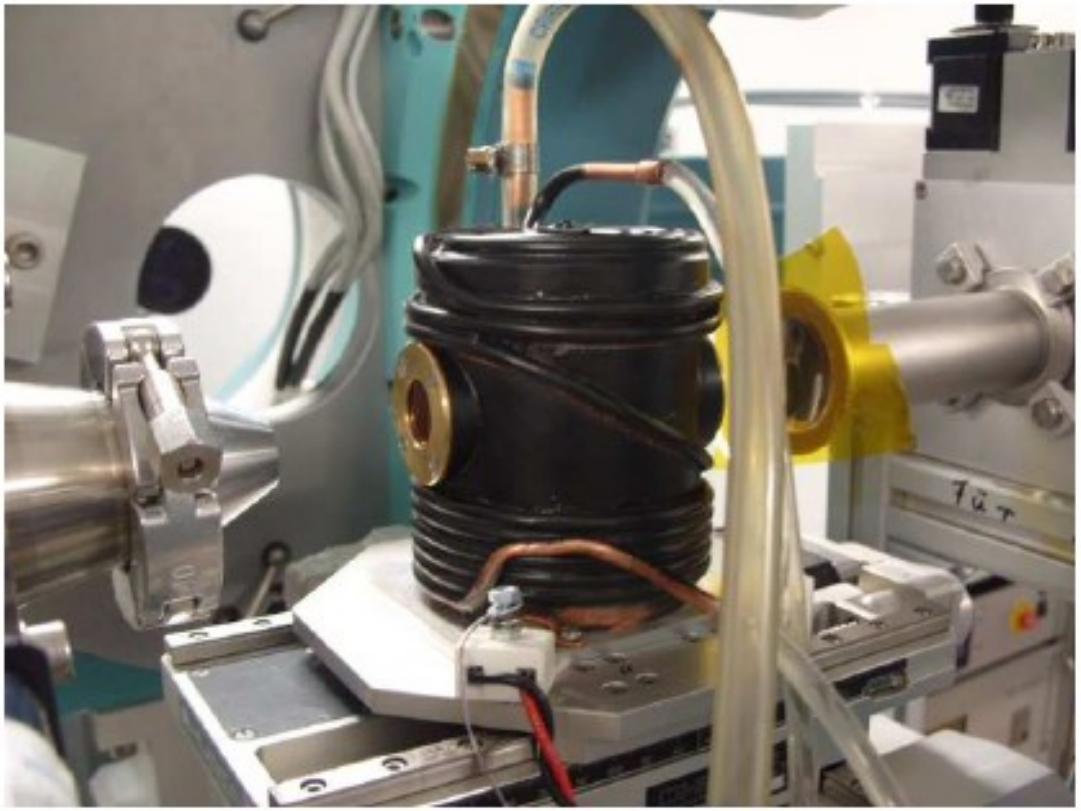
through beam

GISAXS geometry



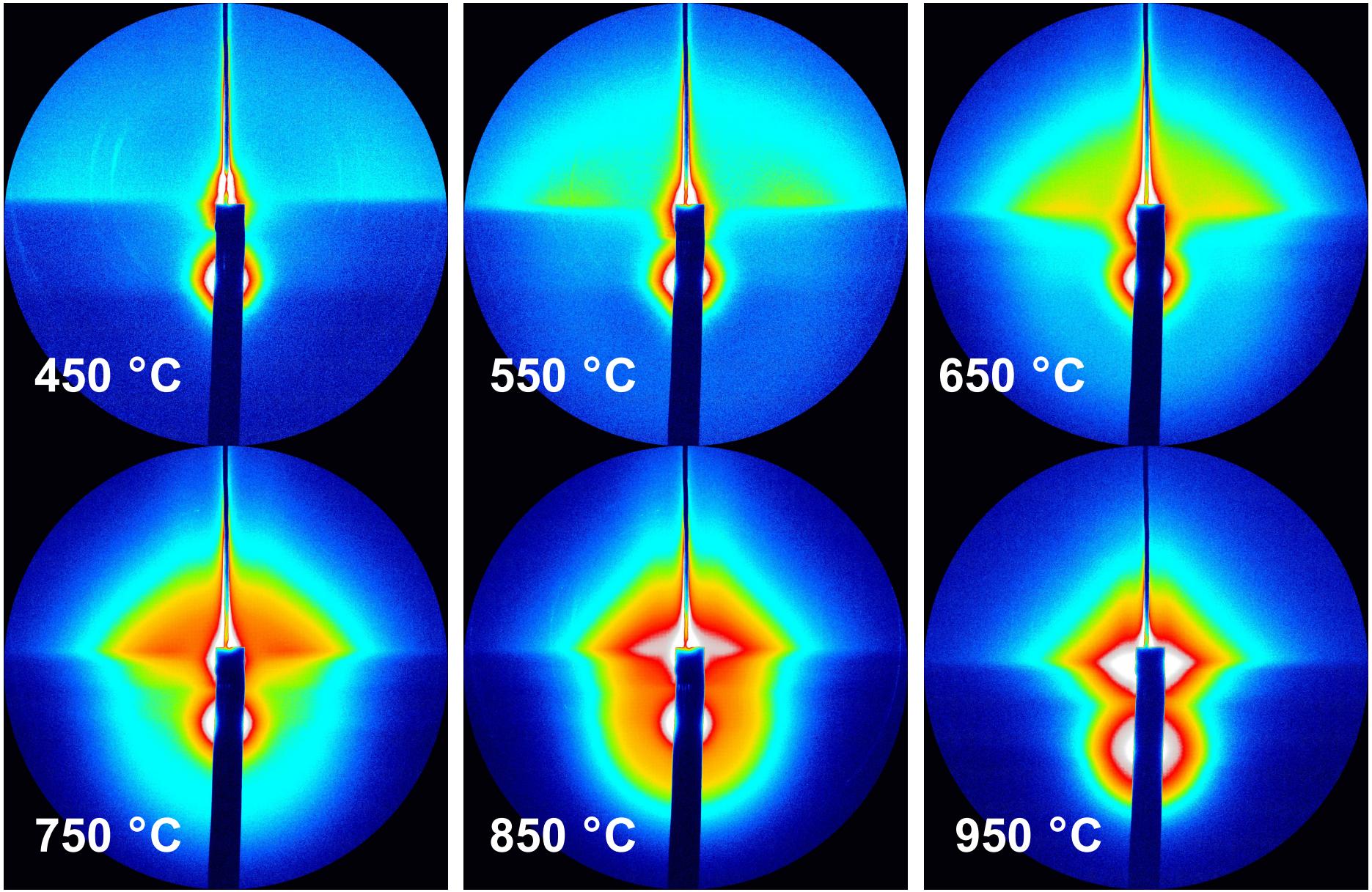
$$\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i = \frac{2\pi}{\lambda} \begin{bmatrix} \cos(\alpha_f)\cos(2\theta_f) - \cos(\alpha_i) \\ \cos(\alpha_f)\sin(2\theta_f) \\ \sin(\alpha_f) + \sin(\alpha_i) \end{bmatrix}$$

