SGK, Geneva, CH
12-09-2017

FNSNF
Swiss National Science Foundation

Universitet Stockholms
Stockholm University

Structure analysis of polycrystalline materials with electrons and X-rays

Stef Smeets

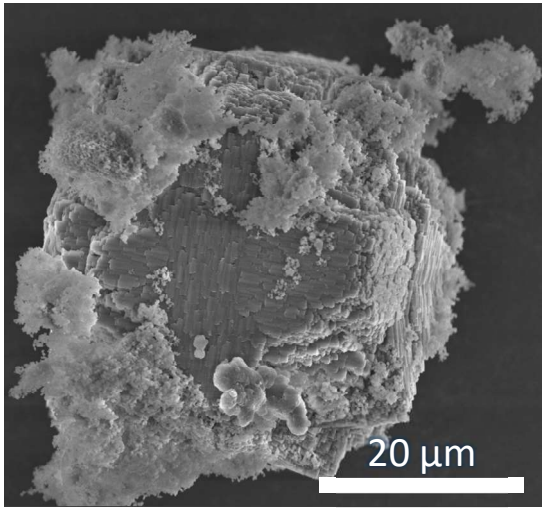
Stockholm University

Outline

- Structure determination of polycrystalline materials
- Structure completion using XRPD

- Serial electron crystallography

X-ray powder diffraction

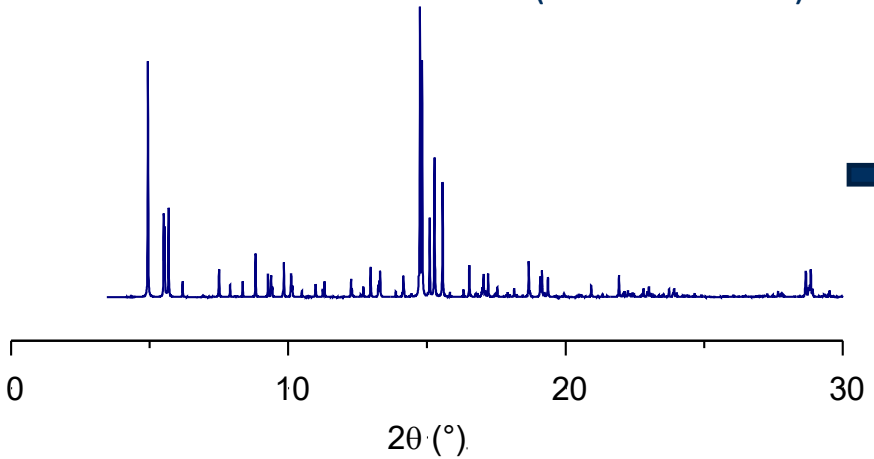


(zeolite Ge-BEC)

Routine
single-crystal
X-ray diffraction

Sample

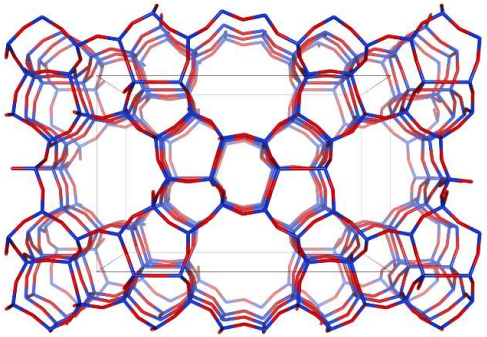
Collect
data



1D diffraction pattern

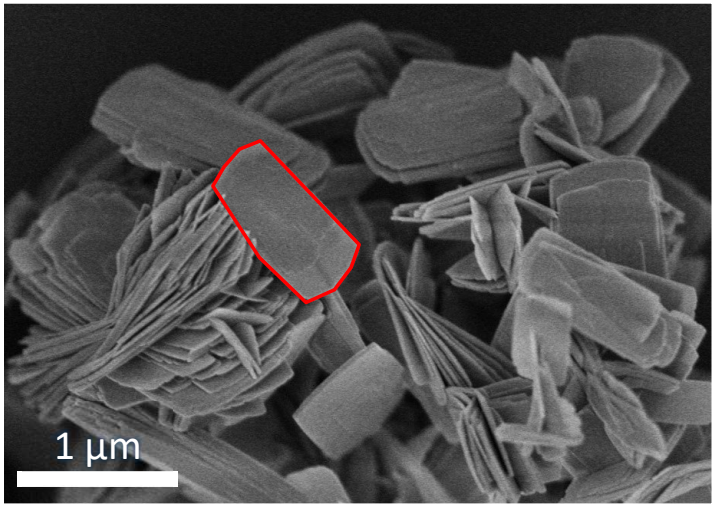
Solve

???



Model

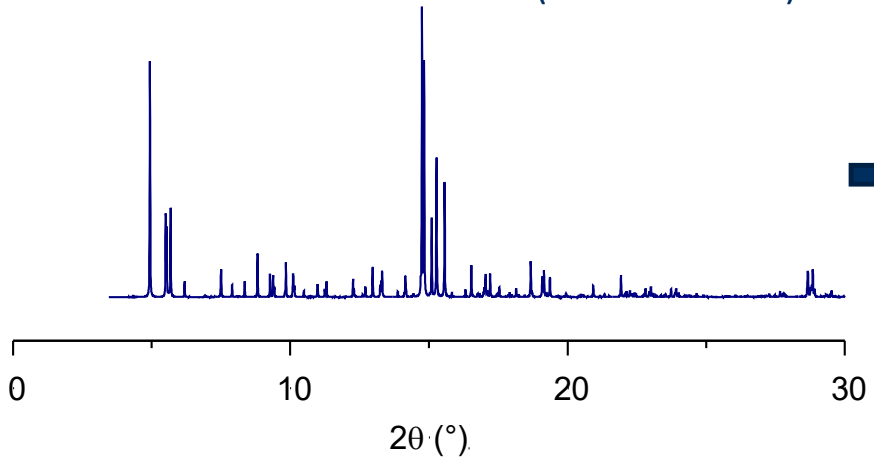
X-ray powder diffraction



(zeolite SSZ-45)

Sample

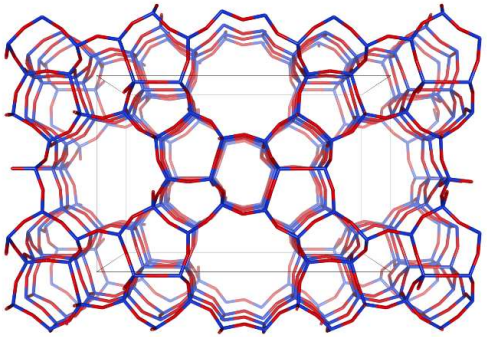
Collect data



1D diffraction pattern

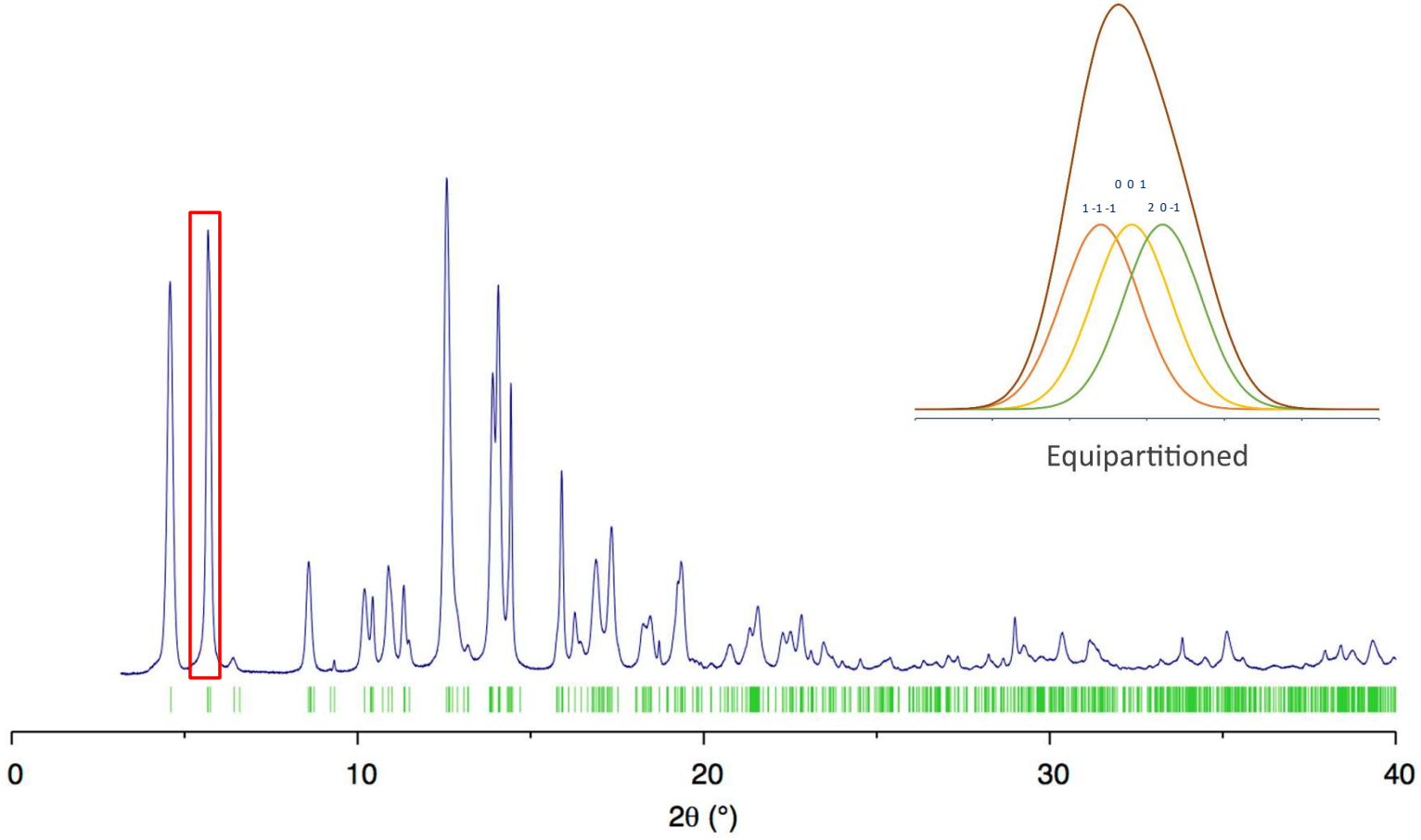
Solve

???



