

# **TMT4301 Materials Characterization**

## **X-ray Characterization of materials**

### **LX8-9: Extra bonus lecture – lab report**

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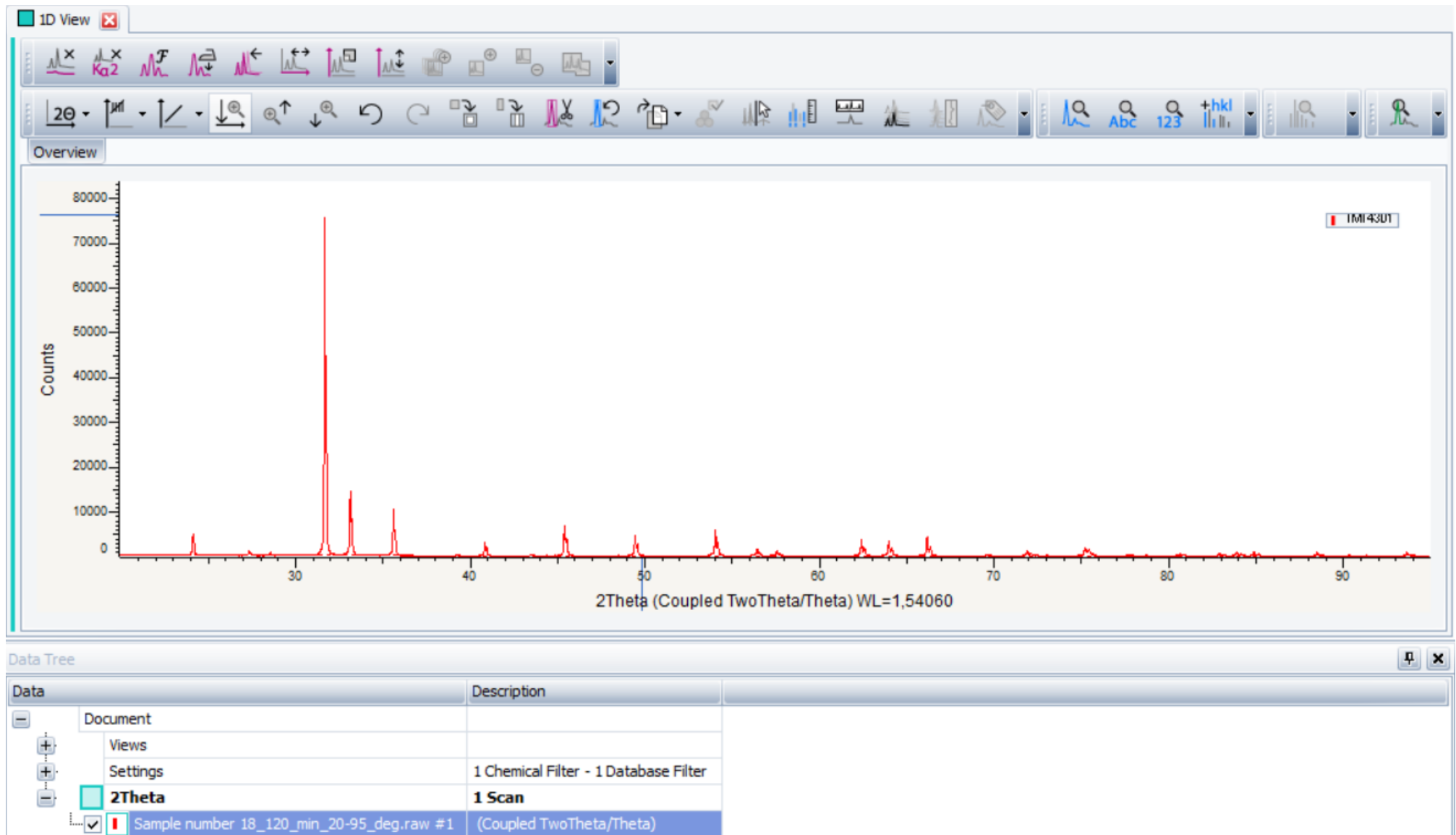


# This lecture

- ◆ Identifying a two-phase sample in EVA
- ◆ Performing Pawley analysis of a two-phase sample in Topas
- ◆ Rietveld refinement of a two-phase sample in Topas

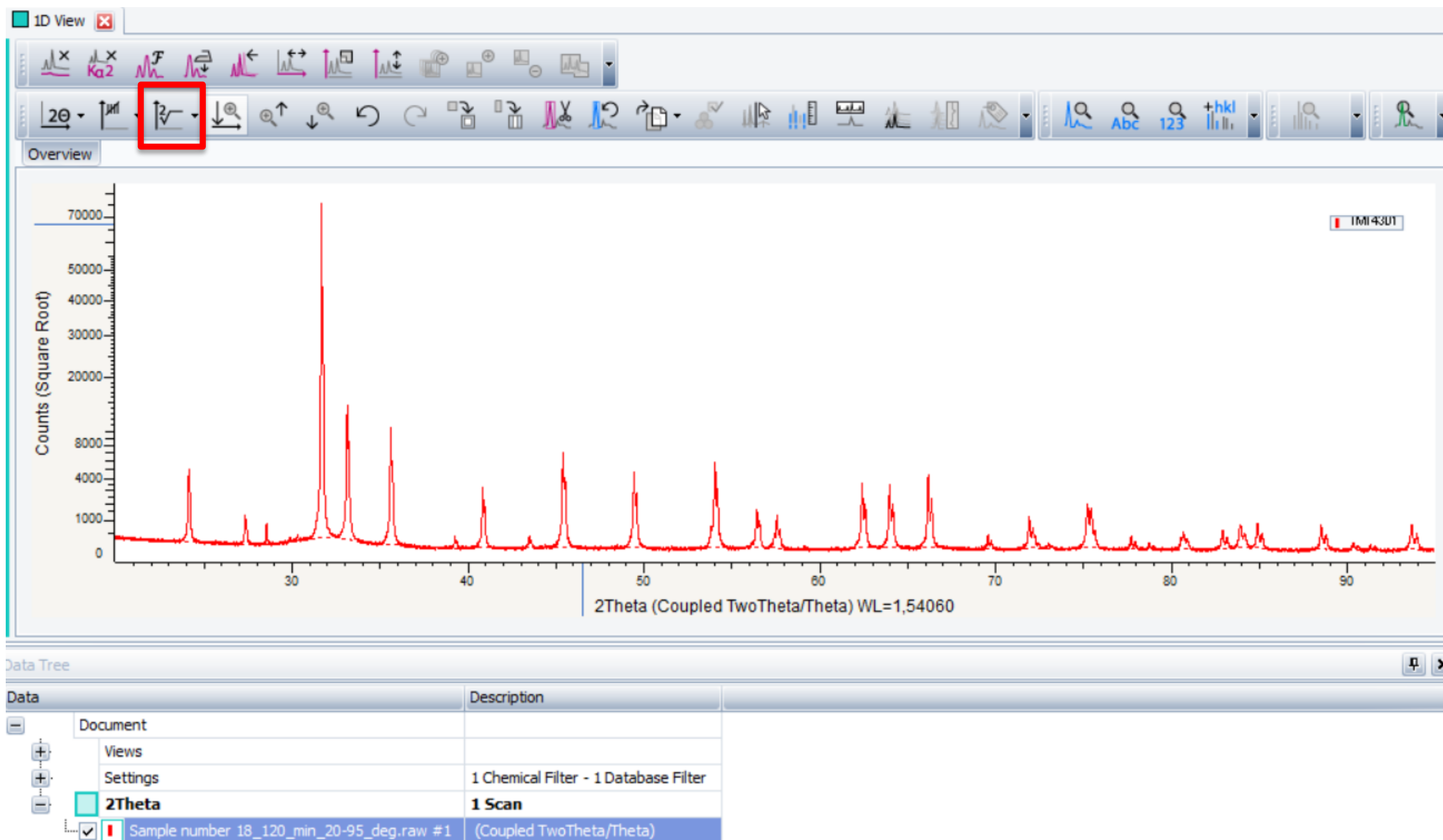
# EVA

- ◆ Import a diffractogram, .raw file.



# EVA

- ◆ Pro tip: use square root y-axis scaling for different peak intensities.





# EVA – search and match

- ◆ Choose the right elements and the right conditions

Search / Match (scan) Sample number 18\_120\_min\_20-95\_deg.raw #1

Rebuild Chemical    Chemical Filter #1 Database    Database Filter #1

Database: Rebuild needed

Chemical Filter Database Filter Candidate List Selected Candidates

H	D																	He														
Li	Be																	B	C	N	O	F	Ne									
Na	Mg																	Al	Si	P	S	Cl	Ar									
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr															
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe															
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn															
Fr	Ra	Ac																	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Lanthanoids/ Actinoids			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Ln																

Discarded At Least One Mandatory Not Checked Reset

# EVA – search and match

- Check promising patterns which can index some of the peaks while you search for a second which can index the rest.

Search / Match (scan) Sample number 18\_120\_min\_20-95\_deg.raw #1

Rebuild Chemical    Chemical Filter #1 Database    Database Filter #1

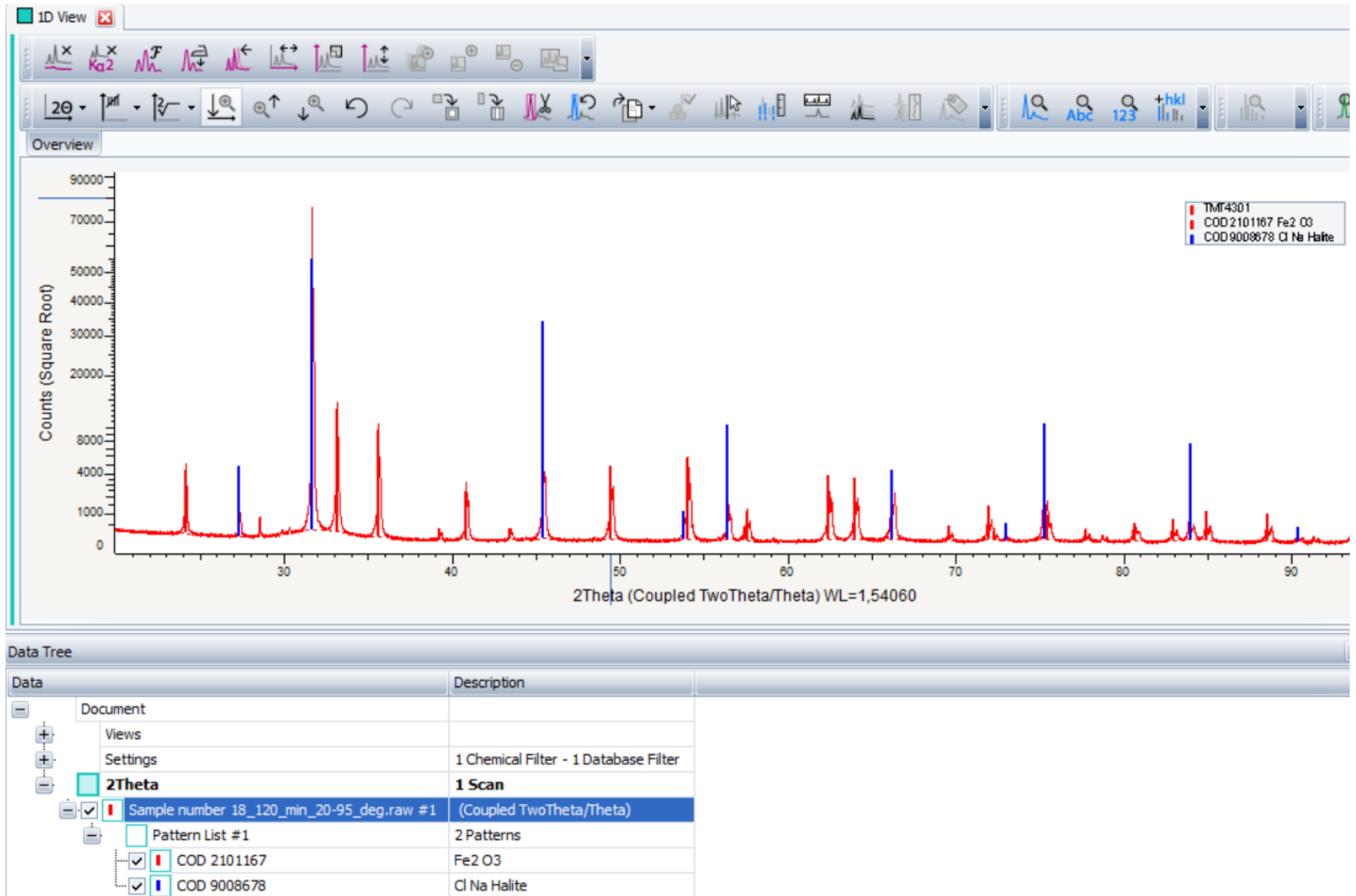
Database COD2016: 352140 - After Filters: 949

Chemical Filter Database Filter Candidate List Selected Candidates

Index ...	0	FOM	Mtc	nM	%	Source	ID	Quality	Status	I/Icor	Mineral	Name	Formula	Crystal System	a	b	c	alpha	beta	gamma	Spacegroup	Z	Volume
<input type="checkbox"/>	1	49,4	22	4	...	COD...	...	Quality Unknown	Stat...	3,82	<input type="checkbox"/>		Fe <sub>2</sub> O <sub>3</sub>	Hexagonal	...	...	...				R -3 c	6	301,87
<input type="checkbox"/>	2	49,4	22	4	...	COD...	...	Quality Unknown	Stat...	3,82	<input type="checkbox"/>		Fe <sub>2</sub> O <sub>3</sub>	Hexagonal	...	...	...				R -3 c	6	301,87
<input type="checkbox"/>	3	49,4	22	4	...	COD...	...	Quality Unknown	Stat...	3,82	<input type="checkbox"/>		Fe <sub>2</sub> O <sub>3</sub>	Hexagonal	...	...	...				R -3 c	6	301,87
<input type="checkbox"/>	4	48,3	23	4	...	COD...	...	Quality Unknown	Stat...	4,01	<input checked="" type="checkbox"/>	He...	Fe <sub>2</sub> O <sub>3</sub>	Hexagonal	...	...	...				R -3 c		301,77
<input type="checkbox"/>	5	31,1	18	6	...	COD...	...	Quality Unknown	Stat...	3,58	<input checked="" type="checkbox"/>	He...	Fe <sub>2</sub> O <sub>3</sub>	Rhombo.R.a...	...		55,28				R -3 c	2	100,79
<input type="checkbox"/>	6	27,6	17	9	...	COD...	...	Quality Unknown	Stat...	2,97	<input type="checkbox"/>		Fe <sub>1.6</sub> ...	Hexagonal	...	...	...				R -3 c	6	301,52
<input type="checkbox"/>	7	26,9	8	3	...	COD...	...	Quality Unknown	Stat...	4,72	<input type="checkbox"/>		Cl Na	Cubic	...						F m -3 m	4	179,34
<input type="checkbox"/>	8	24,9	8	3	...	COD...	...	Quality Unknown	Stat...	5,02	<input checked="" type="checkbox"/>	Halite	Cl Na	Cubic	...						F m -3 m		179,46
<input type="checkbox"/>	9	24,9	18	10	9	COD...	...	Quality Unknown	Stat...	4,01	<input checked="" type="checkbox"/>	He...	Fe <sub>2</sub> O <sub>3</sub>	Hexagonal	...	...	...				R -3 c		299,93
<input type="checkbox"/>	10	24,2	8	3	...	COD...	...	Quality Unknown	Stat...	5,02	<input checked="" type="checkbox"/>	Halite	Cl Na	Cubic	...						F m -3 m		179,42
<input type="checkbox"/>	11	15,7	8	3	...	COD...	...	Quality Unknown	Stat...	5,02	<input checked="" type="checkbox"/>	Halite	Cl Na	Cubic	...						F m -3 m		179,21
<input type="checkbox"/>	12	12,9	13	14	...	COD...	...	Quality Unknown	Stat...	3,58	<input checked="" type="checkbox"/>	He...	Fe <sub>2</sub> O <sub>3</sub>	Rhombo.R.a...	...		55,28				R -3 c		100,24
<input type="checkbox"/>	13	12,3	18	5	...	COD...	...	Quality Unknown	Stat...	4,83	<input checked="" type="checkbox"/>	He...	Fe <sub>2</sub> O <sub>3</sub>	Rhombo.R.a...	...		55,23				R -3 c	2	100,71

