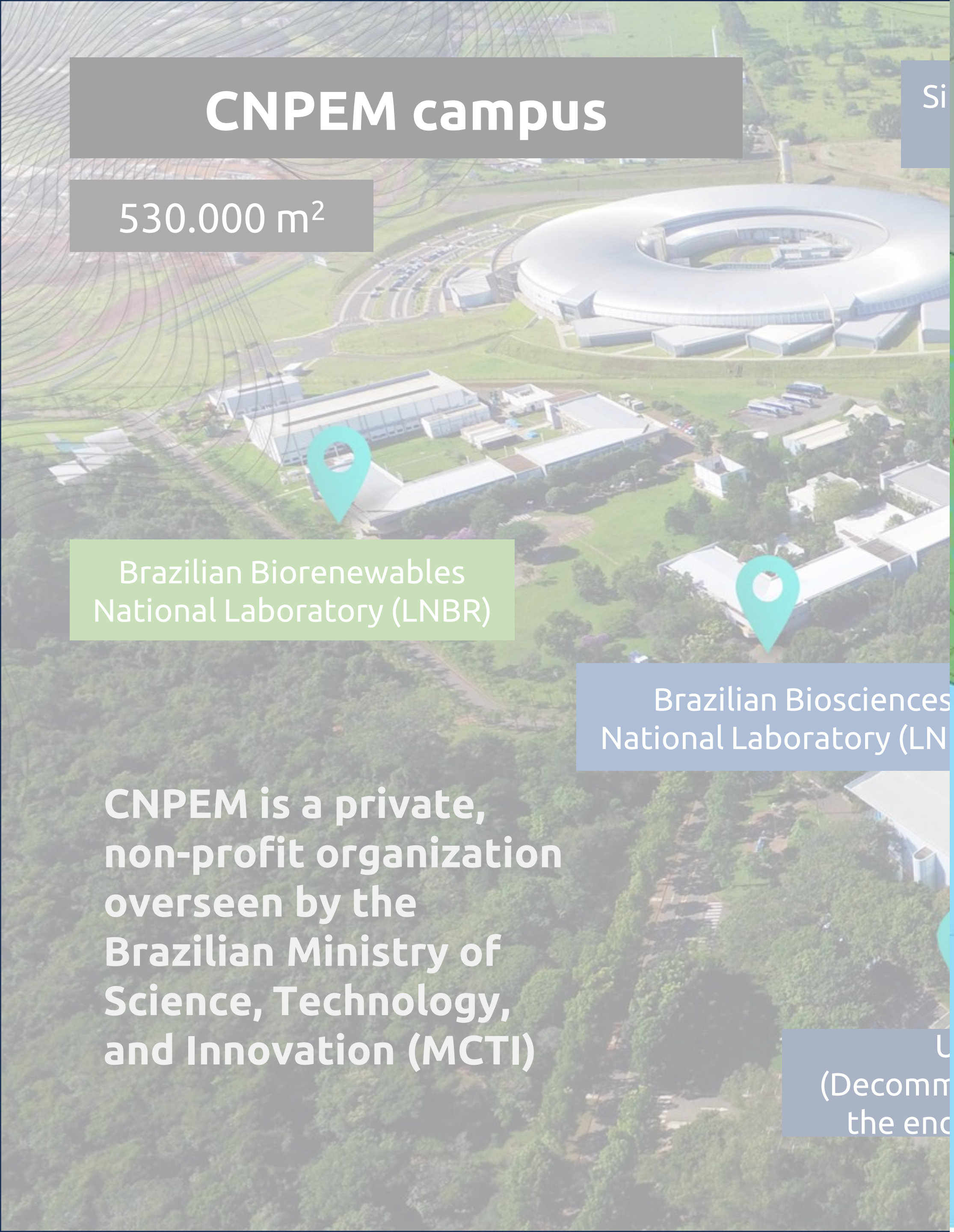
Hands-on at the PAINEIRA Powder Diffraction Beamline at Sirius

Dra. Cristiane B. Rodella
XPD Group Leader
PAINEIRA beamline coordinator

CNPEM campus

530.000 m^2

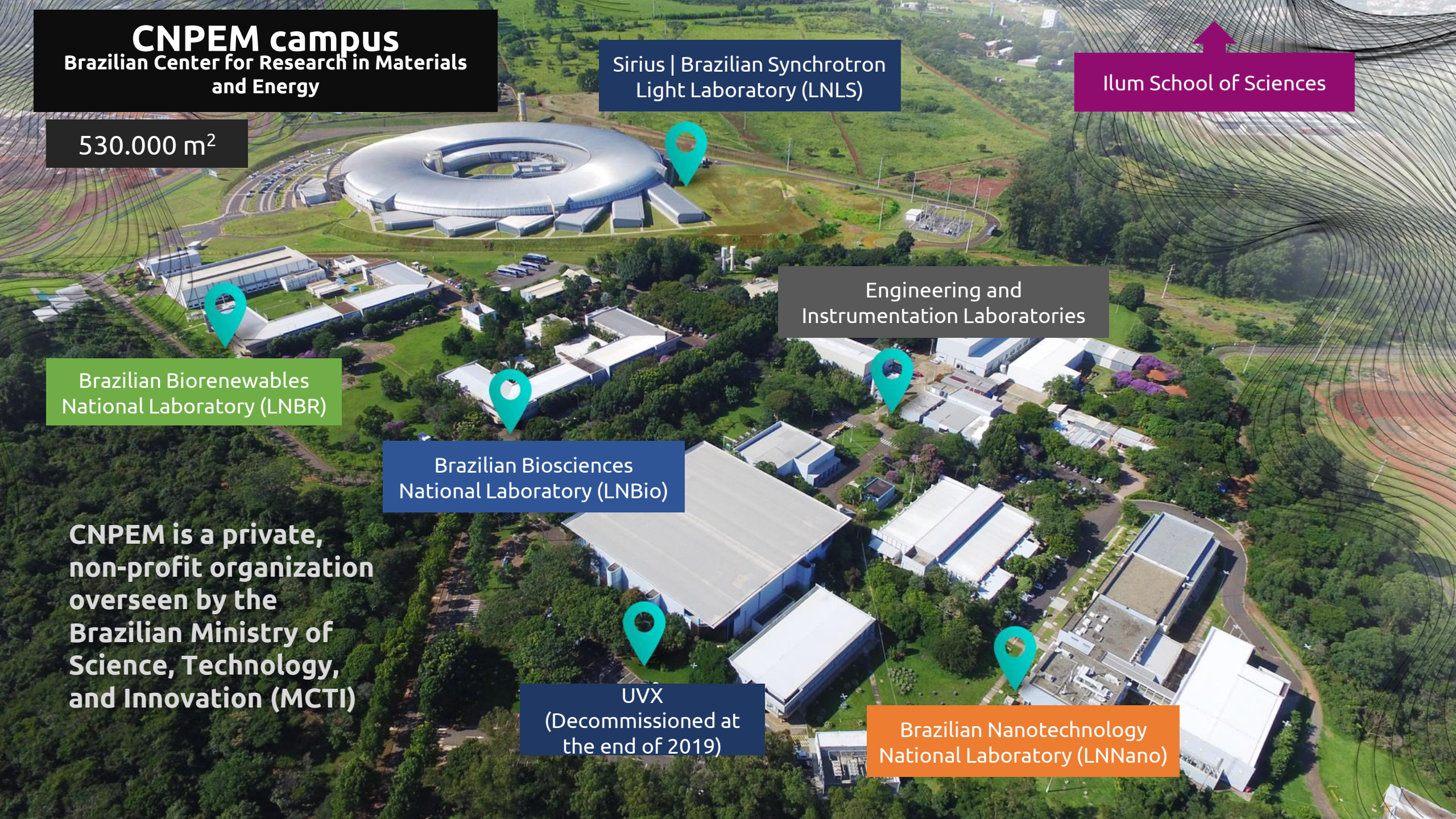


CNPEM is a private, non-profit organization overseen by the Brazilian Ministry of Science, Technology, and Innovation (MCTI)

CNPEM campus

Brazilian Center for Research in Materials and Energy

530.000 m^2



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Sirius Beamlines (2019 - 2028)

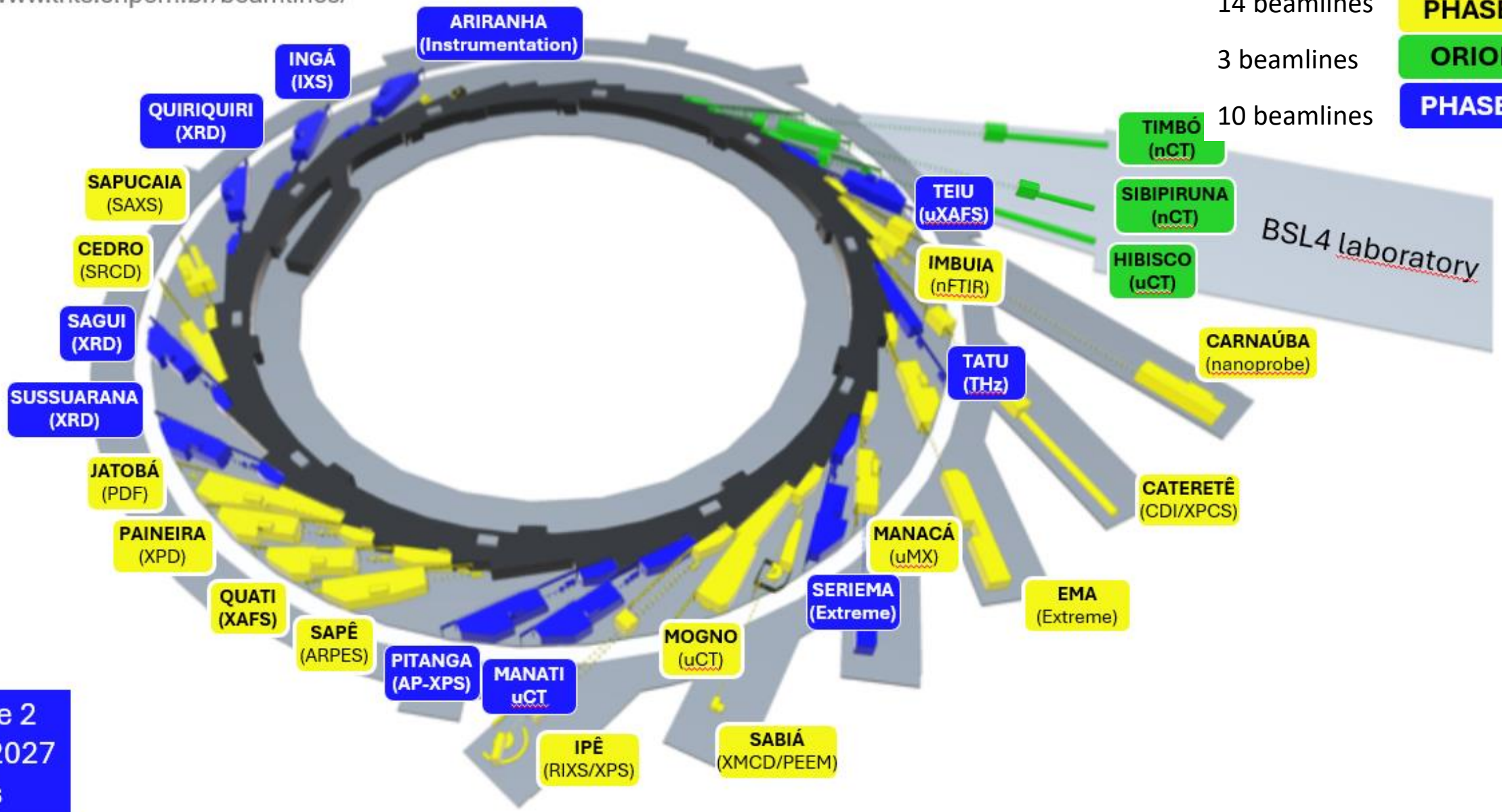
https://www.lnls.cnpem.br/beamlines/

Energy: 3.0GeV
Circumference: 518m

14 beamlines **PHASE I**

3 beamlines **ORION**

10 beamlines **PHASE II**



Sirius Phase 2
PAC 2023-2027
800M Reais

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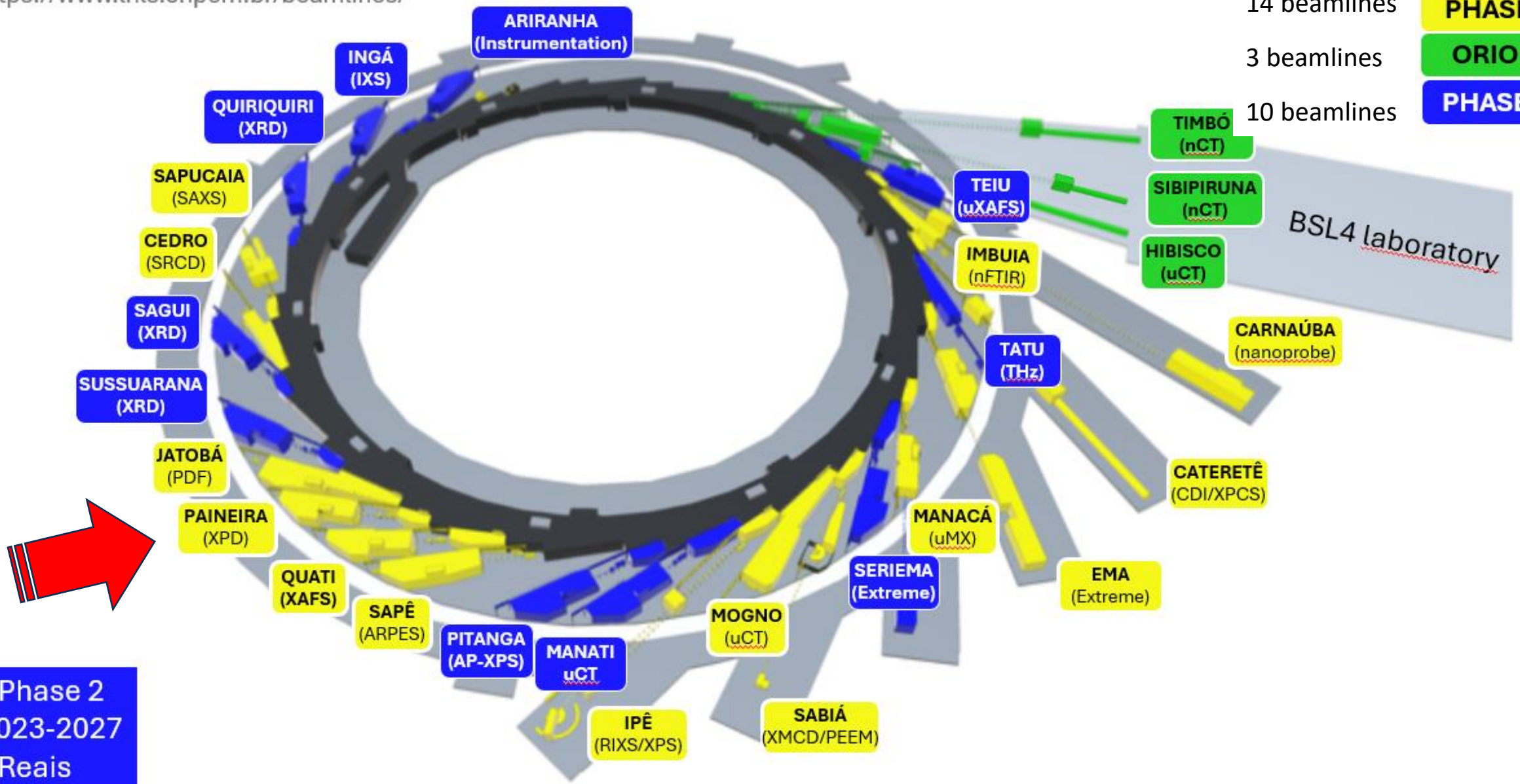

Sirius Phase 2
PAC 2023-2027
800M Reais

Advantages of using synchrotron light for the structural characterization of polycrystalline materials

Advantages of using synchrotron light for the structural characterization of polycrystalline materials

Comparison with a benchtop diffractometer using a regular X-ray source (X-ray tube)

- ✓ High intensity of the X-ray source: 10^{11} - 10^{13} (ph/s/100mA)
- ✓ Fast acquisition time: seconds to minutes (10^3 faster)
- ✓ High angular resolution: 10^2 higher resolution
- ✓ Lower instrumental parameter contribution
- ✓ Better signal-to-noise ratio
- ✓ Energy tunability

- •Larger number of samples analyzed
- •Kinetic studies
- •Identification of transient and unstable phases

- •Separation of phases that appear overlapping
- •Accurate determination of peak position and peak profile: Rietveld Refinement

Identification of minor crystalline phases

Avoid fluorescence

Ressoant scattering

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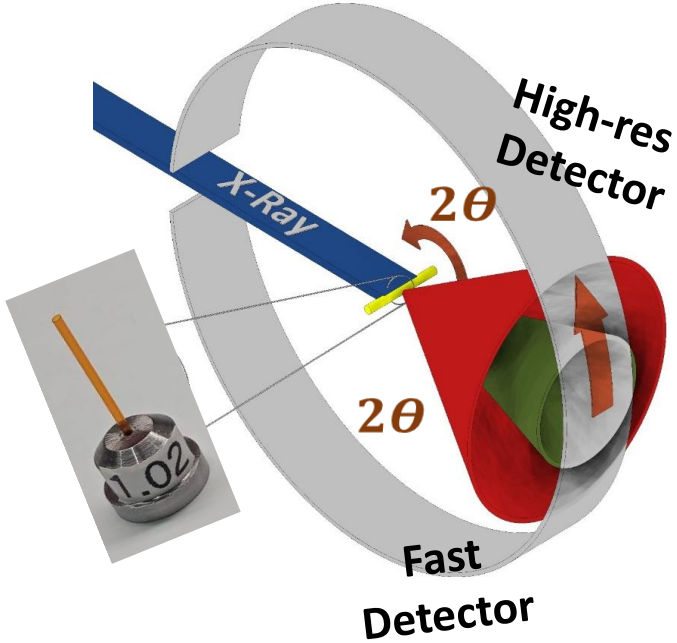
PAINEIRA beamline at SIRIUS