GISAXS furnace

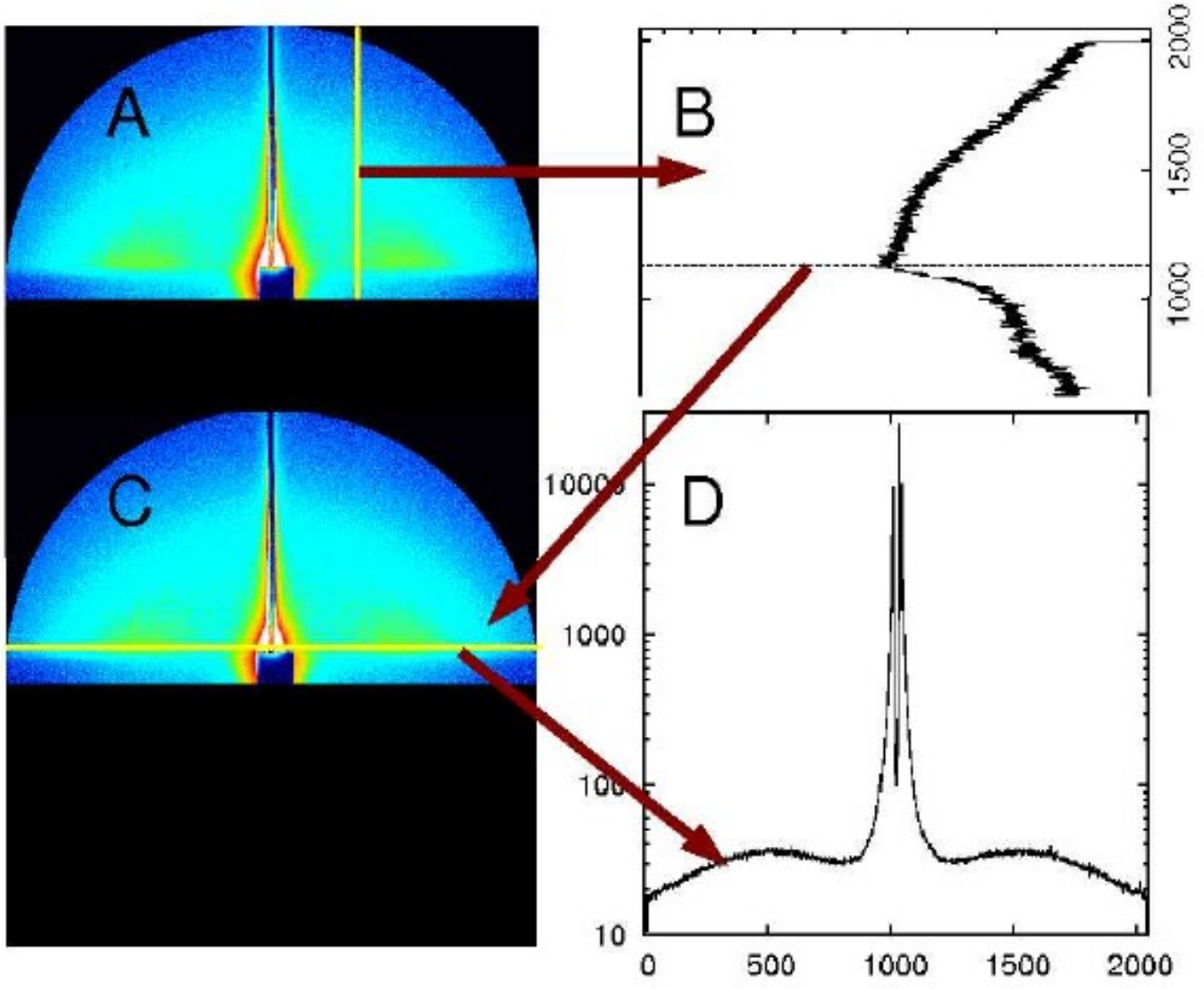


- Kapton windows
- water cooled hood
- He atmosphere possible
- up to 1100°C

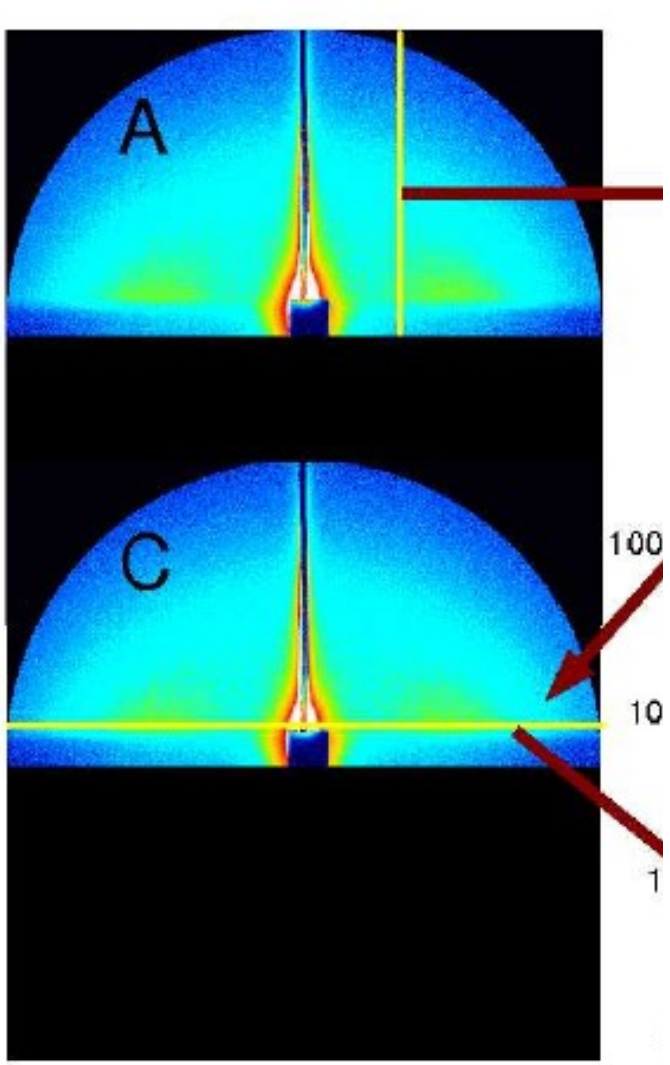
In-situ GISAXS of YSZ film calcination

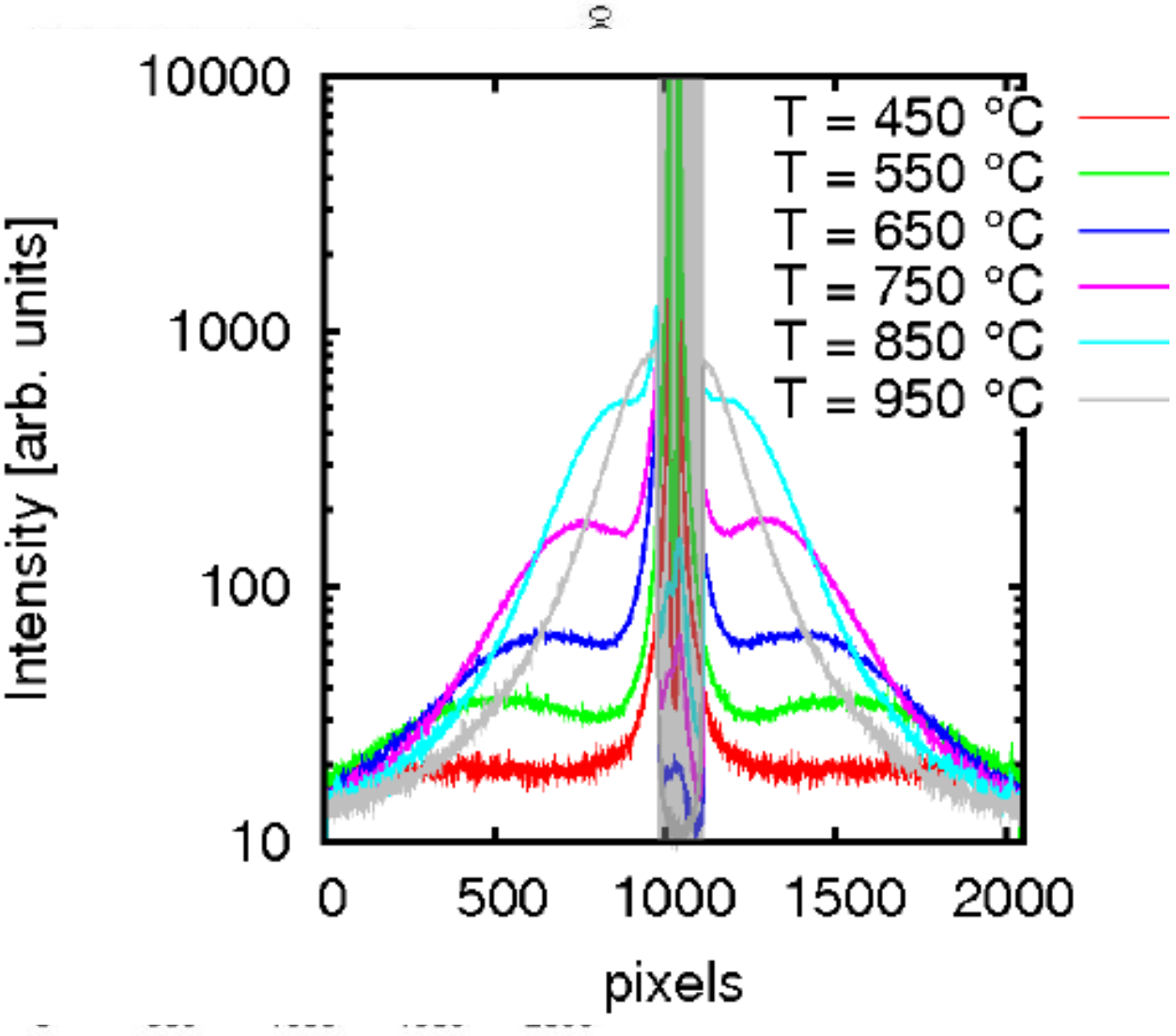


Coping with changing surfaces