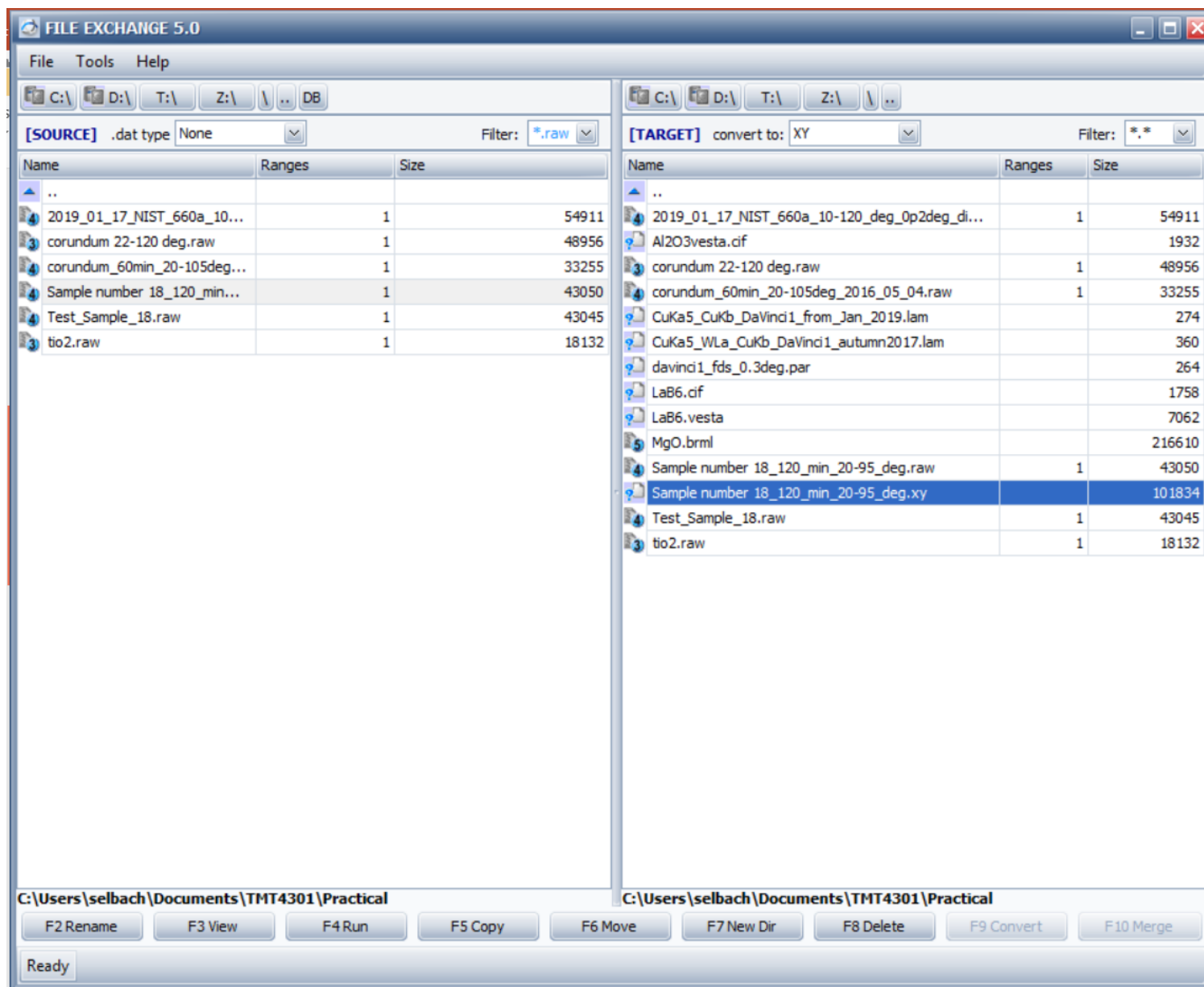
☐ Group Duplicates       Matched 238 / 949 Candidates in 8,8 s.

# EVA – search and match result



# Export your data, from .raw to .xy

- ◆ You can download Bruker Diffraction FileExchange from the Odin server



# Find SG and lattice param. with EVA and COD

Data Command

1D View DB View

**COD 2101167**

Gray all except selection  
Show Selected Patterns in Ruler  
Delete  
Cut  
Copy  
Paste  
Select Parent

**File**

Import from Files

**Tool**

Search / Match (pattern)  
Search by Number  
d x by  
Tune Cell  
Create Kb-Pattern  
Residue  
Auto Residue  
Make Sticks  
Make Peaks  
Make DIF  
Auto-scale  
100% Scale  
User Database  
[hkl] Generator

**Create**

1D View  
DB View  
Stick Column View

Database #: COD 2101167

Fe<sub>2</sub>O<sub>3</sub>

Quality: Quality Unknown

Wavelength: 1,54060

General Comments Authors Additional Subfiles

**Cell Parameters**

System: Hexagonal  
Space group: R -3 c (167)

a (Å): 5,0355 a (°):  
b (Å): β (°):  
c (Å): 13,7471 γ (°):  
a/b: 1,  
c/b: 2,73004 Z: 6

**Crystal Data**

Molecular weight:  
Volume (CD) (Å<sup>3</sup>): 301,87  
Dx: 5,269  
Dm:

**I / Icor**

3,82

d(Å)	2Theta (°)	I fix	h	k	l	Comment
3,68230	24,150	295	-1	1	-2	
2,69930	33,162	999	-1	1	4	
2,51780	35,630	737	-2	1	0	
2,29120	39,291	22	0	0	-6	
2,20660	40,863	178	-2	1	-3	
2,07840	43,508	20	-2	2	2	
1,84110	49,466	360	-2	2	-4	
1,69460	54,073	431	-2	1	-6	
1,63650	56,159	6	-3	1	-1	
1,60280	57,449	23	-3	1	2	
1,59870	57,610	80	-1	1	-8	
1,48620	62,437	283	-3	1	-4	
1,45360	64,001	272	-3	0	0	
1,41370	66,033	3	-3	1	5	
1,34960	69,607	28	-2	2	8	
1,31110	71,963	98	-1	1	10	
1,30590	72,294	16	-2	1	-9	
1,26250	75,199	2	-3	1	-7	
1,25890	75,452	62	-4	2	0	
1,22740	77,745	12	-3	0	-6	
1,22740	77,745	12	-3	0	6	
1,21390	78,776	10	-4	2	-3	

**Data Tree**

Data	Description
Document	
Views	
Settings	1 Chemical Filter - 1 Database Filter
2Theta	1 Scan
Sample number 18_120_min_20-95_deg.raw #1	(Coupled TwoTheta/Theta)
Pattern List #1	2 Patterns
COD 2101167	Fe <sub>2</sub> O <sub>3</sub>
COD 9008678	Cl Na Halite

2Th=42.207 d=2.13938

# Find SG and lattice param. with EVA and COD

You will also find peak positions here.

Database #: COD 9008678

Halite  
Cl Na  
Quality: Quality Unknown  
Wavelength: 1,54060

General Comments Authors Additional Subfiles

**Cell Parameters**

System: Cubic  
Space group: F m -3 m (225)

a (Å): 5,6406    α (°):  
b (Å):            β (°):  
c (Å):            γ (°):

a/b: 1,  
c/b: 1,            Z:

**Crystal Data**

Molecular weight:  
Volume (CD) (Å<sup>3</sup>): 179,46  
Dx: 2,161  
Dm:

**I / Icor**

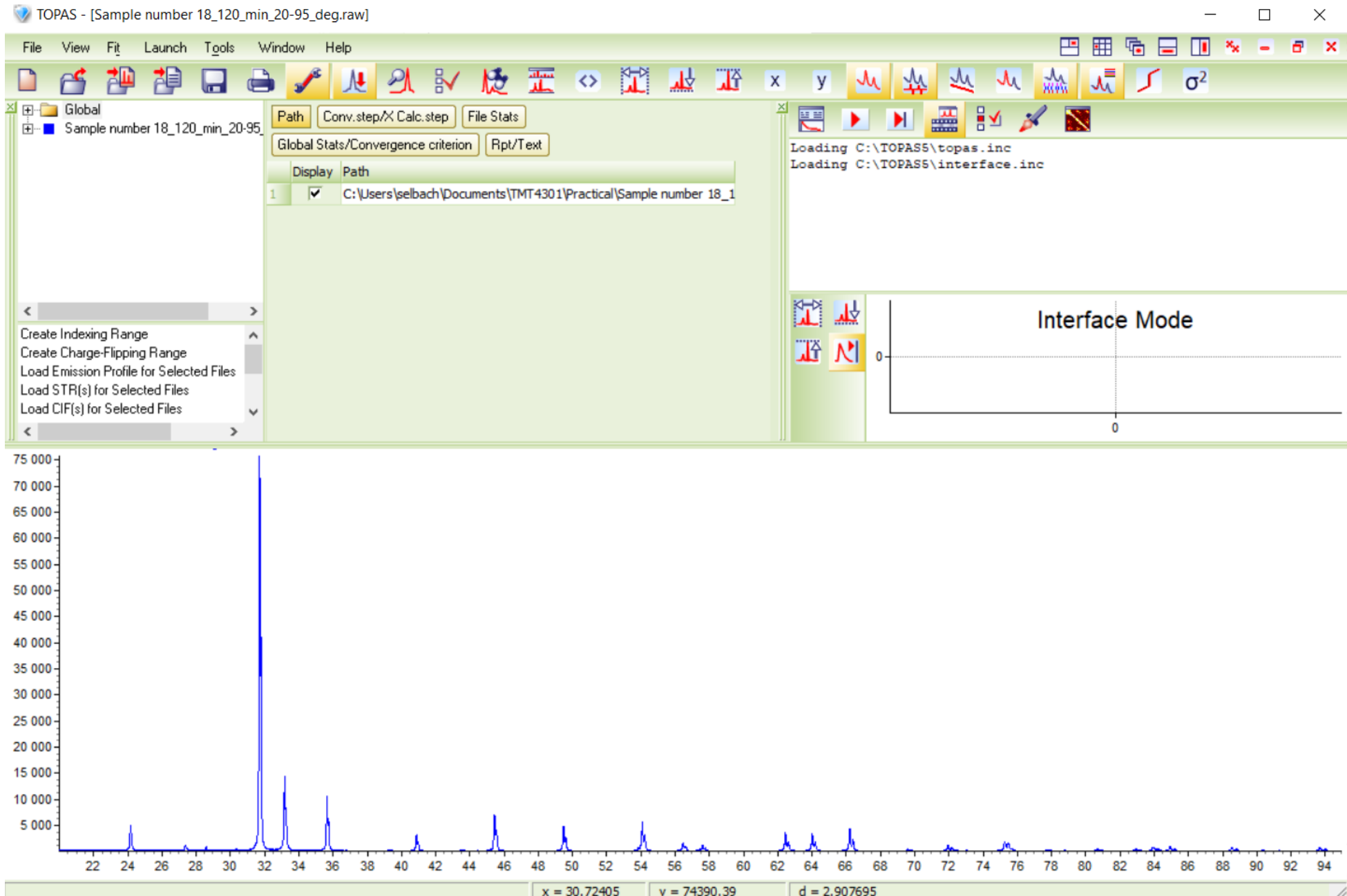
5,02

d(Å)	2Theta (°)	I fix	h	k	l
3,25660	27,364	84	-1	-1	-1
2,82030	31,701	1000	-2	0	0
1,99420	45,445	619	-2	-2	0
1,70070	53,864	19	-3	-1	-1
1,62830	56,468	188	-2	-2	-2
1,41010	66,223	78	-4	0	0
1,29400	73,066	9	-3	-3	-1
1,26130	75,283	194	-4	-2	0
1,15140	83,982	136	-4	-2	-2
1,08550	90,409	7	-5	-1	-1
1,08550	90,409	3	-3	-3	-3

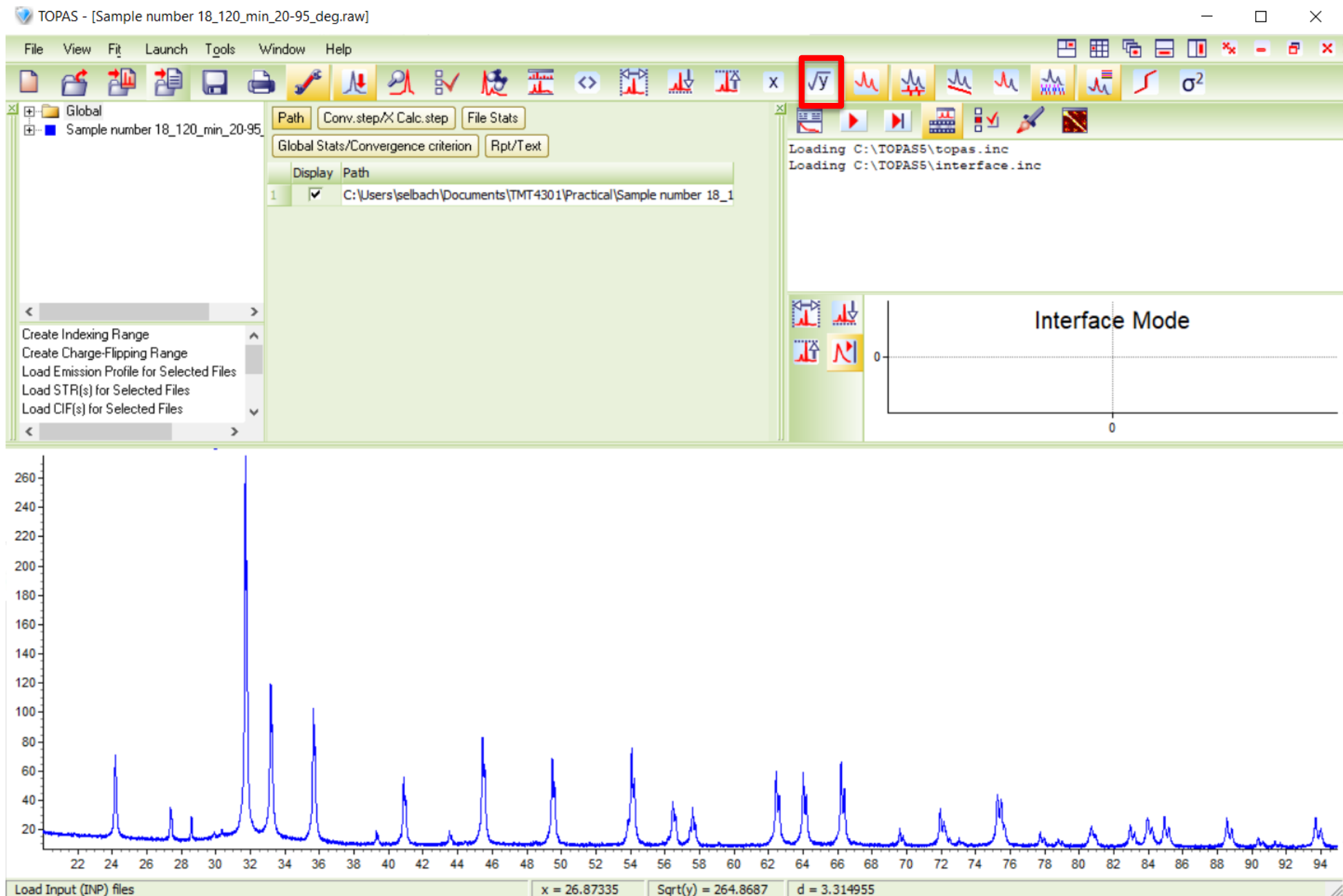
**Data Tree**

Data	Description
Document	
Views	
Settings	1 Chemical Filter - 1 Database Filter
<b>2Theta</b>	<b>1 Scan</b>
Sample number 18_120_min_20-95_deg.raw #1	(Coupled TwoTheta/Theta)
Pattern List #1	2 Patterns
COD 2101167	Fe2 O3
<b>COD 9008678</b>	<b>Cl Na Halite</b>

