Example: Quartz SiO_2

Last update 23.03.2021

Data	Topic	Level
Electron diffraction (sequential continuous rotation)	Data reduction, structure solution + refinement	easy

Input data

Data

Electron diffraction data were measured on a transmission electron microscope FEI Tecnai G2 20 (CCD detector, 200 kV acceleration voltage, λ = 0.02508 Å).
100 frames, each covering a goniometer tilt of $\Delta\alpha$ = 1.0°, exposure time = 2 seconds
Crystal tracking was used to follow the movement of the crystal.

Input files

Folder "EDpatterns": contains 100 measured diffraction patterns in TIF format
Folder "refinements": reference Jana files of all refinement stages
Folder "reference_cif_pets": reference output files from PETS2

Qtz.pts as input file to PETS2:

```
lambda 0.02508
geometry continuous      # data recorded with continuous-rotation geometry
omega 0.0
phi 0.5                  # semi-angle of the covered angular range Δα of one frame
virtualframes 2 1 1      # data from subsequent frames are merged into virtual frames
# The idea of virtual frames is to assure that the dynamical calculation of rocking curves avoids that incomplete or partial intensities are determined. Only fully integrated intensities should contribute to the refinement.

Aperpixel 0.003700
noiseparameters 3.5 70

beamstop no

dstarmax   1.8
dstarmaxps  2.0
i/sigma    5.0   5.0
reflectionsize 10

# The concept of virtual frames is described in Klar et al. (2021) submitted
```

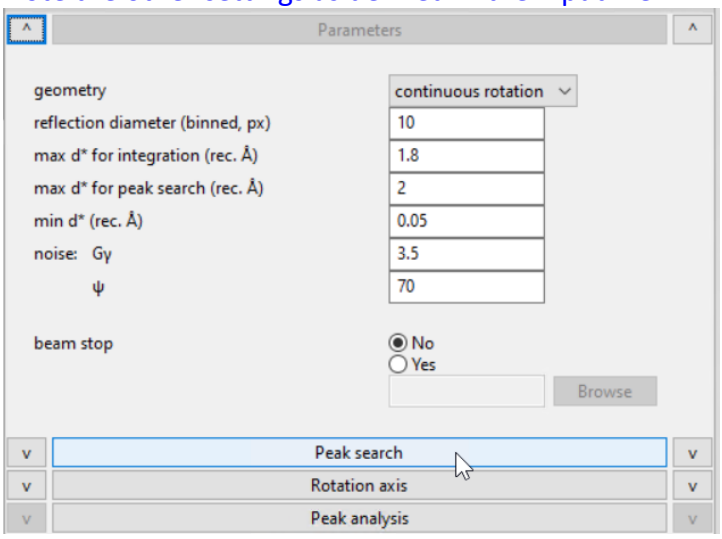
Keywords

Continuous rotation, synthetic nanocrystal

PART 1 - Data treatment in PETS2.0

1. *Peak search*

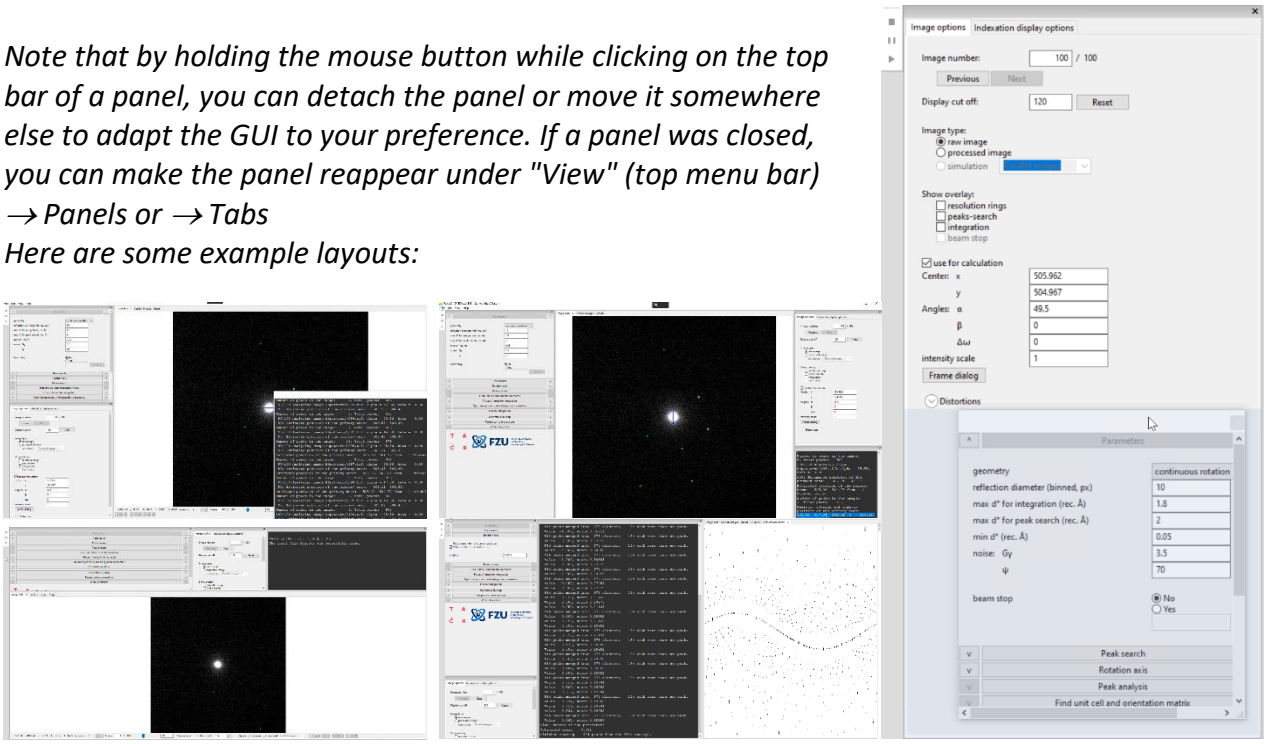
Start PETS2 by double clicking the executable "pets2.exe"
Main menu bar: "File"→"Open"
Locate and open the file Qtz.pts
Open the "Parameters" menu by clicking on the arrow ("v")
Check that the "geometry" is set to "continuous rotation"
Note the other settings as defined in the input file