Dedicated facility for high-resolution and rapid XRD data acquisition from polycrystalline samples



- Crystalline phase determination and quantification
- Micro and nano-features: defects, dislocations, strain and crystal size
- Structural analysis during *in situ* and *operando* experiments (varying gases, liquids, temperature and pressure)
- Multi-analysis: mass spectroscopy and Micro-GC

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PAINEIRA beamline
Powder X-ray Diffraction

Dedicated facility to X-ray diffraction of polycrystalline materials in Debye-Scherrer geometry

Goals

- Operates in High-throughput mode (video)
- Mail-in system
- *In-situ/Operando* experiments

→ Module to control *in situ/operando* experiments for automated operation

→ User-friendly graphical interface to operate the beamline and perform *in situ/operando* experiments of the experiment

→ Software for online data visualization and qualitative data analysis

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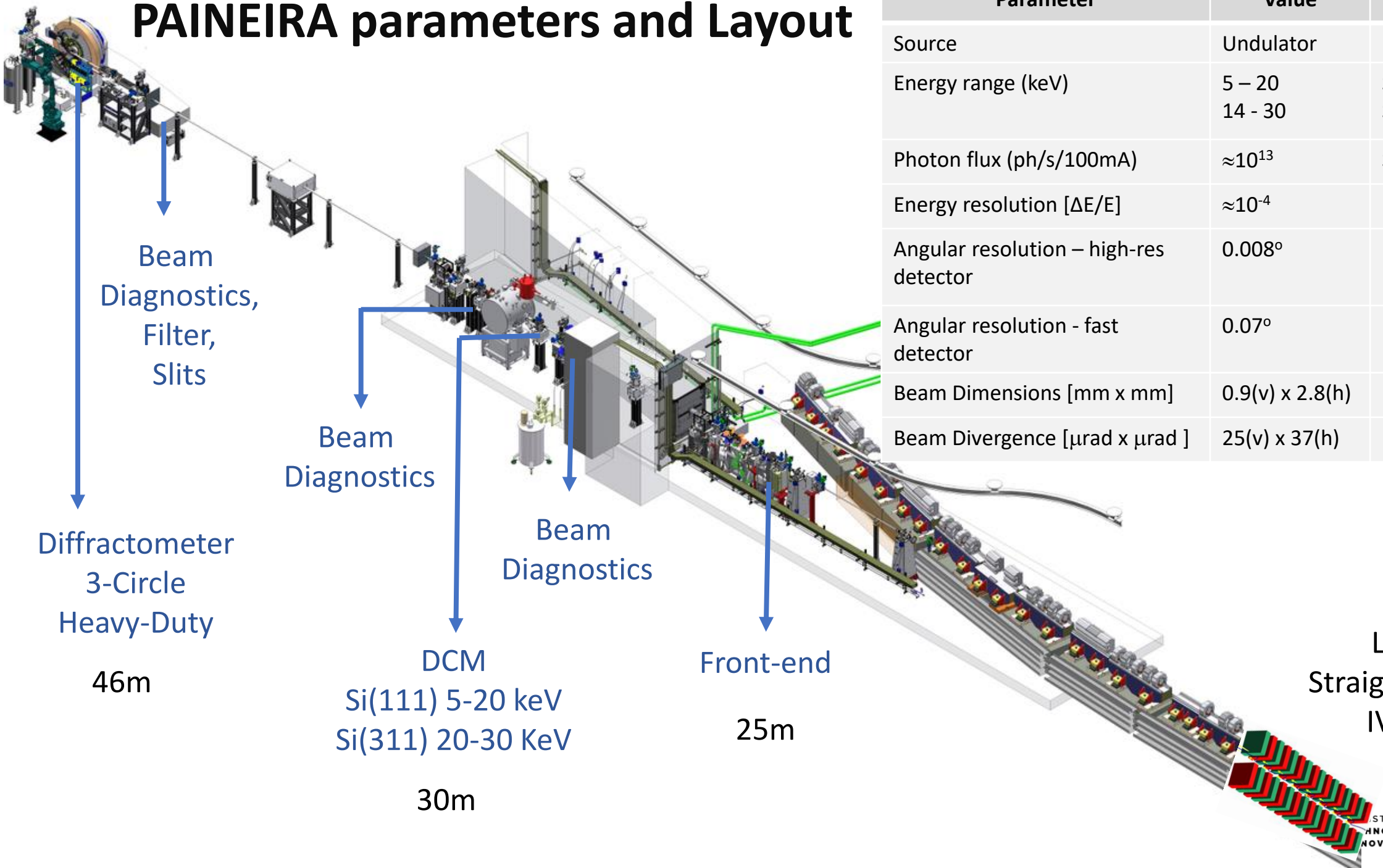
PAINEIRA parameters and Layout

Parameter	Value	Condition
Source	Undulator	IVU 18
Energy range (keV)	5 – 20 14 - 30	Si(111) Si(311)
Photon flux (ph/s/100mA)	$\approx 10^{13}$	Sample at 12 keV
Energy resolution [ΔE/E]	$\approx 10^{-4}$	15 keV
Angular resolution – high-res detector	0.008º	FWHM at 15keV
Angular resolution - fast detector	0.07º	(FWHM)
Beam Dimensions [mm x mm]	0.9(v) x 2.8(h)	(FWHM)
Beam Divergence [µrad x µrad]	25(v) x 37(h)	



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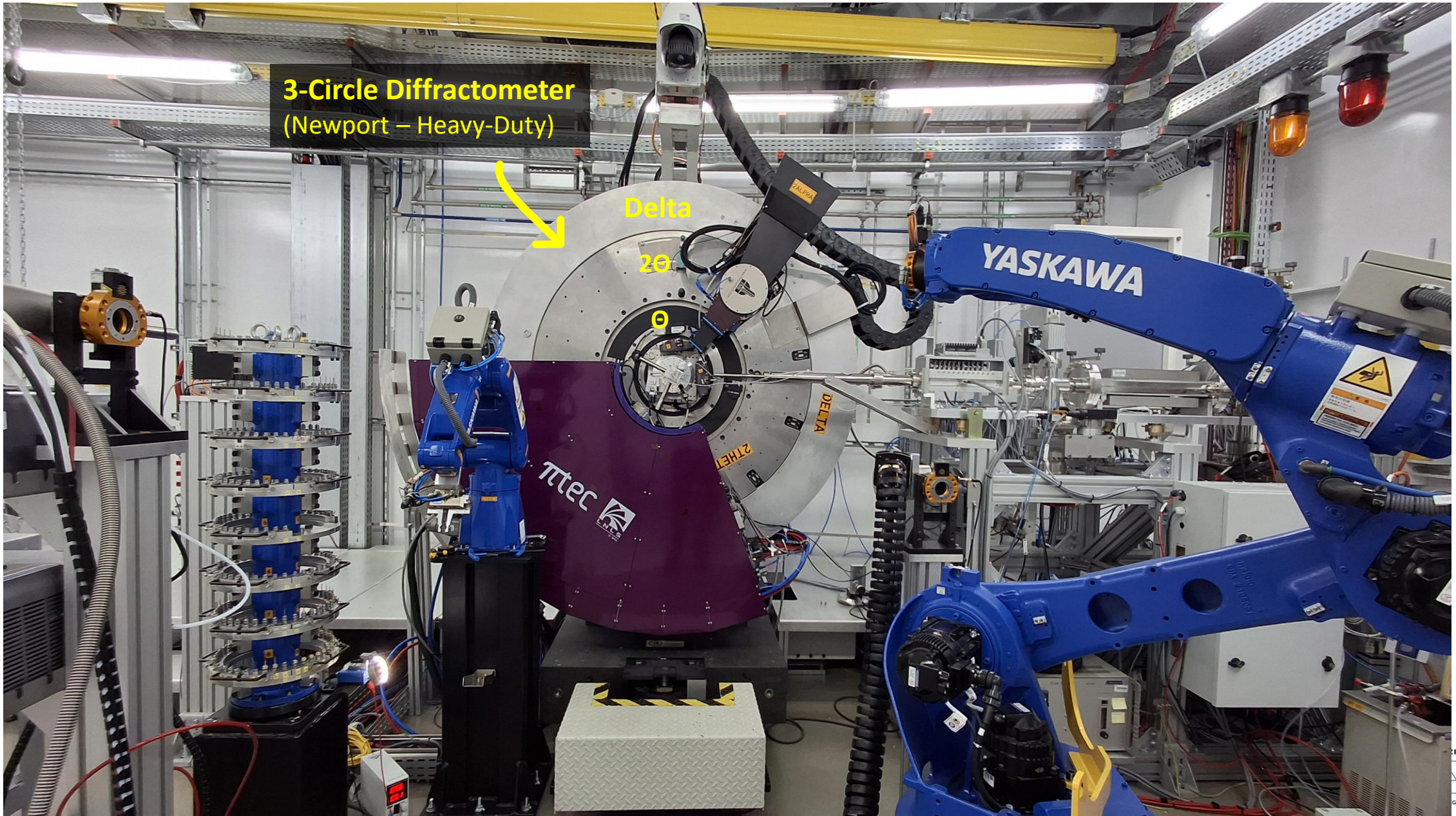
PAINEIRA beamline - Experimental Hutch



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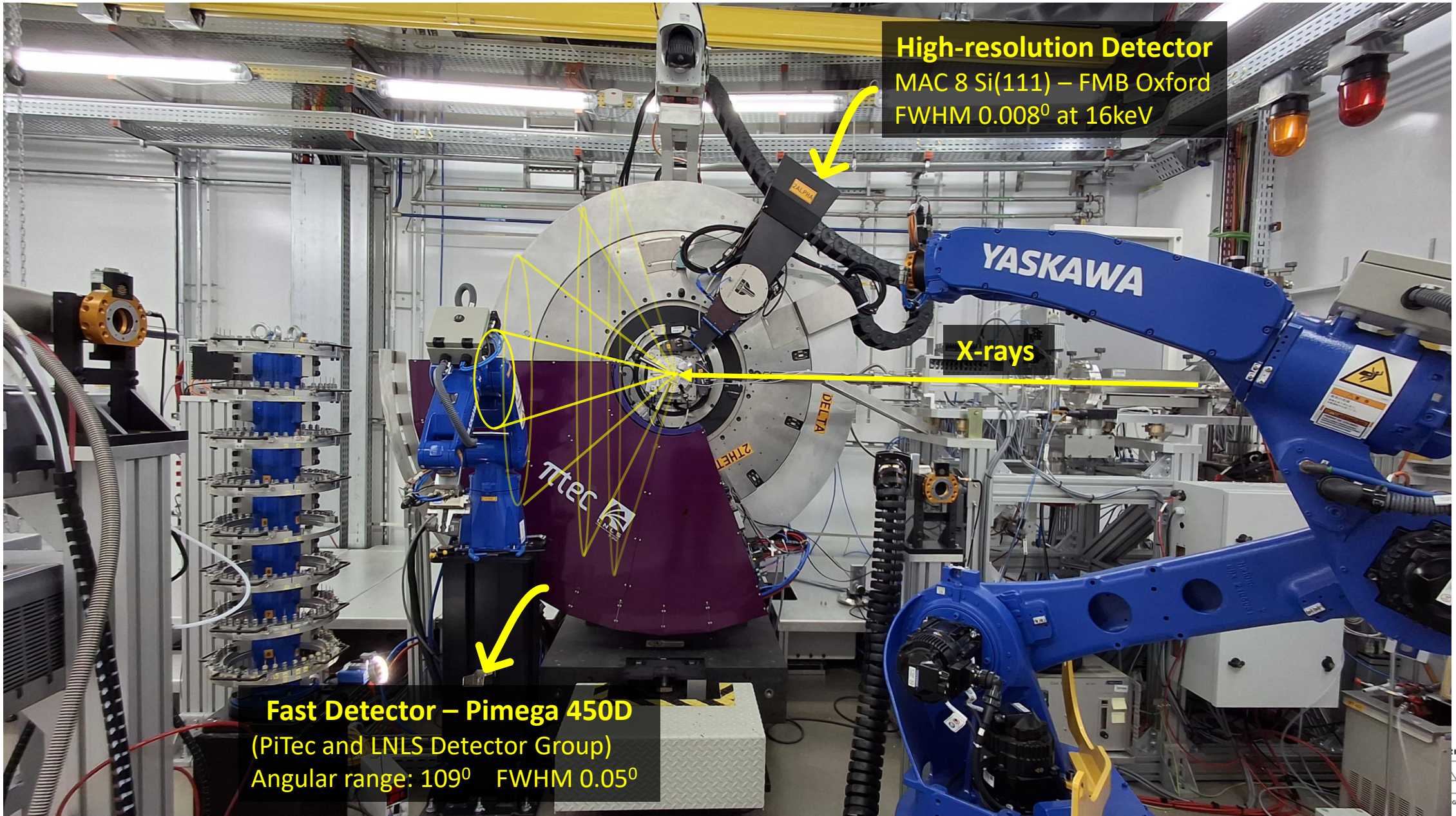
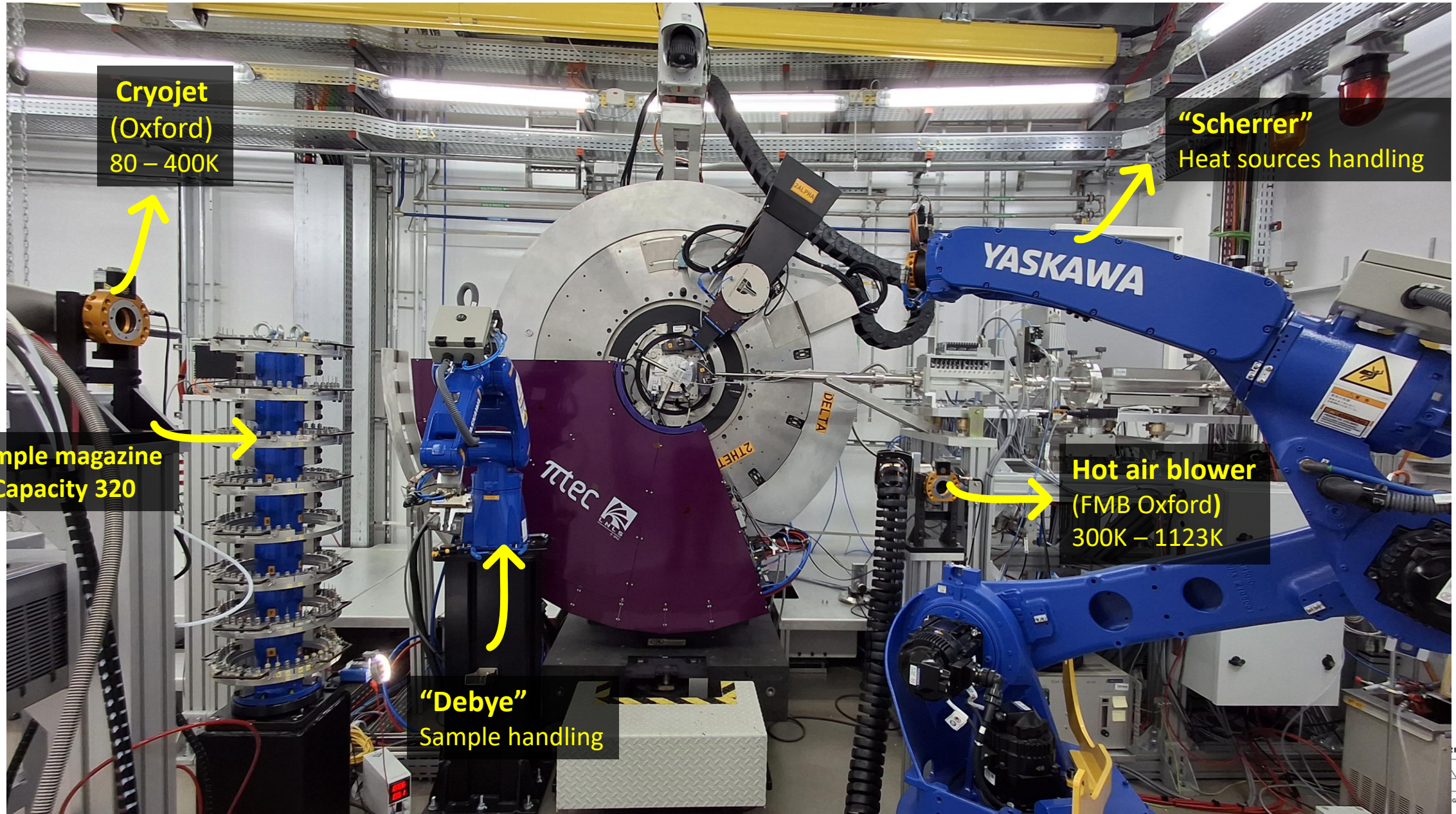
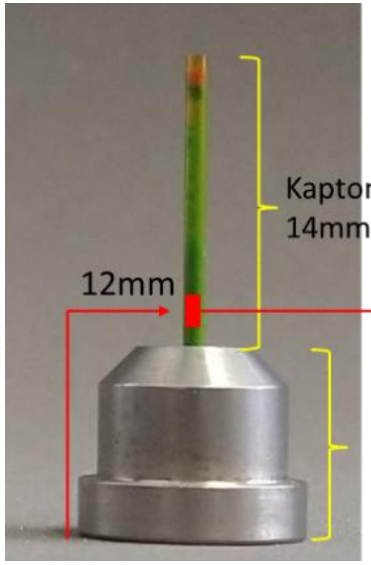


