

Lesson 3

“How-To” Session



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Refinement Strategy: Words of Wisdom

Always refining everything
may lead to good fits,
but the results may be useless.

Release parameters one by one.
When the fit doesn't improve anymore,
don't try to extract more information.

Chose your refinement strategy wisely.
Ask yourself if the results make
physical sense.

Examples

Example 1: Texture, preferred orientation

Example 2: Anisotropic crystallite sizes

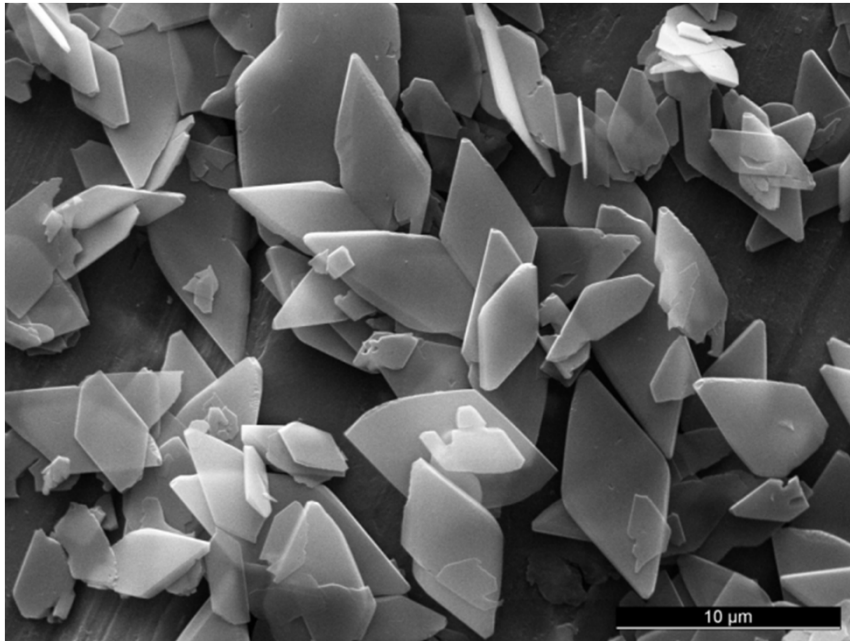
Example 3: Non-existent phases

Example 4: Micro-absorption and Brindley correction

Example 5: Amorphous Content



Texture, Preferred Orientation



Platelets

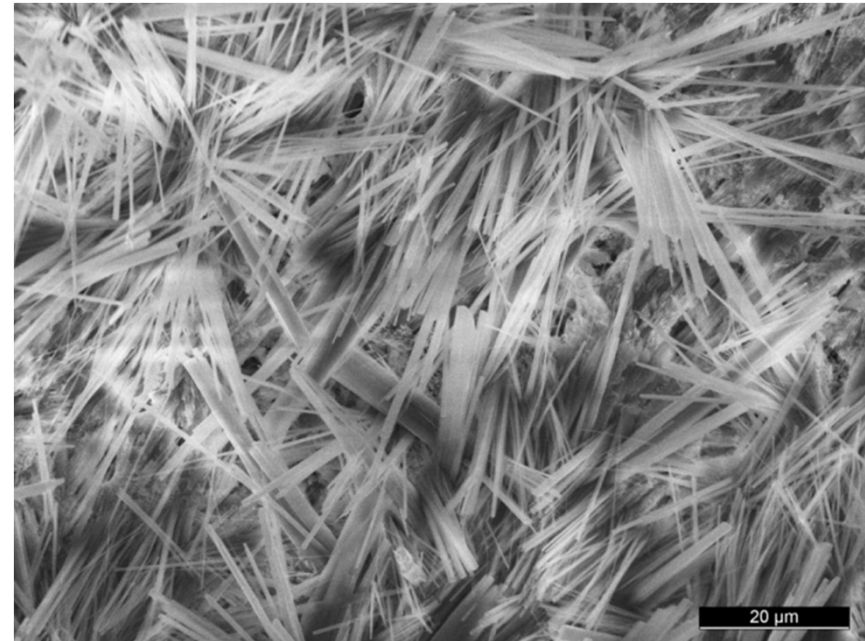
lying flat



Random orientation



Preferred orientation



Needles, Fibers, Whiskers

lying flat

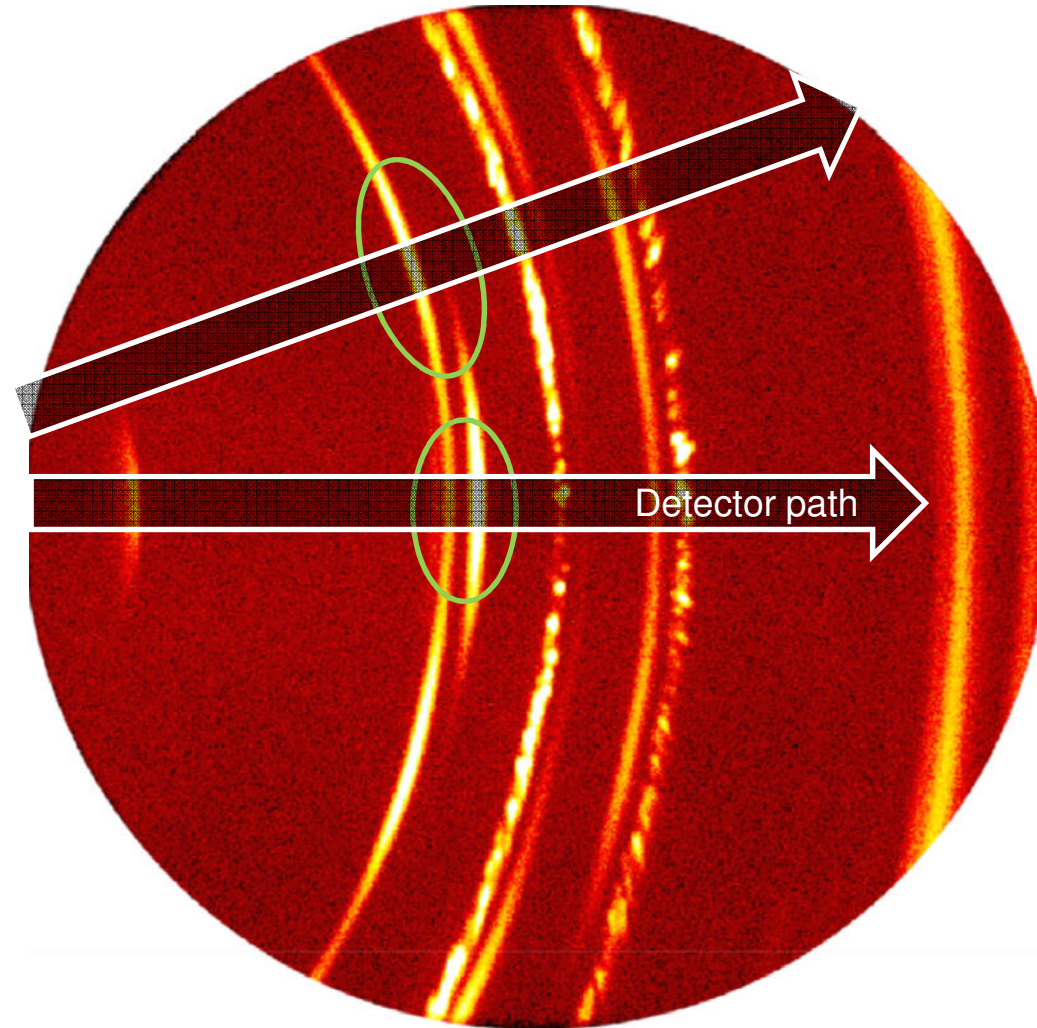
may point in one direction (bundles)



Images: L. Galea, RMS Foundation

Texture, Preferred Orientation

Smooth, but non-continuous
diffraction rings



Some orientations are
over-represented,
others are under-represented.

Texture: Symmetrized Spherical Harmonics

In structure files (*.str) change:

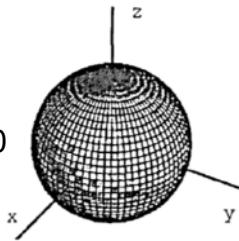
PARAM=GEWICHT=0.1_0

to

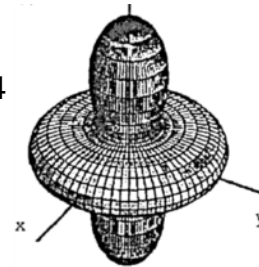
GEWICHT=SPHAR n

($n=0, 2, 4, 6, 8, 10$)

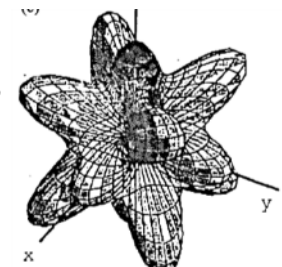
No preferred orientation:
PARAM=GEWICHT=0.1_0
GEWICHT=SPHAR0



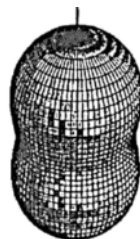
GEWICHT=SPHAR4



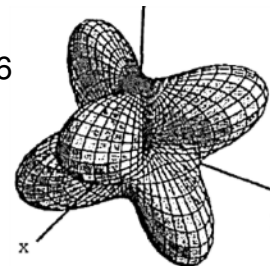
GEWICHT=SPHAR8



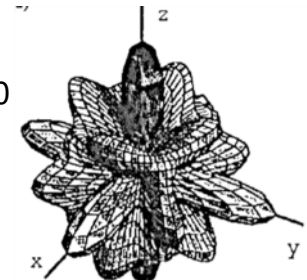
GEWICHT=SPHAR2



GEWICHT=SPHAR6



GEWICHT=SPHAR10



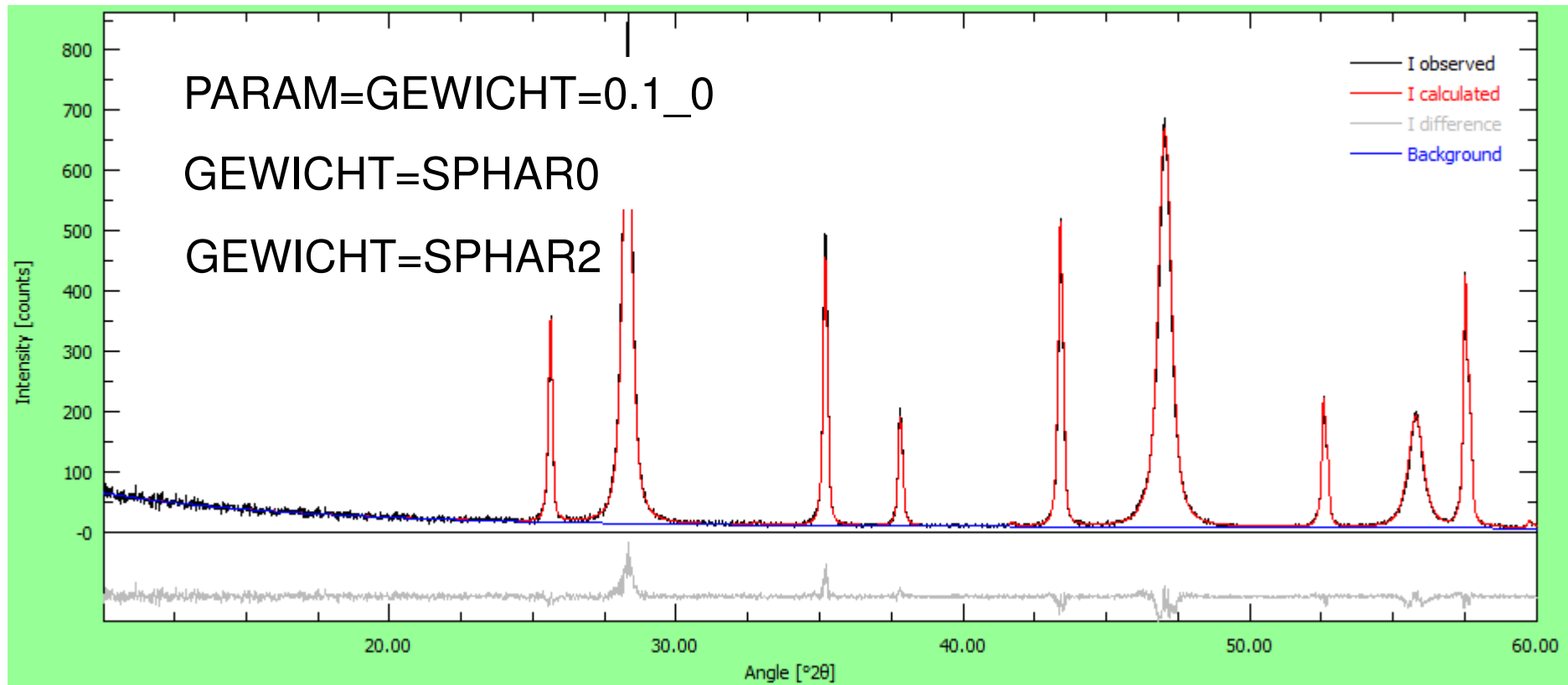
Järvinen, M. Materials Science Forum [278-281], 1998, 184-199.