# TOPAS – import a .raw file

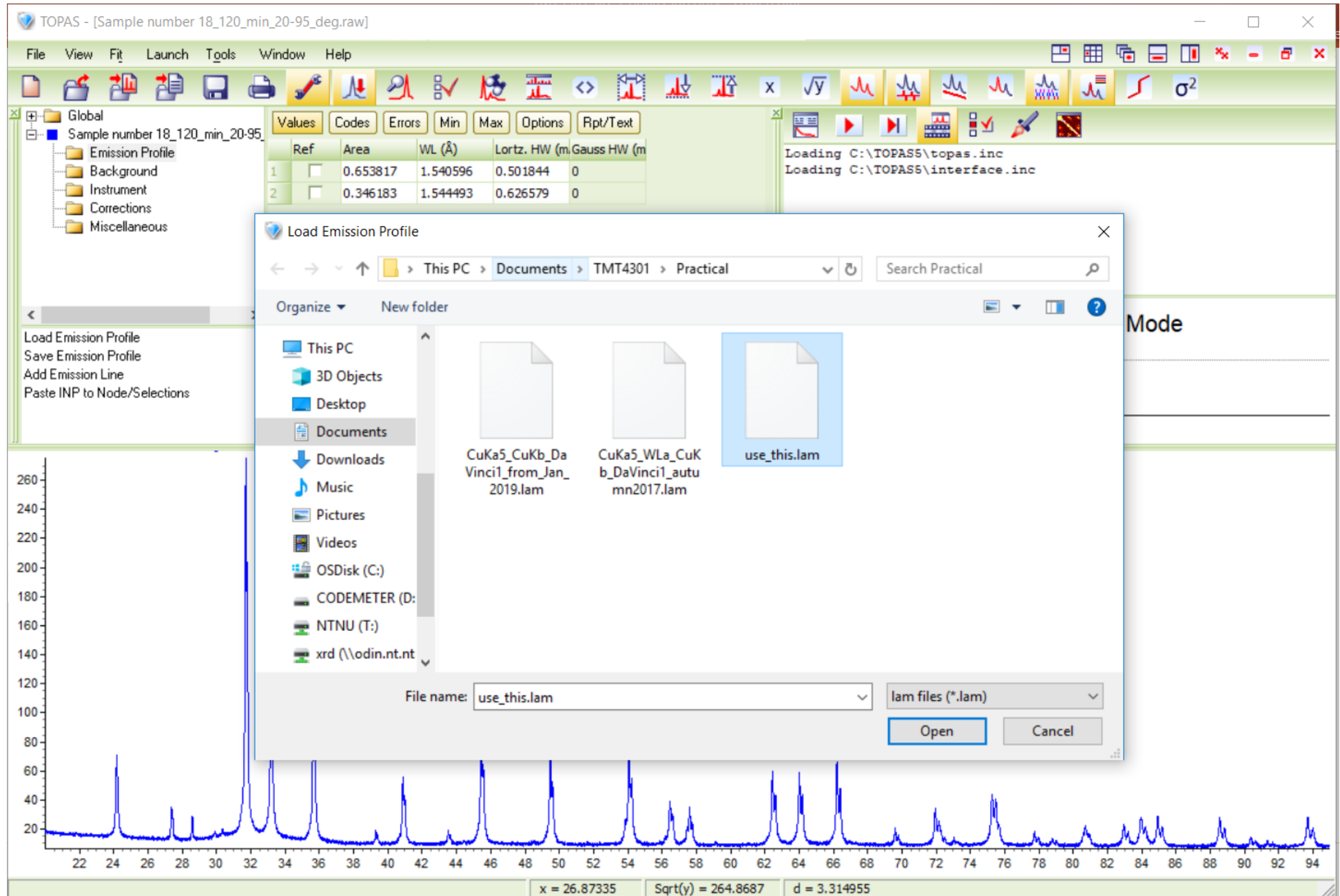


# TOPAS – use square root for y-axis scaling

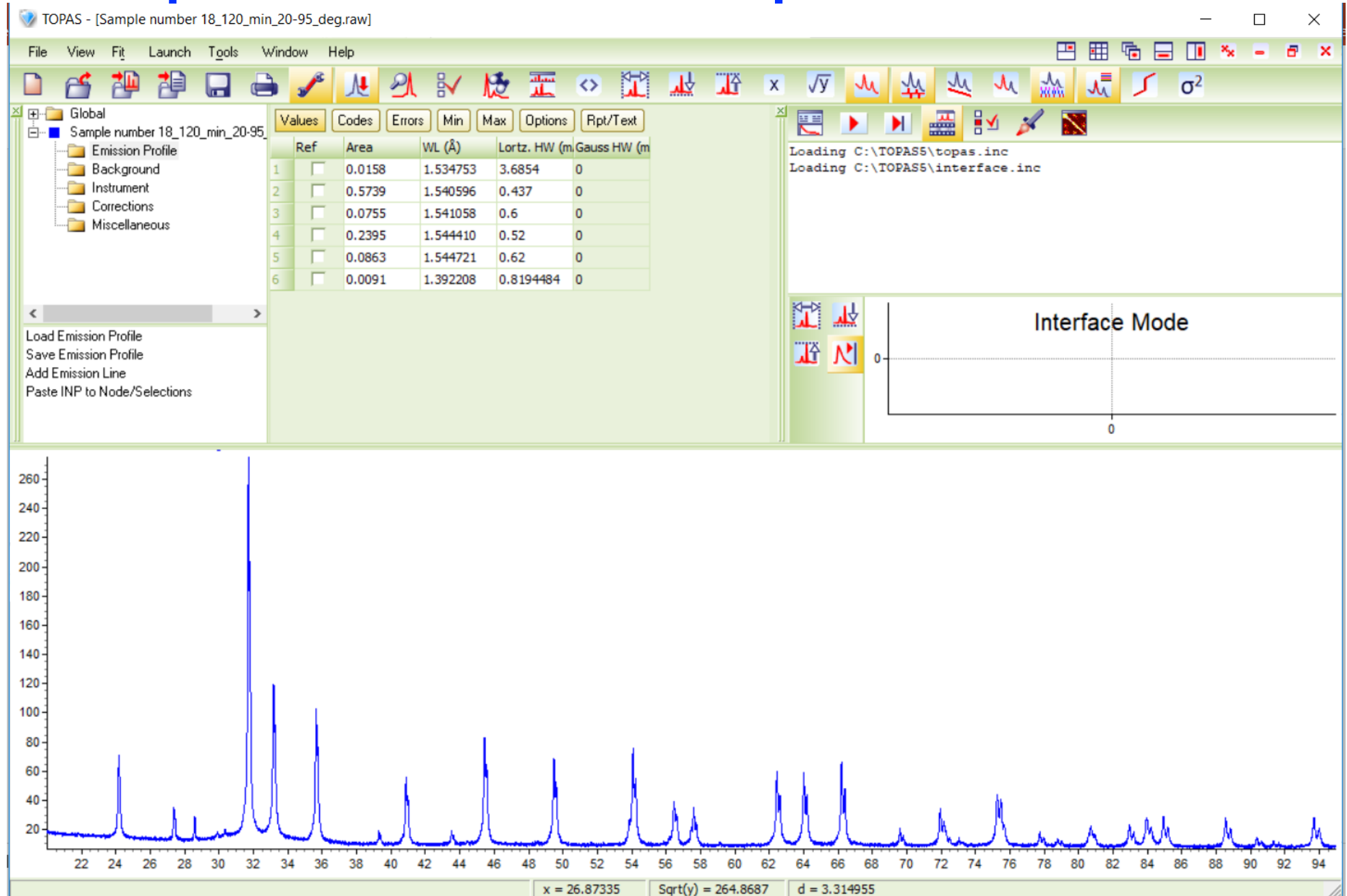




# Topas – load an emission profile



# Topas – load an emission profile



# Topas – load a .par instrumental settings file

TOPAS - [Sample number 18\_120\_min\_20-95\_deg.raw]

File View Fit Launch Tools Window Help

Global  
Sample number 18\_120\_min\_20-95  
Emission Profile  
Background  
Instrument  
Corrections  
Miscellaneous

Divergent beam Additional Convolutions Rpt/Text

	Use	Value	Code	Error
<b>Goniometer radii</b>				
Primary radius (mm)		217.5		
Goniometer (mm)		217.5		

Loading C:\TOPAS5\topas.inc  
Loading C:\TOPAS5\interface.inc

Load Instrument Details  
Save Instrument Details  
Paste INP to Node/Selections

Select Instrument Details File

This PC > Documents > TMT4301 > Practical

Organize New folder

This PC  
3D Objects  
Desktop  
Documents  
Downloads  
Music  
Pictures  
Videos  
OSDisk (C:)  
CODEMETER (D:)  
NTNU (T:)  
xrd (\odin.nt.nt)

davinci1\_fds\_0.3deg.par  
use\_this.par

File name: use\_this.par par files (\*.par)

Open Cancel

Mode

260  
240  
220  
200  
180  
160  
140  
120  
100  
80  
60  
40  
20

22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60 62 64 66 68 70 72 74 76 78 80 82 84 86 88 90 92 94

x = 36.57677 Sqrt(y) = 275.9927 d = 2.454742

# Topas – load a .par file. EVA gives you info too:

TOPAS - [Sample number 18\_120\_min\_20-95\_deg.raw]

File View Fit Launch Tools Window Help

Global  
Sample number 18\_120\_min\_20-95  
Emission Profile  
Background  
Instrument  
Corrections  
Miscellaneous

Divergent beam Additional Convolutions Rpt/Text

	Use	Value	Code
<b>Goniometer radii</b>			
Primary radius (mm)		280	
Secondary radius (mm)		280	
<b>Equatorial Convolutions</b>			
Point detector	<input type="checkbox"/>		
Capillary	<input type="checkbox"/>		
Linear PSD	<input checked="" type="checkbox"/>		
2Th angular range of LPSD (°)		3	Fix
FDS angle (°)		0.4	Fix
Beam spill, sample length (mm)	<input type="checkbox"/>	20	Fix
Tube Tails	<input type="checkbox"/>		
<b>Axial Convolutions</b>			
Full Axial Model	<input checked="" type="checkbox"/>		
Source length (mm)		12	Fix
Sample length (mm)		15	Fix
RS length (mm)		12	Fix
Prim. Soller (°)	<input checked="" type="checkbox"/>	2.5	Fix
Sec. Soller (°)	<input checked="" type="checkbox"/>	2.5	Fix
N Beta		30	
Finger_et_al	<input type="checkbox"/>		

Load Instrument Details  
Save Instrument Details  
Paste INP to Node/Selections

Generator mA 40,0 mA

**Detector**

Detector Name LYNXEYE\_XE (1D ...  
LynxEye 0D ☐  
PSD Opening 2,946 °  
Lower Discrimin 0,218 V  
Upper Discrimin 0,238 V

**Optics**

Primary Soller 2,500 °  
Secondary Soller 2,500 °  
Air-Scatter Screen ☐  
Divergence Slit 0,400 °  
Antiscatter Slit 3,995 °  
Slit Mode Fixed  
Simul. Slit Mode

**Corrections**

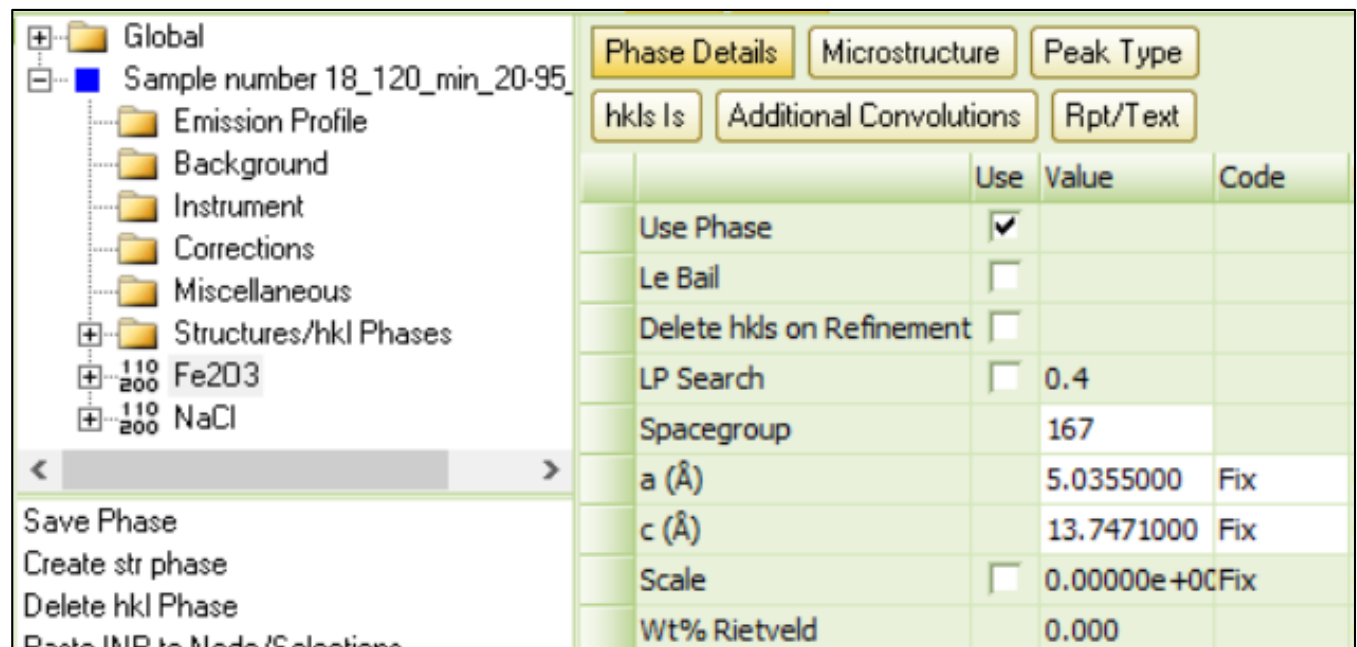
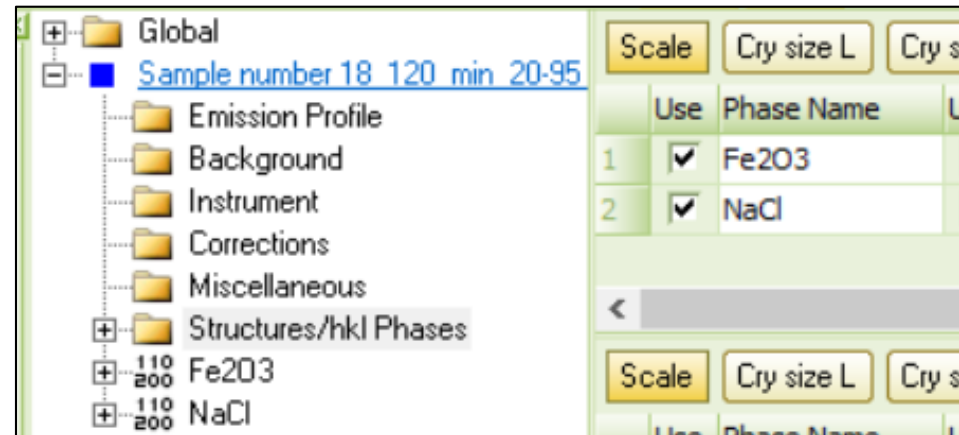
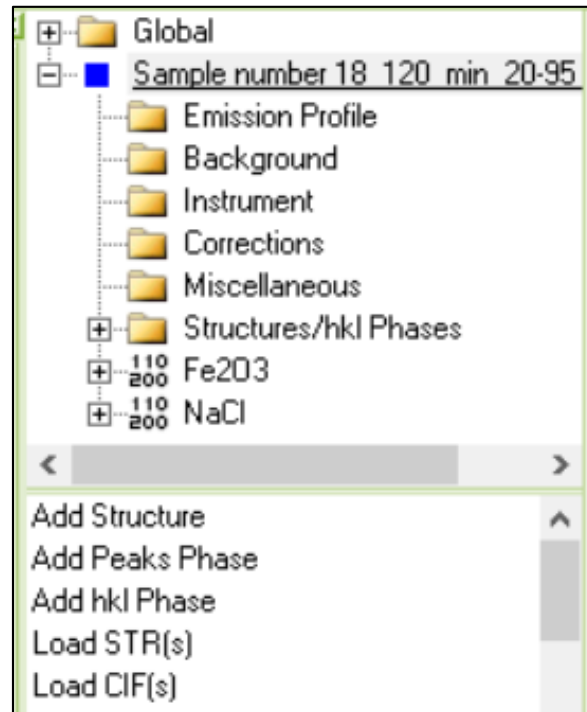
Displacement 0,000 mm  
X-Offset 0,000 °  
Y-Scale Factor 1  
Y-Offset 0 counts

**Background**

Display Original + Ba...  
Curvature 1,000  
Threshold 1,000  
Enhanced ☐  
Color Transp...

# Pawley – add two hkl phases, rename them

- ◆ Note context sensitive menus.



# Pawley – fix all parameters first

The screenshot shows the Pawley software interface. On the left, the 'Global' panel is expanded, showing a tree structure with folders like 'Emission Profile', 'Background', 'Instrument', 'Corrections', 'Miscellaneous', and 'Structures/hkl Phases'. Under 'Structures/hkl Phases', 'Fe2O3' and 'NaCl' are listed. On the right, the 'Phase Details' tab is active. It contains a table with columns 'Use', 'Value', and 'Code'. The table is titled 'Double-Voigt Approach' and lists parameters: 'Crystallite size', 'Cry size L' (checked, 200.0, Fix), 'Cry size G' (unchecked, 200.0, Refine), and 'LVol-IB (nm)' (0.000).

	Use	Value	Code
<b>Double-Voigt Approach</b>			
Crystallite size			
Cry size L	<input checked="" type="checkbox"/>	200.0	Fix
Cry size G	<input type="checkbox"/>	200.0	Refine
LVol-IB (nm)		0.000	

The screenshot shows the Pawley software interface with the 'Fe2O3' and 'NaCl' phases selected in the 'Global' panel. On the right, the 'Phase Details' tab is active. It contains a table with columns 'Use', 'Value', and 'Code'. The table lists parameters: 'LP Search' (unchecked, 0.4), 'Spacegroup' (225), 'a (Å)' (5.6406000, Fix), and 'Scale' (unchecked, 0.000000e+00, Fix).