PAINEIRA beamline - Experimental Hutch
High-throughput system



Sample holders to the High-throughput system

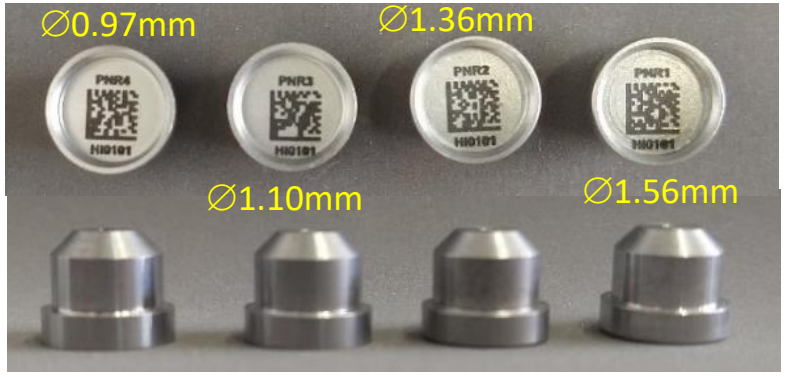
Powder samples

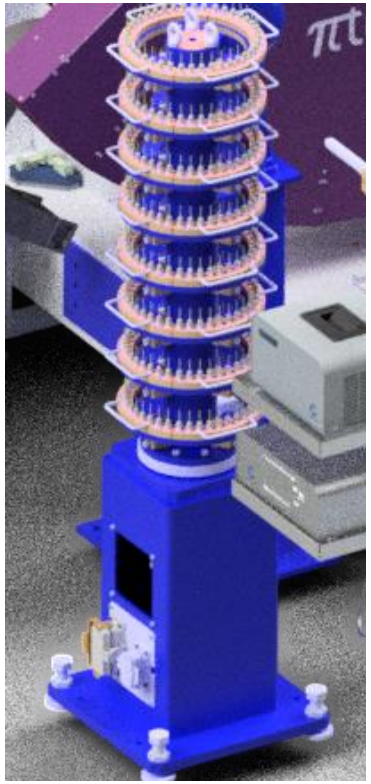


Rotation: 90Hz

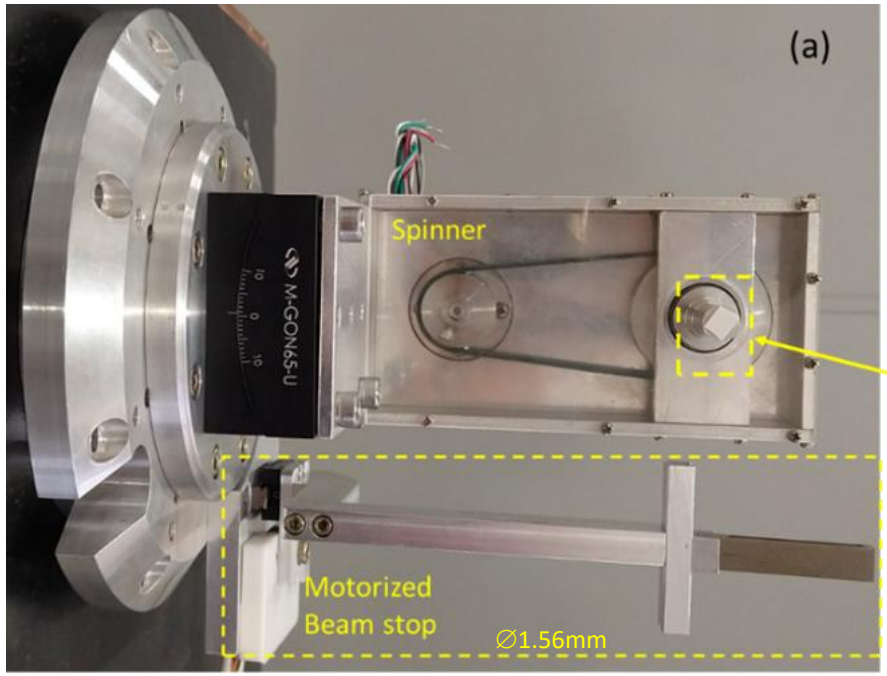
Temperature

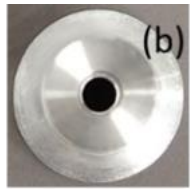
- Ambient
- Cryojet: 80 – 423K
- Blower: 300 – 573K





Pellets – films - rigid samples





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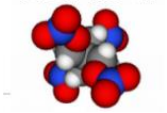
High-Throughput system of Paineira beamline

High-resolution analysis

Fabulous: 13-06-2025
2theta range: 1 - 120^0
Angular step: 0.001^0
Counting time:0.2s/point

Rietveld refinement

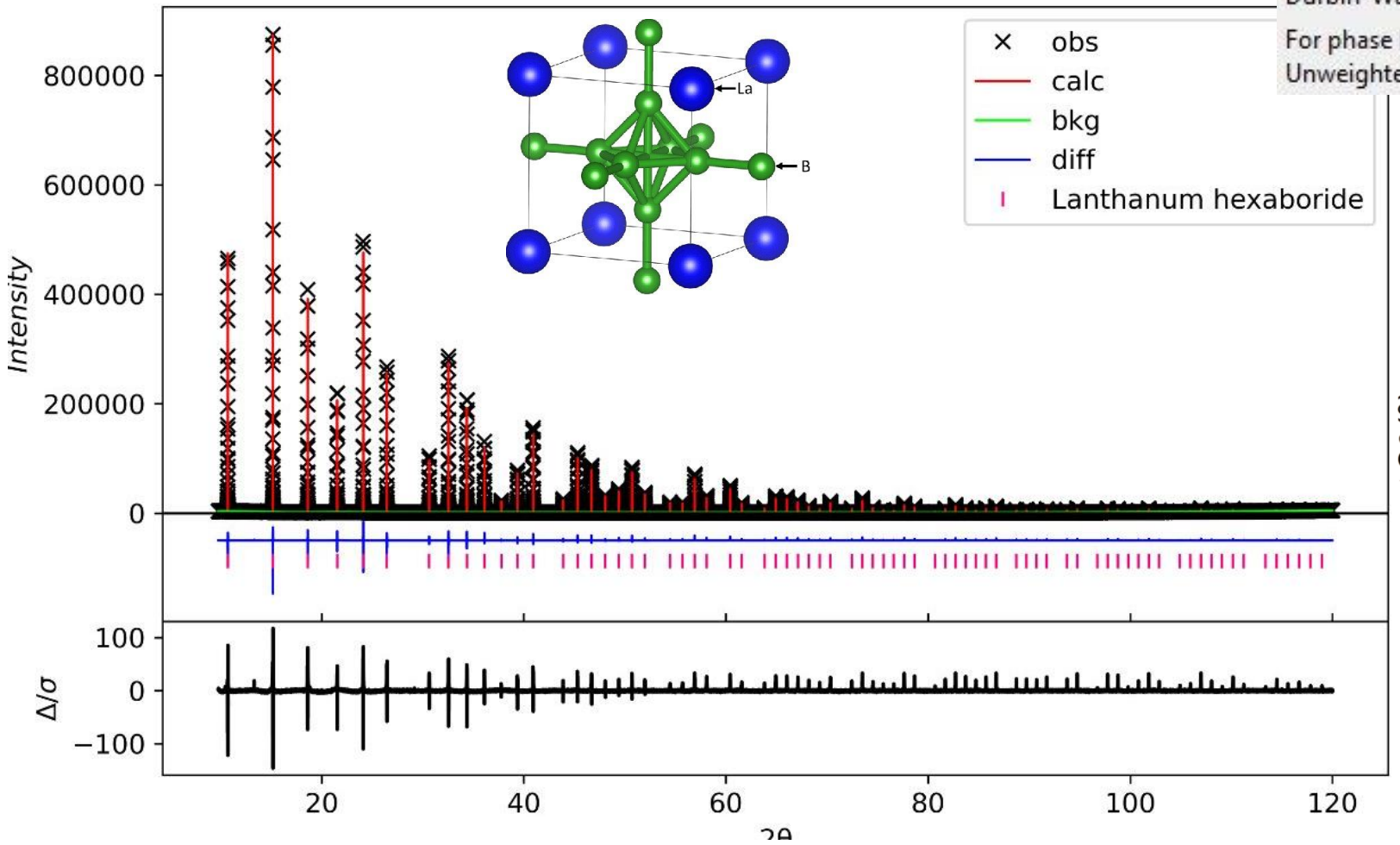
GSAS-II

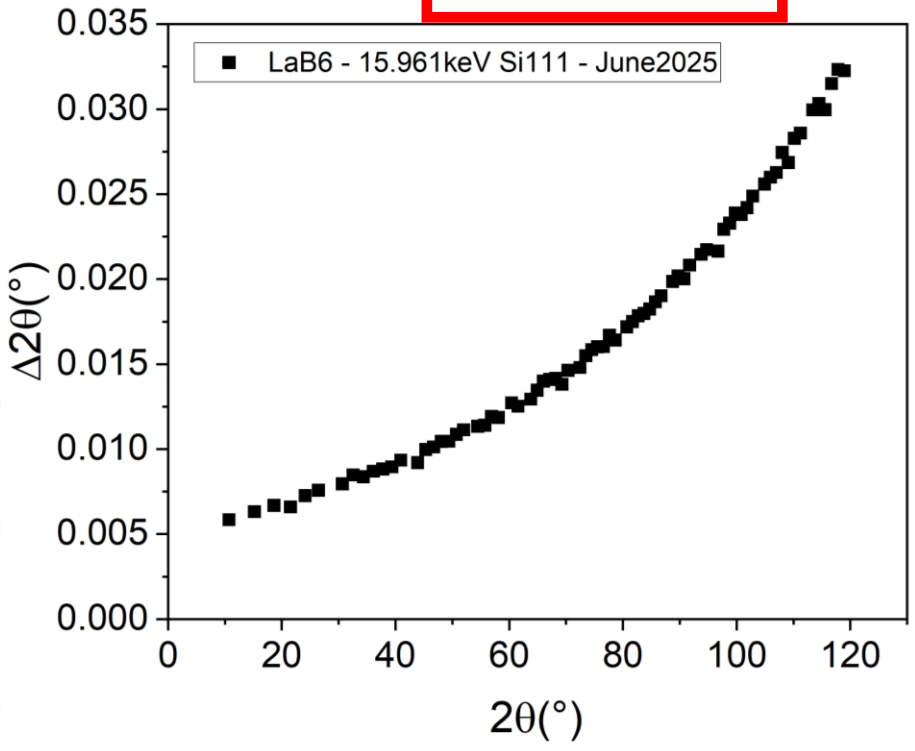


Energy: 15.9610keV (0.776796Å)
Instrumental parameters
Performance of the beamline
Reproducibility

Lam (Å): (0.413263)	0.776796
Zero (0.0000):	0.0003
Polariz. (0.9900):	0.99
U (1.163):	0.366
V (-0.126):	0.138
W (0.063):	0.033
X (0.000):	0.0
Y (0.000):	0.0
Z (0.000):	0.0
SH/L (0.02000):	0.01252

Data residual wR: 8.060% on 110210 observati … f total χ^2
Durbin-Watson statistic: 0.158
For phase Lanthanum hexaboride:
Unweighted phase residuals RF^2: 12.172%, LF: … os





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Example 1: Insertion of graphene in a ceramic (94%Al_2O_3+ (6-x)%Y_2O_3 + multi-layer graphene) to increase hardness

Felipe D. Faglione (PhD) and Flávia R. Estrada (researcher)

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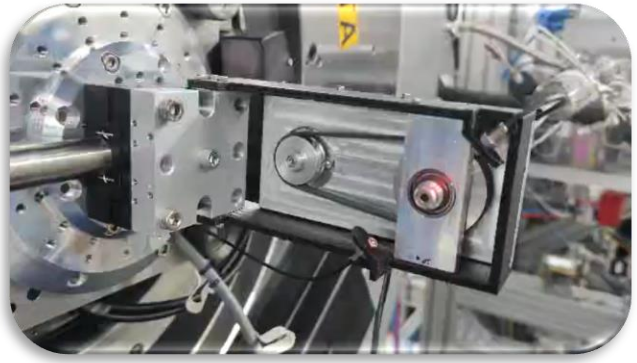
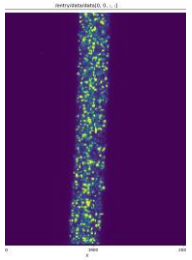


Where is graphene in the ceramic?
Which yttria phase was formed?

Debye ring without sample rotation



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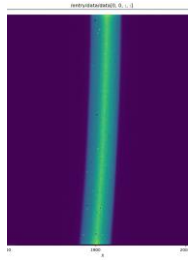

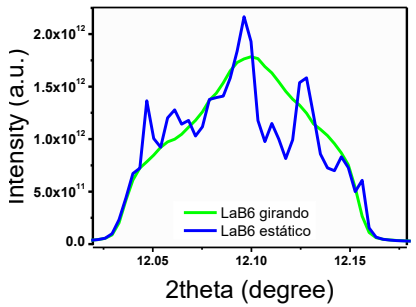

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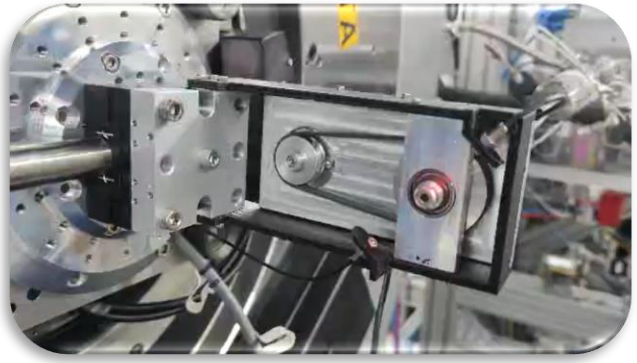

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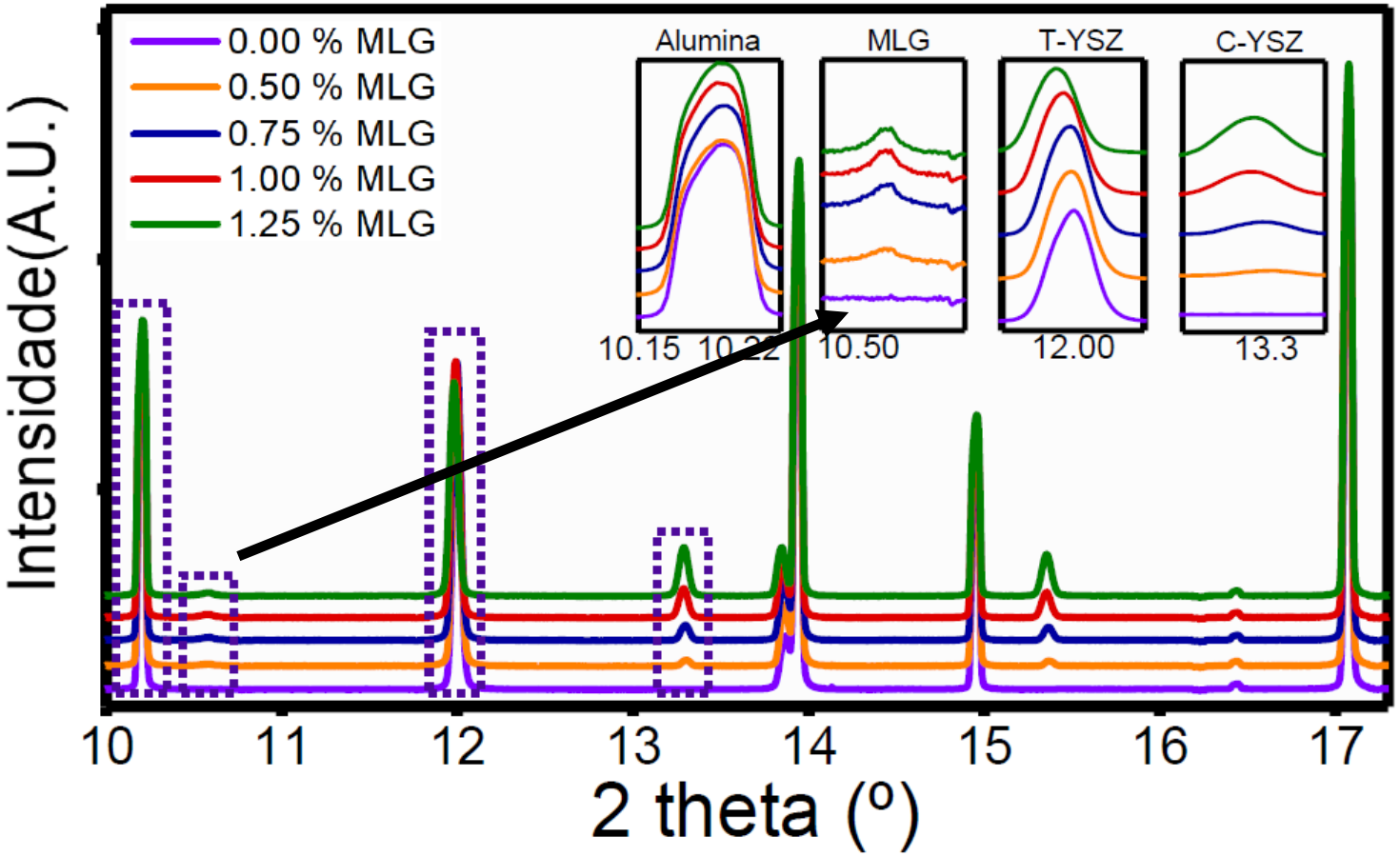
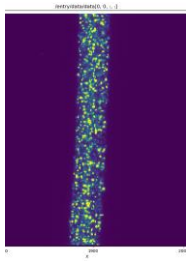
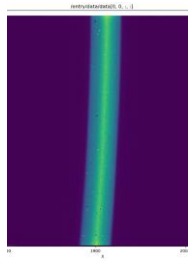
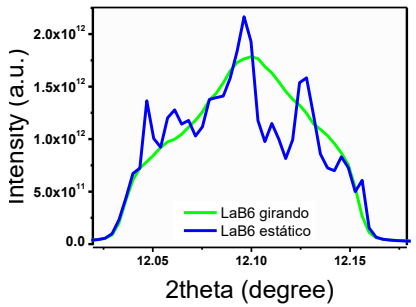


