Not just for experts –
PDF analysis in the home laboratory

Welcome to today's webinar from our Bruker AXS office in Karlsruhe, Germany!

Dr. Michael Evans
Application Scientist XRD

Dr. Christina Drathen
Product Manager XRD

Outline

Introduction
- Why do I need PDF?
- What is PDF & what information can I get from it?

PDF analysis in the home laboratory
- Basic requirements and a simple set-up
- Multi-purpose hard-energy instrument
- Using a single-crystal diffractometer

Wrap-up
- 3 Things to remember
- Question & Answers

Outline

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➢ **Why do I need PDF?**
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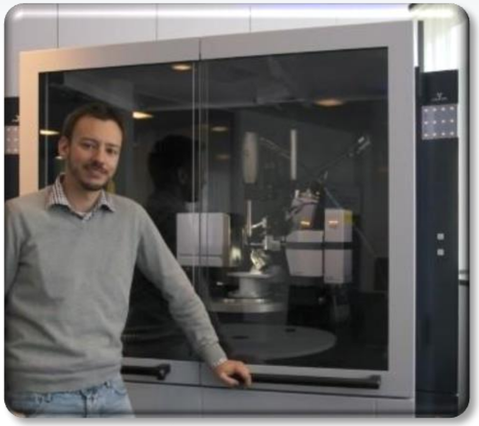
Applications of X-ray diffraction to characterize solid materials



Dr. Chrystal Pickr, *runs analytical service lab*

D8 ADVANCE
- Bragg-Brentano
- Cu tube, slits
- SSD160-2 detector

Main Applications
- Phase-ID
- Quantification

Eddy Current, *PhD student in battery research*

D8 DISCOVER
- Debye-Scherrer
- Cu-TXS, mirror
- LYNXEYE XE-T

Main Applications
- Structure refinement
- Microstructure analysis

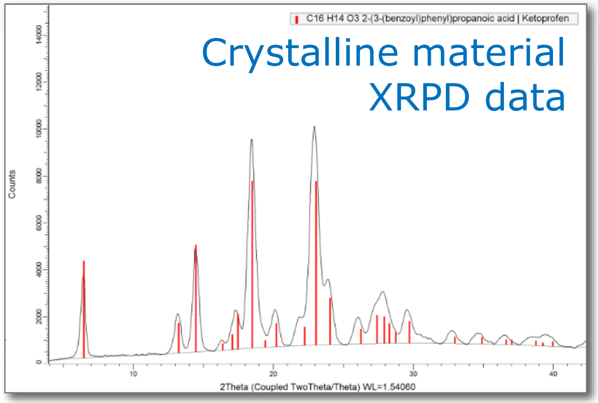
Prof. Max Power, *university crystallographer*

D8 VENTURE
- Kappa goniometer
- Mo/Cu IμS source
- PHOTON II detector

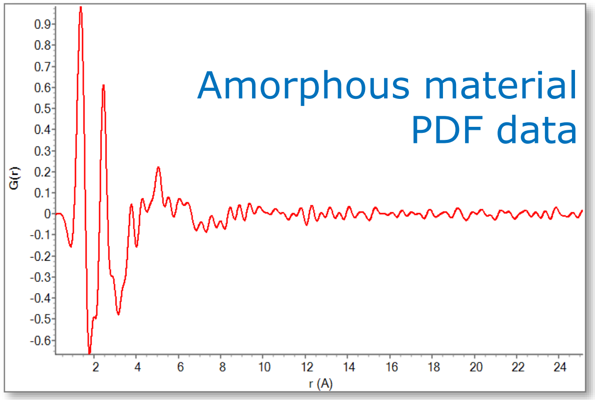
Main Applications
- Crystal structure determination

(Why) Do I need PDF?

- **Powder X-ray diffraction** (PXRD) analysis relies on information in the Bragg peaks:
  - Limited to crystalline materials
  - Less useful for small nanoparticles
  - Not useful for glasses and liquids
  - Provides average structure information

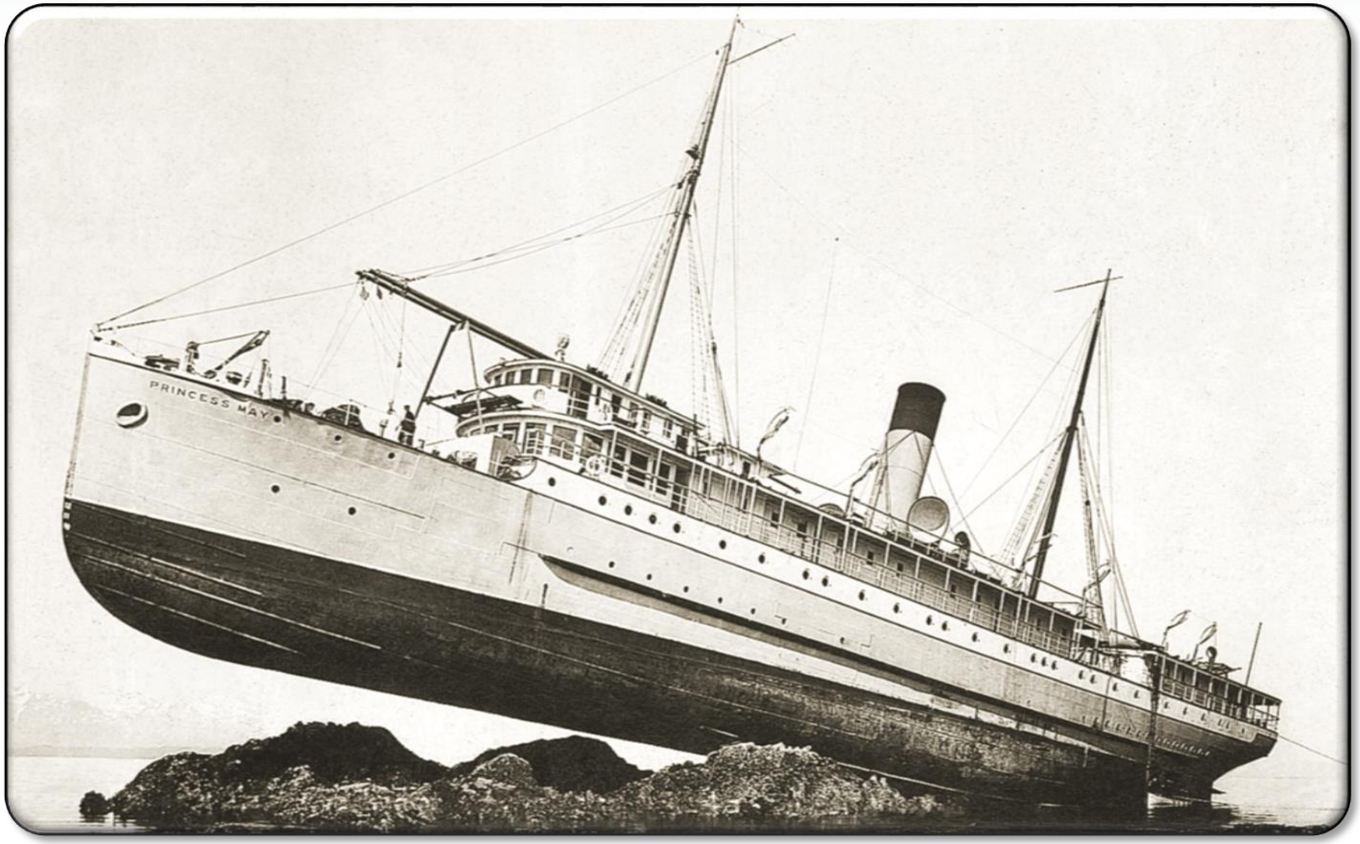


- **Pair Distribution Function analysis** makes use of total scattering data (Bragg peaks and diffuse scattering)
  - Useful for crystalline, nano-crystalline materials as well as liquids and glasses
  - Can provide insights where classic diffraction techniques can't
  - Provides local structure information



Average depth 50 fathom*

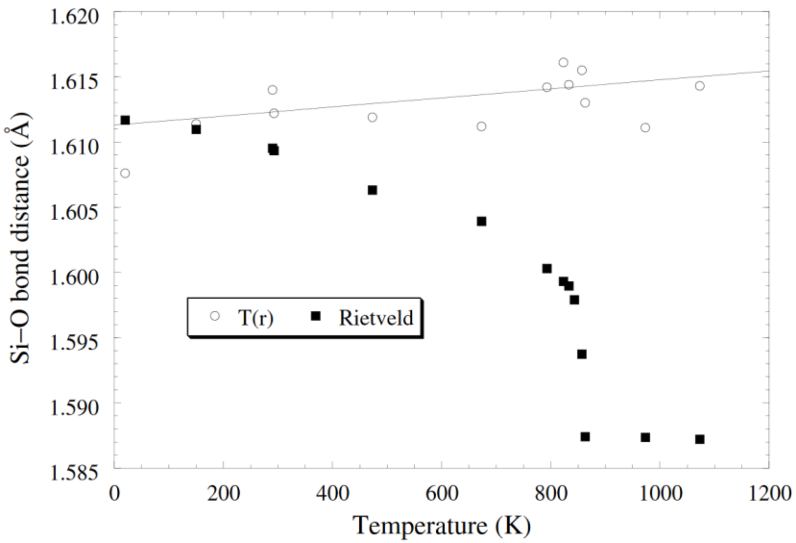
*90m

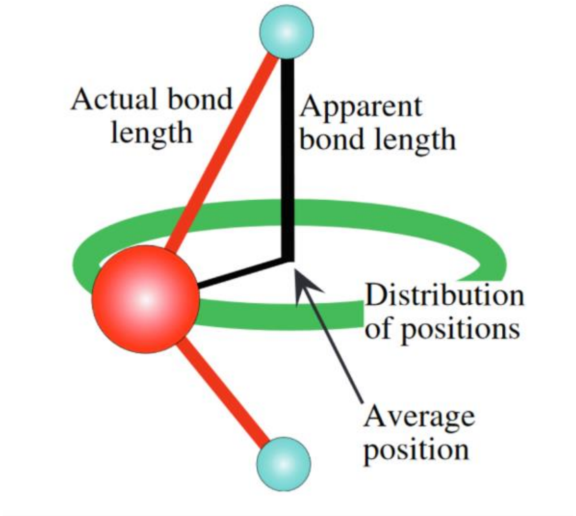


The *Princess May* aground near Sentinel Island, Alaska (1910)

Average vs. local structure

Si-O bond in α-quartz





- **Classic diffraction**
  Distance between averaged positions of pairs of atoms

- **Pair Distribution Function**
  Average distance between pairs of atoms

M.G. Tucker, D.A. Keen and M.T. Dove; Miner. Mag. **65** (2001) 489-507
M.G. Tucker, M.T. Dove and D.A. Keen; J. Phys.: Condens. Matter **12** (2000) L425-L430

For which materials is it relevant?