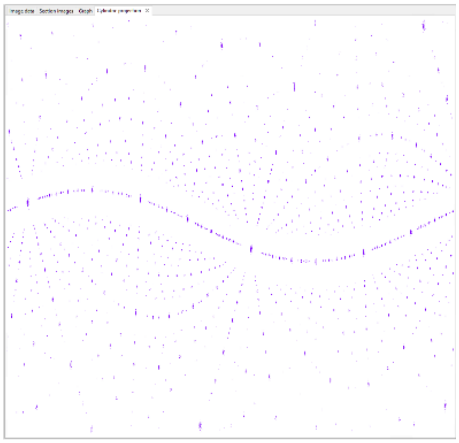
Click the action button “Peak search”.
Use default settings. The progress can be followed in the "Image data" panel.
In the console, for each frame the estimated position of the primary beam, the number of Friedel pairs and the number of significant peaks is given. If you cannot see the console, activate View → Panels → Console. The process ends with the following message in the console:

```
505.92  507.84  509.54  |    504.36  506.26  509.54
Finished reading    914 peaks from the file Qtz.rpl.
```

Note that by holding the mouse button while clicking on the top bar of a panel, you can detach the panel or move it somewhere else to adapt the GUI to your preference. If a panel was closed, you can make the panel reappear under "View" (top menu bar) → Panels or → Tabs
Here are some example layouts:



2. Rotation axis and peak analysis



Click on the action button “Rotation axis”
In the “Cylindric projection” panel, a cylindrical projection of the difference space of the extracted peak positions is displayed. A correct azimuthal angle refinement results in the image containing sharp peaks aligned on sinusoidal curves. This step provides a first estimate of data quality. The refined omega angle is 0.531 degrees.
Click the action button “Peak analysis”.
Click “Peak analysis (continue)”
Click “Peak analysis (continue)”

3. Automatic unit cell and orientation matrix

Click “Find unit cell and orientation matrix”
Click on “Find possible cells automatically”
Open the "Refine cell" menu
Select “hexagonal” symmetry
Click “Refine Cell”
Leave the indexing panel by clicking “Finish”

	a	b	c	α	β	γ
cell:	4.9228	4.9228	5.4011	90.000	90.000	120.000
s.u.:	0.0013	0.0013	0.0010	0.000	0.000	0.000

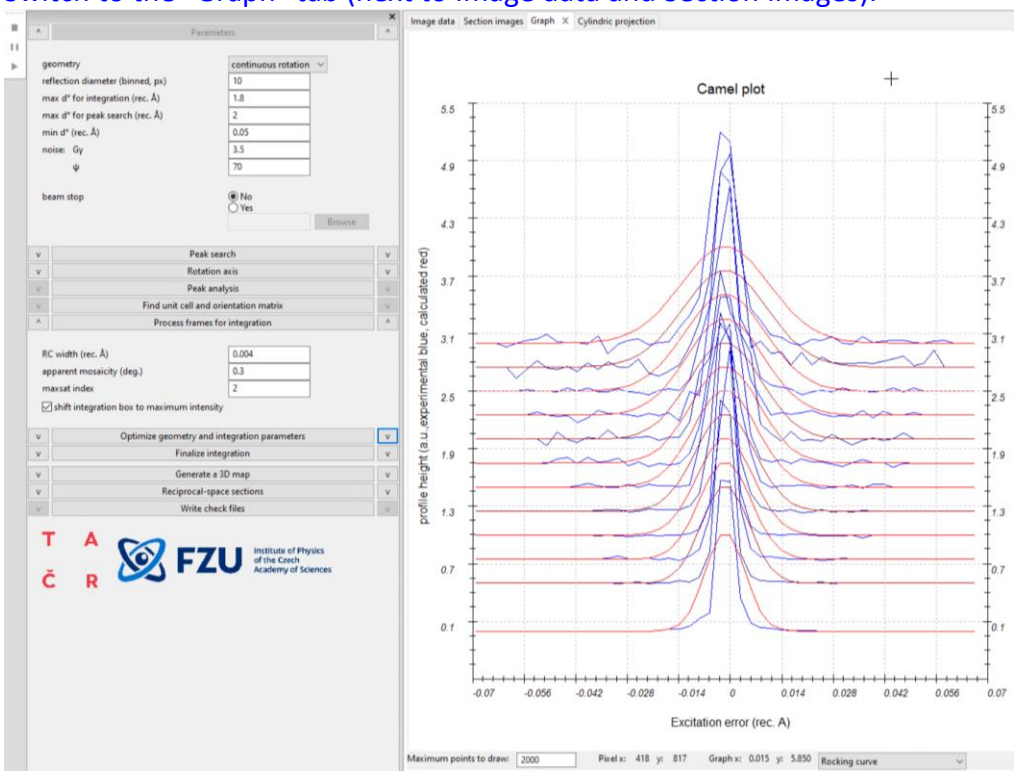
Orientation matrix

0.069796	0.048844	-0.176304
-0.222017	-0.080221	-0.052738
0.029265	0.214938	0.020382

The orientation matrix and unit cell parameters are written to the file qtz.cellist.

4. Integrate intensities

Open the menu "Process frames for integration"
Increase RC width to 0.004 (rec. Å) and the apparent mosaicity to 0.3 (degrees).
We will assume an extremely broad rocking curve to make sure that reflections are integrated on all frames and later adapt the profile parameters.
Click "Process frames for integration"
Switch to the "Graph" tab (next to Image data and Section images).



Typical values of RC width are 0.0005 to 0.002 Å^{-1}. The mosaicity for a very good data set is below 0.05°, but may easily exceed 0.2°. A large mosaicity and irregular profile shape may also indicate incorrect frame orientations. In this case, the nominal frame orientations are quite good. We will now manually adapt the RC width and (apparent) mosaicity until we observe a good fit between the calculated (red) average rocking curve and the observed average rocking curve (blue) for all resolution shells (bottom: lowest-resolution shell, top: highest-resolution shell). We will first adapt the RC width only looking at the lowest-resolution shell (blue curve at the bottom) because the rocking curves of these reflections are least affected by the mosaicity.

