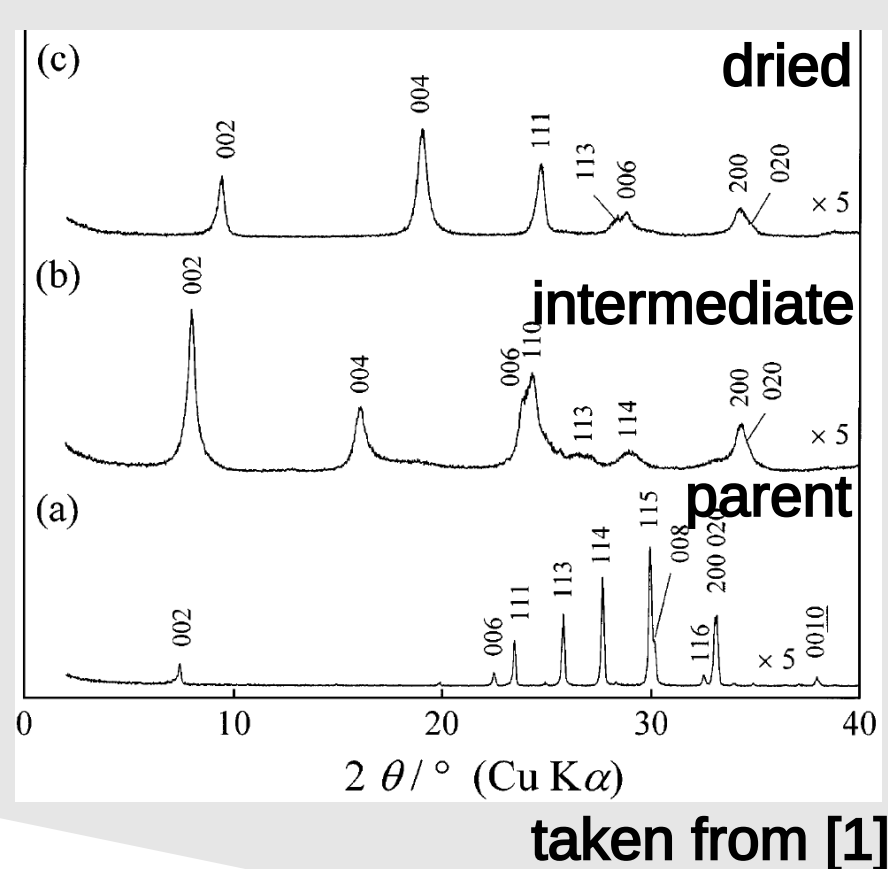
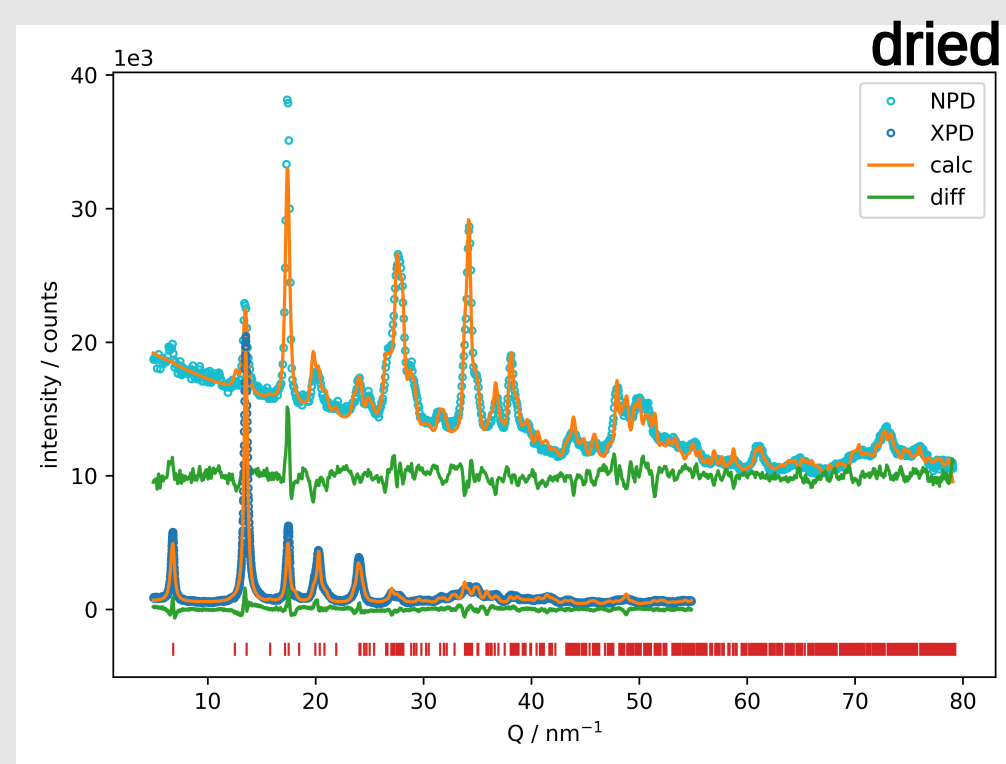