Crystalline materials

- “Unexpected” structure or properties

Disordered materials

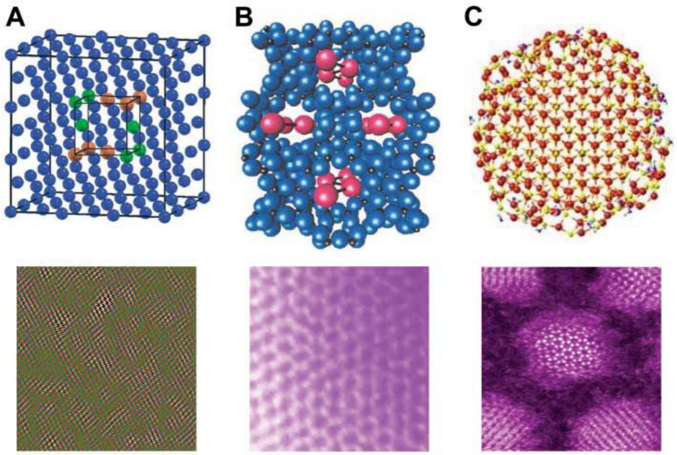
- Physical properties are often dictated by defects or domains of local structure

Nanomaterials

- Long-range order limited to a few nanometers
- Poorly defined Bragg peaks

Non-crystalline materials

- Amorphous materials and polymers



S.J.L. Billinge and I. Levin, **The problem with Determining Atomic Structure at the Nanoscale**, Science 316, 561 (2007)

Introduction

- Why do I need PDF?
- **What is PDF & what information can I get from it?**

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- Basic requirements and a simple set-up
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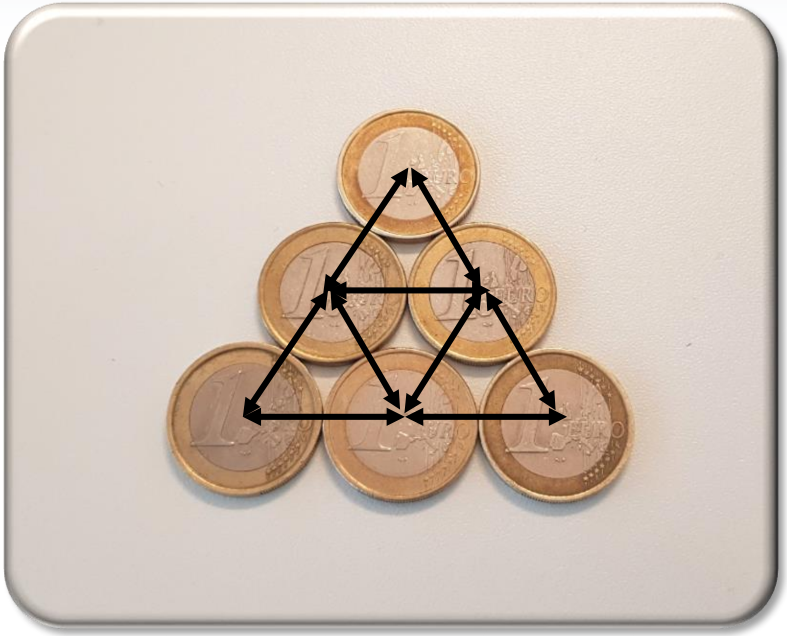
- Using a single-crystal diffractometer

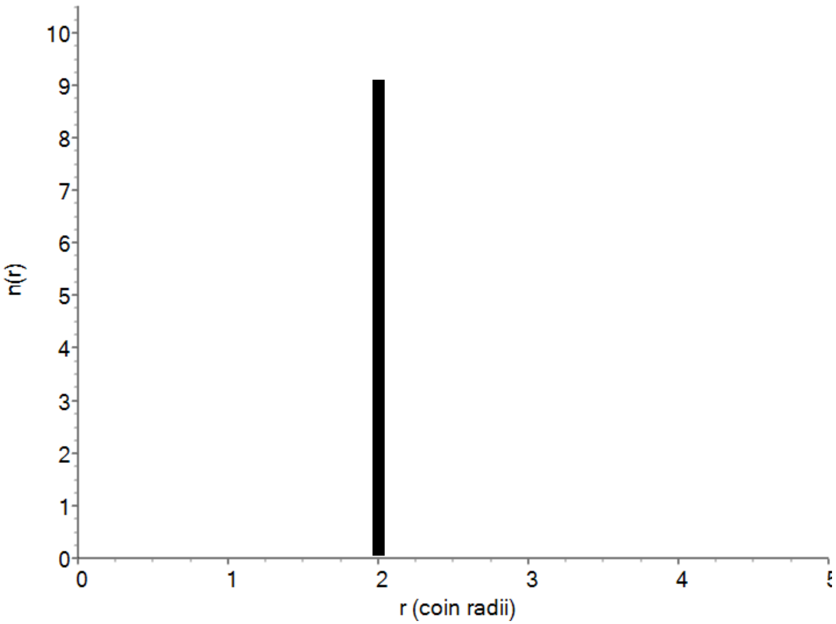
Wrap-up

- 3 Things to remember
- Question & Answers

What is a PDF?
Coins

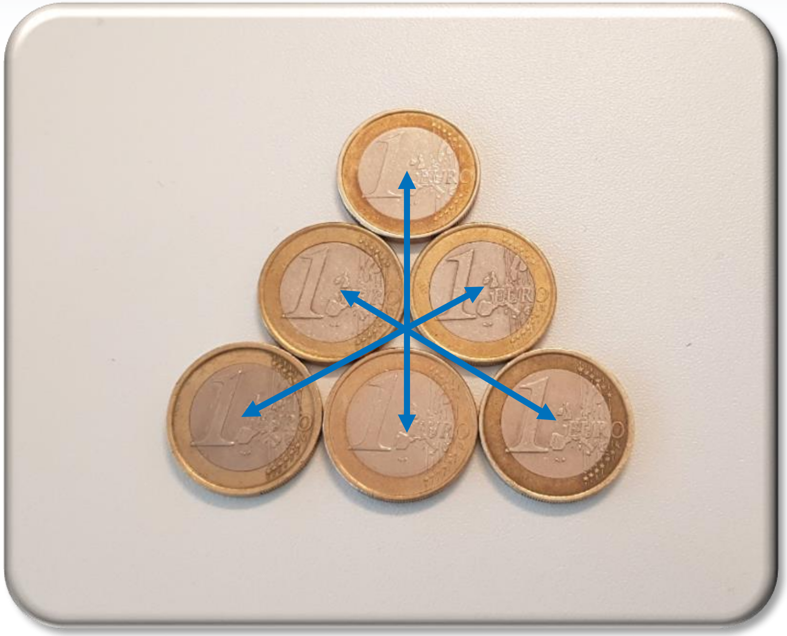


Radial atomic **P**air **D**istribution **F**unction (PDF) gives the interatomic distance distribution, or "probability" of finding atomic pairs of distance *r* apart.



The PDF is a real space function: it tells us where the coins are in relation to each other

What is a PDF?
Coins



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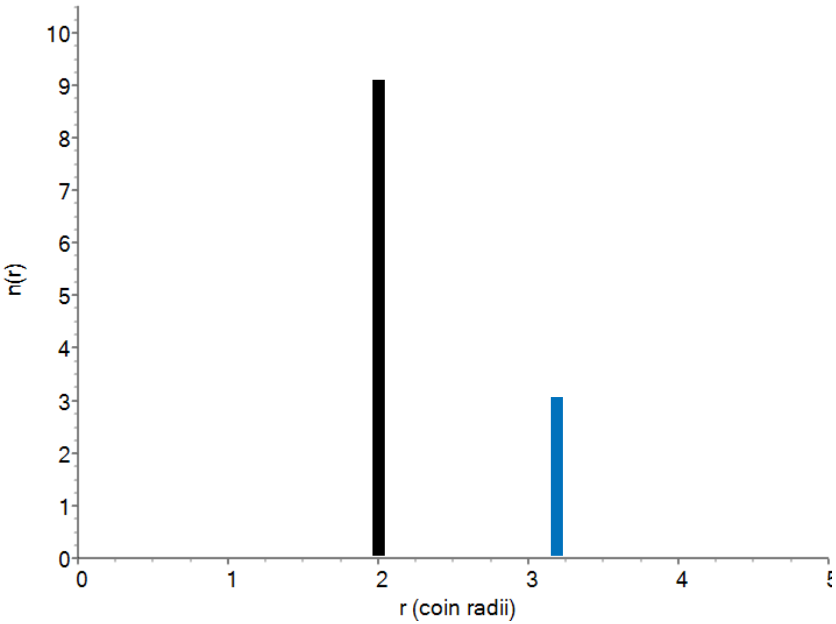

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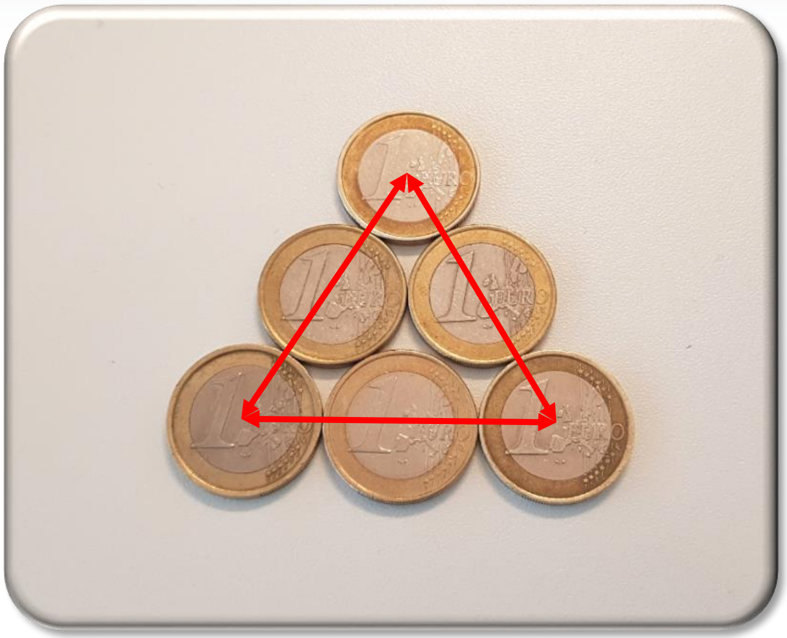