Decrease RC width to 0.002 (rec. Å) and hit enter

The bottom red curve is still a bit too broad

Decrease RC width to 0.0015 (rec. Å) and hit enter

This seems to fit OK

Decrease mosaicity to 0.15 (deg.) and hit enter

The red curve is still too broad at higher resolutions.

Decrease mosaicity to 0.1 (deg.) and hit enter

The red curve is still too broad at higher resolutions.

Decrease mosaicity to 0.05 (deg.) and hit enter

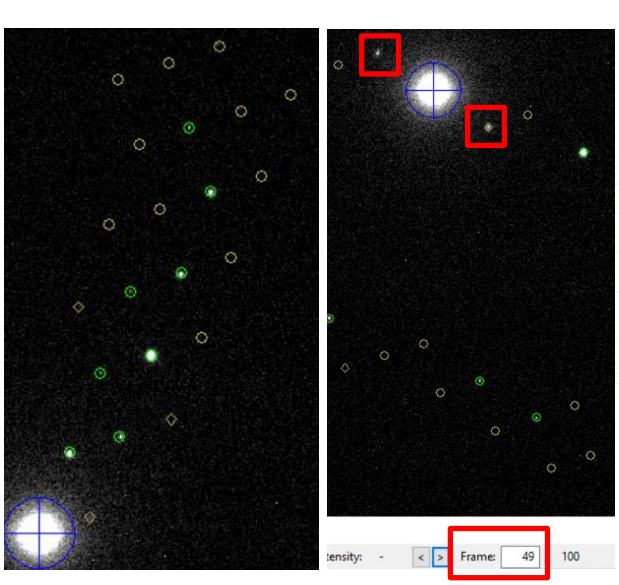
This seems to be OK. As the Δα between frames is 1°, the rocking curves are not well sampled, and it is difficult to determine accurate profile parameters. As the main goal is to correctly place the integration masks, this fit is OK.

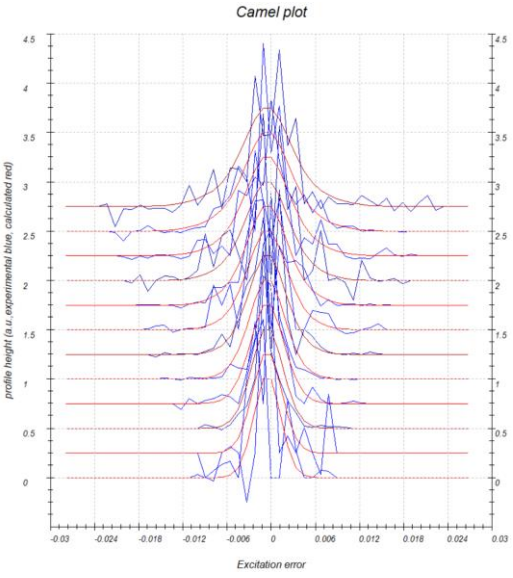
Run again "Process frames for integration" with RC width 0.0015 and mosaicity 0.05

Check the frames and the integration masks in the "Image data" tab.

Every visible reflection should be encircled. On neighboring frames, the circles should disappear (or become diamonds) only if the reflection intensity is 0. Only on frame numbers 48, 49, 50, 55, and 58 there are visible reflections that are not integrated. However, these reflections are the strongest reflections of the data set and in all cases the reflections are integrated on the frames where the reflections are strong.

All reflections seem to be properly integrated. Therefore, we will skip the step of optimizing the frame orientations here as we may expect only a minor improvement. The average rocking curve actually does not look very promising, but this is mainly attributed to the large goniometer steps (1°) combined with a high resolution of the excitation error in this plot.

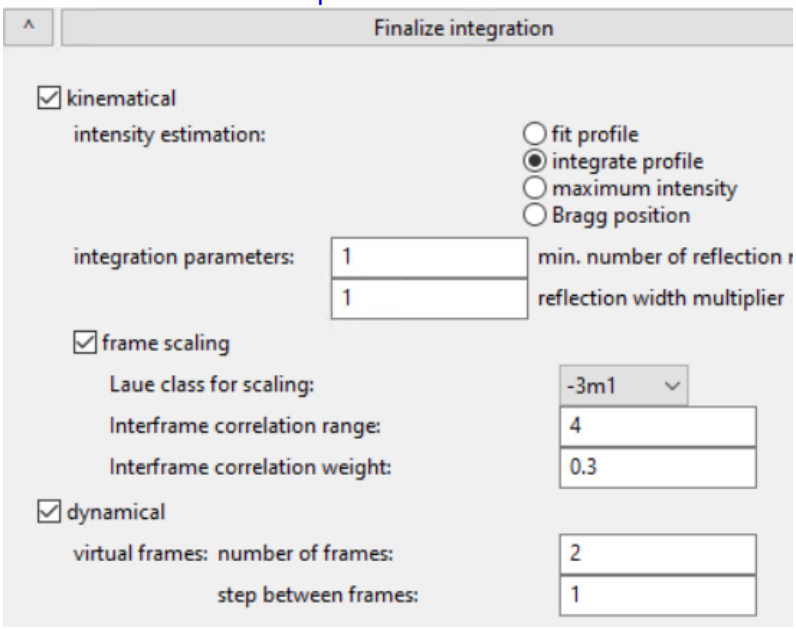




5. *Generate output file for structure determination*

Usually, we would determine first the space group by generating reciprocal-space sections. However, this standard procedure is well described in many other tutorials and is skipped here. From now on, we assume that the point group is -3m1 and the space group is $P3_121$ (or $P3_221$).

Open the "Finalize integration" menu
Check the checkbox "kinematical"
Select the radio button "integrate profile"
Check the checkbox "frame scaling"
Select "Laue class for Scaling": -3m1
"Interframe correlation range": 4
"Interframe correlation weight": 0.3
Check the checkbox "dynamical"
Set the “virtual frames” parameters to number of frames = 2 and step between frames = 1.



