RMS Testing • Research • Consulting

Workshop „Rietveld Refinement with Profex“

Lesson 3: Basics of Rietveld Refinement

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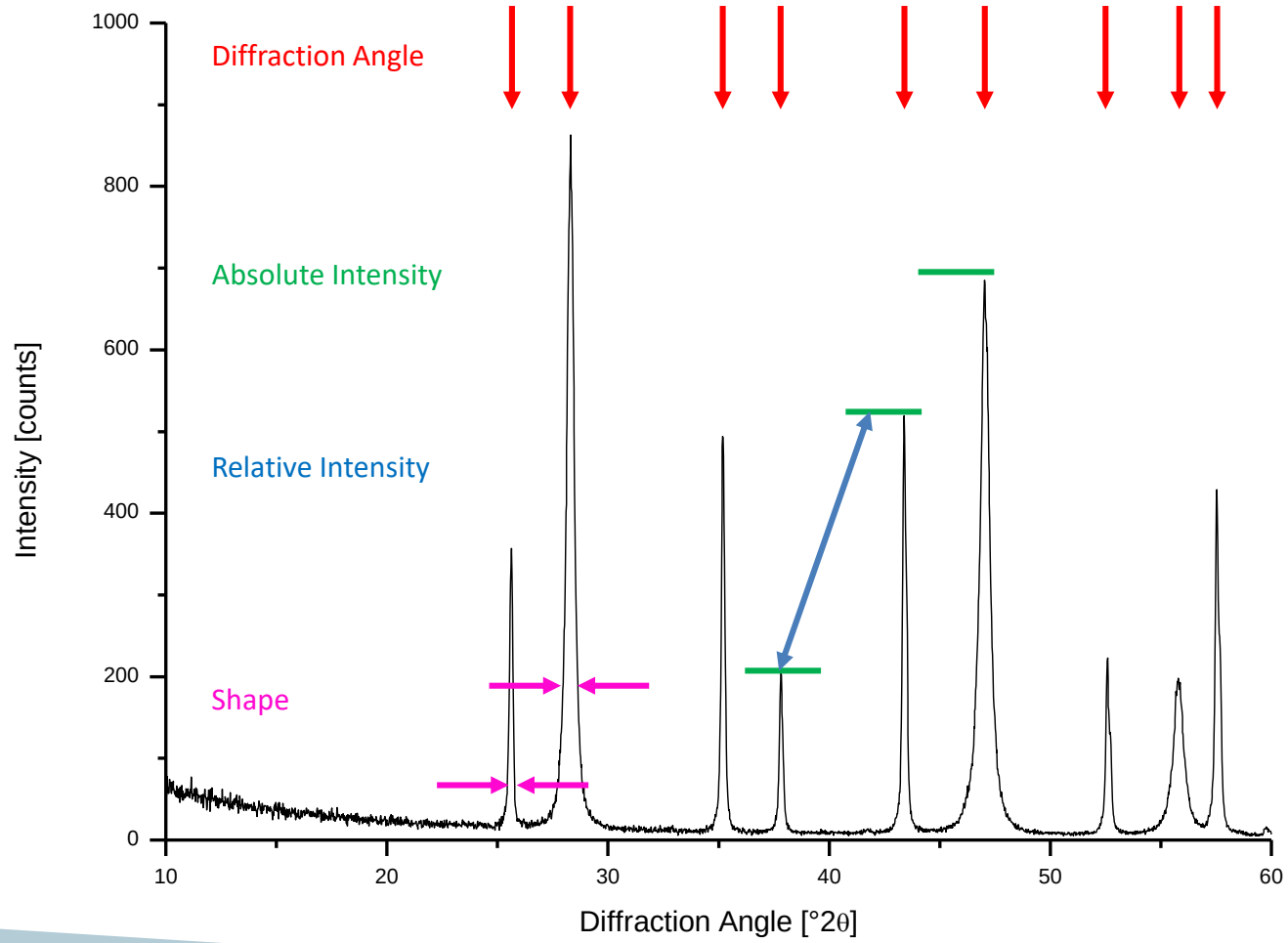
Forschungszentrum Jülich, Germany

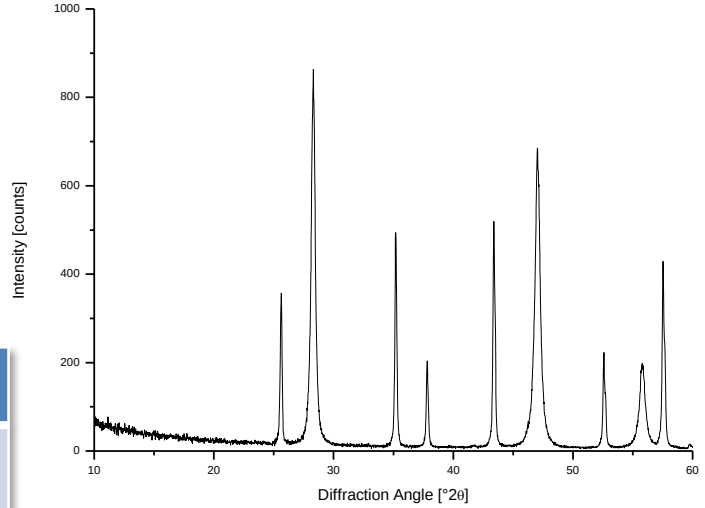
Diffraction Pattern Features

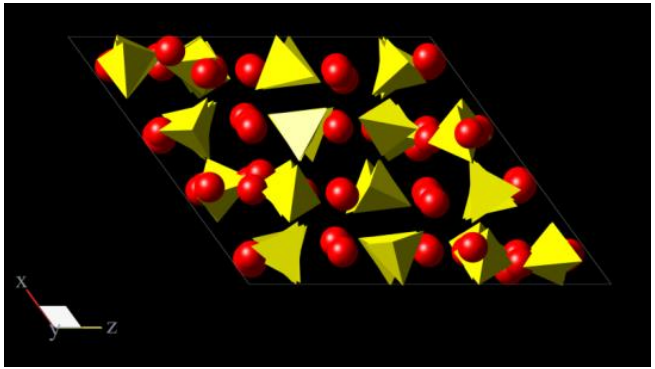


Diffraction Pattern Features

«Pattern Features» originate from crystallographic properties:

Pattern Feature	Origin
Peak positions	- Symmetry of the unit cell (space group) - Dimensions of the unit cell
Relative peak intensities	- Coordinates of atoms in unit cell - Species of atoms
Absolute peak intensities	- Abundance of phase
Peak width	- Crystallite size - Micro-Strain in crystal lattice





Rietveld Refinement

Concept: Fit crystallographic parameters to XRD data

- Unit cell dimensions
- Phase quantities
- Crystallite sizes / shapes
- Atomic coordinates / bond lengths
- Micro-strain in crystal lattice
- Texture effects
- Substitutions / Vacancies

Prof. Hugo Rietveld (1932 – 2016)

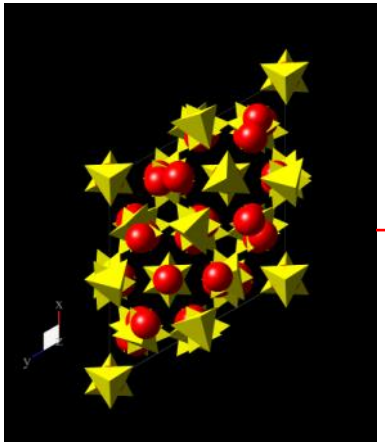
No phase identification!
All phases must be identified first
(unknown phase → no Rietveld refinement)

No structure solution!
(all crystal structures must be known)

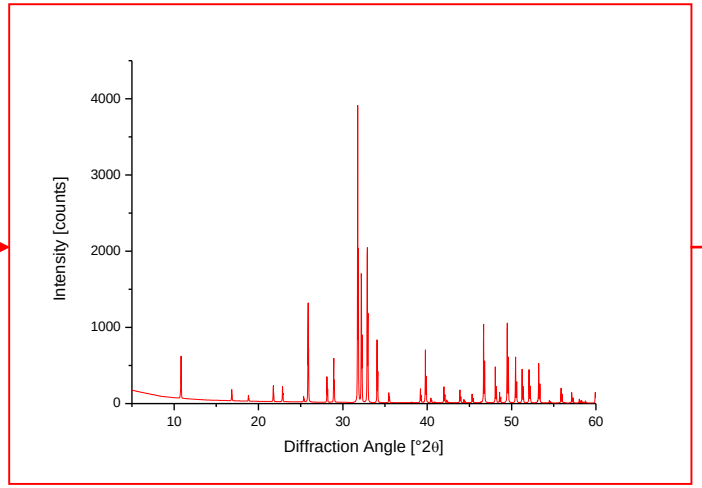
Needs excellent data quality!