Topochemical conversion of layered tungstates: an in-situ Raman and total scattering study

Niels Lefeld¹, Andrea Kirsch², Mathias Gogolin¹, Soham Banerjee³, Thorsten M. Gesing^{1,4}

¹University of Bremen, Institute of Inorganic Chemistry and Crystallography, Bremen, Germany (nile@uni-bremen.de), ²University of Copenhagen, Department of Chemistry, Nanostructure group, Copenhagen, Denmark, ³Deutsches Elektronen-Synchrotron DESY, P21.1, Hamburg, Germany, ⁴University of Bremen, MAPEX Center for Materials and Processes, Bremen, Germany

Introduction



- Parent compound Aurivillius-type $\text{Bi}_2\text{W}_2\text{O}_9$: SG $Pnab$, $a=54.3\text{pm}$, $b=54.1\text{pm}$, $c=237\text{pm}$
- Leaching of BiO-layer with 6M HCl
- Dried end product Ruddlesden-Popper-type $\text{H}_2\text{W}_2\text{O}_7$: SG $P2_1/n$, $a=185\text{pm}$, $b=51.4\text{pm}$, $c=52.6\text{pm}$, $ga=88.8^\circ$

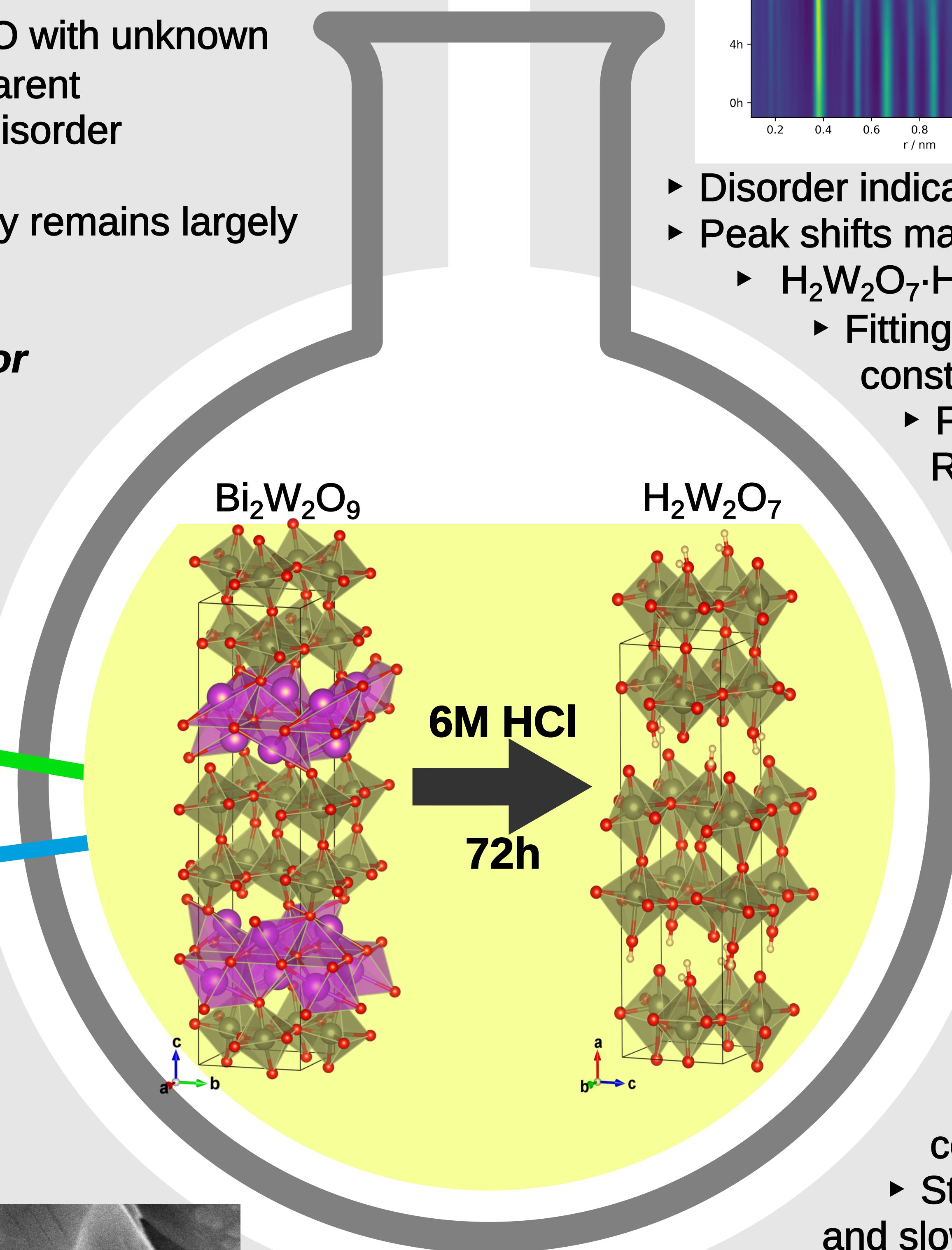
- Intermediate compound $\text{H}_2\text{W}_2\text{O}_7 \cdot \text{H}_2\text{O}$ with unknown structure but comparable cell size to parent
- Hydrotungstates exhibit significant disorder introduced by the leaching process
- Perovskite-like WO-layer presumably remains largely intact, no dissolution of W species [1]

? Can we find structural evidence for preserved WO-layer?
? What is the mechanism for introduced disorder?

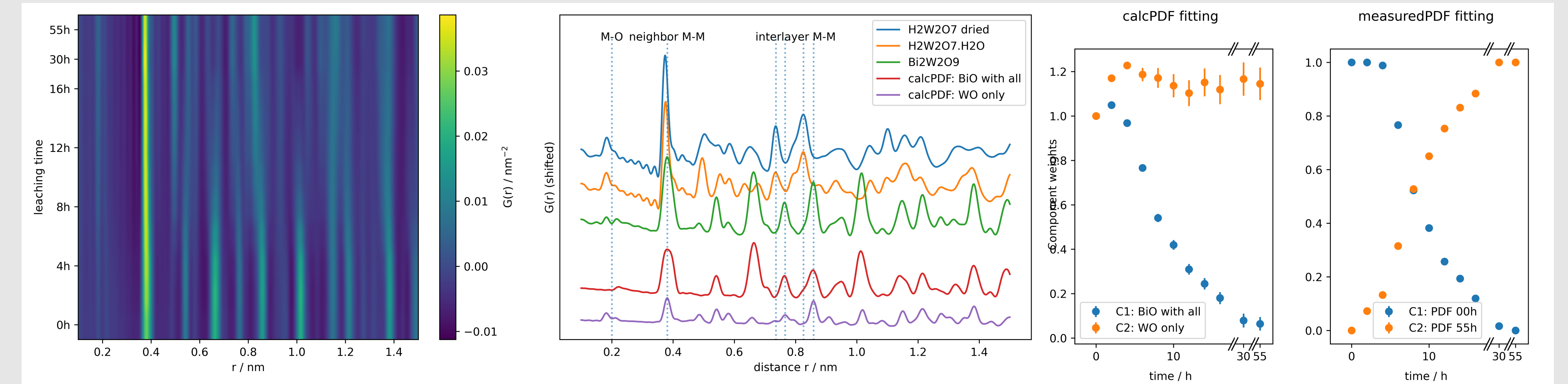
[1] M. Kudo et al., Inorg. Chem. 2003, 42, 4479-4484.

