DISCOVER NON-AMBIENT X-RAY DIFFRACTION

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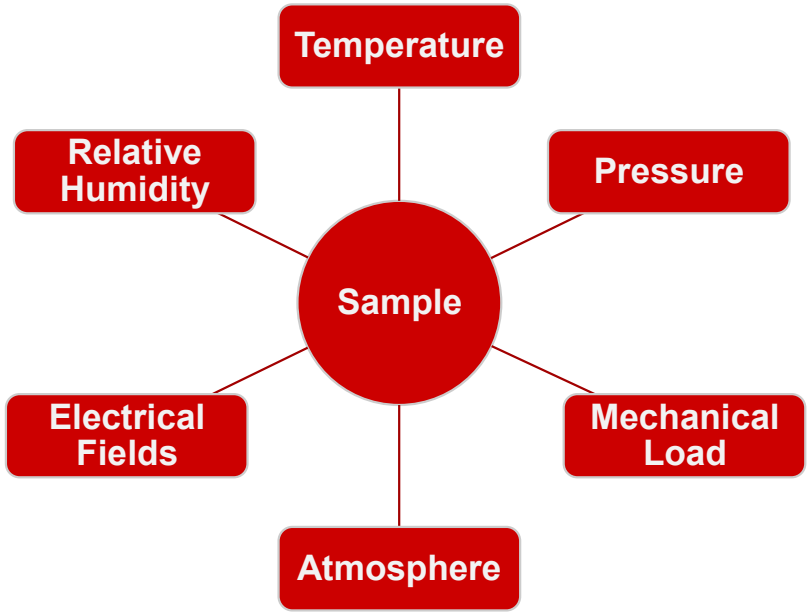
CANADIAN POWDER DIFFRACTION WORKSHOP 19 (CPDW 19)

AGENDA

- Basic principles of Non-Ambient X-ray diffraction
- The typical set-up
- Practical considerations in NA-XRD
  - Temperature accuracy and validation
  - Sample height variations
- Application overview

BASIC PRINCIPLES OF NA-XRD

- Non-ambient X-ray diffraction (NA-XRD) is an indispensable technique to understand the behavior of materials under non-ambient conditions
- Material properties may change significantly when exposed to non-ambient conditions.



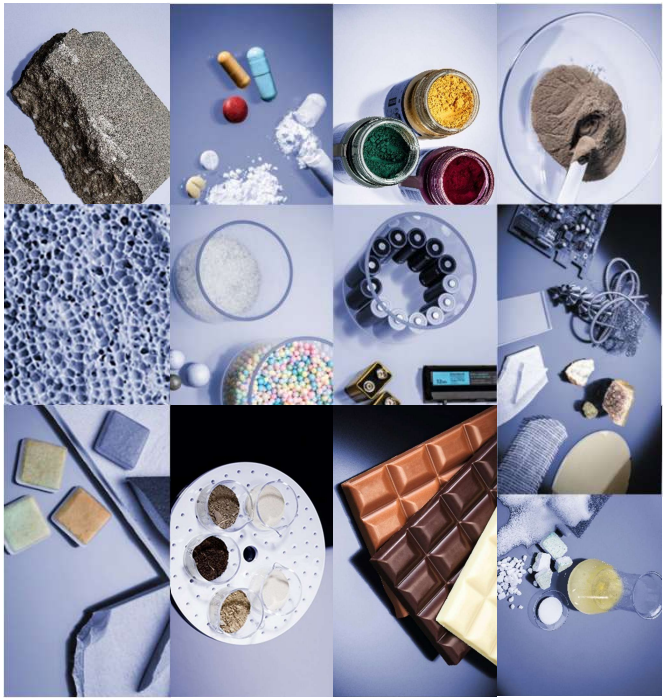
Influence on:

- Crystalline Structure
- Composition
- Crystallite Size
- Internal Stresses
- Surface Layer properties

BASIC PRINCIPLES OF NA-XRD

NA-XRD allows to study a variety of material changes in-situ.

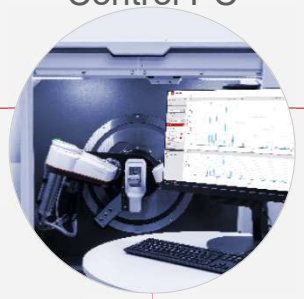
Processes	Application fields
Material formation and structures	Alloys, drug API's, catalysts, minerals..
Annealing due to heat treatment	Alloys, ceramics, polymers..
Calcination and sintering	Catalysts, MOF's, zeolites..
(De-) hydration processes	Building materials, pharmaceuticals, food industry..
Material changes during operation	Catalysts, refractory materials, batteries..



TYPICAL SET-UP FOR NA-XRD

Anton Paar

Control PC



Diffractometer Control

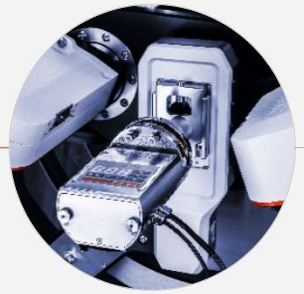
NA-XRD Attachment Control:
- Sending and receiving temperature
- Heating / Cooling power
- Status

DIFFRACTOMETER

Control Unit

Z-stage Control:
- Sample alignment
- Height alignment

Adapter / Z-Stage



Mounted on

Non-Ambient XRD attachment

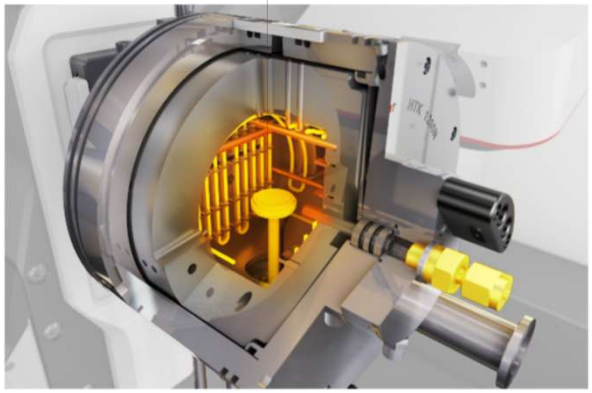
Mounted on

NA-XRD – HEATER DESIGNS

Environmental Heaters

- Heat Transfer from all sides, via surrounding heater
- Capillary, spinner
- RT up to 1500°C