Debye ring without sample rotation



Debye ring with sample rotation





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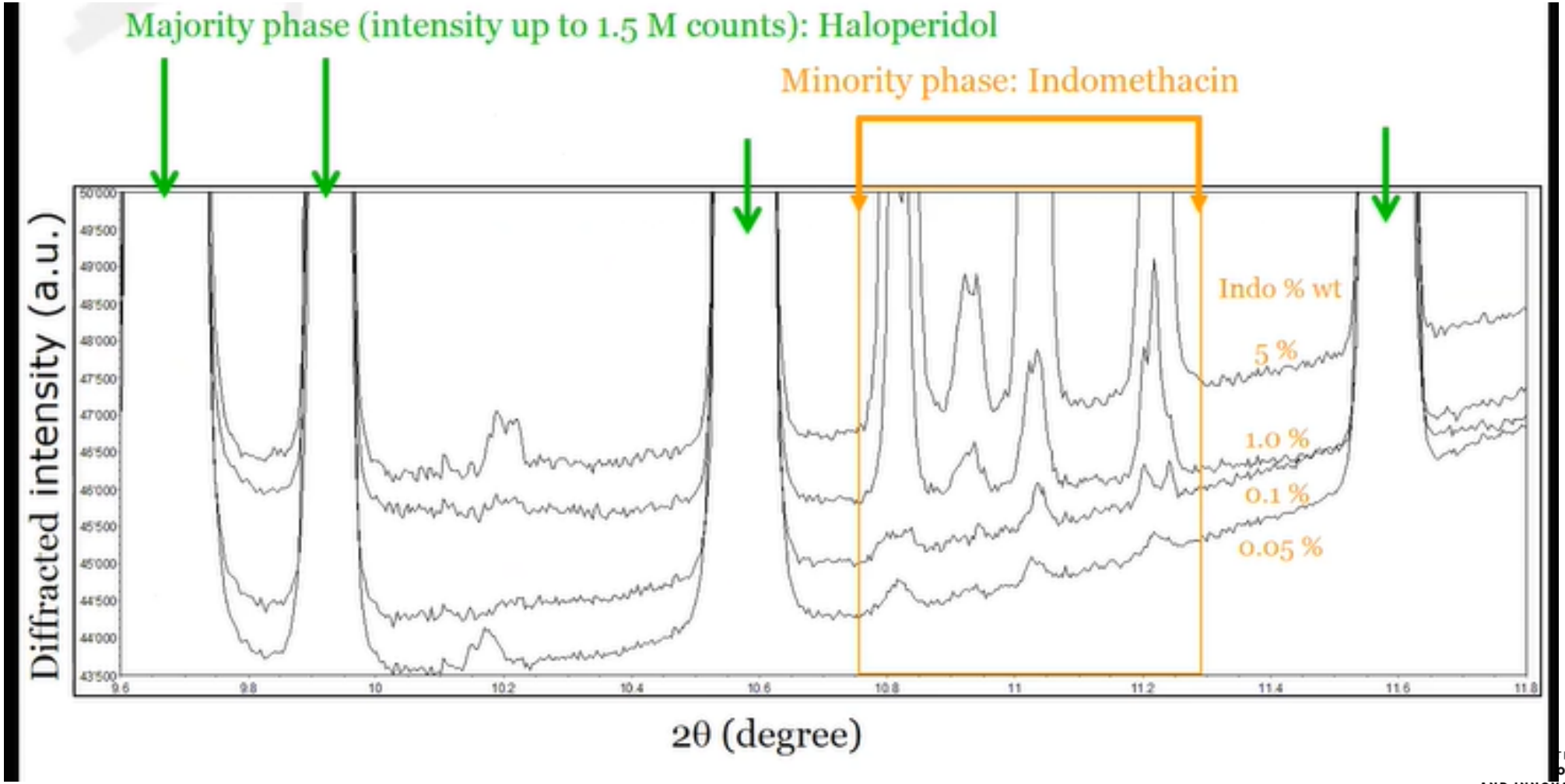
Exemplos

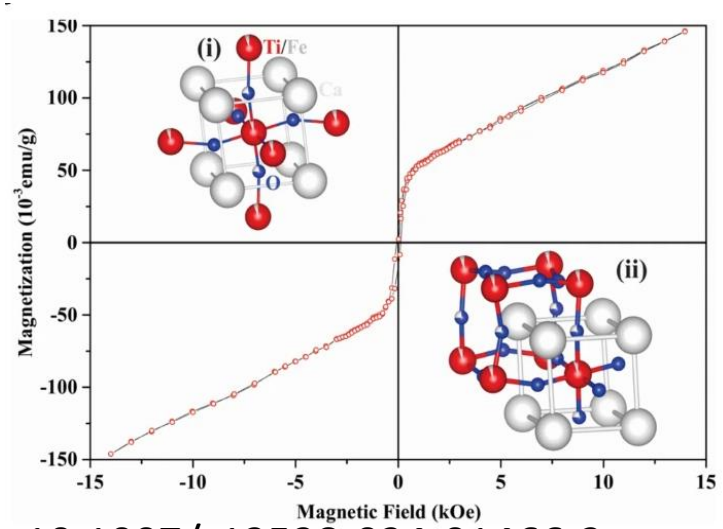
https://www.excelsusss.com/ **CEO Fábia Gozzo**



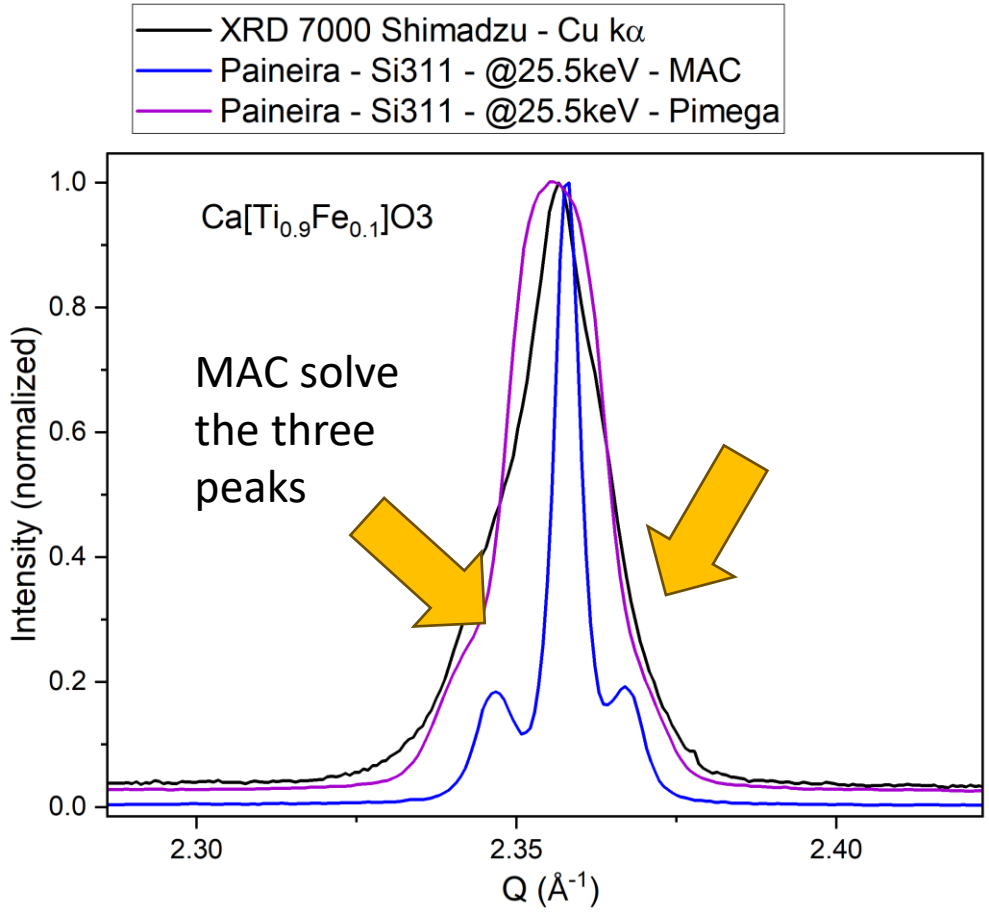
High-resolution application and comparison with fast detection

- Inducing magnetism in the antiferrodistorcive compound $CaTiO_3$ by Fe^{+3} dopping in Ti^{-4} site.
- Aim: evalulate the lattice strain and calculate electric polarization using different crystallographic model.
- Preliminary results:

Freitas - proposal 20250710



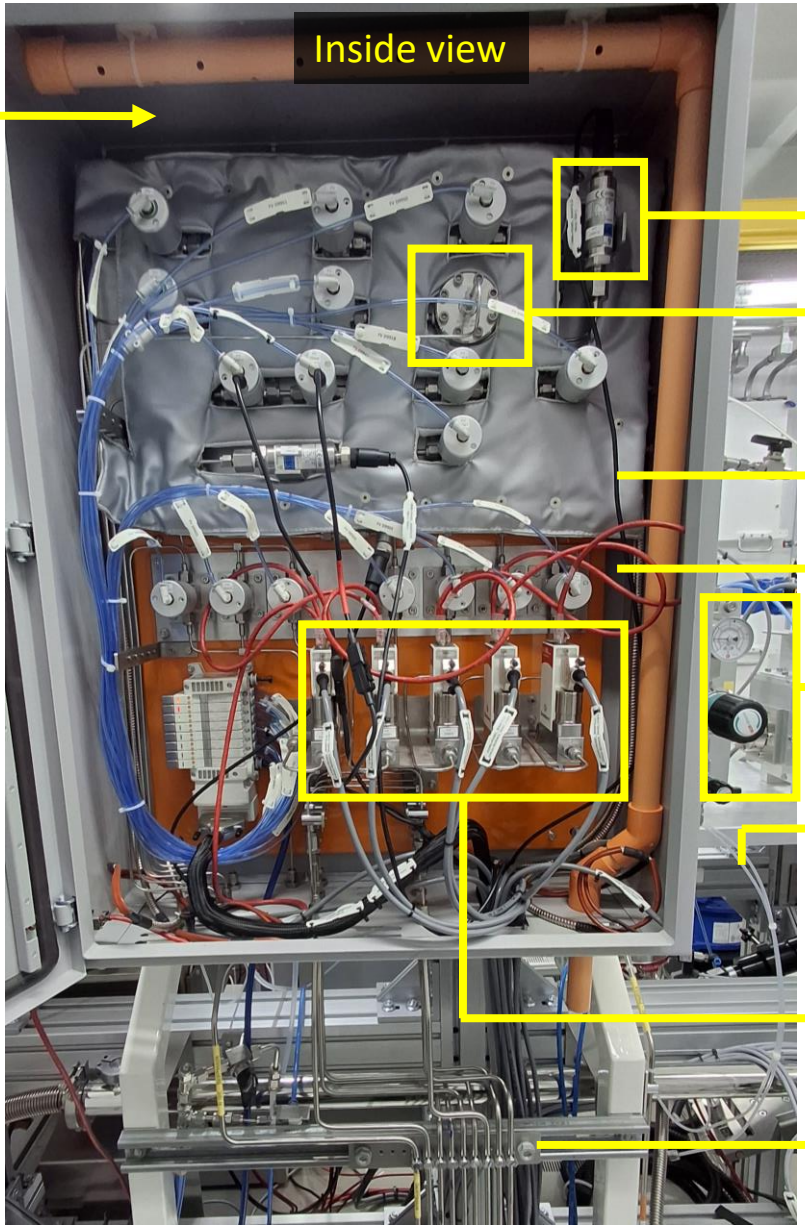
10.1007/s13538-024-01466-2



PAINEIRA beamline - Experimental Hutch
Instrumentation for *In-situ/Operando* experiments

Control module for experimental automation

- Gas
- Liquid
- Vapor
- Pressures up to 100bar



Filter to retain powder

Back pressure for gas and liquid (up to 100bar)

Heater (up to 60^0C)

Solenoid valves

Saturator to produce vapor (ambient pressure), heated up to 60^oC

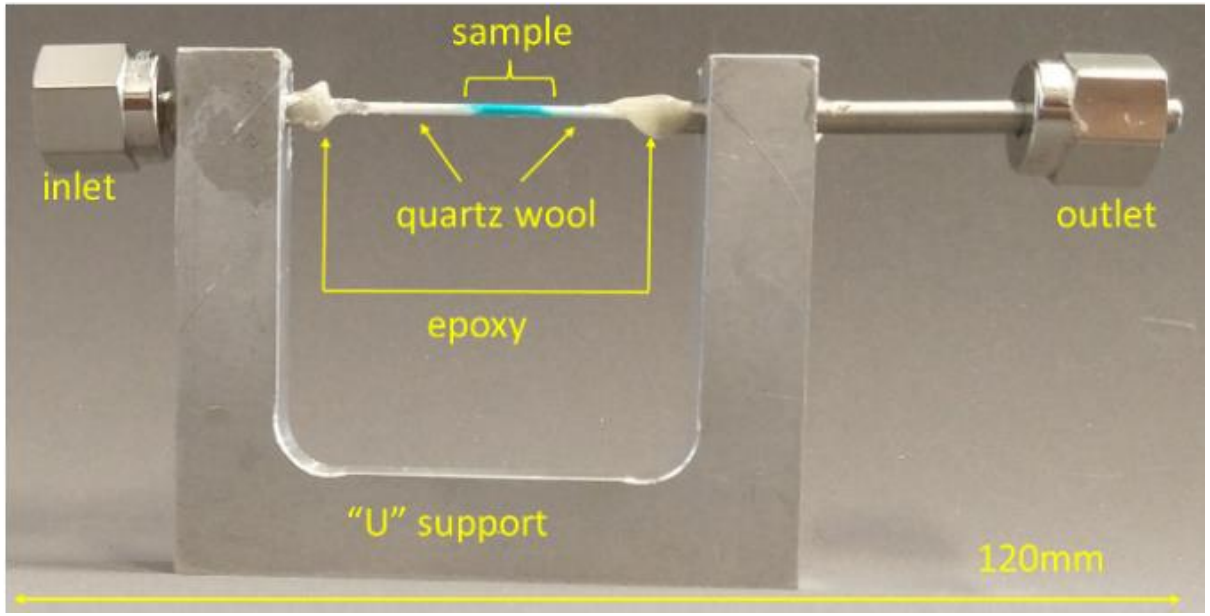
Peristatic pump

5 mass flow meters (Bronkhorst): 0.5 to 50mL/min (Gases: He, H_2, CO_2, 5%CO, CH_4, O_2 , synthetic air, etc.)