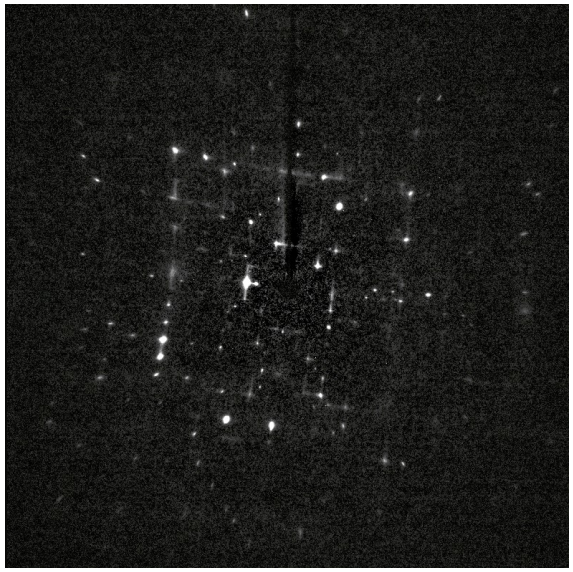
Model

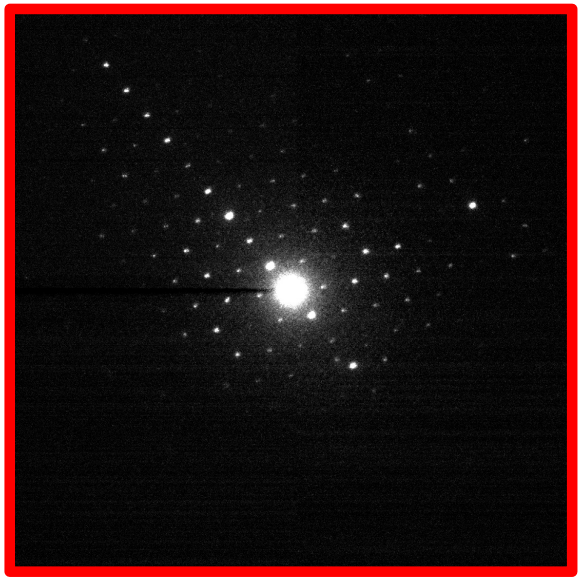
Reflection overlap



X-ray microdiffraction

zeolite SSZ-57
ID-11 @ ESRF (FR)



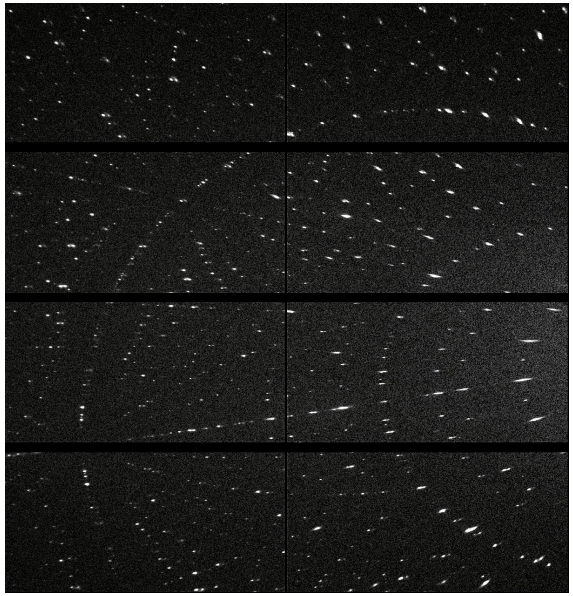


Electron diffraction

zeolite SSZ-45
JEOL JEM-2100 LaB_6

Laue microdiffraction

zeolite ZSM-5
12.3.2 @ ALS (Berkeley, CA)



High-resolution
Electron microscopy

zeolite SSZ-61
JEOL JEM-2100 FEG

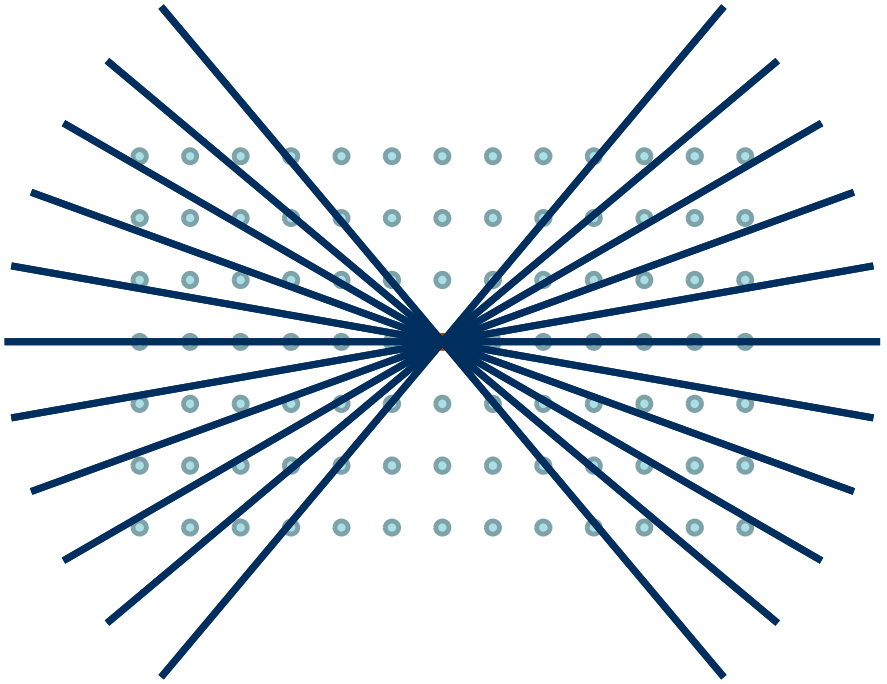
3D electron diffraction

Limitations

- Dynamical scattering
- Beam damage
- Missing wedge

XRPD and ED data have similar problems

	XRPD	3D-ED
Data completeness	100%	40-100%
Extracted intensities	Not kinematical	
Reflection overlap	Yes	No
Sample	Bulk	Single crystal



Tilt range: ±70°
Tilt step: 0.2 °
~30-60 minutes

Automated Diffraction Tomography (ADT): Kolb, *et al.* (2007) *Ultramicroscopy,* 107(6–7):507
Rotation Electron Diffraction (RED): Zhang, *et al.* (2010) *Z. Krist.*, 225(2–3):94;

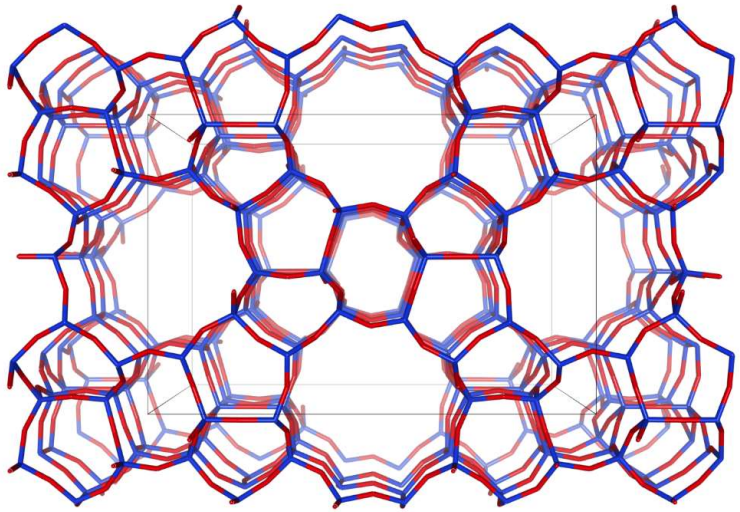
Structure determination from 3D-ED data

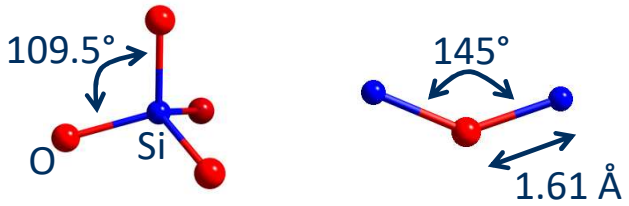
- ~~ShelXS/ShelXT~~
- ~~SIR2017~~

Can FOCUS be used with ED to overcome problems with reflection intensities?
(E. Mugnaioli & U. Kolb, Mainz University, DE)

- FOCUS?
  - Developed for XRPD
  - Use chemical information
  - *Ab-initio*, dual-space method
  - Automated model building

Zeolites





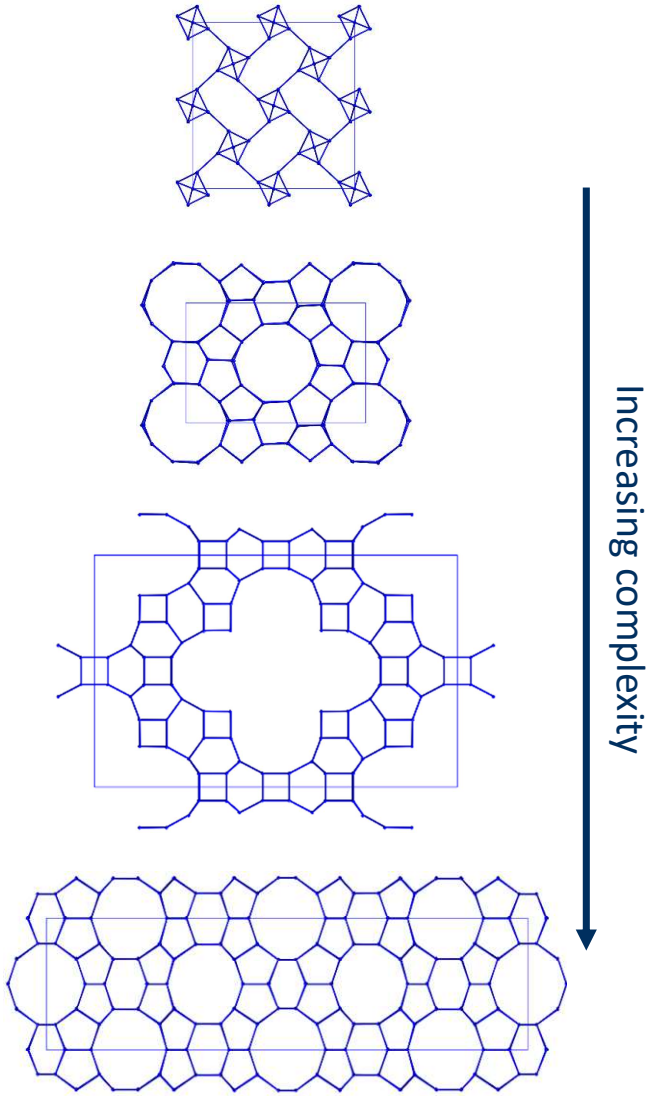
FOCUS: R. W. Grosse-Kunstleve *et al.*, J. Appl. Cryst., 1997