Example 1 - Texture

Instrument: pw1800-fds

Phases: Corundum, Fluorite

Both phases: RP=4 PARAM=k1=0_0^1 PARAM=k2=0_0 PARAM=B1=0_0^0.03 PARAM=GEWICHT=0.1_0 //

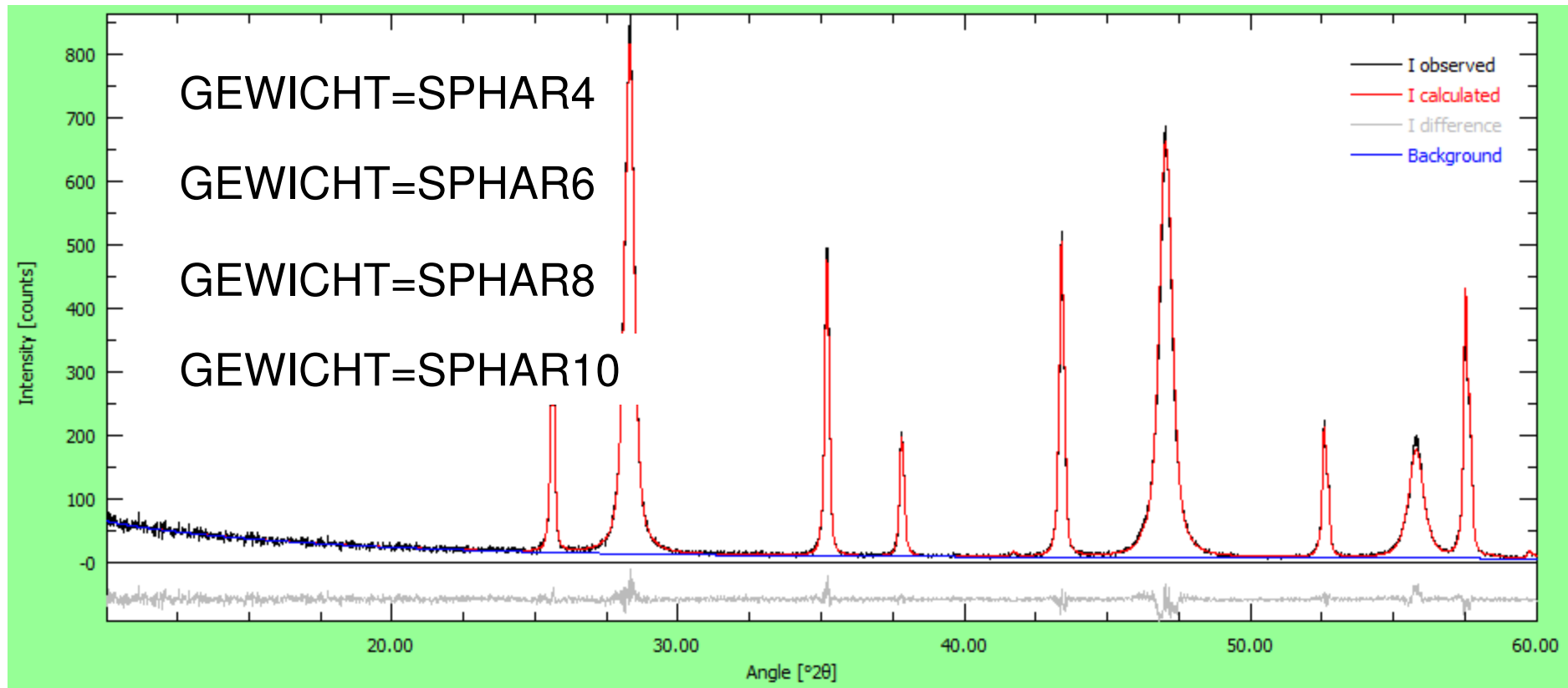


Example 1 - Texture

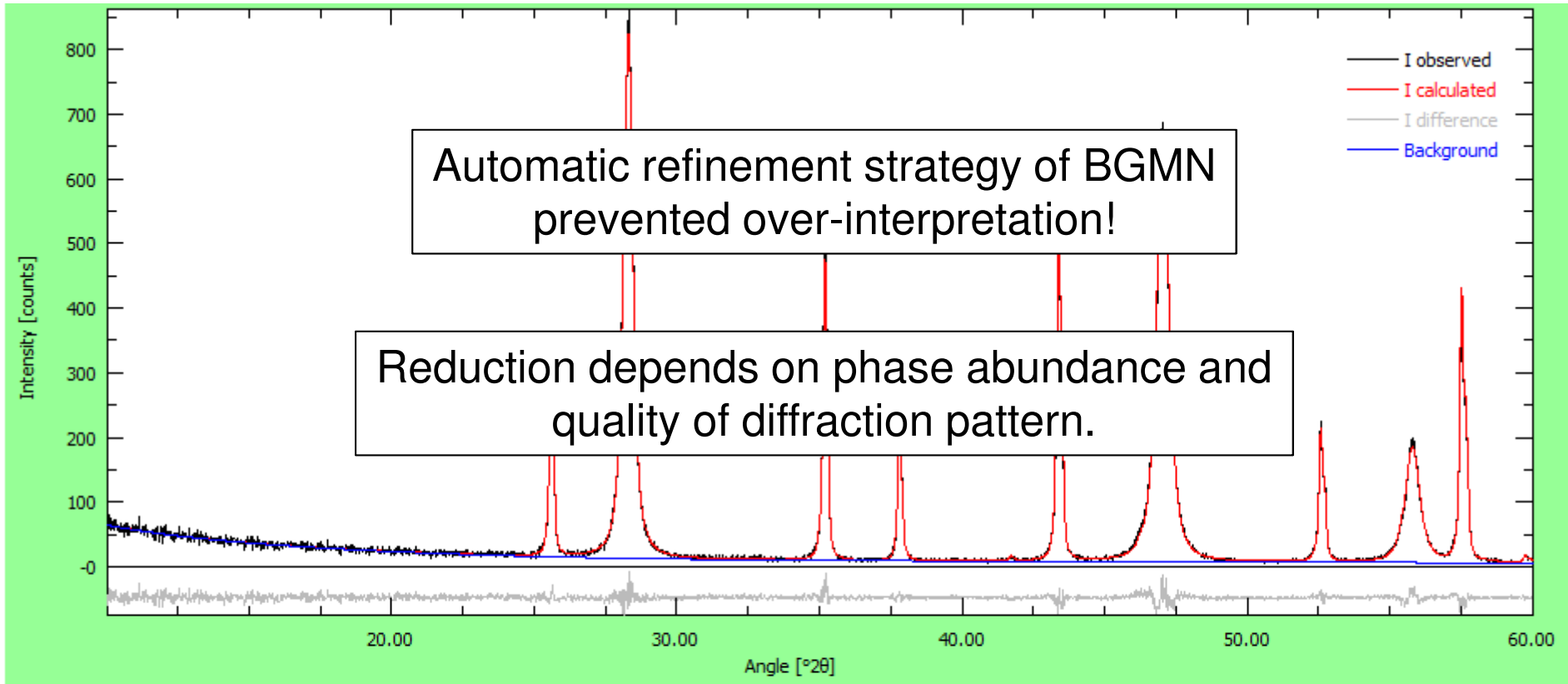
Instrument: pw1800-fds

Phases: Corundum, Fluorite

Both phases: RP=4 PARAM=k1=0_0^1 PARAM=k2=0_0 PARAM=B1=0_0^0.03 **GEWICHT=SPHAR4 //**



Example 1 - Texture



```
-----  
1. phase: texture reduced from SPHAR10 to SPHAR4 due to small contents  
2. phase: texture reduced from SPHAR10 to SPHAR6 due to small contents  
1. phase: initializing SPHAR4...OK  
2. phase: initializing SPHAR6...  
OK
```



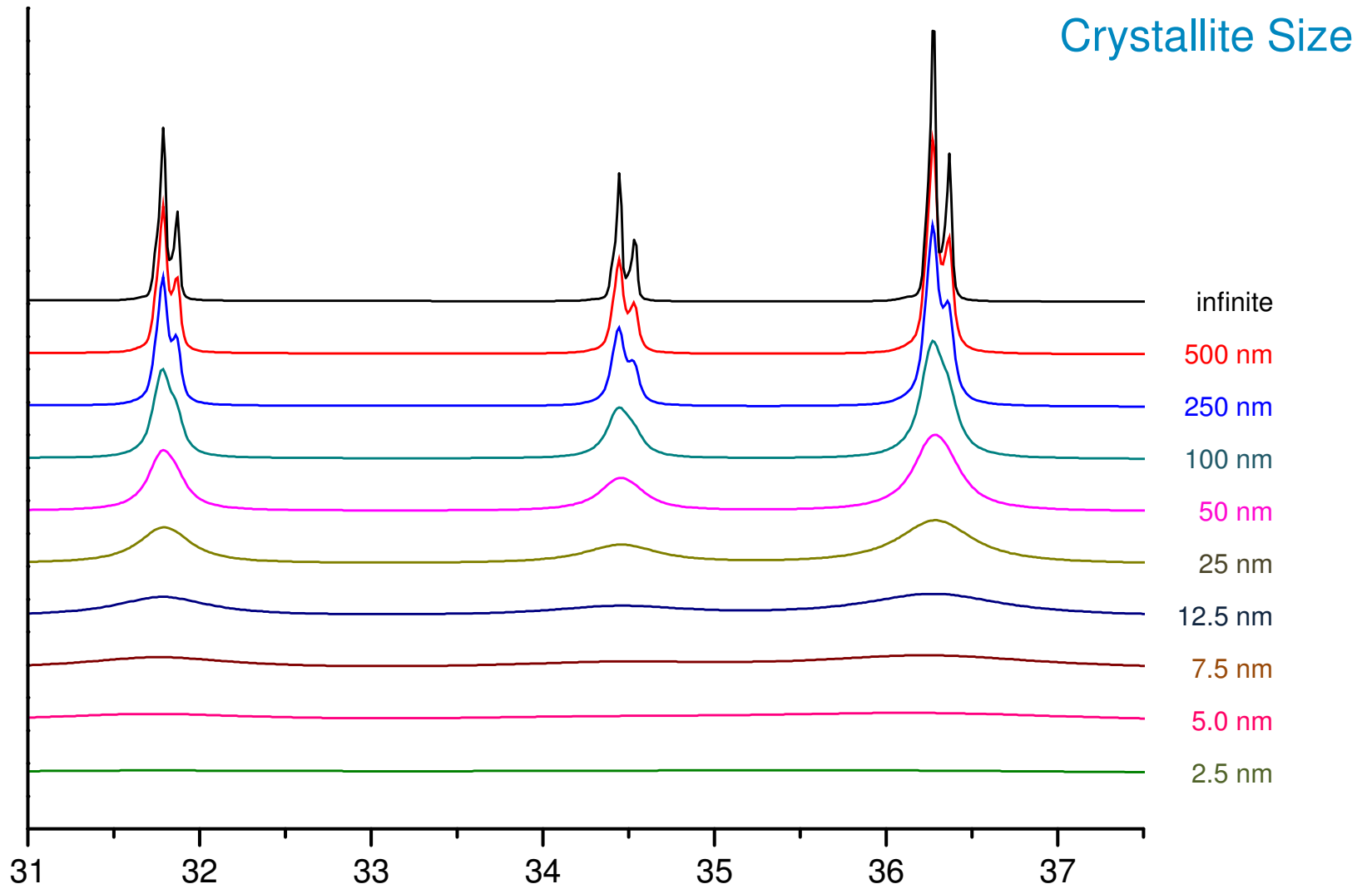
Example 1 - Texture

- Refining «GEWICHT» with symmetrized spherical harmonics functions allows to model texture / preferred orientation.
- Complexity of the polynome can be set in structure file (SPHAR n).
- High order introduce large number of refined parameters.
(→ slow refinement, may get unstable)
- Automatic refinement strategy will protect from over-interpretation.

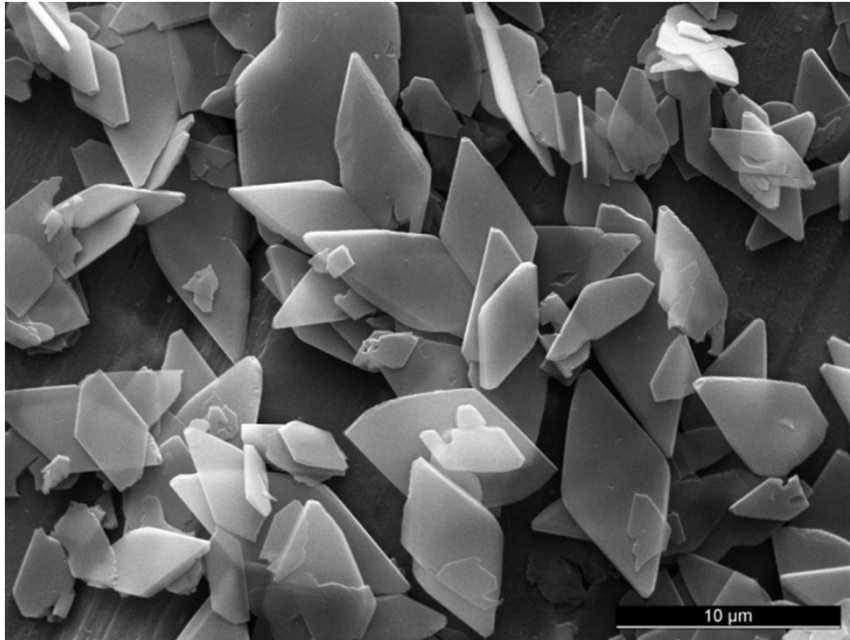
Recommendation:

- Use a moderate order of SPHAR polynomes in your structure files (e.g. SPHAR4)
- Let BGMN reduce the order if necessary
- Only increase the order if the fit really improves