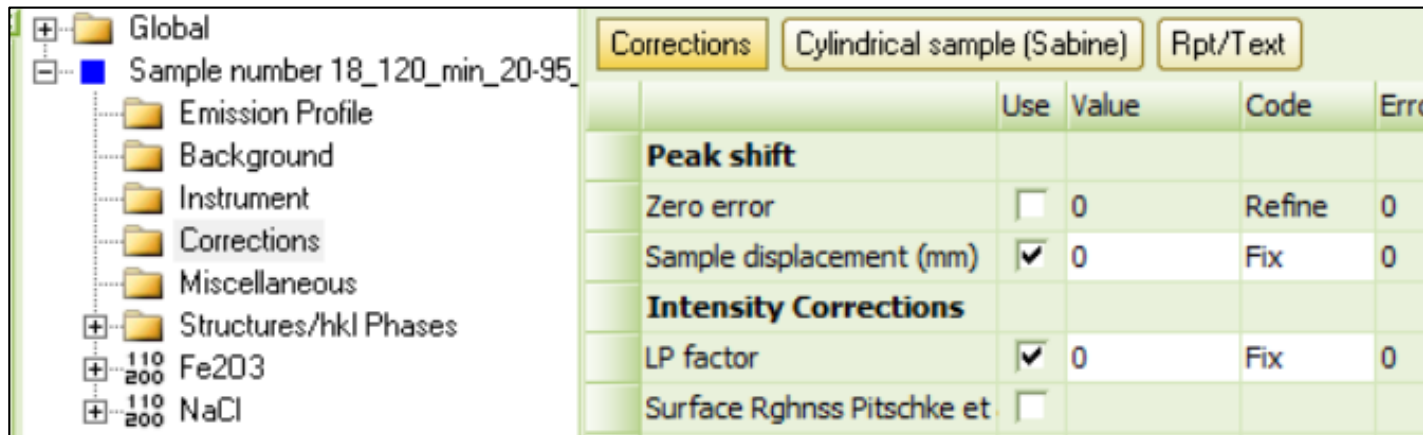
	Use	Value	Code
LP Search	<input type="checkbox"/>	0.4	
Spacegroup		225	
a (Å)		5.6406000	Fix
Scale	<input type="checkbox"/>	0.000000e+00	Fix

The screenshot shows the Pawley software interface. On the left, the 'Global' panel is expanded, showing a tree structure with folders like 'Emission Profile', 'Background', 'Instrument', 'Corrections', 'Miscellaneous', and 'Structures/hkl Phases'. Under 'Structures/hkl Phases', 'Fe2O3' and 'NaCl' are listed. On the right, the 'Phase Details' tab is active. It contains a table with columns 'Use', 'Value', and 'Code'. The table is titled 'Double-Voigt Approach' and lists parameters: 'Crystallite size', 'Cry size L' (checked, 200.0, Fix), 'Cry size G' (unchecked, 200.0, Refine), and 'LVol-IB (nm)' (0.000).

	Use	Value	Code
<b>Double-Voigt Approach</b>			
Crystallite size			
Cry size L	<input checked="" type="checkbox"/>	200.0	Fix
Cry size G	<input type="checkbox"/>	200.0	Refine
LVol-IB (nm)		0.000	

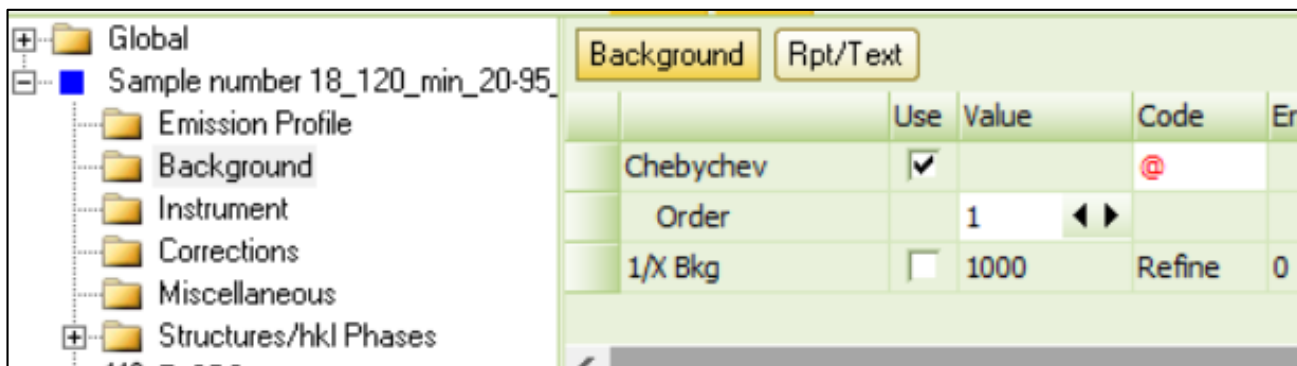
# Pawley – fix all parameters first

- ◆ Exception: allow at least one variable for the background – flat background which gives a crude, but reasonable fit.



The screenshot shows the Pawley software interface with the 'Corrections' tab selected. The left pane displays a tree structure with folders: Global, Sample number 18\_120\_min\_20-95, Emission Profile, Background, Instrument, Corrections, Miscellaneous, Structures/hkl Phases, and a list of phases: Fe2O3 and NaCl. The right pane shows the 'Corrections' settings for the selected sample. The 'Cylindrical sample (Sabine)' button is active. The table below lists the correction parameters:

	Use	Value	Code	Error
<b>Peak shift</b>				
Zero error	<input type="checkbox"/>	0	Refine	0
Sample displacement (mm)	<input checked="" type="checkbox"/>	0	Fix	0
<b>Intensity Corrections</b>				
LP factor	<input checked="" type="checkbox"/>	0	Fix	0
Surface Rghnss Pitschke et	<input type="checkbox"/>			

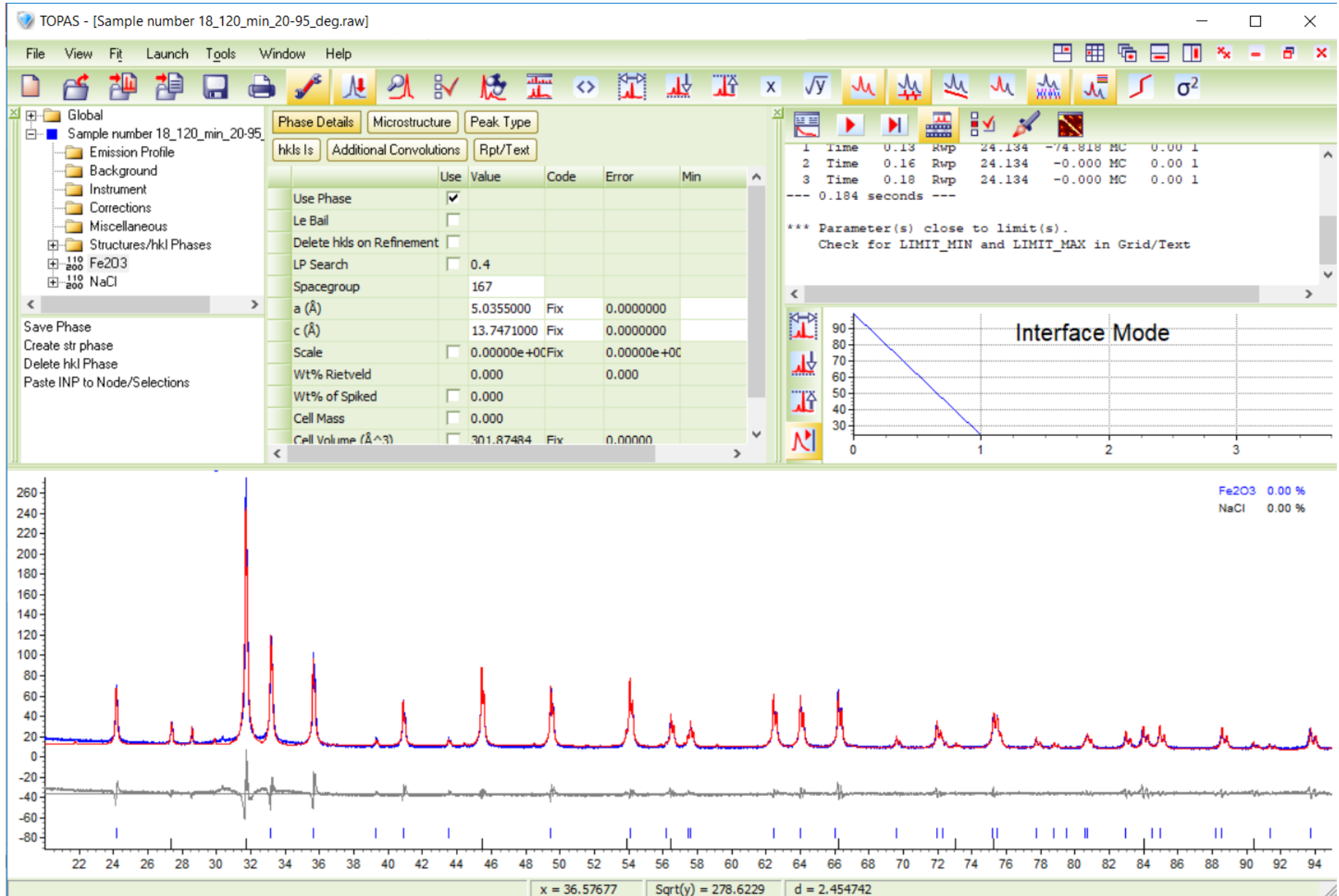


The screenshot shows the Pawley software interface with the 'Background' tab selected. The left pane is the same as the previous screenshot. The right pane shows the 'Background' settings. The table below lists the background parameters:

	Use	Value	Code	Error
Chebychev	<input checked="" type="checkbox"/>		@	
Order		1		
1/X Bkg	<input type="checkbox"/>	1000	Refine	0



# Pawley – first attempt, nothing refined





# Pawley – progressively add variables

- ◆ Add more nodes to the background polynomial – be careful
- ◆ The add variables affecting *peak positions*.

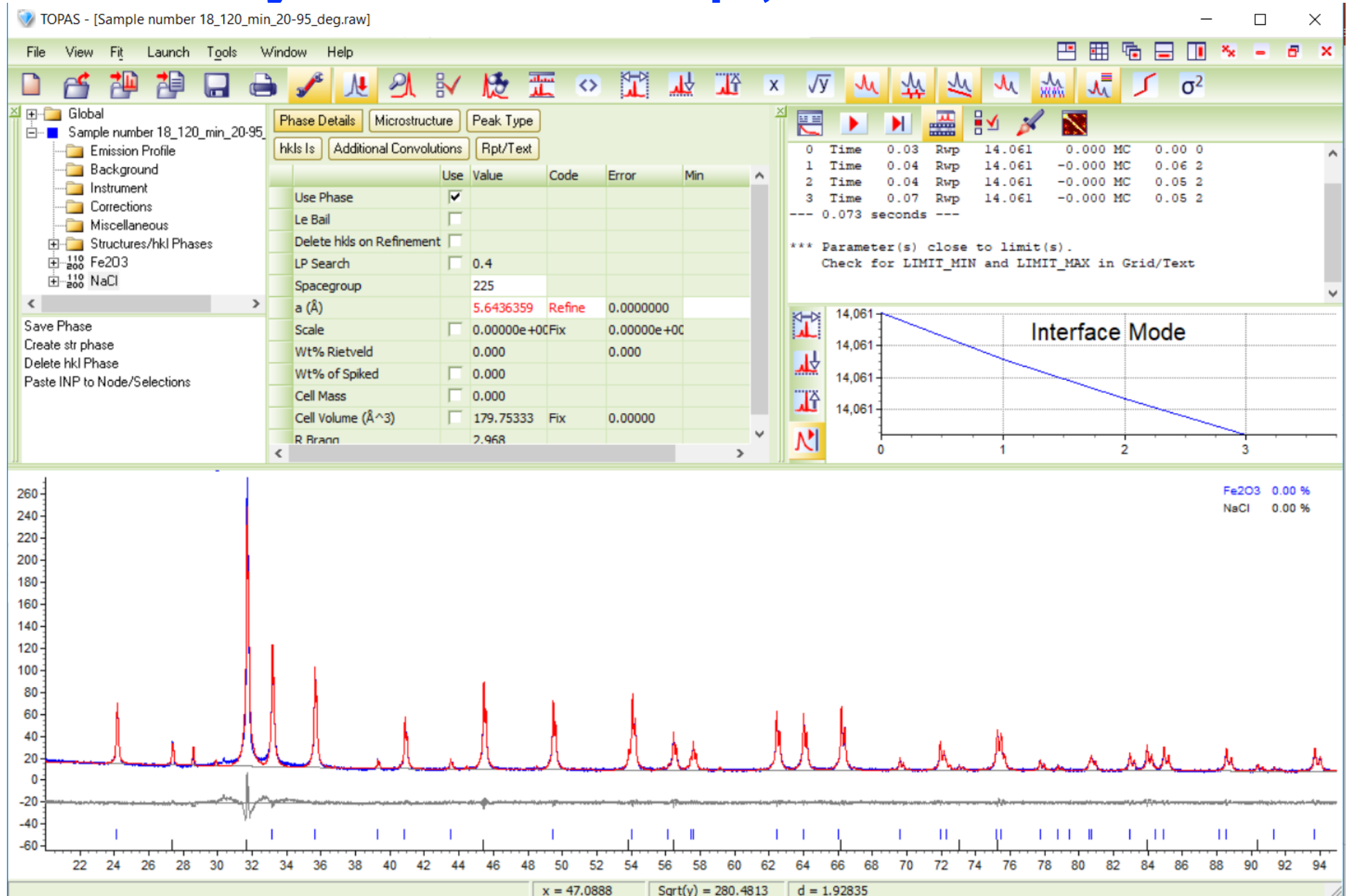
Sample number 18_120_min_20-95_		Use	Value	Code	Er
Emission Profile					
Background	Chebychev	<input checked="" type="checkbox"/>		@	
Instrument	Order		5		
Corrections					

Global	Corrections	Cylindrical sample (Sabine)	Rpt/Text		
Sample number 18_120_min_20-95_		Use	Value	Code	
Emission Profile	<b>Peak shift</b>				
Background	Zero error	<input type="checkbox"/>	0	Refine	
Instrument	Sample displacement (mm)	<input checked="" type="checkbox"/>	-0.02463897	Refine	
Corrections					
Miscellaneous					

Structures/hkl Phases	Delete hkl on Refinement	<input type="checkbox"/>			
110 Fe2O3	LP Search	<input type="checkbox"/>	0.4		
110 NaCl	Spacegroup		167		
	a (Å)		5.0355000	Refine	
	c (Å)		13.7471000	Refine	
	Scale	<input type="checkbox"/>	0.00000e+00	Fix	

110 NaCl	Spacegroup		225		
	a (Å)		5.6406000	Refine	

# Pawley – second attempt, some variables



# Pawley – next add variables for peak shape

Global

Sample number 18\_120\_min\_20-95

- Emission Profile
- Background
- Instrument
- Corrections
- Miscellaneous
- Structures/hkl Phases
  - Fe<sub>2</sub>O<sub>3</sub>
  - NaCl

Phase Details   Microstructure   Peak Type

hkl's Is   Additional Convolutions   Rpt/Text

	Use	Value	Code
<b>Double-Voigt Approach</b>			
Crystallite size			
Cry size L	<input checked="" type="checkbox"/>	177.4	Refine
Cry size G	<input type="checkbox"/>	200.0	Refine
LVol-IB (nm)		112.958	

Miscellaneous

Structures/hkl Phases

- Fe<sub>2</sub>O<sub>3</sub>
- NaCl

Crystallite size			
Cry size L	<input checked="" type="checkbox"/>	276.2	Refine
Cry size G	<input type="checkbox"/>	200.0	Refine
LVol-IB (nm)		175.826	

Strain

Strain L	<input checked="" type="checkbox"/>	0.02228824	Refine	0
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Emission Profile