Rietveld Refinement

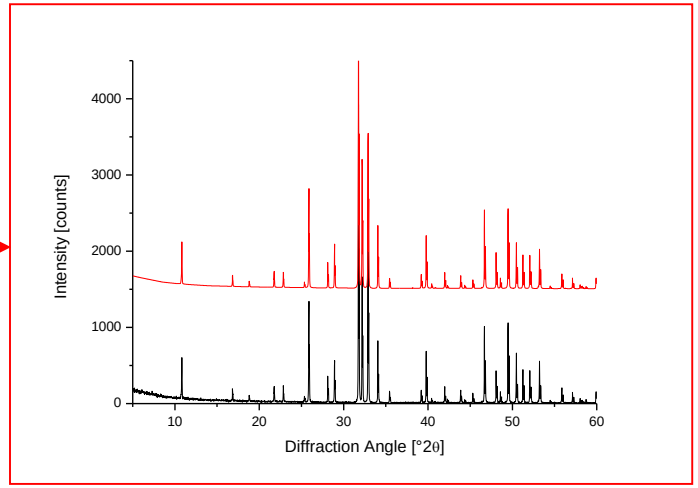
Known structure model



Calculate theoretical diffraction pattern



Compare with measured pattern



Optimize structure model, repeat calculation

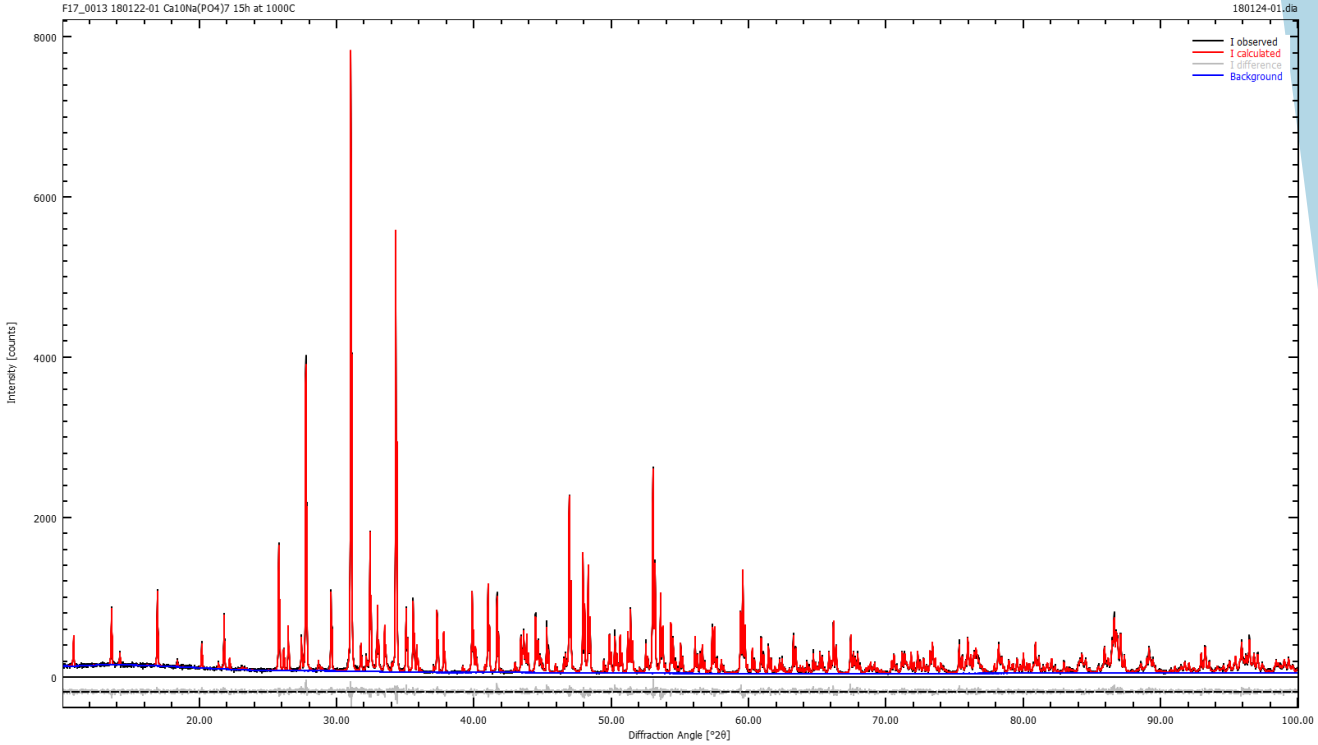
Minimize differences between calculated and observed pattern by least-squares method

Rietveld Refinement

Calculated pattern = Measured pattern

Optimized (refined) crystal structure models = Sample phases

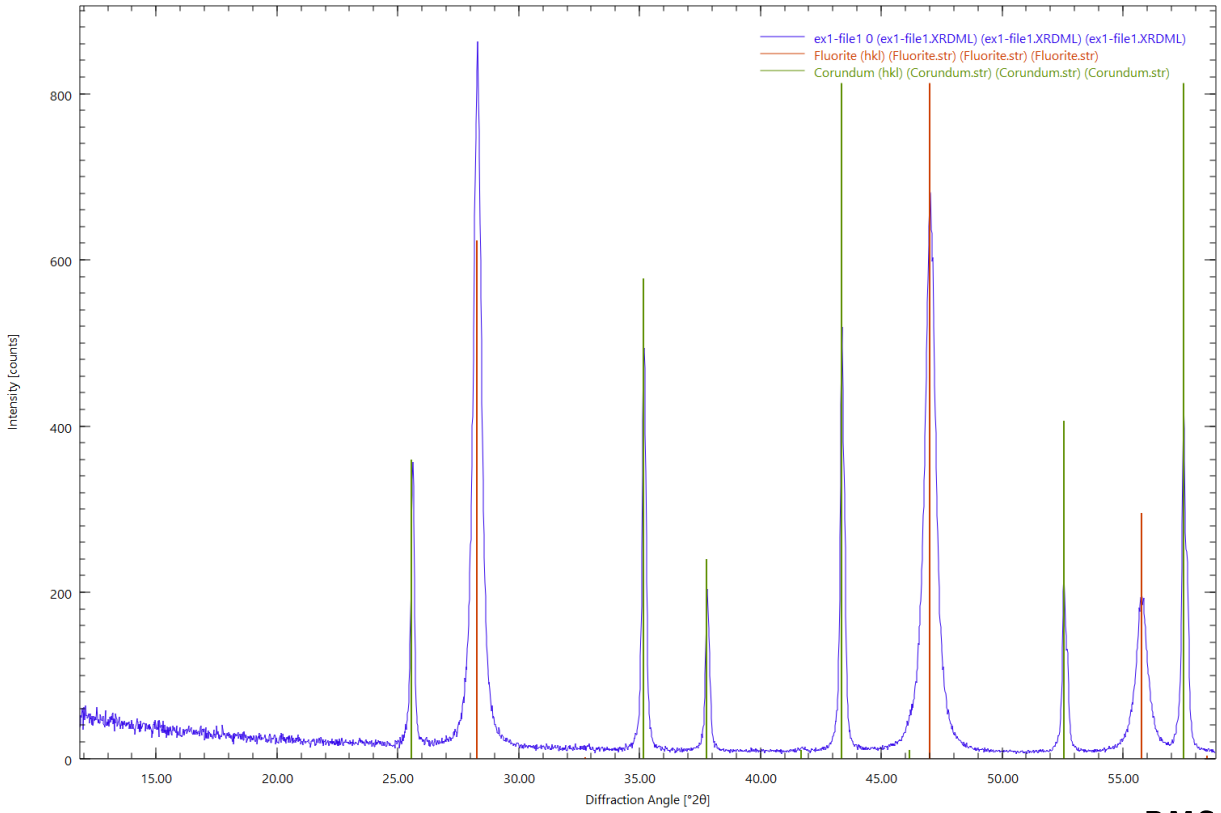
Starting models for all phases required
→ Start with phase identification



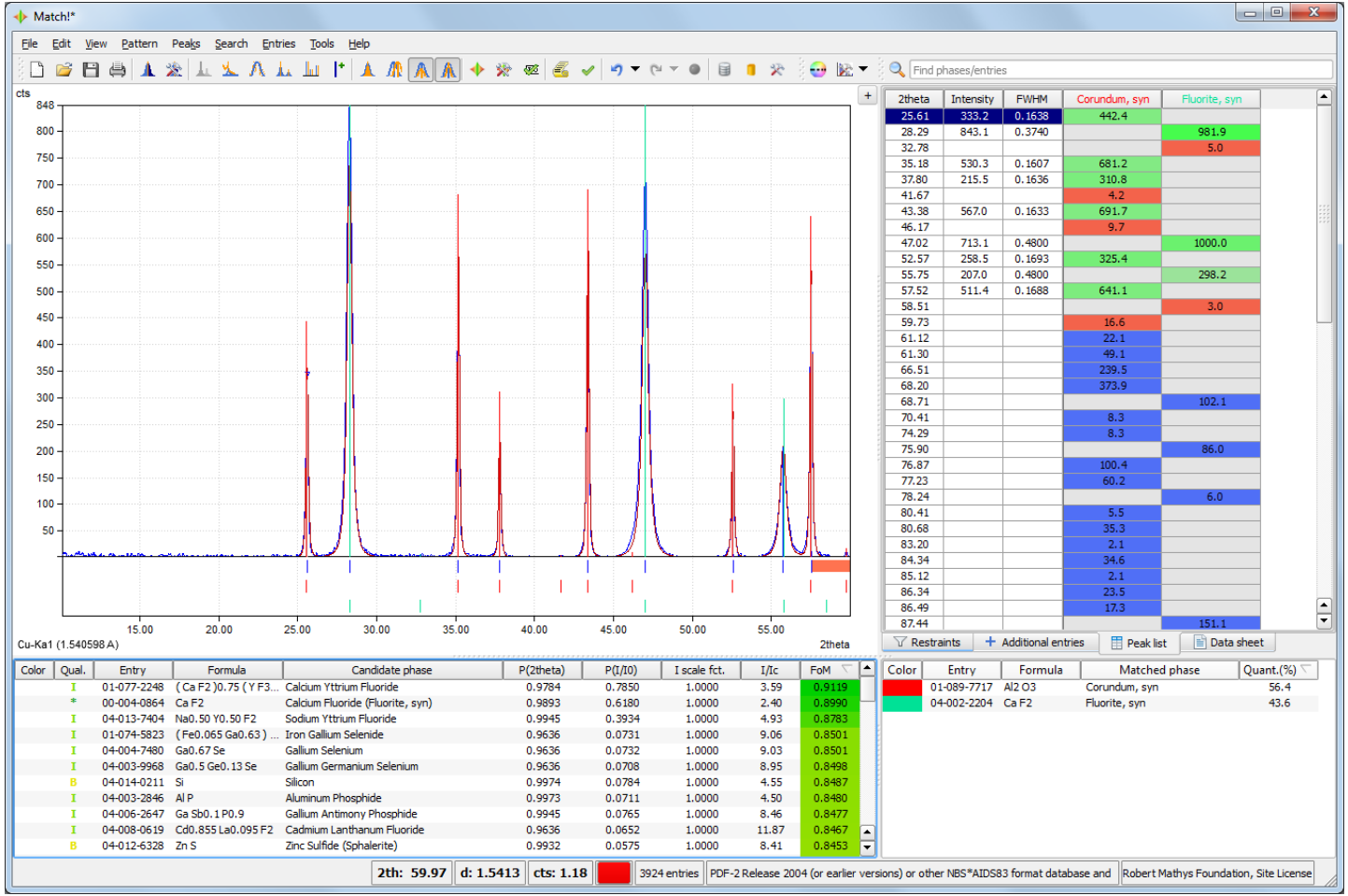
Step 1: Phase Identification

Every crystal structure produces a unique set of diffraction peaks (angle and intensity)

