TMT4301 Materials Characterization X-ray Characterization of materials

LX8-9: Extra bonus lecture – lab report

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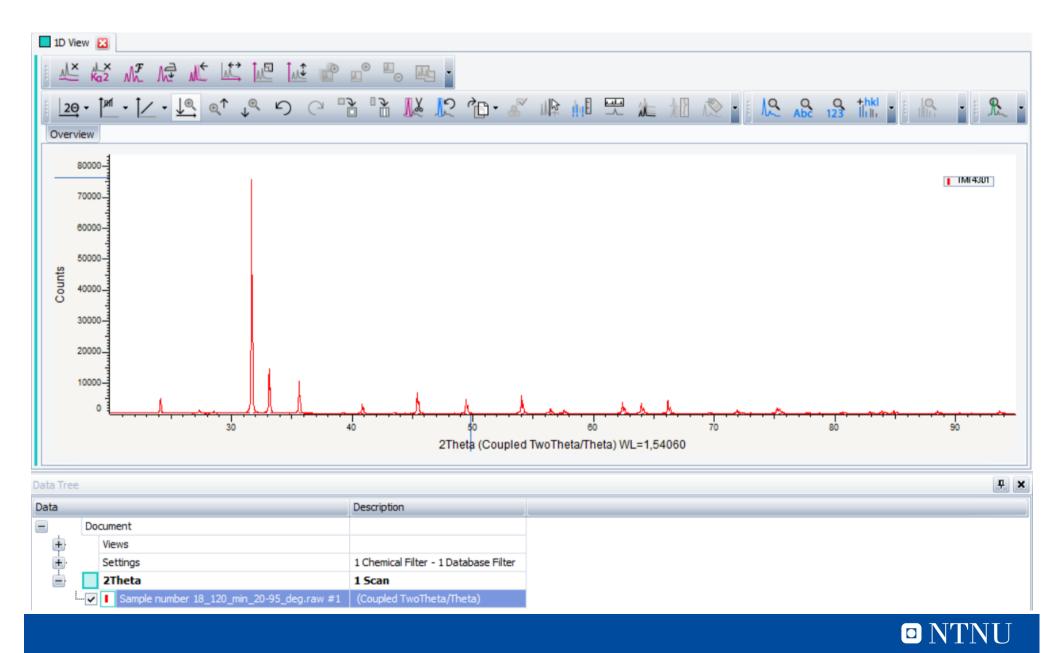
This lecture

- 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



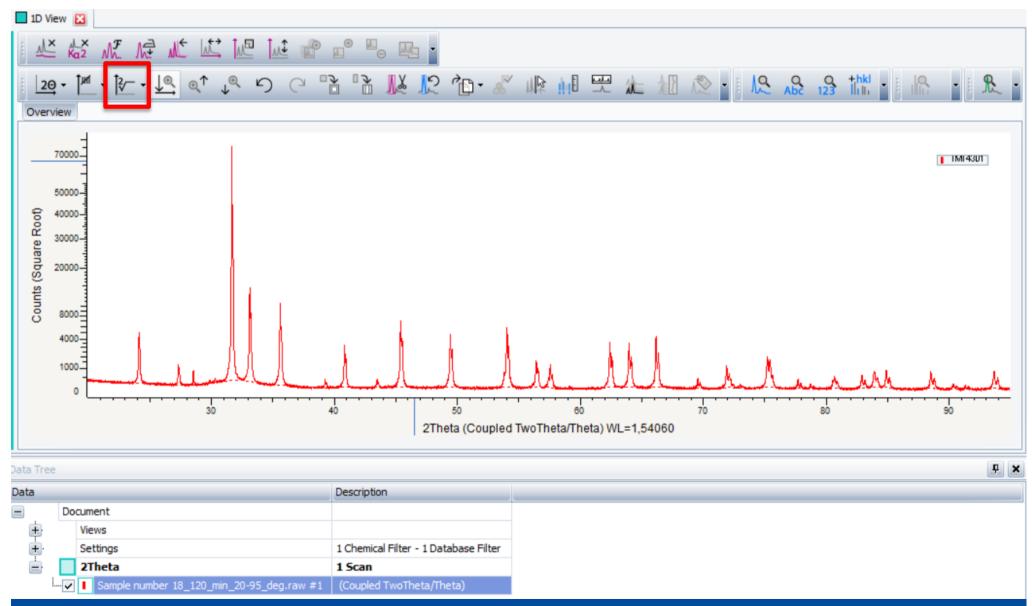
EVA





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	ı (scan) Samp	e number 18	_120_min_2	0-95_deg.ra	w #1												×
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Na	Mg											Al	Si	Р	S	Cl	Ar
K	Са	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	I	Xe
Cs	Ba	La	Hf	Та	w	Re	Os	Ir	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
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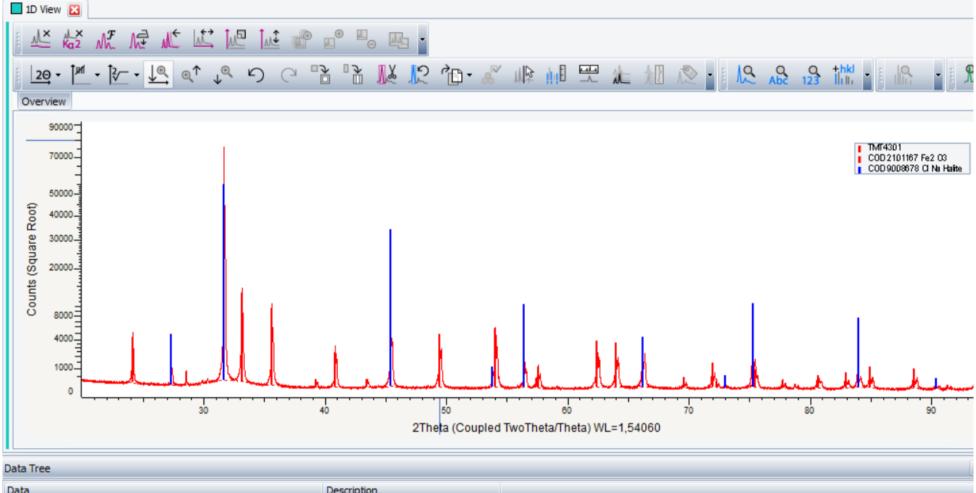
EVA – search and match

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

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index .	û	FOM	Mtc	nM 9	6 S	ource	ID	Quality	Status	I/Icor	Mineral	Name	Formula	Crystal System	а	b	c alp	ha beta	gamma	Spacegroup	Ζ	Volume	
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	4	48,3	23	4.	C	:OD		Quality Unknown	Stat	4,01	~	Не	Fe2 03	Hexagonal						R -3 c		301,77	
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EVA – search and match result



Data		Description					
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E	Views						
E.	Settings	1 Chemical Filter - 1 Database Filter					
È	2Theta	1 Scan					
Ē	✓ I Sample number 18_120_min_20-95_deg.raw #1	(Coupled TwoTheta/Theta)					
	Pattern List #1	2 Patterns					
	COD 2101167	Fe2 O3					
		Cl Na Halite					



Export your data, from .raw to .xy

4

You can download Bruker Diffrac FileExchange from the Odin server

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corundum_60min_20-105deg	1	33255	a corundum 22-120 deg.raw	1	4895
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			avinci 1_fds_0.3deg.par		26
			🔁 LaB6.cif		175
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			S MgO.brml		2166
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			Sample number 18_120_min_20-95_deg.xy		10183
			-	1	
			Sample number 18_120_min_20-95_deg.xy	1	4304
			Sample number 18_120_min_20-95_deg.xy		4304