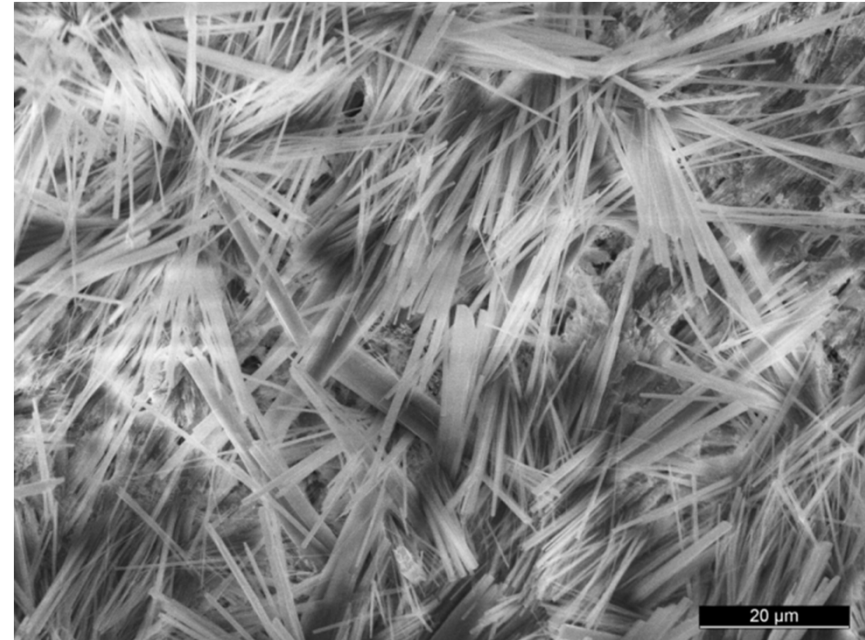
Anisotropic Crystallite Sizes



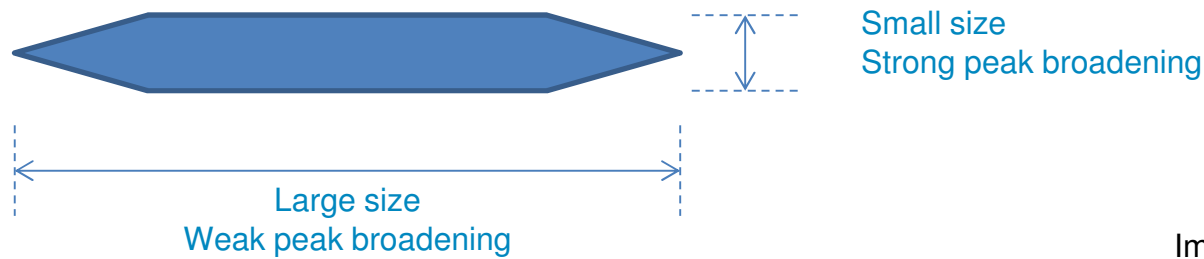
Anisotropic Crystallite Sizes



Platelets

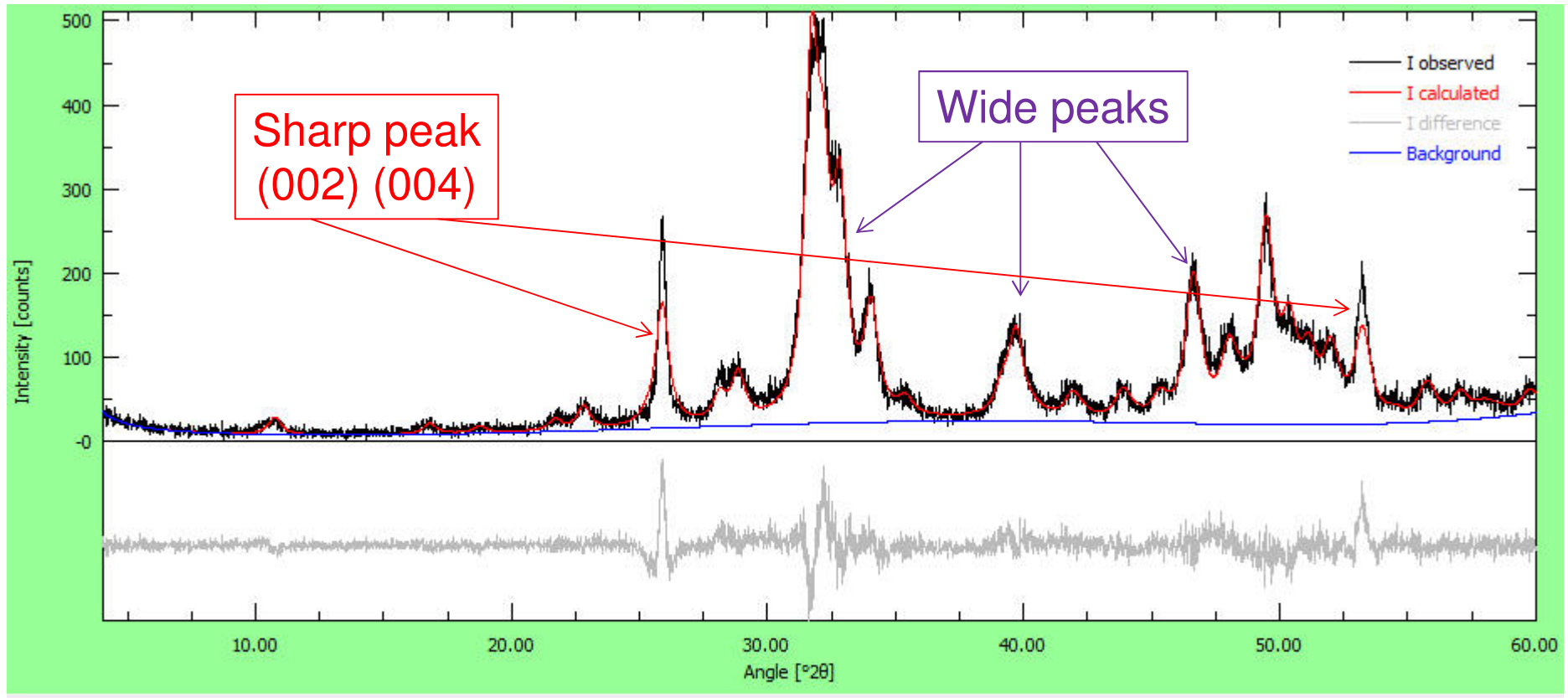


Needles, Fibers, Whiskers



Images: L. Galea, RMS Foundation

Example 2 – Anisotropic Crystallite Size



Sample lesson6-ex2-file1 (C:/xrd/S12_0008/Examples/Lesson 6/Example 2/lesson6-ex2-file1.lst)

Phase	R _{Phase} [%]	Quantity [wt-%]	Mean Gewicht [a.u.]	Crystallite Sizes [nm]	Density [g/cm ³]
Hydroxyapatite	14.91	100.00	0.044979	(0,0,1)14.22 (1,0,0)14.22	3.159

Example 2 – Anisotropic Crystallite Size

Profex - 2.3.1

File Edit View Run Help

Projects: lesson6-ex2-file1.dia lesson6-ex2-file1.sav hydroxylapatite.str lesson6-ex2-file1.lst

```
PHASE=Hydroxyapatite // 01-074-0565
SpacegroupNo=176 HermannMauguin=P6_3/m //
PARAM=A=0.9424 0.9330^0.9518 PARAM=C=0.6879 0.6810^0.6948 //
RP=4 PARAM=k1=0_0^1 PARAM=k2=0_0 PARAM=B1=0_0^0.1 GEWICHT=SPHAR6 //
GOAL=GrainSize(0,0,1) //
GOAL=GrainSize(1,0,0) //
GOAL=my //
GOAL=d //
GOAL:hap=GEWICHT*ifthenelse(ifdef(d),exp(my*d*3/4),1)
E=CA+2 Wyckoff=f x=0.3333 y=0.6667 z=0.0015 TDS=0.00664290
E=CA+2 Wyckoff=h x=0.2468 y=0.9934 z=0.2500 TDS=0.00567436
E=P Wyckoff=h x=0.3987 y=0.3685 z=0.2500 TDS=0.00477426
E=O-2 Wyckoff=h x=0.3284 y=0.4848 z=0.2500 TDS=0.00953535
E=O-2 Wyckoff=h x=0.5873 y=0.4651 z=0.2500 TDS=0.01014069
E=O-2 Wyckoff=i x=0.3437 y=0.2579 z=0.0702 TDS=0.01499127
E=O-2(0.5000) Wyckoff=e x=0.0000 y=0.0000 z=0.1950 TDS=0.00000000
E=H(0.5000) Wyckoff=e x=0.0000 y=0.0000 z=0.0608 TDS=0.02947459
```

Change:

```
RP=4 k1=0 PARAM=k2=0_0 PARAM=B1=0_0^0.1 GEWICHT=SPHAR6 //
```

To:

```
RP=4 k1=0 k2=ANISO4 B1=ANISO^0.1 GEWICHT=SPHAR6 //
```

Use right mouse button or change manually

Angle: 7.019 Intensity: 495.955

Example 2 – Anisotropic Crystallite Size

Profex - 3.3.1

File Edit View Run Instrument Window Help

Projects: ex2-file1.dia, ex2-file1.sav, ex2-file1.lst, hydroxylapatite.str

Name Status
ex2-file1 completed

Rietveld refinement to file(s) ex2-file1.xy
BGMN version 4.2.22, 3733 measured points, 61 peaks, 51 parameters
Start: Fri Jan 9 10:15:27 2015; End: Fri Jan 9 10:15:43 2015
180 iteration steps

Rp=9.66% Rpb=13.94% R=9.09% Rwp=13.37% Rexp=12.31%
Durbin-Watson d=1.71
1-rho=3.08%

Global parameters and GOALS

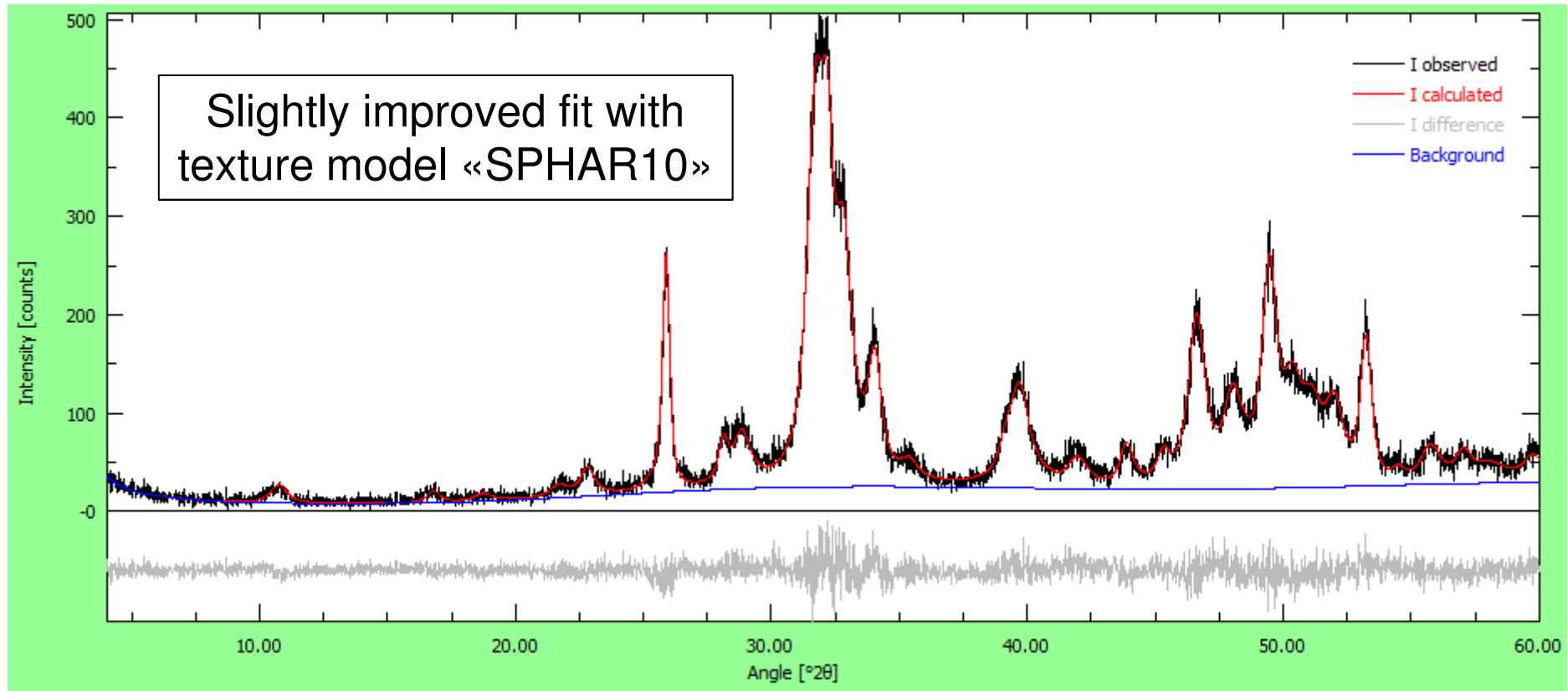
hap/(hap)=1.00000
EPS1=0.0100000
EPS2=-0.009856+-0.000049

Local parameters and GOALS for phase Hydroxyapatite

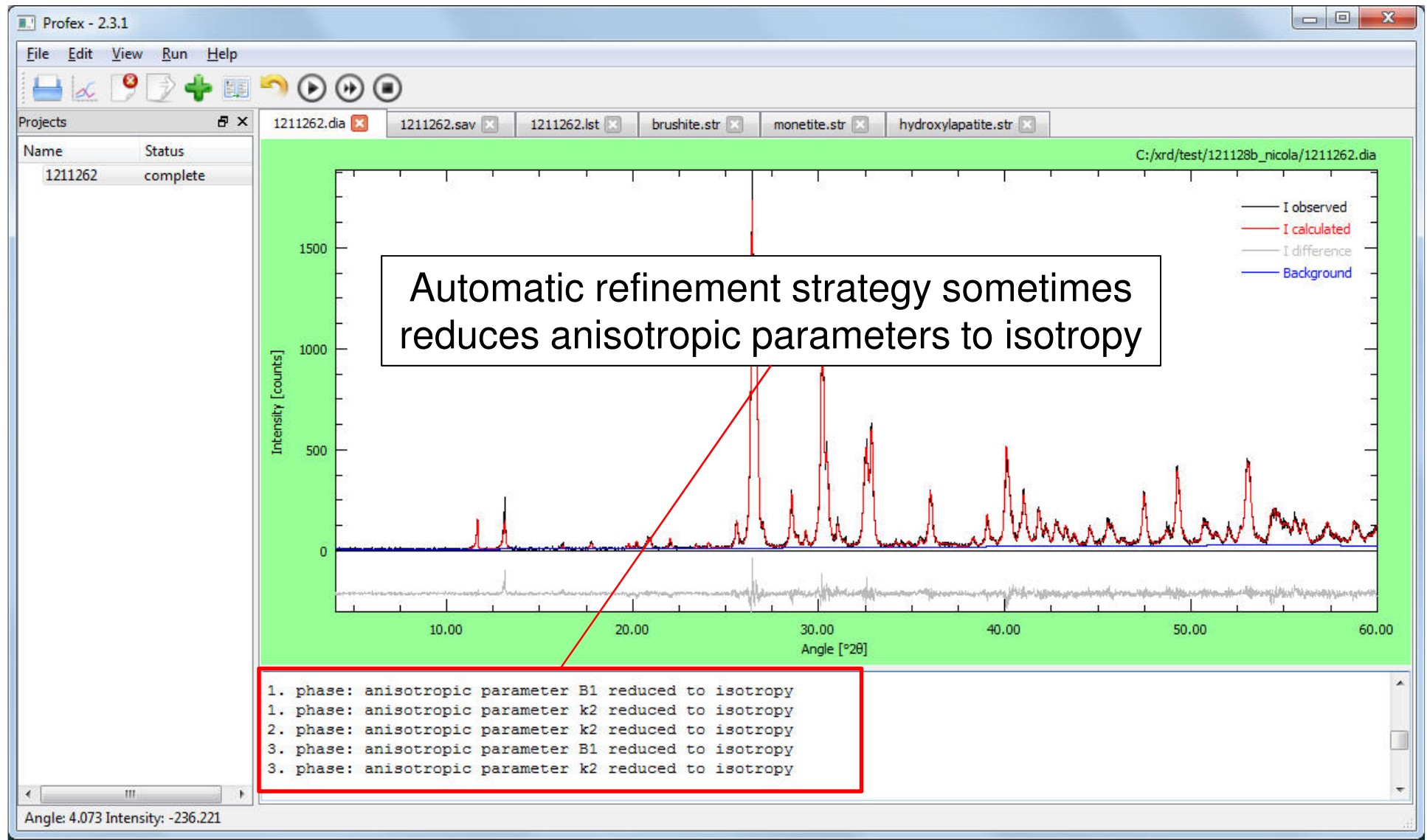
SpacegroupNo=176
HermannMauguin=P6_3/m
XrayDensity=3.159
Rphase=11.43%
UNIT=NM
A=0.94258+-0.00015
C=0.68630+-0.00010
k1=0.52+-0.21
GrainSize(0,0,1)=35.4+-1.9
GrainSize(1,0,0)=11.18+-0.17
my=0.027341+-0.000012
d=ERROR
GEWICHT=SPHAR6, MeanValue(GEWICHT)=0.0437039
B1=ANISOLIN, MeanValue(B1)=0.0255187, sqrt3(det(B1))=0.0212931
k2=ISOTROPIC=0.0000128205

Needle length: 35.4 nm
Diameter: 11.18 nm

Example 2 – Anisotropic Crystallite Size



Example 2 – Anisotropic Crystallite Size



Example 2 – Anisotropic Crystallite Size

Refine anisotropic crystallite sizes with «B1=ANISO»

Refine anisotropic micro-strain with «k2=ANISO4»

Recommendation:

- Do **not** refine micro-strain anisotropically **unless it improves the fit**
- Refine peak broadening anisotropically (**B1=ANISO^{0.01}**), let BGMN handle the reduction to isotropy
- Check if the upper limit of B1 was reached. If yes:
 - increase the limit...
 - ... or see next example (non-existent phases)

Example 3 – Non-existent Phases

Experimental design:

Step 1:

- α -TCP prepared at 1350 °C
- Traces of β -TCP **may** have formed during cooling

Step 2:

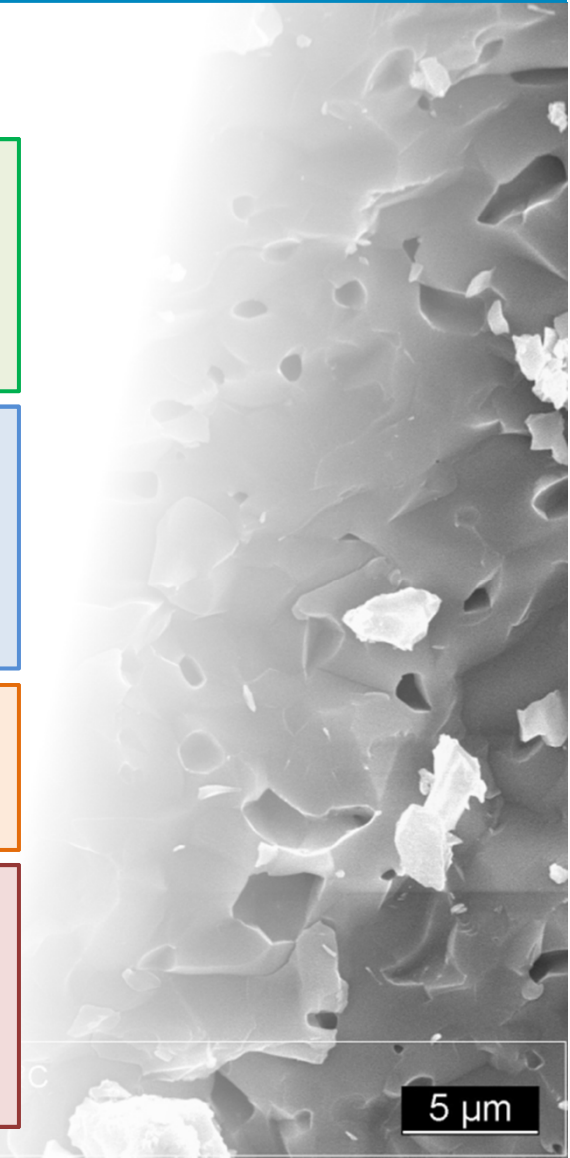
- α -TCP hydrated to Hydroxylapatite
- β -TCP (if present) remains

Question:

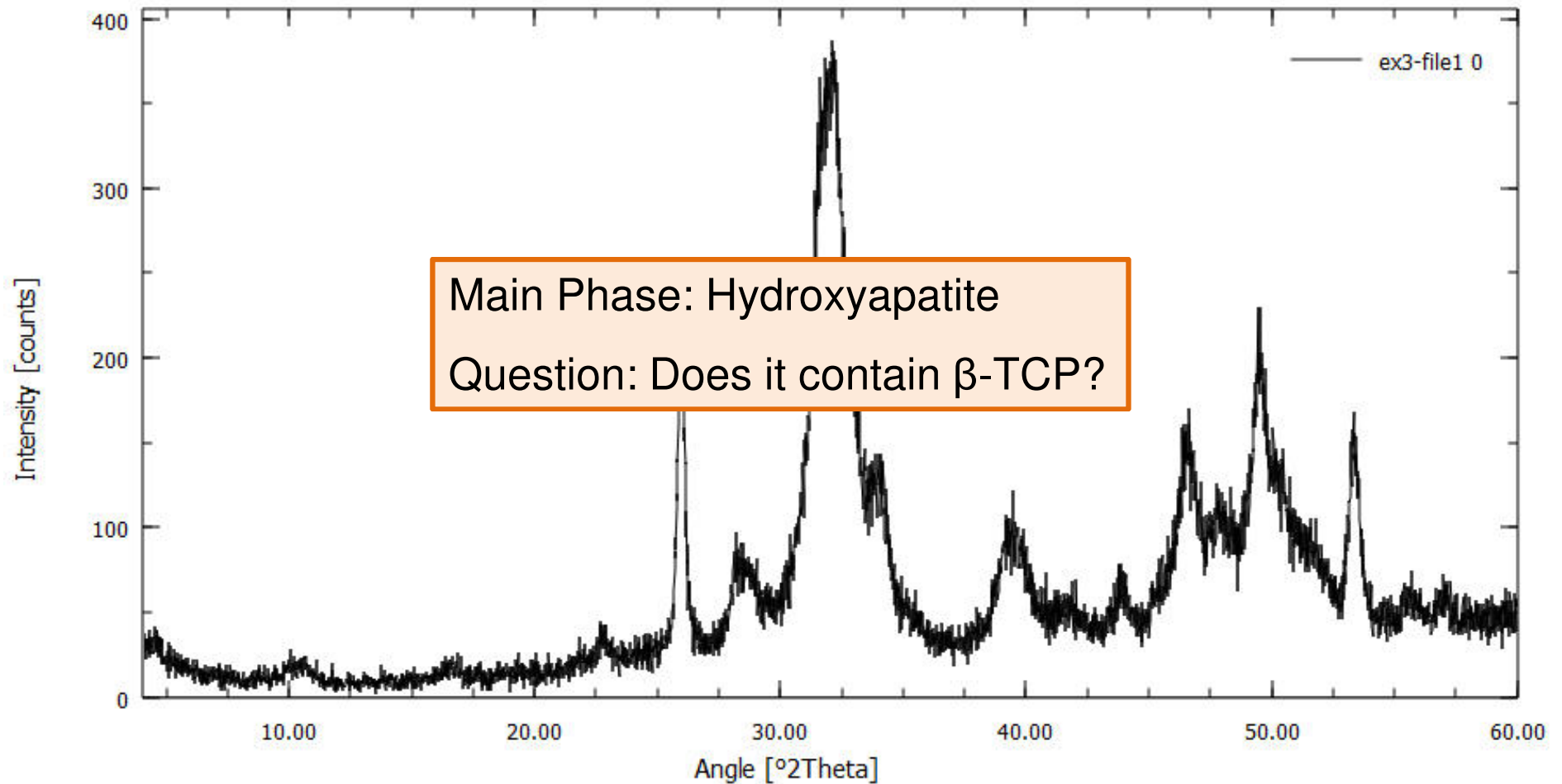
- Is β -TCP present after setting?

Background Information:

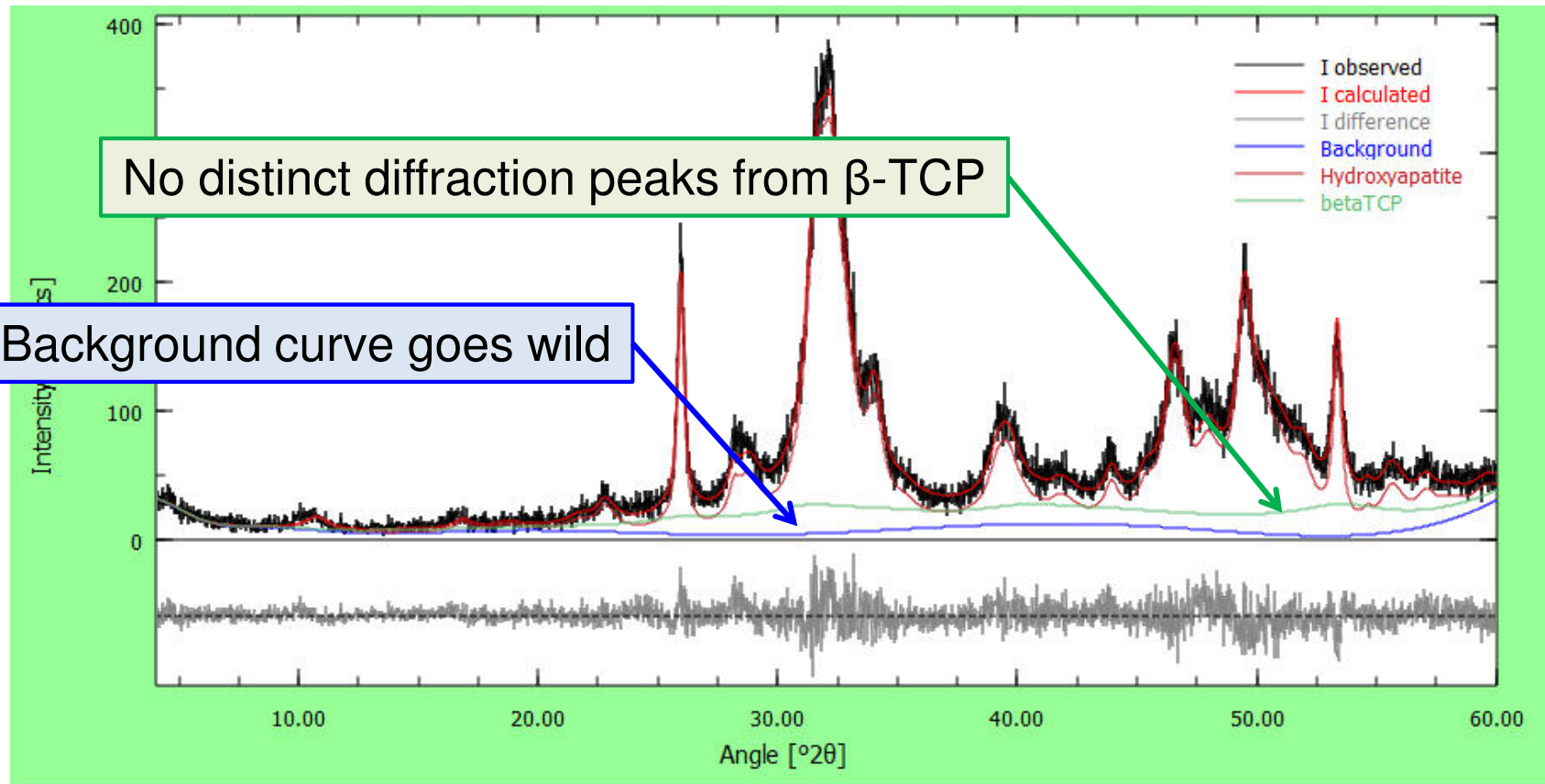
- If β -TCP is present, it has formed at $\sim 1000^\circ\text{C}$
- Must be highly crystalline with large crystallites



Example 3 – Non-existent Phases



Example 3 – Non-existent Phases



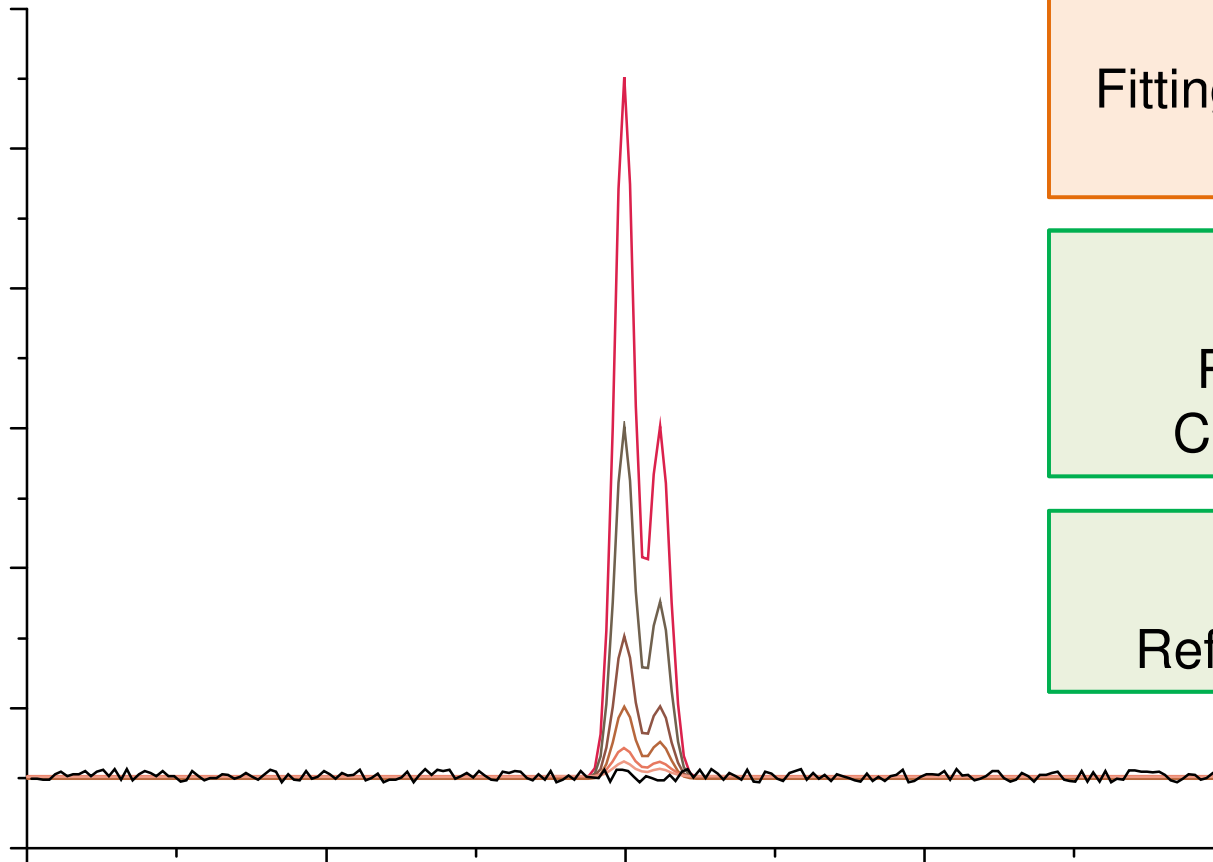
Global Parameters and GOALS ✖

C:\Users\doebelinn\Desktop\Examples-Test\Lesson 7\Example 3\ex3-file1.lst
 $R_{wp}=14.08\%$, $R_{exp}=12.93\%$, $X^2=1.0889$

Parameter / Goal	Value	ESD
hap/(hap+betaTCP)	0.762	0.051
betaTCP/(hap+betaTCP)	0.238	0.051

23.8 wt-% betaTCP (totally wrong!)