SAMPLE placement



Direct Heaters

- Heat Transfer from One side, with heater below the sample

Strip Heaters:
- RT up to 2300°C

Heating Plates / Heater-Cooler Combi
- - 190°C up to 1100°C

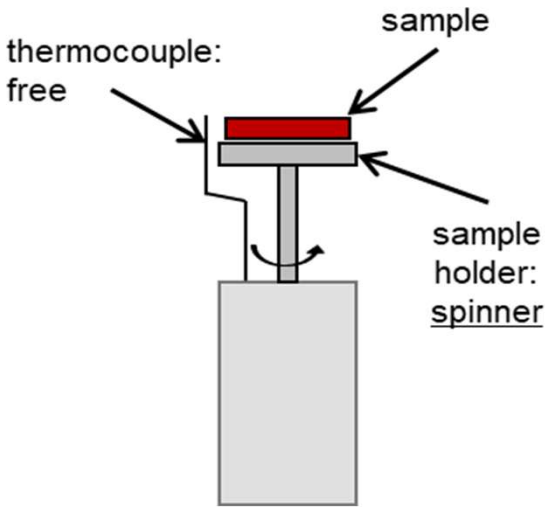
SAMPLE placement

NA XRD – HEATER DESIGNS

Environmental Heaters	Direct Heaters
Advantages	
✓ Good temperature homogeneity	✓ Very high temperatures possible
✓ More accurate sample temperature measurement	✓ Very fast heating / cooling rates
✓ Easy sample exchange	✓ Simpler design
✓ Inert sample holders, Sample spinner available	✓ Temperature-control less dependent on the atmosphere in chamber
Challenges	
× Thermal expansion	× Sample preparation difficult, reactions between sample and sample holder possible (especially for strip heater)
× Slower heating / cooling rates	× Less uniform sample temperatures
× Lower upper T-limit	× Larger sample-temperature deviations

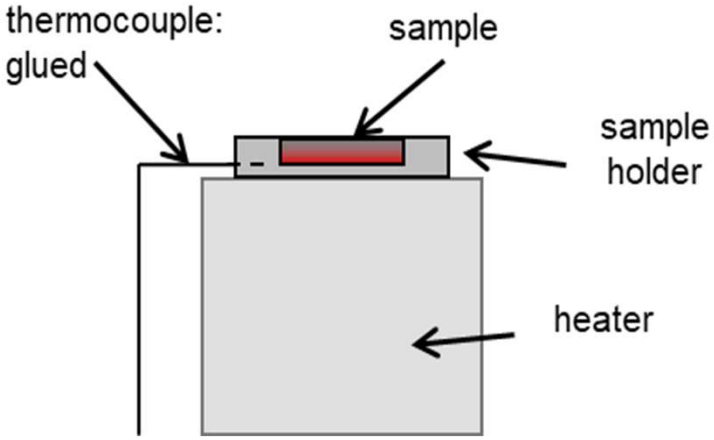
NA XRD – TEMPERATURE MEASUREMENT

TEMPERATURE SENSOR (RTDS OR THERMOCOUPLES) POSITION



Close to the sample but without contact:

- Sample holder rotation possible



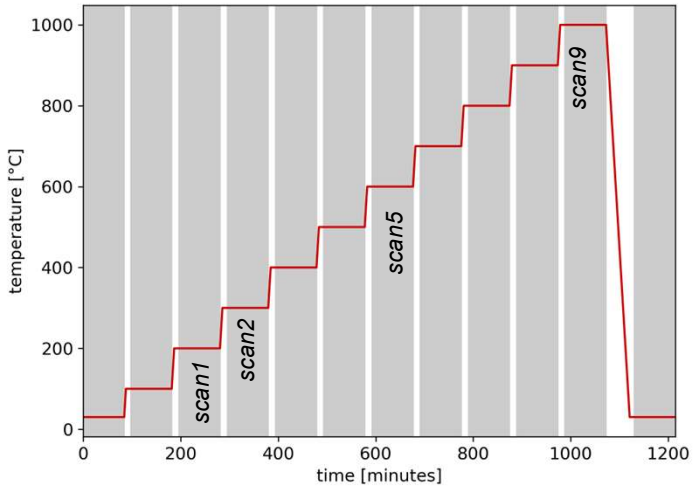
Inside / On the sample holder:

- Thermal contact between sensor and sample holder
- Heat transfer from sample holder to sample