Find SG and lattice param. with EVA and COD

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De Select Parent	General Comments Authors Additional Subfiles		1,69460		431		1	-6	
	Cell Parameters Crystal Data		1,63650		6		1	-1	
File ""	System: Hexagonal Molecular weight:		1,60280	-	23		1	2	
Import from Files	Space group: R -3 c (167) Volume (CD) (Å ³): 301,87		1,59870		80	-1	1	-8	
	a (Å): 5,0355 a (°): Dm:		1,48620		283		1	-4	
Tool	b (Å): β (°):		1,45360 1,41370		272		0	0	
Search / Match (pattern)	c (Å): 13,7471 y (°):		1,34960		28	-2	1	8	
Search by Number	a/b: 1, I / Icor		1,34960		28 98	-2		10	
d x by	c/b: 2,73004 Z: 6 3,82		1,30590		16		1	-9	
7 Tune Cell			1,26250		2		1	-7	
Create Kb-Pattern			1,25890		62			0	
& Residue			1,22740		12		0	-6	
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Create ""	Pattern List #1 2 Patterns								
1D View									
🖯 DB View	CD 9008678 Cl Na Halite								



Find SG and lattice param. with EVA and COD

DR View DR View D

You will also find peak positions here.

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alite				1,99420	45,445	619			
Na						19		-1	
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Navelength: 1,54060	\sim			1,41010	66,223 73,066	78	-4		
				1,29400 1,26130		9 194	-3		
General Comments Authors Addition			_	1,26130		194	-4 -4		
Cell Parameters System: Cubic	Crystal Data			1,13140		7			
-,	Molecular weight			1,08550		3		-1	
Space group: F m -3 m (225)	Volume (CD) (ų)			1,08550	50,105	3	-5	-5	
a (Å): 5,6406 a (°):	Dx:	2,161							
b (Å): β (°):	Dm:								
c (Å): y (°):									
a/b: 1,	I / Icor								
		5.02							
c/b: 1, Z:		5,02							
		5,02							
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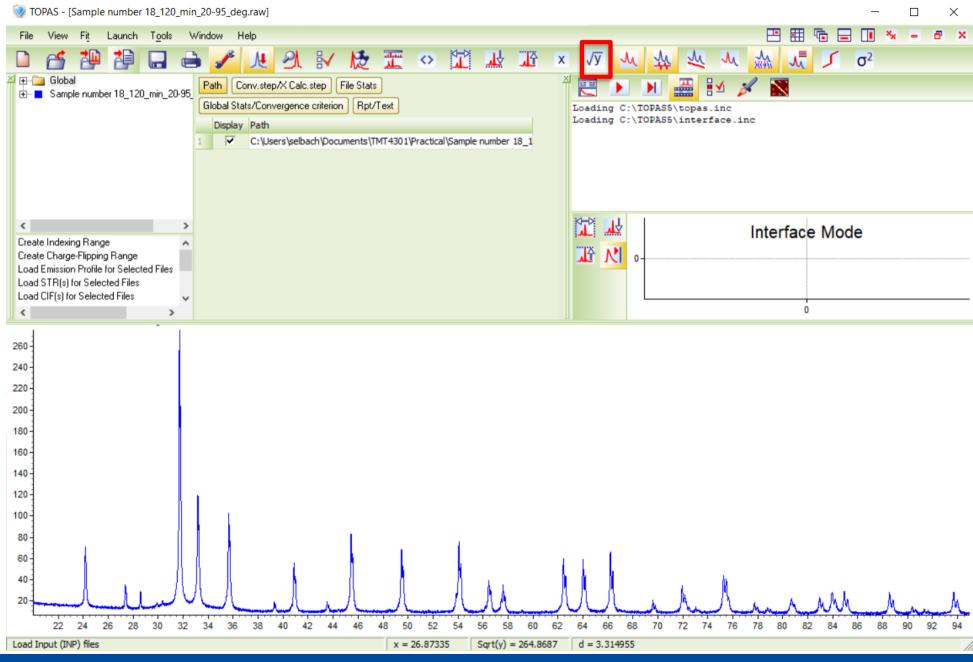
 \Box N

TOPAS – import a .raw file

TOPAS - [Sample number 18_120_min_20-95_deg.raw] \times 🖃 🔳 🦗 🗕 🗗 🗙 • G. File View Fit Launch Tools Window Help P J. ₽ は 王 Ť ΥĻ M M $\langle \mathbf{x} \rangle$ х $\int \sigma^2$ V y M Ä ⊕ 📄 Global Path Conv.step/X Calc.step File Stats \sim ⊕ Sample number 18_120_min_20-95 Global Stats/Convergence criterion Rpt/Text Loading C:\TOPAS5\topas.inc Loading C:\TOPAS5\interface.inc Display Path C:\Users\selbach\Documents\TMT4301\Practical\Sample number 18_1 ~ < Interface Mode Create Indexing Range Create Charge-Flipping Range Load Emission Profile for Selected Files Load STR(s) for Selected Files Load CIF(s) for Selected Files ~ 0 < > 75 000 -70 000 -65 000 · 60 000 -55 000-50 000 -45 000 -40 000 -35 000 -30 000 -25 000· 20 000 -15 000 -10 000 -5 000 -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 = 30.72405 y = 74390.39 d = 2.907695



TOPAS – use square root for y-axis scaling



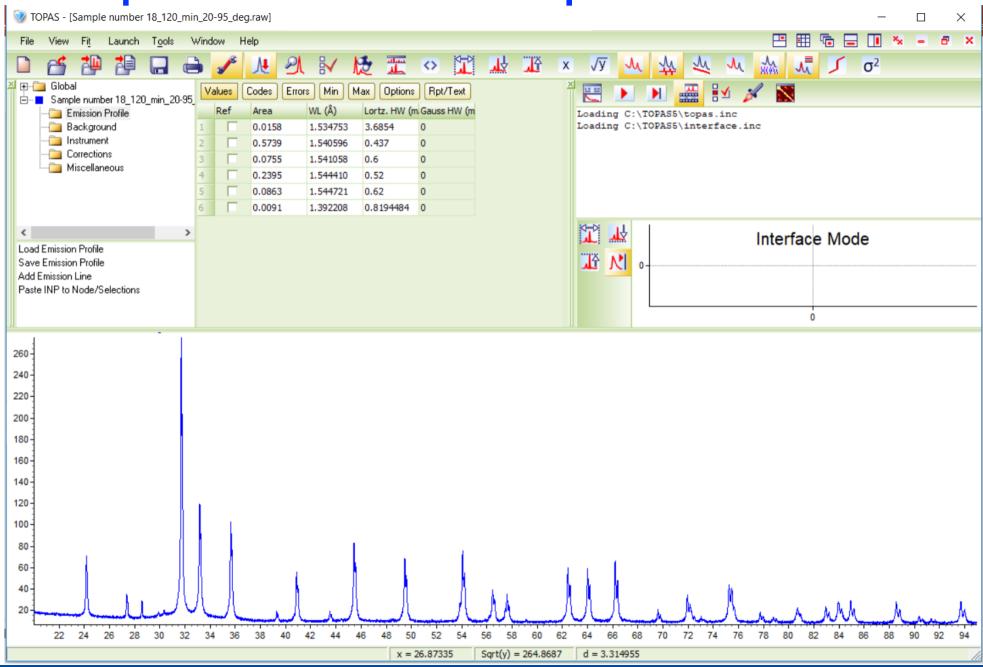
NTNU

Topas – load an emission profile

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Load Emission Profile Save Emission Profile Add Emission Line Paste INP to Node/Selections	 This PC 3D Objects Desktop Documents 	
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	x = 26.87335 Sqrt(y) = 264.8687 d = 3.314955	1.