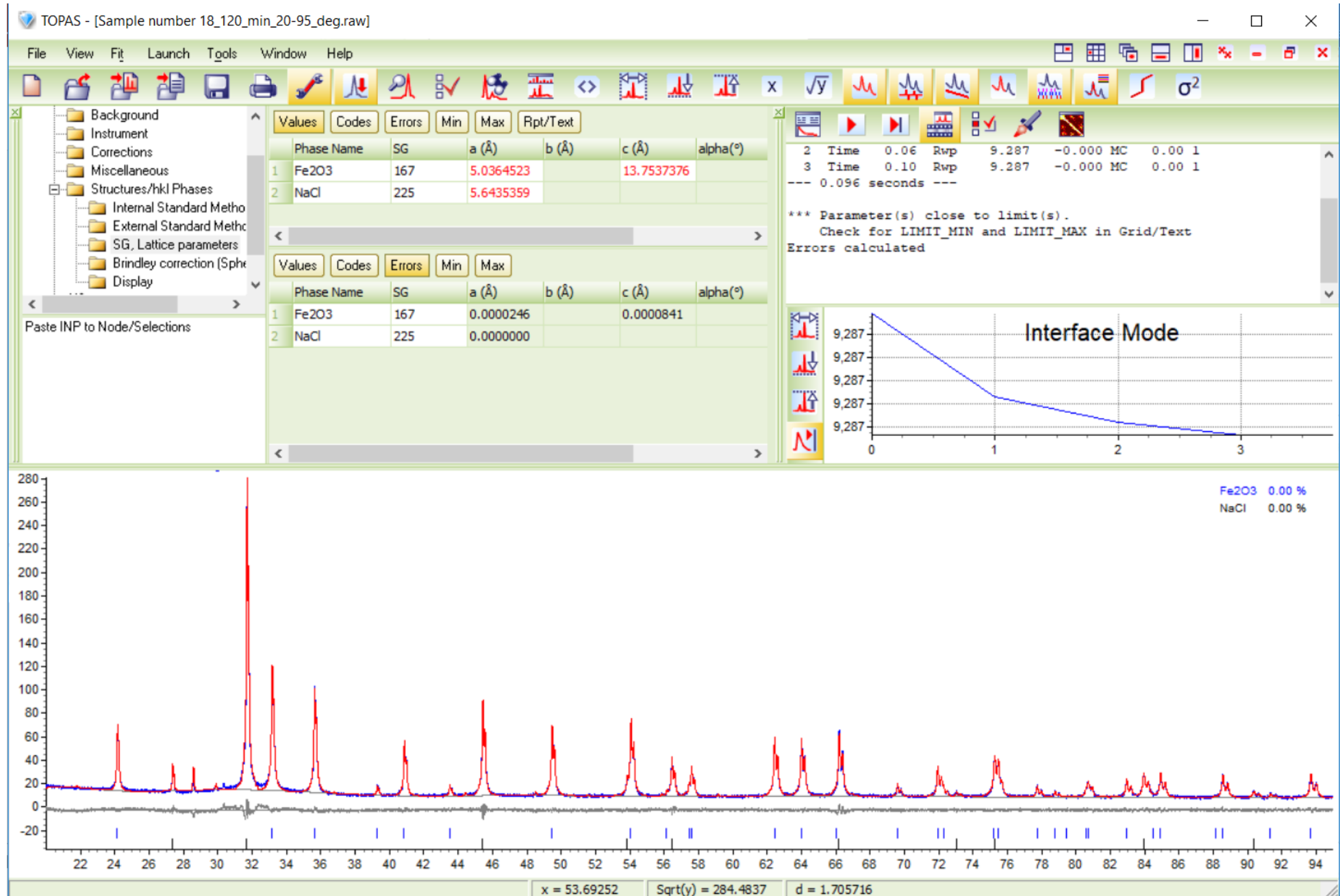
Background

Instrument

Corrections

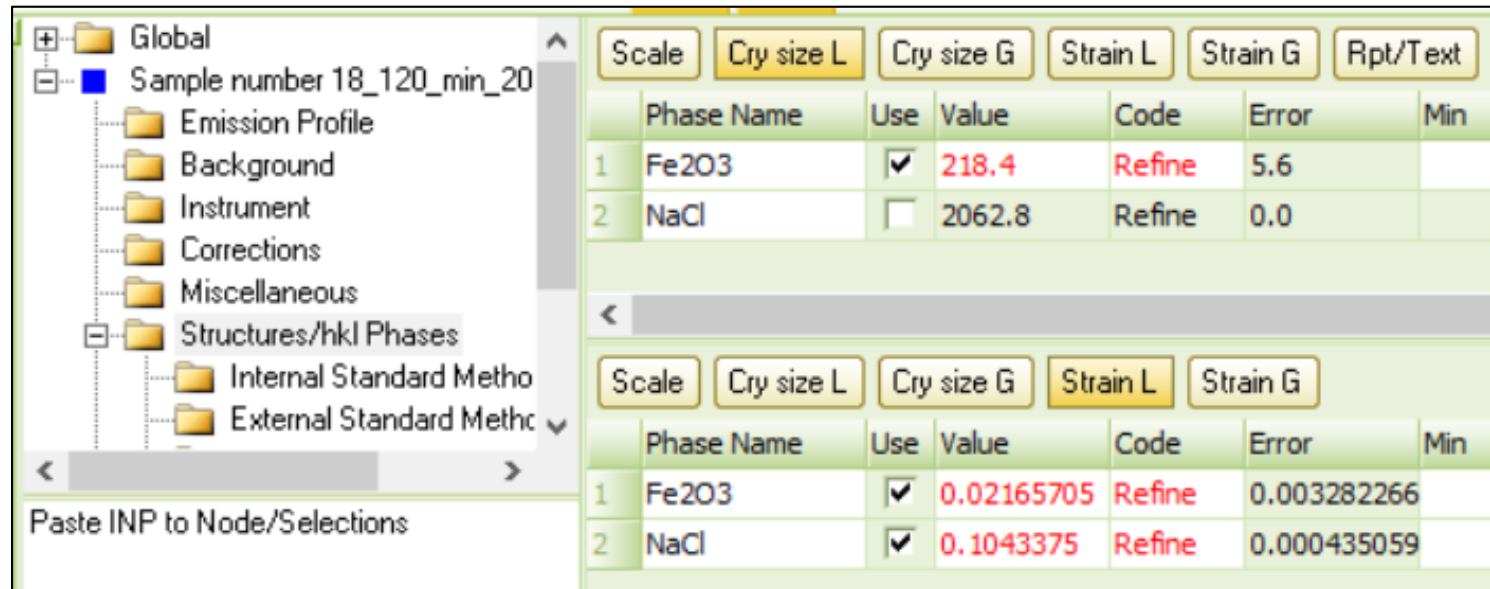
	Use	Value	Code
Chebyshev	<input checked="" type="checkbox"/>		@
Order		13	◀ ▶
1/X Bkg	<input type="checkbox"/>	1000	Refine

# Pawley – a pretty good fit!



# Pawley – summarising results

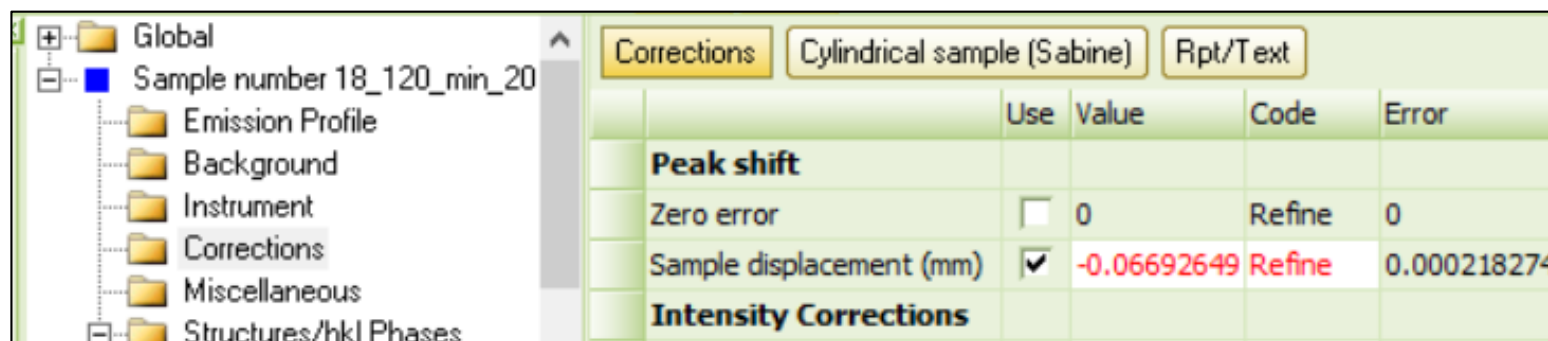
- ◆ Useful for many phases or many diffractograms (under global).



Scale Cry size L Cry size G Strain L Strain G Rpt/Text

	Phase Name	Use	Value	Code	Error	Min
1	Fe2O3	<input checked="" type="checkbox"/>	218.4	Refine	5.6	
2	NaCl	<input type="checkbox"/>	2062.8	Refine	0.0	

Paste INP to Node/Selections

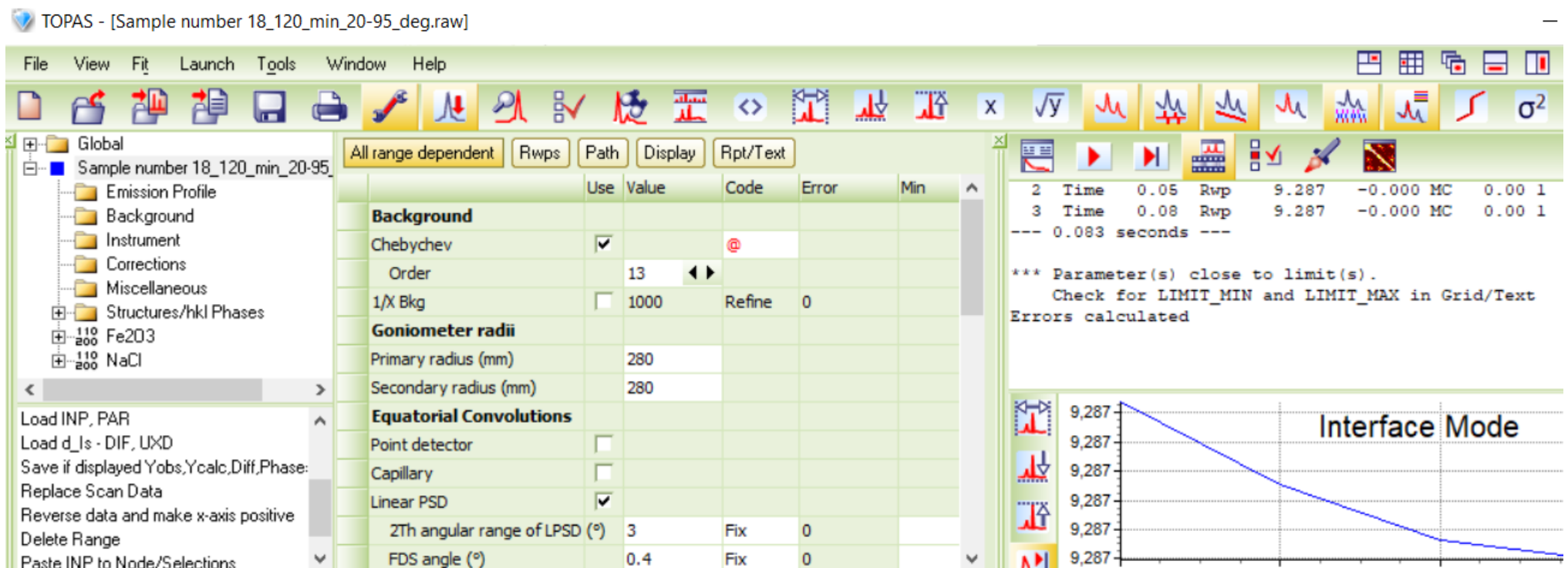


Corrections Cylindrical sample (Sabine) Rpt/Text

	Use	Value	Code	Error
<b>Peak shift</b>				
Zero error	<input type="checkbox"/>	0	Refine	0
Sample displacement (mm)	<input checked="" type="checkbox"/>	-0.06692649	Refine	0.000218274
<b>Intensity Corrections</b>				

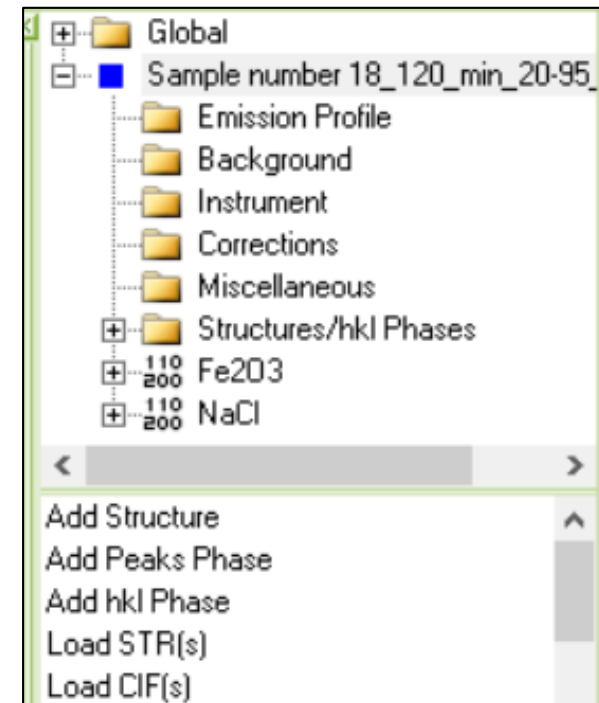
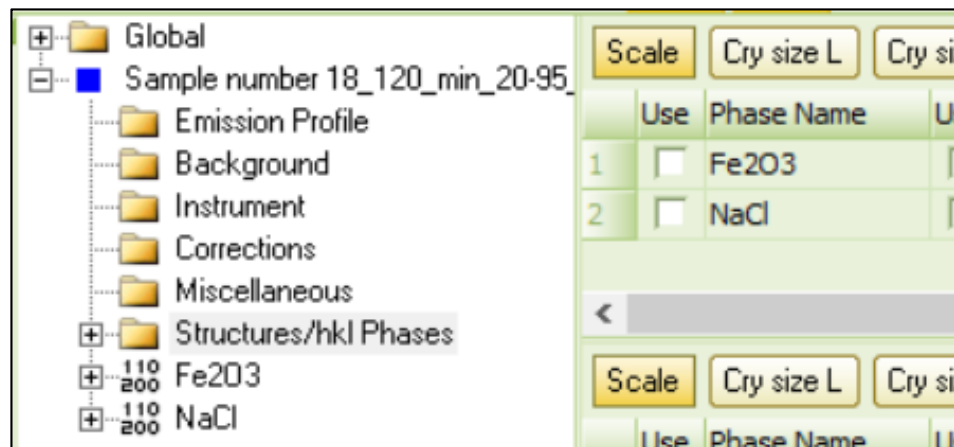
# Pawley – background polynomial

- ◆ You can add more nodes as long as the background does not fit peaks.
- ◆ E.g. 13 is a high number, but unproblematic with broad 2 $\theta$  range and a bulk well-crystallized sample.
- ◆ Can be problematic for small nanocrystallites – why?



# Preparing for Rietveld refinement

- ◆ Uncheck the hkl phases for Pawley
- ◆ Add two new structures
- ◆ You can also load a saver .str file or a downloaded .cif file
- ◆ .cif – Crystallographic Information File





# Add structures for Rietveld refinement

Sample number 18\_120\_min\_20

- Emission Profile
- Background
- Instrument
- Corrections
- Miscellaneous
- Structures/hkl Phases
  - $110_{200}$  Fe2O3
  - $110_{200}$  NaCl
  - Fe2O3
  - NaCl

Structure		Microstructure	Peak Type
hkl	Additional Convolutions	Rpt/Text	
	Use	Value	Code
Use Phase	<input checked="" type="checkbox"/>		
Spacegroup		167	
a (Å)		5.0364524	Fix
c (Å)		13.7537378	Fix
Scale	<input checked="" type="checkbox"/>	1.00000e-00!	@
Wt% Rietveld		0.000	

Structure		Microstructure	Peak Type
hkl	Additional Convolutions	Rpt/Text	
	Use	Value	Code
<b>Double-Voigt Approach</b>			
Crystallite size			
Cry size L	<input checked="" type="checkbox"/>	218.3	Fix

Sample number 18\_120\_min\_20

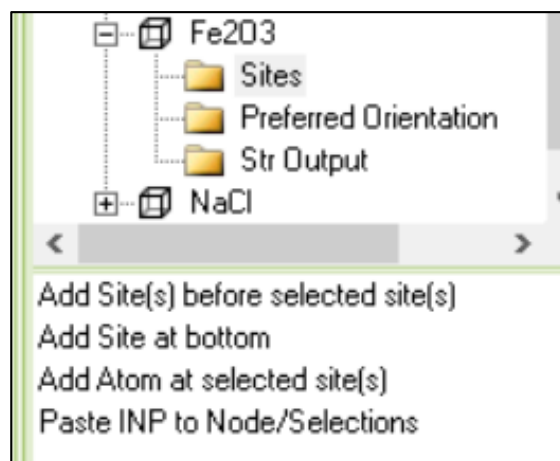
- Emission Profile
- Background
- Instrument
- Corrections
- Miscellaneous
- Structures/hkl Phases
  - $110_{200}$  Fe2O3
  - $110_{200}$  NaCl
  - Fe2O3
  - NaCl

Structure		Microstructure	Peak Type
hkl	Additional Convolutions	Rpt/Text	
	Use	Value	Code
Use Phase	<input checked="" type="checkbox"/>		
Spacegroup		225	
a (Å)		5.6435341	Fix
Scale	<input checked="" type="checkbox"/>	1.00000e-00!	@
Wt% Rietveld		0.000	
Wt% of Spiked	<input type="checkbox"/>	0.000	

Strain			
	Use	Value	Code
Strain L	<input checked="" type="checkbox"/>	0.104205	Fix



# Structures for Rietveld – atomic positions



Background

Instrument

Corrections

Miscellaneous

Structures/hkl Phases

110

200

Fe2O3

110

200

NaCl

Fe2O3

Sites

Preferred Orientation

Str Output

NaCl

Values

Codes

Errors

Min

Max

Rpt/Text

	Site	Np	x	y	z	Atom	Occ.	Beq.
1	Fe	0	0.00000	0.00000	0.35500	Fe+3	1	1
2	O	0	0.699	0.00000	0.25000	O-2	1	1

<

>

Values

Codes

Errors

Min

Max

	Site	Np	x	y	z	Atom	Occ.	Beq.
1	Fe	0	Fix	Fix	Fix	Fe+3	Fix	Fix
2	O	0	Fix	Fix	=1/4	O-2	Fix	Fix

# Structures for Rietveld – atomic positions

Structures/hkl Phases

110  
200

Fe2O3

110  
200

NaCl

Fe2O3

Sites

Preferred Orientation

Str Output

NaCl

Sites

Preferred Orientation

Str Output

Values

Codes

Errors

Min

Max

Rpt/Text

	Site	Np	x	y	z	Atom	Occ.	Beq.
1	Na	0	0.00000	0.00000	0.00000	Na+1	1	1
2	Cl	0	0.50000	0.50000	0.50000	Cl-1	1	1

< >

Values

Codes

Errors

Min

Max

	Site	Np	x	y	z	Atom	Occ.	Beq.
1	Na	0	Fix	Fix	Fix	Na+1	Fix	Fix
2	Cl	0	=1/2	=1/2	=1/2	Cl-1	Fix	Fix