NA-XRD – Measurement Strategies

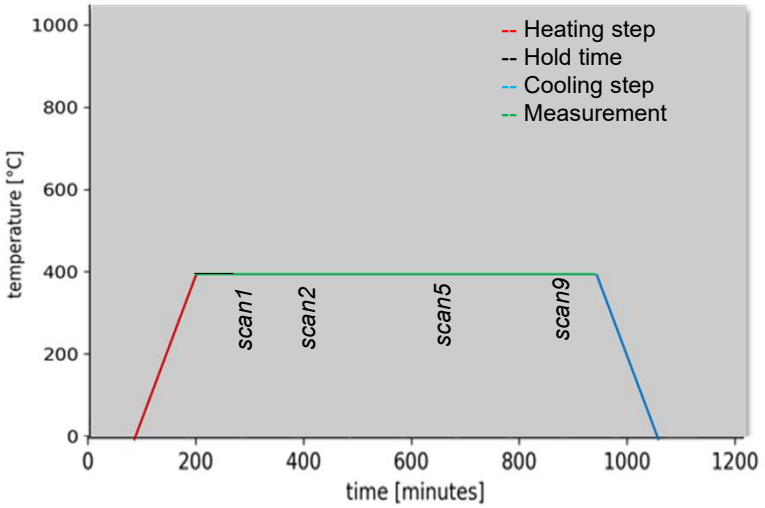
- Temperature-dependent measurements

e.g. phase-transistion



- Time-dependent measurements

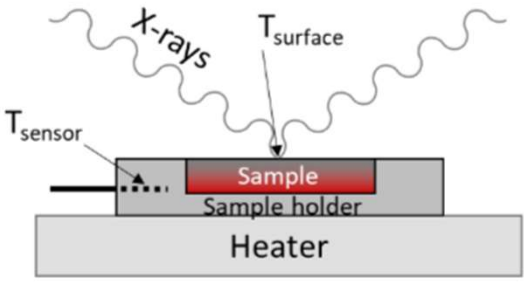
e.g. reaction kinetics



PRACTICAL CONSIDERATIONS IN NA-XRD

SAMPLE TEMPERATURE ACCURACY

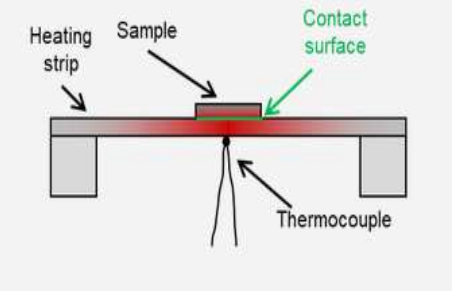
- Specified temperatures always refer to the temperature of the sample holder and **NOT** the sample
- The location of the temperature measurement and the area under investigation are different
- Deviation between the measured temperature and the sample surface temperature is expected

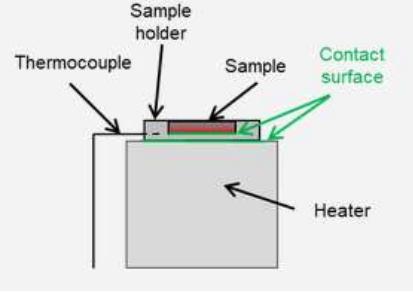


SAMPLE TEMPERATURE ACCURACY

INFLUENCES ON TEMPERATURE DEVIATION

- Design of non-ambient XRD attachment
  - Direct or environmental heater
- Applied atmosphere
  - Vacuum or gas atmosphere
- Thermal properties of the sample
  - Heat conductivity, sample thickness
- Thermal contact
  - Surface between heater and sample is crucial





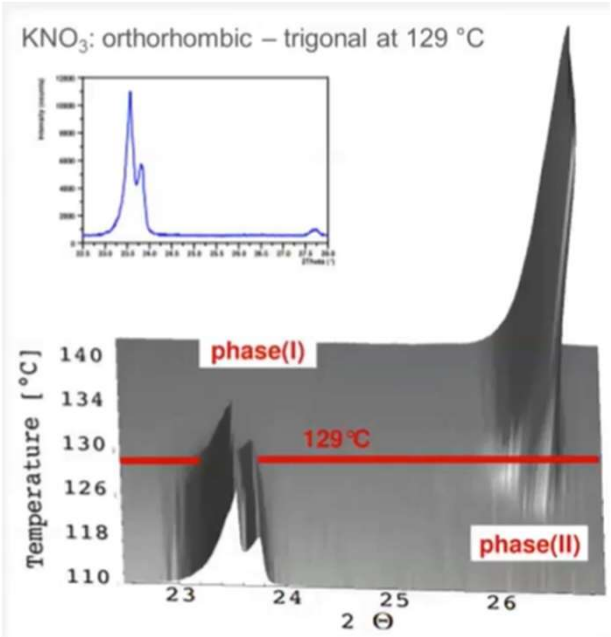
NA XRD – TEMPERATURE VALIDATION

- Temperature validation: Correlating the sensor temperature with the true sample surface temperature

Validation methods:

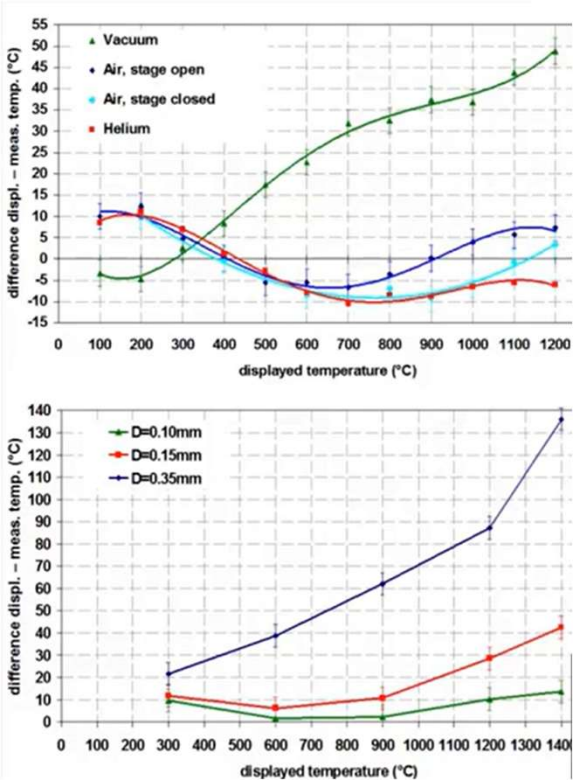
1. Phase transition**:** Monitor a crystallographic transformation or sample melting and compare the measured transition temperature with tabulated values

2. Thermal expansion**:** Measure the change of the lattice parameter(s) during heating / cooling and compare it with thermal expansion curves from literature



NA XRD – TEMPERATURE VALIDATION

- Validation must be done under the same conditions as the measurements (gas type, pressure, sample thickness, …)
- The validation/ reference sample should have similar thermal properties as the sample (color, type of material, …)
- Validation only makes sense if the temperature deviation is reproducible.