DNTNU

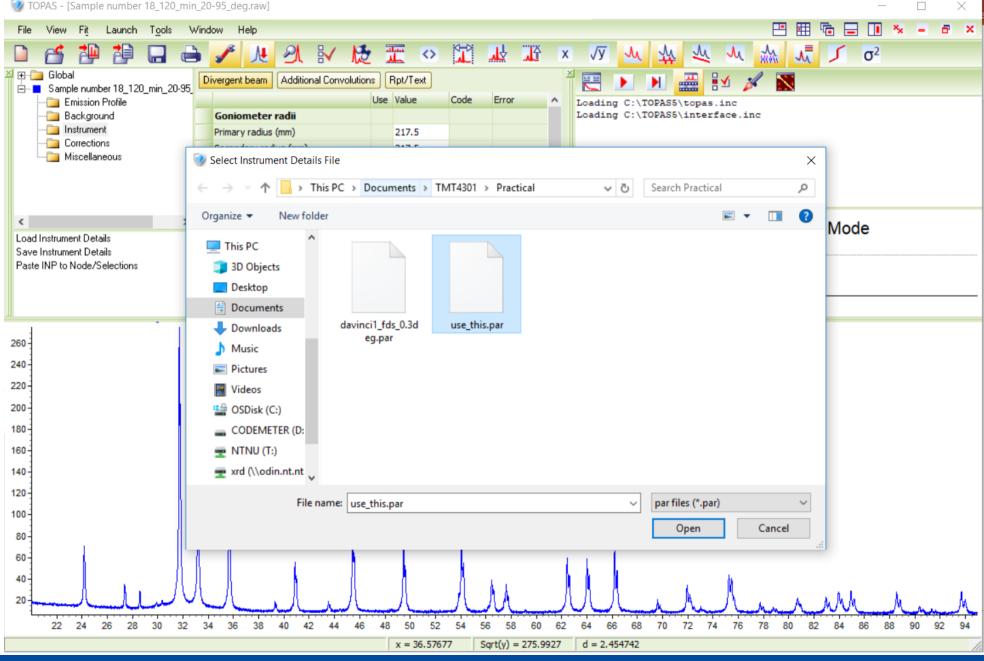
Topas – load an emission profile



 \Box NTNU

Topas – load a .par instrumental settings file

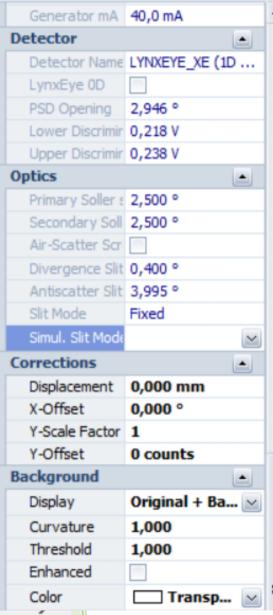
📝 TOPAS - [Sample number 18 120 min 20-95 deg.raw]



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

TOPAS - [Sample number 18_120_min_20-95_deg.raw]

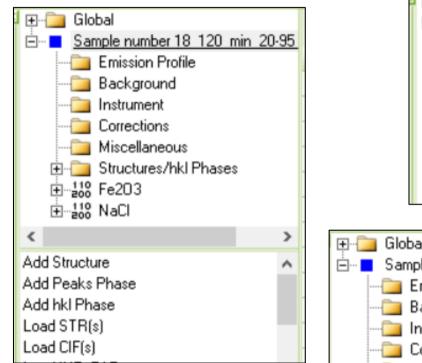
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Tube Tails Image: Convolutions						FDS angle (°)			0.4	Fix	C	Simul. S
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Pawley – add two hkl phases, rename them

Note context sensitive menus.





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Pawley – fix all parameters first

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it 118 Fe2O3		Cry size G		200.0	Refine
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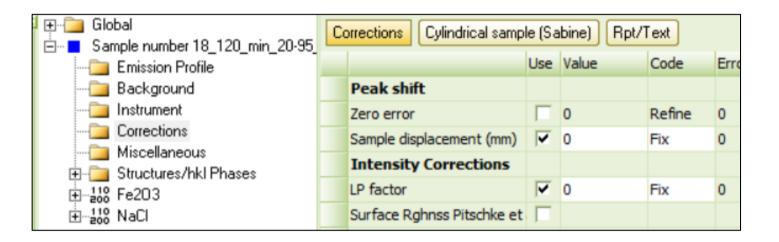
± 100 Fe203		LP Search	0.4	
±		Spacegroup	225	
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Save Phase		Scale	0.00000e+00	Fix

Global Global Sample number 18_120_min_20-95_ Emission Profile	nase Details Microstructu Is Is Additional Convolut		Peak Type Rpt/Text	
Background		Use	Value	Code
	Double-Voigt Approac	h		
Miscellaneous	Crystallite size			
🗄 🚞 Structures/hkl Phases	Cry size L	\checkmark	200.0	Fix
±18 Fe2O3	Cry size G		200.0	Refine
i lination NaCl	LVol-IB (nm)		0.000	



Pawley – fix all parameters first

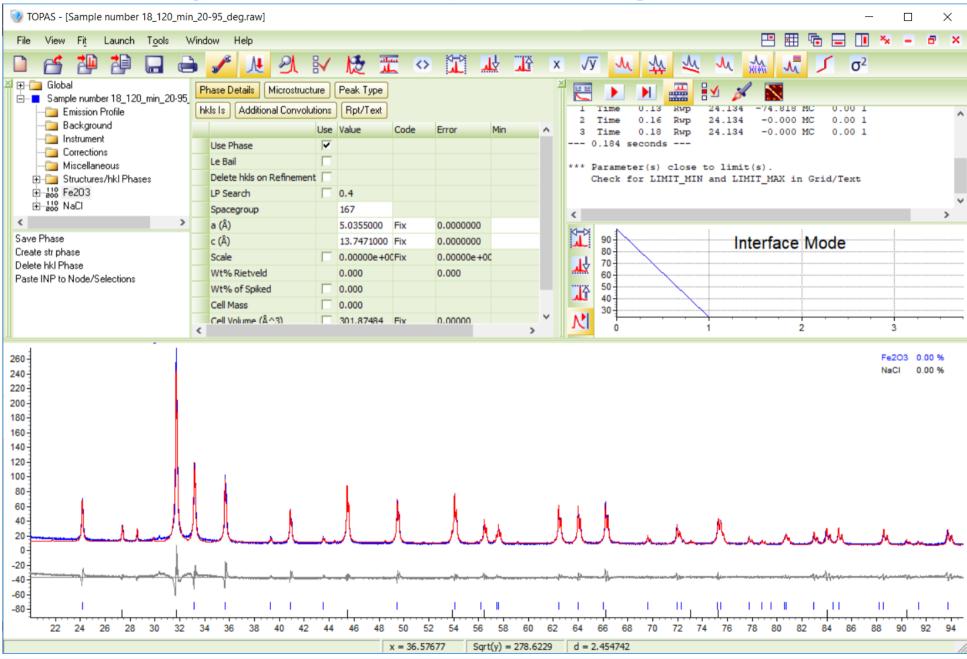
Exception: allow at least one variable for the background – flat background which gives a crude, but reasonable fit.