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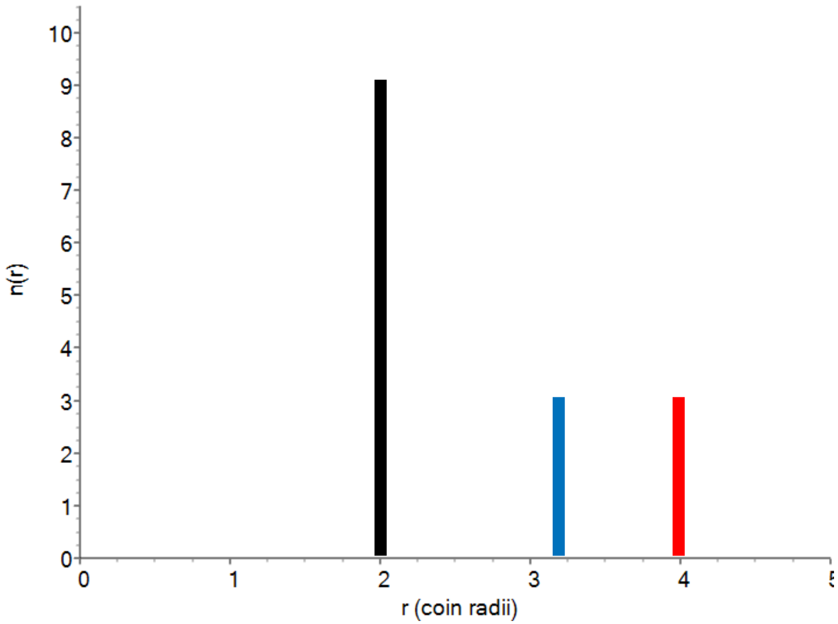


The PDF is a real space function: it tells us where the coins are in relation to each other

How does the PDF look?
Information content

Peak positions

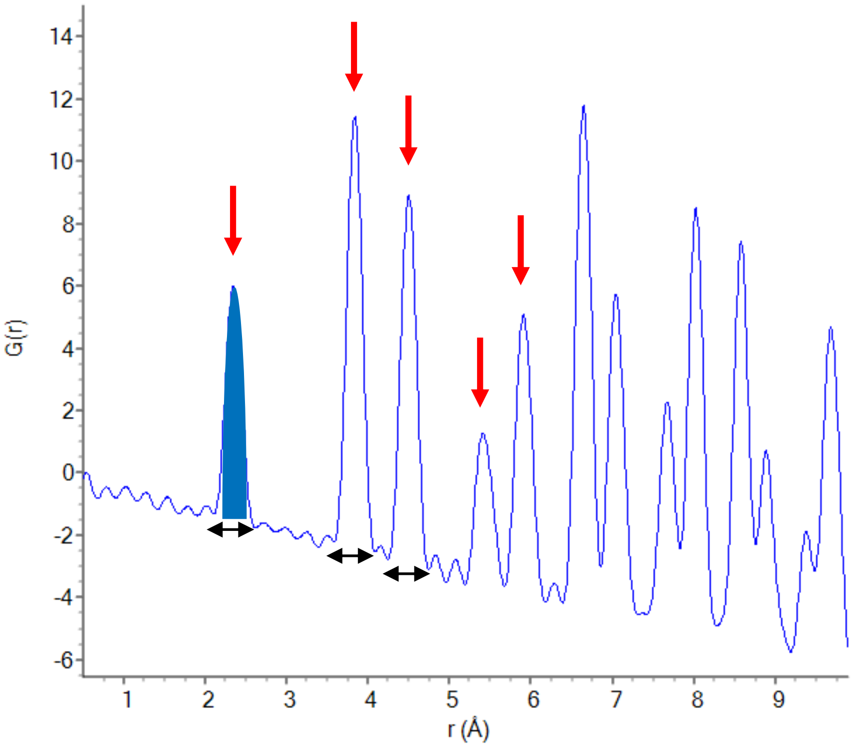
- Bond lengths, interatomic distances

Peak areas

- Coordination number

Peak widths

- Dynamic disorder (ADPs)
- Static disorder



How does the PDF look?
Information content

Peak positions

- Bond lengths, interatomic distances

Peak areas

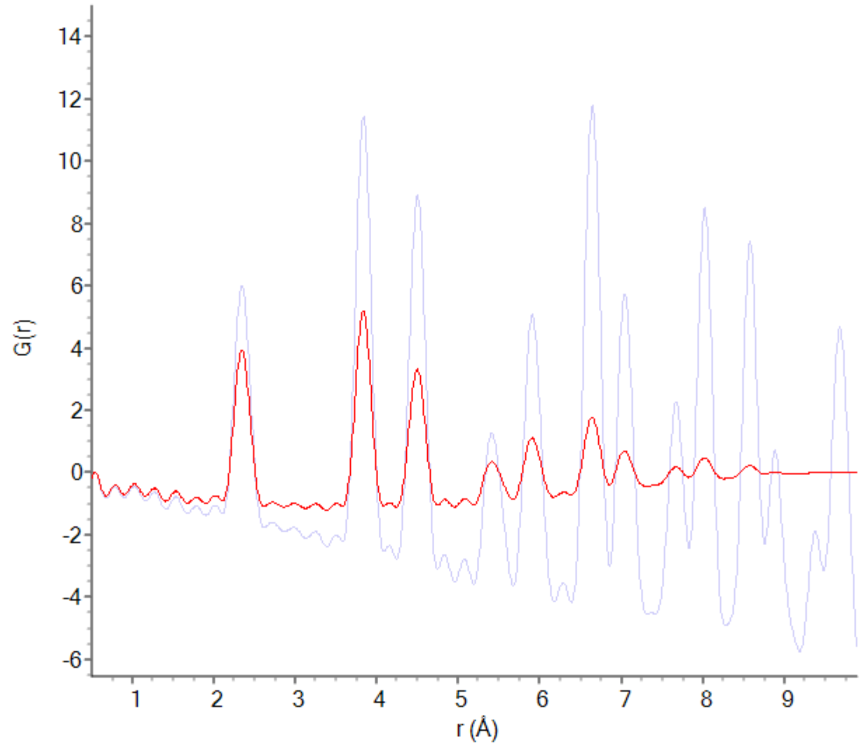
- Coordination number

Peak widths

- Dynamic disorder (ADPs)
- Static disorder

PDF peak damping

- Crystallite size



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PDF on a typical powder diffractometer

Dr. Chrystal Pickr, *manages an analytical service lab*

D8 ADVANCE
- Bragg-Brentano
- Cu tube
- Divergence slits
- Sample-changer
- SSD160-2 detector

change to:

→ Mo (Ag) tube

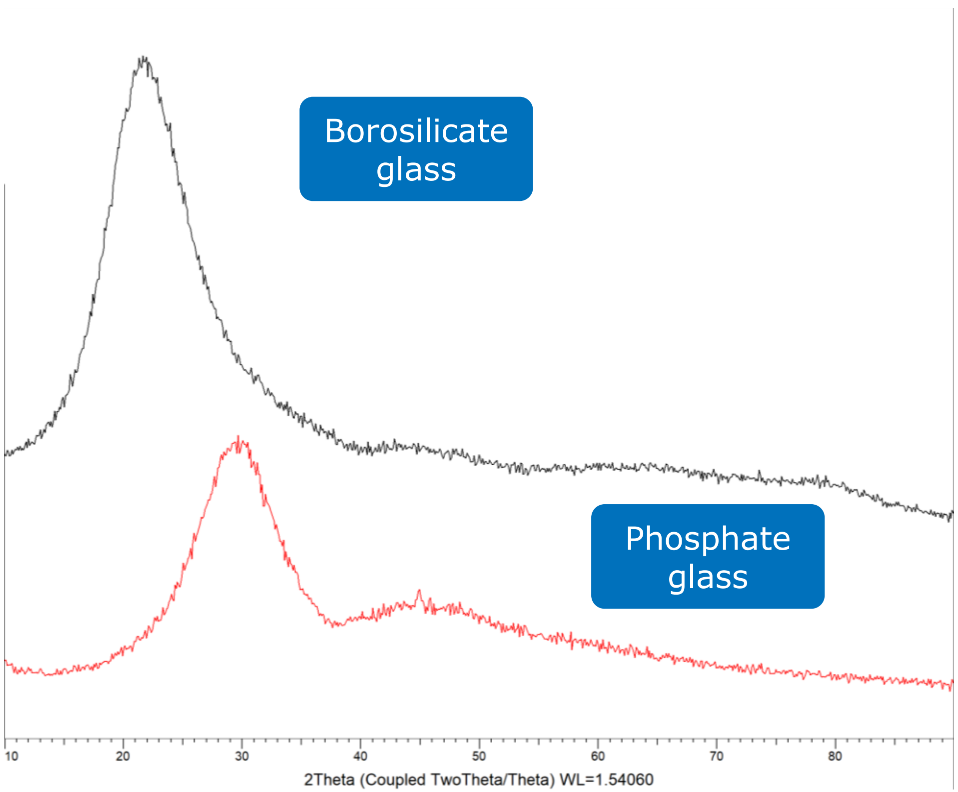
→ Capillary stage

Benefits

- Low entry point (Mo or Ag tube only) to access PDF in your lab
- Tube and stage change in < 10 min
- Use standard divergence slits as high resolution data (sharp peaks) not needed for PDF analysis
- Great for occasional PDF measurements of amorphous (liquids, glasses) or crystalline samples

Application Example
Glass

- Glasses: amorphous materials with no long-range atomic ordering
- Diffraction patterns show only broad features, no Bragg peaks
- What structural information can be extracted?



Oxide	(%)
SiO_2	81
B_2O_3	13
Na_2O	3.5
Al_2O_3	2.3
K,Ca	< 1

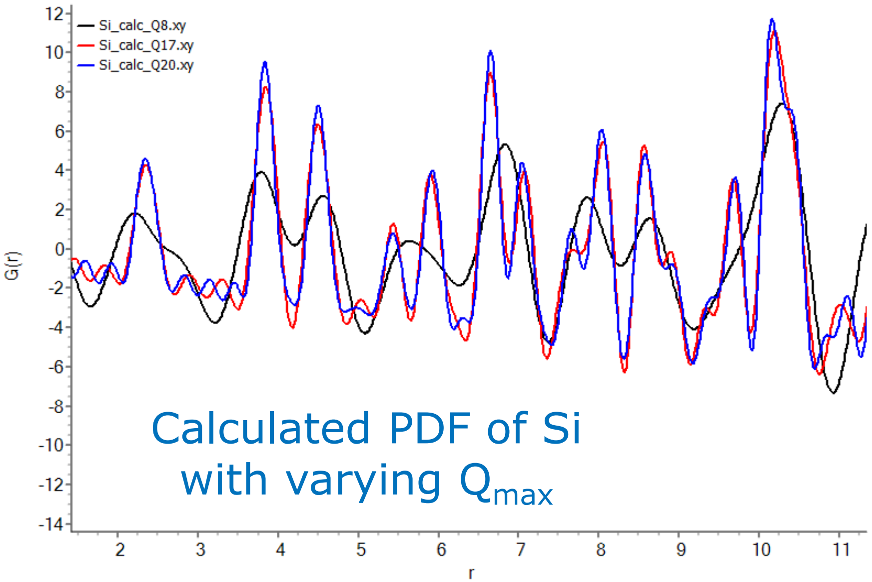
Oxide	(%)
P_2O_5	30
SrO	20
ZnO	20
CaO	20
Na_2O	10

PDF Analysis
Why is Cu not suitable?