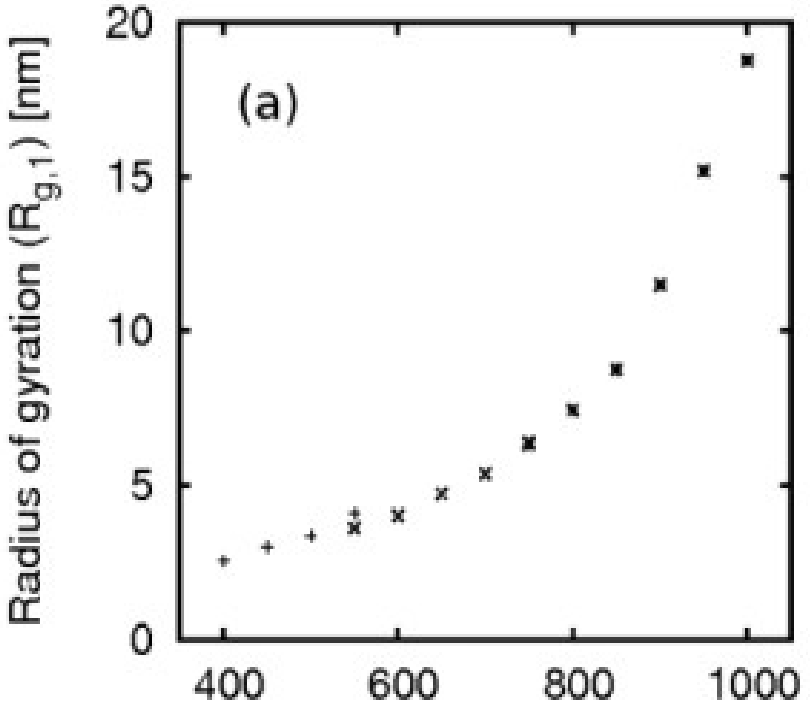
Lateral scattering patterns: film morphology

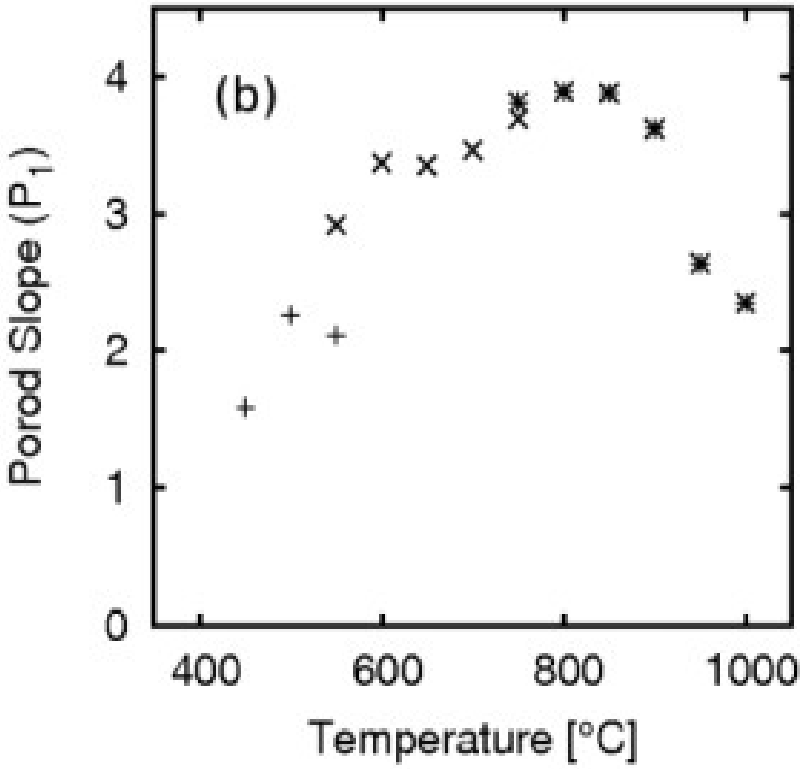


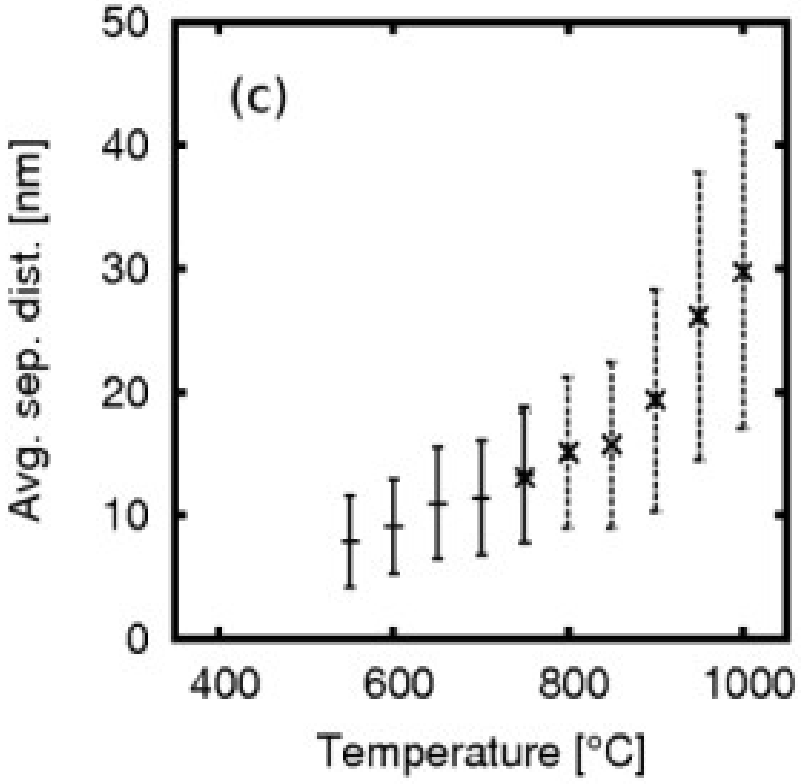


with
Dragomir Tatchev (BAS Sofia)
Sylvio Haas, Armin Hoell (HZB Berlin)

K Hoydalsvik et al.
Phys Chem Chem Phys (2010) adv. art.