	Ba	ackground Rpt/Tex	ĸt				
Emission Profile			Use	Value		Code	Err
Background		Chebychev	$\mathbf{\nabla}$			0	
Instrument		Order		1	4 b		
		1/X Bkg	Г	1000		Refine	0
- Miscellaneous							
Structures/hkl Phases	<						



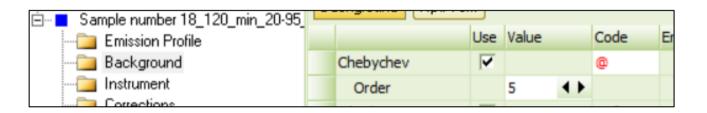
Pawley – first attempt, nothing refined



NTNU

Pawley – progressively add variables

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



⊈ ⊕… 🧰 Global ⊡… 📕 Sample number 18_120_min_20-9	5	Corrections Cylindrical sample		le (Sa	(Sabine) Rpt/Text		
Emission Profile	~			Use	Value	Code	
Background			Peak shift				
			Zero error		0	Refine	
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		Delete hkis on Refinement					
⊕ 100 Fe2O3		LP Search		0.4			
i±…iii NaCl		Spacegroup		167			
>		a (Å)		5.0355000	Refine		
ve Phase		c (Å)		13.7471000	Refine		
eate striphase lata kki Phase		Scale	\Box	0.00000e+00	Fix		

±		Spacegroup	225	
D	>	a (Â)	5.6406000	Refine (

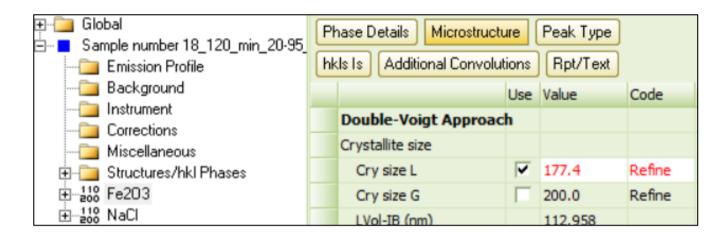


Pawley – second attempt, some variables

TOPAS - [Sample number 18 120 min 20-95 deg.raw] X P Ŧ G. 🚺 🛰 - 🗗 🗙 File View Launch Tools Window Help Fit 3 مىيان. مىلە ЧĻ Ť Martin 1 P \mathbf{O} √у $\int \sigma^2$ х J. 💐 🕀 🛅 Global Phase Details Microstructure Peak Type Sample number 18_120_min_20-95 hkls Is Additional Convolutions Rpt/Text 🛅 Emission Profile 0 Time 0.03 Rwp 14.061 0.000 MC 0.00 0 -0.000 MC 0.06 2 1 Time 0.04 Rwp 14.061 🛅 Background Use Value Code Error Min 0.05 2 Time 14.061 -0.000 MC 2 0.04 Rwp - Instrument ~ Use Phase 3 Time 0.07 14.061 -0.000 MC 0.05 2 Rwp Corrections --- 0.073 seconds Le Bail Miscellaneous Delete hkls on Refinement 🗄 🛅 Structures/hkl Phases *** Parameter(s) close to limit(s). ± 18 Fe2O3 LP Search 0.4 Check for LIMIT MIN and LIMIT MAX in Grid/Text ± 18 NaCl 225 Spacegroup < a (Â) 5.6436359 Refine 0.0000000 14,061 K-D: Save Phase Interface Mode Scale 0.00000e+00Fix 0.00000e+00 J. Create str phase 14.061 Wt% Rietveld 0.000 0.000 ل<mark>ل</mark>ه Delete hkl Phase Wt% of Spiked 0.000 14.061 Paste INP to Node/Selections Ĩ Cell Mass 0.000 14.061 Cell Volume (Å^3) 179.75333 Fix 0.00000 マ 2,968 R Brann 0 2 3 < > Fe2O3 0.00 % 260 NaCI 0.00 % 240-220-200-180 160 140-120 100 80 **60** · 40-20 0--20 -40ш -60 22 24 26 28 30 32 42 48 50 52 54 56 58 72 74 76 78 82 90 92 34 36 38 40 44 60 62 64 66 68 70 80 84 86 88 94 x = 47.0888 Sqrt(y) = 280.4813d = 1.92835

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Pawley – next add variables for peak shape



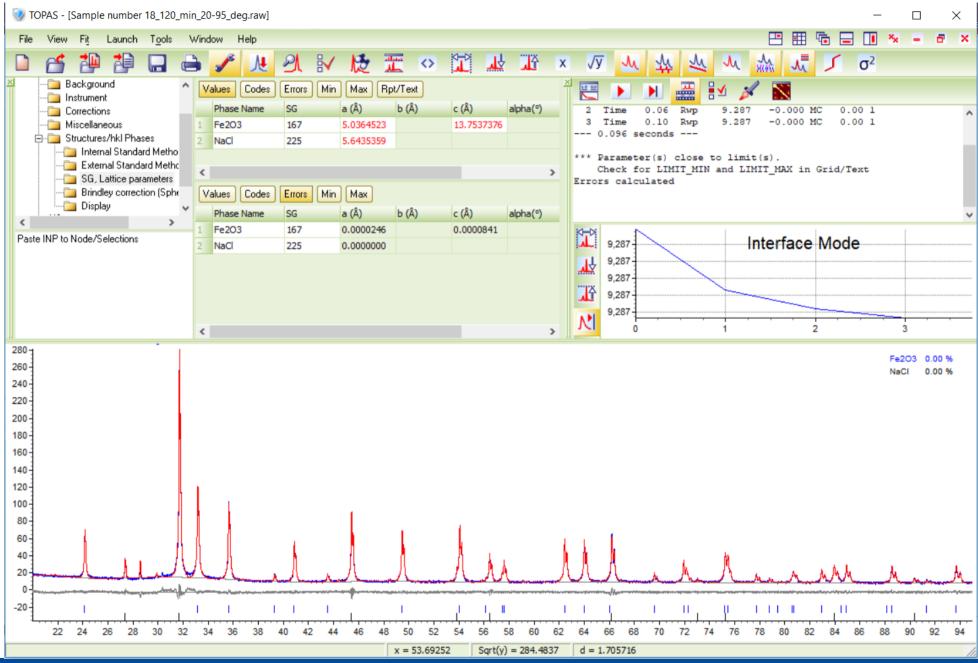
- 🔁 Miscellaneous	Crystallite size			
🗄 🛅 Structures/hkl Phases	Cry size L	${\color{black} \checkmark}$	276.2	Refine
± 18 Fe2O3	Cry size G		200.0	Refine
±	LVol-IB (nm)		175.826	

Strain				
Strain L	$\overline{\mathbf{v}}$	0.02228824	Refine	0
	-			

Emission Profile		Use	Value		Code	E
Background	Chebychev	\mathbf{V}			0	Π
Instrument	Order		13	••		
	1/X Bkg		1000		Refine	C



Pawley – a pretty good fit!



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Pawley – summarising results

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

🖅 💼 Global 🔹 🧥	S	cale Cry size L	Cry	size G Stra	ain L Str	ain G Rpt/1	[ext			
🖻 🗧 Sample number 18_120_min_20							_			
Emission Profile		Phase Name	Use	Value	Code	Error	Min			
Background	1	Fe2O3	\checkmark	218.4	Refine	5.6				
Instrument	2	NaCl		2062.8	Refine	0.0				
Corrections										
🖃 🛅 Structures/hkl Phases	<									
Internal Standard Metho	S	Scale Cry size L Cry size G Strain L Strain G								
External Standard Methc 🗸		Phase Name	Use	Value	Code	Error	Min			
	1	Fe2O3	$\overline{\mathbf{v}}$	0.02165705	Refine	0.003282266	5			
Paste INP to Node/Selections	2	NaCl	$\overline{\checkmark}$	0.1043375	Refine	0.000435059)			

I ⊞ ⊡i Global ^ ⊡ I Sample number 18_120_min_20	Co	orrections Cylindrical samp	le (Sa	abine) Rpt/1	[ext	
Emission Profile			Use	Value	Code	Error I
Background		Peak shift				
🛅 Instrument		Zero error		0	Refine	0
		Sample displacement (mm)	\checkmark	-0.06692649	Refine	0.000218274
Miscellaneous Structures/hkl Phases		Intensity Corrections				



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 2q range and a bulk well-crystallized sample.
- Can be problematic for small nanocrystallites why?