Source	$E_{K\alpha 1}$	$\lambda_{K\alpha 1}$	$2\theta_{max}$	Q_{max}
Cu	8.05 keV	1.541Å	160°	8.0 $Å^{-1}$
Mo	17.48 keV	0.708Å	160°	17.5 $Å^{-1}$
Ag	22.16 keV	0.559Å	160°	22.0 $Å^{-1}$

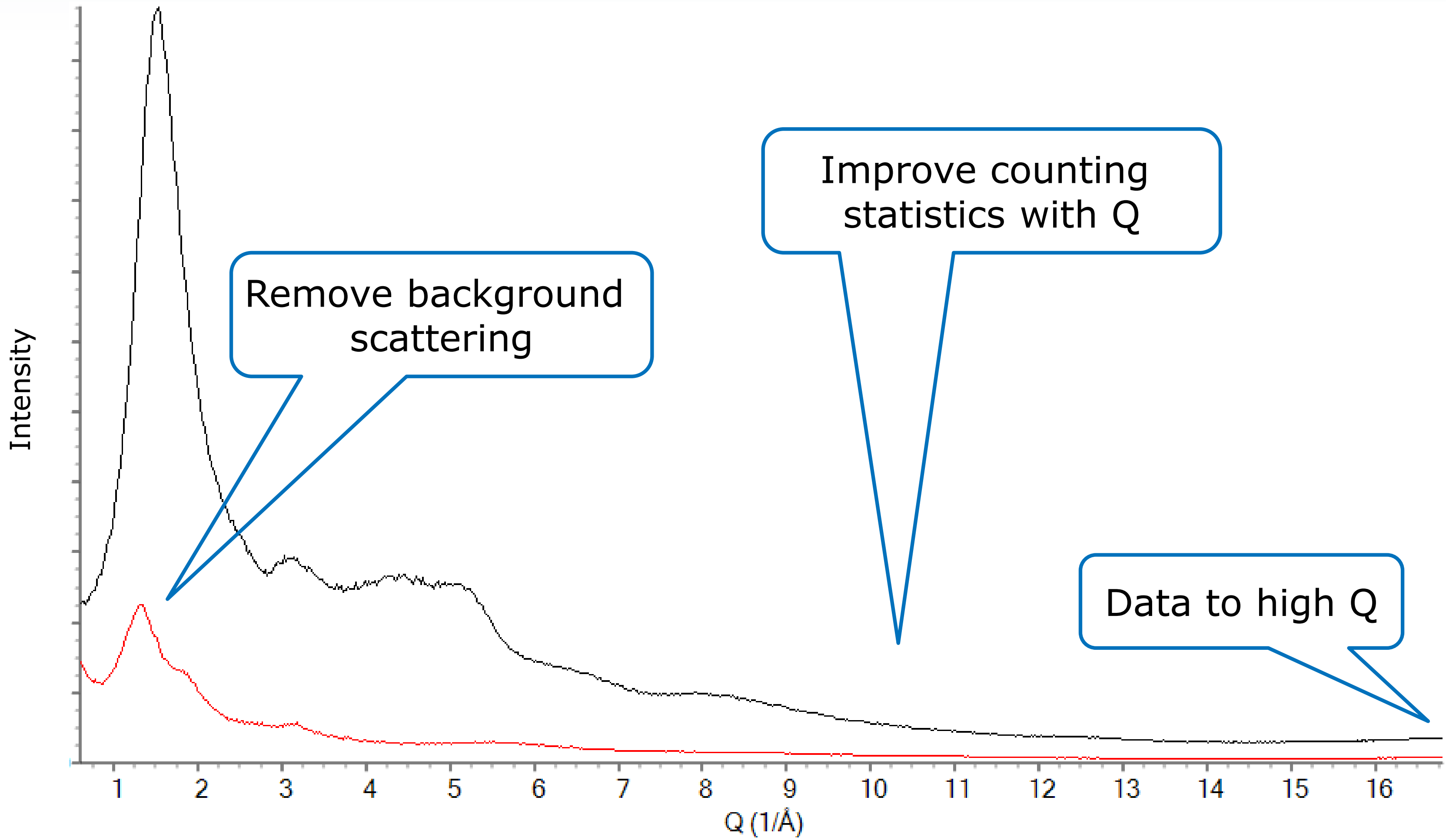
$$Q = \frac{4\pi \sin\theta}{\lambda}$$

The real-space resolution of the PDF depends on the extent of the diffraction pattern (Q_{max}) in reciprocal space.



Calculated PDF of Si with varying Q_{max}

PDF Analysis
Data Collection Requirements



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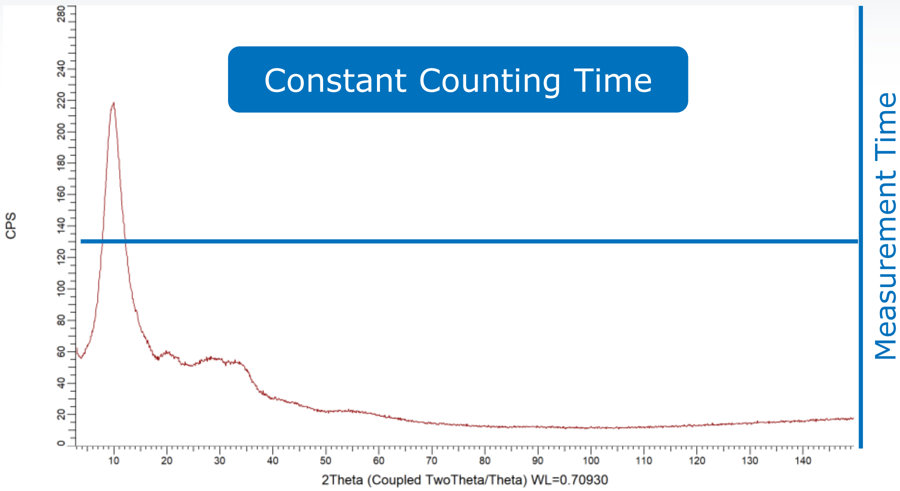
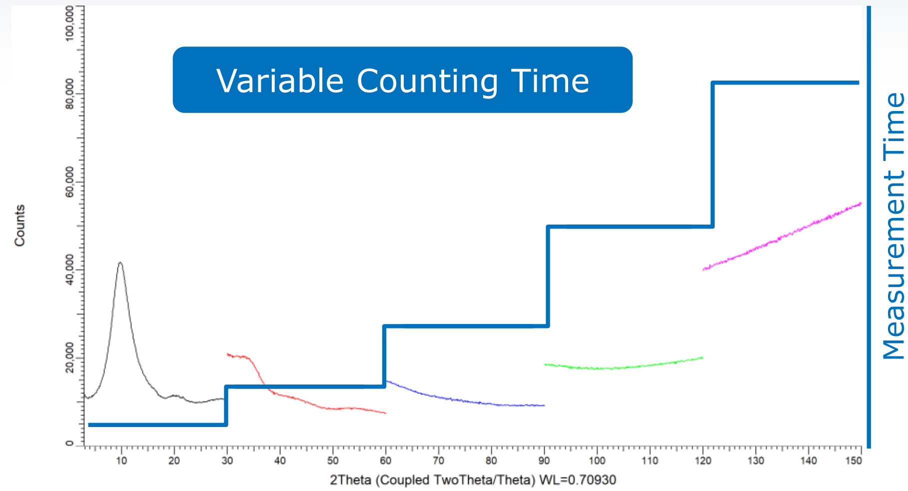
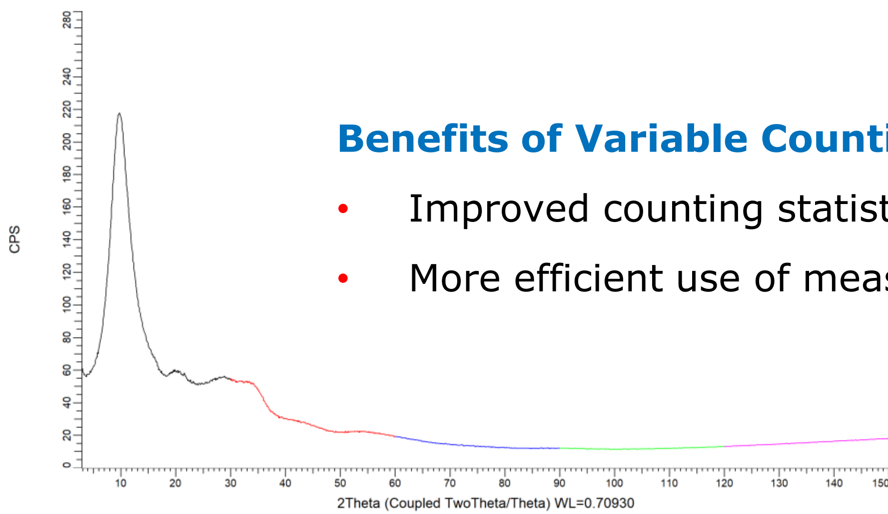