Compare measured peak positions and intensities with a database



Step 1: Phase Identification



2theta	Intensity	FWHM	Corundum, syn	Fluorite, syn
25.61	333.2	0.1638	442.4	
28.29	843.1	0.3740		981.9
32.78				5.0
35.18	530.3	0.1607	681.2	
37.80	215.5	0.1636	310.8	
41.67			4.2	
43.38	567.0	0.1633	691.7	
46.17			9.7	
47.02	713.1	0.4800		1000.0
52.57	258.5	0.1693	325.4	
55.75	207.0	0.4800		298.2
57.52	511.4	0.1688	641.1	
58.51				3.0
59.73			16.6	
61.12			22.1	
61.30			49.1	
66.51			239.5	
68.20			373.9	
68.71				102.1
70.41			8.3	
74.29			8.3	
75.90				86.0
76.87			100.4	
77.23			60.2	
78.24				6.0
80.41			5.5	
80.68			35.3	
83.20			2.1	
84.34			34.6	
85.12			2.1	
86.34			23.5	
86.49			17.3	
87.44				151.1

Color	Qual.	Entry	Formula	Candidate phase	P(2theta)	P(I/I0)	I scale fct.	I/Ic	FoM
	I	01-077-2248	(Ca F2)0.75 (Y F3...	Calcium Yttrium Fluoride	0.9784	0.7850	1.0000	3.59	0.9119
	*	00-004-0864	Ca F2	Calcium Fluoride (Fluorite, syn)	0.9893	0.6180	1.0000	2.40	0.8990
	I	04-013-7404	Na0.50 Y0.50 F2	Sodium Yttrium Fluoride	0.9945	0.3934	1.0000	4.93	0.8783
	I	01-074-5823	(Fe0.065 Ga0.63) ...	Iron Gallium Selenide	0.9636	0.0731	1.0000	9.06	0.8501
	I	04-004-7480	Ga0.67 Se	Gallium Selenium	0.9636	0.0732	1.0000	9.03	0.8501
	I	04-003-9968	Ga0.5 Ge0.13 Se	Gallium Germanium Selenium	0.9636	0.0708	1.0000	8.95	0.8498
	B	04-014-0211	Si	Silicon	0.9974	0.0784	1.0000	4.55	0.8487
	I	04-003-2846	Al P	Aluminum Phosphide	0.9973	0.0711	1.0000	4.50	0.8480
	I	04-006-2647	Ga Sb0.1 P0.9	Gallium Antimony Phosphide	0.9945	0.0765	1.0000	8.46	0.8477
	I	04-008-0619	Cd0.855 La0.095 F2	Cadmium Lanthanum Fluoride	0.9636	0.0652	1.0000	11.87	0.8467
	B	04-012-6328	Zn S	Zinc Sulfide (Sphalerite)	0.9932	0.0575	1.0000	8.41	0.8453

Color	Entry	Formula	Matched phase	Quant.(%)
	01-089-7717	Al2 O3	Corundum, syn	56.4
	04-002-2204	Ca F2	Fluorite, syn	43.6

Step 2: Obtain Crystal Structure Models

For each phase, a structure model must be obtained.

The model contains:

- Space group
- Cell parameters
- Atomic positions:
  - Scattering factor
  - Fractional coordinates
  - Thermal displacement parameter

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data_04-004-2852
#Copyright 2024 International Centre
#for Diffraction Data. All rights reserved.

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_cell_angle_gamma                      120
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O2 O 0.30624 0.0 0.25 0.00343 18 e 1.0
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#for Diffraction Data. All rights reserved.

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_atom_site_fract_z
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F2 F 0.25 0.25 0.25 . 8 c 1.0
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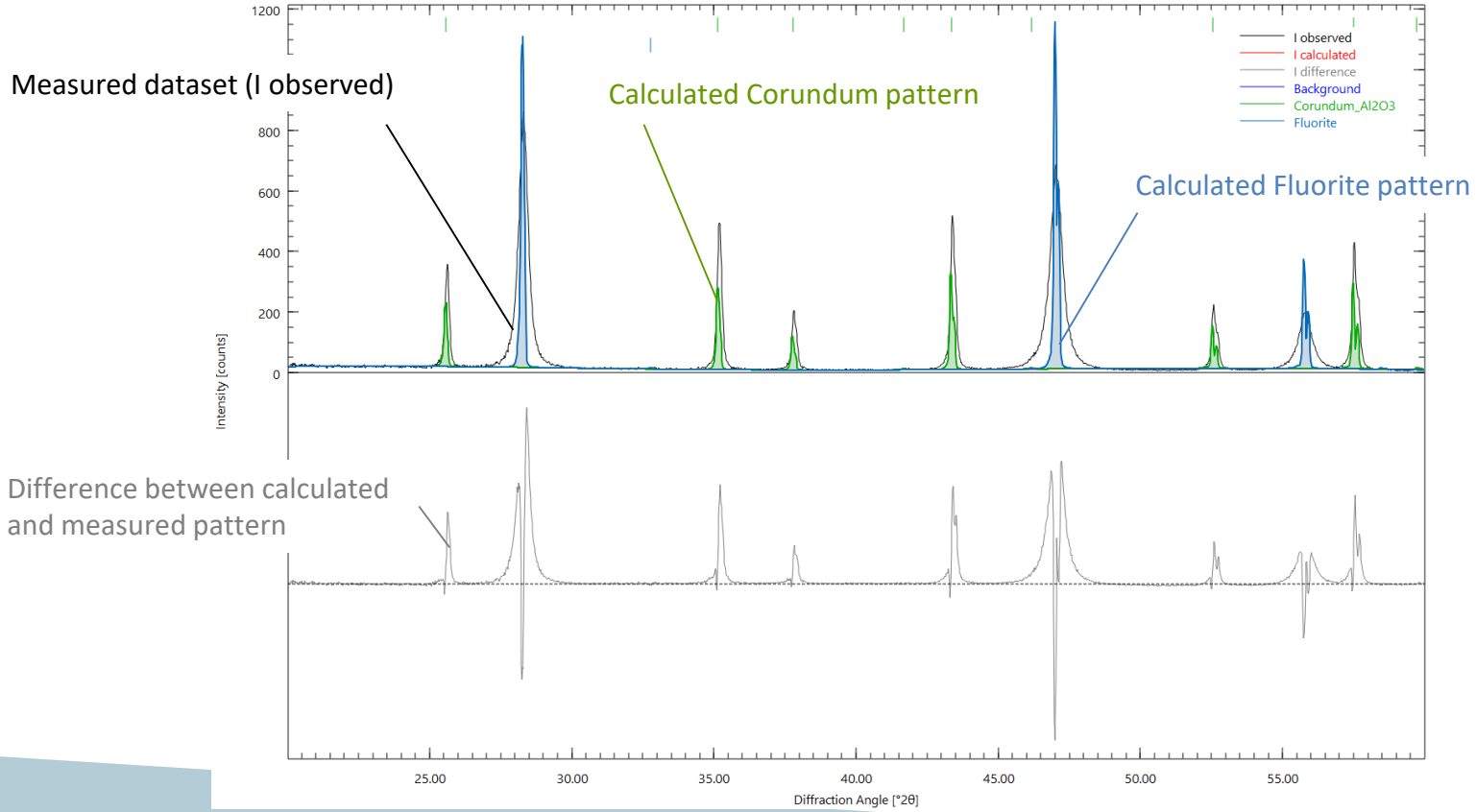
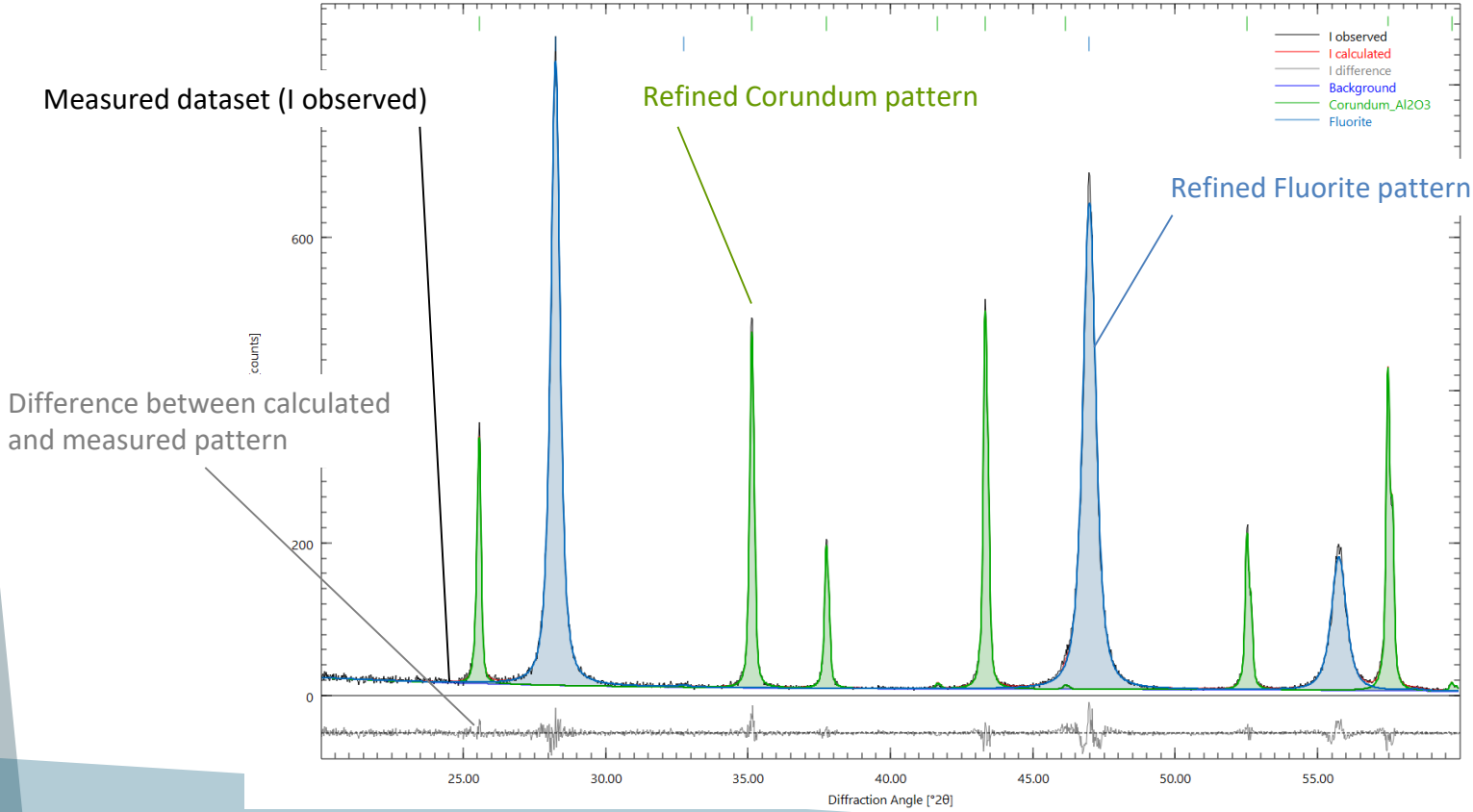
Step 3: Rietveld Refinement 1st Iteration