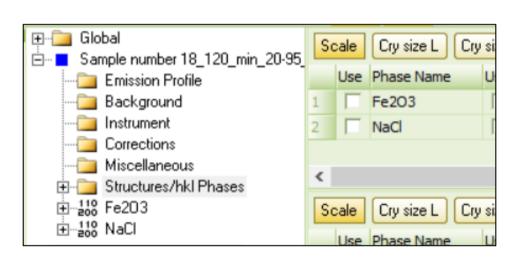
File View Fit Launch Tools Wir	ndow Help					
🗅 🖆 🏥 🖨 🖨	🖌 🥂 A 🕅	' kt 🗄			X	 √y <u>M</u> <u>M</u> <u>M</u> <u>M</u> <u>M</u> <u>M</u> <u>J</u> σ²
[≦] ⊞ <mark>]a</mark> Global ⊟ ■ Sample number 18_120_min_20-95	All range dependent Rwps	Path Displa	y Rpt/Tex	t		ž 🚬 🕨 🛲 🛃 💉 🔊
Emission Profile		Use Value	Code	Error	Min 🔺	2 Time 0.05 Rwp 9.287 -0.000 MC 0.00 1
Background	Background					3 Time 0.08 Rwp 9.287 -0.000 MC 0.00 1
Instrument	Chebychev	V	0			0.083 seconds
- Corrections	Order	13	41			*** Parameter(s) close to limit(s).
Miscellaneous	1/X Bkg	1000	Refine	0		Check for LIMIT_MIN and LIMIT_MAX in Grid/Text
⊡ - ⊡ Structures/hkl Phases ⊡ - 100 Fe2O3	Goniometer radii					Errors calculated
	Primary radius (mm)	280				
< >	Secondary radius (mm)	280				
Load INP, PAR	Equatorial Convolutions					9,287 Interface Mode
Load d_Is - DIF, UXD	Point detector					9,287
Save if displayed Yobs,Ycalc,Diff,Phase:	Capillary					9,287
Replace Scan Data	Linear PSD	V				9,287
Reverse data and make x-axis positive Delete Range	2Th angular range of LPSD	(°) 3	Fix	0		9,287
Paste INP to Node/Selections	FDS angle (°)	0.4	Fix	0	~	9,287

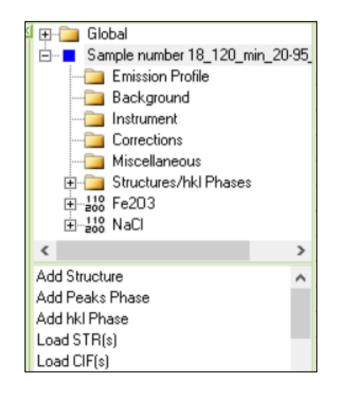
TOPAS - [Sample number 18_120_min_20-95_deg.raw]



Preparing for Rietveld refinement

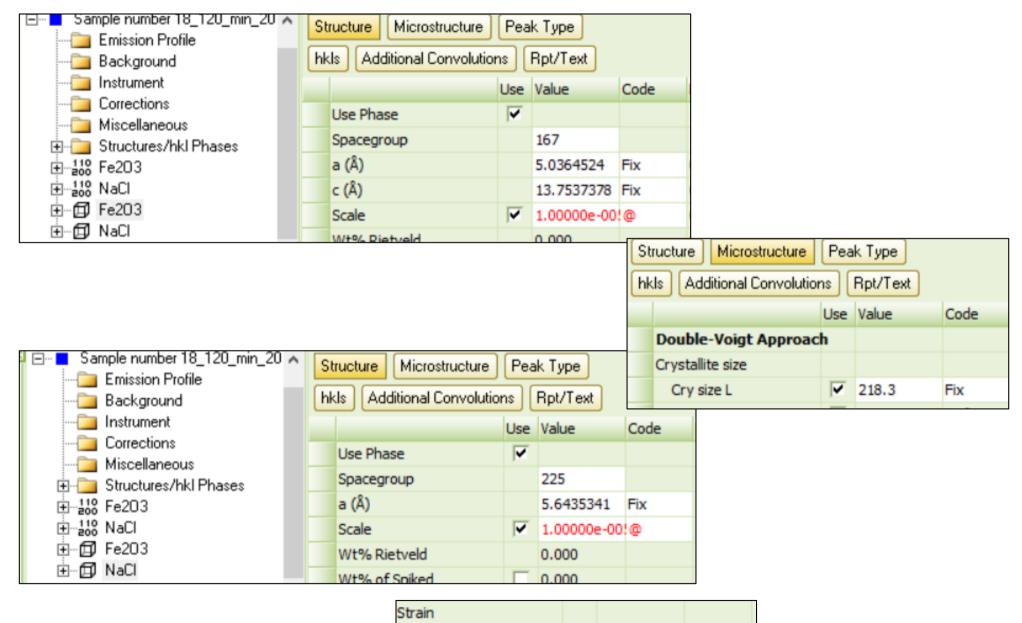
- Uncheck the hkl phases for Pawley
- Add two new structures
- You can also load a saver .str file or a downloaded .cif file
- .cif Crystallographic Information File







Add structures for Rietveld refinement



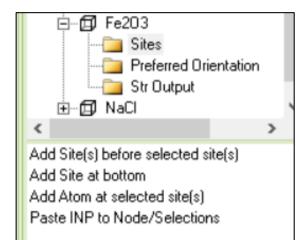
Strain L

✓ 0.104205

Fix

N	ΓN	ΤT
ТЛЛ		\mathbf{U}

Structures for Rietveld – atomic positions



	Background Instrument	^	Va	alues 0	Codes	Errors	lin Max F	Rpt/Text		_	1
	- 🛅 Corrections			Site	Np	x	у	z	Atom	Occ.	Beq.
			1	Fe	0	0.00000	0.00000	0.35500	Fe+3	1	1
	吏 🛅 Structures/hkl Phases		2	0	0	0.699	0.00000	0.25000	0-2	1	1
	i∃…108 Fe2O3										
			<								>
	⊡…∰ Fe2O3			alues	Codes	Errors	lin Max				
	Preferred Orientation			Site	Np	х	у	z	Atom	Occ.	Beq.
	⊡⊡ D NaCl	~	1	Fe	0	Fix	Fix	Fix	Fe+3	Fix	Fix
<	>		2	0	0	Fix	Fix	=1/4	0-2	Fix	Fix