Click on “Finalize integration”

```
Laue class   Rint(obs)    Rint(all)    Nobs/Nall   redundancy
-3             17.59        20.11     292/  468        3.338
-31m           42.21        44.14     195/  272        5.743
-3m1           18.70        20.99     204/  294        5.313
6/m            42.81        44.51     187/  256        6.102
6/mmm          43.43        44.86     138/  177        8.825
```

From these stats we expect that the point group symmetry is -3m1.

Two output files (apart from the log files) are generated:
Qtz.cif_pets is the list of reflections for structure solution and kinematical refinement.
Qtz_dyn.cif_pets is the list of reflections for dynamical refinement.

PART 2 – Structure solution and kinematical refinement

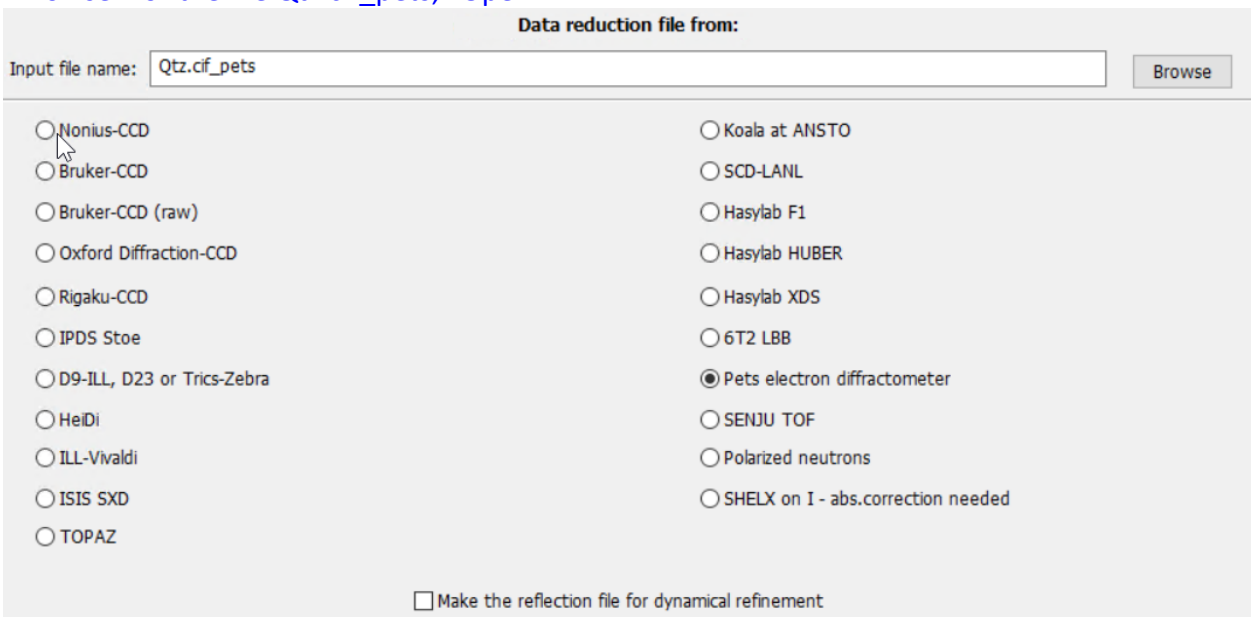
1. *Create new structure*

Important! The data-processing procedure is almost never perfectly reproducible. Small differences in the indexing and cell refinement procedure may result in small differences of integrated intensities. If you want to be sure that you can reproduce the following part of the tutorial, do not use the file Qtz.cif_pets that you have just created, but use the file from the

folder "reference_cif_pets" provided with the example files. Using your own cif_pets file is also possible, but your results may differ from the results described in this tutorial.
Create a new subfolder “Jana” and copy Qtz.cif_pets into this folder
Start Jana2020
Main menu bar: "Structure" → "New"
Locate the folder Jana
Enter “quartz” as filename; “open”
This starts a new structure determination with jobname quartz in the new subfolder “Jana”.

2. Import Wizard

The data import is automatically started.
[On the screen: Specify type of the file to be imported]
Select “known diffractometer formats”; NEXT
Select the format: “Pets electron diffractometer”
"Browse" for the file Qtz.cif_pets; “Open”



NEXT
[On the screen: Complete/correct experimental parameters]
The unit cell parameters, radiation type and wavelength are correctly set. The sample was measured at room temperature.
NEXT
[On the screen: Define the reference cell]
We do not want to change anything here.
NEXT
`1562 input reflections were properly handled.`
OK
[On the screen: Define parameters for absorption and scaling procedure]
NEXT
`The import wizard is complete. As a next step you can import another or modify the previously imported ones.`
FINISH; OK;

3. *Symmetry wizard*

The symmetry wizard starts automatically after the import wizard. The symmetry wizard can be started separately by expanding "Reflection file" in the Command tree and selecting "Make space group test".

NEXT

We may adapt the tolerances for the determination of the crystal system and space group recognition. In this case, this is not needed.

Deselect "Search for higher symmetrical supercell"

NEXT;

Select "Ordered by R(int)"

Select Laue point group

Crystal system	Point group	Rint(obs/all)	#averaged(obs/all)	Redundancy
Triclinic	-1	11.74/14.08	460/805	1.94
Trigonal	-3	17.46/20.11	288/468	3.338
Trigonal	-3m1	18.61/20.98	203/294	5.313
Monoclinic-setting "c"	2/m	35.93/37.98	334/510	3.063
Orthorhombic-setting "-a-b,a-b"	mmm	37.79/39.72	289/417	3.746
Orthorhombic-setting "b,-2a+b"	mmm	38.03/39.94	233/332	4.705
Orthorhombic-setting "a,a+2b"	mmm	41.30/43.22	236/352	4.438
Trigonal	-31m	42.18/44.16	193/272	5.743
Hexagonal	6/m	42.74/44.52	187/256	6.102
Hexagonal	6/mmm	43.34/44.88	137/177	8.825

○ Ordered by Laue symmetry Details

◉ Ordered by R(int)

Assuming that we have never heard of quartz before and we do not know the structure, we expect trigonal or hexagonal symmetry from the unit cell parameters. From the Rint overview during the data reduction with PETS2.0 we expect the point group -3m1, which also has a reasonable Rint in this overview.