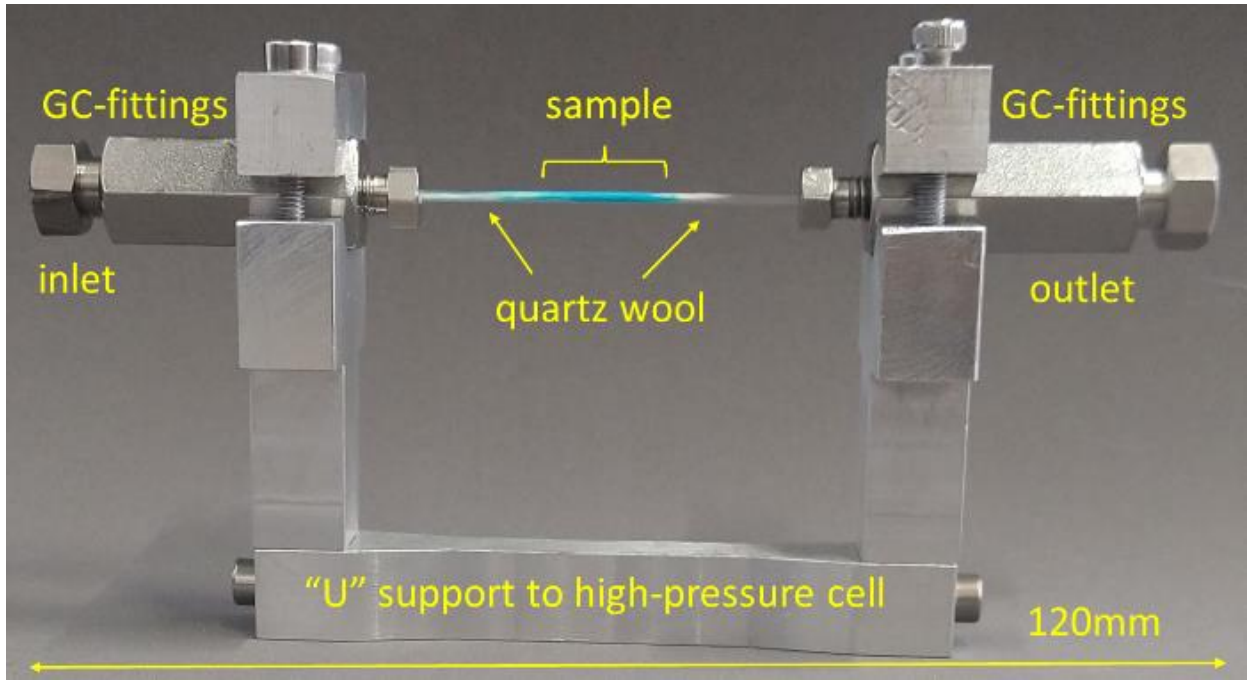
8 stainless steel tubing

Capillary cell for *in situ* experiments

Ambient pressure



Pressure up to 95bar

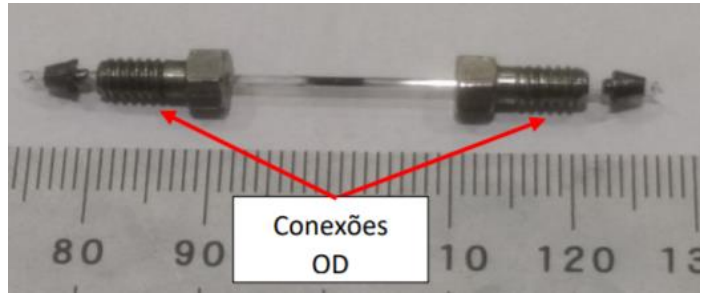


- Gas
- Liquid
- Vapor

Temperature

- Ambient
- Cryojet: 80 – 423K
- Blower: 300 – 1073K

- Mass spec
- Micro-GC



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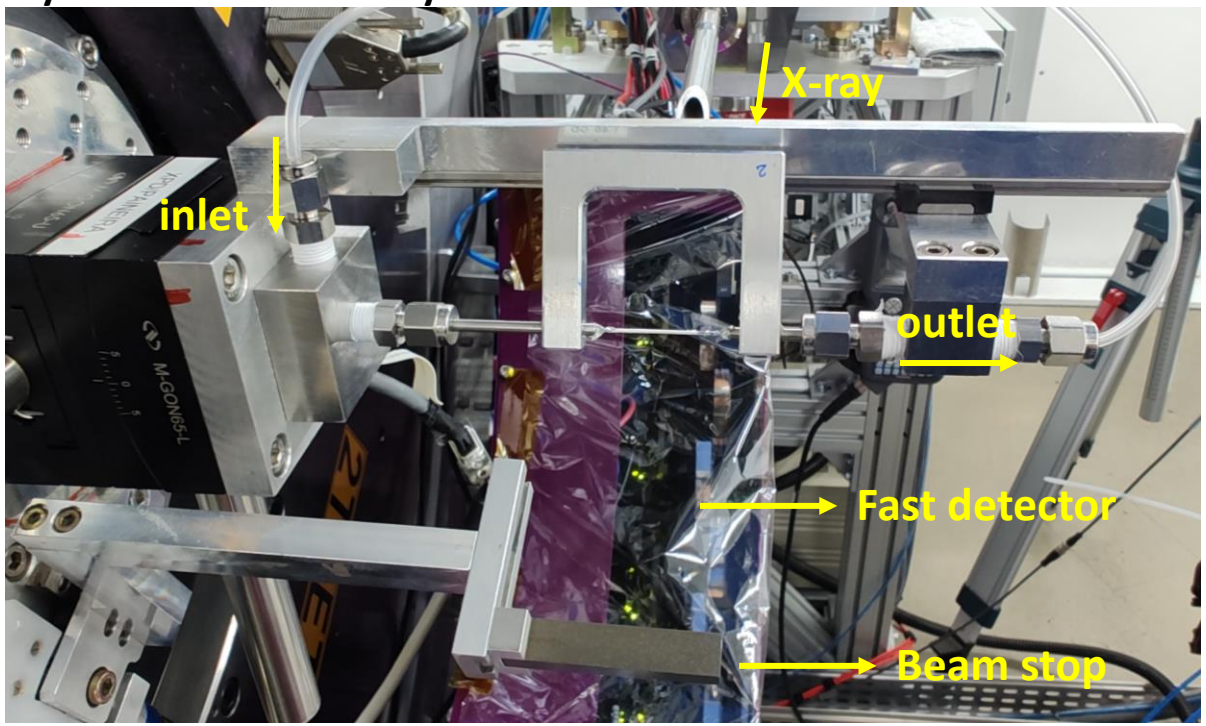
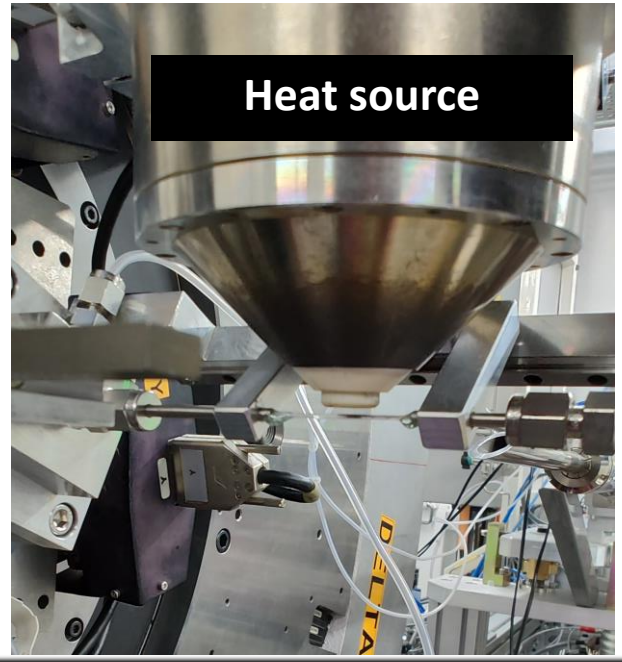
Instrumentation for *in-situ/operando* experiments

Capillary cell reactor assembly installed on the theta circle of the diffractometer





(Tmax. = 1123K at sample position)

Liquid injection

- **flow: 0.001 - 12 mL/min**
- **pressure: 0 - 18000 psi**

Gas analysis

Micro-GC

mass spectrometer

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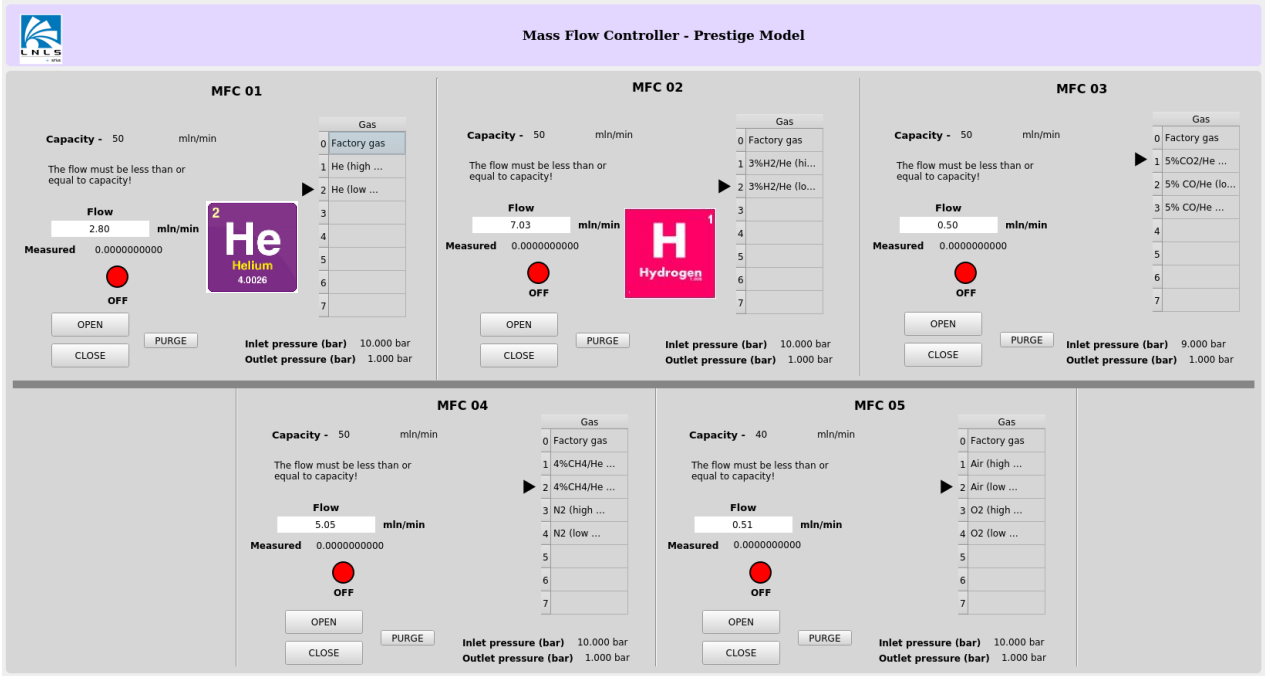
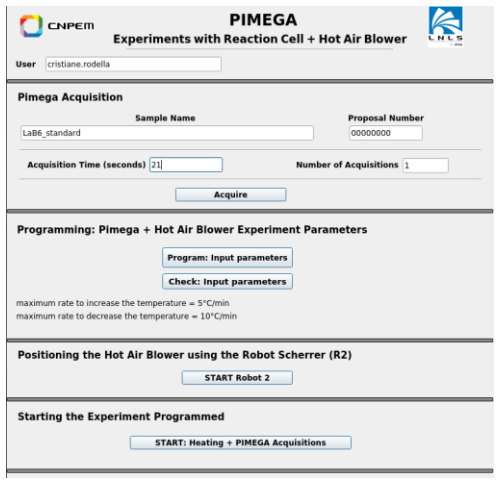
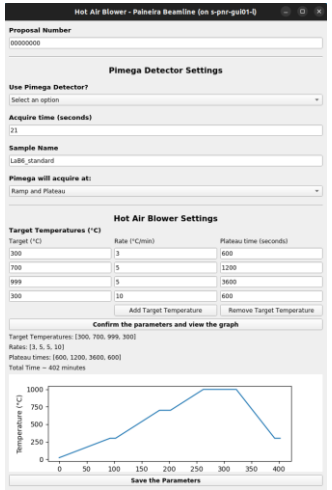
PAINEIRA beamline - Workstation control system to *in-situ* experiments







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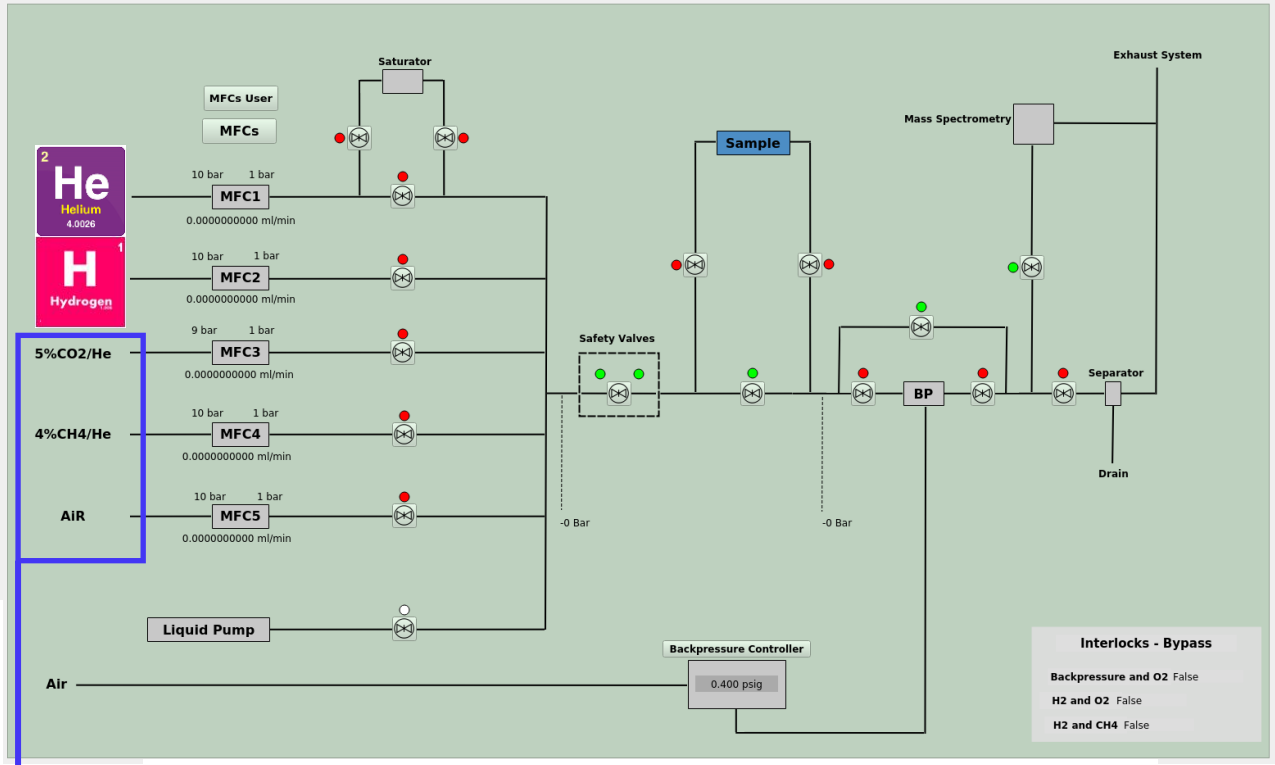
Module for in situ experiments



Two different gas cylinders connected
Open/Close a valve to select the gas
- More versatility to the gases supplied for the experiment

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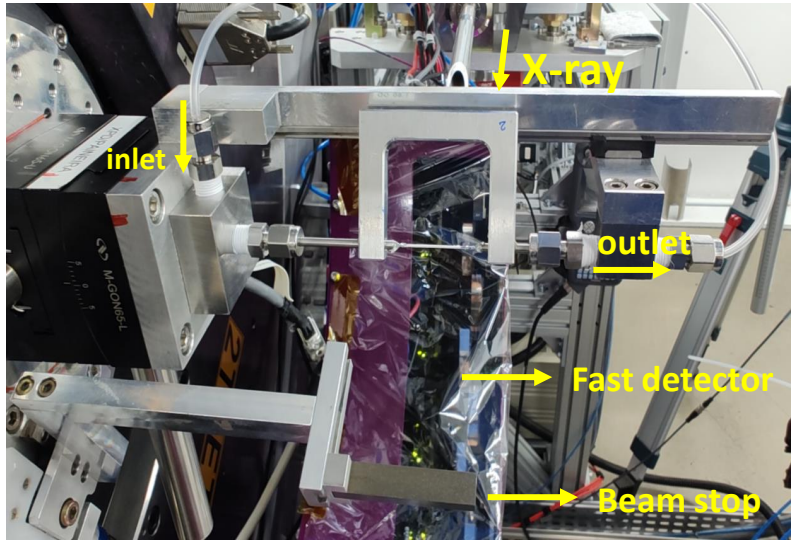
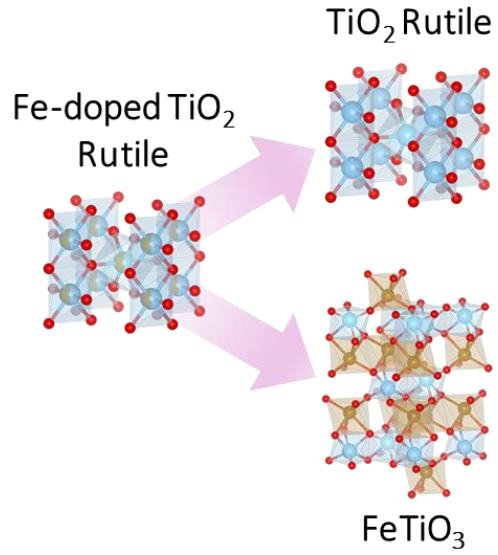
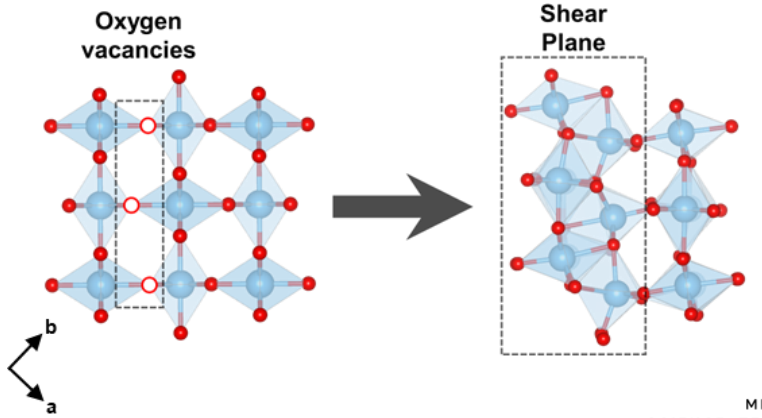
Example 3: *In situ* XRD analysis of Fe-doped TiO_2 rutile catalyst under a 3% H_2/He atmosphere to probe the structural evolution during the activation process