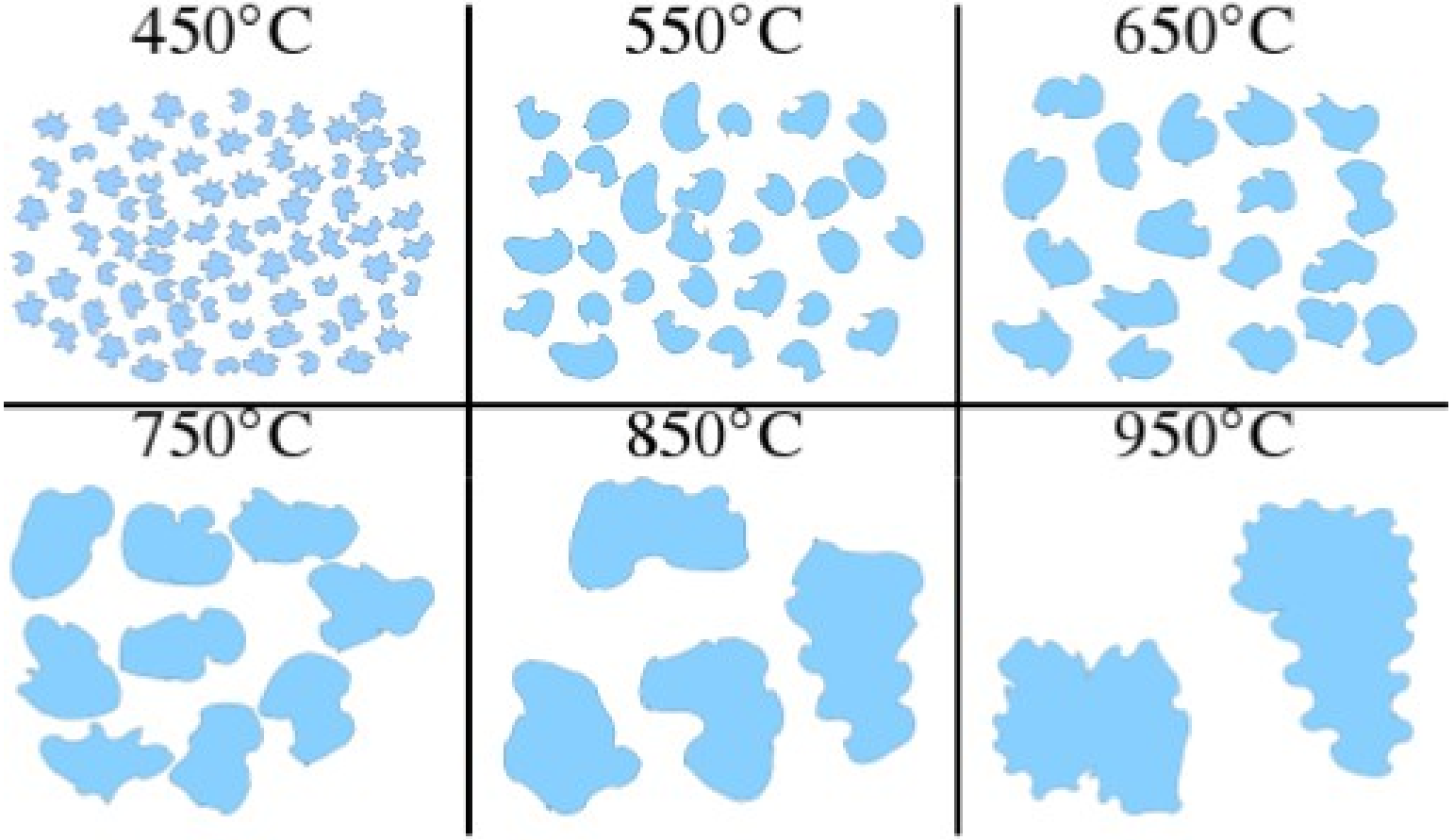


- particle size increases

- internal surfaces become smoother, then rougher again

- particle distance increases

Visualisation of film calcination process



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- **Combined in-situ techniques**
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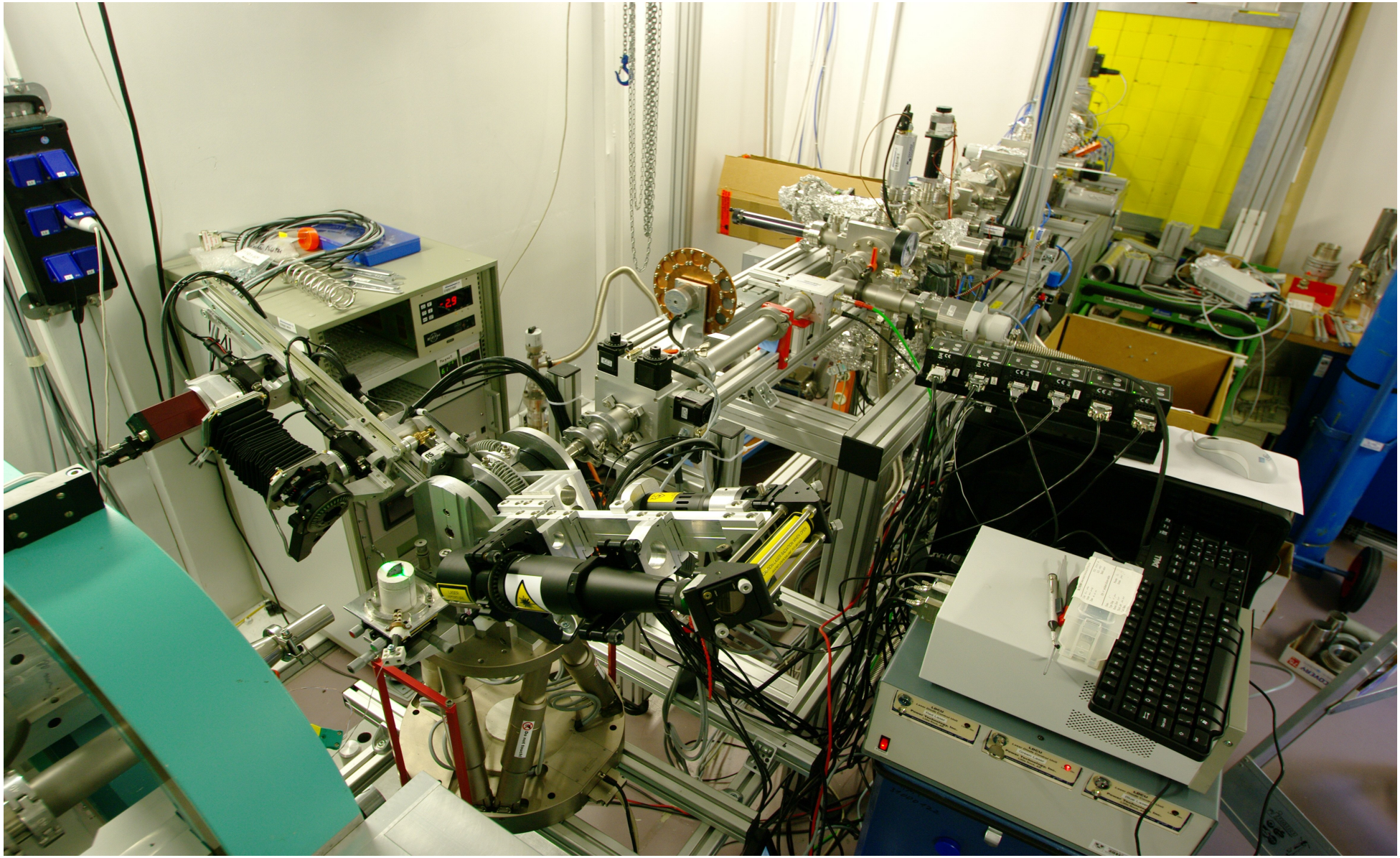
Combining scattering and imaging