- Calculate theoretical diffraction pattern from structure models
- Compare with measured pattern

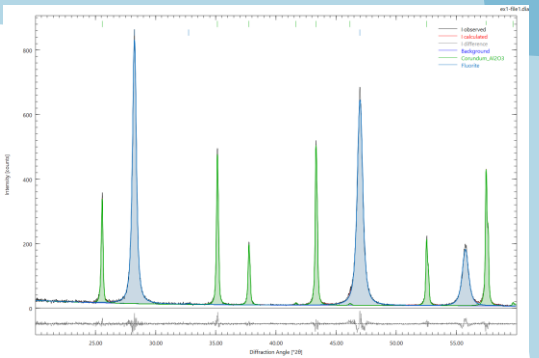


Step 3: Rietveld Refinement Curve Fitting

- Optimize crystallographic parameters in structure models
- Minimize difference between observed and calculated pattern



Step 3: Rietveld Refinement Curve Fitting



Optimize crystallographic parameters in structure models represent sample composition:

- Phase quantities
- Cell parameters
- Crystallite size
- Lattice strain
- Atomic coordinates
- Atomic site occupancy factors
- Thermal displacement parameters

Refined Parameters

Parameter	Value	ESD
Statistics		
Rwp	7.58	
Rexp	14.01	
χ^2	0.29	
GoF	0.54	
Background Coefficients	6	
Global GOALs		
corundum/sum	0.4958	0.0041
fluorite/sum	0.5042	0.0041
Local GOALs		
Corundum_Al2O3		
Refined Composition	AL12 O18	
A	0.47610	0.00003
C	1.29960	0.00008
UNIT	NM	
GrainSize(1,1,1)	124.1	5.0
UNIT	NM	
Fluorite		
Refined Composition	CA4 F8	
A	0.54677	0.00003
UNIT	NM	
GrainSize(1,1,1)	42.4413	
UNIT	NM	

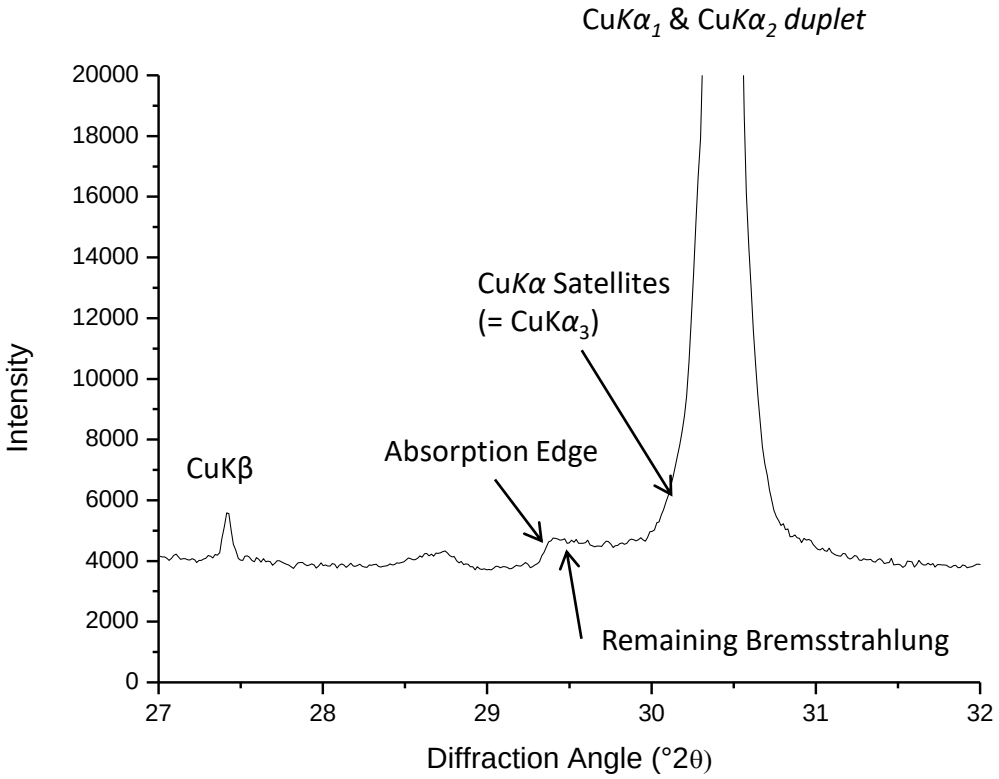
Modelling the Peak Profile

Mathematical model to describe the peak profile is needed.

Two different approaches:

- Use empirical function
  - Pseudo-Voigt
  - Pearson-IIV
  - …
- Simulate peak profile from instrument configuration
  - Convolute the effect of every optical element

= Fundamental Parameters Approach (FPA)

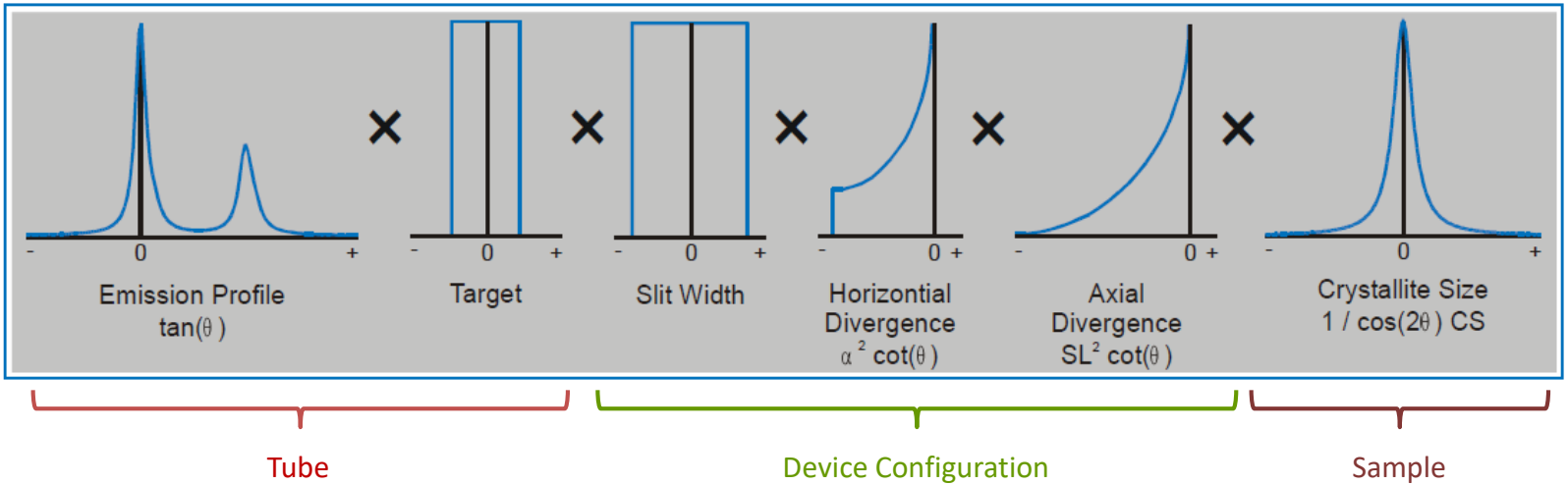


Fundamental Parameters Approach (FPA)