Application to test samples

- Modify FOCUS to work with ED
- Test with ED data on different zeolites (Smeets *et al.*, *J. Appl. Cryst.*, 2013)

	Space group	Vol. (Å^3)	uniq. T atoms
natrolite	Fdd2	2245	3
ZSM-5	Pnma	5375	12
ITQ-43	Cmmm	14038	11
IM-5	Cmcm	16260	24

- Application to new zeolites
  - SSZ-45 (Smeets *et al.*, *Chem. Mater.*, 2014)
  - SSZ-87 (Smeets *et al.*, *JACS*, 2015)
  - CIT-13 (Kang *et al.*, *Chem. Mater.*, 2016)
  - SSZ-27 (With Lukas Palatinus, FZU Prague)

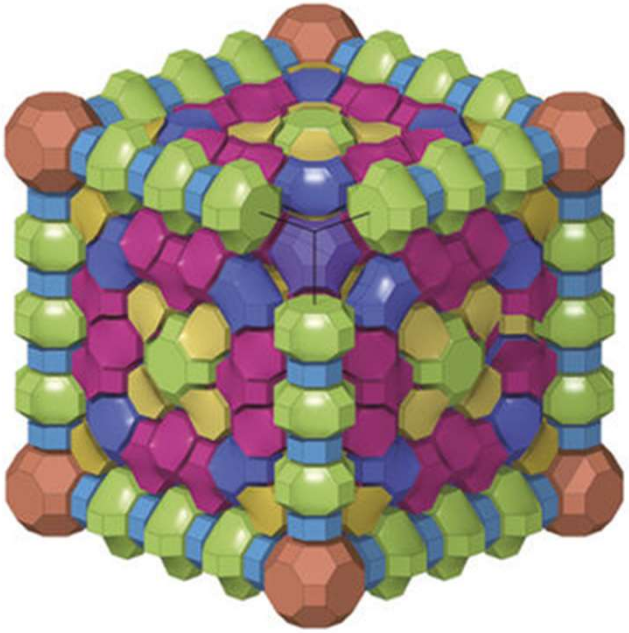


FOCUS Example 1: ZSM-25

The three-dimensional (3D) RED data revealed that ZSM-25 is body-centred cubic (unit-cell edge length $a = 42.3$ Å) with Laue symmetry $m\bar{3}m$. However, electron beam damage causes low data resolution and prevents structure solution using direct methods.

Im-3m	a = 42.3 Å
Unique T-atoms	16
Composition	$Si_{1440}O_{2880}$
RED data	d_{min} = 2.5 Å Compl. = 100%

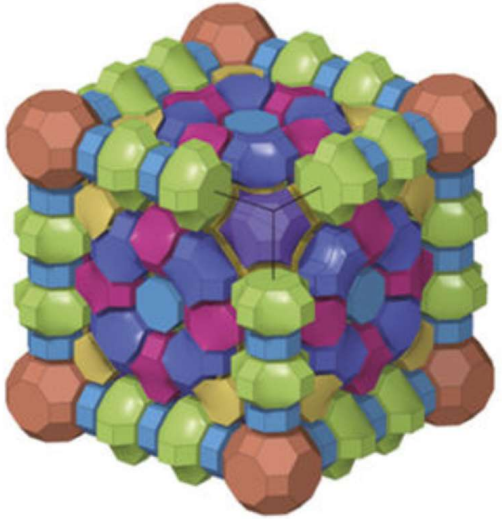
ZSM-25



Guo & Shin *et al.*, *Nature*, 2015
'A zeolite family with expanding structural complexity and embedded isoreticular structures'

FOCUS Example 1: ZSM-25

Paulingite



Im-3m a = 42.3 Å

Unique T-atoms 16

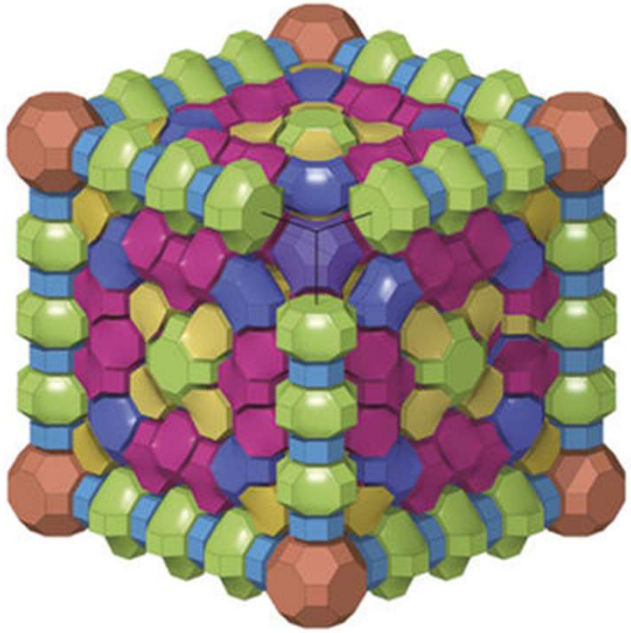
Composition $Si_{1440}O_{2880}$

RED data d_{min} = 2.5 Å, Compl. = 100%

"strong reflections approach"

FOCUS

ZSM-25



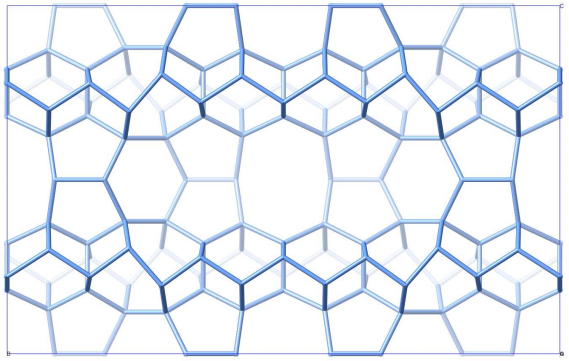
Guo & Shin *et al.*, *Nature*, 2015

FOCUS Example 2: SSZ-45

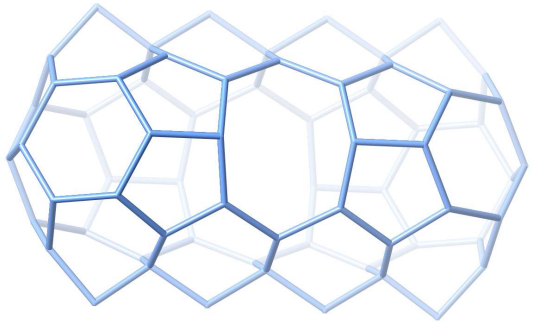
- Smeets *et al.*, *Chem. Mater.*, 2014

Fmmm

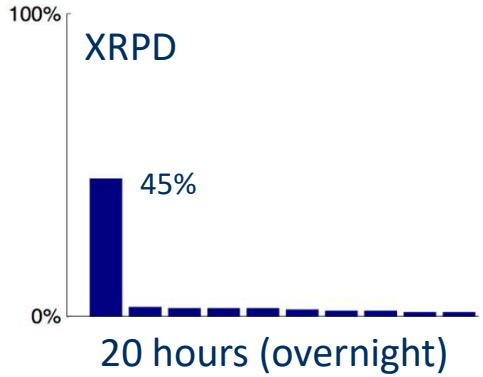
Volume	10678 Å^3
Unique T-atoms	10
Composition	$Si_{200}O_{400}$



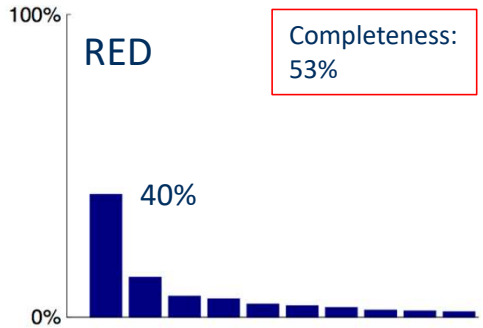
One dimensional, 8-ring channels



12-ring supercages



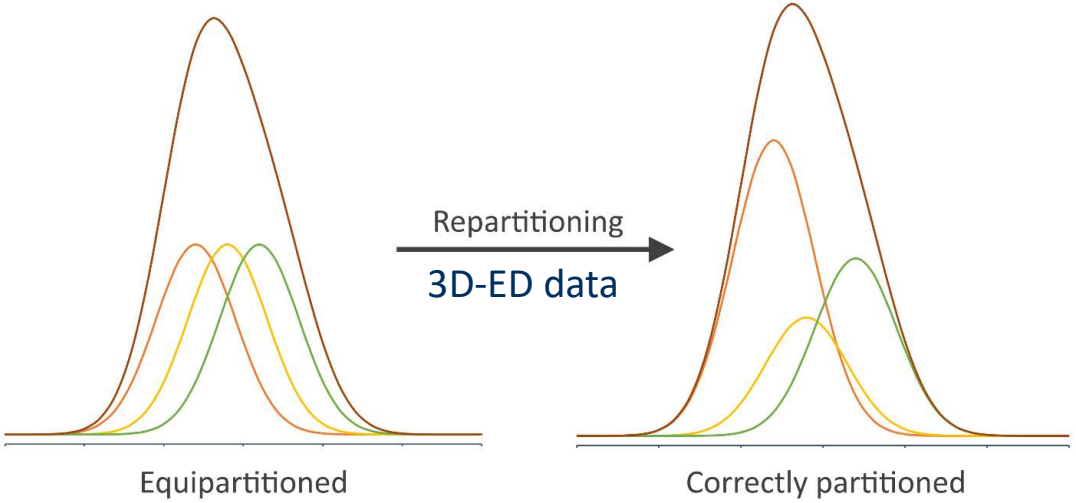
20 hours (overnight)