PAINEIRA

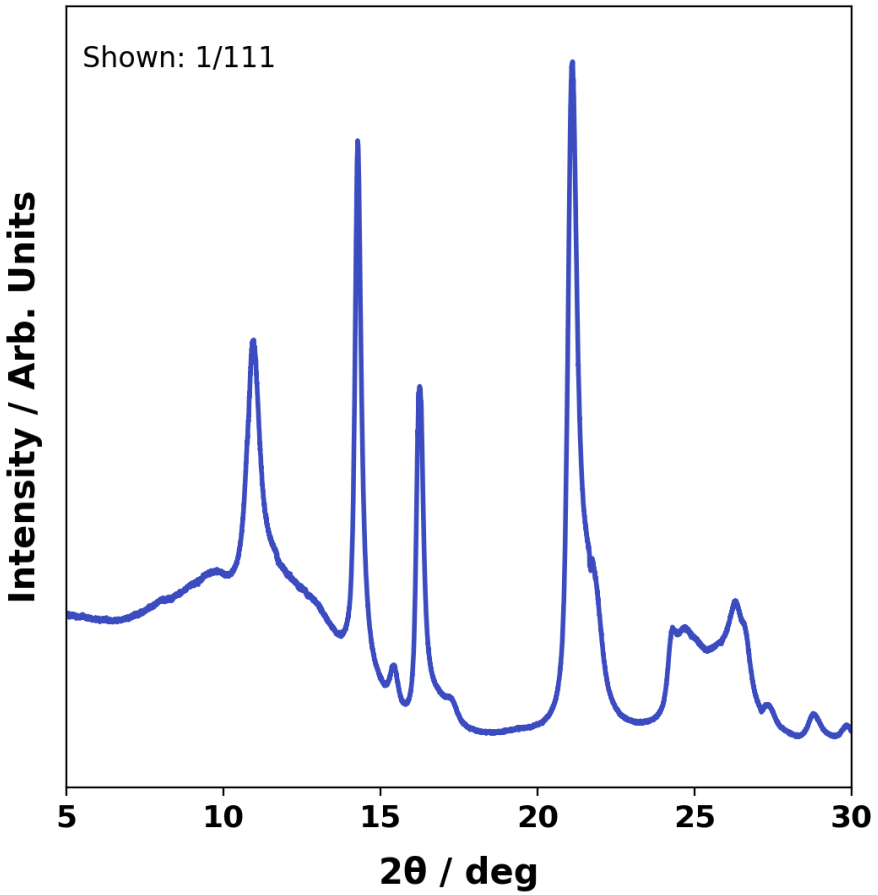


Hypothesis: formation of two crystalline phases



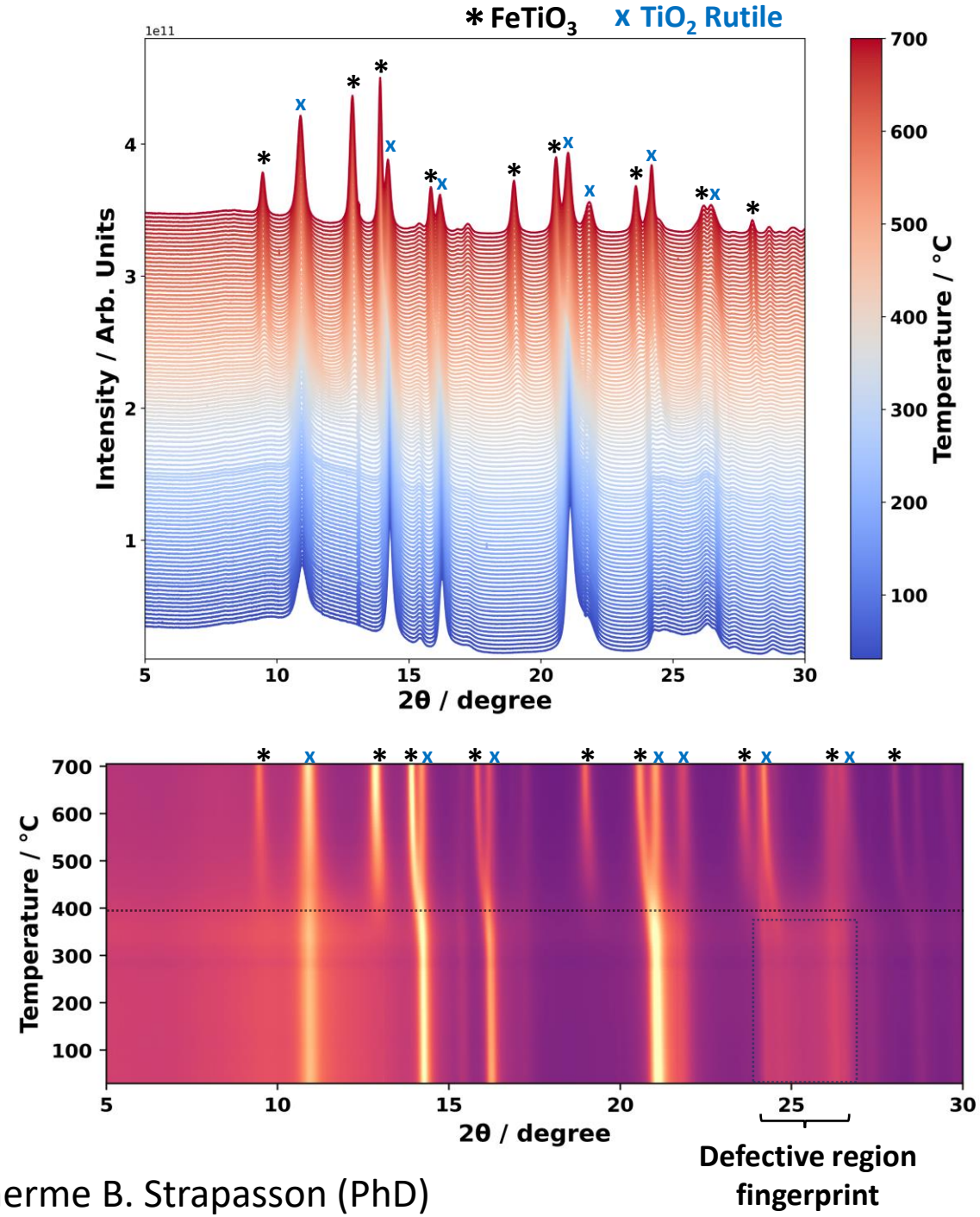


Each diffractogram was collected in 20 seconds and immediately visualized during the experiment



IGUAPE - PAINEIRA Graphical User Interface for Kinetic Experiments

JAC COMPUTER PROGRAMS
J. Appl. Cryst. (2025). **58**, 1061-1067
https://doi.org/10.1107/S1600576725003309



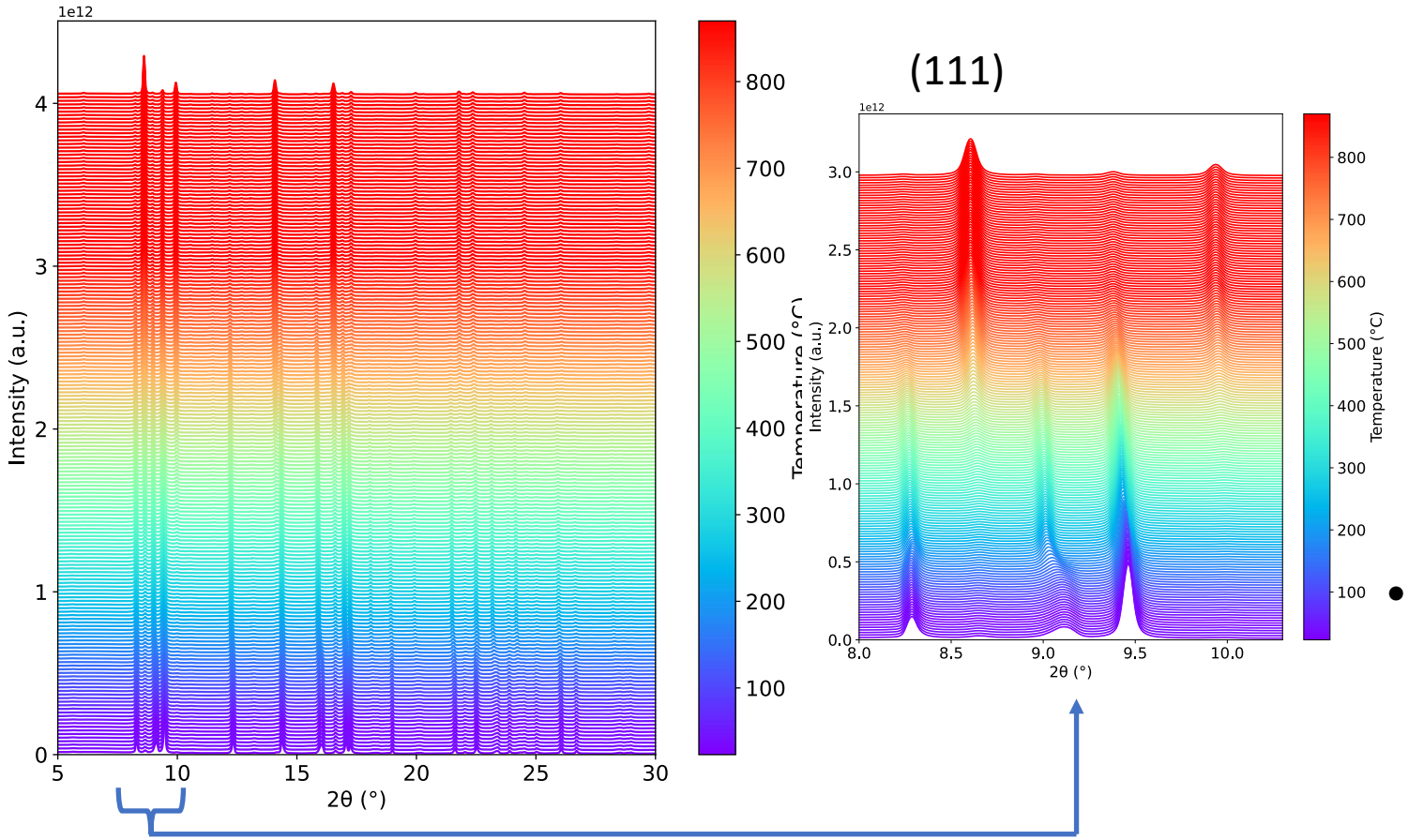
Credit: Guilherme B. Strapasson (PhD)

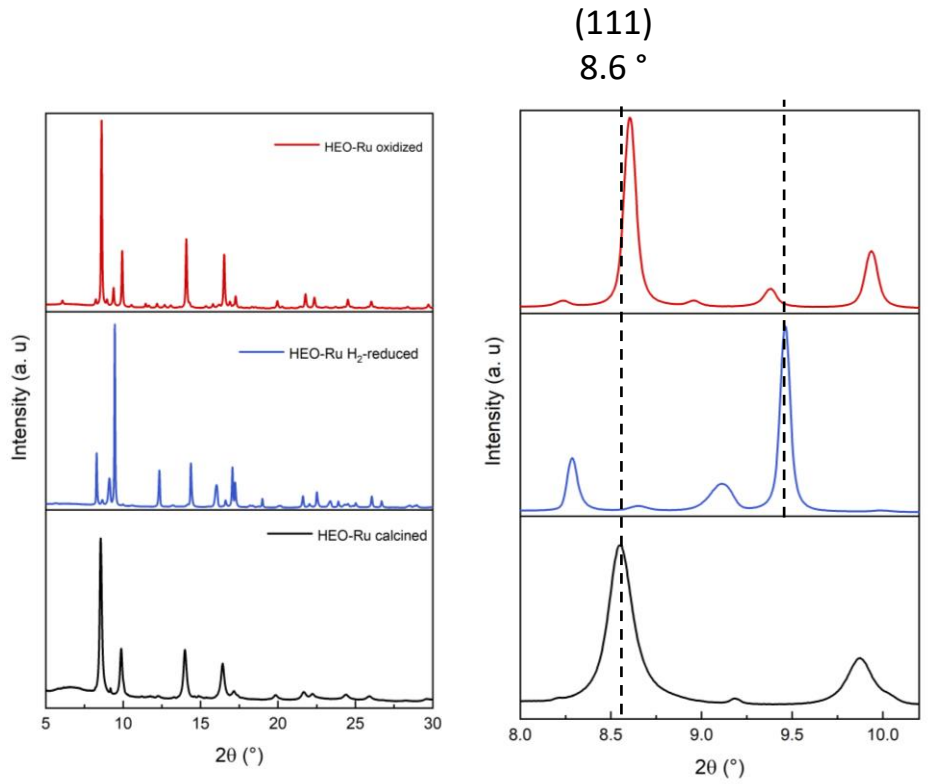
Data analysis for *in-situ* experiments

IGUAPE - PAINEIRA Graphical User Interface for Kinetic Experiments

Calcination: 800 °C, 2 h (5 °C·min^{-1})
Reduction: pure-H2, 800 °C, 6 h
Heating ramp: 5 °C.min^{-1} in air (5 mL·min^{-1})
Isothermal step: 800 °C, 60 min in air

$Ru_{0.01}$-$Ce_{0.198}La_{0.198}Nd_{0.198}Ca_{0.198}Mg_{0.198}O_{2-\delta}$

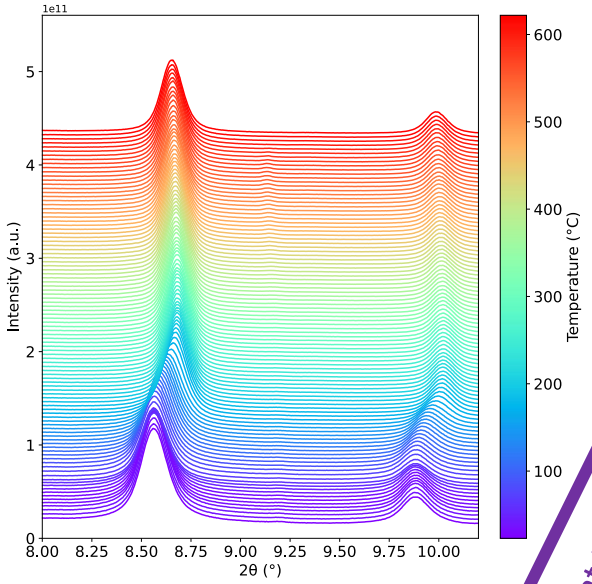


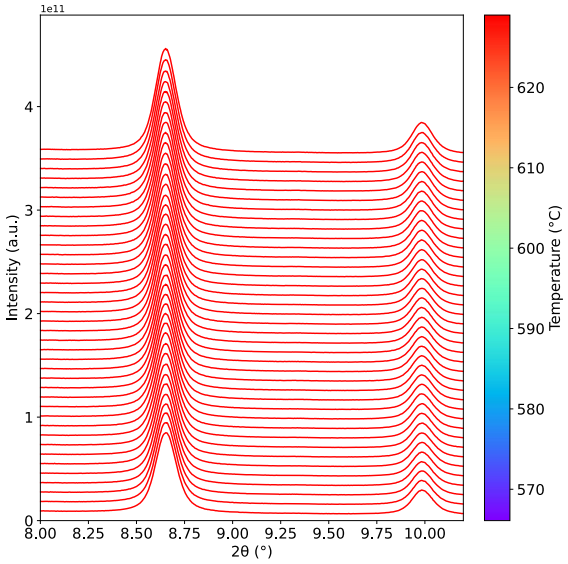


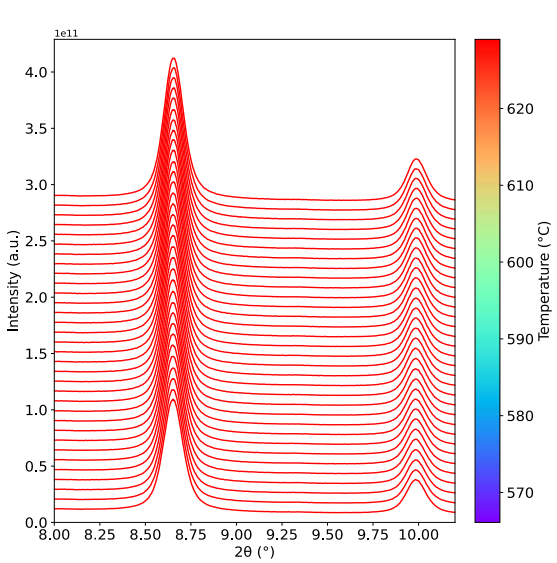
- Oxidation: recovery of an apparently more fluorite phase, but with an additional crystalline phase (minor proportion)

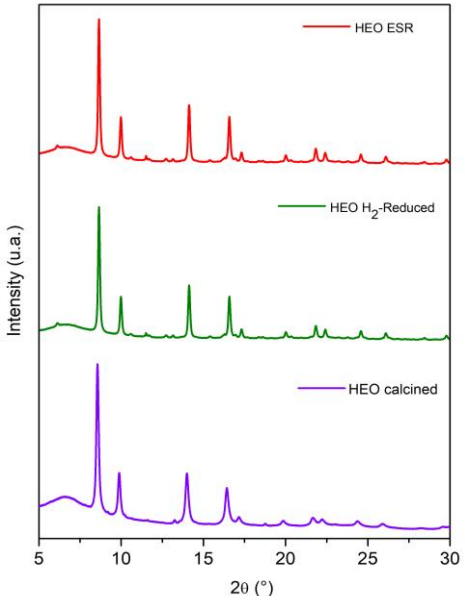
Data analysis for *in-situ* experiments

IGUAPE - PAINEIRA Graphical User Interface for Kinetic Experiments







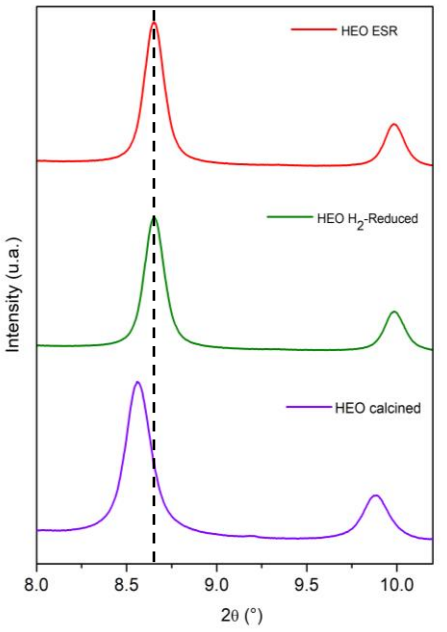


Activation at 600 °C under under H_2 flow of 5 mL.min^{-1}

ESR Reaction at 600 °C under H_2O:EtOH 3:1 flow of 10 mL.min^{-1} 50 min

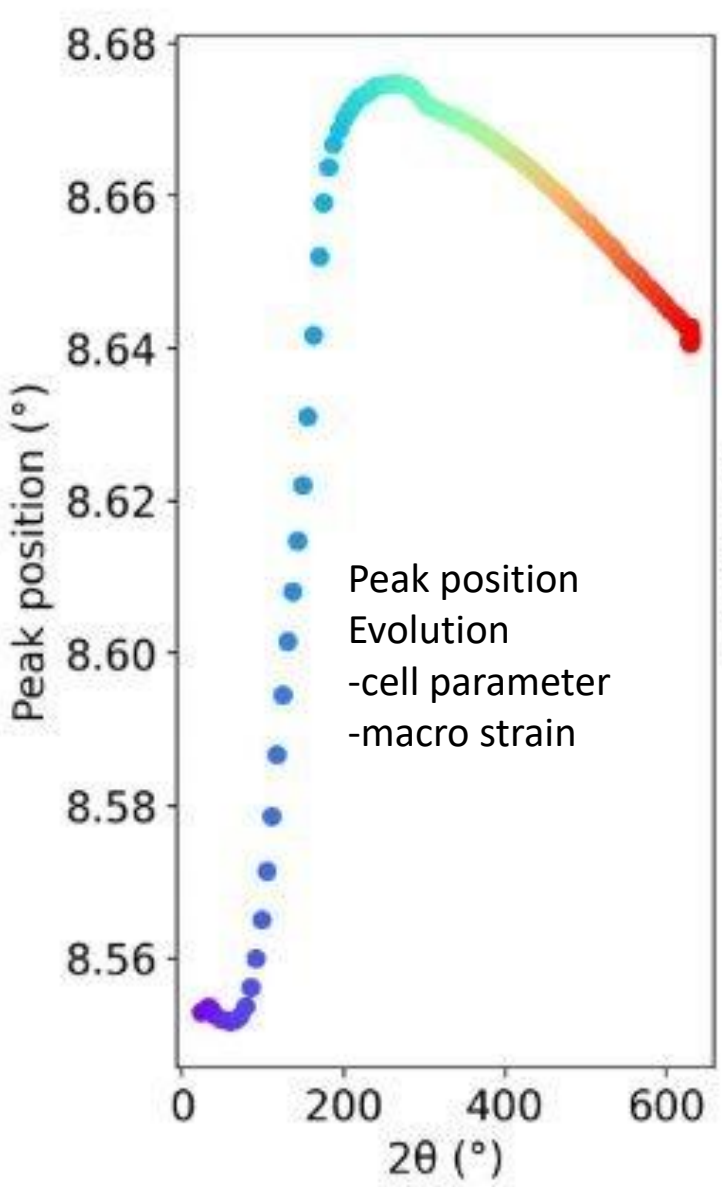
Heating ramp at 5 °C.min^{-1} under 3% H_2/He flow of 5 mL.min^{-1}