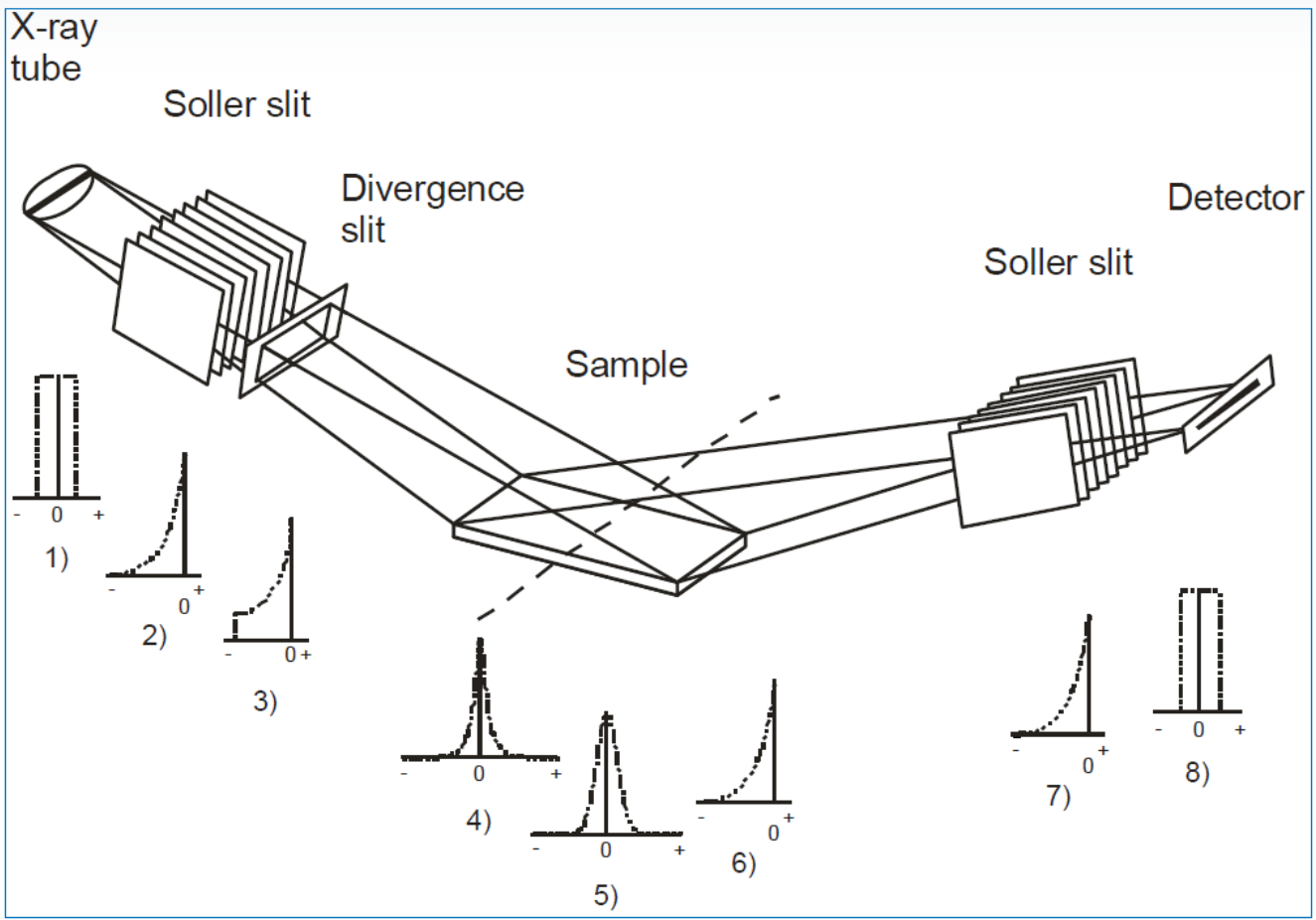
Calculate the peak profile from the device configuration

Take into account the contributions of:

- Source emission profile (X-ray wavelength distribution from Tube)
- Every optical element in the beam path (position, size, etc.)
- Sample contributions (peak broadening due to crystallite size & strain)

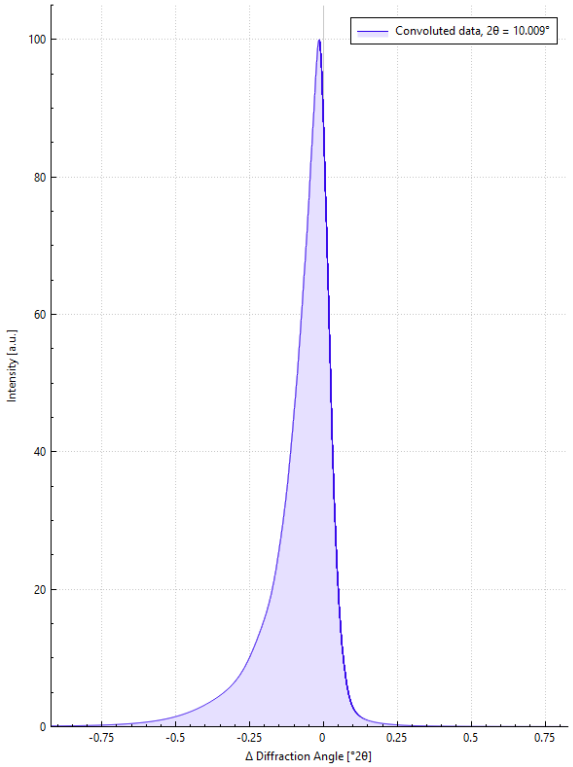


Fundamental Parameters Approach (FPA)

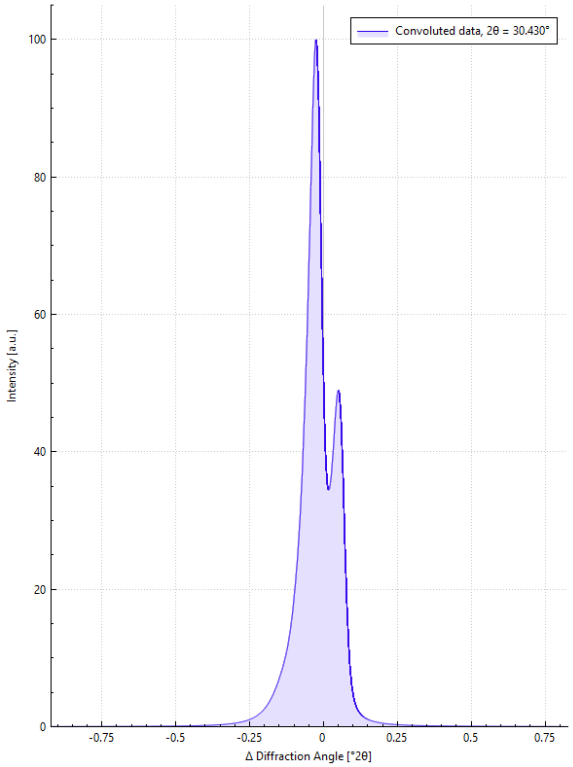


Fundamental Parameters Approach (FPA)