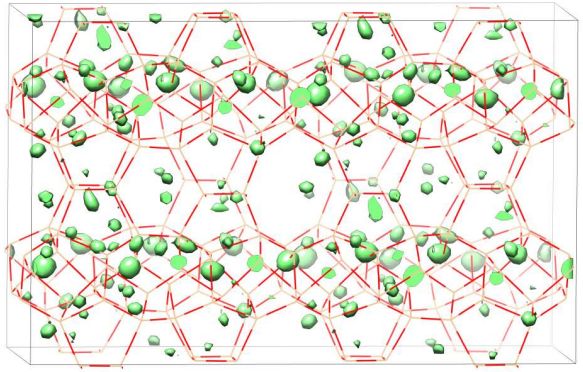
5 min (coffee break)

Combine XRPD and ED data

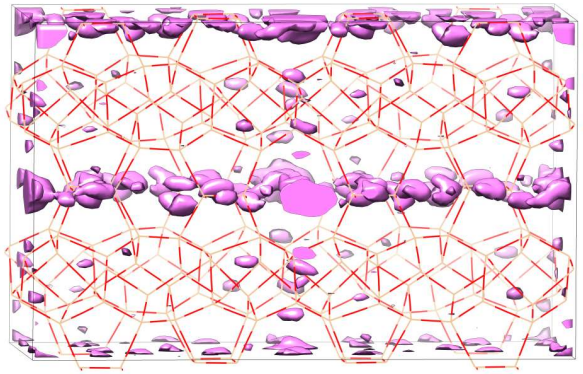
	XRPD	3D-ED
Data completeness	100%	40-100%
Reflection intensities	Kinematical	Dynamical
Reflection overlap	Yes	No
Sample	Bulk	Single crystal



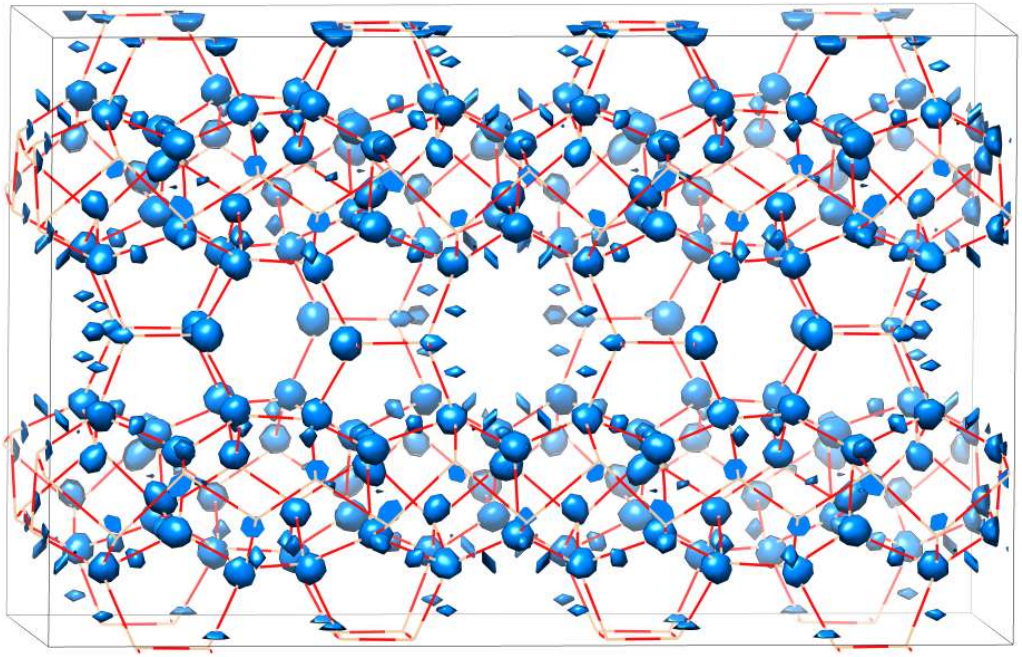
Combine XRPD and ED data (SSZ-45)



XRPD



3D-ED

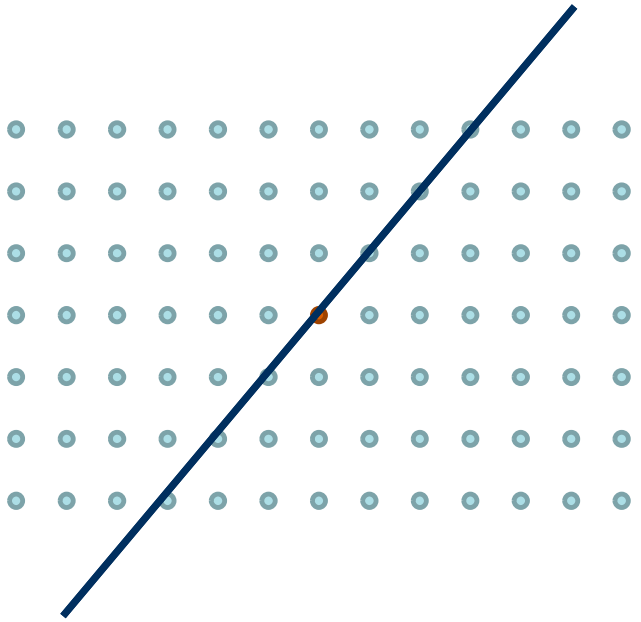


Combined

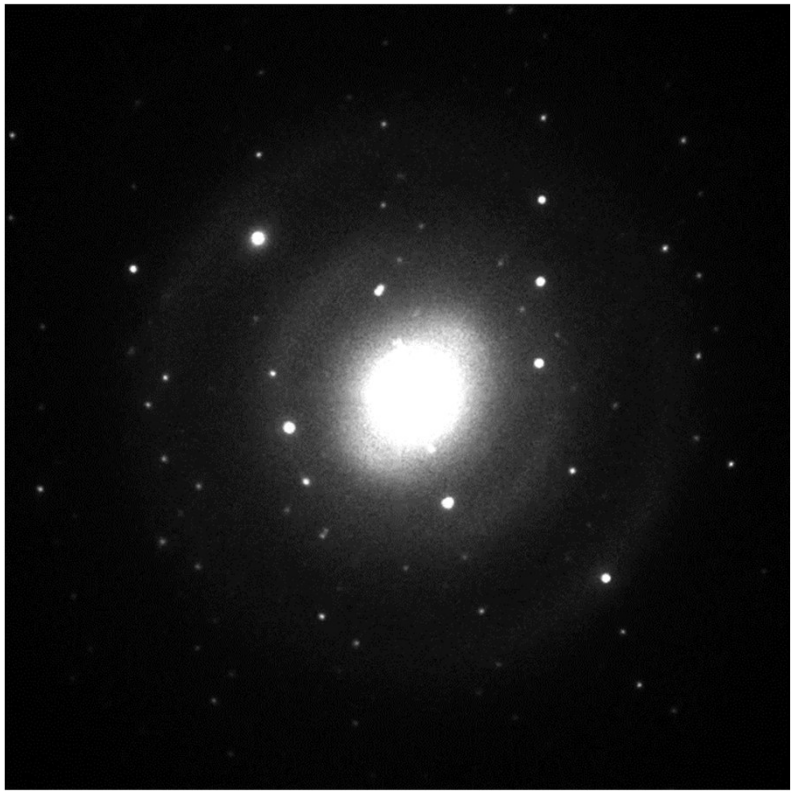
Continuous rotation electron diffraction (2017)

Fast electron diffraction tomography
Gemmi *et al.*, J. Appl. Cryst. (2015). 48, 718-727

ASI Timepix Camera @ 120 hz

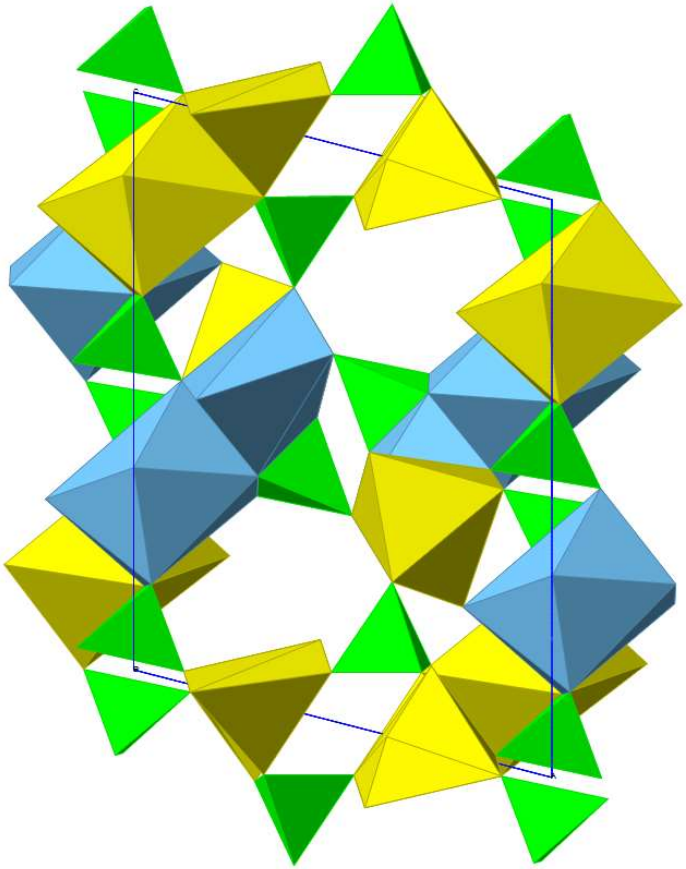


Continuous rotation electron diffraction (2017)



150 images
1.5 minutes
Tilt range: ±55°

ShelXS



Structure completion

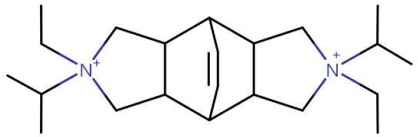
Structure completion

Zeolite SSZ-87

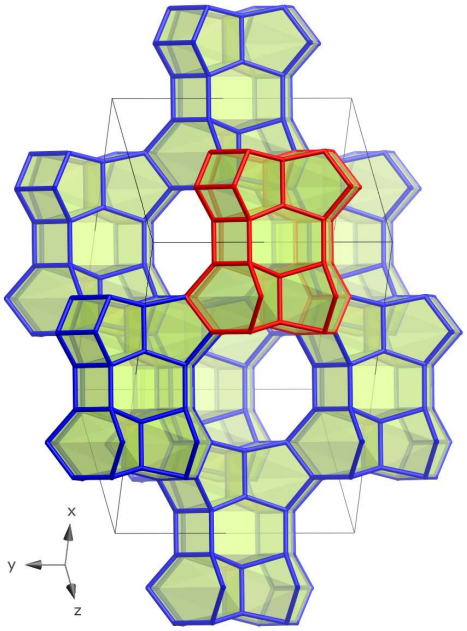
S. I. Zones, US Patent 8,545,800 (2013)