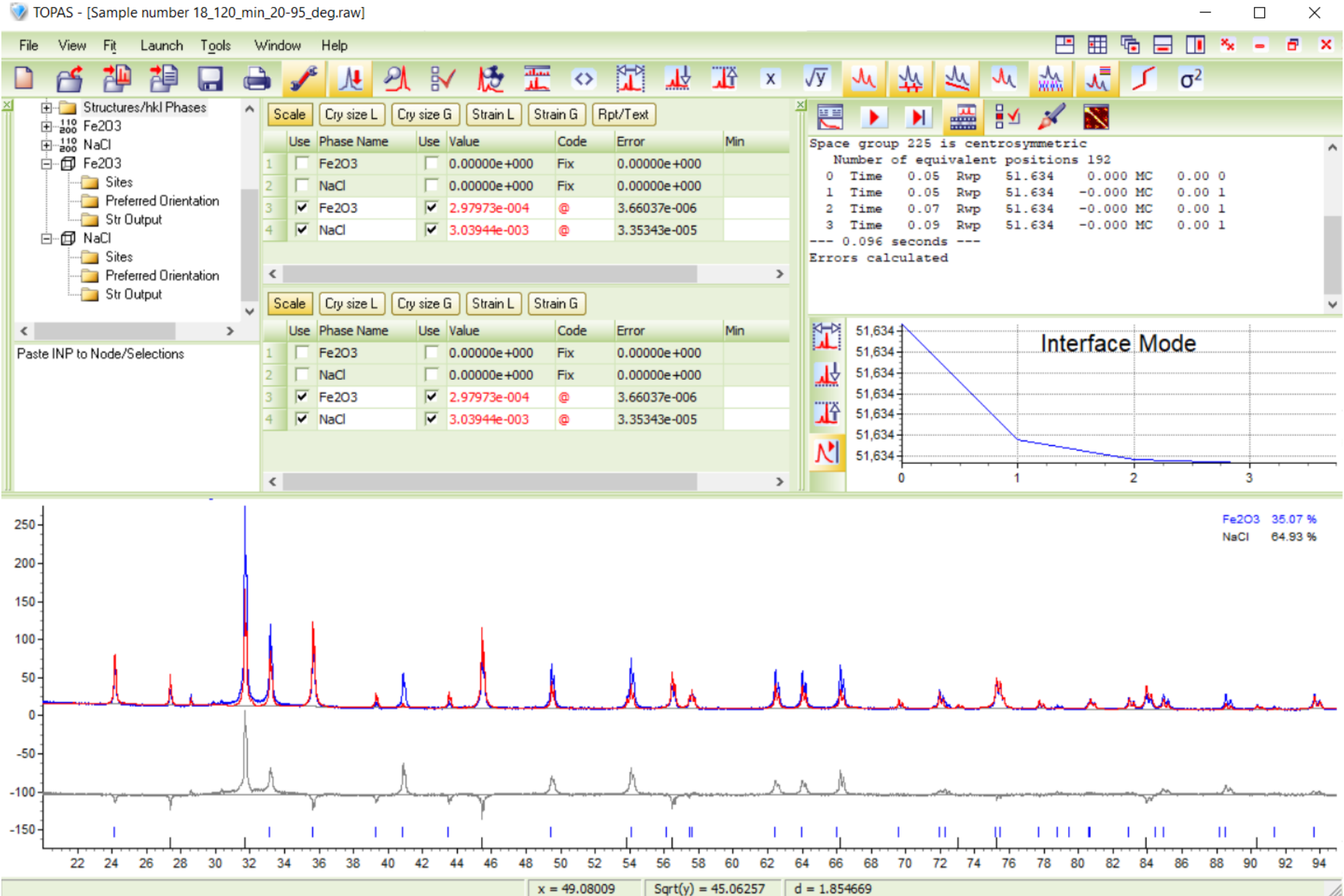
Add Site(s) before selected site(s)

Add Site at bottom

Add Atom at selected site(s)

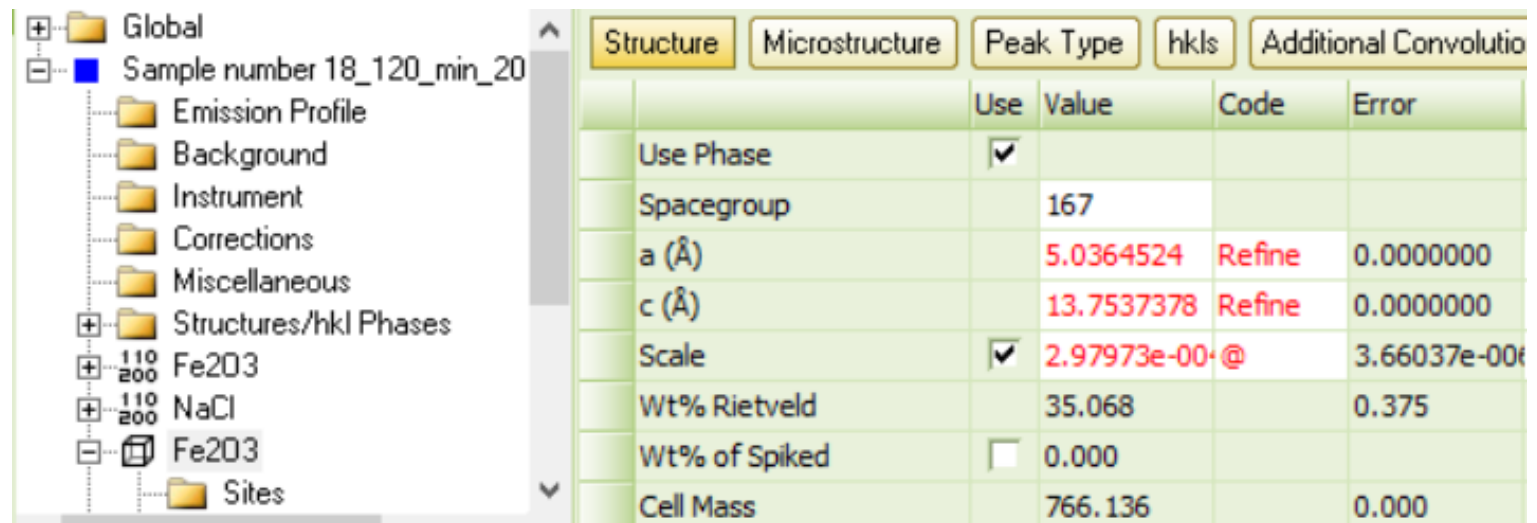
Paste INP to Node/Selections

## Rietveld – first attempt with Pawley results

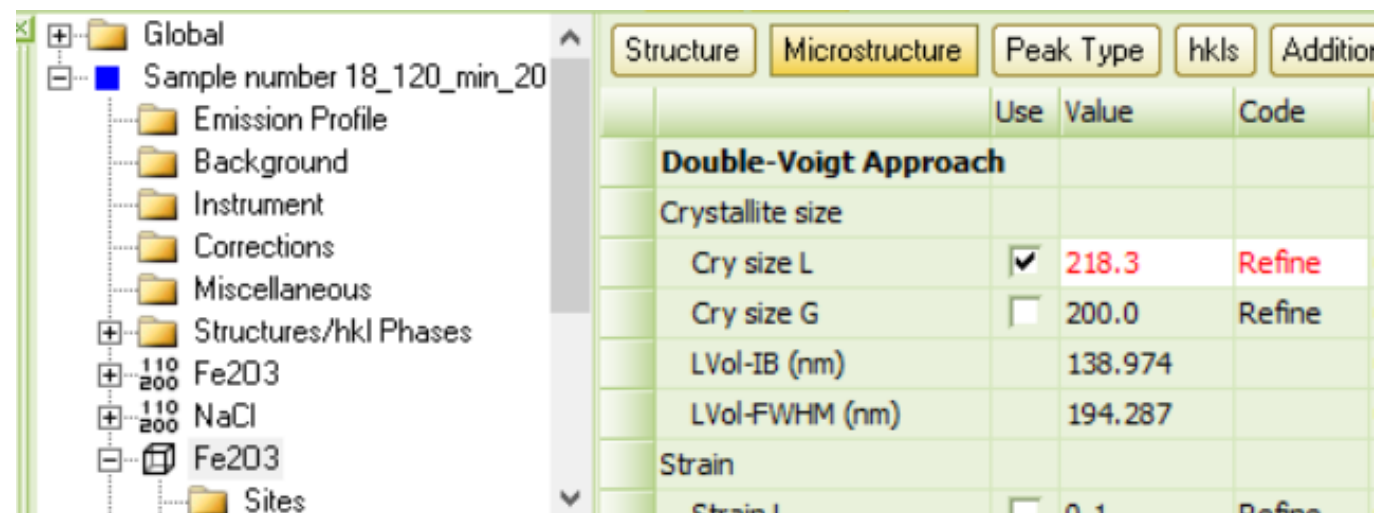


# Rietveld refinement

- ◆ Start with lattice parameters – peak *positions*.
- ◆ Proceed with size/strain – peak *shapes*.

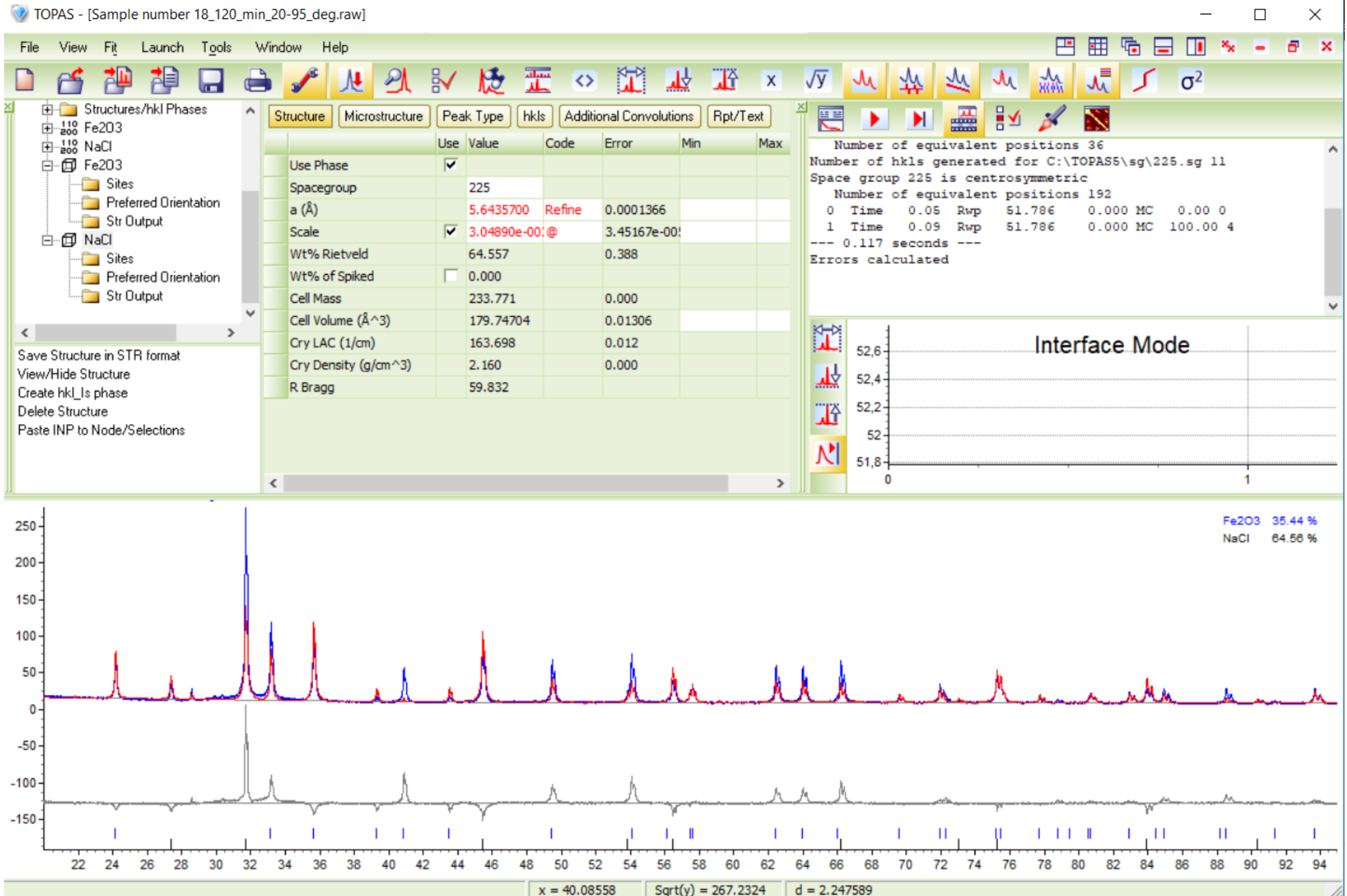


	Use	Value	Code	Error
Use Phase	<input checked="" type="checkbox"/>			
Spacegroup		167		
a (Å)		5.0364524	Refine	0.0000000
c (Å)		13.7537378	Refine	0.0000000
Scale	<input checked="" type="checkbox"/>	2.97973e-004		3.66037e-006
Wt% Rietveld		35.068		0.375
Wt% of Spiked	<input type="checkbox"/>	0.000		
Cell Mass		766.136		0.000



	Use	Value	Code
<b>Double-Voigt Approach</b>			
Crystallite size			
Cry size L	<input checked="" type="checkbox"/>	218.3	Refine
Cry size G	<input type="checkbox"/>	200.0	Refine
LVol-IB (nm)		138.974	
LVol-FWHM (nm)		194.287	
Strain			
Strain L	<input type="checkbox"/>	0.1	Refine

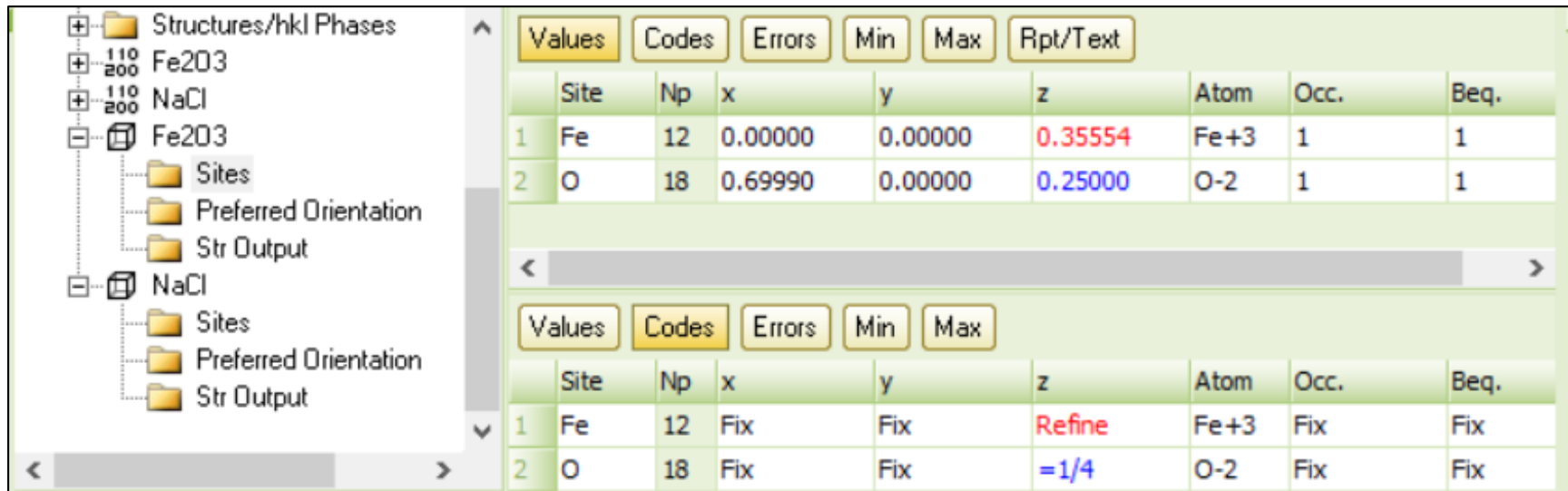
# Rietveld refinement, peak pos./shape included





# Rietveld refinement – atomic positions

- Start with heaviest atomcs, proceed with lighter.
- If more what one Wyckoff position: start with highest multiplicity.