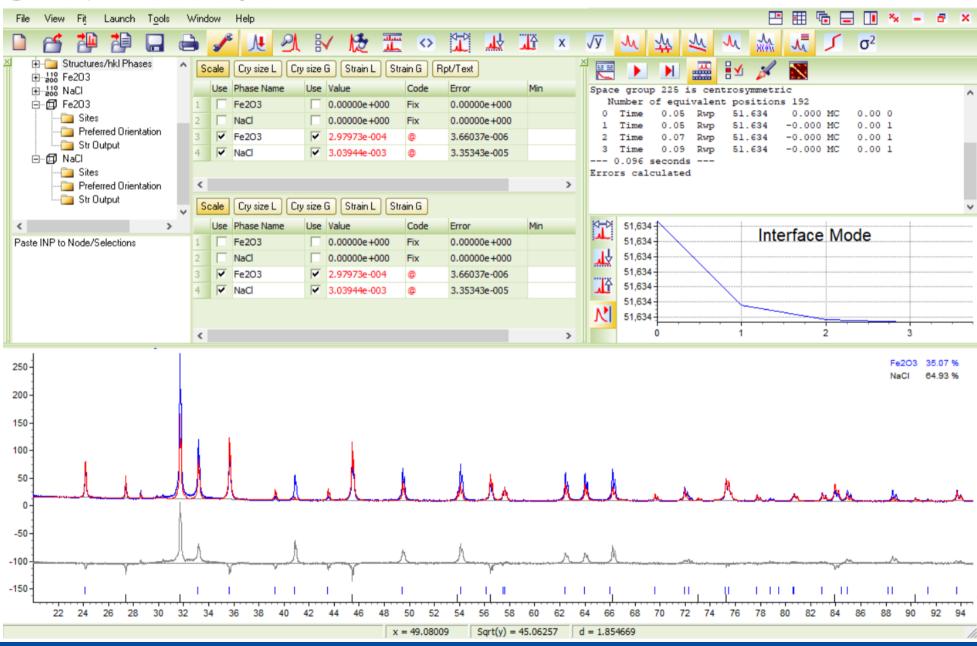
Structures for Rietveld – atomic positions

d ⊕…j_ Structures/hkl Phases ⊕…j_% Fe203	^	Values Codes Errors Min Max Rpt/Text								
			Site	Np	х	у	z	Atom	Occ.	Beq.
⊟ ⊡ Fe2O3		1	Na	0	0.00000	0.00000	0.00000	Na+1	1	1
🛅 Sites		2	Cl	0	0.50000	0.50000	0.50000	Cl-1	1	1
Preferred Orientation										
⊡-⊡ NaCl		<	<							
Sites		Values Codes Errors Min Max								
Str Output			Site	Np	х	у	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

TOPAS - [Sample number 18_120_min_20-95_deg.raw]

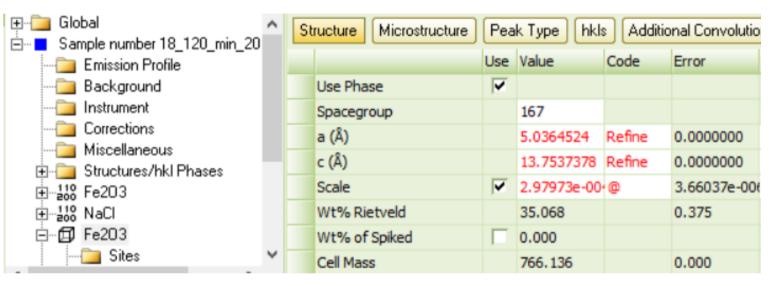


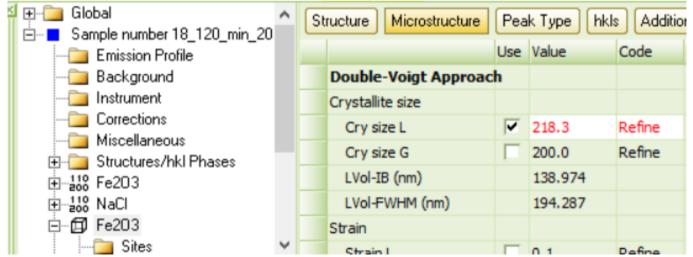
 \square NTNI

X

Rietveld refinement

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

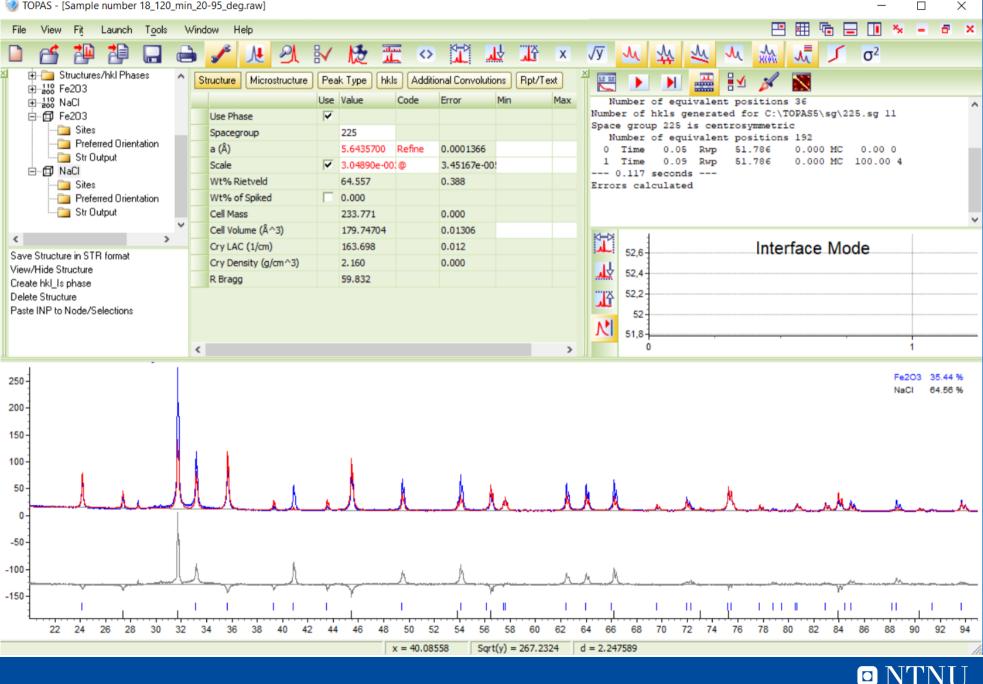






Rietveld refinement, peak pos./shape included

TOPAS - [Sample number 18 120 min 20-95 deg.raw]



Rietveld refinement – atomic positions

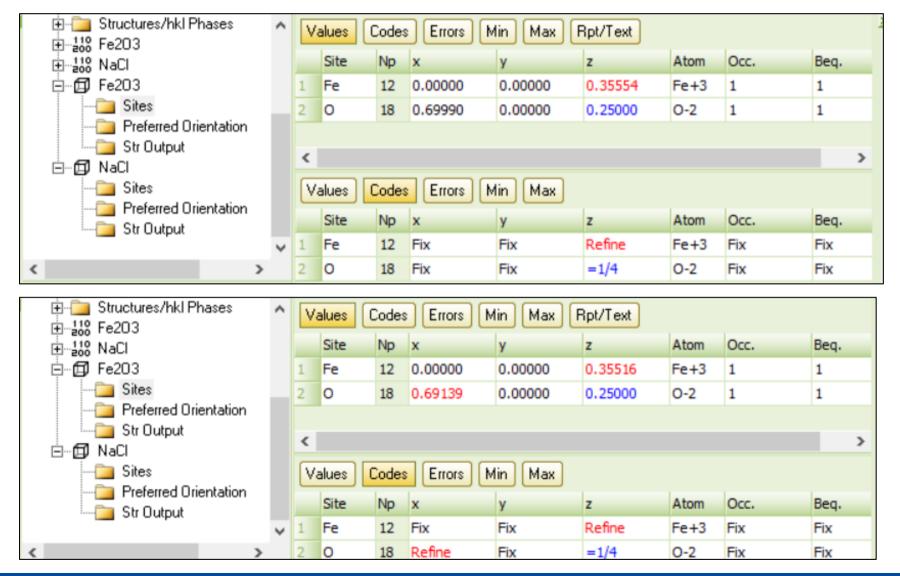
- Always start with locked atomic positions.
- Lattice parameters and size/strain MUST converge before you add atomic positions as variables.