in-situ Grazing-incidence SAXS and 2D imaging ellipsometry



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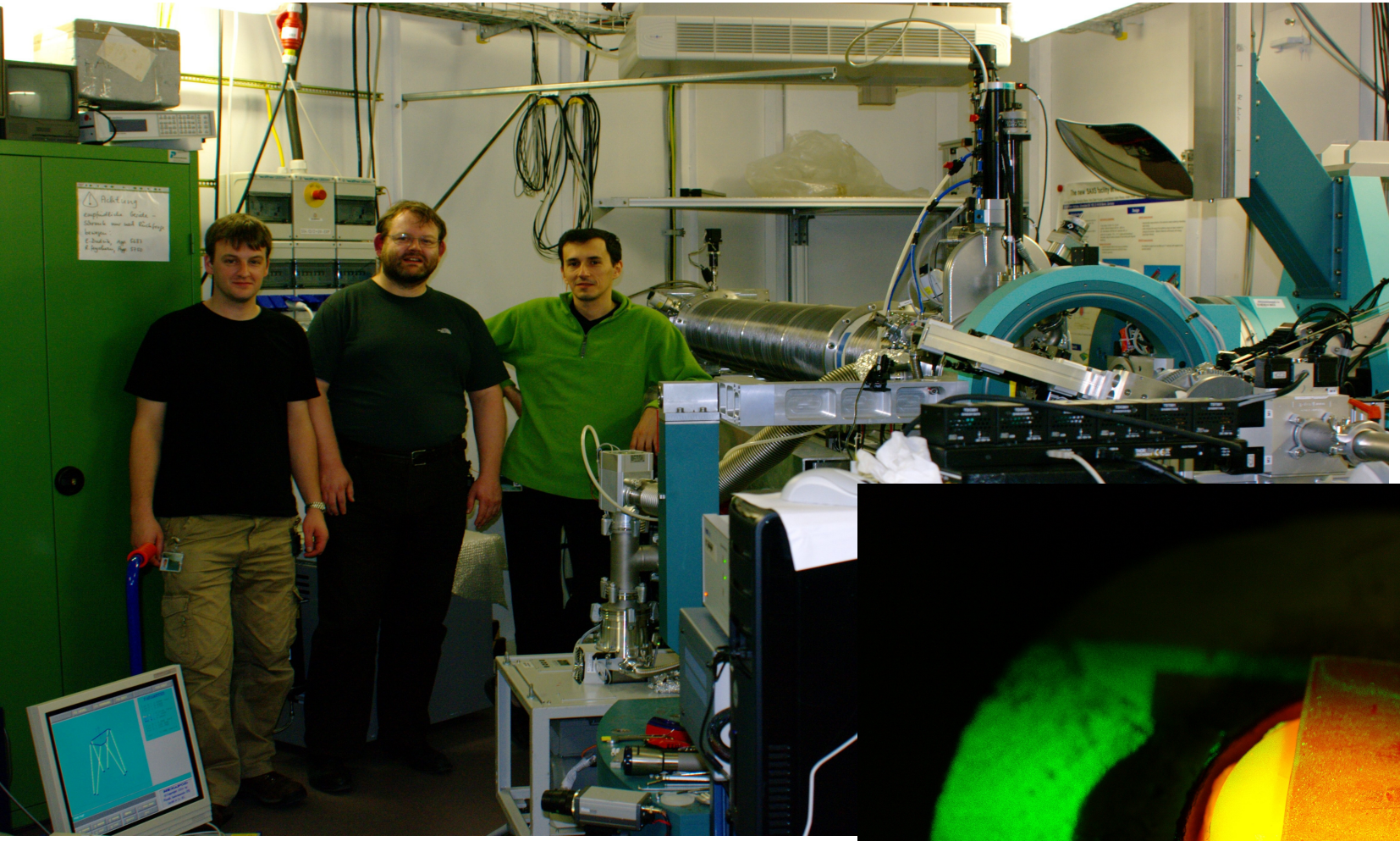
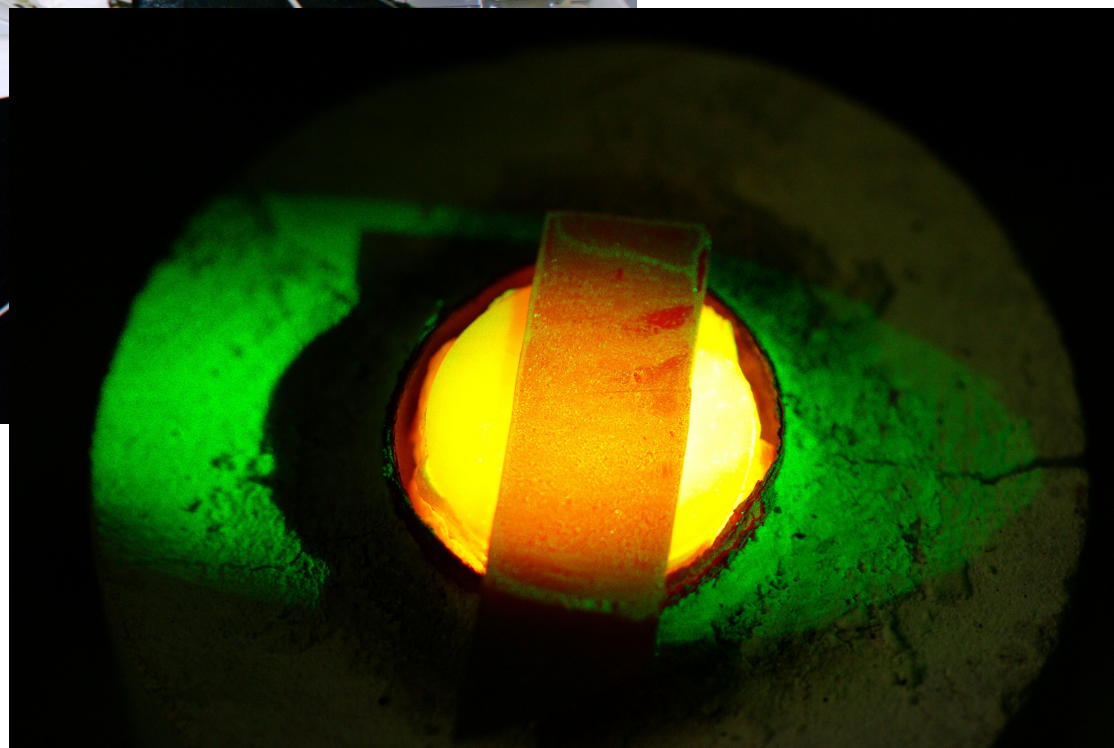
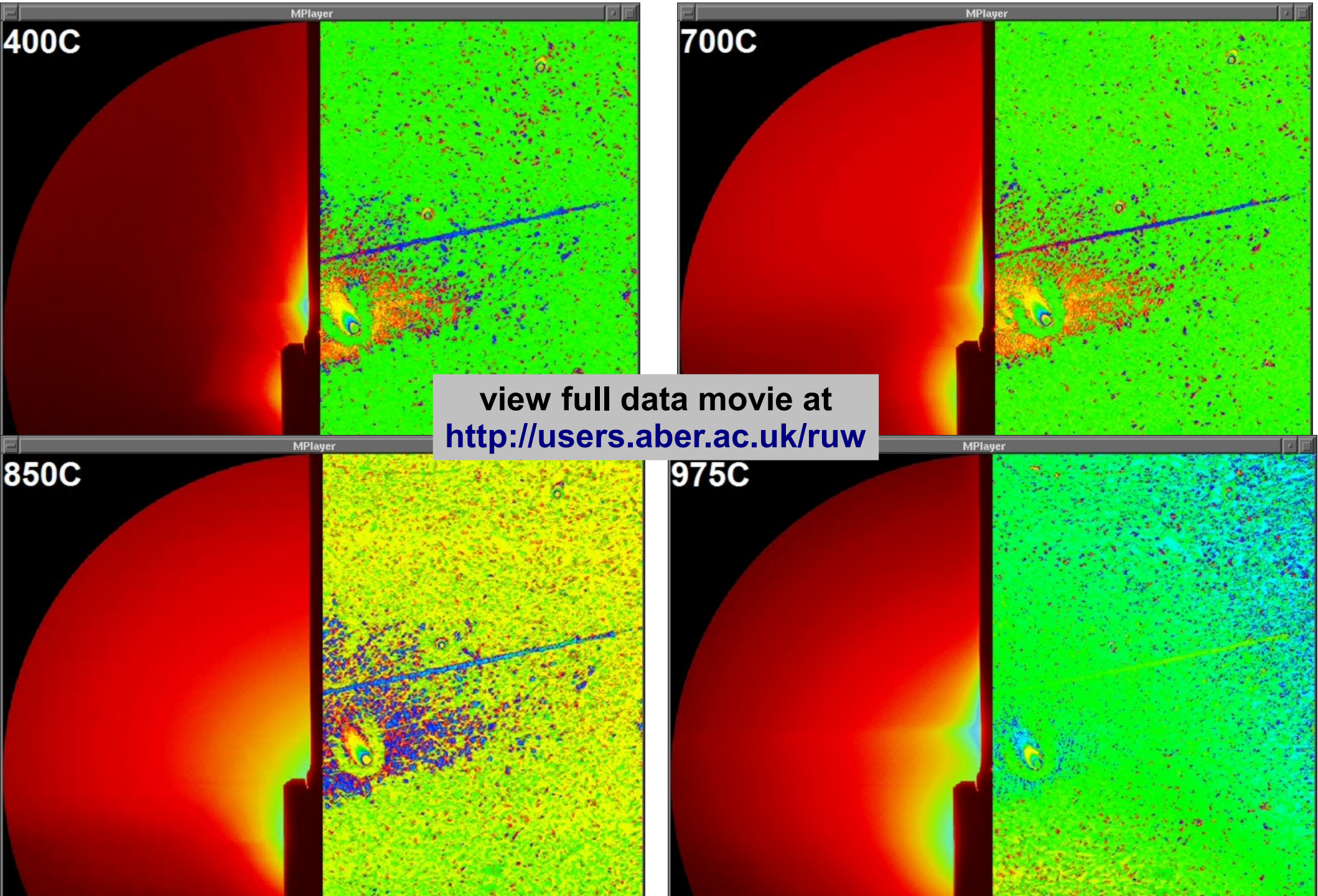




with
Matt Gunn, Dave Langstaff (Aber)
Dragomir Tatchev (BAS Sofia)
Sylvio Haas, Armin Hoell (HZB Berlin)

in-situ Grazing-incidence SAXS and 2D imaging ellipsometry



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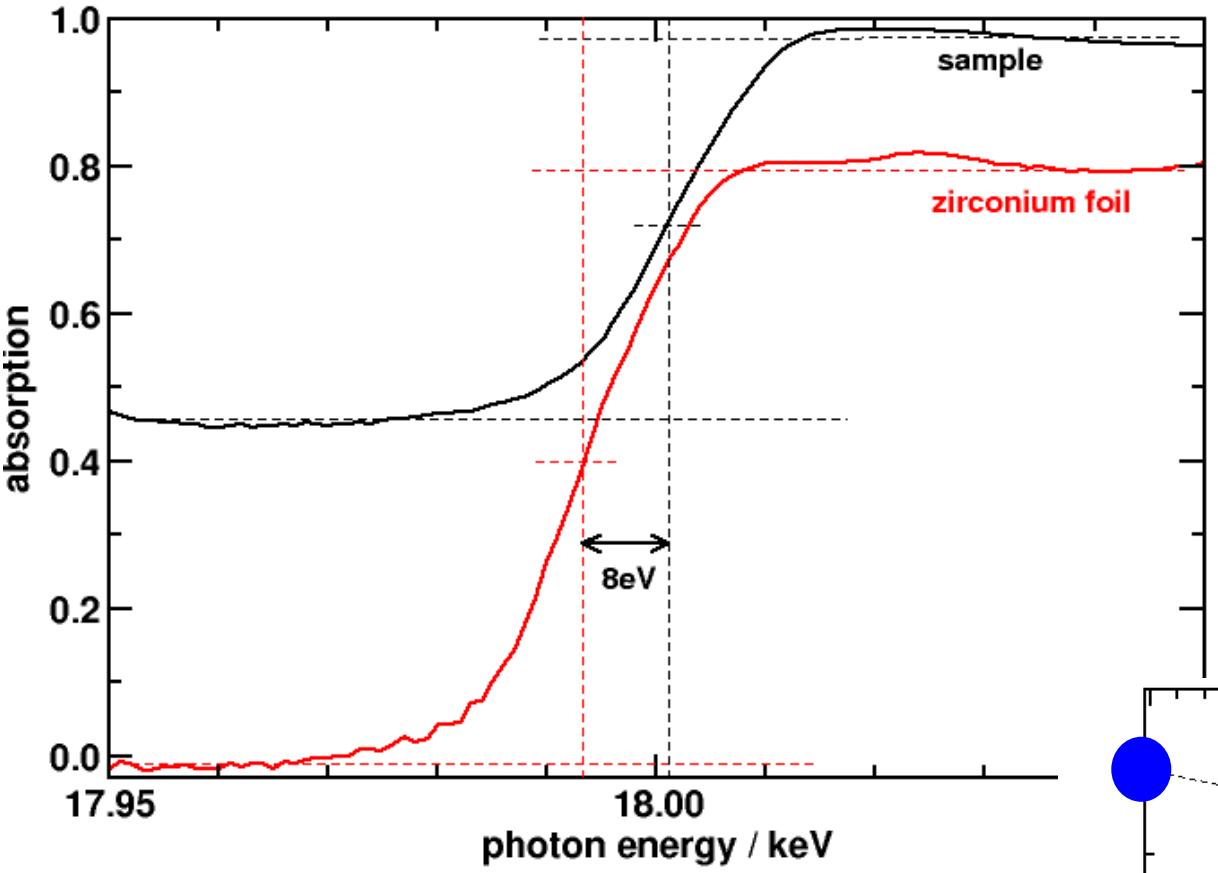
Chemical contrast