Example 3 – Non-existent Phases



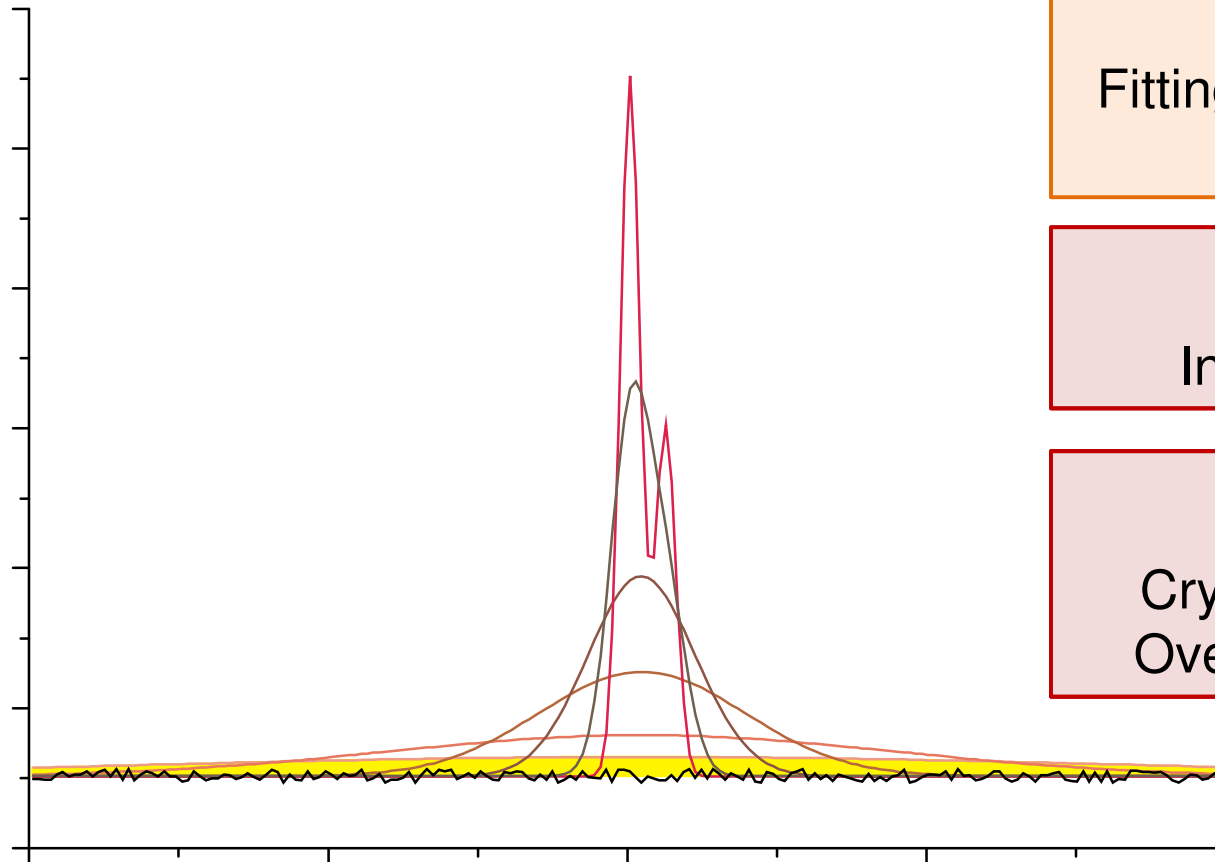
Problem:
Refining non-existing phases
=
Fitting a calculated pattern
to random noise

Solution 1:
Reducing intensity
Constant peak width

Result:
Refined quantity \rightarrow 0 %

Correct result

Example 3 – Non-existent Phases



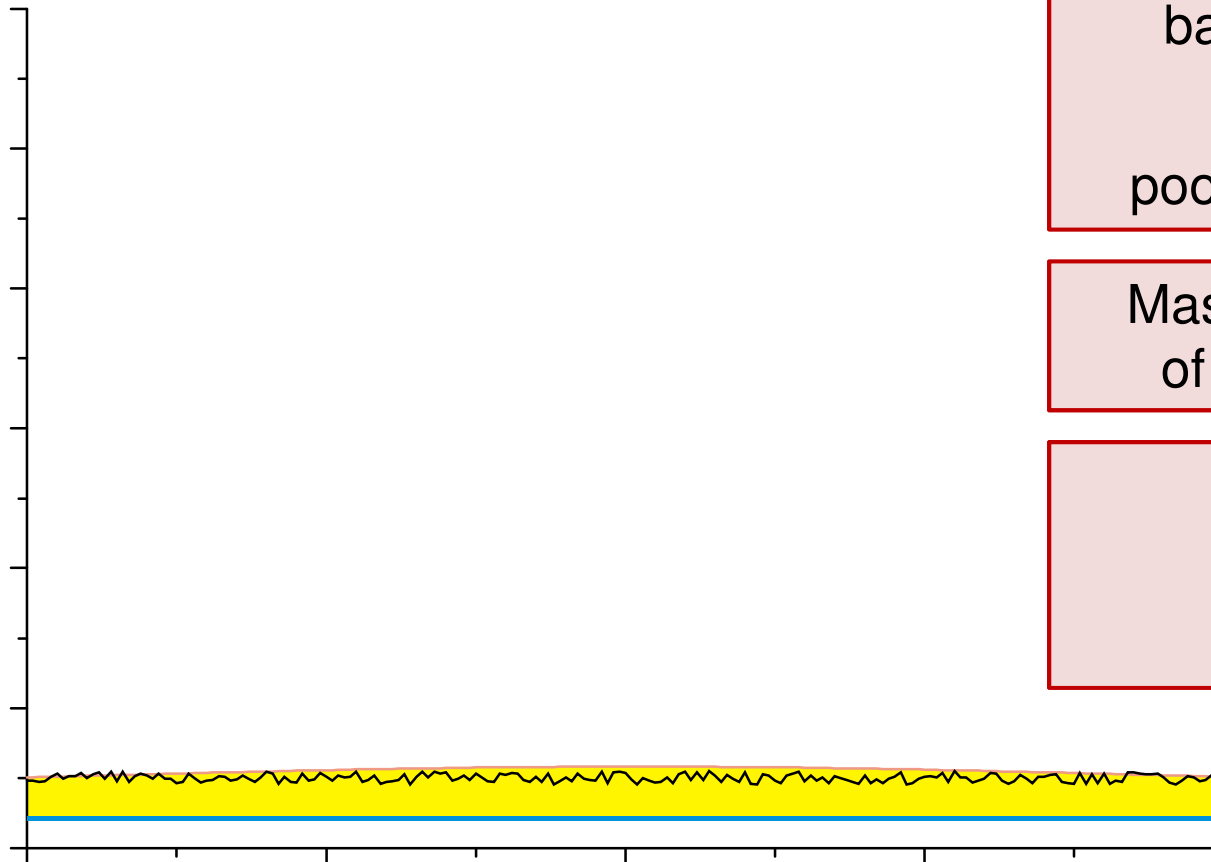
Problem:
Refining non-existing phases
=
Fitting a calculated pattern
to random noise

Solution 2:
Increase peak width

Result:
Crystallite Size \rightarrow 0 nm
Over-estimated quantity

Wrong result

Example 3 – Non-existent Phases

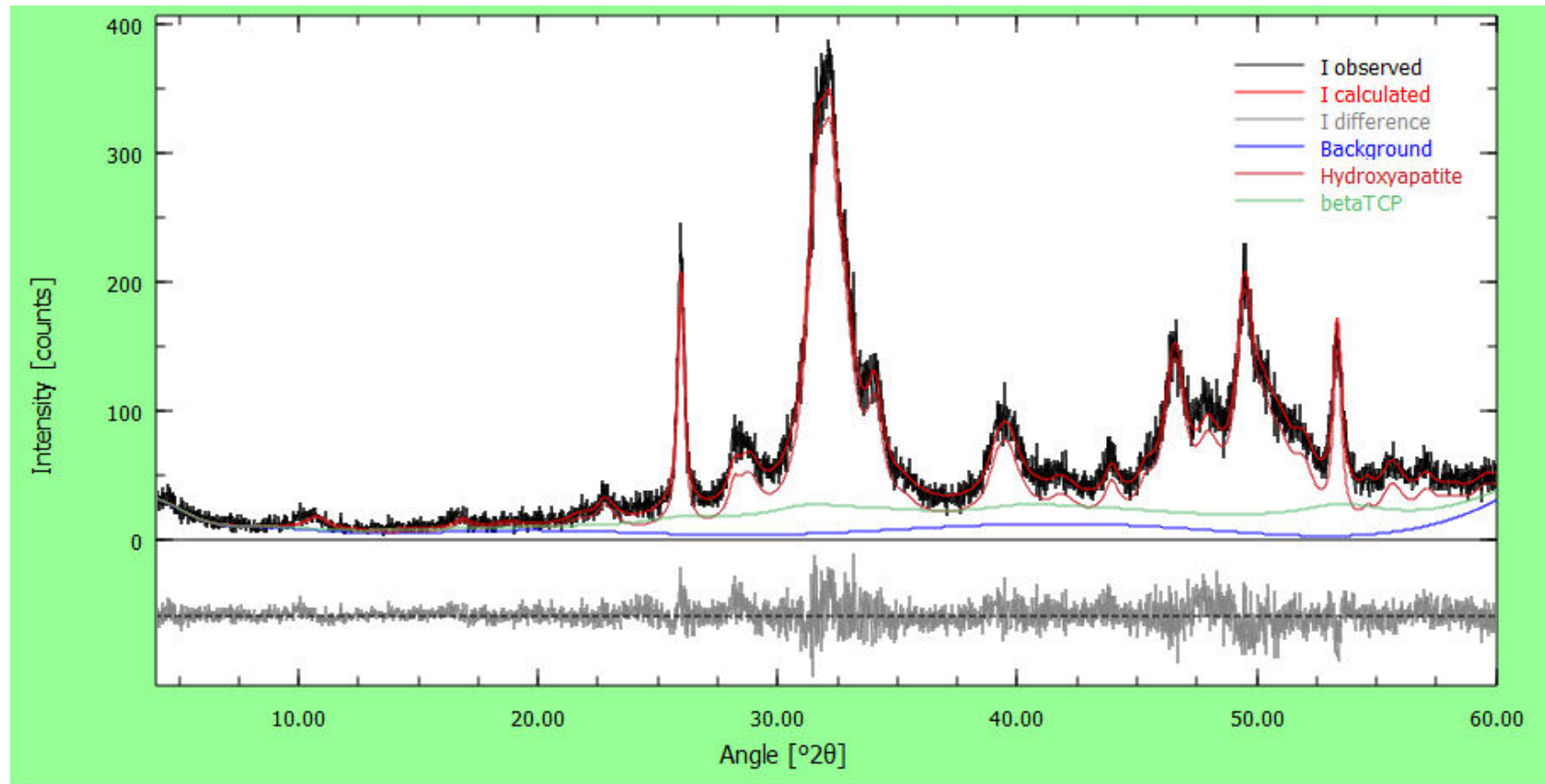


Even worse:
No anchor points for background anymore
Background is poorly/randomly defined

Massive over-estimation of non-existing phase

Result:
Totally wrong!
Unpredictable!

Example 3 – Non-existent Phases



Global Parameters and GOALS

C:\Users\doebelinn\Desktop\Examples-Test\Lesson 7\Example 3\ex3-file1.lst
 $R_{wp}=14.08\%$, $R_{exp}=12.93\%$, $X^2=1.0889$

Parameter / Goal	Value	ESD
hap/(hap+betaTCP)	0.762	0.051
betaTCP/(hap+betaTCP)	0.238	0.051

GrainSize(1,1,1) = 2.47+-0.44

Example 3 – Non-existent Phases

Solutions:

- Use a reasonable upper limit for B1 (peak broadening, crystallite size)
- Don't trust very small crystallite sizes (e.g. < 20 nm)
- Repeat the refinement without the questionable phase (Does the fit really look worse? Or just as good?)
- Use additional information:
 - Sintered samples: very small crystallites are unlikely
 - Cement samples: very small crystallites are reasonable

Example 3 – Non-existent Phases

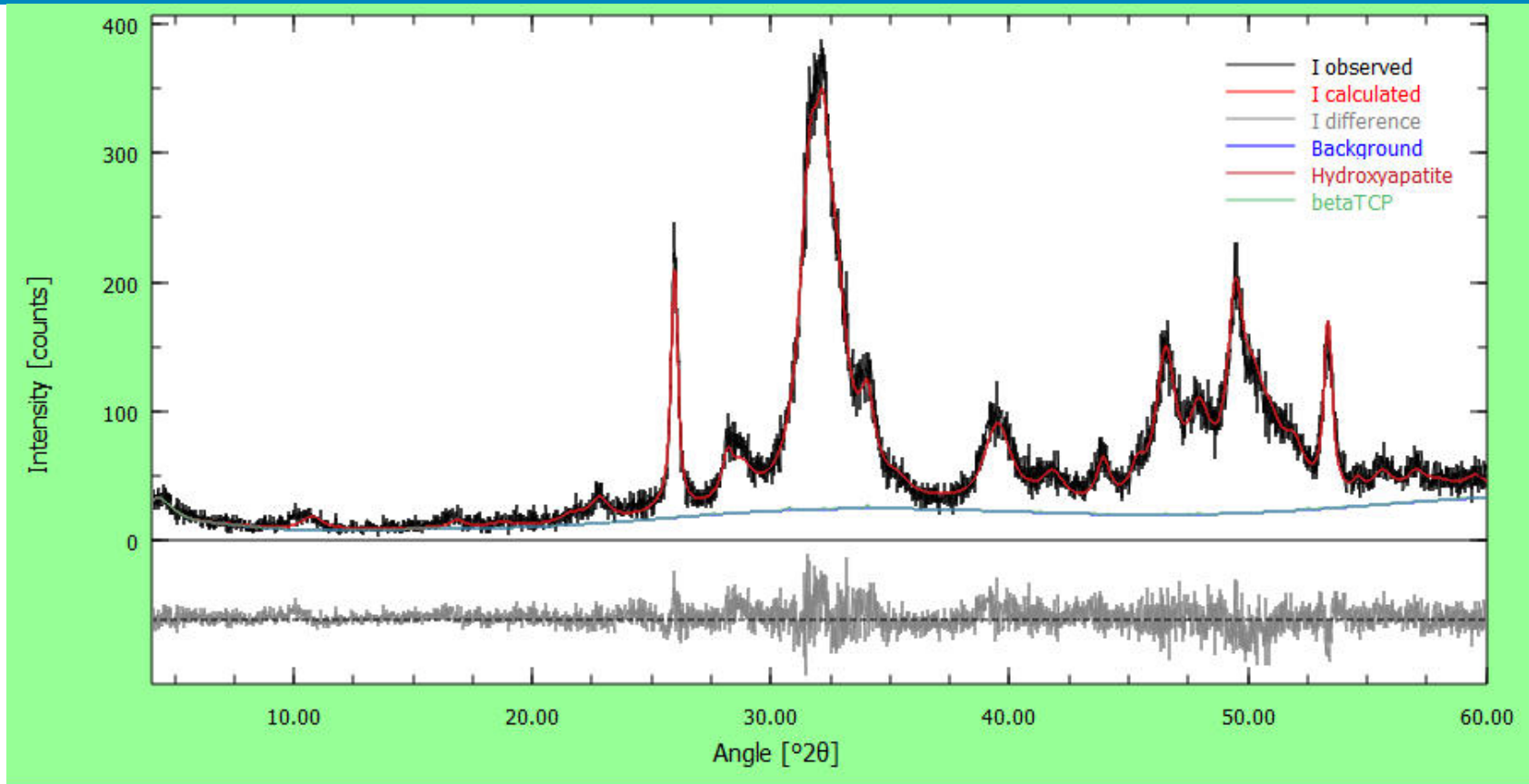
1. Edit betaTCP.str

PHASE=betaTCP // 04-008-8714
SpacegroupNo=161 HermannMauguin=R3c //
PARAM=A=1.0439 1.0335 1.0543 PARAM=C=3.7375_3.7001^3.7749 //
RP=4 k1=0 k2=0 PARAM=B1=0_0A0.005 GEWICHT=SPHAR4 //
GOAL=GrainSize(1,1,1) //
GOAL=my //
GOAL=d //
GOAL:betaTCP=GEWICHT*ifthenelse(ifdef(d),exp(my*d*3/4),1)
E=CA+2 Wyckoff=b x=-0.2766 y=-0.1421 z=0.1158 TDS=0.00686924
E=CA+2 Wyckoff=b x=-0.3836 y=-0.1775 z=-0.0336 TDS=0.00673765
E=CA+2 Wyckoff=b x=-0.2721 y=-0.1482 z=0.0606 TDS=0.0187390
E=CA+2(0.5000) Wyckoff=a x=0.0000 y=0.0000 z=-0.0850 TDS=0.
E=CA+2 Wyckoff=a x=0.0000 y=0.0000 z=-0.2658 TDS=0.01150138
E=P Wyckoff=a x=0.0000 y=0.0000 z=0.0000 TDS=0.00886948
E=O-2 Wyckoff=b x=0.0070 y=-0.1366 z=-0.0136 TDS=0.02092356
E=O-2 Wyckoff=a x=0.0000 y=0.0000 z=0.0400 TDS=0.02031823
E=P Wyckoff=b x=-0.3109 y=-0.1365 z=-0.1320 TDS=0.00802728
E=O-2 Wyckoff=b x=-0.2736 y=-0.0900 z=-0.0926 TDS=0.0247398
E=O-2 Wyckoff=b x=-0.2302 y=-0.2171 z=-0.1446 TDS=0.0231606
E=O-2 Wyckoff=b x=-0.2735 y=0.0053 z=-0.1523 TDS=0.00752722
E=O-2 Wyckoff=b x=-0.4777 y=-0.2392 z=-0.1378 TDS=0.0165283
E=P Wyckoff=b x=-0.3465 y=-0.1537 z=-0.2333 TDS=0.00526379
E=O-2 Wyckoff=b x=-0.4031 y=-0.0489 z=-0.2211 TDS=0.0111855
E=O-2 Wyckoff=b x=-0.4246 y=-0.3056 z=-0.2152 TDS=0.0118435
E=O-2 Wyckoff=b x=-0.1814 y=-0.0805 z=-0.2233 TDS=0.0107644
E=O-2 Wyckoff=b x=-0.3696 y=-0.1748 z=-0.2735 TDS=0.0138174

2. Change
PARAM=B1=0_0
to
PARAM=B1=0_0^0.005

3. Run Refinement...

Example 3 – Non-existent Phases



Global Parameters and GOALS

C:\Users\doebelinn\Desktop\Examples-Test\Lesson 7\Example 3\ex3-file1.lst
 $R_{wp}=14.23\%$, $R_{exp}=12.94\%$, $X^2=1.0997$

Parameter / Goal	Value	ESD
hap/(hap+betaTCP)	0.9973	0.0021
betaTCP/(hap+betaTCP)	0.0027	0.0021

< 1 % vs. 23.8 %!