Substance	Transition Temp [°C]:	Type [1]	Lit. [2]	Substance	Transition Temp [°C]:	Type [1]	Lit. [2]
NH_4NO_3	54	p.t.	1	SiO_2	573	p.t.	1
NH_4NO_3	127	p.t.	1	Li_2SO_4	577,85	p.t.	3
KNO_3	128,7	p.t.	2	K_2SO_4	584	p.t.	1
In	156,5985	m.p.	3	Sb	630,5	m.p.	4
$RbNO_3$	166	p.t.	2	Rb_2SO_4	653	p.t.	5
$RbNO_3$	222,7	p.t.	2	Al	660,323	m.p.	3
Sn	231,928	m.p.	3	KCl	776	m.p.	4
Bi	271,4	m.p.	2	NaCl	804	m.p.	4
$RbNO_3$	285	p.t.	1	Bi_2O_3	820	m.p.	4
$KClO_4$	299,4	p.t.	2	Ag	961,78	m.p.	3
Cd	321	m.p.	2	NaF	988	m.p.	4
Pb	327,46	m.p.	3	Au	1064,18	m.p.	3
KNO_3	334	m.p.	2	K_2SO_4	1069	m.p.	4
Zn	419,527	m.p.	3	Cu	1083	m.p.	4
$AgSO_4$	426,4	p.t.	2	CaF_2	1360	m.p.	4
CuCl	430	m.p.	4	Ca_2SiO_4	1425	p.t.	4
CsCl	476	p.t.	1	Fe	1535	m.p.	4

Validation methods:

Phase transition – Well known references

NA XRD – TEMPERATURE VALIDATION

Phase Transition	Thermal Expansion
Advantages	
✓ No special requirements with regards to data quality	✓ Complete temperature range can be validated with one sample material
✓ Straight-forward data evaluation	✓ Method can be applied up to very high temperatures
Challenges	
× Only one (max. a few) temperature value per reference material	× Data evaluation can be complex
× Limited availability of feasible phase transformations (especially at low temperatures)	× Inaccurate at low temperatures (< 400°C), due to small lattice expansion

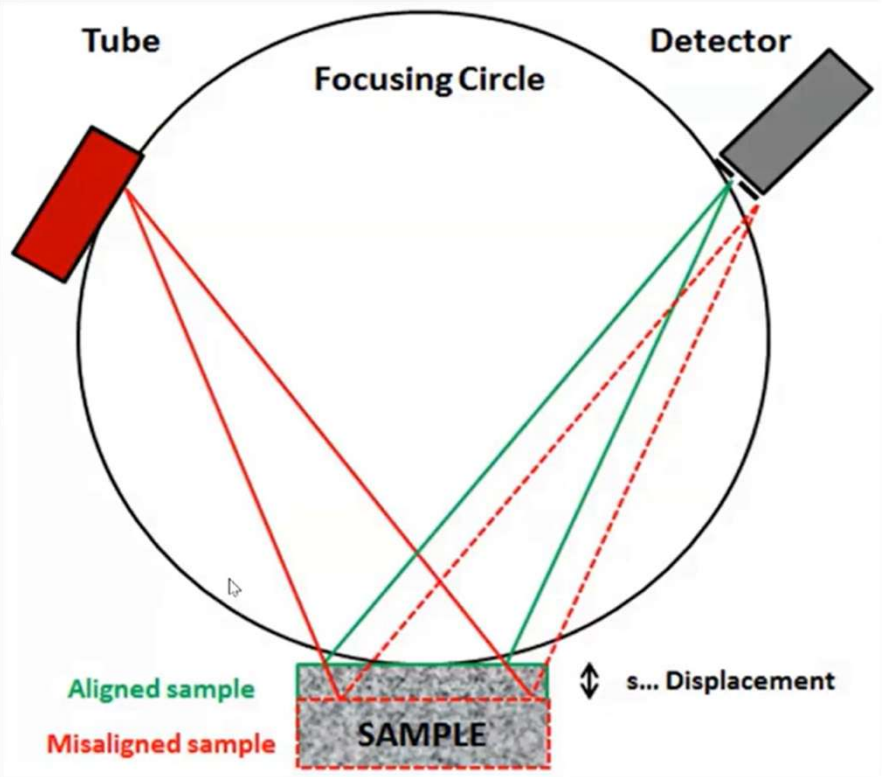
THERMAL EXPANSION OF THE SAMPLE HOLDER

Effect of sample height variation:

- Heating leads to thermal expansion of materials
- Thermal expansion of sample holder results in misalignment of the sample height → peak shift in diffraction pattern

$$\Delta 2\theta = \frac{-2s\cos\theta}{R}$$

s… magnitude of displacement
R… radius of goniometer
θ… scattering angle in radians



SAMPLE HEIGHT VARIATIONS

Fig.: Typical sample holder for HTK 1200N

Possible approaches:

! Ignore the effect

! Correct during data analysis

! Use a parallel beam geometry

Recommended:

✓ **Correct the displacement during the measurement**

› Manual re-alignment

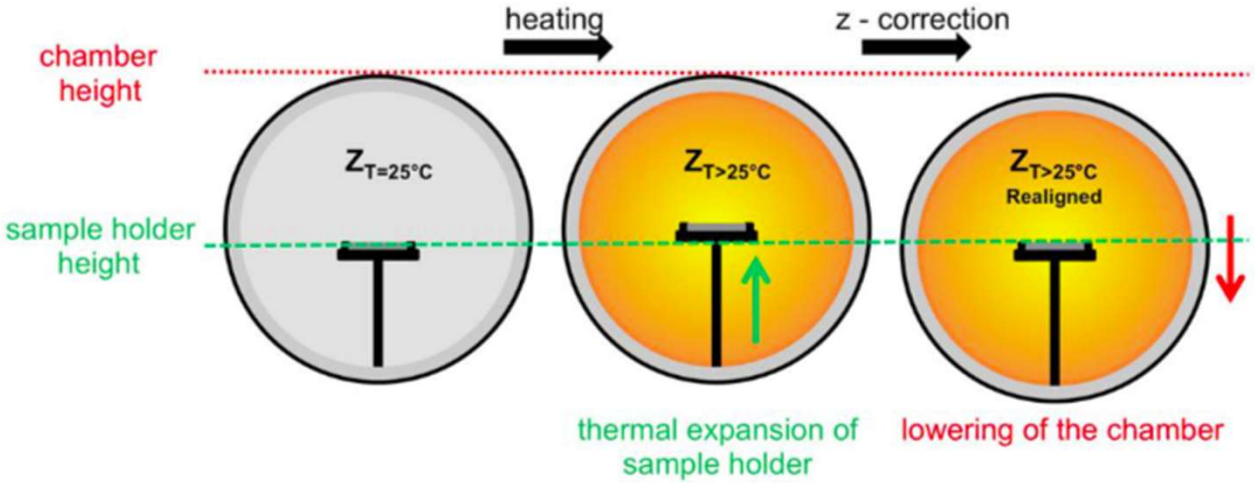
› Automated Z-stage compensation

SAMPLE HEIGHT VARIATIONS
REALIGNMENT (Z-ALIGNMENT)

Correct height alignment is highly important for good diffraction data!