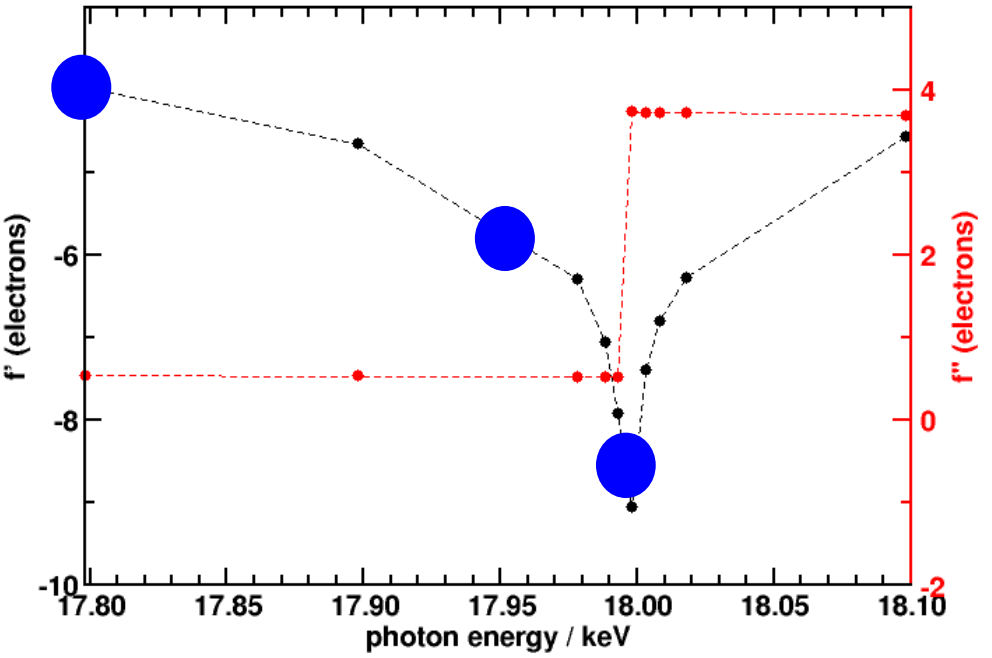


ASAXS:

3 energies below the edge

=> determine partial structure factors

but: chemical edge shift

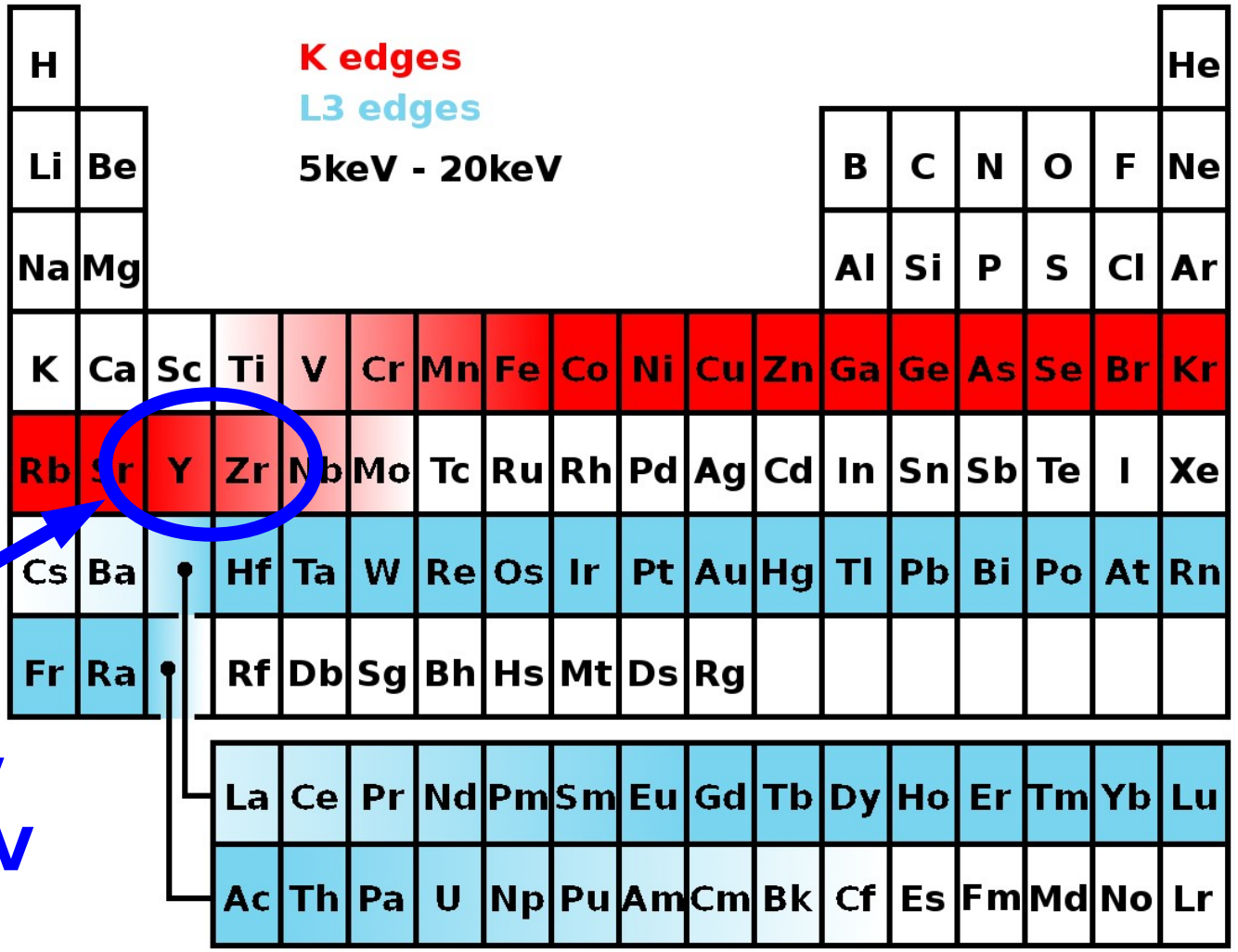


- **photon energy calibrated to Zr foil at 17.993keV**
- **8eV chemical shift of edge in unreacted sample**
- **edge shifts by several eV as reaction progresses**