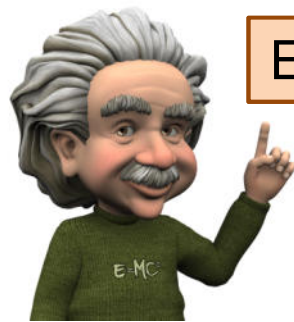
Example 3 – Non-existent Phases

How to choose the upper limit for B1?

Upper limit B1	Crystallite Size β -TCP	Quantity β -TCP
None	2 nm	23.8 wt-%
0.1	4 nm	14.6 wt-%
0.05	8 nm	7.0 wt-%
0.01	42 nm	0.4 wt-%
0.005	85 nm	0.8 wt-%
0.001	424 nm	0.2 wt-%
0.0005	849 nm	0.2 wt-%
0	∞	0.2 wt-%

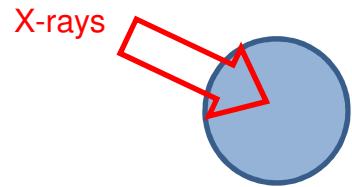
Sample was sintered at 1350°C:

- Crystallites of several 100 nm diameter expected
- Any other useful data available?
 - Other samples which **do** contain β -TCP?
 - Before cement reaction?

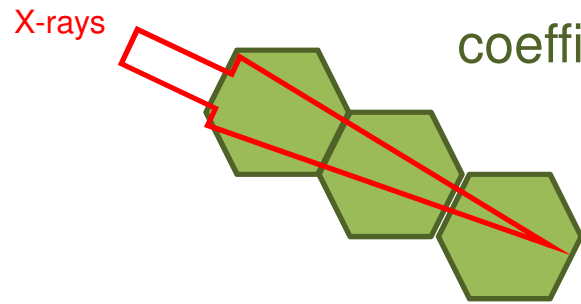


Educated Guess!

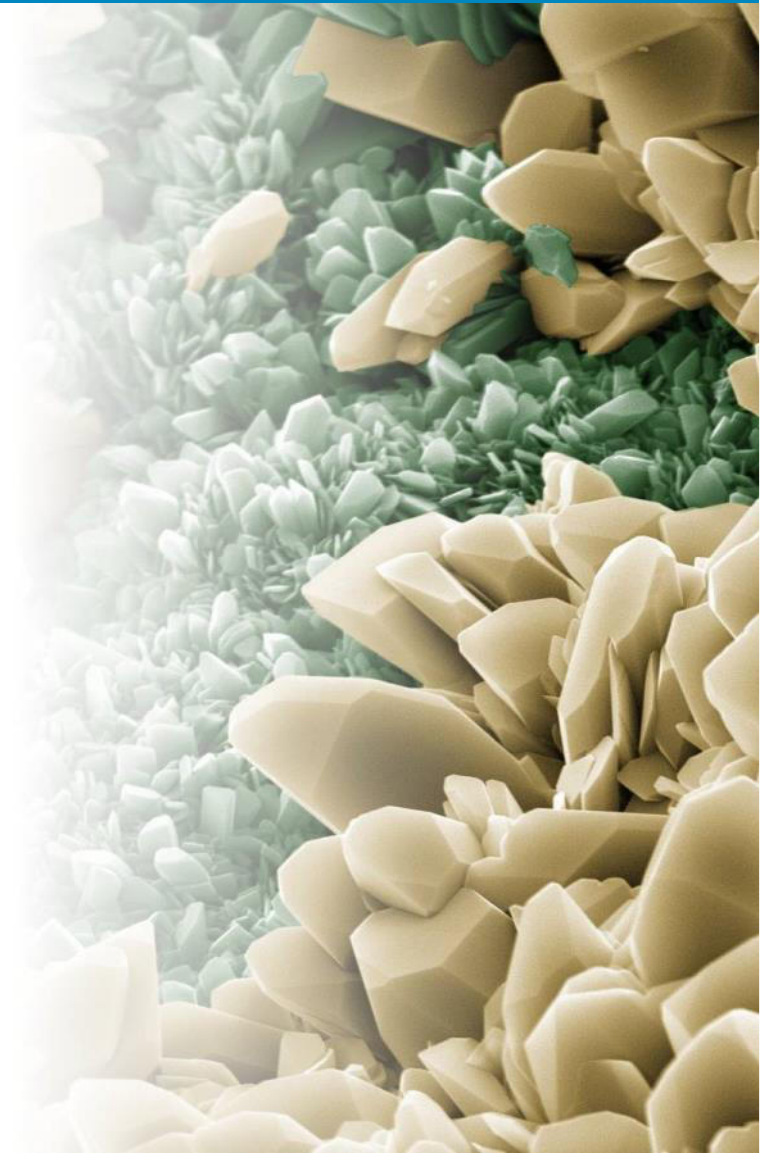
Micro-absorption



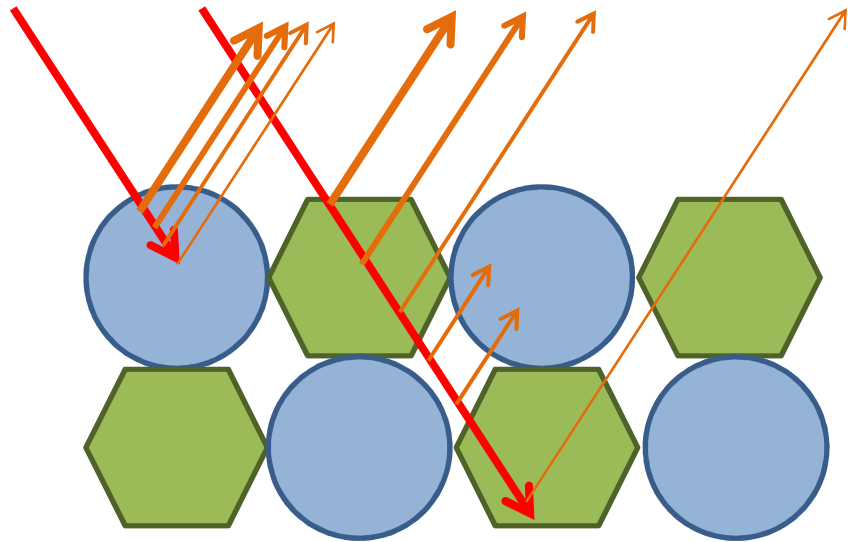
Phase 1: High absorption coefficient for X-radiation



Phase 2: Low absorption coefficient for X-radiation

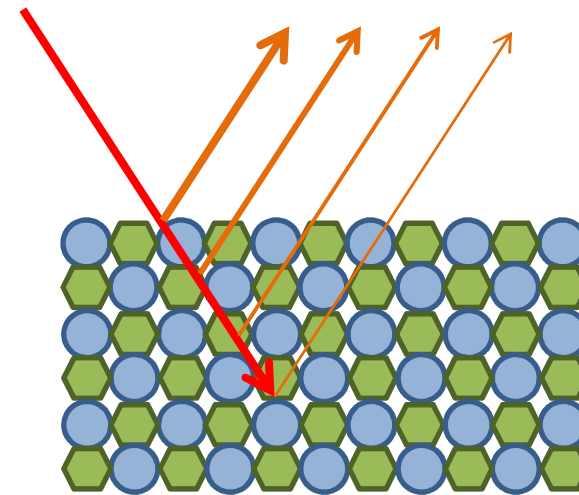


Micro-absorption



Strong attenuation by phase 1
Large particles absorb significant part of the radiation.
→ Small volume of interaction

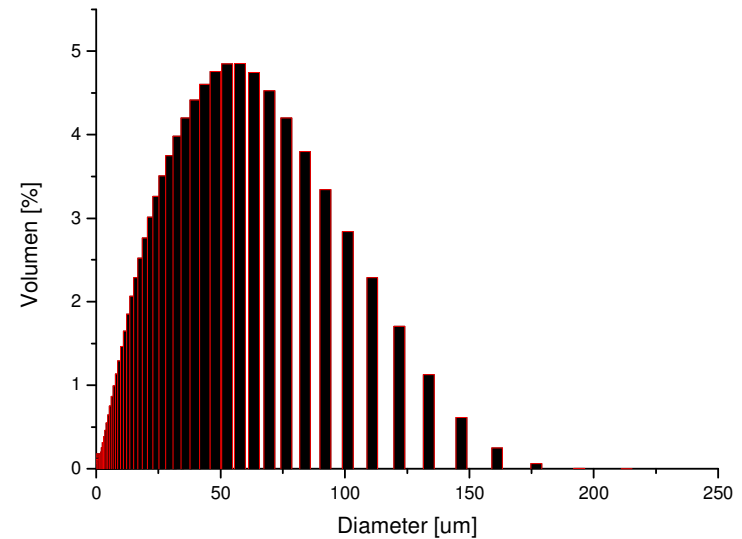
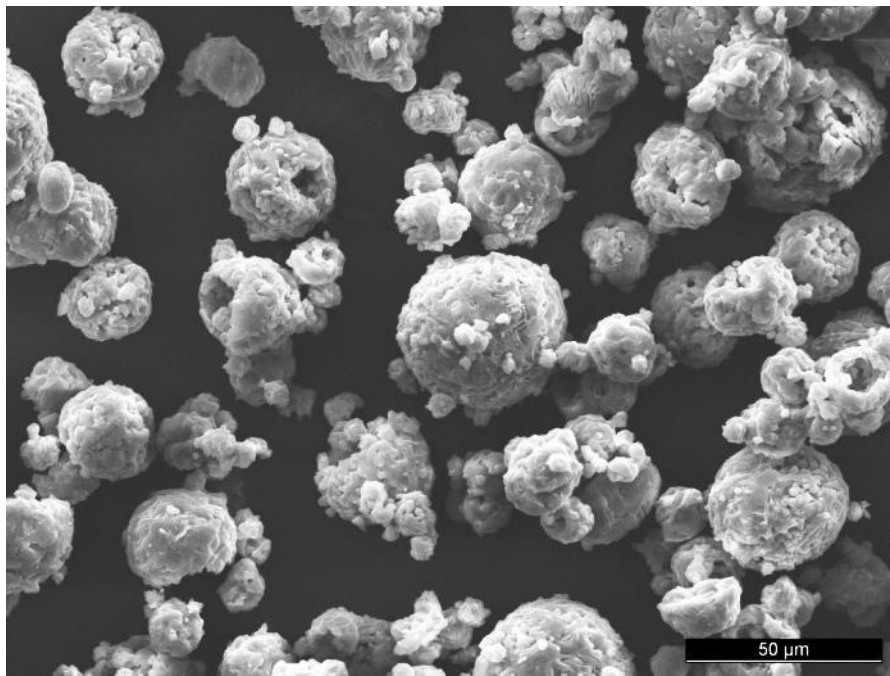
Weak attenuation by phase 2
→ Large volume of interaction



Small particles absorb insignificant part of the radiation.
→ Volumes of interaction with phases 1 & 2 are representative for phase composition

Micro-absorption and Brindley Correction

Micro-absorption can be corrected,
but mean particle* size must be known.



*not crystallite size

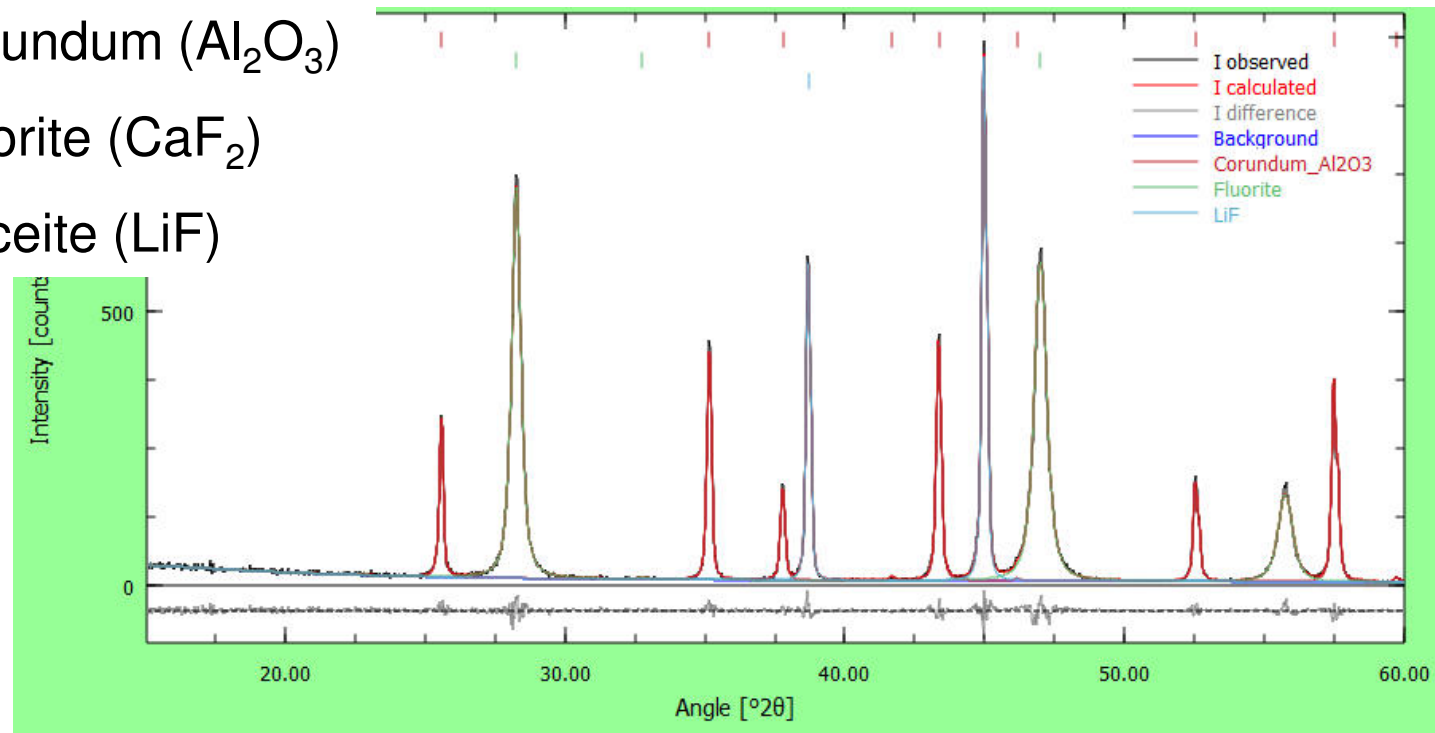
Example 4 – Micro-Absorption

Reference mixture:

33.33 wt-% Corundum (Al_2O_3)

33.33 wt-% Fluorite (CaF_2)

33.33 wt-% Griceite (LiF)



Global Parameters and GOALS

C:\Users\doebelinn\Desktop\Examples-Test\Lesson 7\Example 4\ex4-file1.lst

$R_{wp}=7.54\%$, $R_{exp}=13.39\%$, $X^2=0.5631$

Parameter / Goal	Value	ESD
corundum/(corundum+fluorite+lif)	0.3348	0.0038
fluorite/(corundum+fluorite+lif)	0.3001	0.0029
lif/(corundum+fluorite+lif)	0.3651	0.0034

Wrong phase quantities

Example 4 – Micro-Absorption

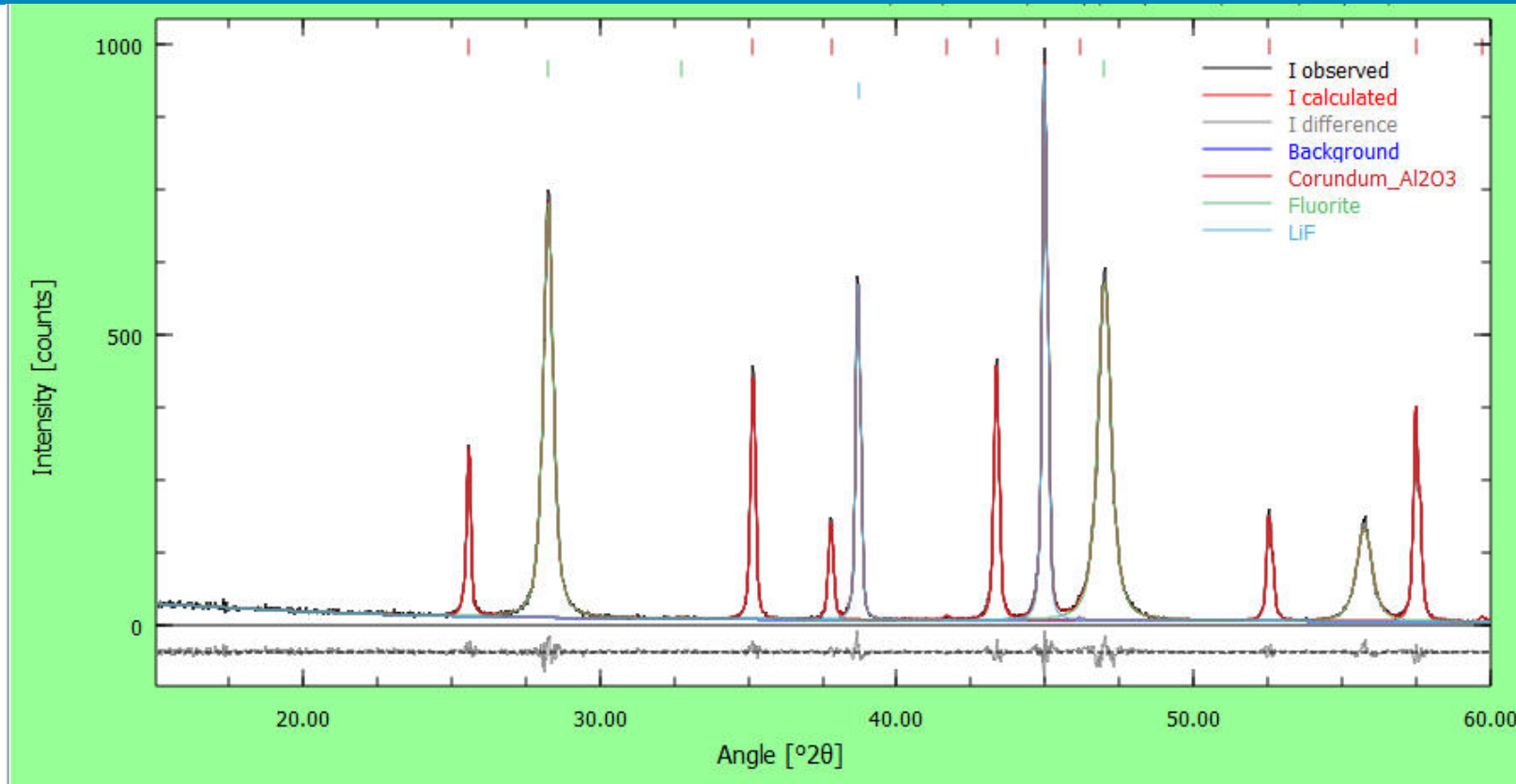
Add mean particle diameter (μm) to structure files:

```
lesson5-ex4-file1.dia x lesson5-ex4-file1.sav x lesson5-ex4-file1.lst x Corundum.str x Fluorite.str x LiF.str x
PHASE=Corundum_Al2O3 // 04-004-2852
SpacegroupNo=167 Setting=1 HermannMauguin=R-32/c //
PARAM=A=0.4760_0.4712^0.4808 PARAM=C=1.2993_1.2863^1.3123 //
RP=4 PARAM=k1=0_0^1 k2=ANISO4 B1=ANISO^0.01 GEWICHT=SPHAR8 //
GOAL=GrainSize(1,1,1) //
d=12 //
GOAL=d //
GOAL=my //
GOAL:corundum=GEWICHT*ifthenelse(ifdef(d), exp(my*d*3/4), 1)
E=AL Wyckoff=c x=0.0000 y=0.0000 z=0.3522 TDS=0.00224764
E=O-2 Wyckoff=e x=0.3062 y=0.0000 z=0.2500 TDS=0.00271875
```

Corundum: 12 μm
Fluorite: 10 μm
LiF: 9 μm

μy (μ) = mass absorption coefficient
(calculated automatically by BGMN)

Example 4 – Micro-Absorption



Global Parameters and GOALS

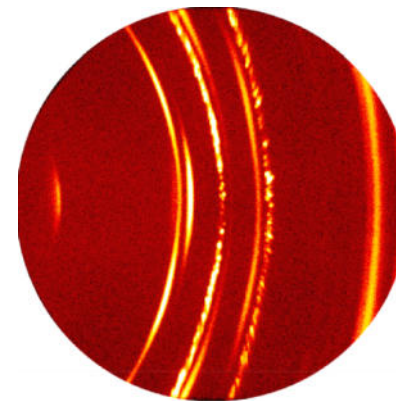
C:\Users\doebelinn\Desktop\Examples-Test\Lesson 7\Example 4\ex4-file1.lst
 $R_{wp}=7.54\%$, $R_{exp}=13.39\%$, $\chi^2=0.5631$

Parameter / Goal	Value	ESD
corundum/(corundum+fluorite+lif)	0.3337	0.0038
fluorite/(corundum+fluorite+lif)	0.3347	0.0031
lif/(corundum+fluorite+lif)	0.3317	0.0033

Example 4 – Micro-Absorption

Micro-Absorption and Brindley correction:

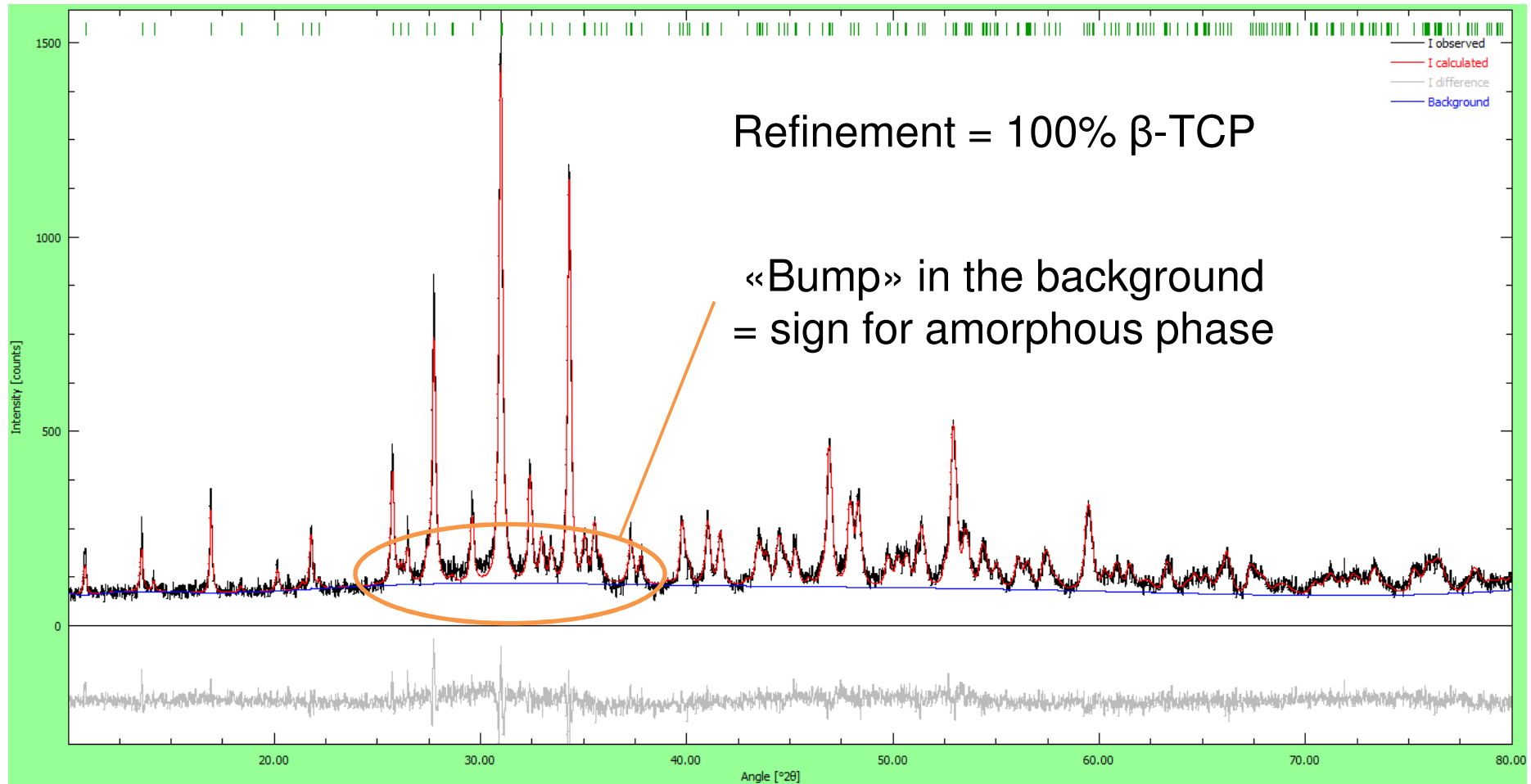
- Try to avoid the problem in the first place (keep particle size close to 1 μm)
- Additional information (particle size from SEM, PSD analysis) required for all refined phases!
- Large particles still lead to grainy diffraction patterns. Brindley-correction does **not** solve this problem!



Bruker AXS

Example 5 – Amorphous Content

Question: Does this sample contain amorphous material?

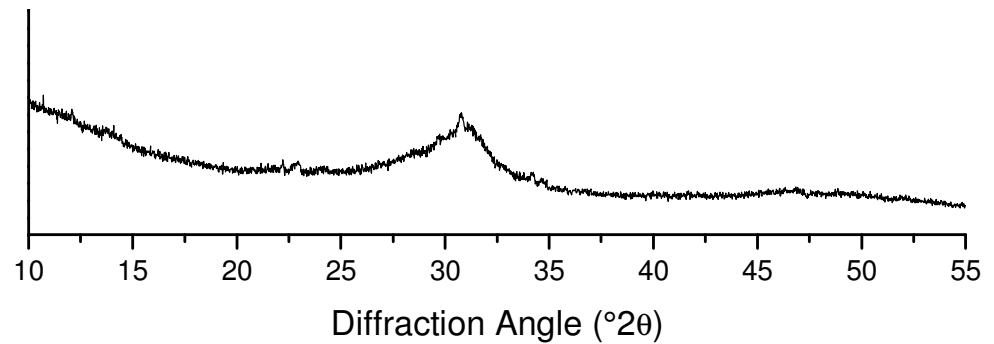


Example 5 – Amorphous Content

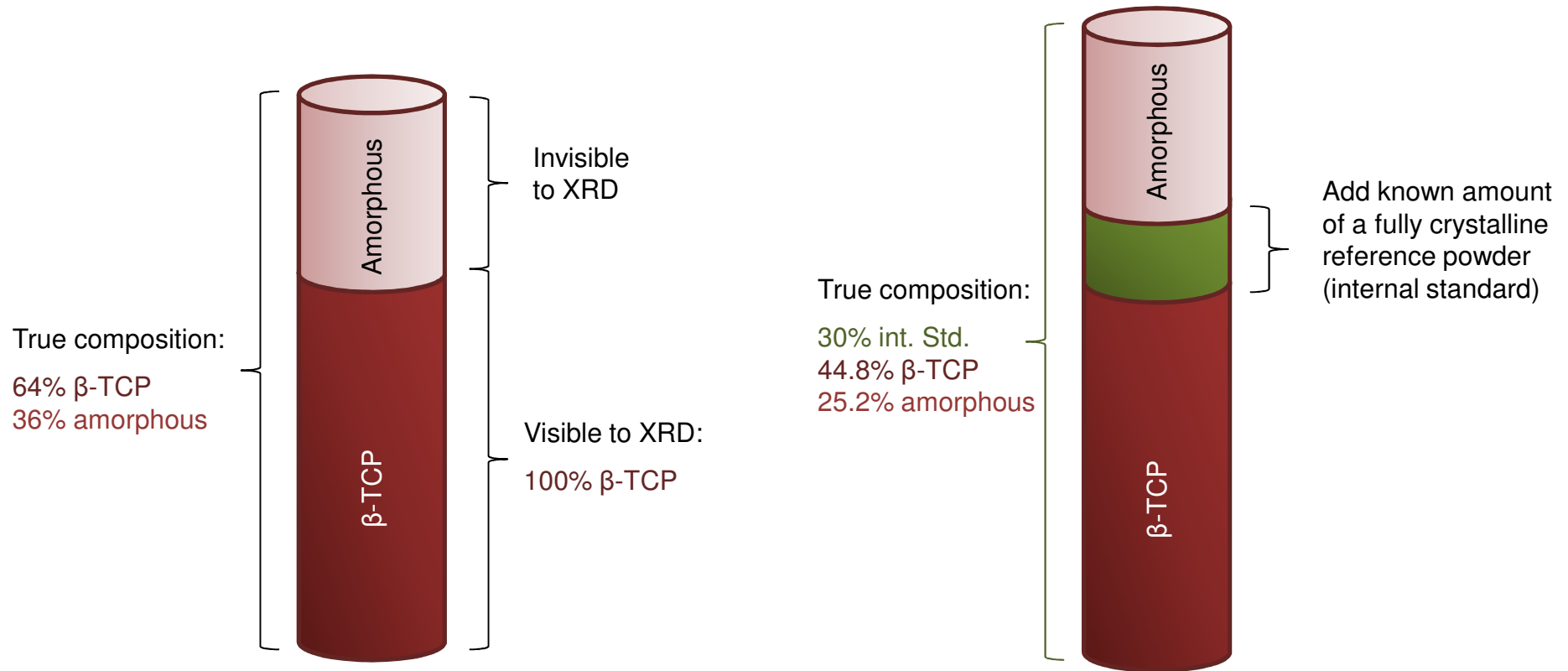
Problem: Amorphous phases

- Don't produce a distinct diffraction pattern
- Create a broad bump around $30^\circ 2\theta$