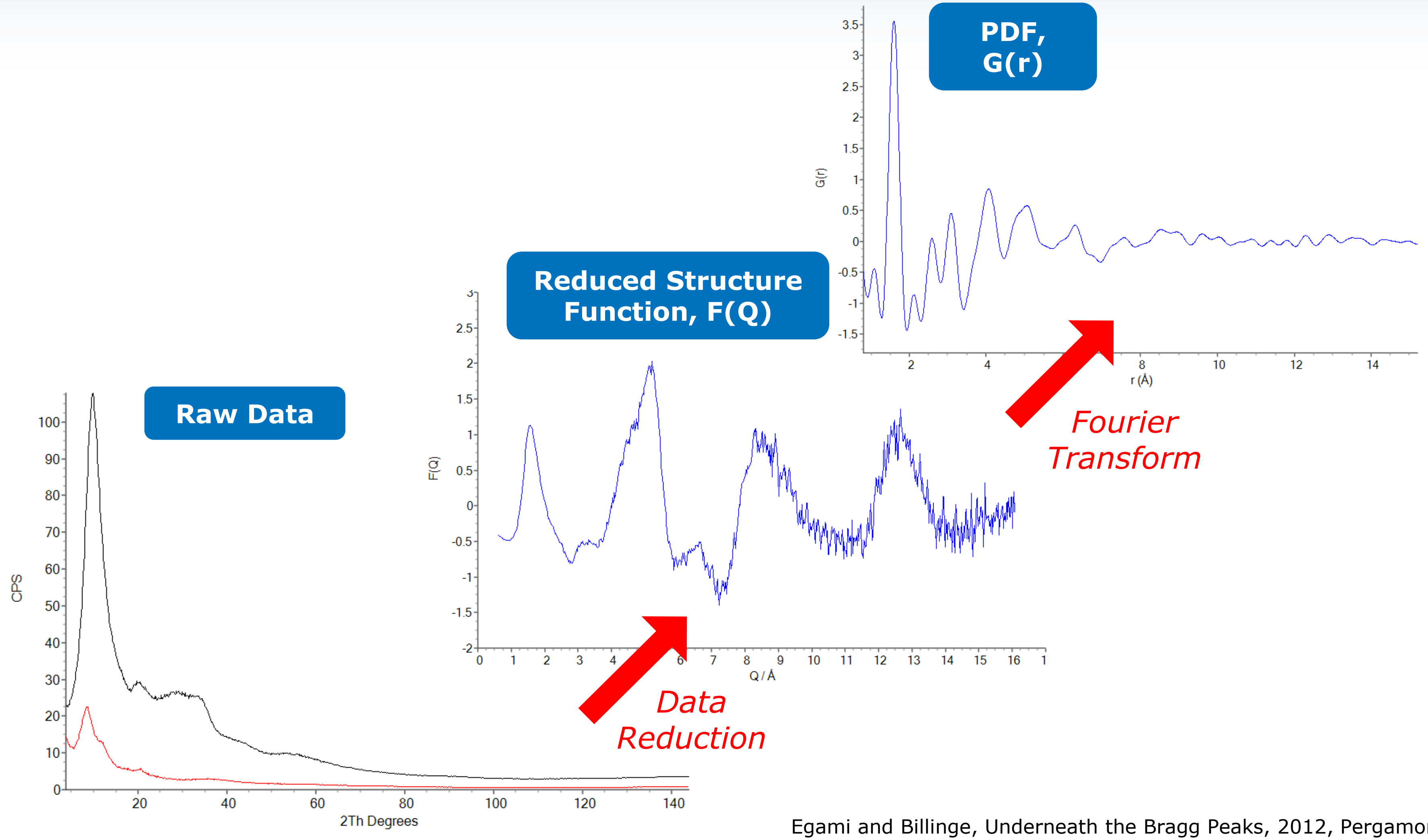




Benefits of Variable Counting Time (VCT)

- Improved counting statistics as function of Q
- More efficient use of measurement time

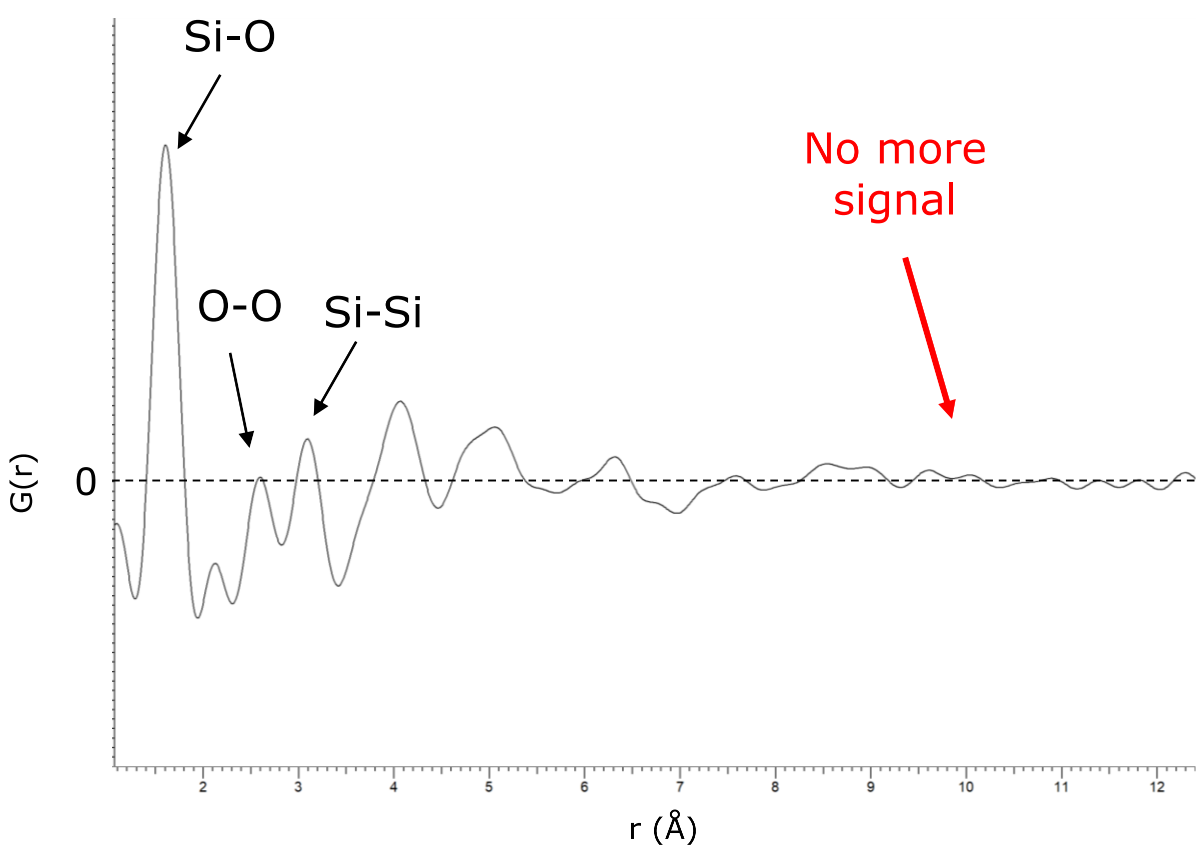
PDF Analysis
How do we obtain the PDF?

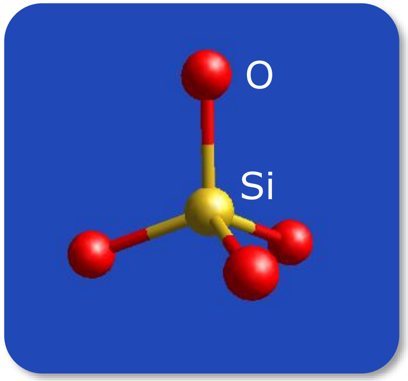


Egami and Billinge, Underneath the Bragg Peaks, 2012, Pergamon

Application Example
Borosilicate Glass

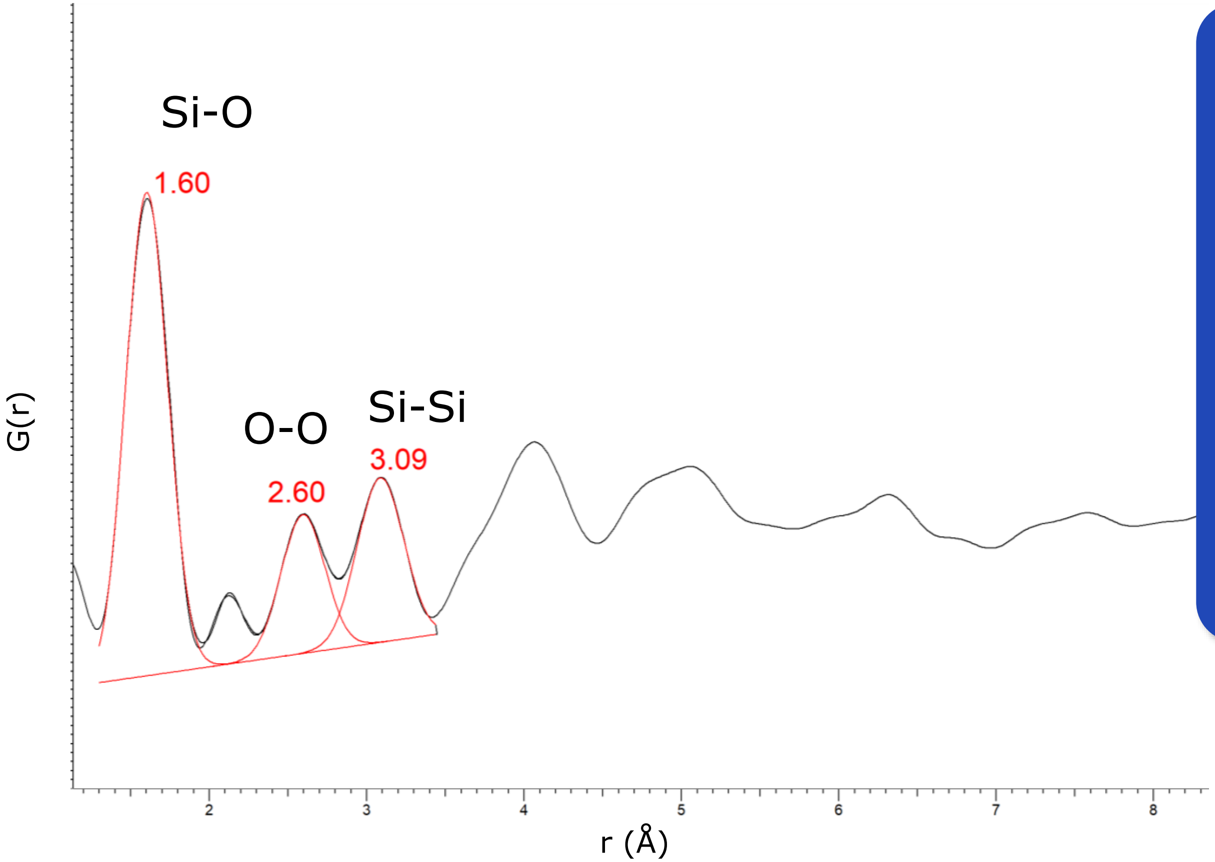
- Direct information: what can we see just by looking at the PDF