Choose the point group "-3m1"; NEXT

[On the screen: Select cell centering]

Select "P"

We assume a primitive unit cell without R centering

NEXT

[On the screen: Select space group]

Space group	Characteristics for systematically absent reflections		
	#obs/#all	ave(I/sig(I))	Figure of merit
P-3m1	0/0	--------/--------	1.00000
P3m1	0/0	--------/--------	1.00000
P321	0/0	--------/--------	1.00000
P3221	4/12	7.395/3.192	2.76820
P3121	4/12	7.395/3.192	2.76820

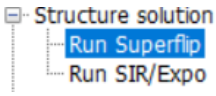
4 observed reflections violate the space group $P3_221$ and $P3_121$. This may be attributed to dynamical diffraction effects.

Choose the space group "P3121"

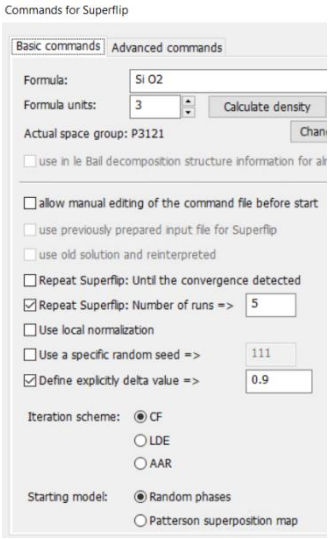
Note that $P3_221$ and $P3_121$ form a pair of chiral space groups. Successful structure solutions in the two space groups are related by mirror symmetry and exhibit different absolute structure.

Within the kinematical approximation, the two corresponding enantiomorphs cannot be distinguished because both result in identical R factors. We will determine the correct absolute structure later when we perform the dynamical refinement.
NEXT
[On the screen: Final step of space group test]
FINISH
[On the screen: Processing refinement reflection file for Block1…]
In the next step the reflection file is generated from the hkl input file taking the determined symmetry into account.
NEXT;
`782/1562 reflections read from input file`
OK; OK;
Select "Perform averaging"
(At the bottom) "Sigma(I(ave)) from": Equivalents
PETS provides uncertainties based on detector and counting statistics. Due to the systematic errors introduced by the kinematical approximation, it is often advantageous to determine the standard uncertainties from reflection intensity statistics
NEXT
`Summary after averaging`
`Rint(obs/all) = 10.88/20.19 for 186/466 reflections …`
OK; FINISH
OK

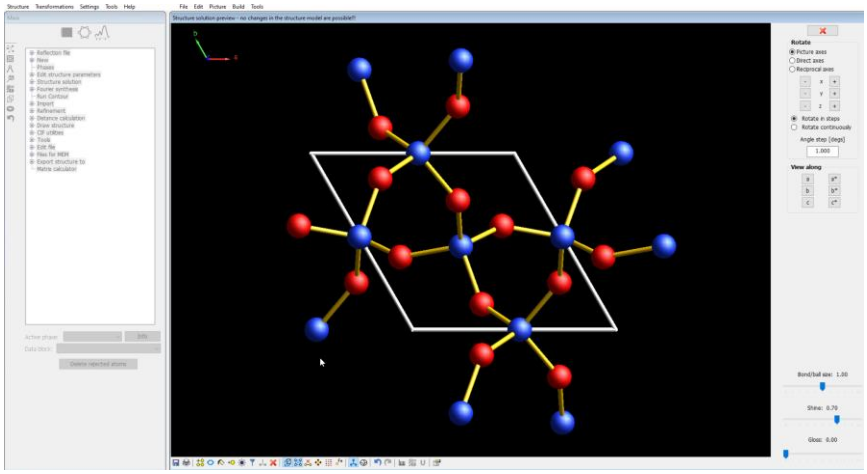
4. Structure solution

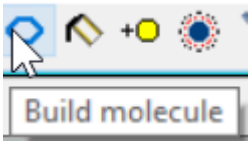


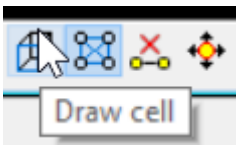
After finishing the symmetry wizard, the structure solution program starts automatically. If you need to start it manually, expand "Structure solution" in the Command tree of Jana2020 and double click "Run Superflip".



Enter the chemical formula: Si O2
Formula units: 3
Repeat superflip: Number of runs: 5
Iteration scheme: CF
Starting model: Random phases
For peak search use: EDMA – fixed composition
“Run superflip”
The structure is solved by superflip.
OK
“Draw structure”
Use the “Build molecule” and “draw cell” option at the bottom to get a clearer visualiization.



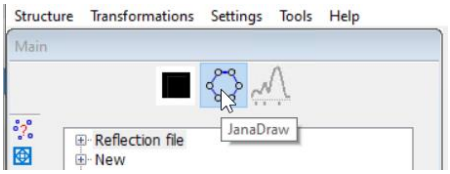




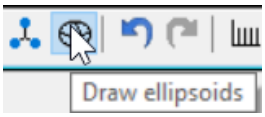
The tetrahedral network looks like a reasonable structure solution.
Klick on the red “X” (top right) to close JanaDraw
“Accept last solution”
[refinements/quartz_4+solution is the current state of the Jana files]

5. *Kinematical refinement*

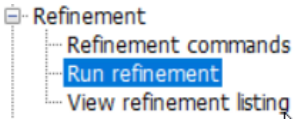
Activate "JanaDraw" mode by clicking on the 6-ring above the command tree
In the command tree expand "Refinement"
Double click "Refinement commands"
Set "Number of cycles" to 20
Uncheck "Refinements on F(obs)**2"
OK; YES+START



The refinement converges with R(obs)= 19.17% and wR(all)= 22.27%
Right click a red atom in JanaDraw -> "Define/Edit atom parameters"
ADP parameter(s): select "harmonic (anisotropic)"
Click "Select atom(s) from list"
Select "Si1"; OK
ADP parameter(s): select "harmonic (anisotropic)"; OK
In JanaDraw click the icon "Draw ellipsoids"