- This is done by lowering the complete NA-XRD attachment (importance of heigh-alignment stage) according to a predefined correlation table (instrument specific) or temperature vs. height change.

Fig.: Typical sample holder for HTK 1200N



APPLICATIONS

STRUCTURAL CHANGES IN BENTONITE DURING HEATING

APPLICATION 1

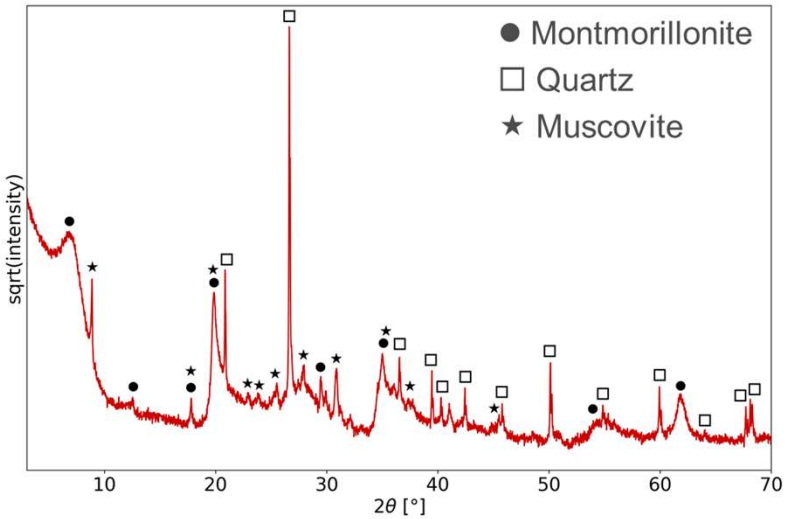
- Bentonite is a naturally occurring swelling clay that can absorb large amounts of water.
- Its application include drilling muds, casting sands, ceramics, catalysts, adsorbents and geological barrier materials.
- In-situ XRD measurements with an environmental heater monitors structural and phase changes during heating up to 1000 °C.

HTK 1200N: environmental heater with high temperature homogeneity _ Temperature range: 25 °C to 1200 °C Atmospheres: Air, inert gas, vacuum (10^{-4} mbar), O_2

STRUCTURAL CHANGES IN BENTONITE DURING HEATING

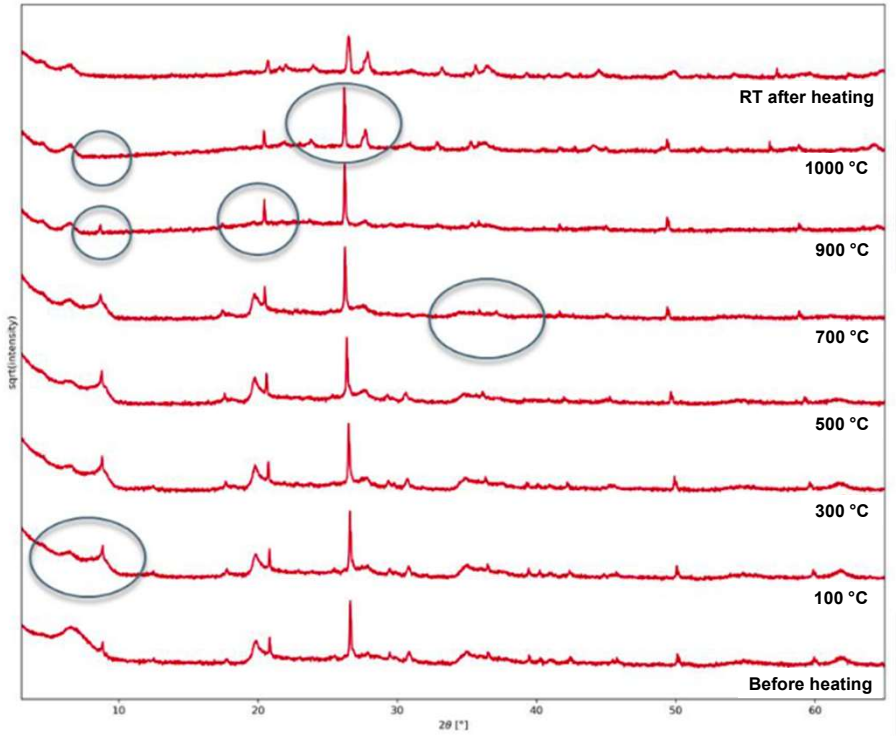
APPLICATION 1

Room temperature



Diffractogram of the starting material consisting of montmorillonite, quartz and muscovite.

In-situ heating



Selected diffractograms from the in-situ experiment.

EFFECT OF HYDROPHOBIC SURFACES ON WATER FREEZING

APPLICATION 2

- Water covers approx. 70% of the planet and a significant amount of water exists as vapor in the atmosphere.
- Water is the only non-metallic substance that expands as it freezes.
- Expanding water can damage materials or surfaces and can lead to bursting of containers or pipes
- Frozen roads also lead to many car accidents every year.

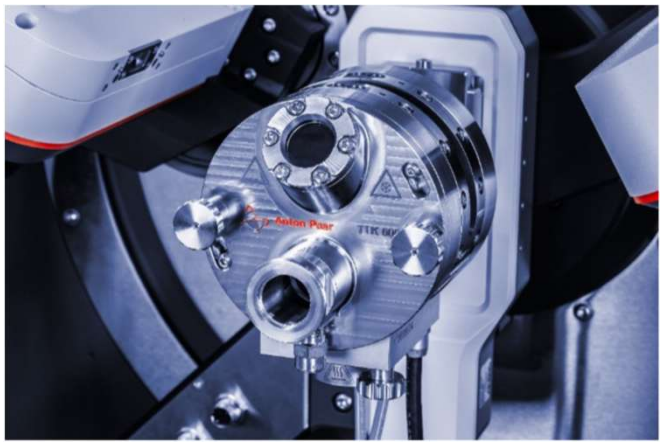
EFFECT OF HYDROPHOBIC SURFACES ON WATER FREEZING

APPLICATION 2

Experiment

- The correlation between hydrophobicity of surfaces and the freezing point of water droplets deposited on the surface was investigated:

- Experiments were performed with low temperature chamber with liquid nitrogen cooling from -5 °C to -25 °C.