Horiba LabAramis 532 nm Laser SuperHead external probe

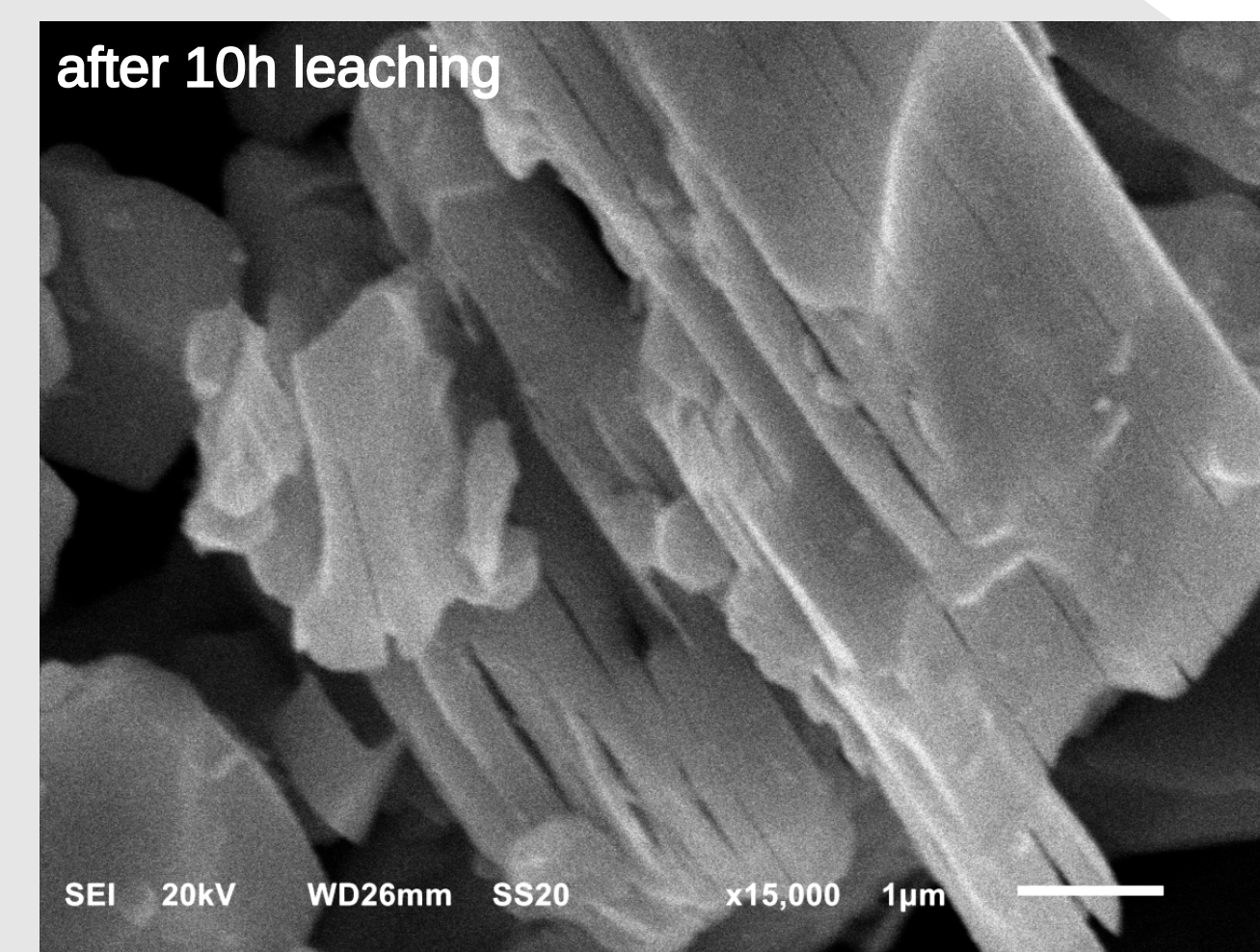