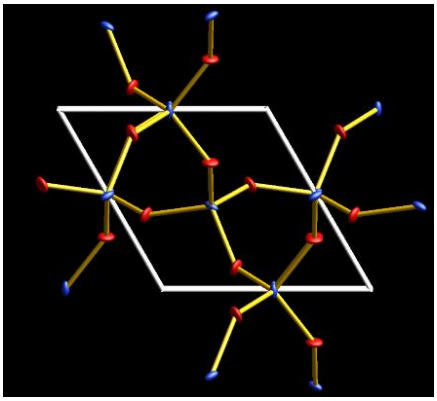


During the next refinement cycles you can follow the structural changes after each refinement cycle.
Double click "Run refinement"

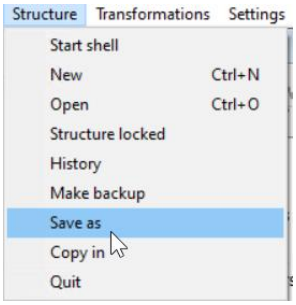


Alternatively, you can use the quick button on the left

`R(obs)= 21.85, wR(all)= 20.46`
The ADP tensors of O1 and Si1 are non-positive definite. This is most likely a result of the systematic errors introduced by the kinematical approximation.
Expand "Edit structure parameters" in the Command tree
Double click "Edit extinction parameters"
Select radio button "SHELX model"
Activate the checkbox next to "EXTI"
OK; YES
Run refinement
The refinement converges with R(obs)= 16.90% and wR(all)= 17.39%



In the literature, kinematical refinements are frequently published with applied extinction correction, which improves the resulting model in terms of R factors and displacement parameters. However, a systematic and thorough investigation of this aspect is not reported in the literature (as far as we know). Thus, this correction should be applied with care. For example, the resulting anisotropic displacement parameters (ADPs) are not necessarily representative for the thermal motion of the atoms. [refinements/quartz_5+adp_exti is the final state of the kinematical refinement]



In the top menu bar: "Structure" → "Save as"
File name: "quartz_dyn"; SAVE
[On screen: Do you want to continue with the new structure?]
YES

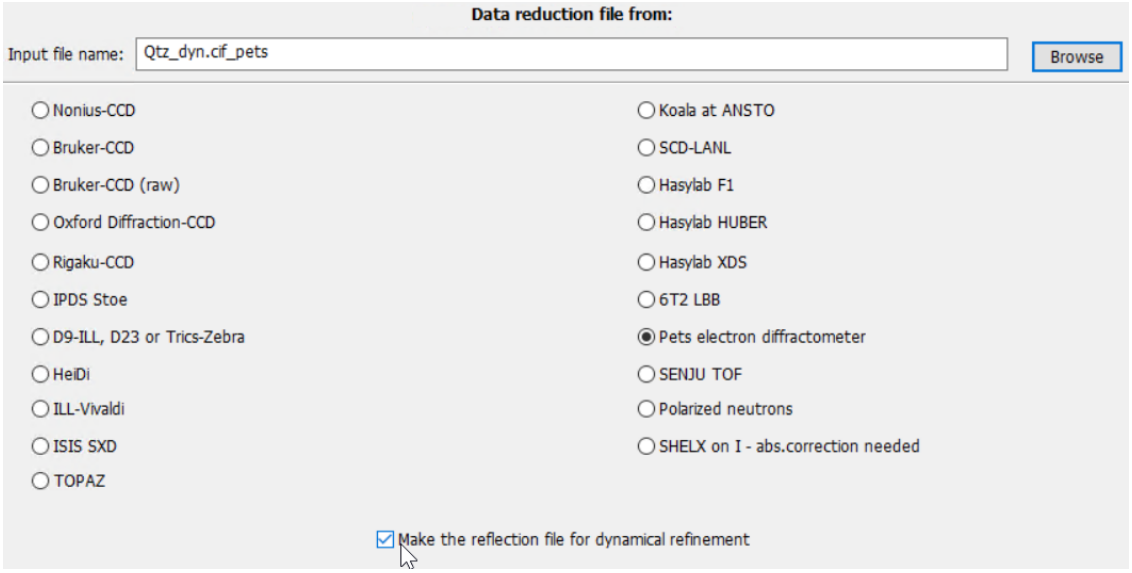
PART 3 – Dynamical refinement

Important! If you want to be sure that you can reproduce the following part of the tutorial, use the file from the folder "reference_cif_pets" provided with the example files. Otherwise there may be minor differences. You may also continue with a copy of "refinements/quartz_5+adp_exti"

6. Import reflection file for dynamical refinement

Copy "Qtz_dyn.cif_pets" from the folder of the data reduction with PETS to the folder "Jana"
In Jana2020: Expand "Reflection file" -> "Import/modify reflection file" (double click)
Click "Delete"; OK;
"Reflection file" -> "Import/modify reflection file" (double click)

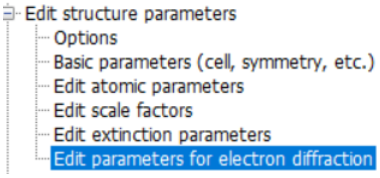
Select "Single crystal": "known diffractometer formats"; NEXT
Select "Pets electron diffractometer"
Click "Browse"; Locate "Qtz_dyn.cif_pets"; OPEN
Check "Make the reflection file for dynamical refinement"; NEXT