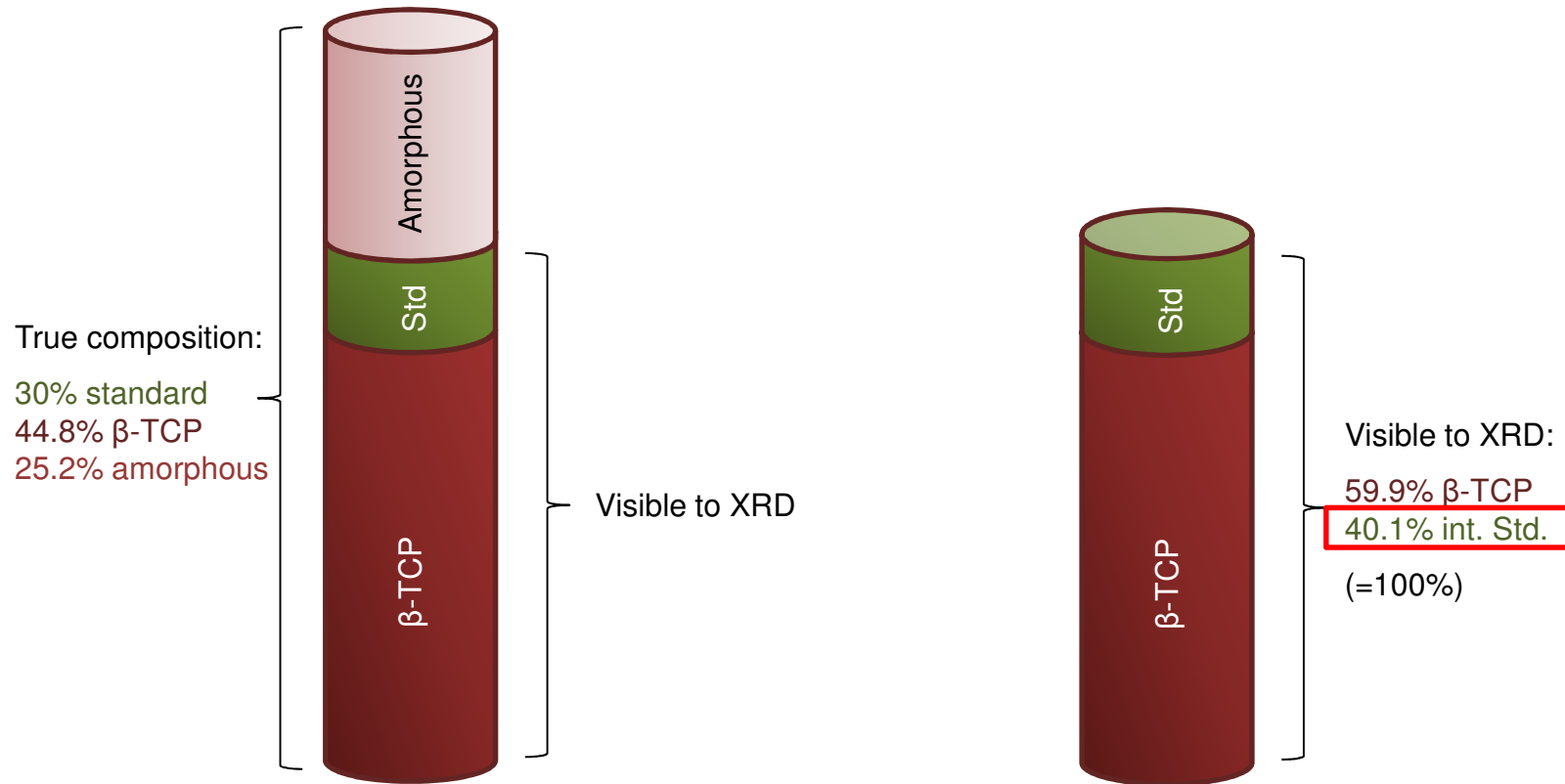
Most common solution:
Internal Standard



Example 5 – Amorphous Content

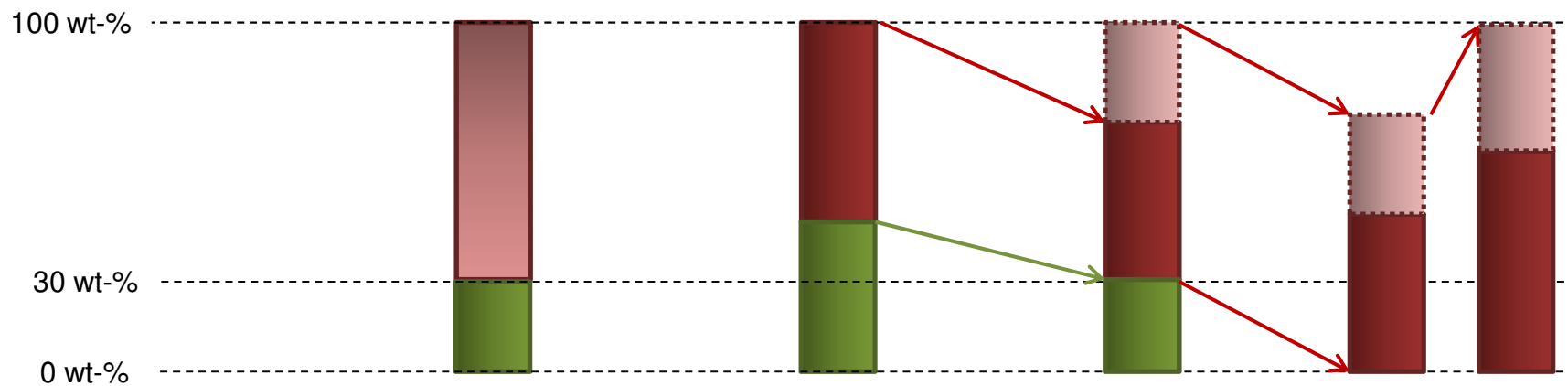


Example 5 – Amorphous Content



Example 5 – Amorphous Content

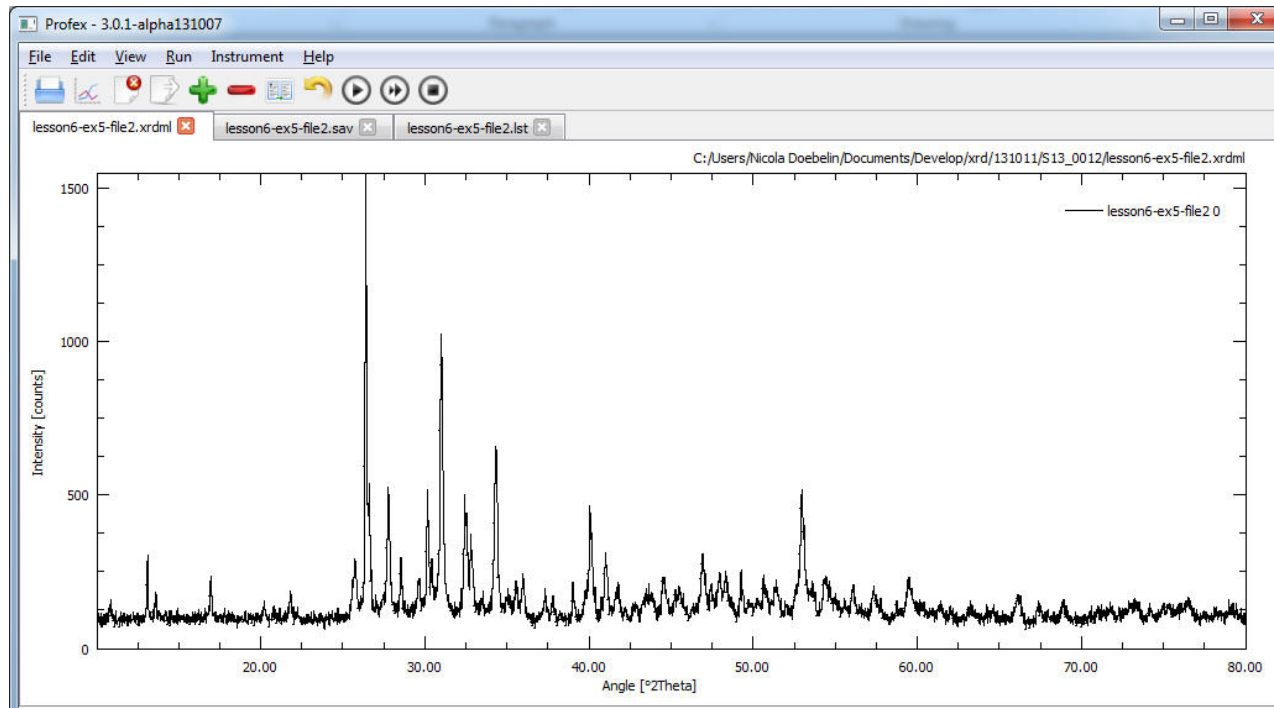
Phase	Mixed	Refined	Normalized to int. Std.	Normalized w/o int. Std.
Amorphous	?	-	Fill up to 100% = 25.2 wt-%	36 wt-%
β -TCP	?	59.9 wt-%	$59.9 * 0.748 =$ 44.8 wt-%	64 wt-%
Internal Standard	30.0 wt-%	40.1 wt-%	$40.1 * 0.748 =$ 30.0 wt-%	-



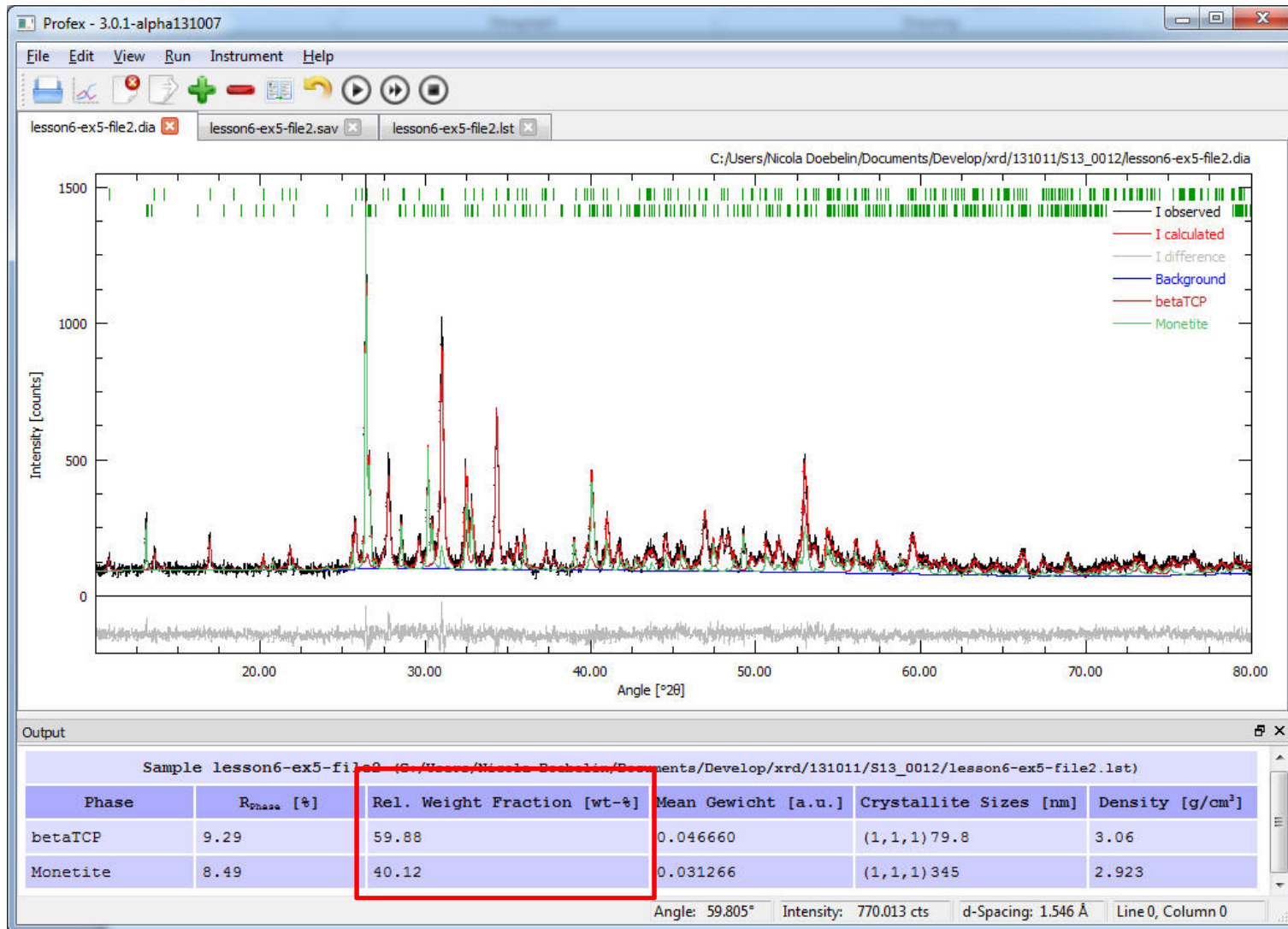
Example 5 – Amorphous Content

Example 5 File 2

Sample	β -TCP + amorphous phase	70 wt-%
Internal Standard	Monetite	30 wt-%

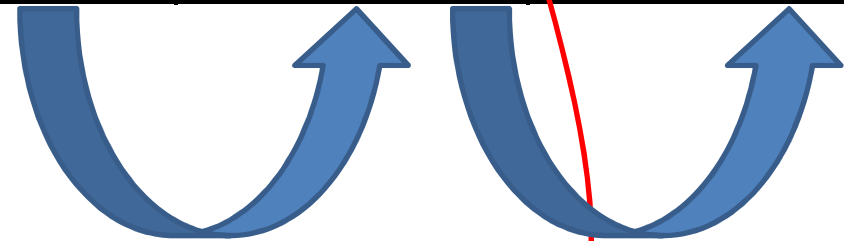


Example 5 – Amorphous Content



Example 5 – Amorphous Content

Phase	Mixed	Refined	Normalized to int. Std.	Normalized w/o int. Std.
Amorphous	?	-	25.22	36.03
b-TCP	?	59.88	44.78	63.97
Internal Standard	30.00	40.12	30.00	-



$$* \frac{30.00}{40.12}$$

$$* \frac{100.00}{70.00}$$

Gap between (44.78 + 30)% and 100%

Example 5 – Amorphous Content

Challenge: Selection of internal standard material:

- Must be 100% crystalline
- Simple structure (cubic)
- No texture or micro-absorption problems
- Absorption coefficient similar to matrix
- Absolutely homogeneous mixing
- Must not react with sample matrix

Common materials:

- Si
- LiF

Monetite was a bad choice:

- Triclinic
- Large crystals (micro-absorption)
- Severe texture effects