The anomalous scatterer's periodic table

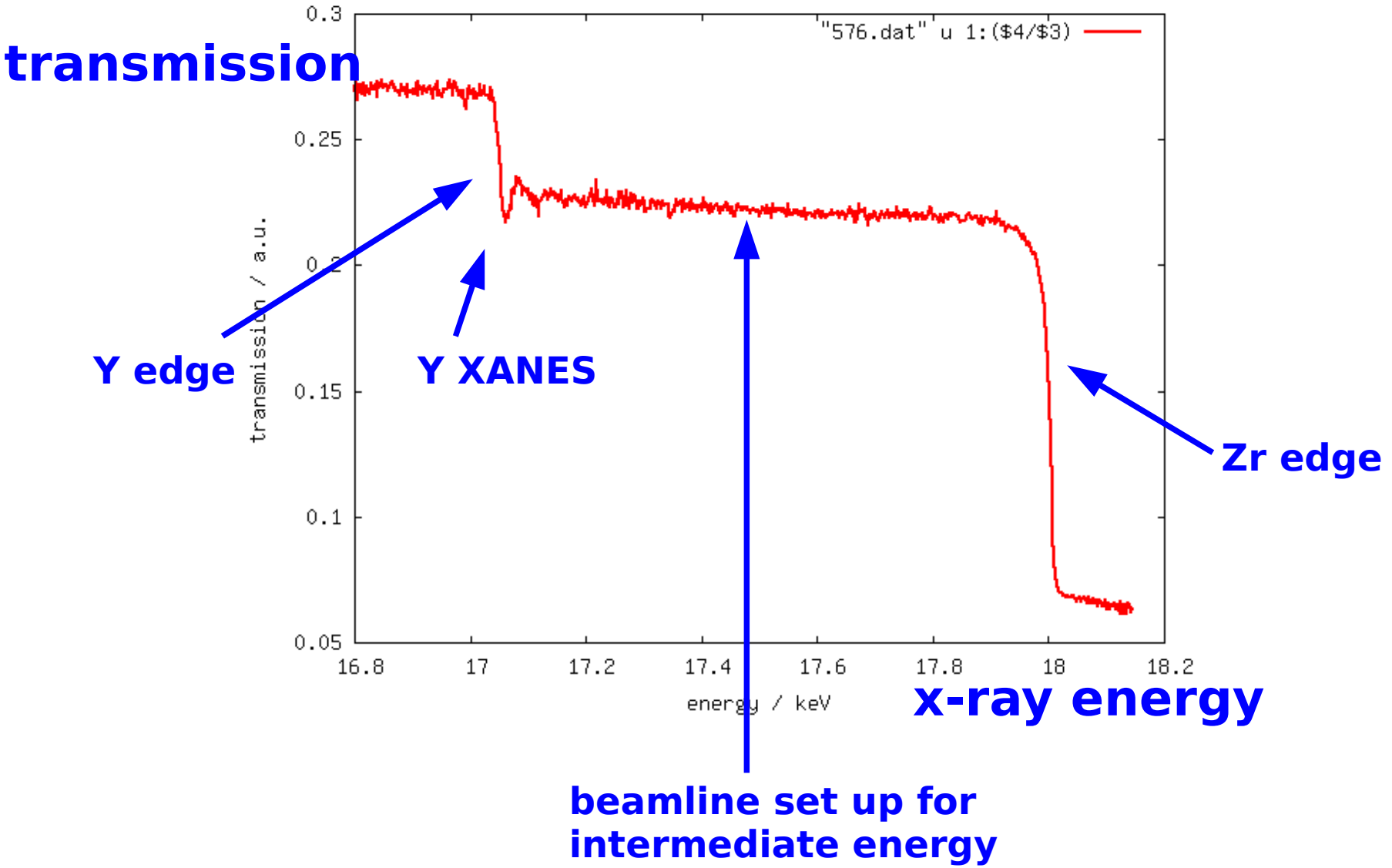
low-energy limit:
- absorption
- air scatter

high-energy limit:
- monochromator coating
- limited q range



Double ASAXS:
Y *K* edge: 17keV
Zr *K* edge: 18keV

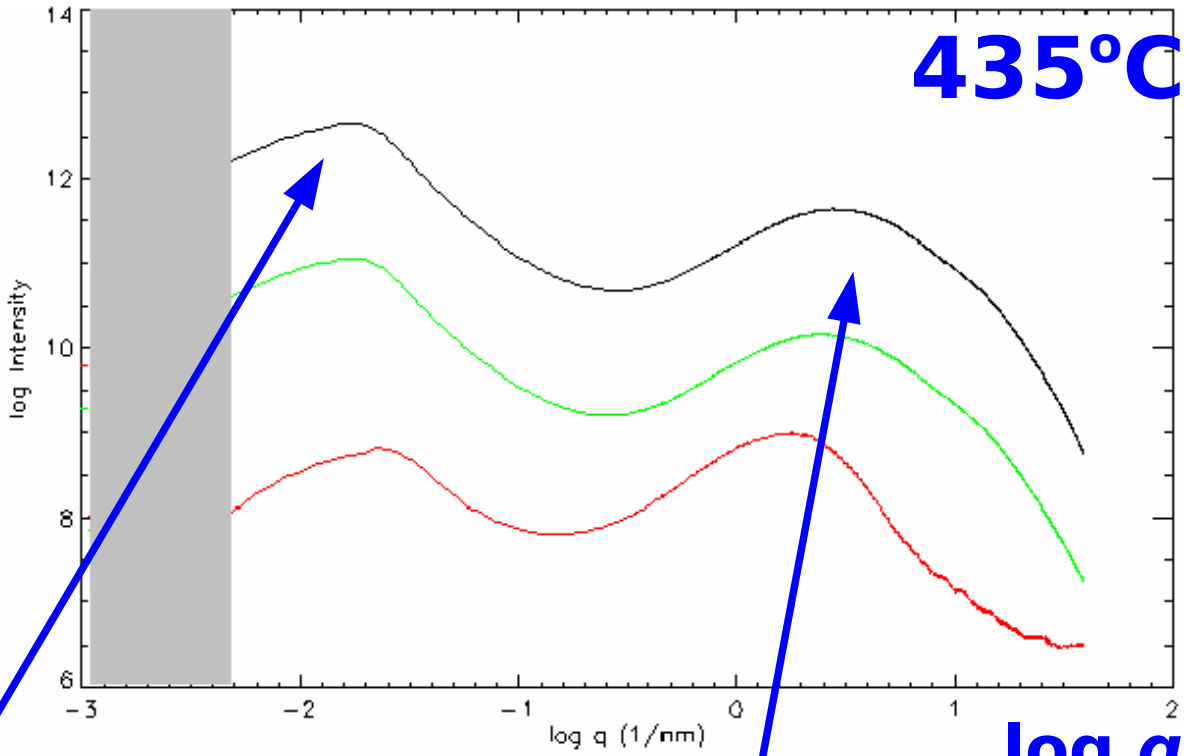
Double edge experiments



with Chris Martin, Graham Clark (STFC)