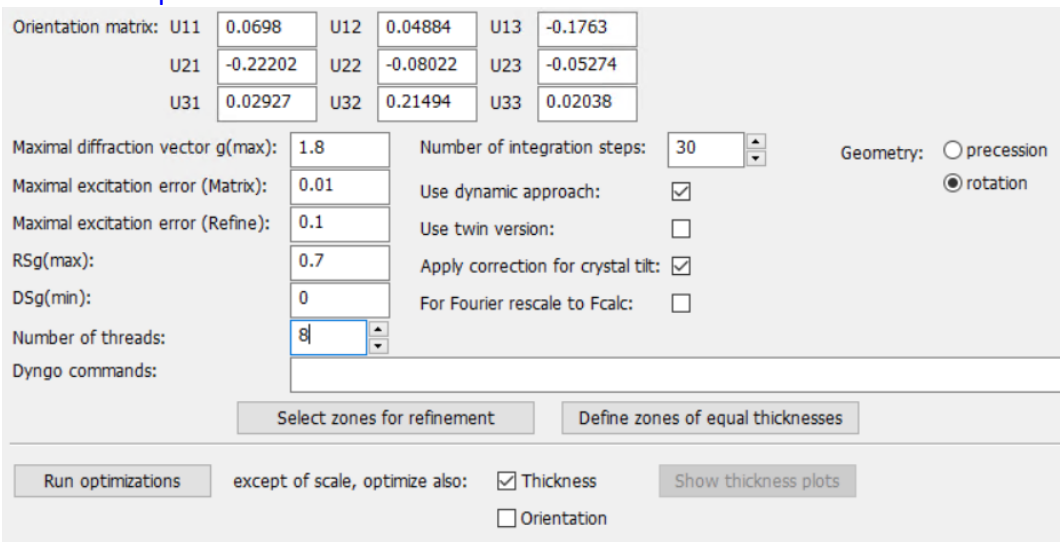
[On the screen: Complete/correct experimental parameters]
Leave the default settings unchanged.
NEXT; NEXT;
`All 6131 input reflections were properly handled`

OK; NEXT; FINISH; OK
[On the screen: Processing refinement reflection file for: Block1…]
Make sure that "Make the reflection file for dynamical refinement" is checked.
NEXT
`2833/6131 reflections read from input file …`
OK; OK; FINISH

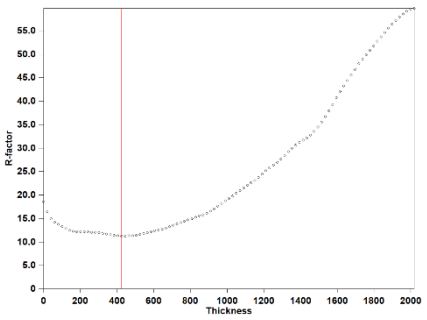
7. *Dynamical refinement setup*



In the command tree (left), expand "Edit structure parameters"
→ "Edit parameters for electron diffraction" (double click)
In the top section on the left:
Set "Maximal diffraction vector g(max)" to 1.8
This g(max) is related to the resolution of the dynamical calculations, which should in general be a bit higher than the resolution of the highest reflections used in the refinement.
Set "RSg(max)" to 0.7
Set "DSg(min)" to 0.0015 ($Å^{-1}$)
RSg(max) and DSg(min) filter out reflections for which an incomplete or unreliable rocking curve integration is expected, e.g. reflections that lie on or are close to the goniometer rotation axis.
Set "Number of threads" to the number of physical cores of your processor
In the top section on the right:
Set "Number of integration steps" to 30
Set "Geometry" to "rotation"
In the section in the middle:
"except of scale, optimize also": check "Thickness"
Click "Run optimizations"



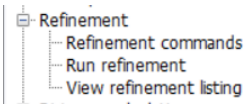
The dependence of R factors of individual virtual frames on the thickness is determined. The initial thickness estimation is necessary to get a stable starting point for the dynamical refinement and to avoid getting stuck in a local minimum.
Click "Show thickness plots"
There are many different curves. Curvers with a well-defined minimum suggest a thickness between 200 and 600 Å.
Close the plot (red X)



Click on “Select zones for editing”; “Select all”; OK.
The EDThick box is yellow and locked because the parameter is not the same for all selected zones.
Click EDThick box; click Unlock and change the value to 400.
This changes EDThick for all zones to 400 Å.
Click on “Select zones for editing”; “Refresh”; OK
By changing number of zone by “Zone#” textbox, we can see that all zones have EDThick 400 Å
Uncheck the checkbox “Thickness”
Click on “Run optimizations”
This will optimize the scale factor for each frame based on a thickness of 400 Å.
OK; YES to save m42 file.
[The current state of the Jana files is refinements/quartz+7_setup]

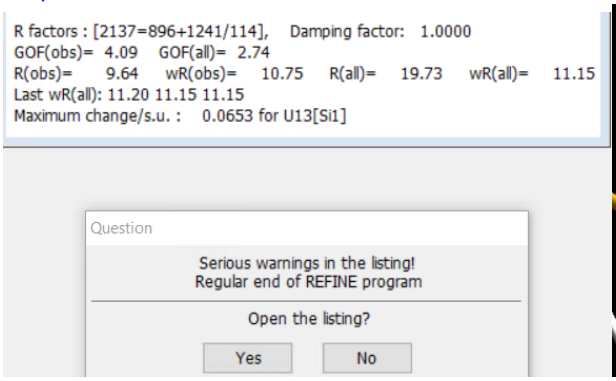
8. *Dynamical refinement and absolute structure determination*

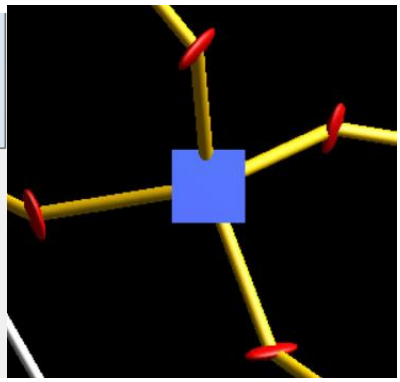
Expand "Edit structure parameters" in the Command tree
Double click "Edit extinction parameters"
Select radio button "None"
OK; YES
Activate JanaDraw mode to see the structural changes after each refinement cycle.
Expand "Refinement" -> "Refinement commands" (double click)



Set "Check for convergence: stop if " 0.2 (in 1 consecutive cycle.)