Borosilicate

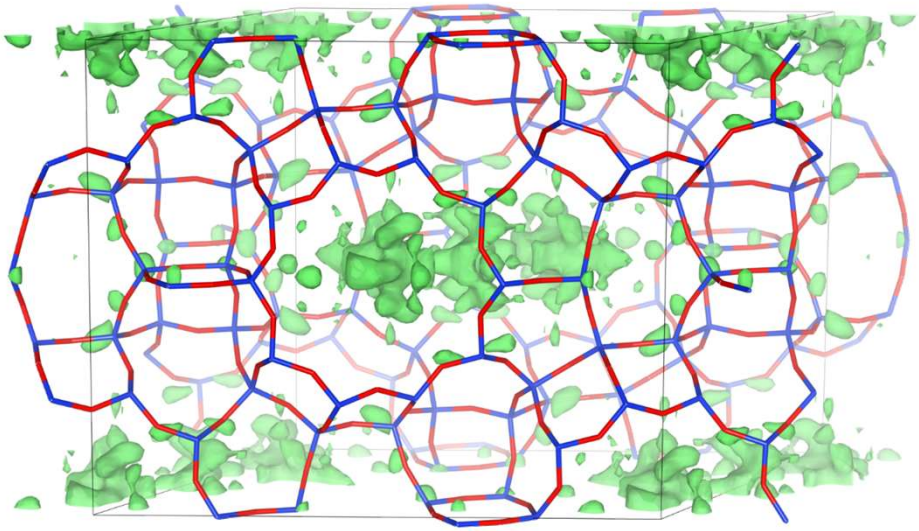
Organic structure-directing agent



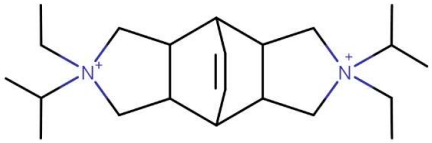
Solved using FOCUS with RED data

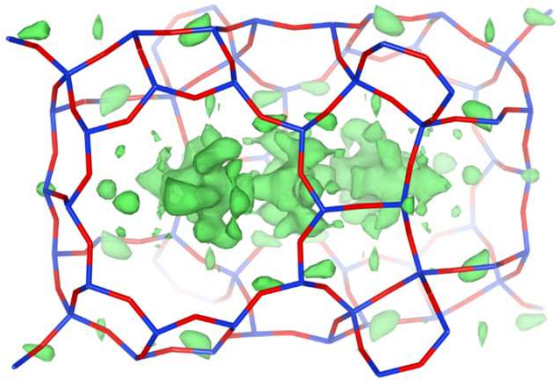


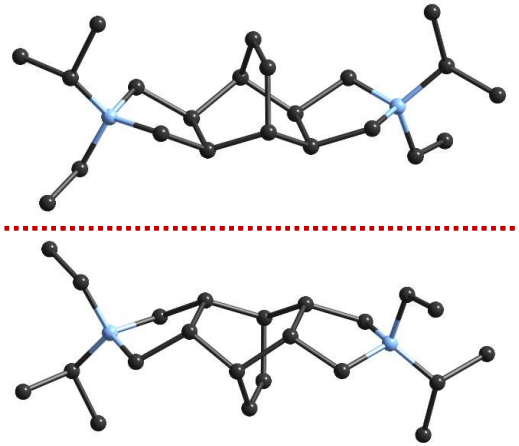
Difference map



Locating the OSDA





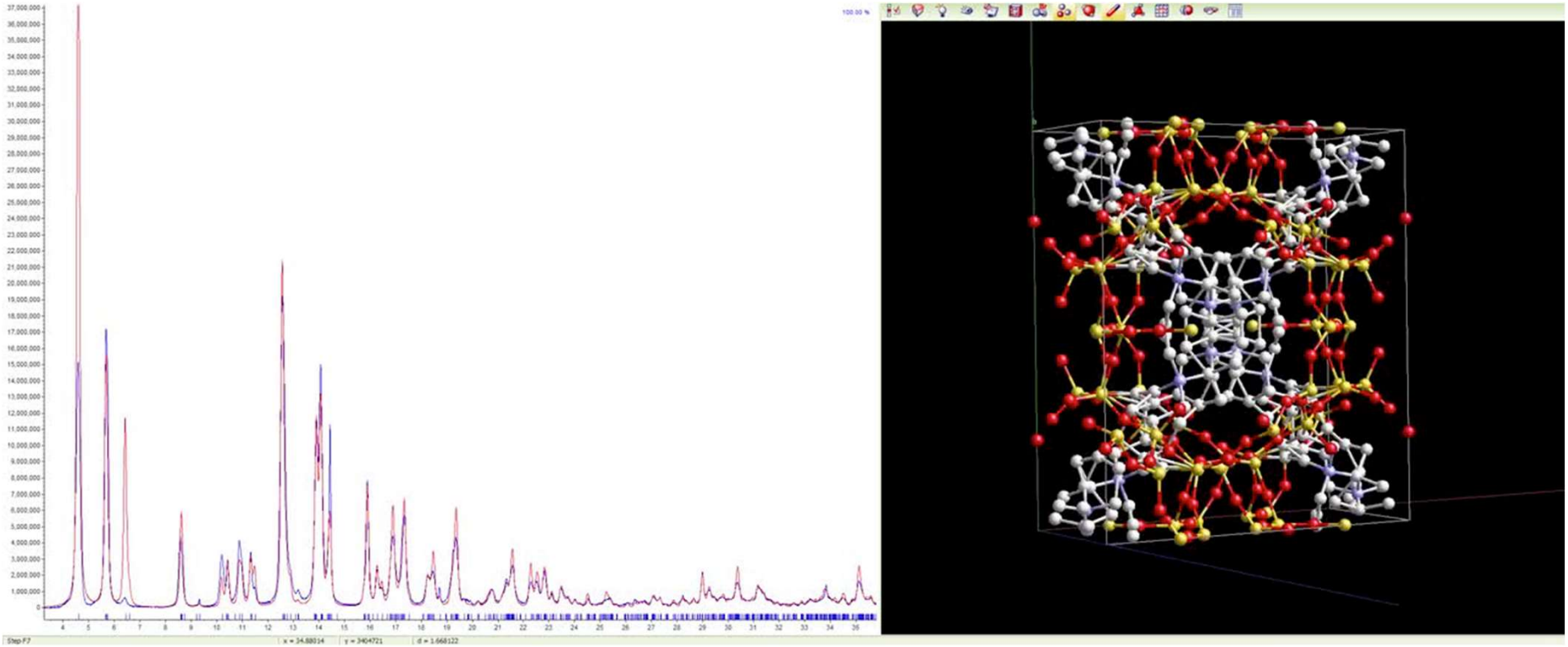


50%

50%

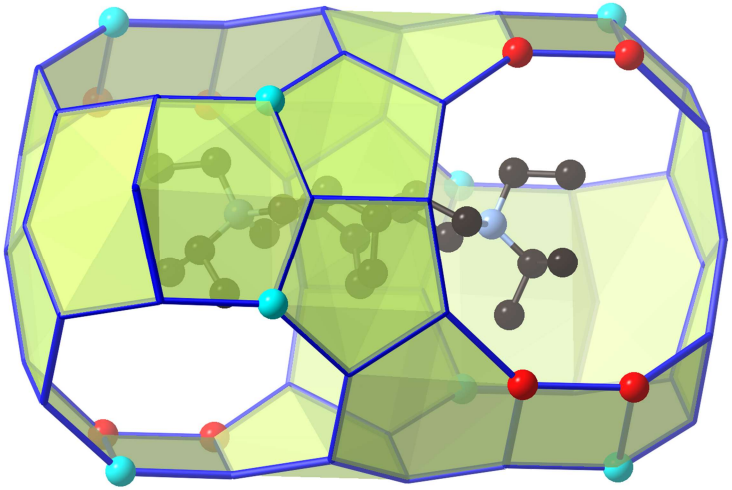
Symmetry of the OSDA does not follow the symmetry of the framework

Locating the OSDA using simulated annealing



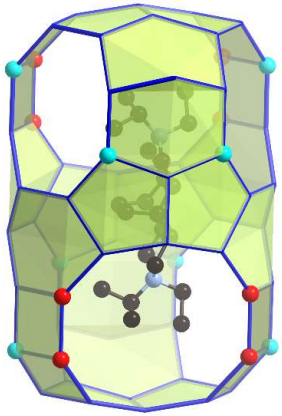
S. Smeets, L. B. McCusker, C, Baerlocher, S. Elomari, D. Xie, and S. I. Zones,
J. Am. Chem. Soc. **138**, 7099-7106 (2016)

Rietveld refinement

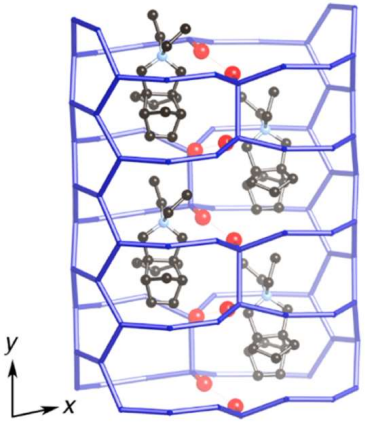


Locating the OSDA using simulated annealing

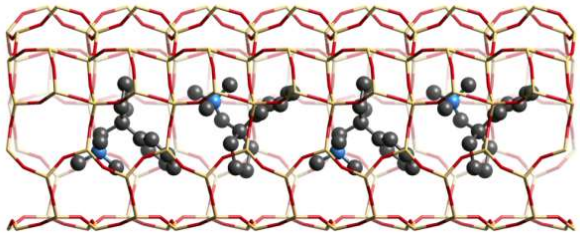
Using simulated annealing:
A systematic approach to locate the OSDA in zeolites from XRPD data