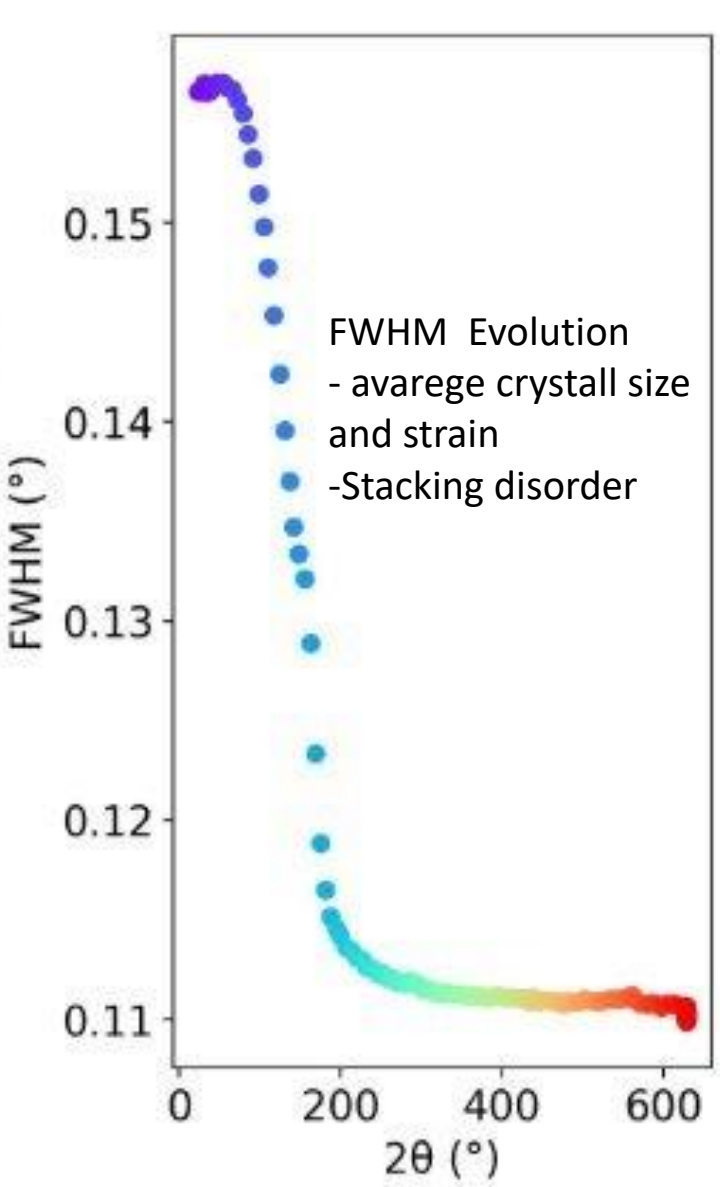
In Situ PXRD for 3% H_2/He activation and ESR reaction of calcined $Ce_{0.20}La_{0.20}Nd_{0.20}Ca_{0.20}Mg_{0.20}O_{2-\delta}$

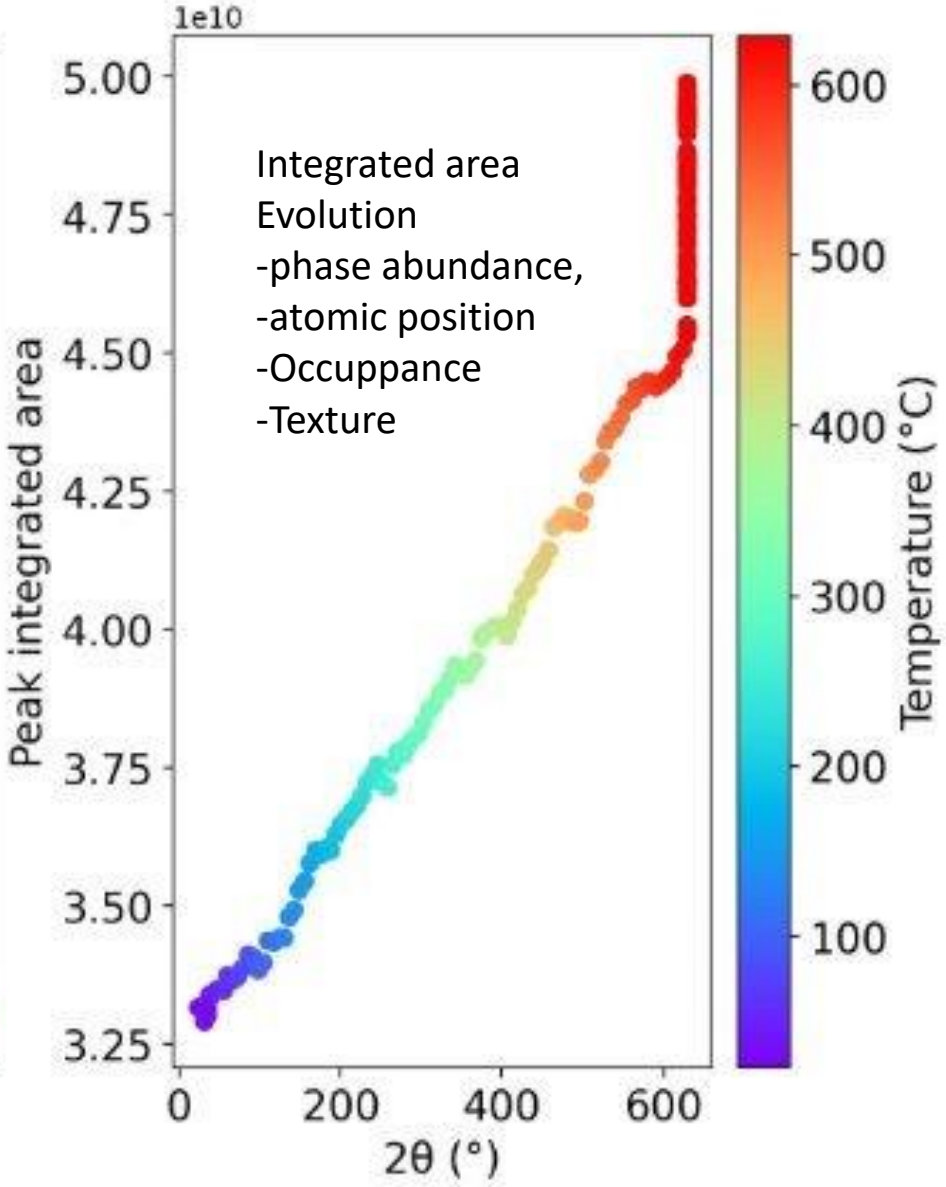


Data analysis for *in-situ* experiments

IGUAPE - Paineira Graphical User Interface for Kinetic Experiments

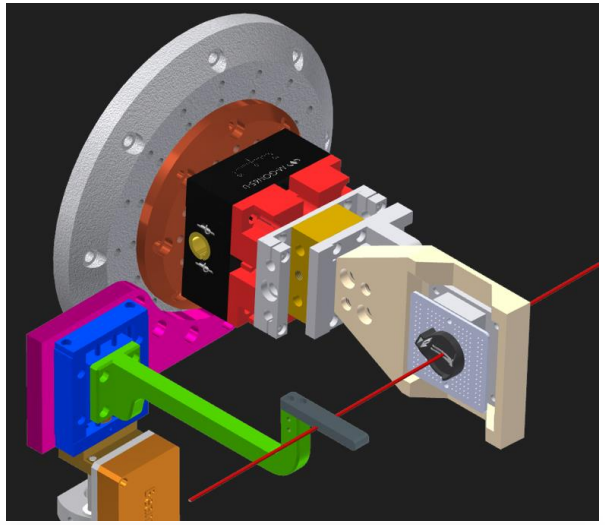


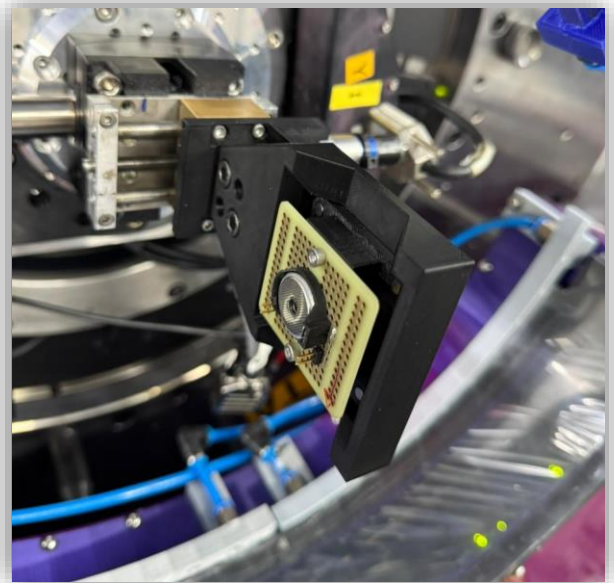




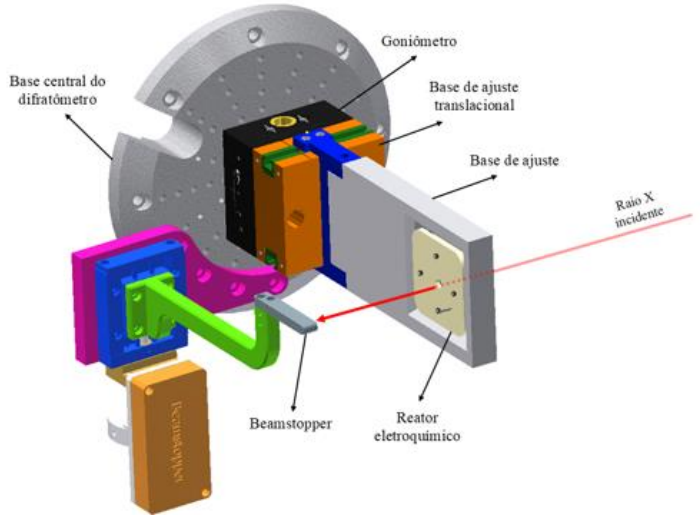
Supports and sample holders for in situ/operando studies of batteries

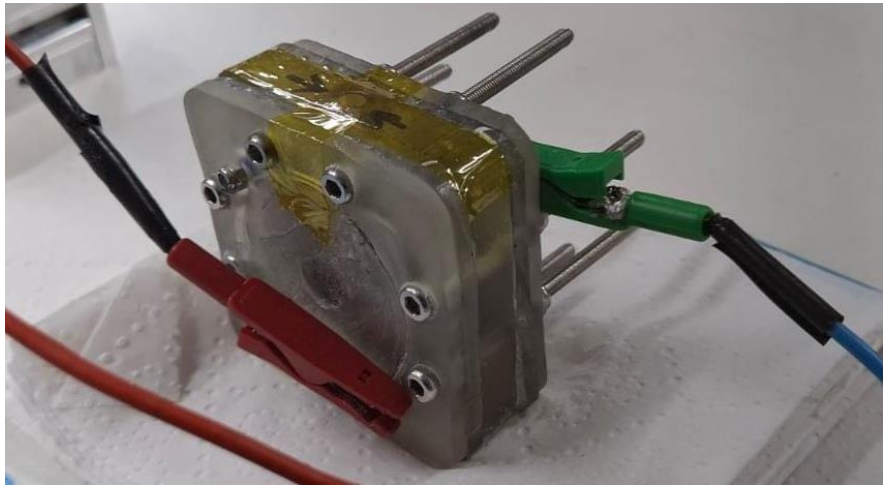
Coin cell battery





Flow cell battery





Concluding Remarks

- PAINEIRA has been developed to provide high-resolution and quality SR-PXRD data, using a high-throughput operational system, which implies efficiency for the beamtime. Moreover, it can handle a large number of samples and users.
- The infrastructure for kinetics SR-PXRD experiments with fluids (gas, liquid, and vapor), temperature, and pressure variation is robust and user-friendly.
- The PAINEIRA team will keep investing efforts to create new sample environments to promote in situ and operando experiments for the user's community

Thank you

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MINISTRY OF SCIENCE, TECHNOLOGY AND INNOVATION

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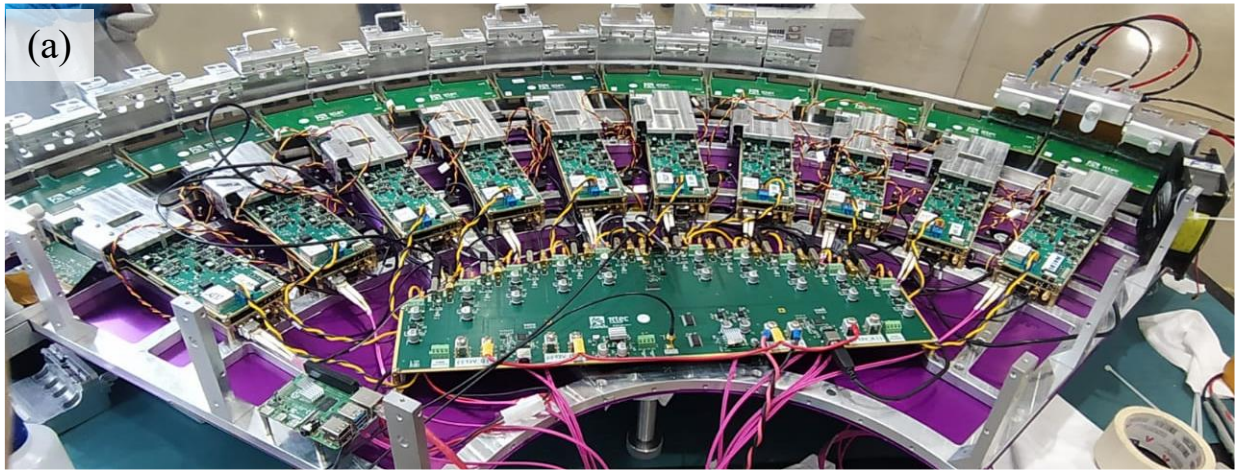
Fast detector - Pimega 450D

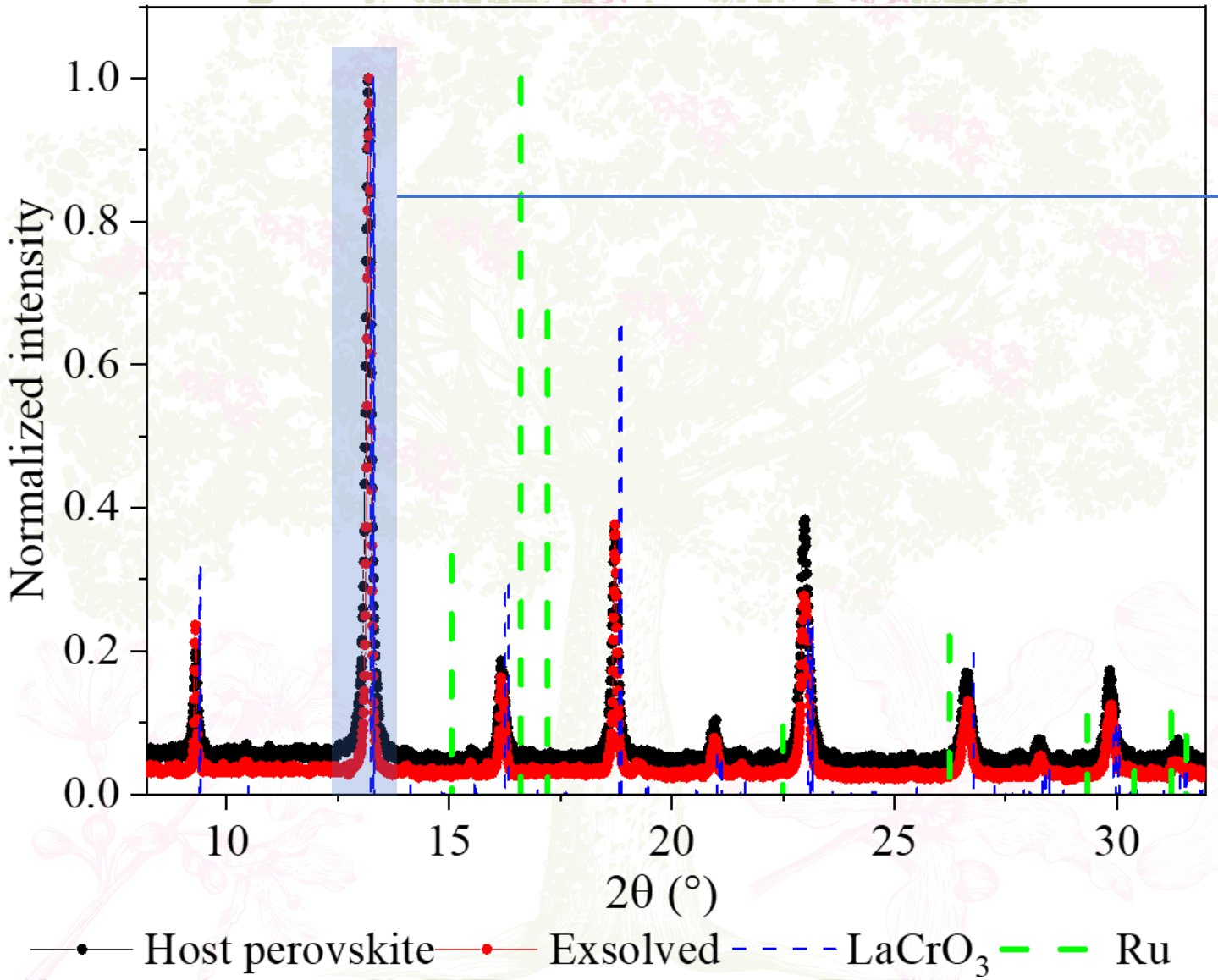


Figures. Pimega 450D pictures (a) the electronic; (b) the sensors placed in zigzag; and (c) the case of the detector closed and ready to be installed at the diffractometer.