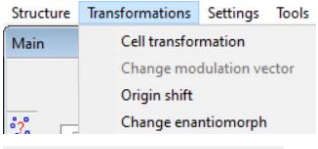
OK; YES+START

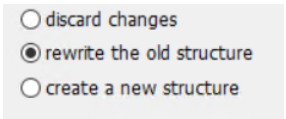




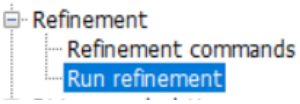
The refinement converges with wR(all)= 11.15%. ADP tensor of Si1 is non-positive definite. This is very surprising for a simple structure. At this initial stage of a dynamical refinement of a non-centrosymmetric structure it is necessary to also refine the inverted structure because at the stage of the structure solution we had no indications about the correct absolute structure. In this case we actually set the absolute structure when we chose $P3_121$ and not $P3_221$ because the space groups themselves are chiral. Jana offers a simple option to invert the structure. The space group is automatically adapted if necessary, i.e., if the space group is chiral.
[The current state of the Jana files is refinements/quartz+8_wrong_enantiomorph]

Structure (top main menu bar) → Save as
Save the structure as “inverted_model”; SAVE
[On the screen: “Do you want to continue with the new structure?”]
YES
Transformations (top main menu bar) → Change enantiomorph
Select “rewrite the old structure”
OK



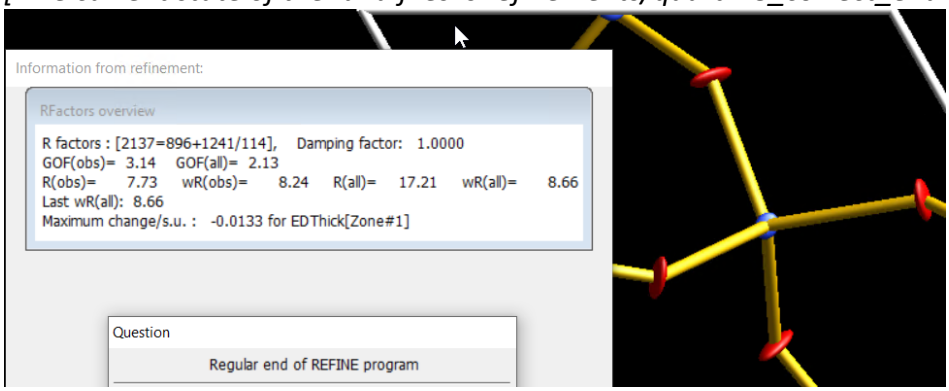


Double-click “Run refinement” in the command tree



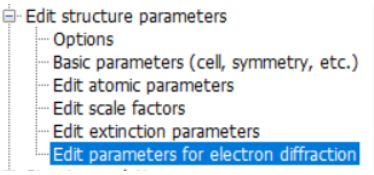
The refinement converges with R(obs) 7.73% and wR(all) 8.66%. The R factors improved significantly, and the ADPs are physically meaningful. These are clear indications, that the absolute structure is now correct.

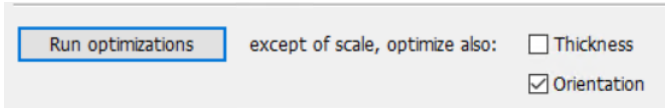
[The current state of the Jana files is refinements/quartz+8_correct_enantiomorph]



9. *Optimize frame orientation*

In the Command tree, expand "Edit structure parameters "
"Edit parameters for electron diffraction" (double click)
Activate "Orientation" and then "Run optimizations"

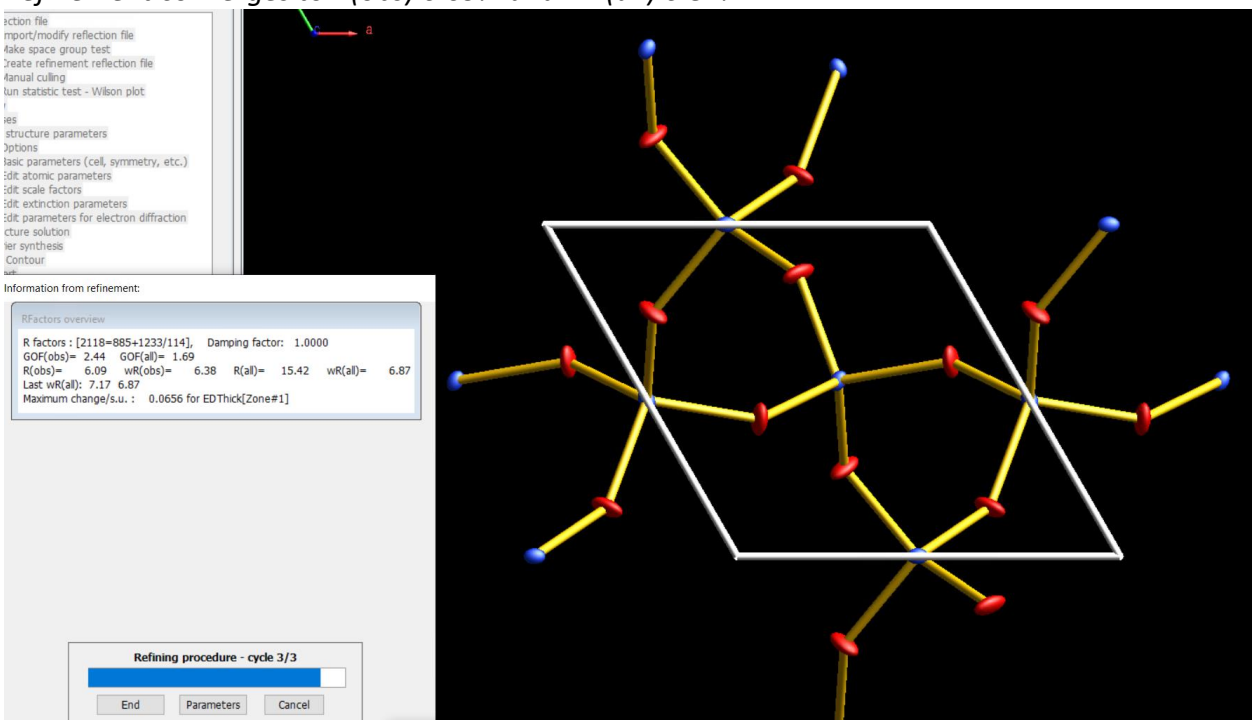




This will adapt the orientation of the frames by minimizing the R factors of all frames. The correction is defined by an azimuth angle "EDphi" and a tilt "EDtheta" for each frame.

"Run refinement" (quick button on the left: )

Refinement converges to R(obs) 6.09% and wR(all) 6.87%.



[The final state of the Jana files is refinements/ quartz_9+orientation_opt]