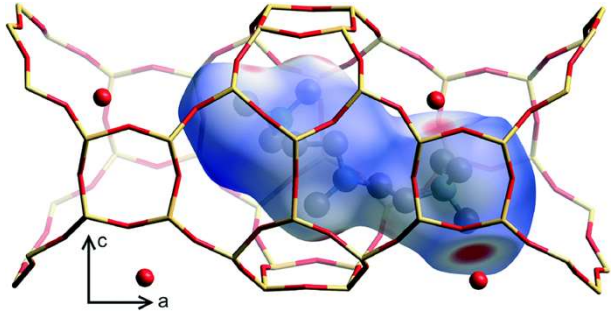
SSZ-87
JACS, 2014



SSZ-61
Angew. Chem., 2015



SSZ-53
JACS, 2016



Ge-**BEC**
CrystEngComm, 2015

Increasing flexibility

Smeets & McCusker. *Location of Organic Structure-Directing Agents in Zeolites using Diffraction Techniques* in *Structure and Bonding* (2017), doi: 10.1007/430_2017_7

Serial electron crystallography

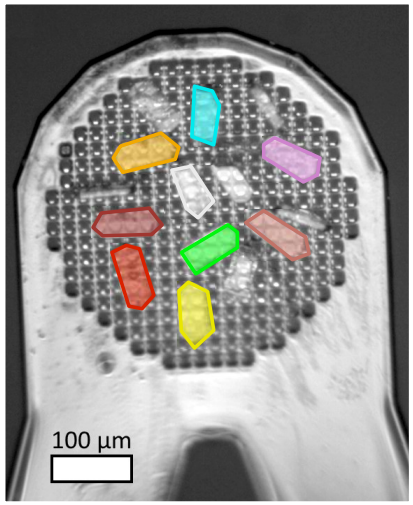
SwissFEL broad bandpass diffraction

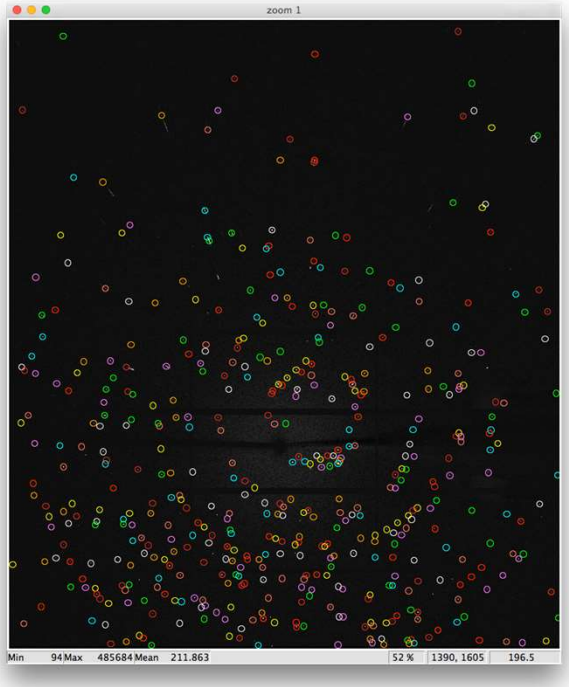
Can the 4% bandpass beam mode be used for structure analysis?

Yes!

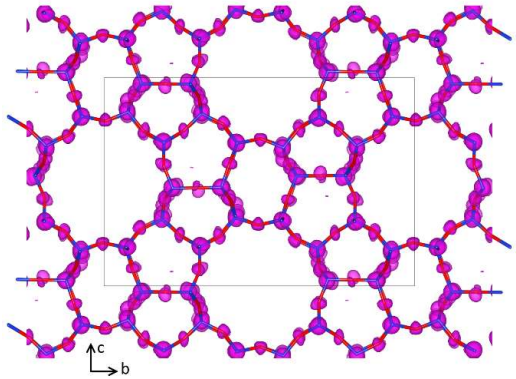
Dejoie, Smeets, *et al.*, *IUCrJ*, **2**, 361-37 (2015)

(C. Dejoie, ETH Zurich)

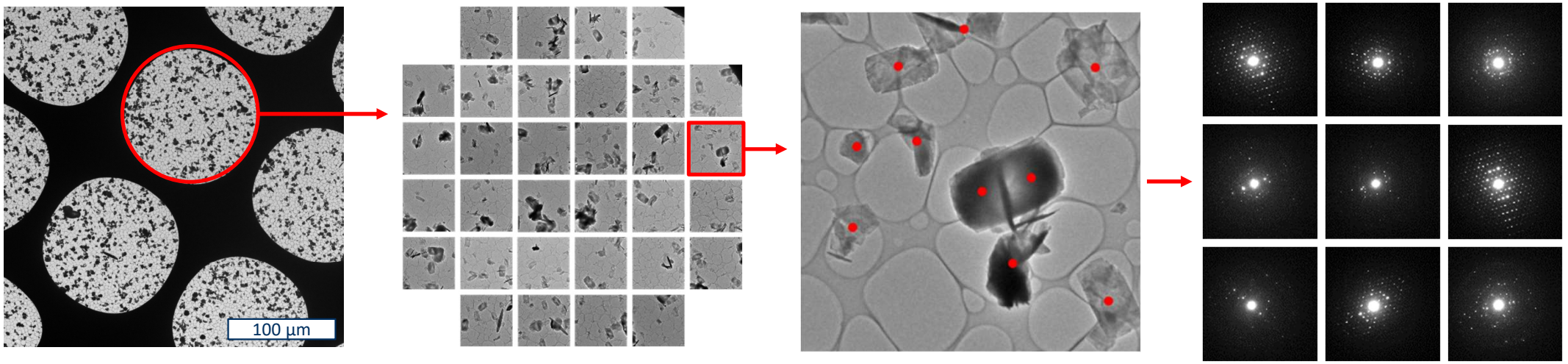




548 reflections (9 crystals)



Serial electron crystallography



Randomly oriented crystals

1 crystal = 1 diffraction pattern

Combine data from many crystals

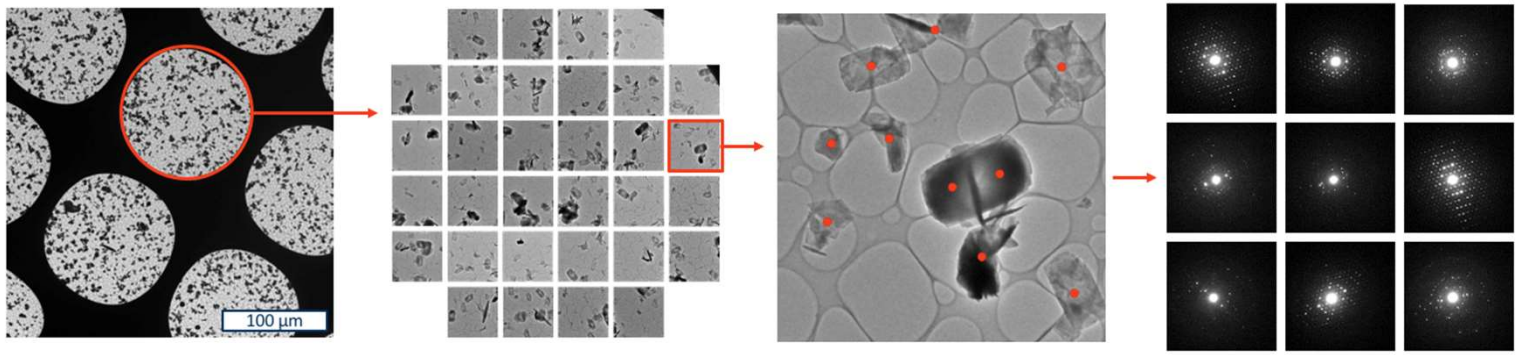
Serial electron crystallography

Why use a TEM?

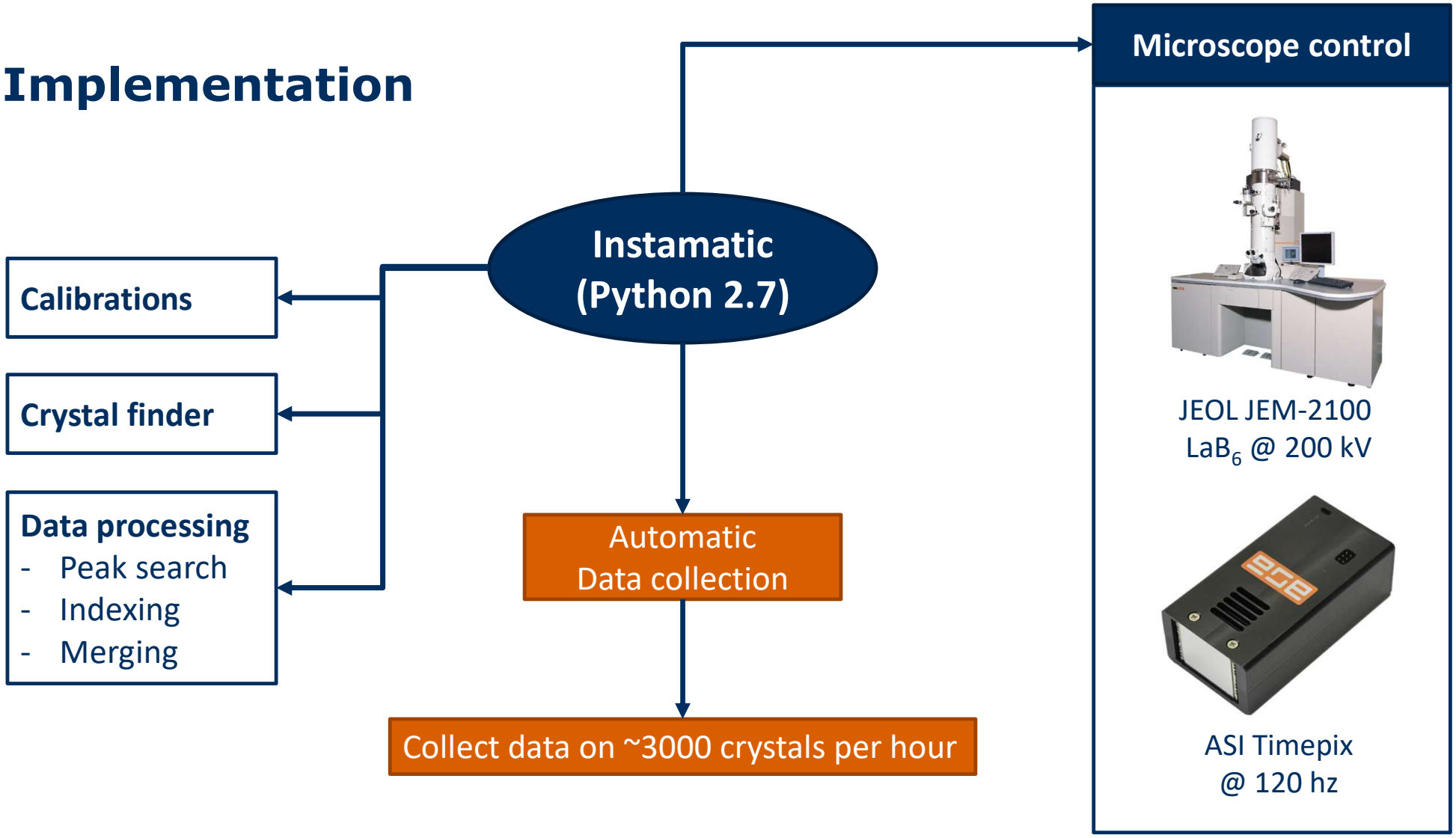
- Electron beam is very intense
- Crystals can be located from images
- TEMs can be programmed
- There is one in many labs