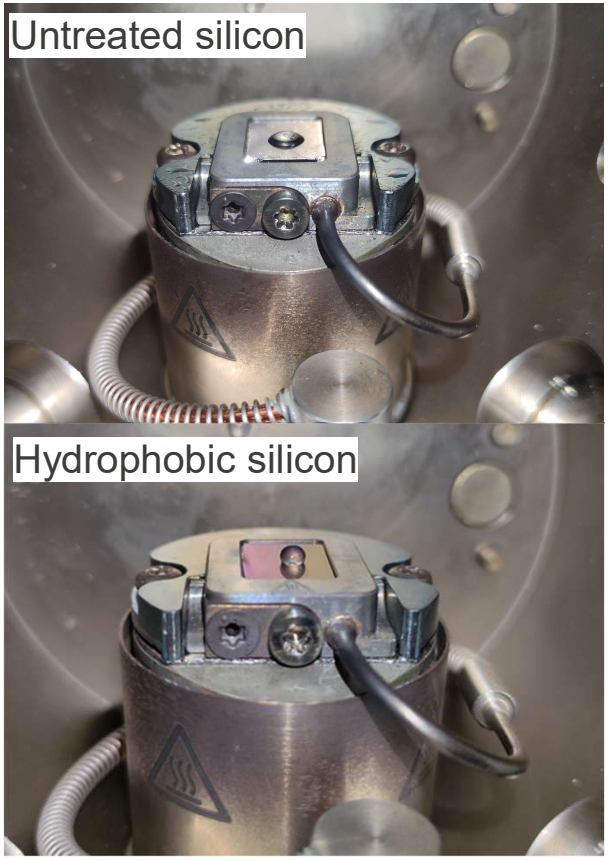


TTK 600: Low-Temperature Chamber
Temperature range: -190°C to 600°C.
Measurements can be performed in air, inert gas or high vacuum (10-4 mbar)

EFFECT OF HYDROPHOBIC SURFACES ON WATER FREEZING

APPLICATION 2

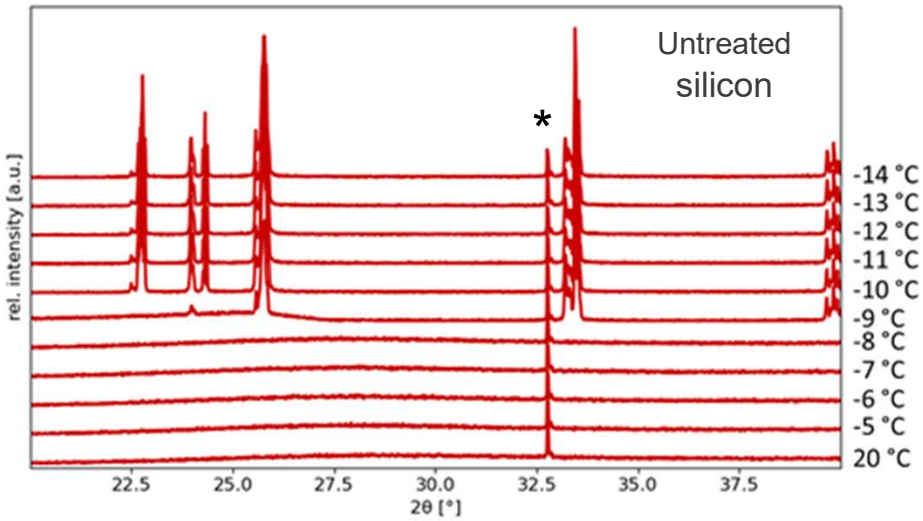
- Silicon (Si) wafers were used as substrates.
  - One plate was untreated and served as reference to determine the change of the freezing point.
  - On silicon plate featured hydrophobic surface coating (grad100)
- Water droplet (0.1 mL) was deposited on surface.



EFFECT OF HYDROPHOBIC SURFACES ON WATER FREEZING

APPLICATION 2

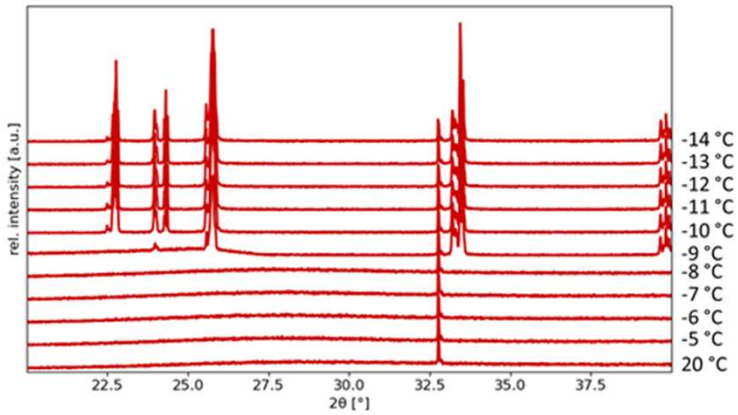
- As expected, no crystalline reflections of water are visible at 20 °C.
- The freezing point of water on the untreated surface is at -9 °C.
- The reflection labeled * is most likely Si 200, which is often observed in (111) oriented Si wafers.



EFFECT OF HYDROPHOBIC SURFACES ON WATER FREEZING

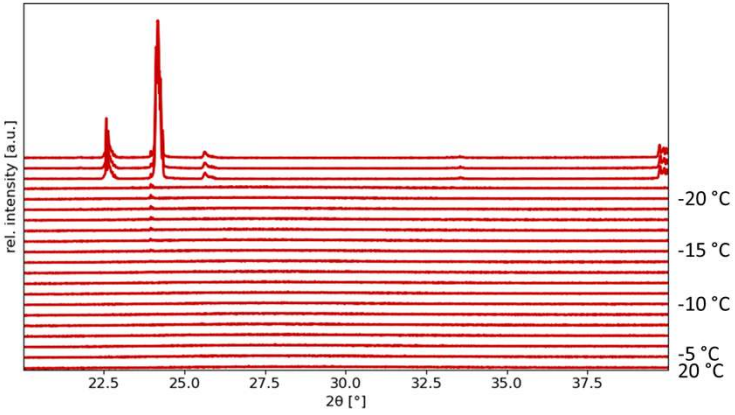
APPLICATION 2

Untreated silicon

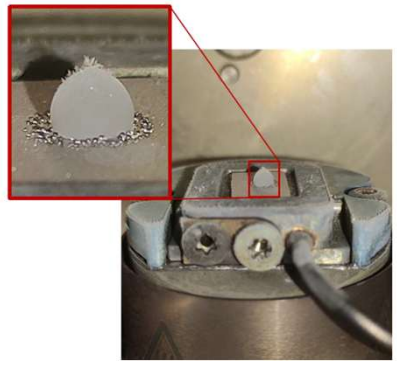


The freezing point of water on the untreated surface is at -9 °C.