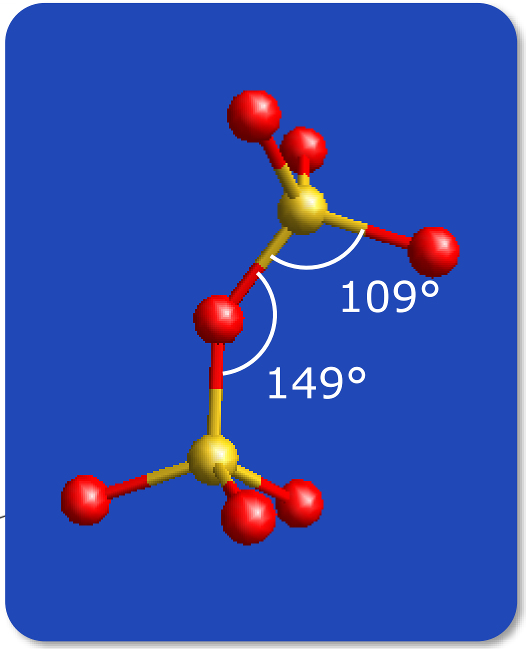




Application Example
Borosilicate Glass

- Peak fitting in DIFFRAC.EVA to obtain bond lengths

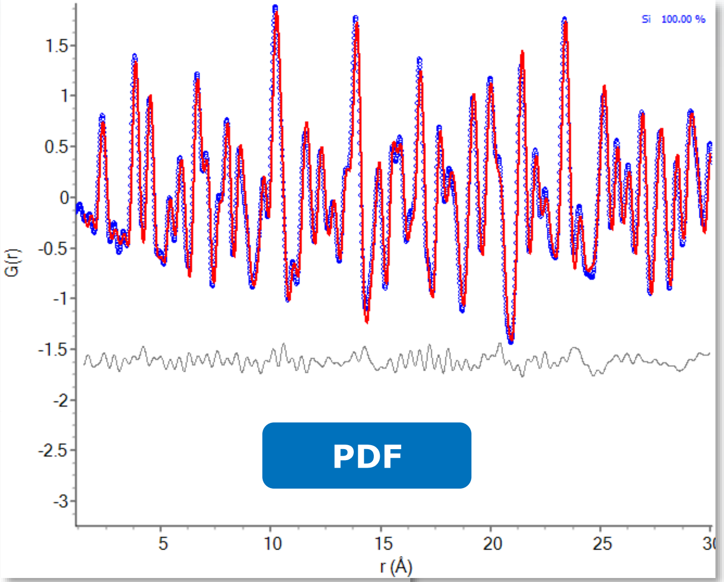


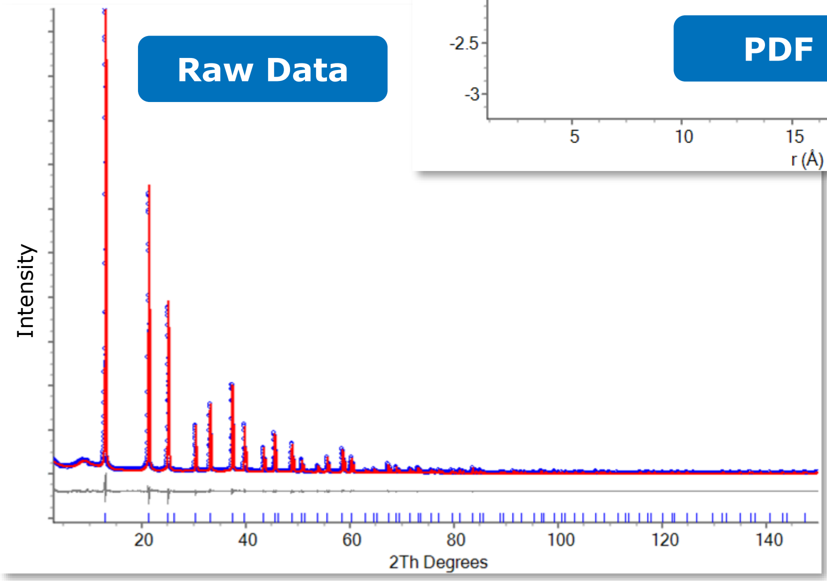


Application Example
Crystalline materials

- Also for crystalline materials, this simple set-up delivers great PDF data

- Both Bragg-data and real-space PDF can be modelled in **DIFFRAC.TOPAS** to extract detailed information:
  - Average and local structures
  - Lattice parameters
  - Bond distances
  - Microstructure
  - Particle size
  - …





Silicon powder;
13h scan time

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- **Multi-purpose hard-energy instrument**
- Using a single-crystal diffractometer

Wrap-up

- 3 Things to remember
- Question & Answers

PDF for those keen on structure analysis

Eddy Current, *PhD-Student in battery research*

D8 DISCOVER	**Change to:**
• Debye-Scherrer	
• Cu-TXS, mirror	→ Mo-TXS, mirror
• Capillary stage	
• LYNXEYE XE-T	→ EIGER2 R 500K*

Benefits

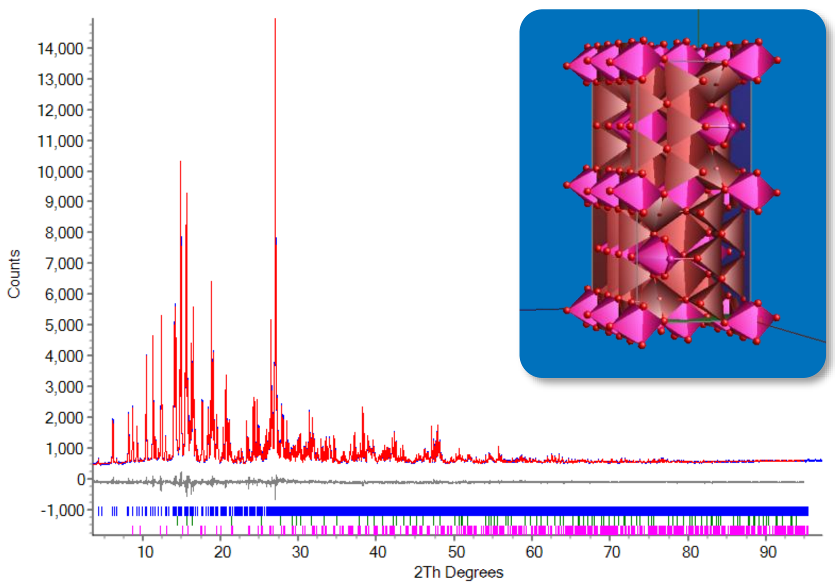
- Higher penetration in absorbing samples with hard radiation, e.g. for in-situ studies of batteries
- 10x faster measurements with larger 2D detector
- Keep the same set-up for structural work and PDF analysis

*optional

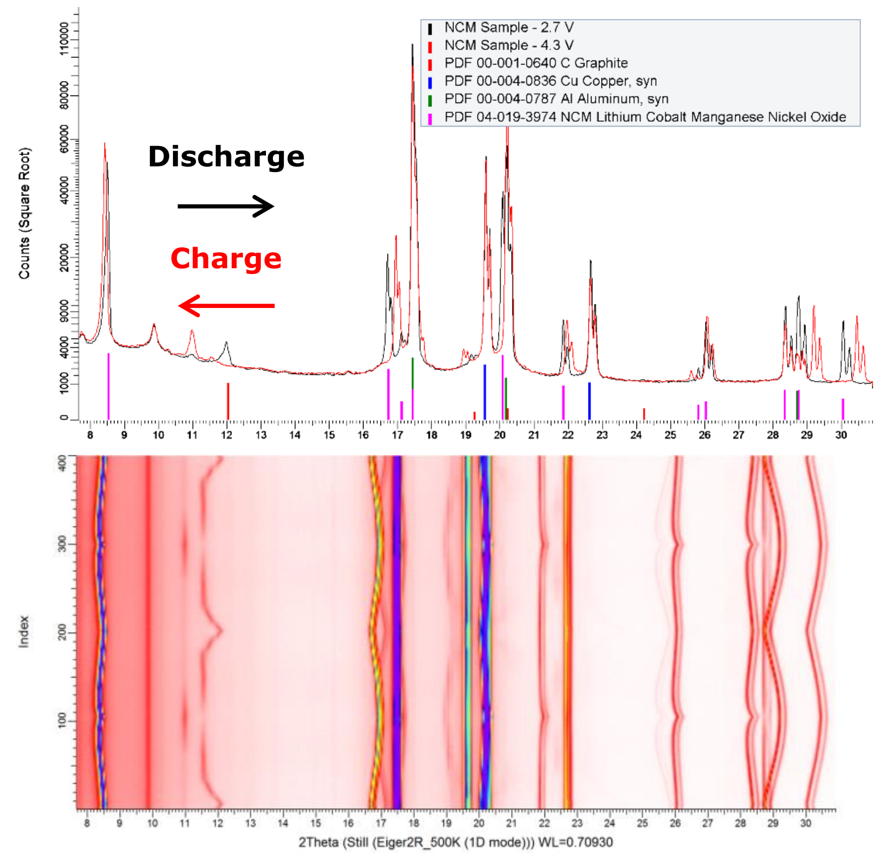
D8 Family with EIGER2 R 500K
Hard Radiation Applications

- Versatile configuration for multiple applications

Structure Solution/Refinement

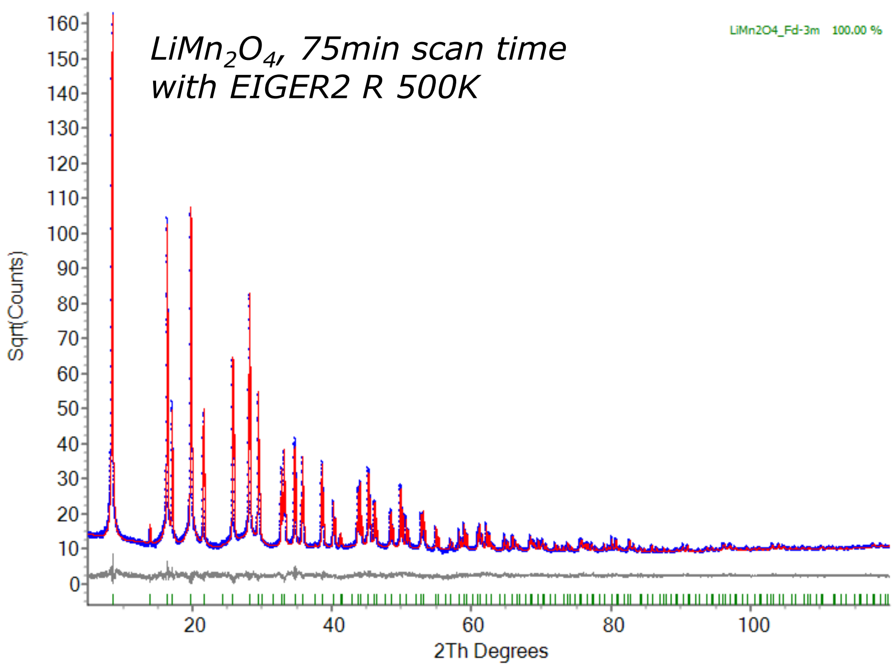


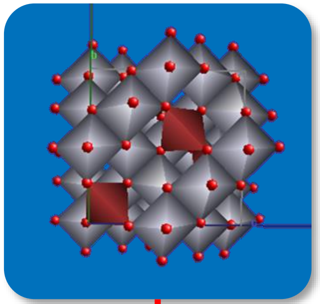
In-situ Experiments - Battery Cells



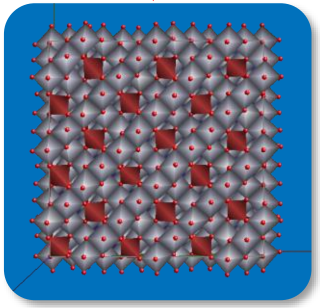
Iso-intensity plot, 2 charge/discharge cycles

Cathode Material $LiMn_2O_4$
Combined Rietveld + PDF Analysis





260 K



Room Temperature

- Cubic *Fd*-3*m*
- Average valence $Mn^{3.5+}$
- 6 equivalent Mn-O bonds = 1.95 Å