T Barnardo et al., J Phys Chem C 113 (2009) 10021

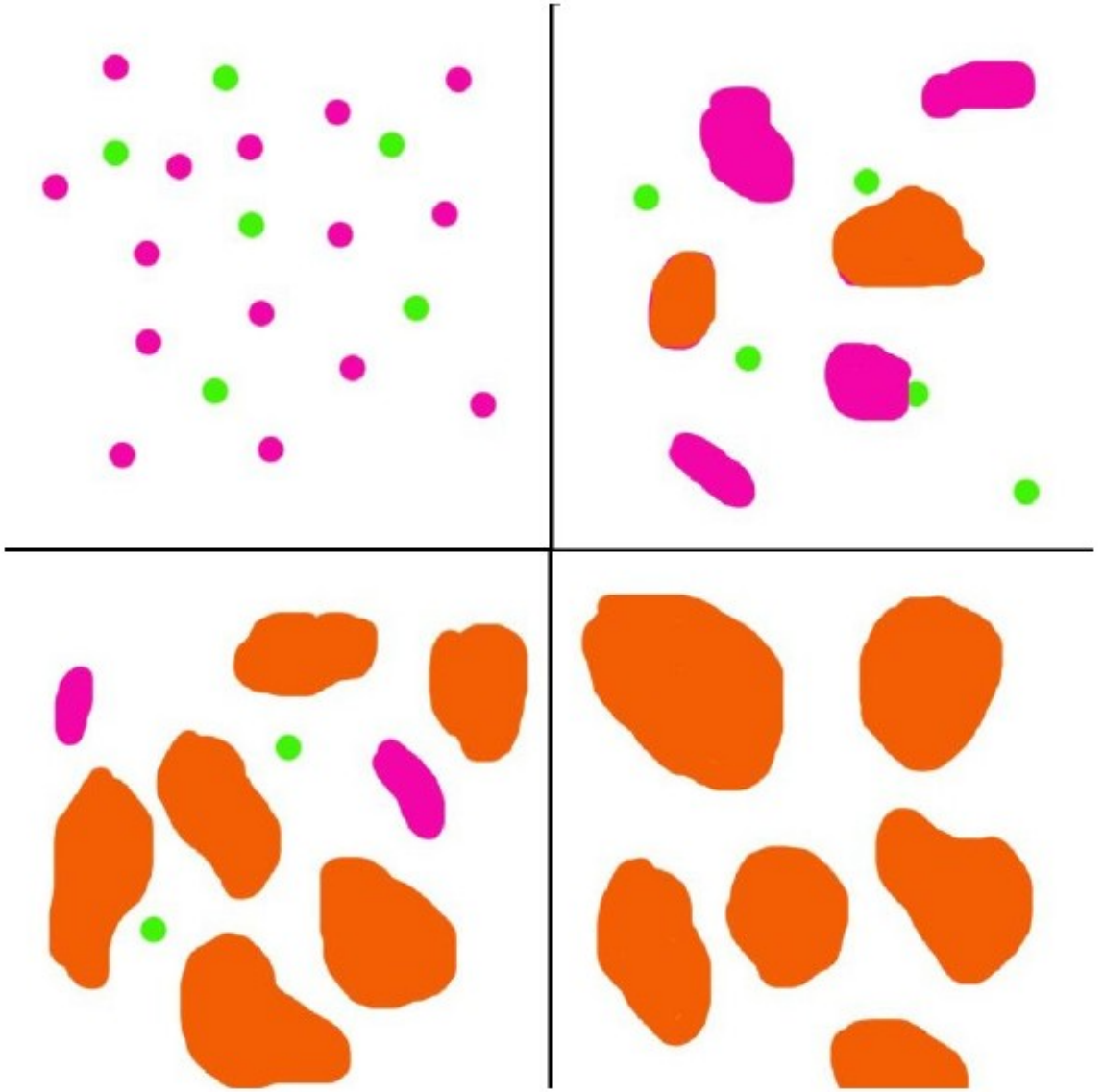
Calcination of bulk YSZ gel



macro-scatter increases in magnitude only

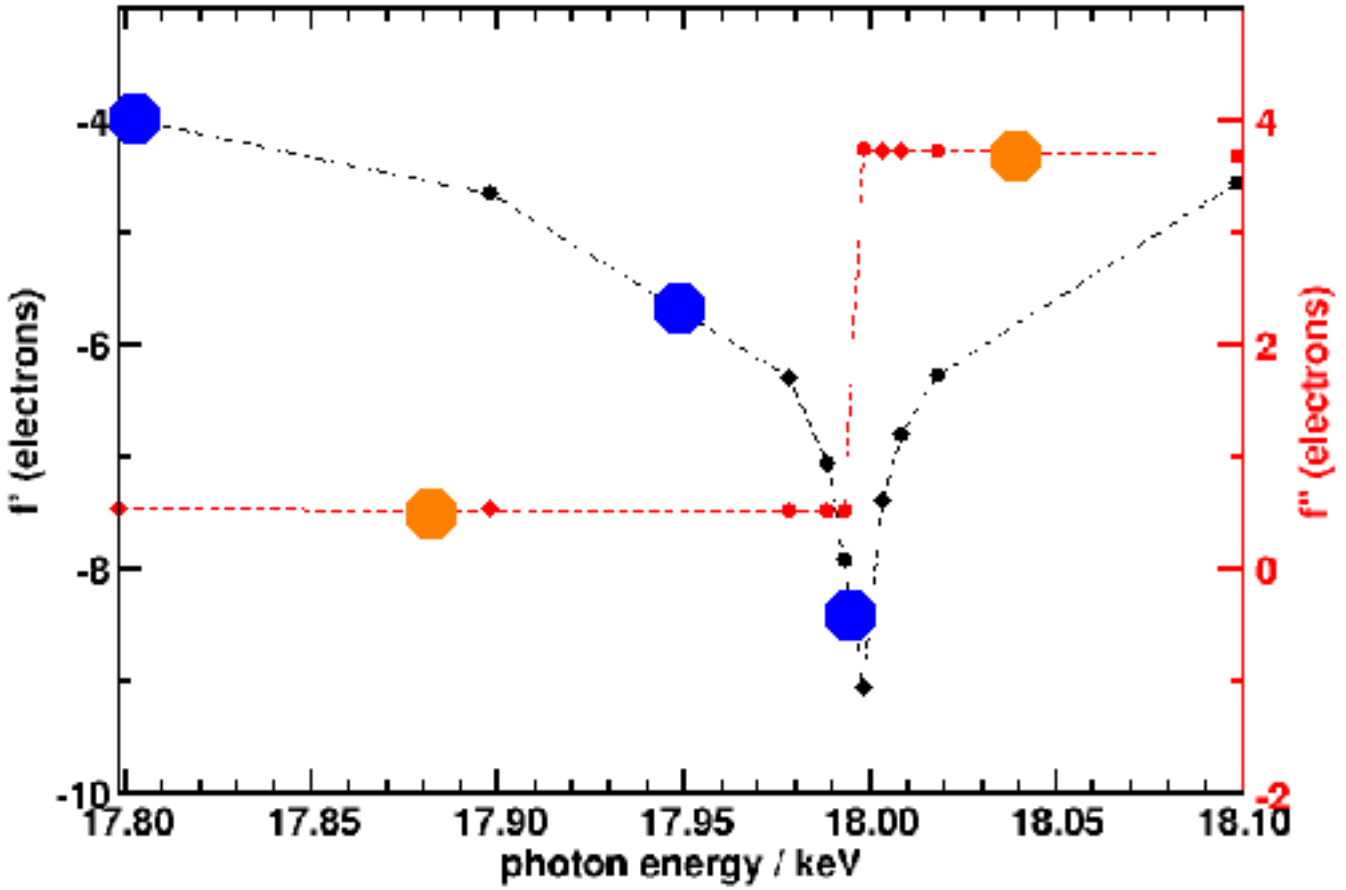
structure factor moves left:
=> *nucleation*
Note difference in resonant term!

Calcination of bulk YSZ gel



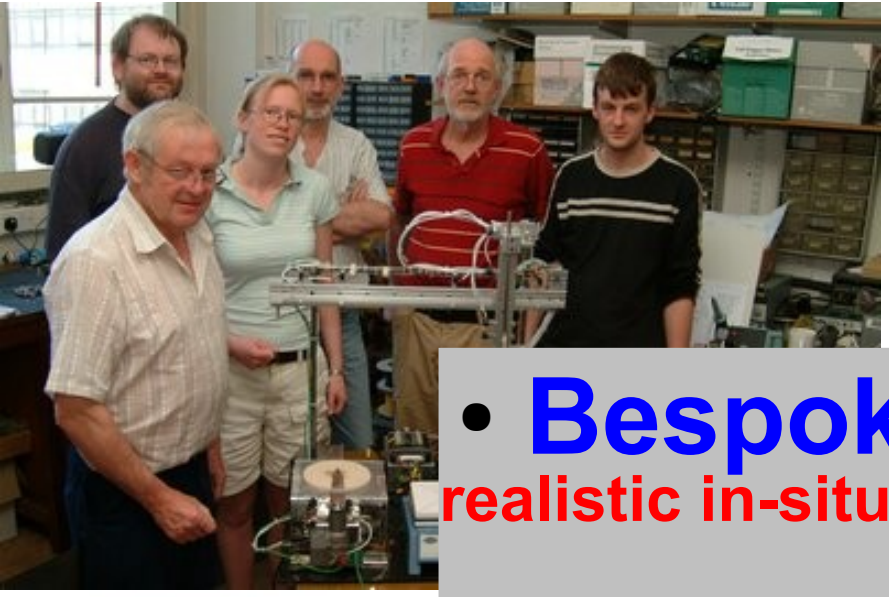
Chemical contrast

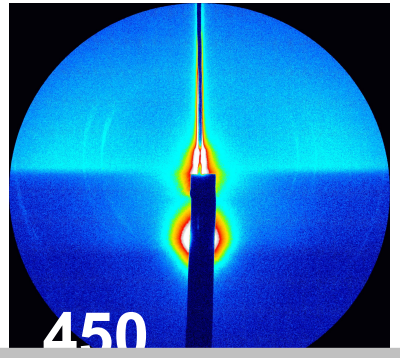
by Absorption-Contrast Scattering

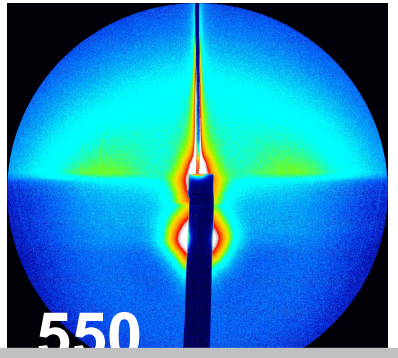


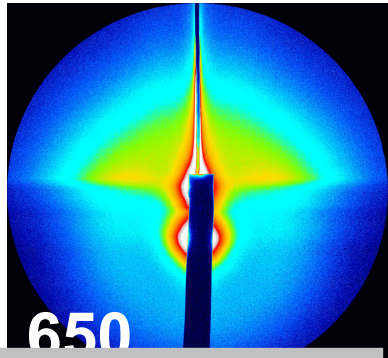
- **measure and subtract fluorescence explicitly**
- ***spectroscopic scattering***

with Simon Cooil (Aber)
Nick Terrill, Tobias Richter, Marc Malfois (Diamond)









- **Bespoke sample environments**

realistic in-situ conditions modelled on use conditions

- **Dynamic GISAXS**

film nanostructure changes during deposition or use

- **Combined in-situ techniques**

in-situ scattering with imaging

- **Chemical contrast**

grasping chemically complex multi-phase systems