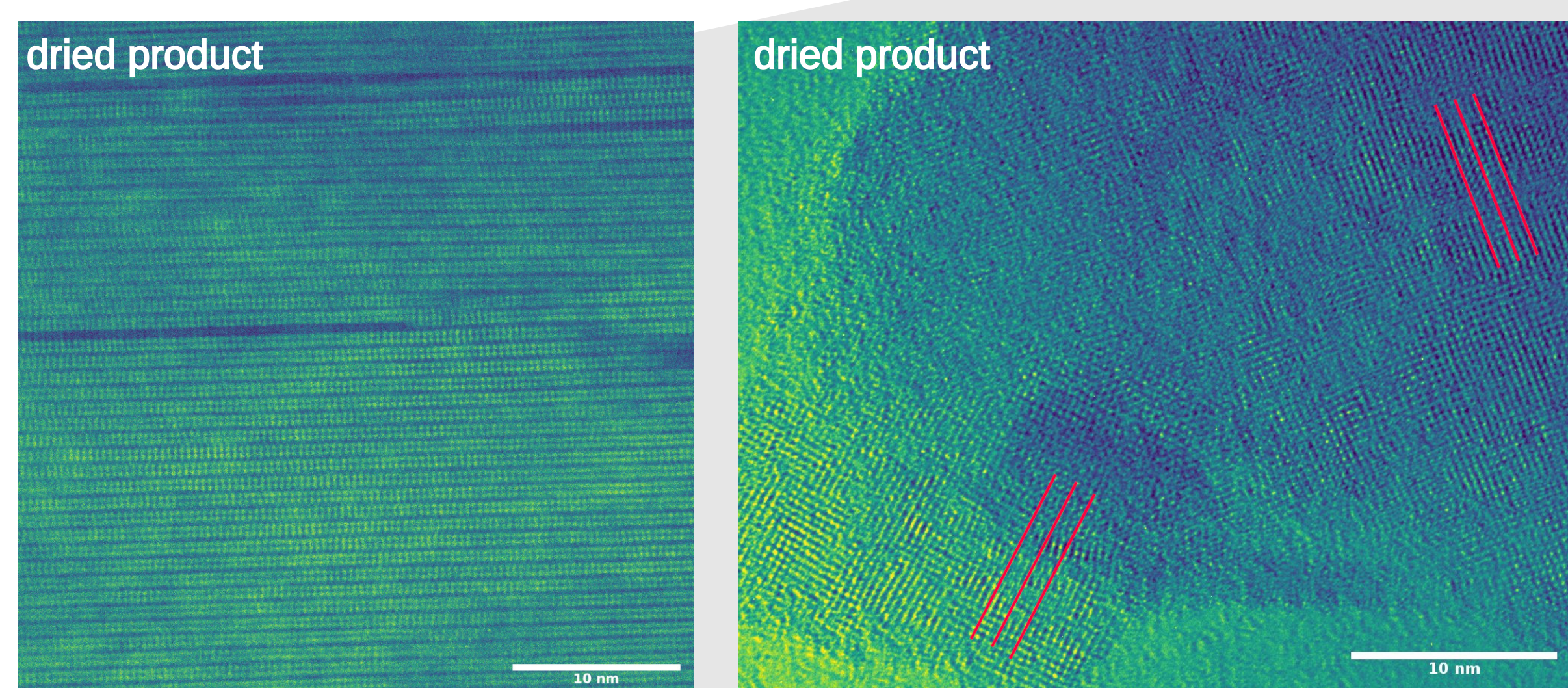
DESY Beamline P21.1 $E = 101.2\text{keV}$ RAPDF setup