×	ia - 🔁 Structures/hkl Phases ia - 118 Fe2O3	^	V	Values Codes Errors Min Max Rpt/Text								
				Site	Np	x	у	z	Atom	Occ.	Beq.	
			1	Na	4	0.00000	0.00000	0.00000	Na+1	1	1	
			2	Cl	4	0.50000	0.50000	0.50000	Cl-1	1	1	
	Str Output		<	<							>	
	⊡…∰ NaCl ⊡ Sites ⊡ Preferred Orientation		V	Values Codes Errors Min Max								
	Str Output			Site	Np	x	у	z	Atom	Occ.	Beq.	
		¥	1	Na	4	Fix	Fix	Fix	Na+1	Fix	Fix	
<	2	•	2	Cl	4	=1/2	=1/2	=1/2	Cl-1	Fix	Fix	



Rietveld refinement – atomic positions

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





Rietveld refinement – B-factors

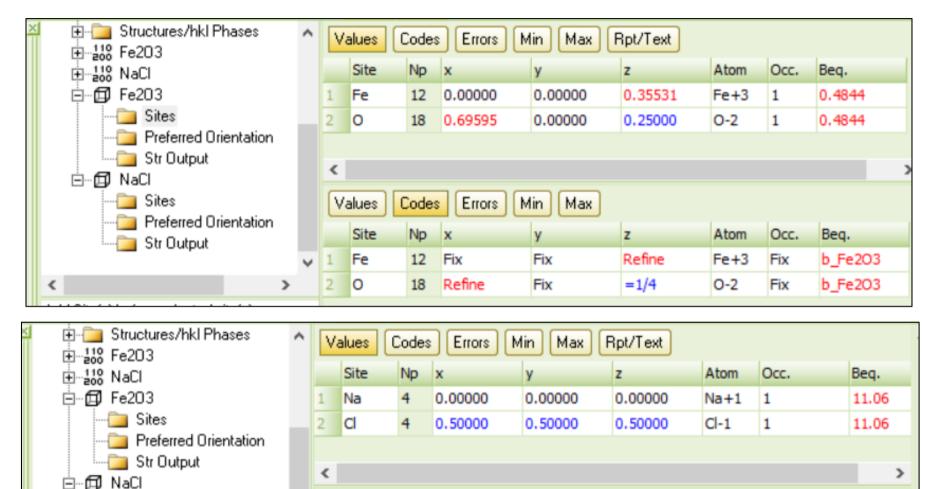
Start with linking parameters, see example below.

Sites

<

🛅 Str Output

Preferred Orientation



Errors

Min

y

Fix

=1/2

Max

z

Fix

=1/2

Codes

Np

4

4

X

Fix

=1/2

Values

Site

Na

C

≻

Cl-1 Fix B_NaCl

Beg.

B NaCl

Occ.

Fix

Atom

Na+1

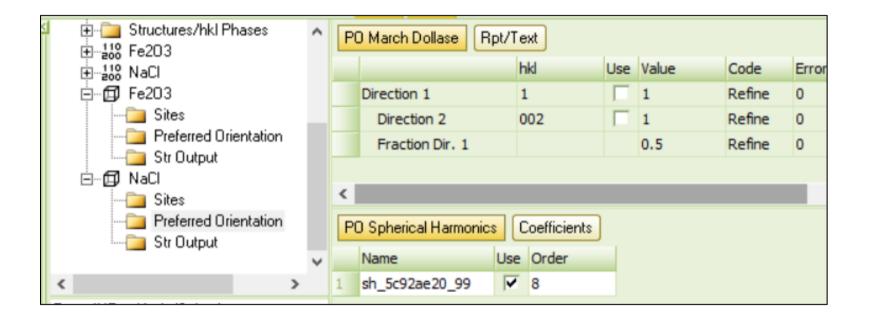
Peak intensities wrong and B-factors too high...

TOPAS - [Sample number 18 120 min 20-95 deg.raw] П \times Fit Launch Tools Window Help PP. G. 8 X File View 1 P 13 ΥĻ Ť √у 4 σ^2 김희 <> X r M h m 🗄 🛅 Structures/hkl Phases ^ Values Errors Min Max Rpt/Text Codes ±-18 Fe2O3 Site Np z Atom Occ. ± 18 NaCl Beg. X v Space group 225 is centrosymmetric Number of equivalent positions 192 Ė~67 Fe203 4 0.00000 0.00000 Na+1 11.06 Na 0.00000 1 0 Time 0.06 Rwp 36.203 0.000 MC 0.00 0 - 🗀 Sites CI 2 0.50000 0.50000 0.50000 Cl-1 11.06 4 1 Time Rwp 36.203 -0.000 MC 0.30 3 1 0.07 Preferred Orientation 2 Time 0.11 Rwp 36.203 -0.000 MC 1.28 3 - 🛅 Str Output 3 Time 0.14 Rwp 36.203 -0.000 MC 0.81 2 < > 🗄 🗇 🕅 NaCl --- 0.146 seconds ---Sites Values Codes Errors Min Max Errors calculated Preferred Orientation Atom Occ. Site Np v Z Beg. X - 🛅 Str Output B_NaCl Na 4 Fix Fix Fix Na+1 Fix CI < =1/2 B_NaCl > 4 =1/2=1/2Cl-1 Fix 36,203-Interface Mode 36.203 Add Site(s) before selected site(s) Add Site at bottom γŗ 36,203 Add Atom at selected site(s) 36,203 Paste INP to Node/Selections Â 36,203 36.203 36,203 0 2 3 < > Fe2O3 24.39 % 250 75.61 % NaCI 200 150 100 50-0. -50 -100 Ш 11 22 24 26 28 30 32 34 36 40 42 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 38 44 x = 50.43265Sqrt(y) = 248.2478d = 1.808054

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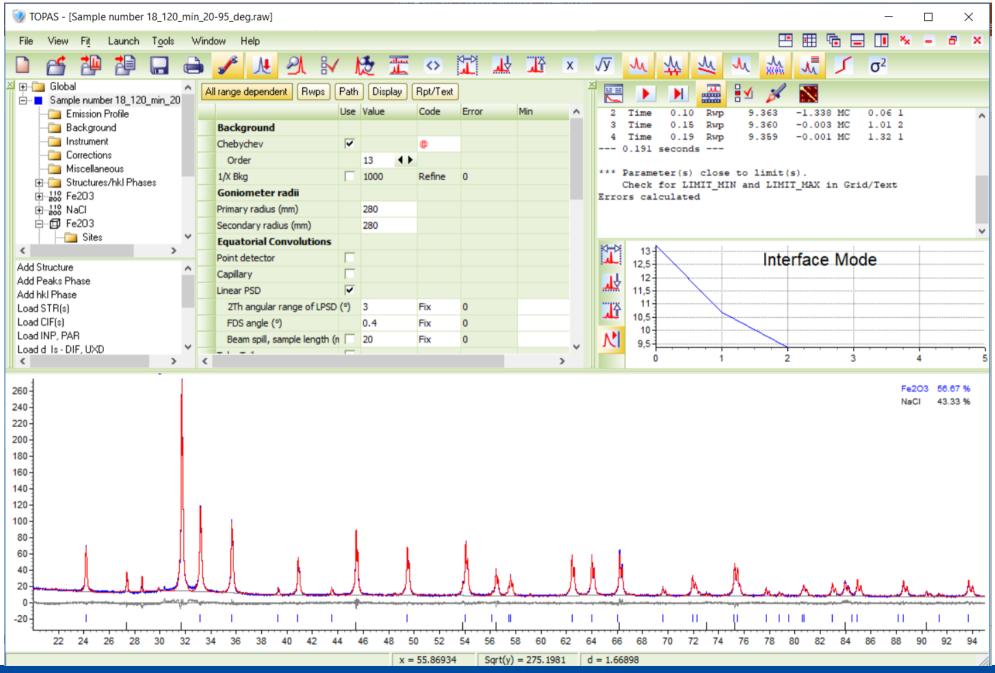
Preferential orientation in powder