- Development of the LNLS detector group in partnership with PiTec (https://www.pitec.co/).
- frame rate of 1000 fps;
- pixel size of 55 μm ;
- 10 modules, each with 2 silicon chips placed in a zigzag orientation to avoid gaps between the sensors;
- wide angular coverage : 109° in 2θ;
- 0.07° resolution (FWHM) in 2θ;
- Estimate 10s to obtain a whole diffraction pattern

Results and Discussion

SR - High-resolution XRD analysis



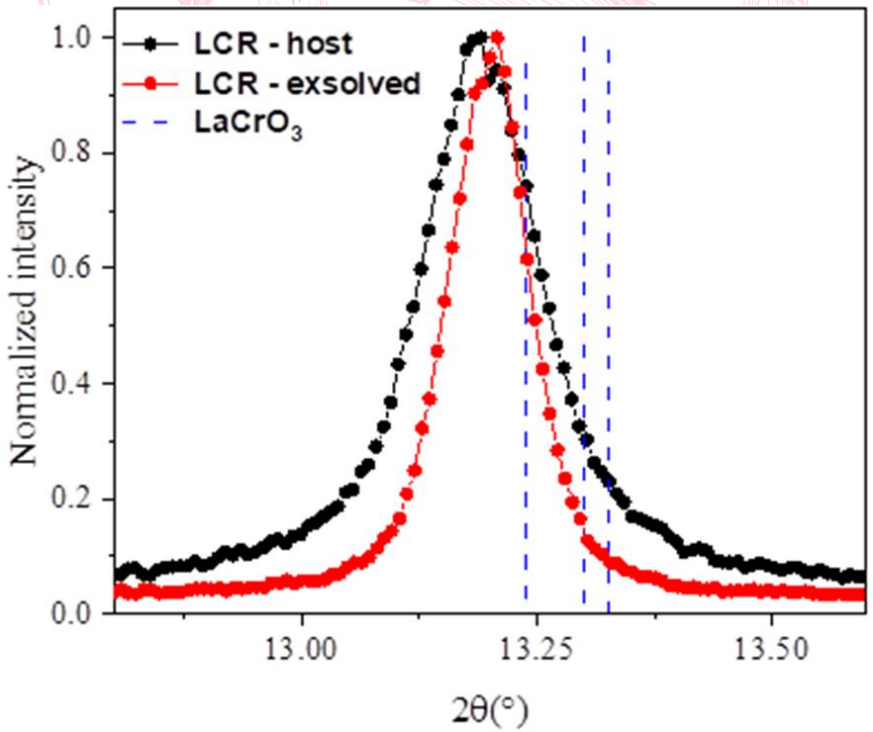
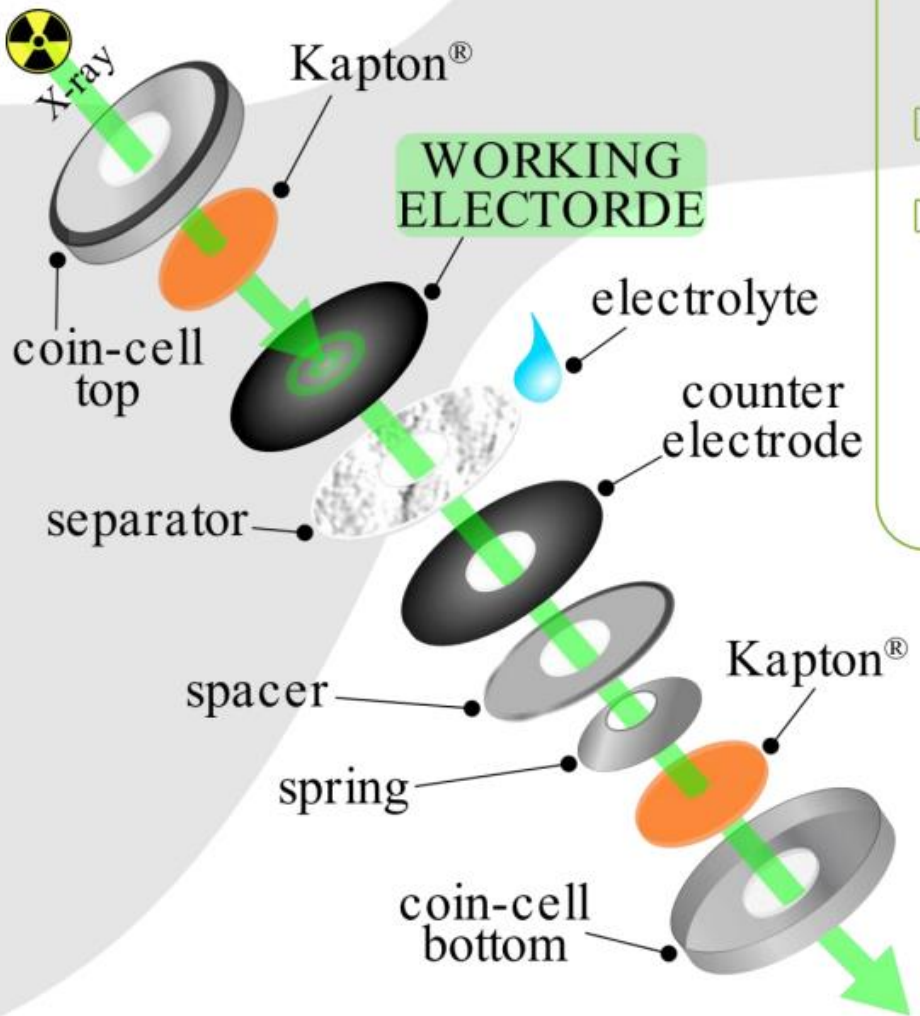


Figure 3. SR-High-resolution XRD pattern of the perovskite matrix (black) and after the exsolution thermochemical treatment (red).

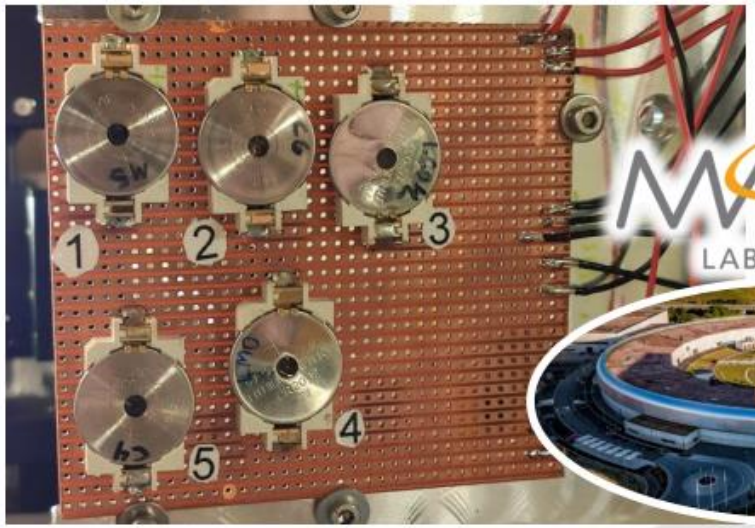
Experimental



Assembly

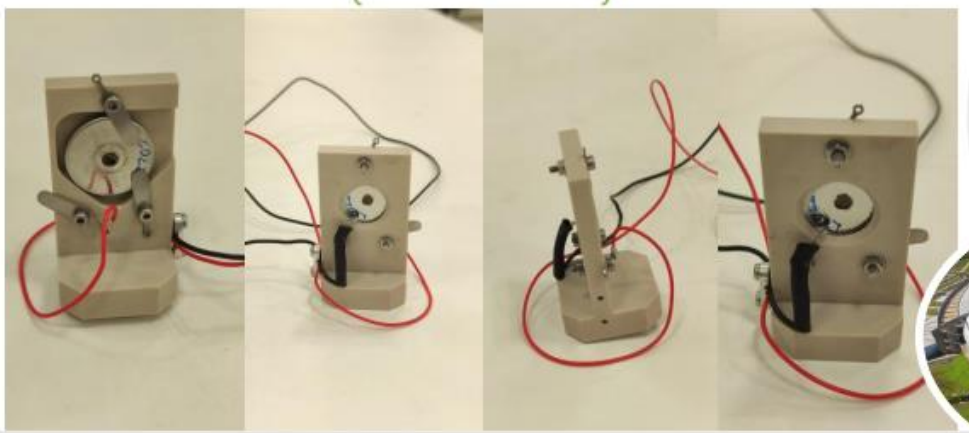
- Asymmetric cell:
  - W. E. – $LiCoO_2$: MWCNT
  - C. E. – AC : MWCNT
- Electrolyte: Li_2SO_4 1M
- *Operando*
  - Kapton window
  - Transmission geometry
  - The same configuration was used for the *Operando* XRD and XAS

XRD holder



MAX IV LABORATORY

XAS holder



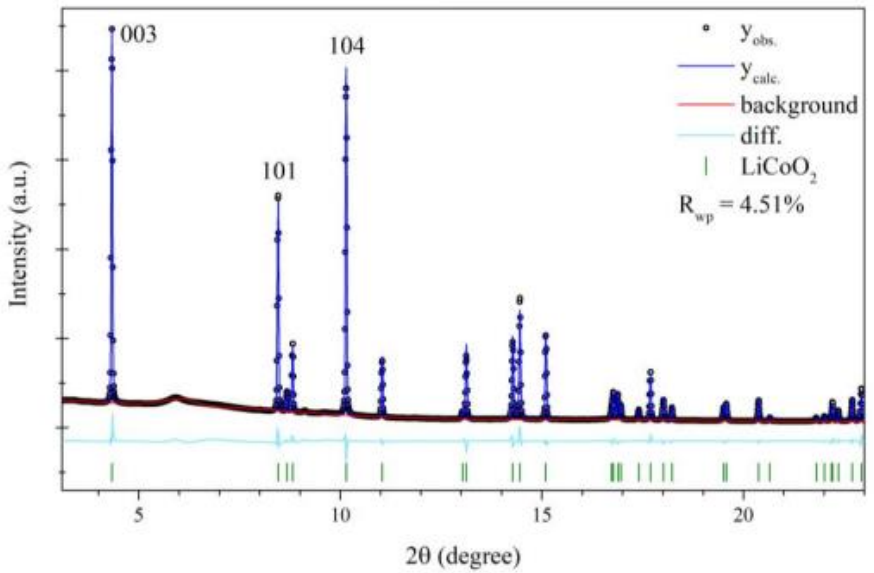
LNLS Brazilian Synchrotron Light Laboratory

sirius

Results and discussion

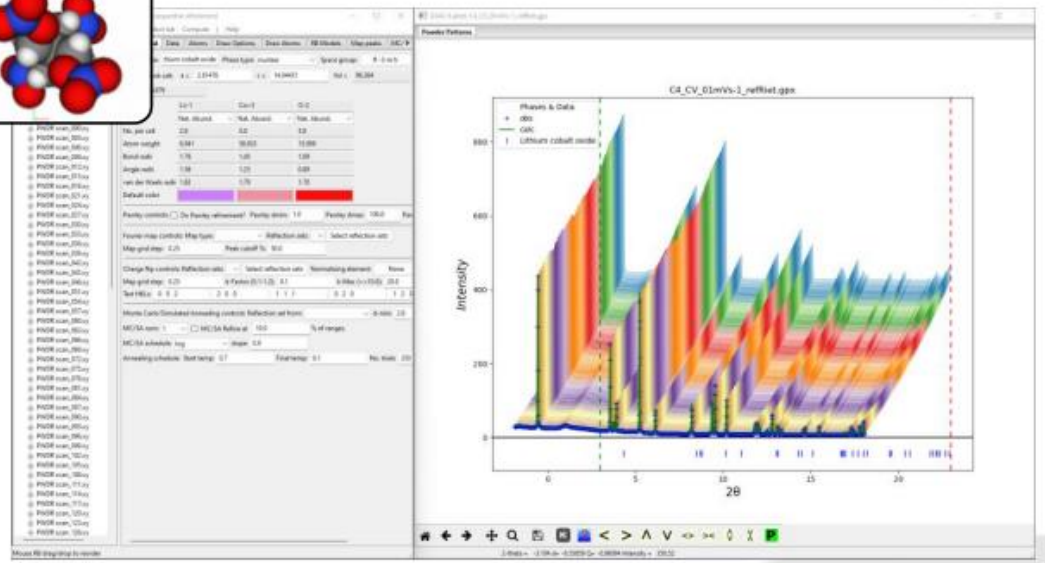
Software

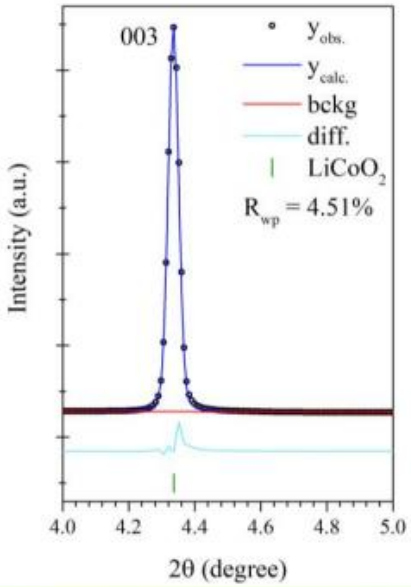
GSAS-2



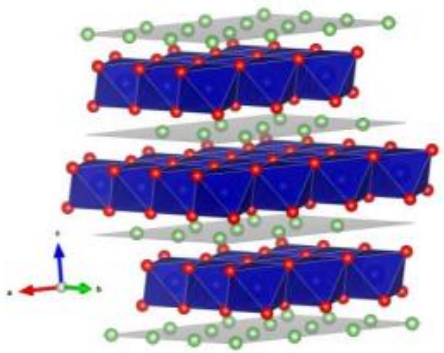
XRD *Refinement*

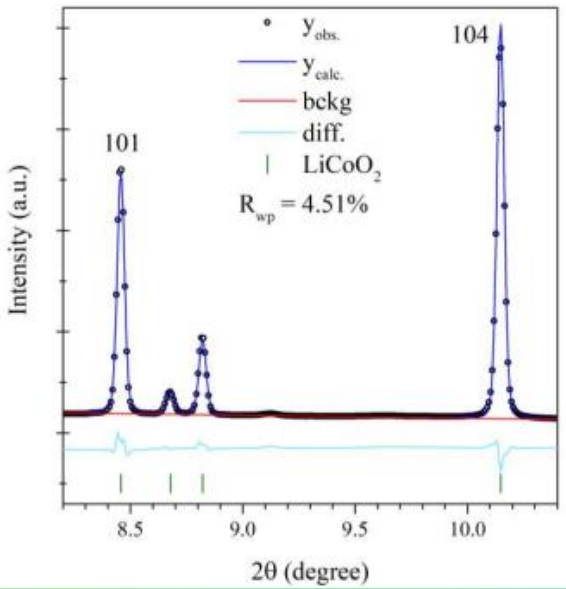
- $LiCoO_2$: identification phases 👍
- Refinement result:
  - R_{wp}: 4.51 %





003





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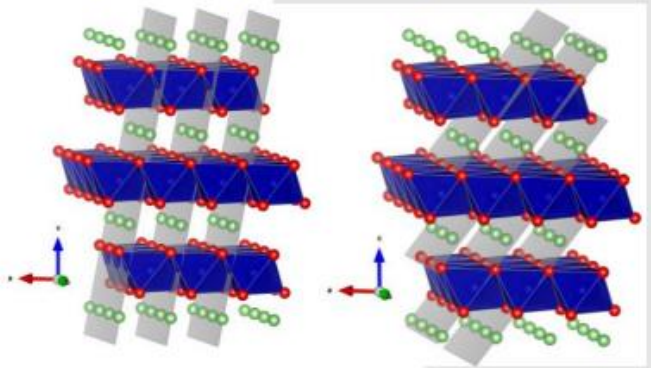
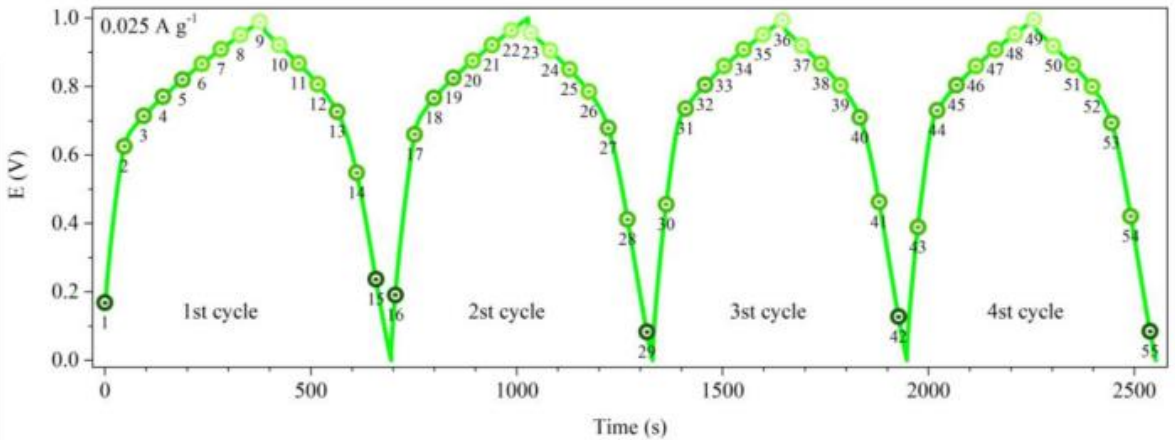


Results and discussion

XRD operando [GCD 0.025 A g^{-1}]



Unit cell parameters

- $a = b = 2.8147$ Å
- $c = 14.0457$ Å
- Vol. = 96.37 Å^3