	Site	Np	x	y	z	Atom	Occ.	Beq.
1	Fe	12	0.00000	0.00000	0.35554	Fe+3	1	1
2	O	18	0.69990	0.00000	0.25000	O-2	1	1

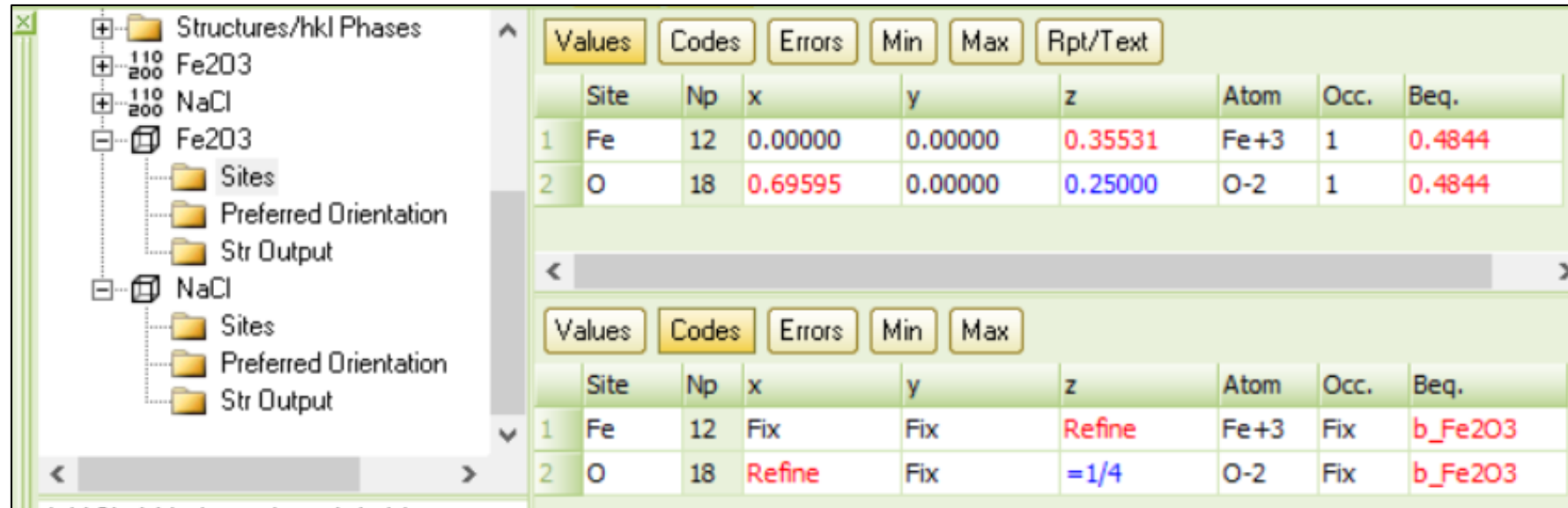


	Site	Np	x	y	z	Atom	Occ.	Beq.
1	Fe	12	0.00000	0.00000	0.35516	Fe+3	1	1
2	O	18	0.69139	0.00000	0.25000	O-2	1	1



# Rietveld refinement – B-factors

- Start with linking parameters, see example below.



Values Codes Errors Min Max Rpt/Text

	Site	Np	x	y	z	Atom	Occ.	Beq.
1	Fe	12	0.00000	0.00000	0.35531	Fe+3	1	0.4844
2	O	18	0.69595	0.00000	0.25000	O-2	1	0.4844

Values Codes Errors Min Max

	Site	Np	x	y	z	Atom	Occ.	Beq.
1	Fe	12	Fix	Fix	Refine	Fe+3	Fix	b_Fe2O3
2	O	18	Refine	Fix	=1/4	O-2	Fix	b_Fe2O3



Values Codes Errors Min Max Rpt/Text

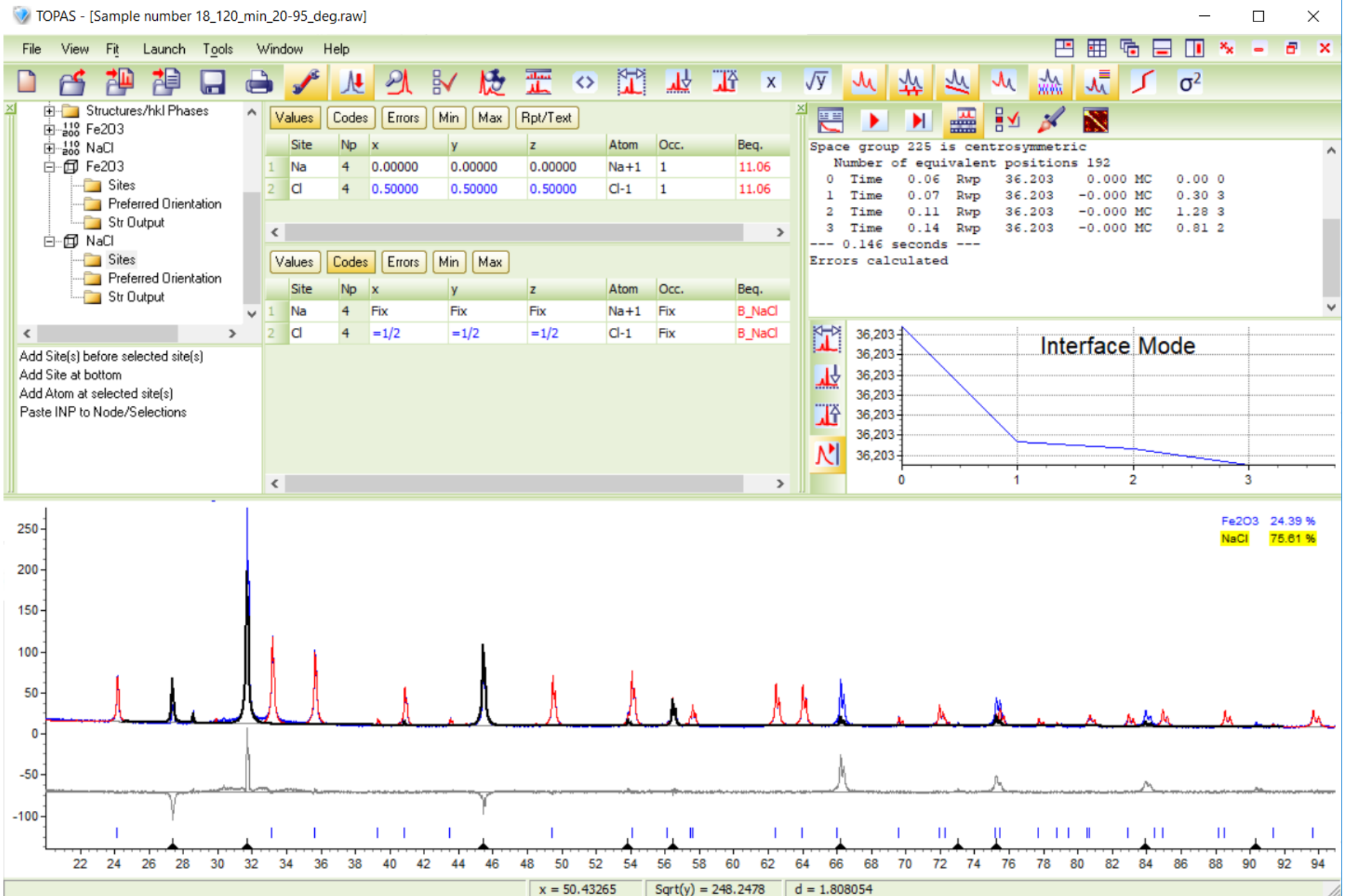
	Site	Np	x	y	z	Atom	Occ.	Beq.
1	Na	4	0.00000	0.00000	0.00000	Na+1	1	11.06
2	Cl	4	0.50000	0.50000	0.50000	Cl-1	1	11.06

Values Codes Errors Min Max

	Site	Np	x	y	z	Atom	Occ.	Beq.
1	Na	4	Fix	Fix	Fix	Na+1	Fix	B_NaCl
2	Cl	4	=1/2	=1/2	=1/2	Cl-1	Fix	B_NaCl

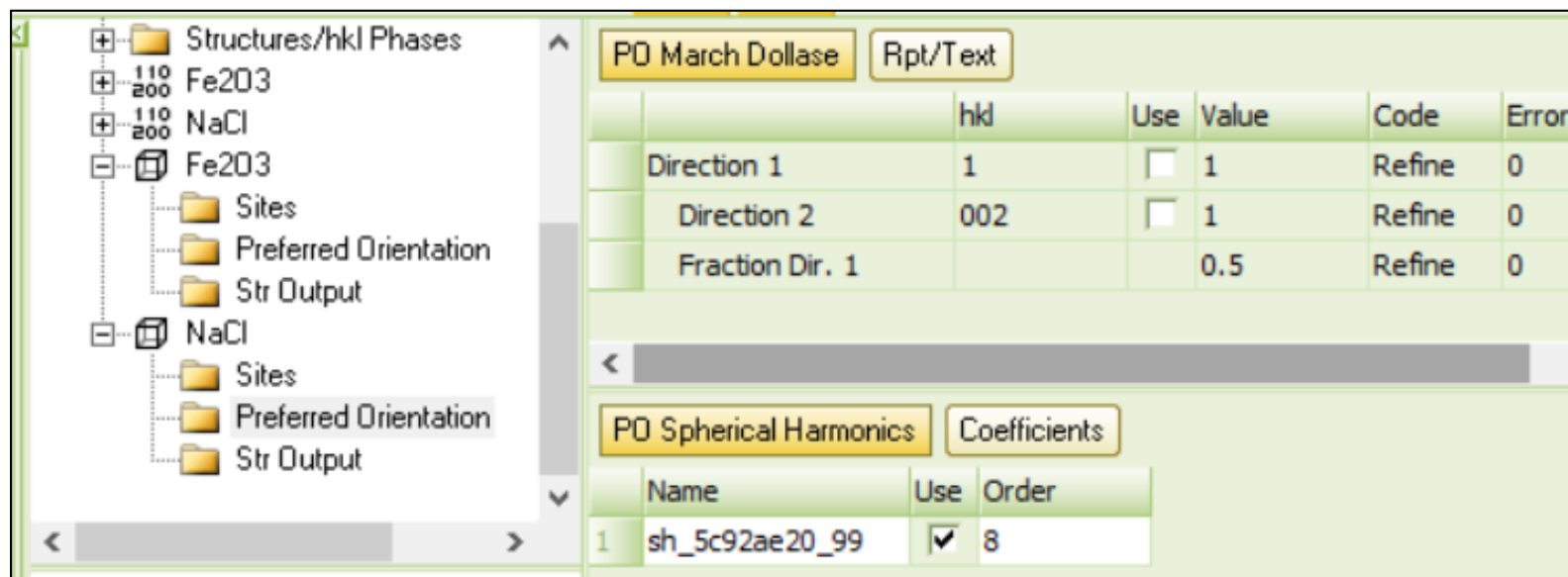


# Peak intensities wrong and B-factors too high...



# Preferential orientation in powder

- ◆ Use this with care and make sure you know what you are doing!
- ◆ (I know what I'm doing – and I made the sample...)



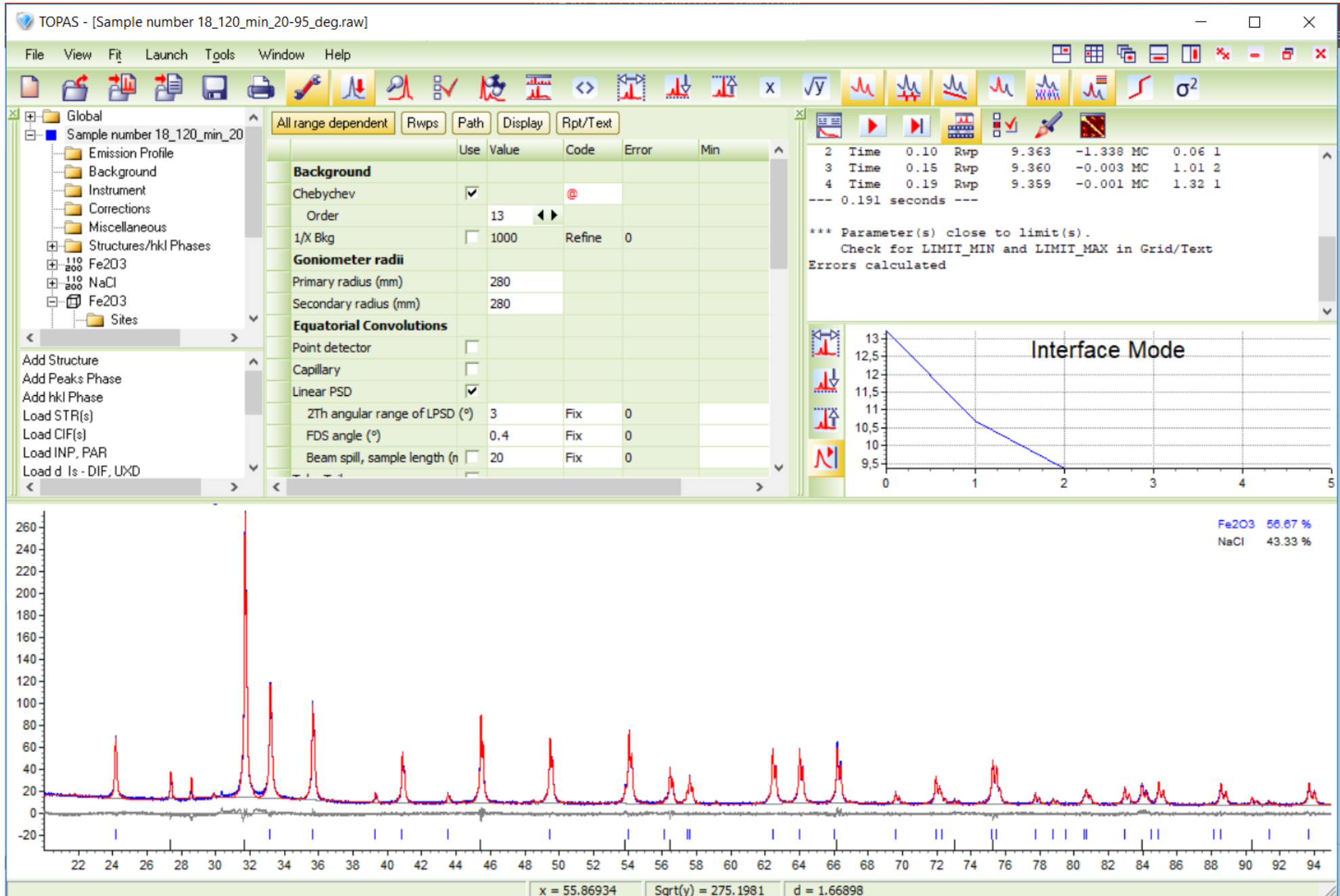
The screenshot displays a software interface for preferential orientation analysis. On the left, a tree view shows the project structure under 'Structures/hkl Phases'. It includes two main entries: 'Fe203' and 'NaCl'. Each entry has sub-folders for 'Sites', 'Preferred Orientation', and 'Str Output'. The 'Fe203' entry is expanded, showing its 'Preferred Orientation' folder. On the right, the 'PO March Dollase' tab is active, displaying a table of parameters. The table has columns for 'hkl', 'Use', 'Value', 'Code', and 'Error'. The parameters are: 'Direction 1' (hkl: 1, Use: ☐, Value: 1, Code: Refine, Error: 0), 'Direction 2' (hkl: 002, Use: ☐, Value: 1, Code: Refine, Error: 0), and 'Fraction Dir. 1' (hkl: , Use: , Value: 0.5, Code: Refine, Error: 0). Below this, the 'PO Spherical Harmonics' tab is active, showing a table of coefficients. The table has columns for 'Name', 'Use', and 'Order'. The parameters are: 'sh\_5c92ae20\_99' (Name: sh\_5c92ae20\_99, Use: ☒, Order: 8).

hkl	Use	Value	Code	Error
Direction 1	<input type="checkbox"/>	1	Refine	0
Direction 2	<input type="checkbox"/>	1	Refine	0
Fraction Dir. 1		0.5	Refine	0