Hydrophobic silicon



The freezing point of water on the hydrophobic surface is at -22 °C.



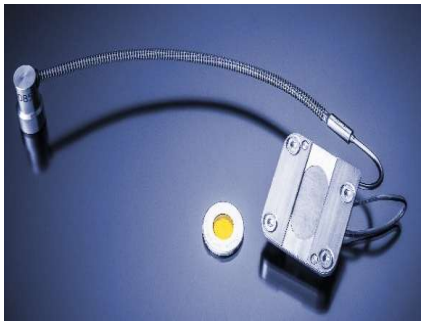
OPERANDO XRD UNDER NON-AMBIENT CONDITIONS

APPLICATION 3

Objective:

Monitor XRD peak shifts during electrochemical charge cycling.

Evaluate structural changes over a temperature range of −5 °C to 55 °C.



Battery sample holder (Reflection)

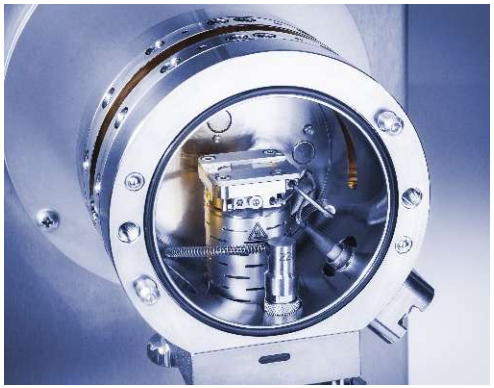
Measurement configuration:

- Cu X-ray tube
- Bragg-Brentano geometry using a monochromator
- External potentiostat for for operando charge/discharge cycling

Sample:

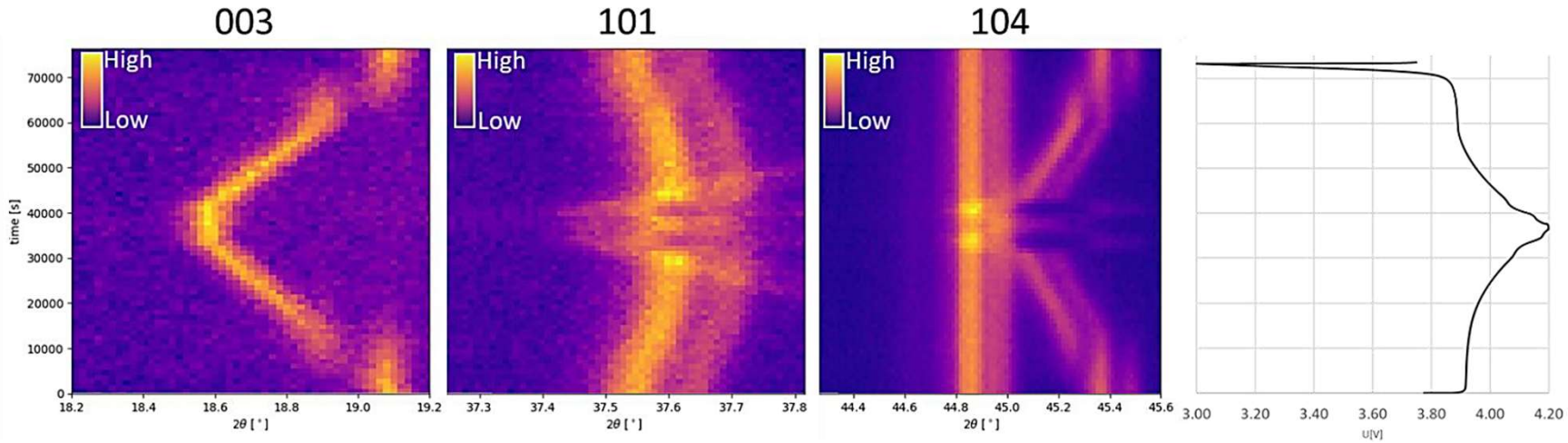
LiCoO2 (LCO) half-cell in coin cell format

- Li metal anode
- Positive electrode: aluminum foil coated with LCO



TTK 600 Low Temperature Chamber for in situ and in operando XRD studies with temperature range of -180 to +130 °C.

PEAK SHIFTS DURING BATTERY CYCLING



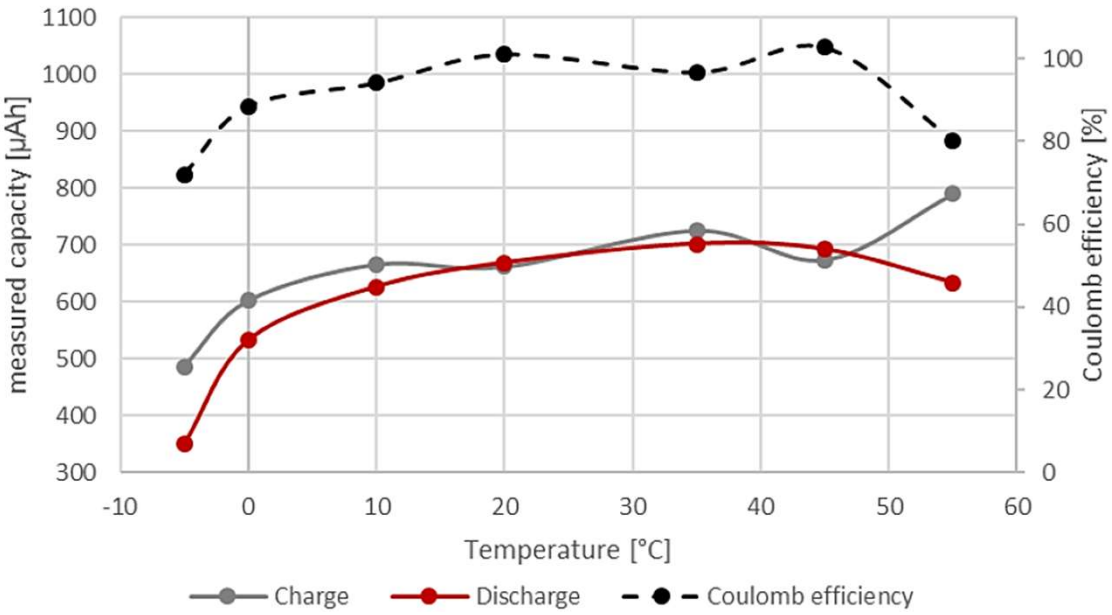
Heat maps of XRD scans for 003, 101, and 104 reflection of LCO during battery cycling (left), and charging/discharging curve (right).