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





Rietveld refinement – final result



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Rietveld refinement – fit statistics

∯ ⊕ 🛅 Global	^	A	Irange dependent Rwps Path	Display Rpt/Text
🖻 🗉 Sample number 18_120_min_20		<u> </u>		
Emission Profile				Value
Background			GOF	1.97
			Rexp	4.96
			Rwp	9.76
Miscellaneous E Structures/hkl Phases			Rp	6.97
			Rexp-dash	6.11
±			Rwp-dash	12.02
Ė ∰ Fe2O3			Rp-dash	9.51
Sites	~		Weighted Durbin Watson	0.57
< >				



Rietveld refinement - results

Emission Profile	^	So	cale Cry size L	Cry	size G Stra	ain L Str	ain G Rpt/1	「ext
			Phase Name	Use	Value	Code	Error	Min
Corrections		1	Fe2O3		218.3	Refine	4.2	
Miscellaneous		2	NaCl	Г	2062.8	Refine	0.0	
🖻 🧰 Structures/hkl Phases		3	Fe2O3	\checkmark	217.5	Refine	4.4	
Internal Standard Metho External Standard Metho		4	NaCl		4143.9	@	1257.1	
Brindley correction (Sphe								
⊡ <mark>i</mark> iii Display ⊡iiii Fe2O3	¥	So	cale Cry size L	Cry	size G Stra	ain L Str	ain G	
< >			Phase Name	Use	Value	Code	Error	Min
Paste INP to Node/Selections		1	Fe2O3	\mathbf{V}	0.134611	Refine	0.001841314	ŧ
		2	NaCl	$\overline{\checkmark}$	0.104205	Refine	0.000460946	5
		3	Fe2O3	$\overline{ \checkmark }$	0.02137314	Refine	0.002042238	3
		4	NaCl	\mathbf{V}	0.1055814	Refine	0.000486459)



Rietveld refinement - results

Emission Profile	^	Va	alues Codes	Errors Min	Max Rp	t/Text		
- instrument			Phase Name	SG	a (Å)	b (Â)	c (Å)	а
Corrections		1	Fe2O3	167	5.0364248		13.7537028	
Miscellaneous		2	NaCl	225	5.6435341			
E Structures/hkl Phases		3	Fe2O3	167	5.0364513		13.7537742	
Internal Standard Metho		4	NaCl	225	5.6435355			
SG, Lattice parameters								
⊡ Brindley correction (Sphe ⊡⊡ Display ⊕ 188 Fe2O3	~	< [Va	alues Codes	Errors Min	Max			
< >			Phase Name	SG	a (Â)	b (Â)	c (Å)	а
Paste INP to Node/Selections		1	Fe2O3	167	0.0001347		0.0006824	
		2	NaCl	225	0.0000000			
		3	Fe2O3	167	0.0000241		0.0000925	
		4	NaCl	225	0.0000290			



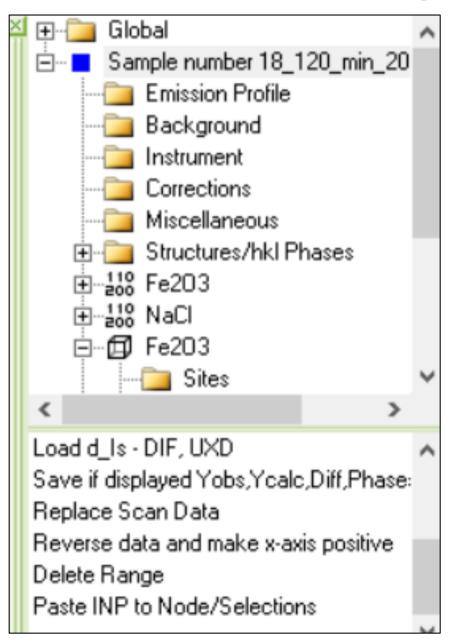
Rietveld refinement - results



Structures/hkl Phases ± <u>11</u> 8 Fe2D3	^	V	alues (Codes	Errors	fin Max I	Rpt/Text			
			Site	Np	х	у	z	Atom	Occ.	Beq.
⊨ ⊡ Fe2O3		1	Na	4	0.00000	0.00000	0.00000	Na+1	1	0.5961
🚞 Sites		2	Cl	4	0.50000	0.50000	0.50000	Cl-1	1	0.5961
Str Output		<								>
⊡…∰ NaCl ⊡ Sites ⊡ Preferred Orientation		V	Values Codes Errors Min Max							
Str Output			Site	Np	x	У	z	Atom	Occ.	Beq.
Ou buiput	~	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	^	S	tructure) Mici	rostruct	ure F	eak Type	kls Additional	Convolutions	Rpt/Text
			h	k	1	m	d	th2	F^2	
Miscellaneous										
⊡		1	0	1	2	6	3.68310	24.14436	15.353	
i		2	1	0	4	6	2.70013	33.15139	98.719	
⊞ 18 NaCl		3	1	1	0	6	2.51808	35.62540	82.192	
⊡…∰ Fe2O3		4	0	0	6	2	2.29217	39.27357	2.550	
Preferred Orientation		5	1	1	3	12	2.20706	40.85428	35.846	
Str Output		6	2	0	2	6	2.07870	43.50116	3.603	
⊡…∰ NaCl		7	0	2	4	6	1.84155	49.45303	94.142	
Sites	~	8	1	1	6	12	1.69506	54.05737	143.826	
		9	2	1	1	12	1.63676	56.14967	1.781	
Save Structure in STR format View/Hide Structure		10	1	2	2	12	1.60305	57.43860	8.486	
Create hkl_Is phase		11	0	1	8	6	1.59937	57.58339	29.380	
Delete Structure		12	2	1	4	12	1.48646	62.42471	129.999	
Paste INP to Node/Selections		13	0	3	0	6	1.45382	63.99001	134.967	

⊕ <mark>ial</mark> Structures/hkl Phases ⊕ i al Fe203	^	S	tructure	Mic	rostruct	ure F	eak Type	nkls Additiona	l Convolutions	Rpt/Text
±			h	k	1	m	d	th2	F^2	
🖻 🗇 Fe2O3		1	1	1	1	8	3.25814	27.35099	7.324	
- 🚞 Sites		2	0	0	2	6	2.82163	31.68541	109.569	
Preferred Orientation		3	0	2	2	12	1.99520	45.42118	153.293	
⊡⊡ Str Output		4	3	1	1	24	1.70151	53.83600	7.334	
Sites		5	2	2	2	8	1.62907	56.43829	78.200	
Preferred Orientation		6	0	0	4	6	1.41082	66.18532	47.222	
🛄 Str Output		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 2θ 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 2θ .
 - ✤ 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.
 - → Z² 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: $PbZr_{0.2}Ti_{0.8}O_3$ and Fe_3O_4 .
- ✤ Link parameters when sensible user understanding required.
- Do not over-fit your data! Mind R_{wp} , R_{exp} and χ^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% Fe_2O_3 and 50% NaCl.
- 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...