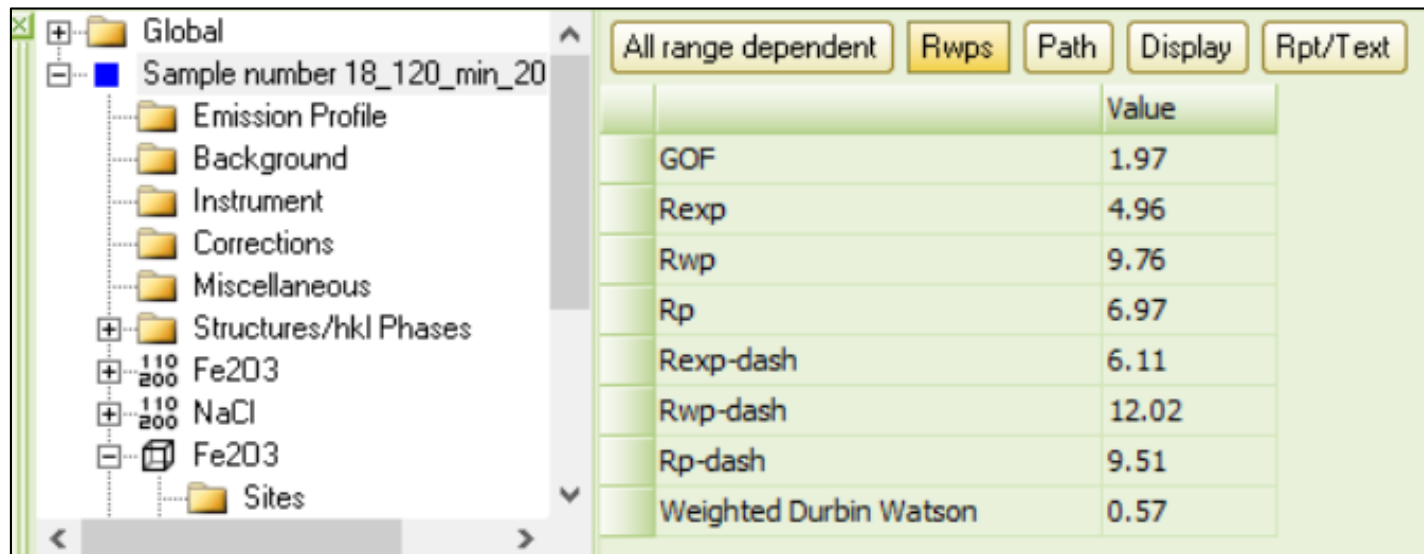
  

Name	Use	Order
sh_5c92ae20_99	<input checked="" type="checkbox"/>	8

# Rietveld refinement – final result



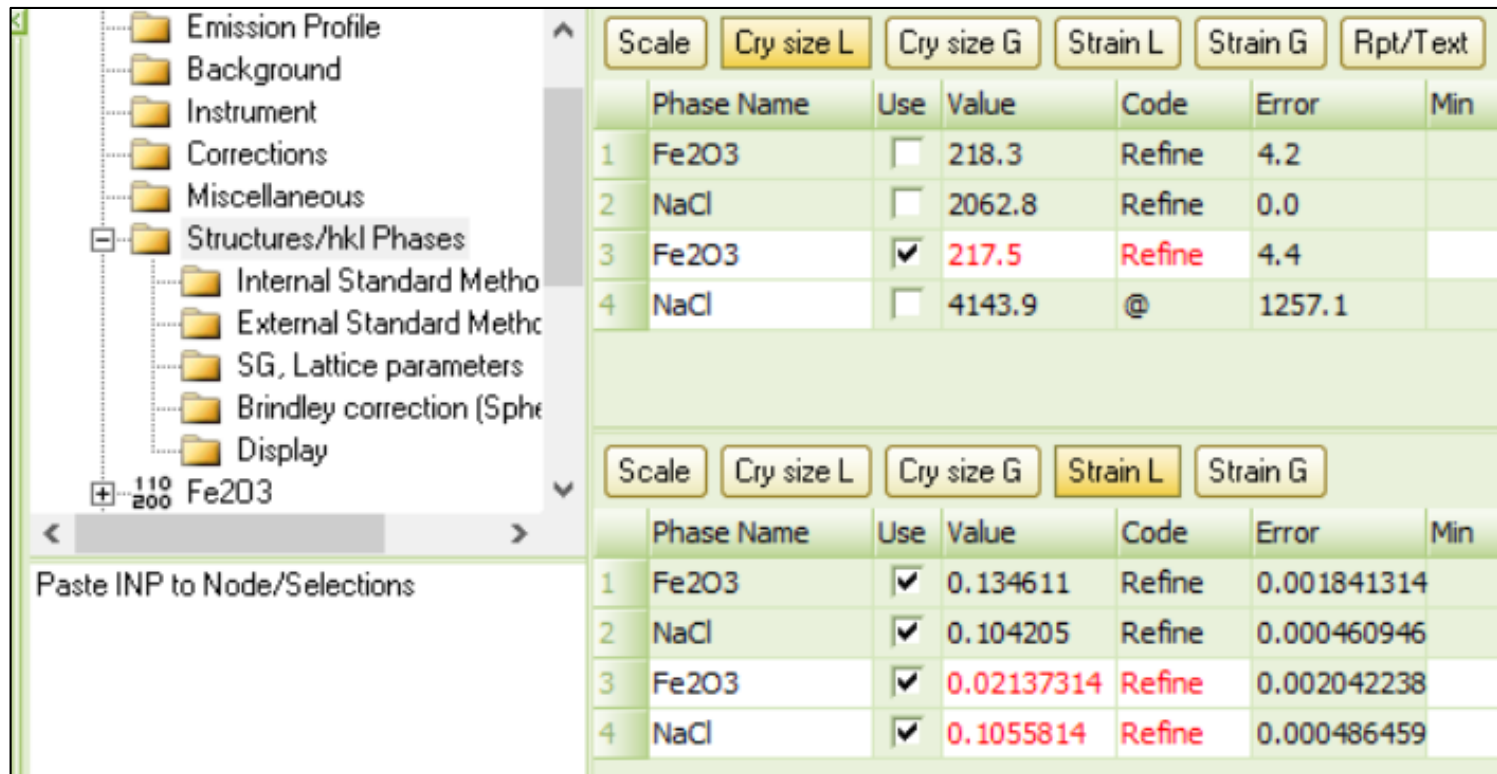
# Rietveld refinement – fit statistics



The screenshot shows a software interface for Rietveld refinement. On the left is a tree view of the project structure. The main panel on the right displays fit statistics in a table. Above the table are five buttons: 'All range dependent', 'Rwps', 'Path', 'Display', and 'Rpt/Text'. The table has two columns: the first column lists the statistics, and the second column, labeled 'Value', shows the corresponding numerical results.

	Value
GOF	1.97
Rexp	4.96
Rwp	9.76
Rp	6.97
Rexp-dash	6.11
Rwp-dash	12.02
Rp-dash	9.51
Weighted Durbin Watson	0.57

# Rietveld refinement - results



Scale Cry size L Cry size G Strain L Strain G Rpt/Text

	Phase Name	Use	Value	Code	Error	Min
1	Fe2O3	<input type="checkbox"/>	218.3	Refine	4.2	
2	NaCl	<input type="checkbox"/>	2062.8	Refine	0.0	
3	Fe2O3	<input checked="" type="checkbox"/>	217.5	Refine	4.4	
4	NaCl	<input type="checkbox"/>	4143.9	@	1257.1	

Scale Cry size L Cry size G Strain L Strain G

	Phase Name	Use	Value	Code	Error	Min
1	Fe2O3	<input checked="" type="checkbox"/>	0.134611	Refine	0.001841314	
2	NaCl	<input checked="" type="checkbox"/>	0.104205	Refine	0.000460946	
3	Fe2O3	<input checked="" type="checkbox"/>	0.02137314	Refine	0.002042238	
4	NaCl	<input checked="" type="checkbox"/>	0.1055814	Refine	0.000486459	

Paste INP to Node/Selections

# Rietveld refinement - results

<div> <div>Emission Profile</div> <div>Background</div> <div>Instrument</div> <div>Corrections</div> <div>Miscellaneous</div> <div>Structures/hkl Phases</div> <div>Internal Standard Metho</div> <div>External Standard Methc</div> <div>SG, Lattice parameters</div> <div>Brindley correction (Sph</div> <div>Display</div> <div>110 200 Fe2O3</div> </div>	<div> <div>Values</div> <div>Codes</div> <div>Errors</div> <div>Min</div> <div>Max</div> <div>Rpt/Text</div> </div>					
	Phase Name	SG	a (Å)	b (Å)	c (Å)	a
	1 Fe2O3	167	5.0364248		13.7537028	
	2 NaCl	225	5.6435341			
	3 Fe2O3	167	5.0364513		13.7537742	
<div> <div>Values</div> <div>Codes</div> <div>Errors</div> <div>Min</div> <div>Max</div> </div>	<div> <div>Values</div> <div>Codes</div> <div>Errors</div> <div>Min</div> <div>Max</div> </div>					
	Phase Name	SG	a (Å)	b (Å)	c (Å)	a
	1 Fe2O3	167	0.0001347		0.0006824	
	2 NaCl	225	0.0000000			
	3 Fe2O3	167	0.0000241		0.0000925	
	4 NaCl	225	0.0000290			

# Rietveld refinement - results

Values Codes Errors Min Max Rpt/Text									
	Site	Np	x	y	z	Atom	Occ.	Beq.	
1	Fe	12	0.00000	0.00000	0.35507	Fe+3	1	0.4949	
2	O	18	0.69341	0.00000	0.25000	O-2	1	0.4949	

Values Codes Errors Min Max									
	Site	Np	x	y	z	Atom	Occ.	Beq.	
1	Fe	12	0.00000	0.00000	0.00004	Fe+3	0	0.02096	
2	O	18	0.00037	0.00000	0.00000	O-2	0	0.02096	

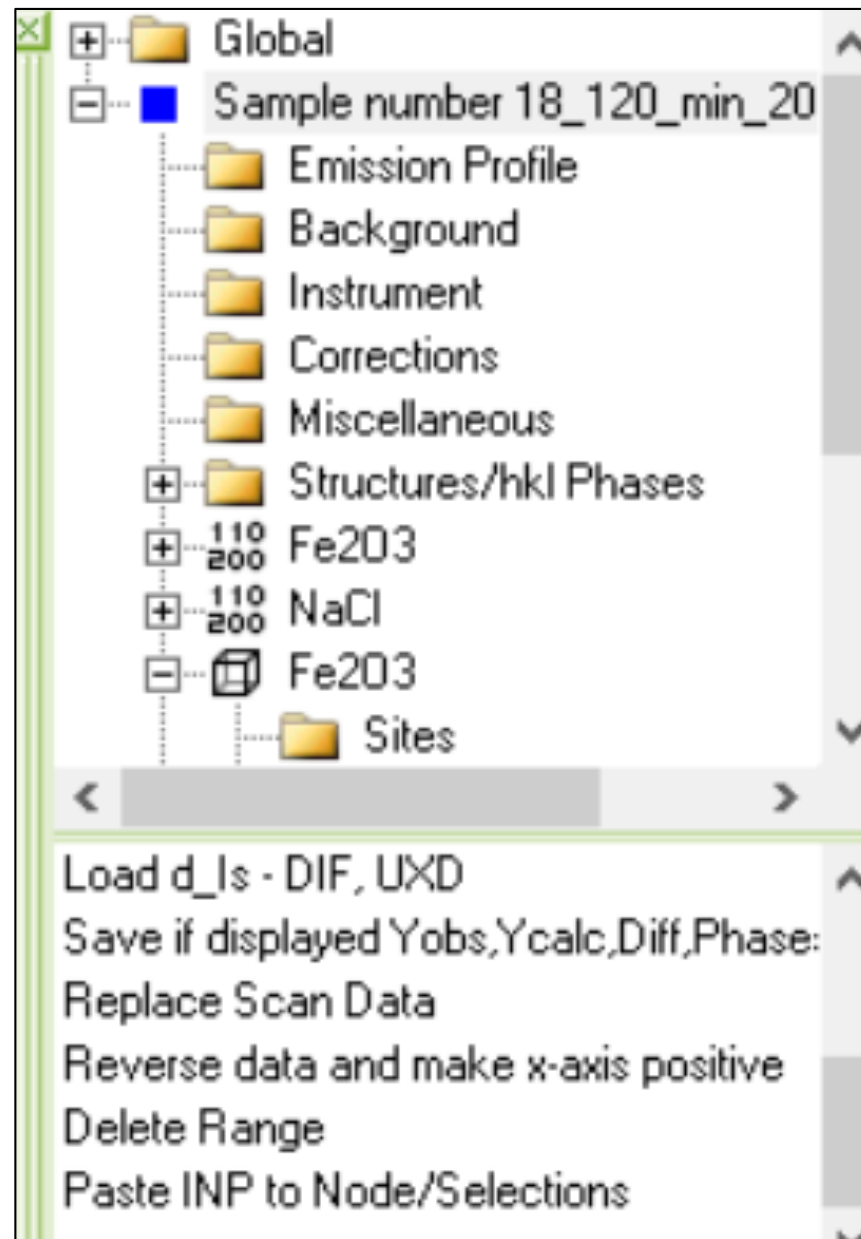
Values Codes Errors Min Max Rpt/Text									
	Site	Np	x	y	z	Atom	Occ.	Beq.	
1	Na	4	0.00000	0.00000	0.00000	Na+1	1	0.5961	
2	Cl	4	0.50000	0.50000	0.50000	Cl-1	1	0.5961	

Values Codes Errors Min Max									
	Site	Np	x	y	z	Atom	Occ.	Beq.	
1	Na	4	0.00000	0.00000	0.00000	Na+1	0	0.0329	
2	Cl	4	0.00000	0.00000	0.00000	Cl-1	0	0.0329	



# Rietveld refinement – export your data



# Getting the positions of the hkl ticks

Instrument

Corrections

Miscellaneous

Structures/hkl Phases

110  
200

Fe2O3

110  
200

NaCl

Fe2O3

Sites

Preferred Orientation

Str Output

NaCl

Sites

Save Structure in STR format

View/Hide Structure

Create hkl phase

Delete Structure

Paste INP to Node/Selections

Structure

Microstructure

Peak Type

hkl

Additional Convolutions

Rpt/Text

	h	k	l	m	d	th2	F <sup>2</sup>
1	0	1	2	6	3.68310	24.14436	15.353
2	1	0	4	6	2.70013	33.15139	98.719
3	1	1	0	6	2.51808	35.62540	82.192
4	0	0	6	2	2.29217	39.27357	2.550
5	1	1	3	12	2.20706	40.85428	35.846
6	2	0	2	6	2.07870	43.50116	3.603
7	0	2	4	6	1.84155	49.45303	94.142
8	1	1	6	12	1.69506	54.05737	143.826
9	2	1	1	12	1.63676	56.14967	1.781
10	1	2	2	12	1.60305	57.43860	8.486
11	0	1	8	6	1.59937	57.58339	29.380
12	2	1	4	12	1.48646	62.42471	129.999
13	0	3	0	6	1.45382	63.99001	134.967

+

Structures/hkl Phases

+

$\frac{110}{200}$  Fe2O3

+

$\frac{110}{200}$  NaCl

-

Fe2O3

Sites

Preferred Orientation

Str Output

-

NaCl

Sites

Preferred Orientation

Str Output

Structure

Microstructure

Peak Type

hkl

Additional Convolutions

Rpt/Text

	h	k	l	m	d	th2	F <sup>2</sup>
1	1	1	1	8	3.25814	27.35099	7.324
2	0	0	2	6	2.82163	31.68541	109.569
3	0	2	2	12	1.99520	45.42118	153.293
4	3	1	1	24	1.70151	53.83600	7.334
5	2	2	2	8	1.62907	56.43829	78.200
6	0	0	4	6	1.41082	66.18532	47.222
7	3	3	1	24	1.29465	73.02296	6.736

# Pawley refinement – hkl phases

- ◆ Advantages:
  - ◆ Data quality requirement limited compared to Rietveld
    - ◆ Uncertainty will still depend on collection time and  $2\theta$  range
  - ◆ Lattice parameters often the most important information
    - ◆ E.g. high symmetry structures have no/little degrees of freedom in atomic positions
  - ◆ Crystallite size the essential information for nanocrystalline powder
  - ◆ Lattice strain the essential information for disordered or strained materials, or chemically complex solid solutions.
- ◆ Disadvantages:
  - ◆ No information about atomic positions or occupancies
  - ◆ No quantification of phase fractions

# Rietveld refinement – structure models

- ◆ Advantages:
  - ◆ Atomic positions, occupancies and B-factors extracted.
  - ◆ Quantitative information about phase fractions obtained.
  - ◆ Necessary information to publish or report new or novel structures.
- ◆ Disadvantages:
  - ◆ High quality data necessary – long collection time and broad  $2\theta$ .
  - ◆ More variables, more possibilities of making mistakes.

# General refinement strategy for Pawley

- ◆ Start with the most important things, proceed with less important when convergence is reached for the most important.
- ◆ In other words: do NOT refine all variables at once!
- ◆ TOPAS has no chemical/physical knowledge – you have.
- ◆ Set background to 3, increase it later if necessary.
- ◆ Make sure your emission profile and instrumental parameters are right.
- ◆ Make sure your simulated Bragg peaks “hit” the measured.
  - ◆ Lock size and strain with FP.
  - ◆ Follow the position of the hkl ticks.
  - ◆ Use d-spacing for the x-axis and the formulas from previous lectures and adjust the initial guess value.
  - ◆ Refine lattice parameters and sample displacement simultaneously.
- ◆ Add crystallite size and/or strain to fit the peaks shapes with FP.

# General refinement strategy for Rietveld

- ◆ As for Pawley +:
- ◆ Lattice parameters (peak positions) and size/strain (peak shape) must converge before you refine atomic positions.
- ◆ ONLY refine atomic positions where the space group has a degree of freedom.
  - ◆ How do you know which positions have degrees of freedom?
  - ◆ Use fractions for high symmetry positions in codes field
  - ◆ Wyckoff sites – test with VESTA to be certain!
- ◆ Start with the position that affects the peak intensities the most.
  - ◆  $Z^2$  x multiplicity/stoichiometry
  - ◆ Start with the heaviest atoms
  - ◆ Reach convergence before you add progressively lighter atoms.
  - ◆ Exceptions may apply, a sound understanding is required.
- ◆ Occupancies – be careful! Examples:  $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ .
- ◆ Link parameters when sensible – user understanding required.
- ◆ Do not over-fit your data! Mind  $R_{\text{wp}}$ ,  $R_{\text{exp}}$  and  $\chi^2$ !

## Take-home messages from *bonus* lecture LX8-9

- ◆ This is the essence of what you should do for your lab report.
- ◆ The nominal composition was 50%  $\text{Fe}_2\text{O}_3$  and 50% NaCl.
  - ◆ +/- 5-10% is the typical error in mass% for Rietveld refinement.
- ◆ Serious preferred orientation of the NaCl crystallites –
  - ◆ or simply too large/few crystallites
    - ◆ Wrong peak intensities with position sensitive detector
    - ◆ Spots in Debye rings on a 2D plate detector
  - ◆ Had to use corrections to obtain a reasonable result
  - ◆ Note how the B-factors tell you if something is wrong
- ◆ Never underestimate visual inspection, more important than R-factors!
- ◆ Rietveld refinement still not trivial after 15 years...