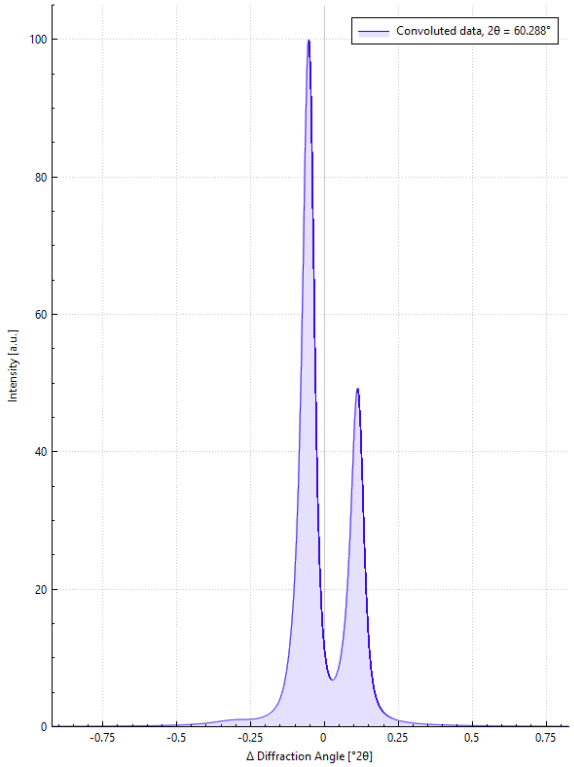
Calculated Peak Profiles



2θ=10°



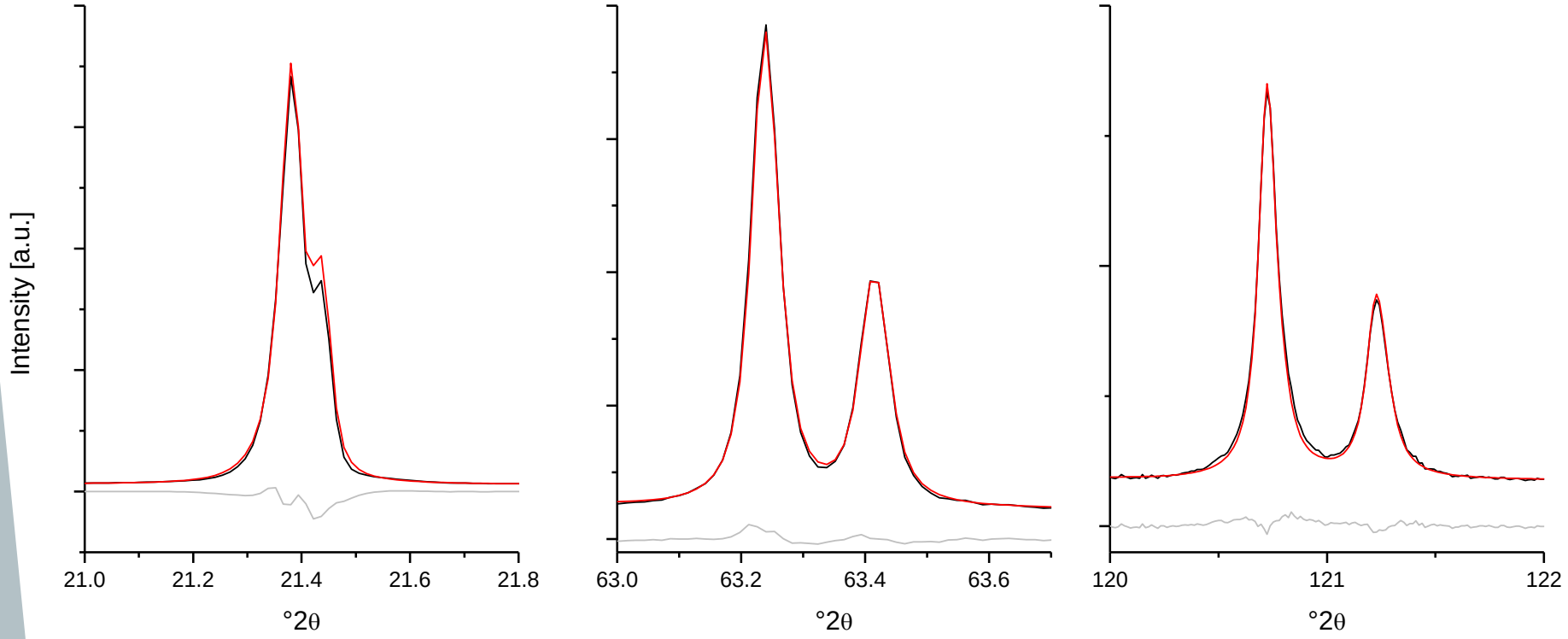
2θ=30°



2θ=60°

Fundamental Parameters Approach

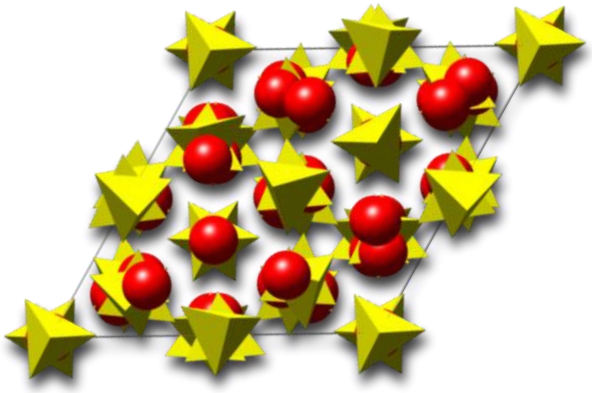
If done properly:



Very good description of the peak profile

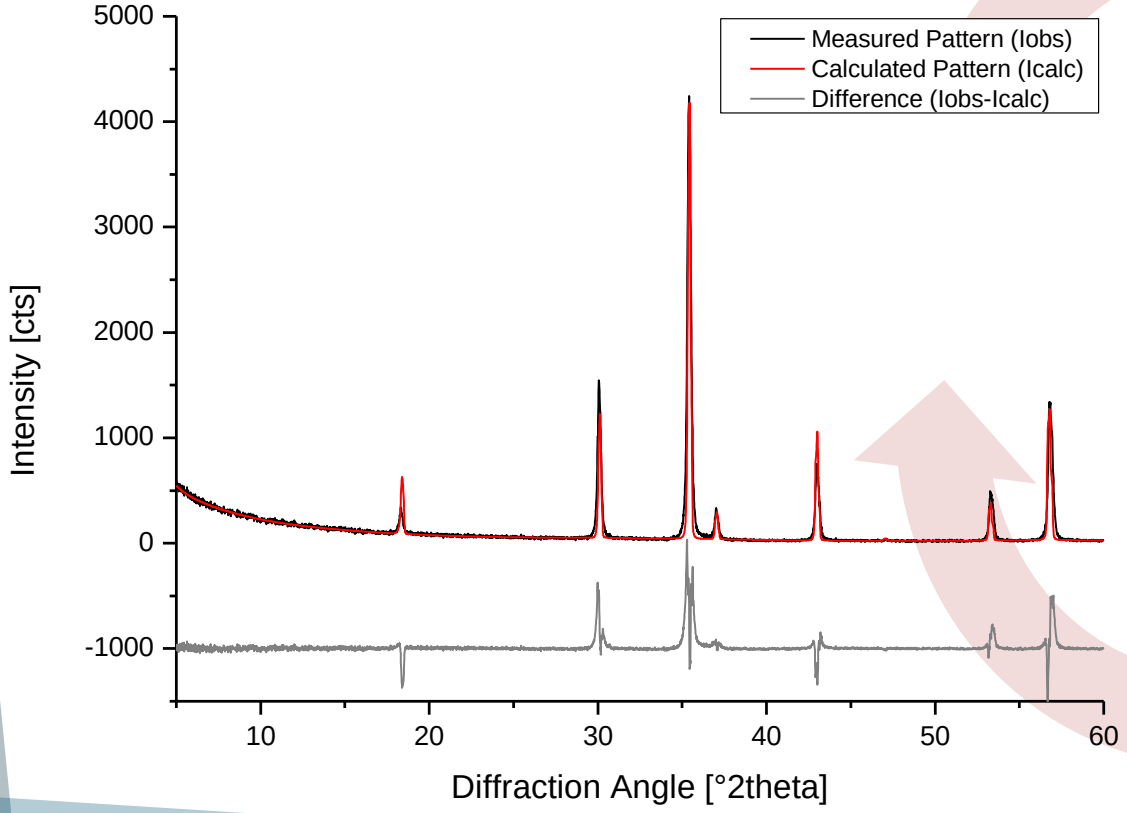
Summary: Rietveld Refinement Basics

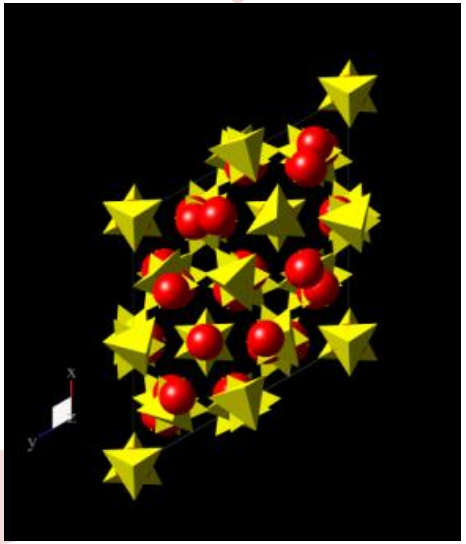
- Step 1: Phase identification
- Step 2: Obtain crystal structure models for all phases
- Step 3: Rietveld refinement:
  - Calculate XRD pattern from model structure
  - Minimize differences between calculated and measured pattern
- Accurate mathematical description of peak profile required:
  - Classical Rietveld approach: Fit a peak shape function (PV or similar) to reference pattern
  - Fundamental Parameters Approach: Calculate peak profile from device configuration