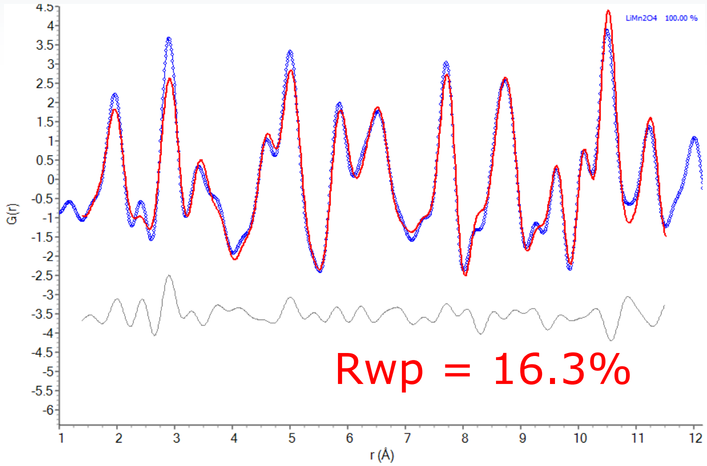
Low Temperature

- Orthorhombic *Fddd*
- Mn^{3+}/Mn^{4+} ordering
- Mn-O bonds between 1.82 to 2.23 Å
- Superlattice reflections, ($3a \times 3a \times a$) cell

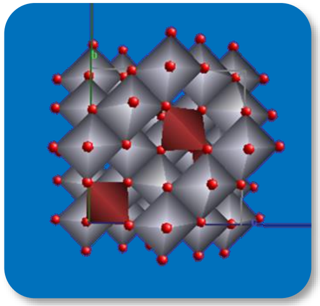
Kodama, K. et al., J. Phys. Soc. Jpn. 82, 094601 (2013)

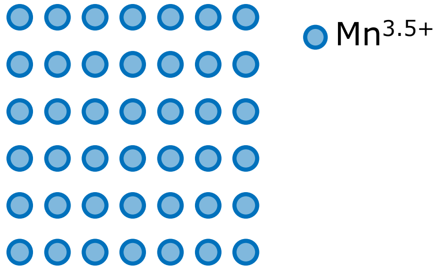
Cathode Material $LiMn_2O_4$

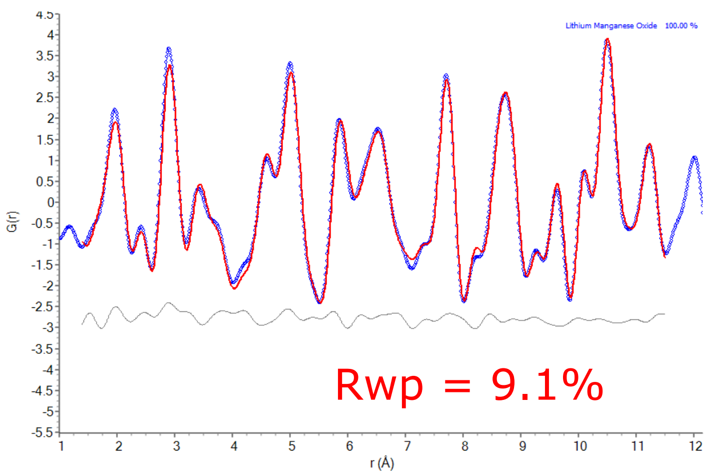
Local Structure at room temperature



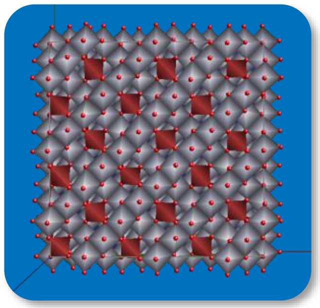
Cubic – disordered $Mn^{3.5+}$

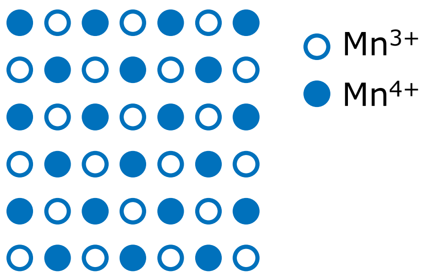




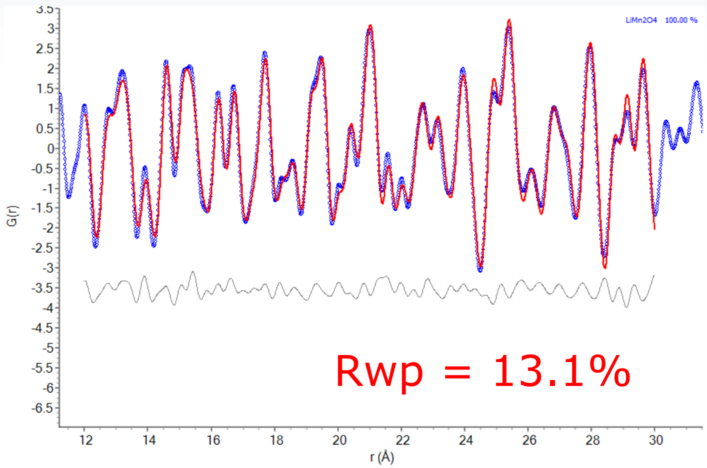


Orthorhombic - ordered Mn^{3+}/ Mn^{4+}

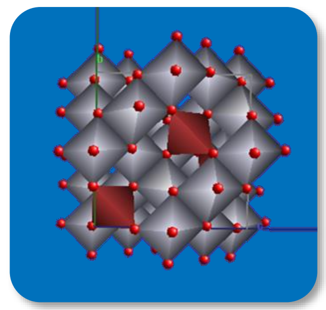


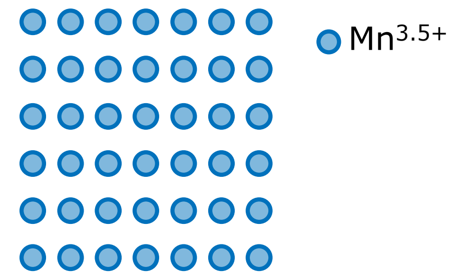


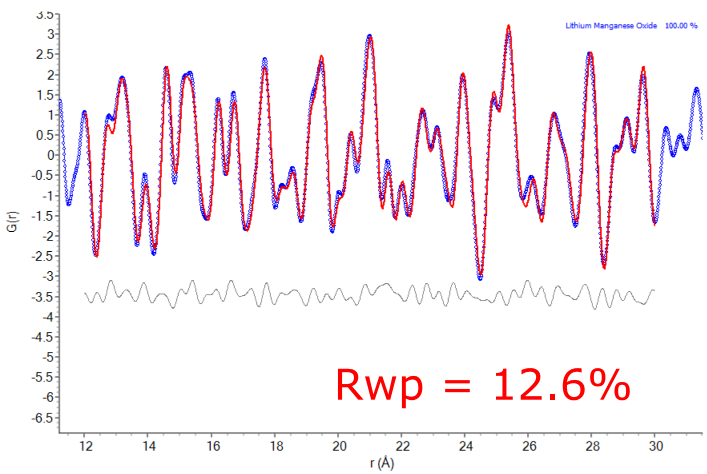
Cathode Material $LiMn_2O_4$
Local Structure at room temperature



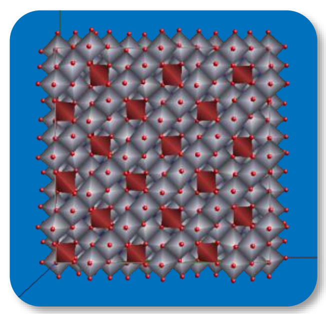
Cubic – disordered $Mn^{3.5+}$ on long range

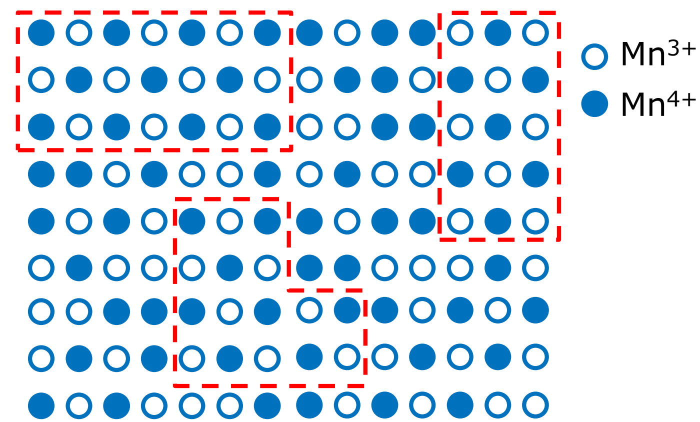






Orthorhombic - ordered Mn^{3+}/ Mn^{4+} domains





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- Why do I need PDF?
- What is PDF & what information can I get from it?

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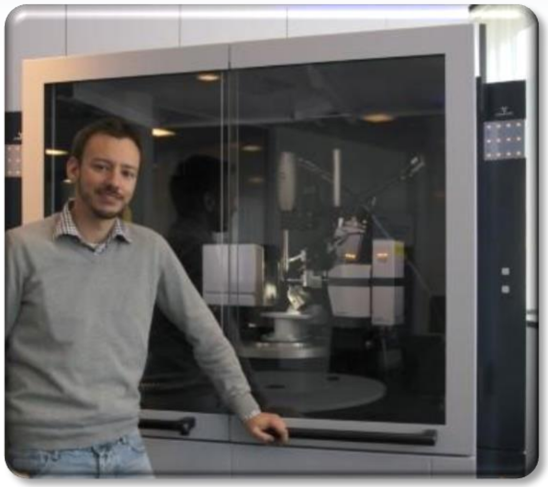
- Basic requirements and a simple set-up
- Multi-purpose hard-energy instrument
- ➢ **Using a single-crystal diffractometer**

Wrap-up

- 3 Things to remember
- Question & Answers

PDF possible & extra benefits for SCD



Prof. Max Power, *university crystallographer*

D8 VENTURE

- KAPPA4 goniometer
- Cu/Mo IμS
- PHOTON II

Change to:

→ PHOTON III*

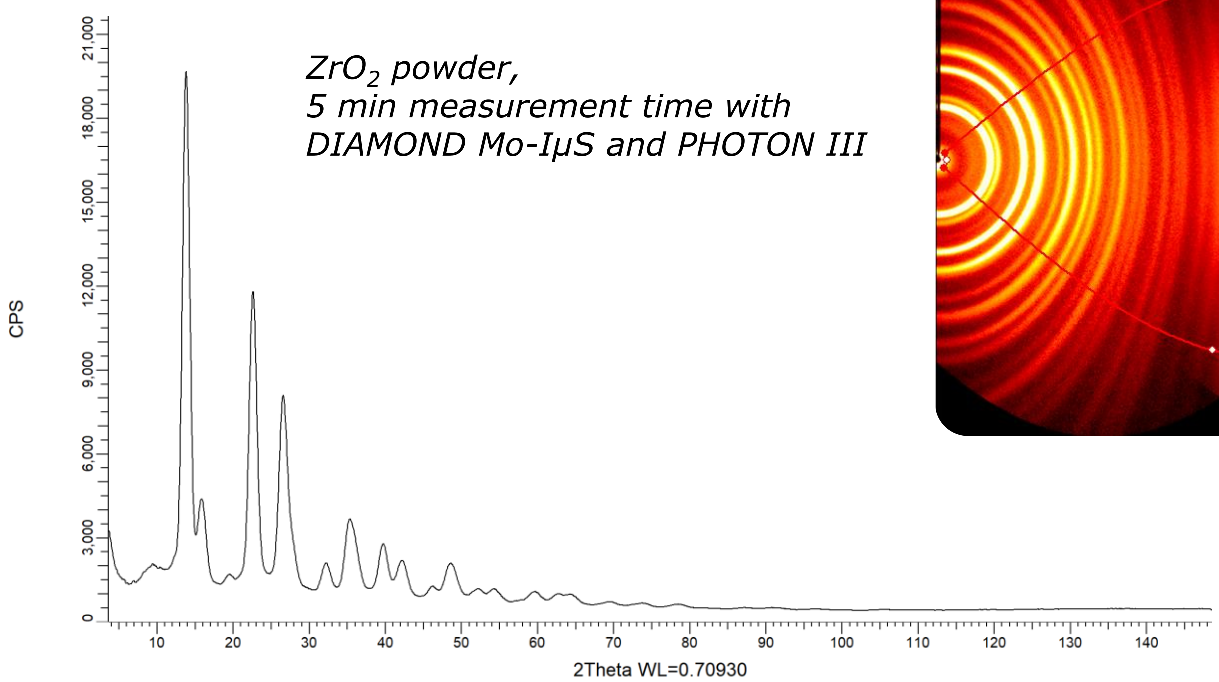
Benefits

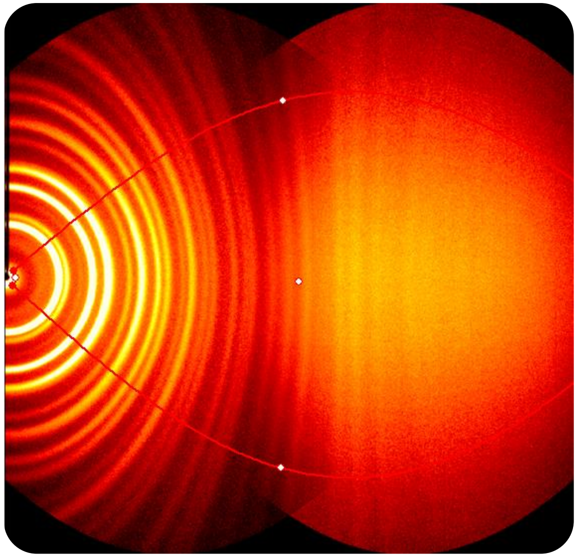
- Use your existing D8 QUEST or D8 VENTURE diffractometers also for PDF analysis.
- Only tiny sample amounts are required when working with highly focused high-brilliance point-focus beams of the IμS microfocus sources.
- PHOTON III for highest sensitivity for weakest signals and hard radiation.

*optional

Nanoparticles: ZrO_2
PDF Measurements on D8 VENTURE

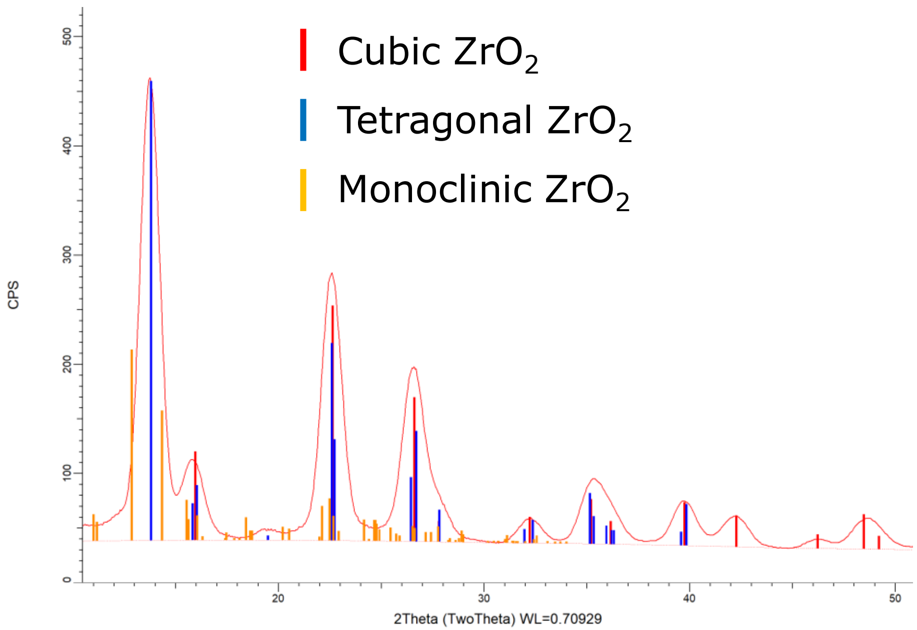
- Sample loaded in capillary and rotated during measurement
- Single frame coverage of 86º 2θ with PHOTON III C14 detector
- Entire PDF dataset collected in 2 frames
- Total measurement time: 5 min



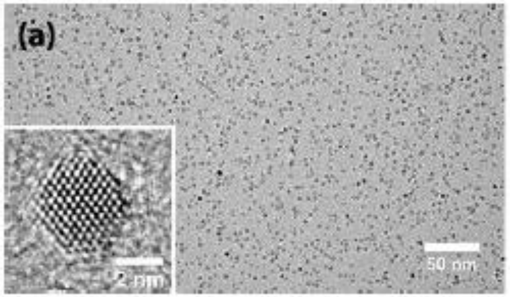


Nanoparticles: ZrO_2
Bragg peaks can tell us something…

- There are Bragg peaks, so there is some information to extract from the raw data



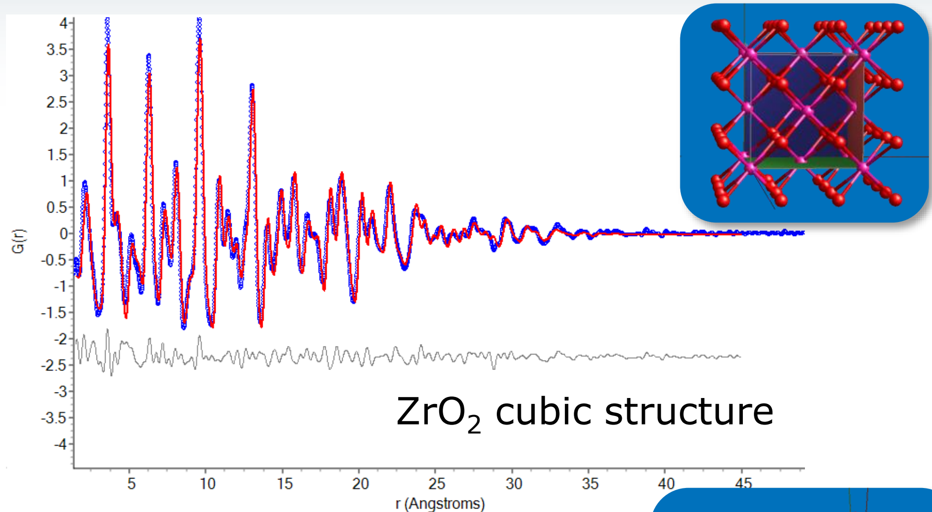
- ZrO_2 exists as 3 different polymorphs
- Each differs in catalytic activity and selectivity
- Crystallite size: around 4nm

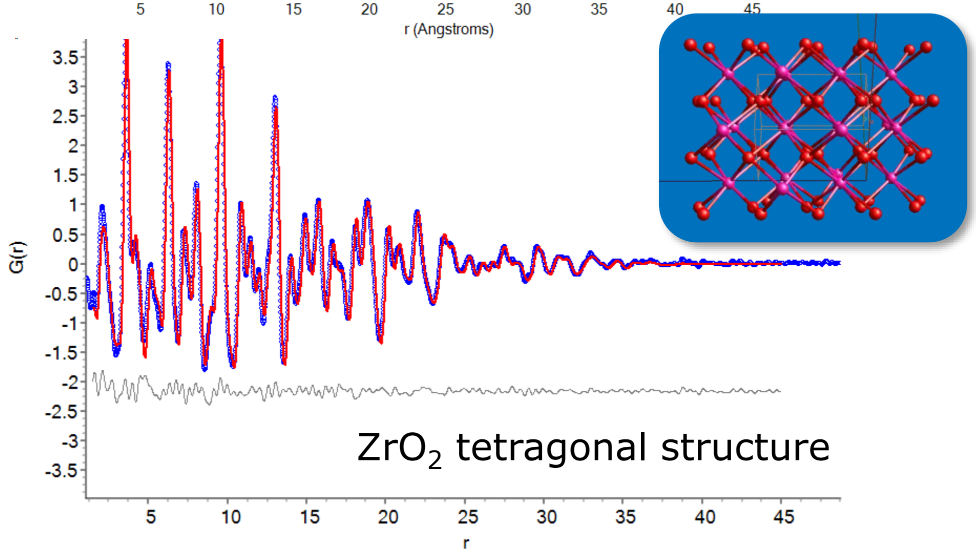


Sample courtesy of Jonathan De Roo, Univ. of Basel
Rijckaert, H. et al., *Materials* **2018,** *11* (7), 1066.

Nanoparticles: ZrO_2

…but the PDF can tell us more!





	ZrO_2 (cub)	**ZrO_2 (tet)**
SG	*Fm-3m*	$P4_2/nmc$
a (Å)	5.1256(4)	3.6054(2)
c (Å)		5.1925(7)
V (Å^3)	134.66(3)	67.50(1)
B_{Zr}	1.03(2)	0.97(1)
B_O	5.64(5)	2.61(4)
dia. (Å)	3.9(1)	4.1(1)
R_{wp} (%)	16.2	11.3

Introduction

- Why do I need PDF?
- What is PDF & what information can I get from it?

PDF analysis in the home laboratory

- Basic requirements and a simple set-up
- Multi-purpose hard-energy instrument
- Using a single-crystal diffractometer

Wrap-up

- 3 Things to remember
- Question & Answers

PDF is possible – also in your Lab!
3 Things to remember

1. Start using PDF by simply exchanging your tube from Cu to Mo or Ag
   → measure PDF overnight

2. Increase speed and performance with dedicated optics and large 2D detectors
   → measure PDF in a few hours

3. Work with your existing SCD instrument or add some components for extra intensity
   → measure PDF in <1h

Any Questions?

Take part in the poll & let us know how useful you would rate PDF for your work

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