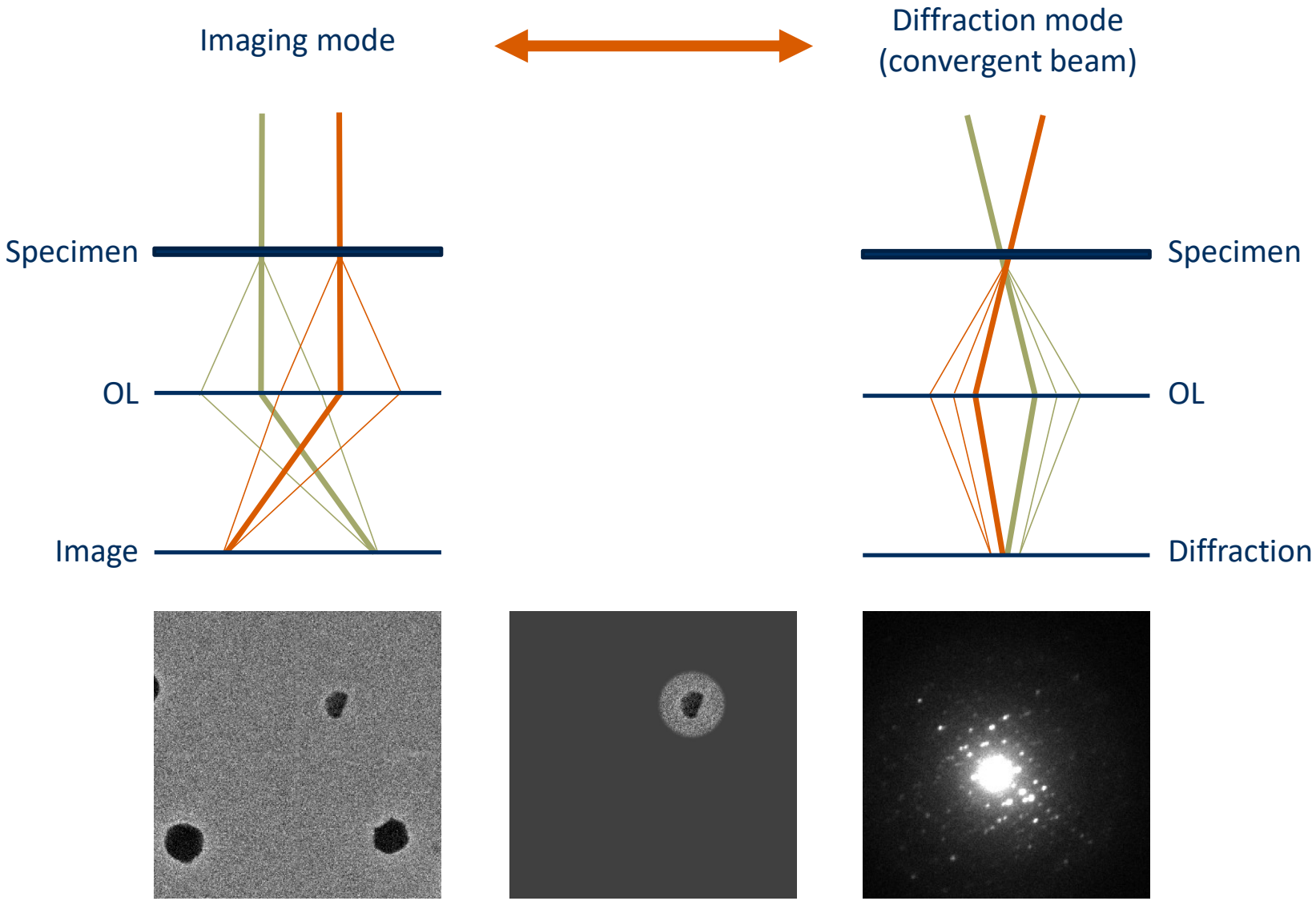
Advantages

- Beam damage is avoided
- Simple alignment, no rotation
- Fully automatic data collection
- Obtain bulk information



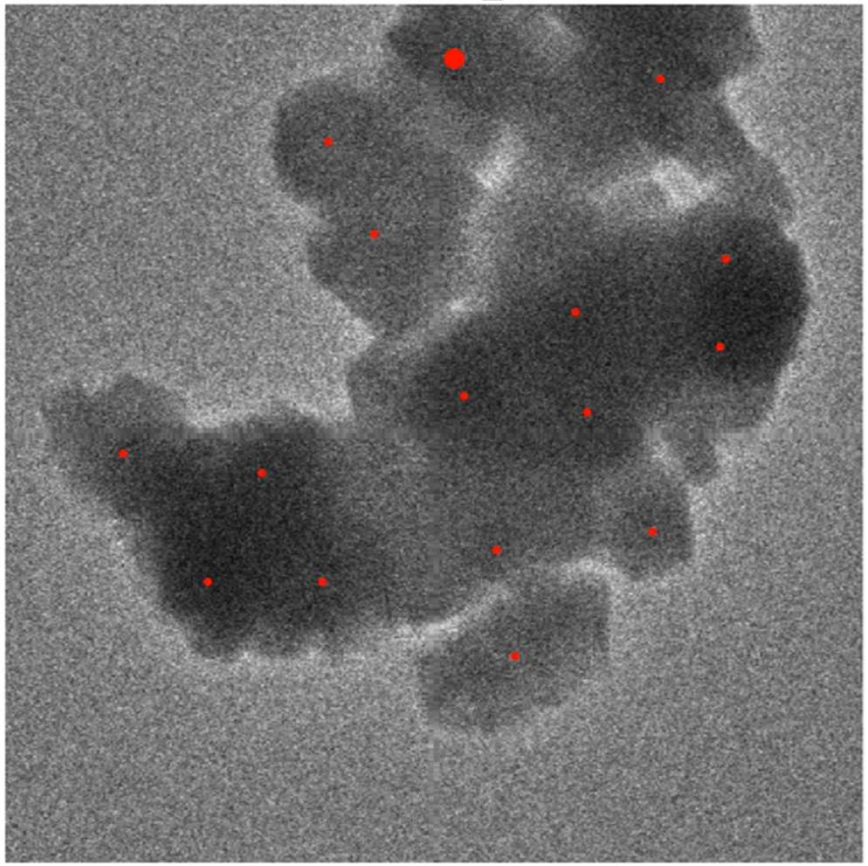
Implementation



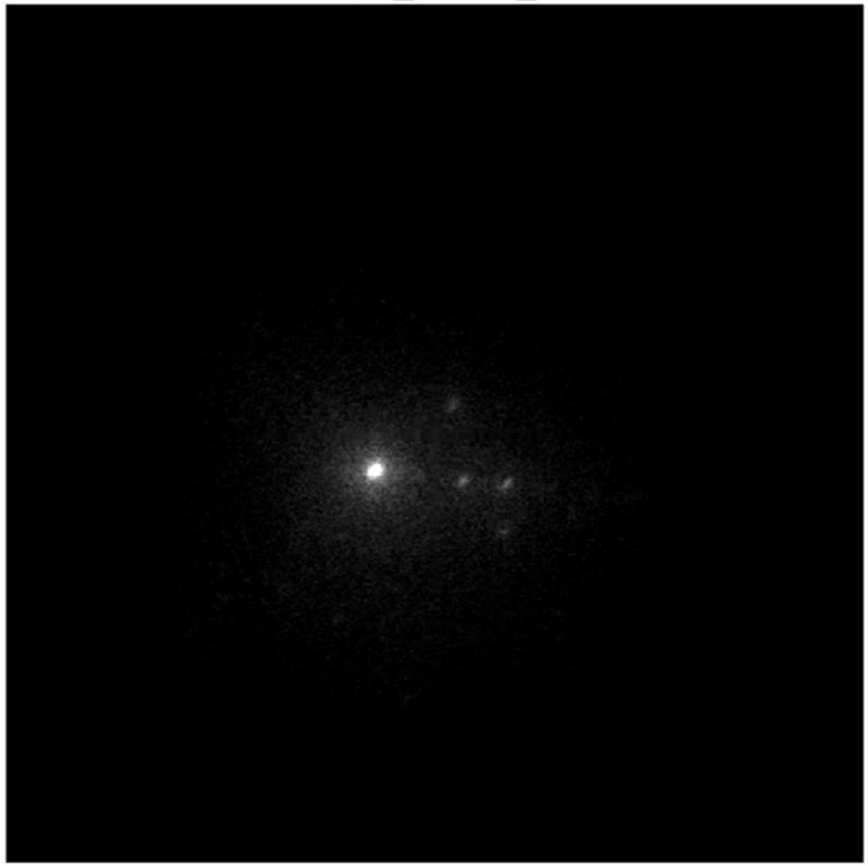

Imaging mode
Diffraction mode
(convergent beam)
Specimen
OL
Image
Specimen
OL
Diffraction