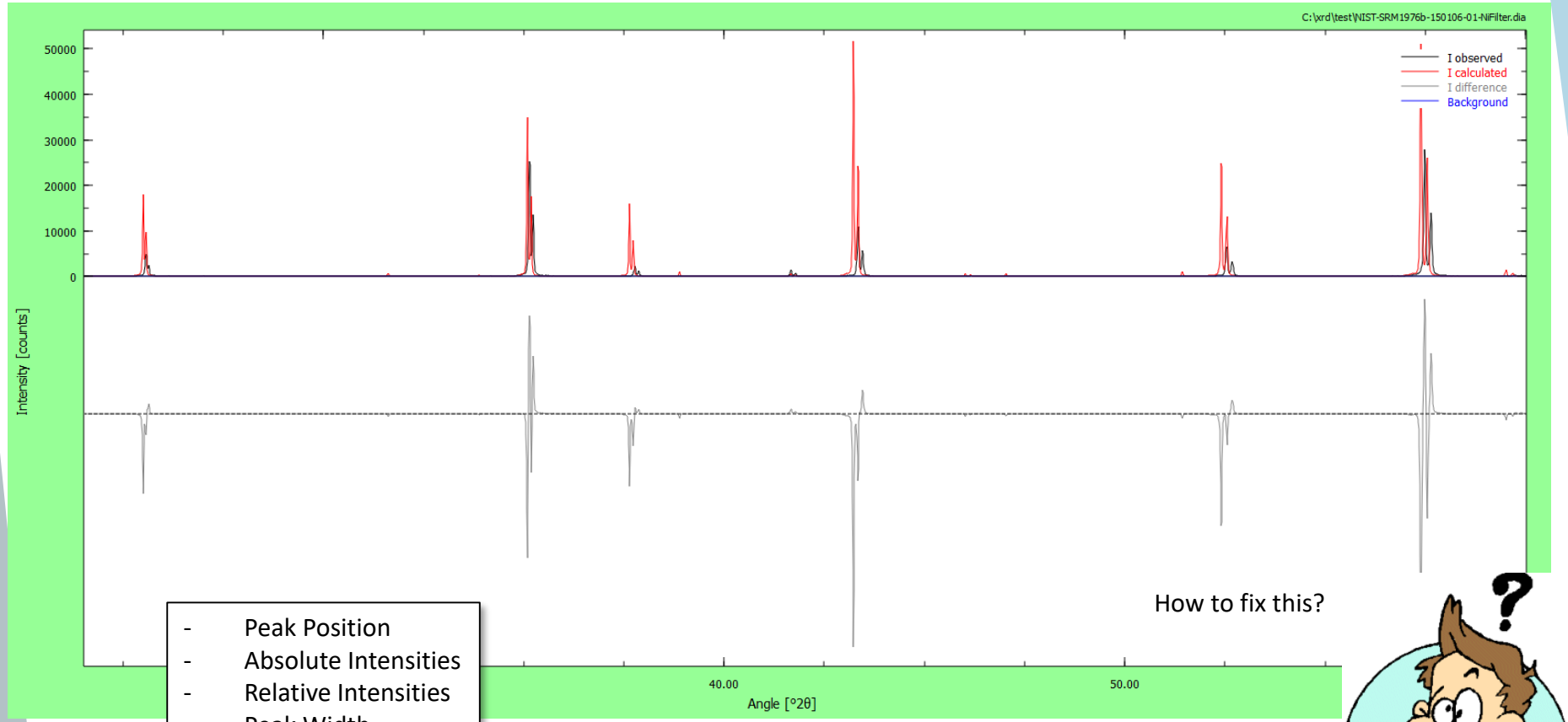
Refinement Strategies

Relation between Pattern Features and Structural Features





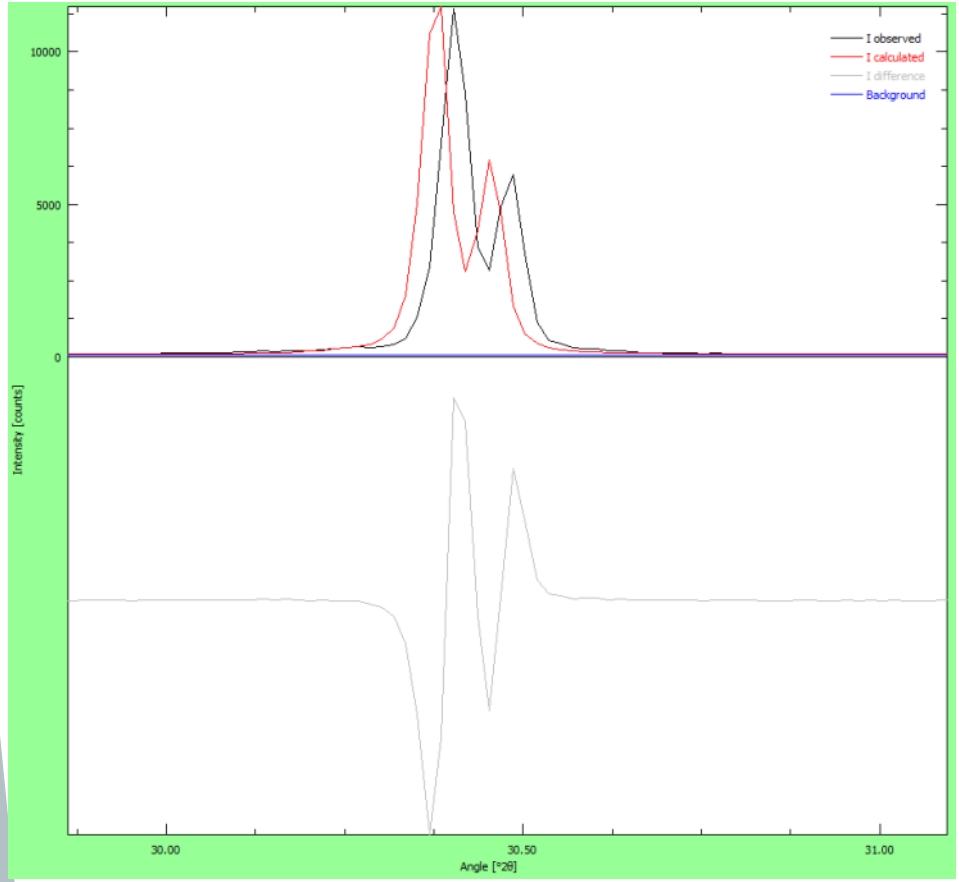
Refinement Strategies



- Peak Position
- Absolute Intensities
- Relative Intensities
- Peak Width

How to fix this?

Refinement Strategies



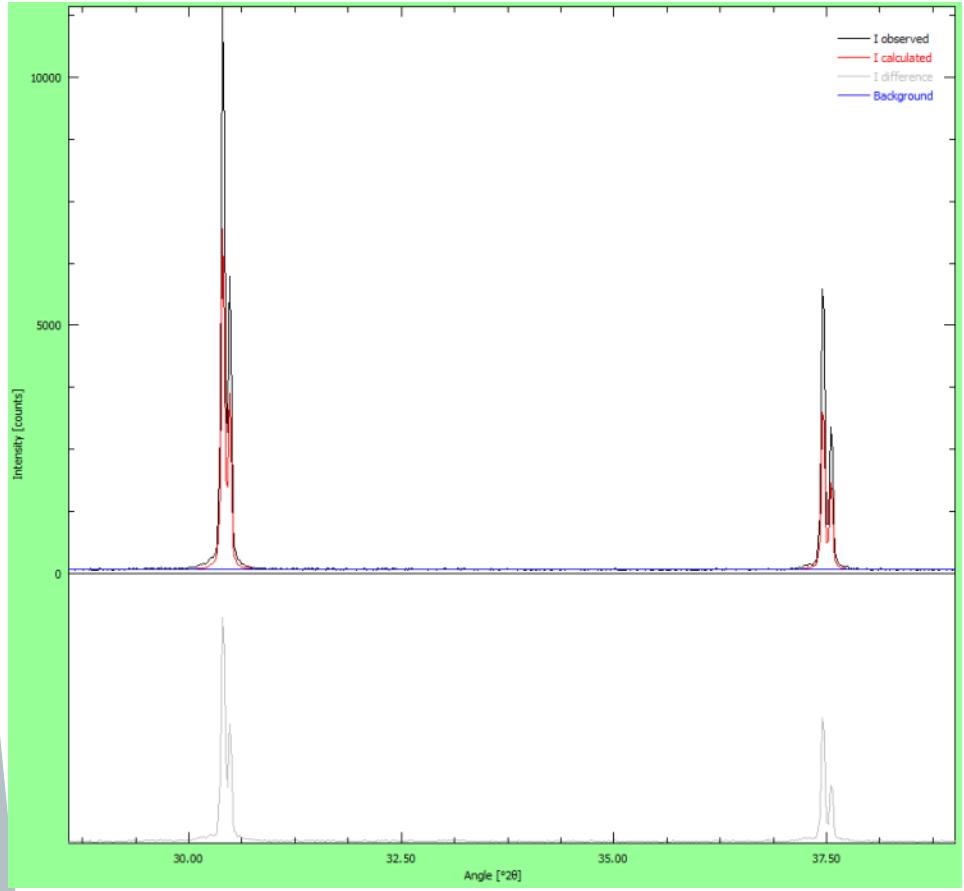
Wrong peak positions

Cause:

- Cell parameters
- Sample height displacement
- Instrument misalignment

Solution:
Refine cell parameters
(and sample height displacement)

Refinement Strategies



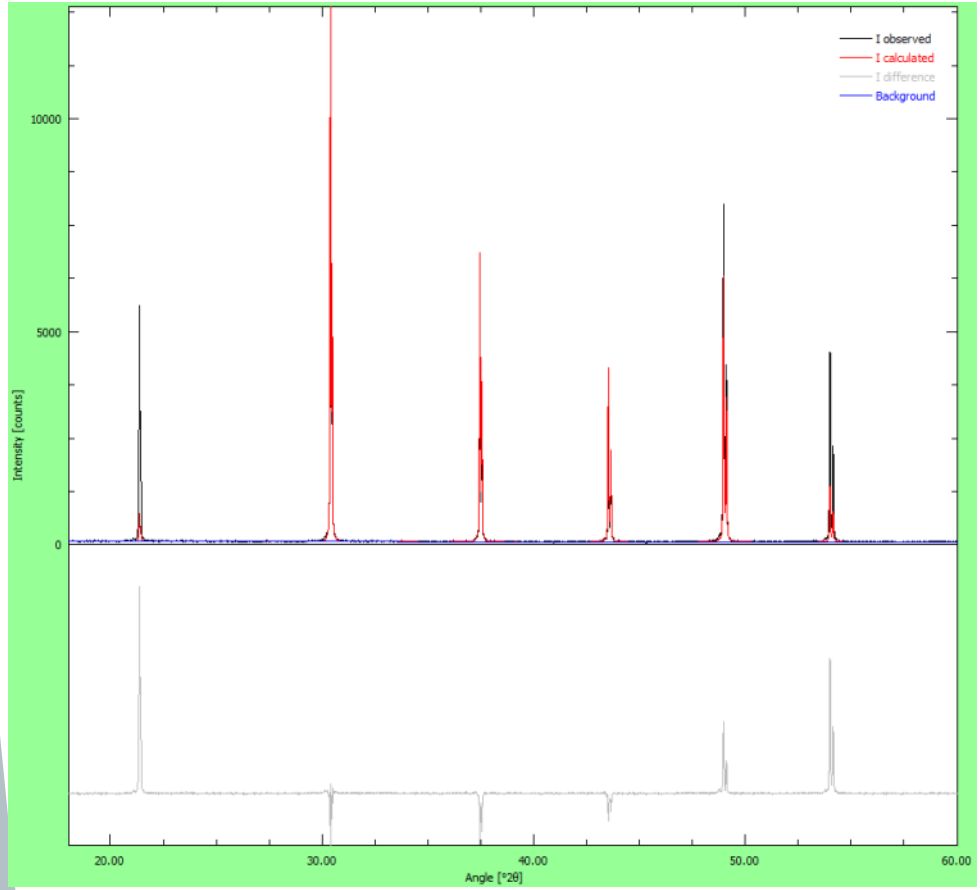
Wrong absolute intensities

Cause:

- Weight fraction (scaling)

Solution:
Refine phase scale factor

Refinement Strategies



Wrong relative intensities

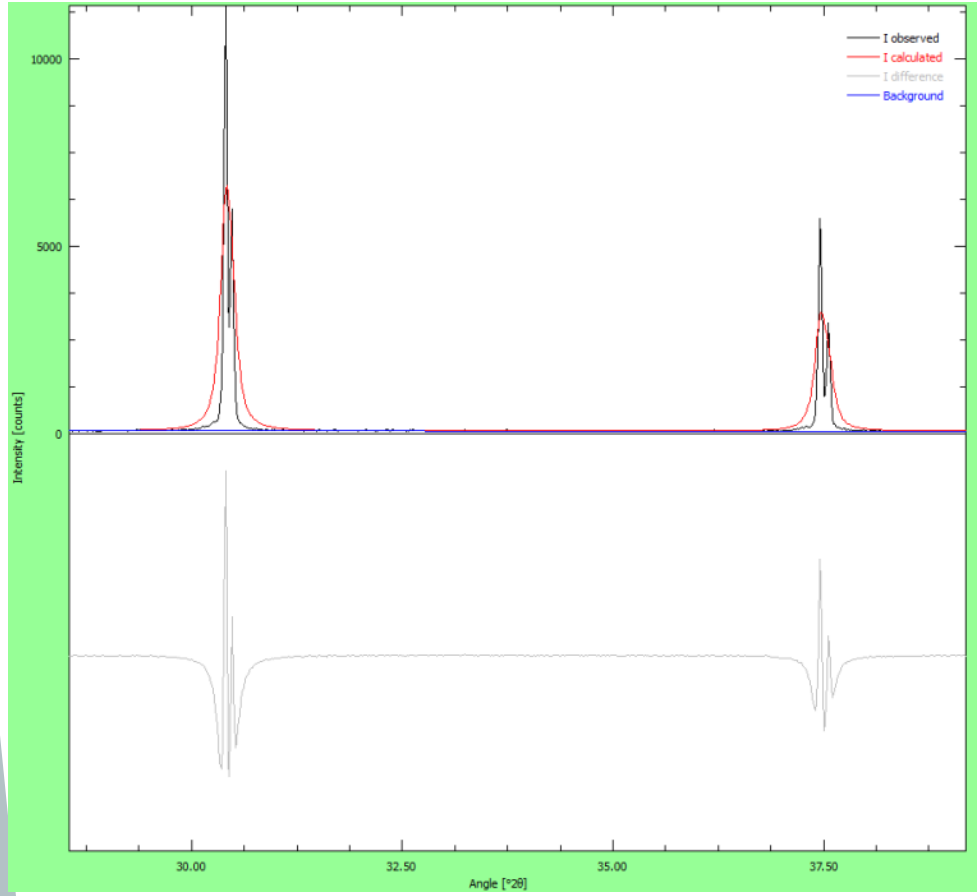
Cause:

- Texture / Preferred orientation
- Graininess
- Atomic species / substitutions
- Atomic coordinates / site occupancies / thermal displacement

Solution:

1. Check sample quality
2. Refine texture
3. Full structure refinement (atomic parameters)

Refinement Strategies



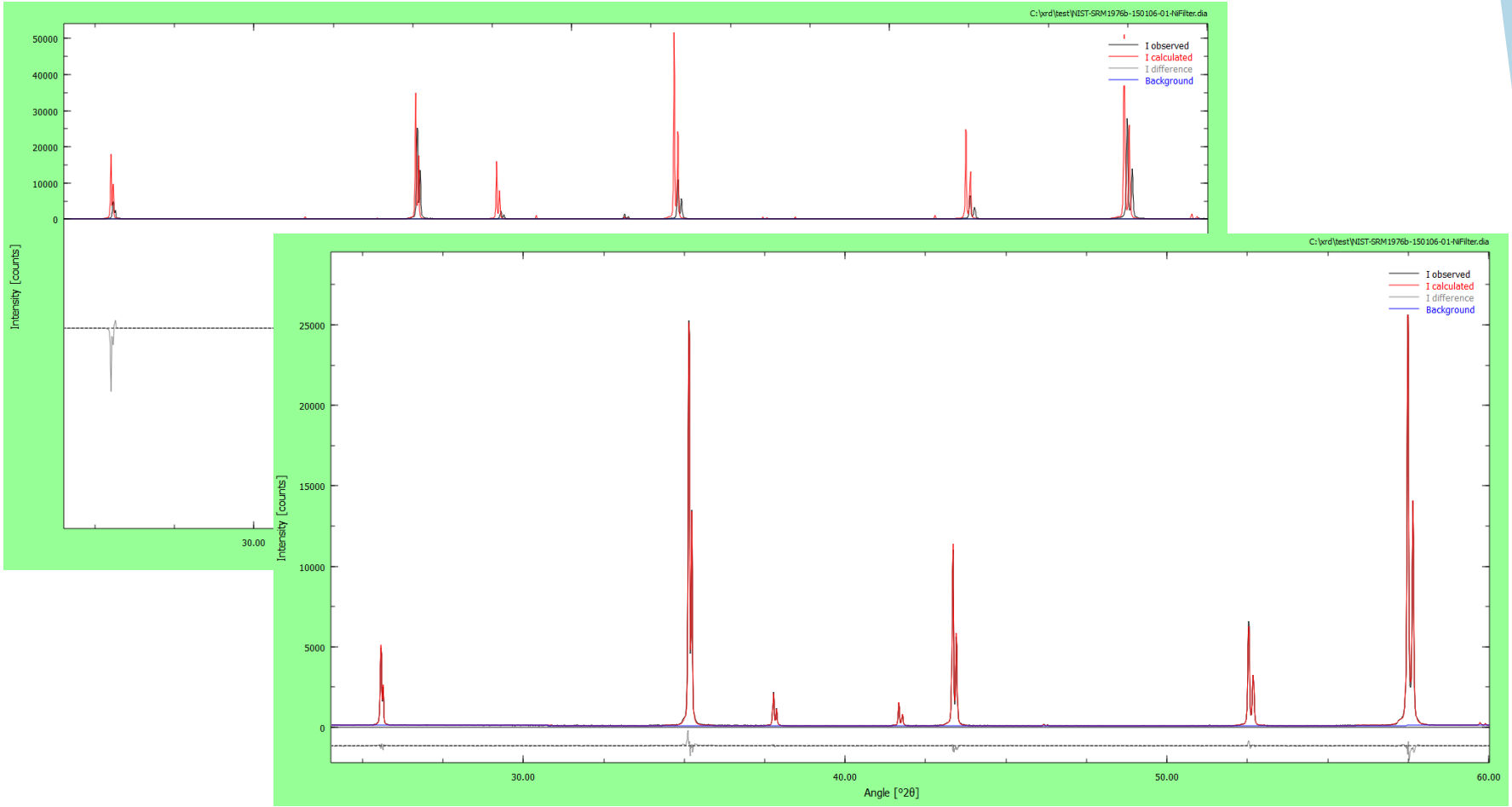
Wrong peak width

Cause:

- Crystallite size
- Micro-strain
- Surface roughness
- Sample transparency

Solution:
Refine crystallite size and / or micro-strain

Refinement Strategies



Refinement Strategies

Phase composition: 100% Al_2O_3 Corundum

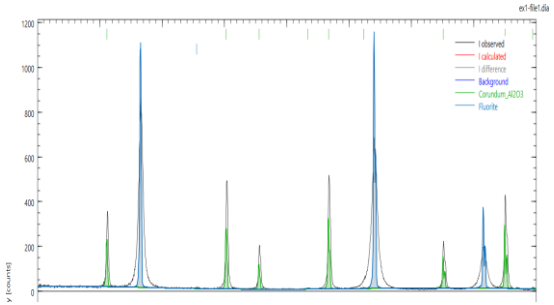
Starting Model

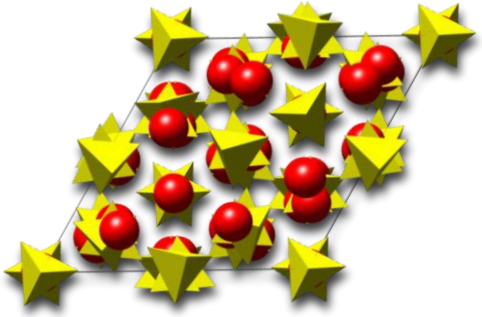
Parameter	Value
Unit cell *a*	0.4775 nm
Unit cell *c*	1.2993 nm
Crystallite Size	Inf.
Atomic Coordinates Al	0.0 / 0.0 / 0.3522
Atomic Coordinates O	0.3062 / 0.0 / 0.25

Refined

Parameter	Value
Unit cell *a*	0.4760127 +- 0.0000028 nm
Unit cell *c*	1.2995974 +- 0.0000077 nm
Crystallite Size	1267 +- 138 nm
Atomic Coordinates Al	0.0 / 0.0 / 0.3522
Atomic Coordinates O	0.3062 / 0.0 / 0.25

Summary: Refinement Strategies





Observation in diffraction pattern	Origin in crystal structure model
Wrong peak positions	Unit cell dimensions Sample height displacement
Wrong absolute intensities	Weight fraction (scaling)
Wrong relative intensities	Preferred orientation Atomic species / substitutions / vacancies Atomic coordinates / displacement parameters
Wrong peak width	Crystallite size Micro-strain