In situ XRD monitor the structural changes in real time:

- Peak shifts
- Lattice parameter changes
- Phase transitions

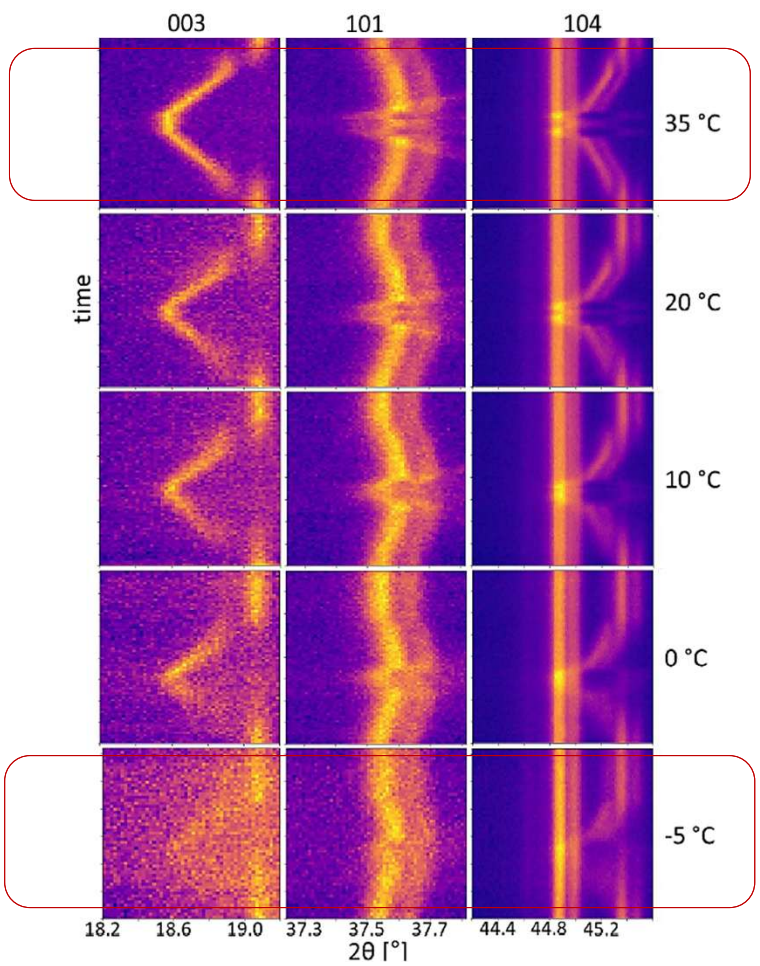
NON-AMBIENT CYCLING OF LCO

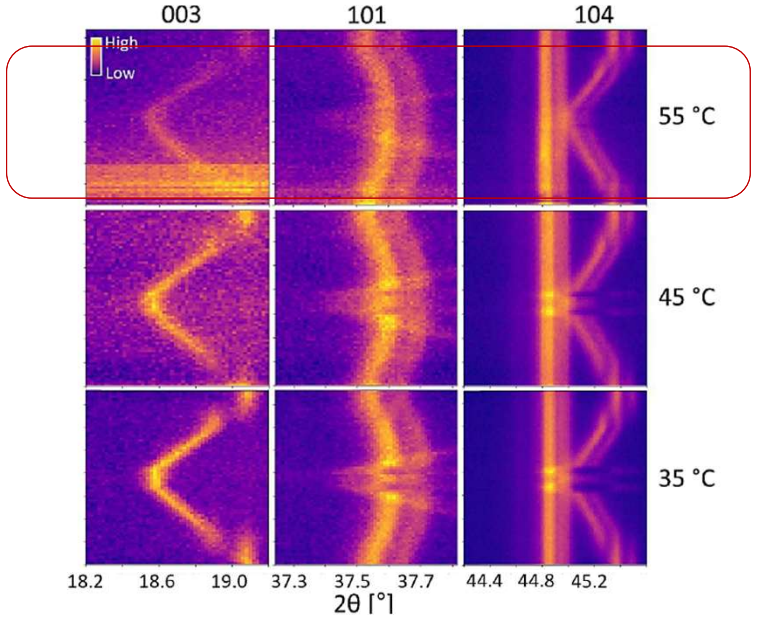
- Capacity decreases at low temperatures
- Capacity is relatively stable between 10 °C and 45 °C
- At higher temperatures:
  - capacity measured during discharge drops
  - capacity obtained during charging seems to increase.



Capacity and Coulomb efficiency of LCO coin cell at different temperatures.

NA CYCLING OF LCO





Temperature-dependent contour plots of XRD scans for 003, 101 and 104 reflection of LCO during battery cycling.

NA XRD – summary

- Non-ambient XRD enables the investigation of structural changes under realistic operating conditions.
- Reliable measurements require careful control of temperature, sample alignment, and experimental conditions.
- From heating and cooling to operando battery cycling, non-ambient XRD provides direct insight into the relationship between structure and material performance.

NON-AMBIENT XRD SPECIFICATION RANGE

COVERING A HUGE RANGE OF NON-AMBIENT CONDITIONS