ex-situ total scattering | PDF



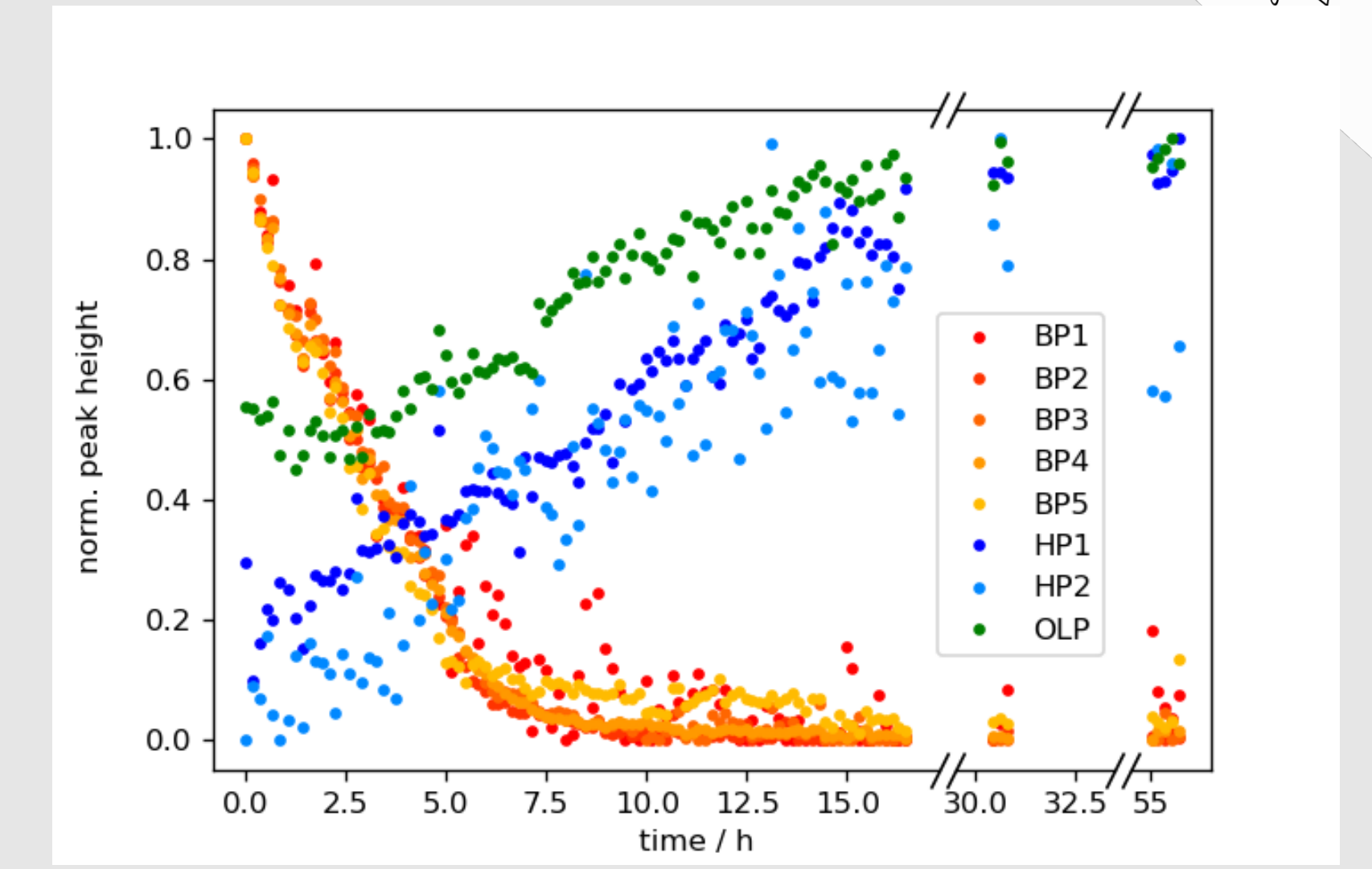
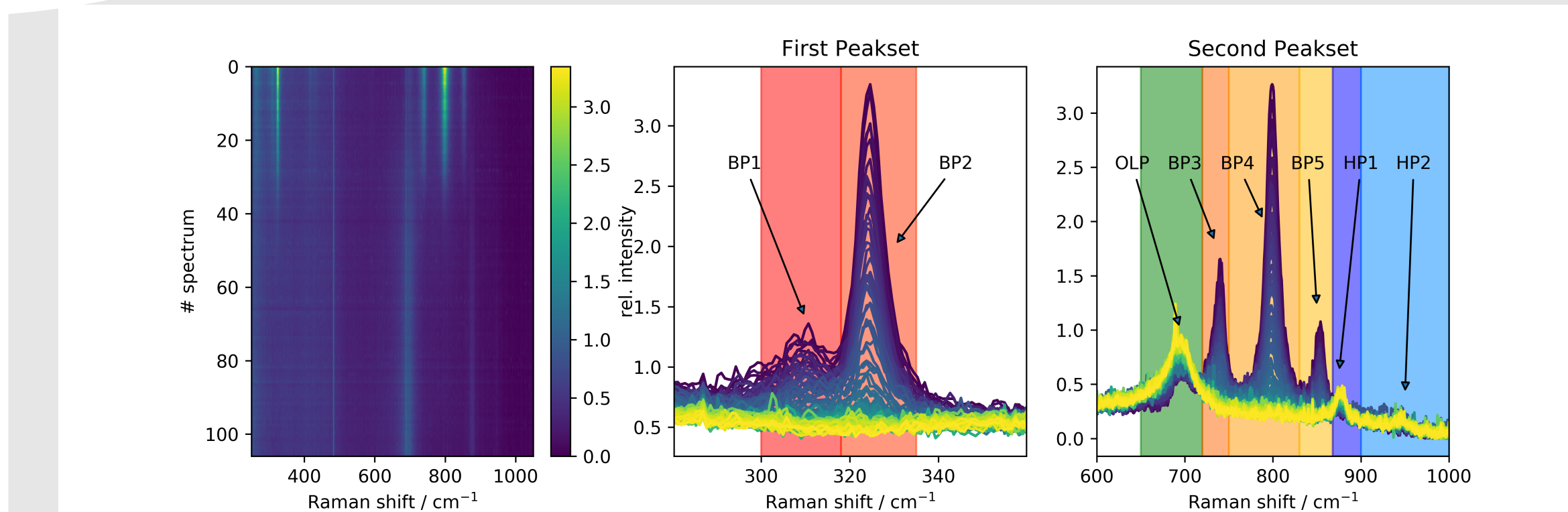
- Disorder indicated by loss of correlations in high r-range
- Peak shifts mainly in interlayer correlations, also some intralayer reorientation
 - $\text{H}_2\text{W}_2\text{O}_7 \cdot \text{H}_2\text{O}$ structure is not just $\text{H}_2\text{W}_2\text{O}_7$ with larger layer spacing
 - Fitting of calculated PDFs: relative weight of WO-layer remains constant but fails to describe intermediate structure satisfactorily
 - Fitting with end members shows different behaviour than Raman, maybe due to changes in scattering contributions or bulk sensitivity



- Delamination and crack formation during leaching
- TEM of dried product indicate rotation of layers, e.g. turbostratic disorder

SEM | TEM

- No peak shifting, distinct two-phase system
- In-plane vibrations (OLP peak) constantly present, layer remains intact
- Structural decoherence due to rapid BiO dissolution and slower evolution of intermediate structure peaks



Outlook

- Can we tune the reaction to reduce disorder, e.g. with time, molarity, temperature?
- Can we describe the local changes in the WO layer, e.g. PDF decomposition?
- Can we model the reaction interface and its propagation, also for drying process?

in-situ Raman spectroscopy