Data collection (Zeolite Y)

images\image_0000.h5

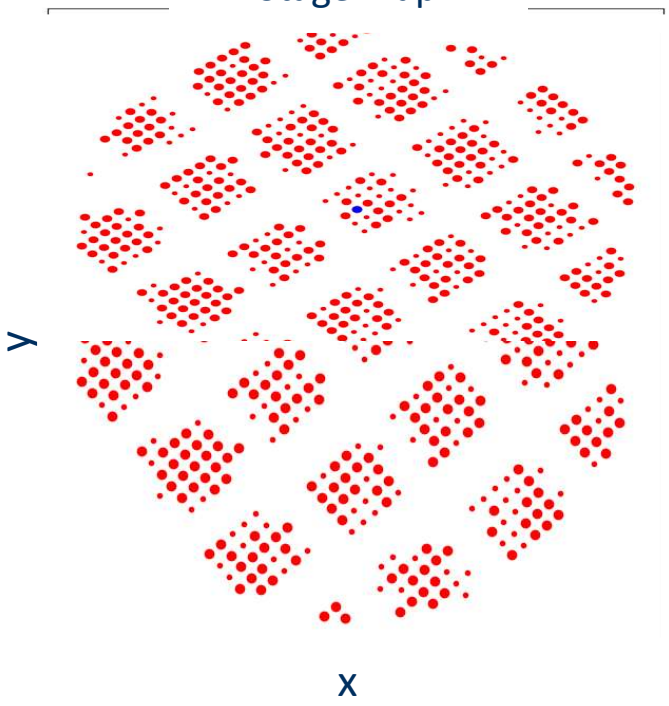


data\image_0000_0000.h5



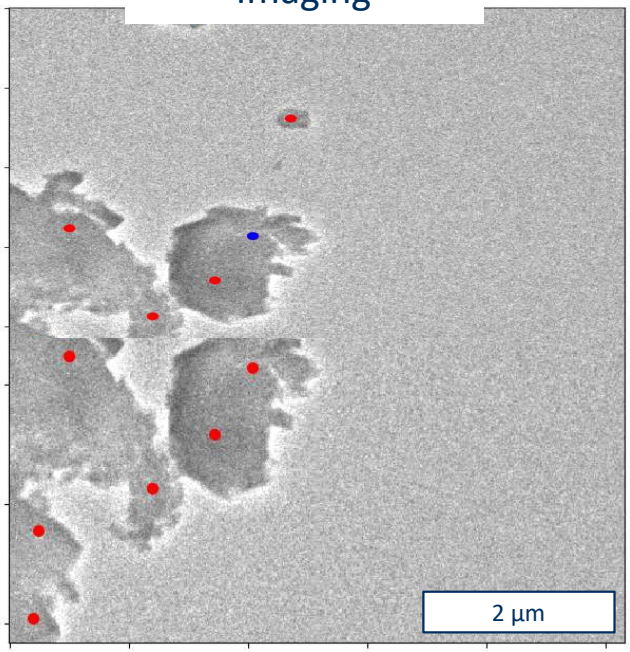
Data collection (zeolite A)

Stage map



200 x 200 µm
484 images
35 minutes

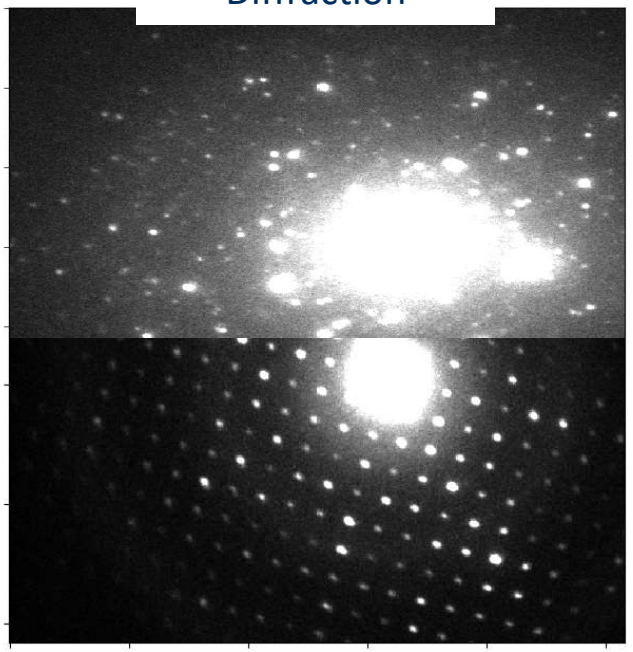
Imaging



Locate crystals

Probe size ~500 nm

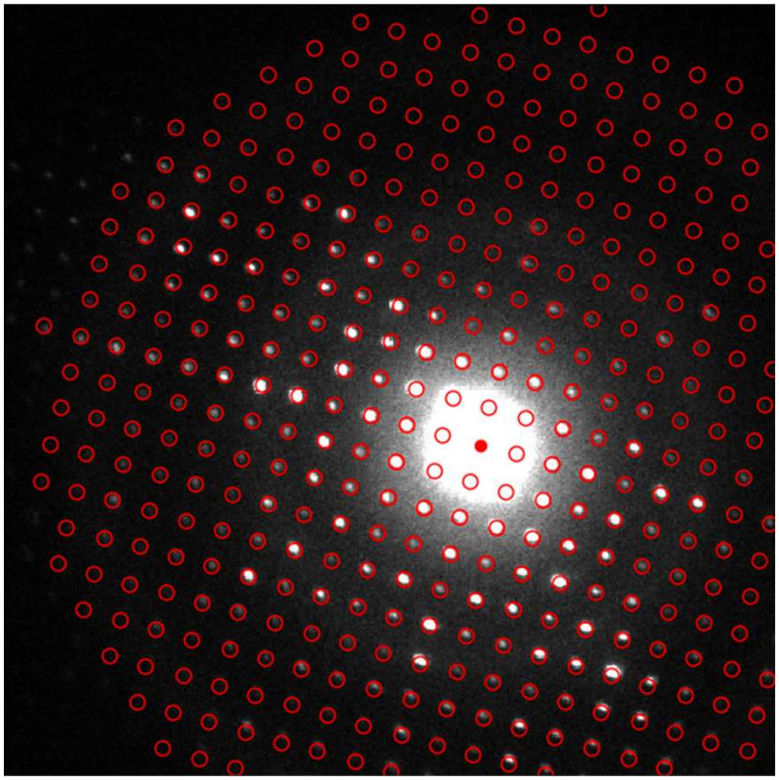
Diffraction

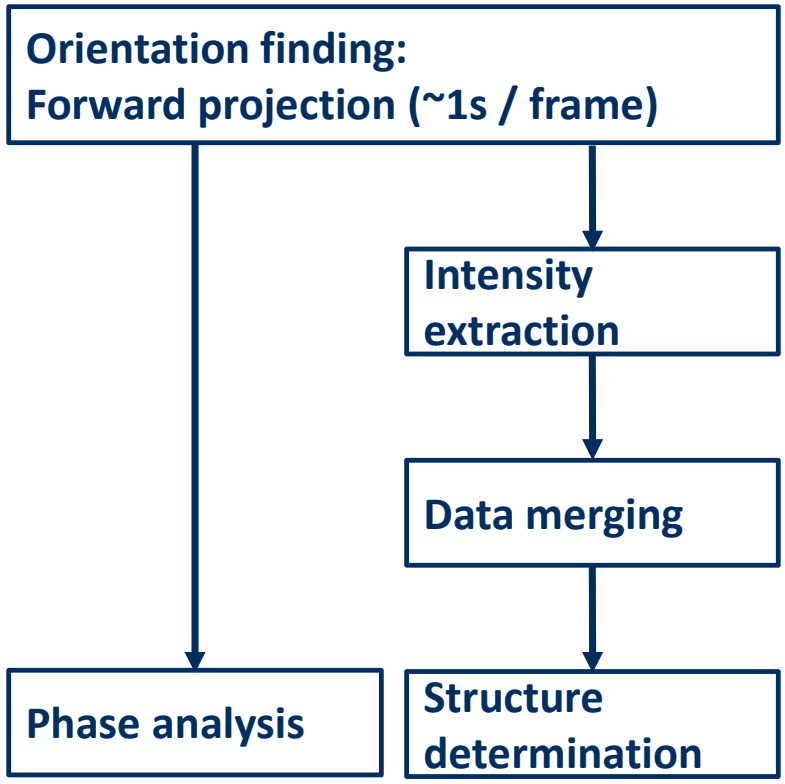


Collect data

Total: 1107 patterns

Data processing





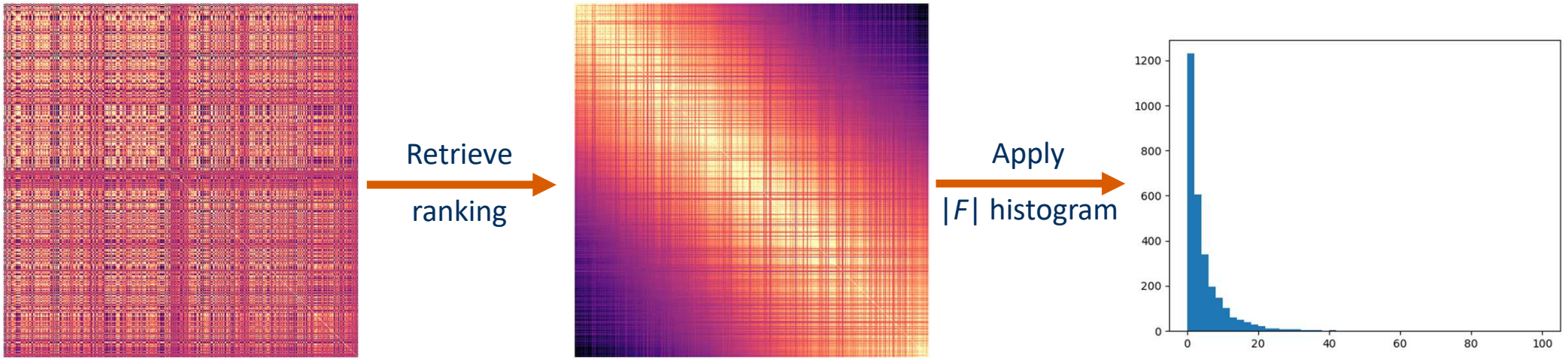
Data Merging

Challenges

- Scaling
- Dynamical effects
- Reflection partiality

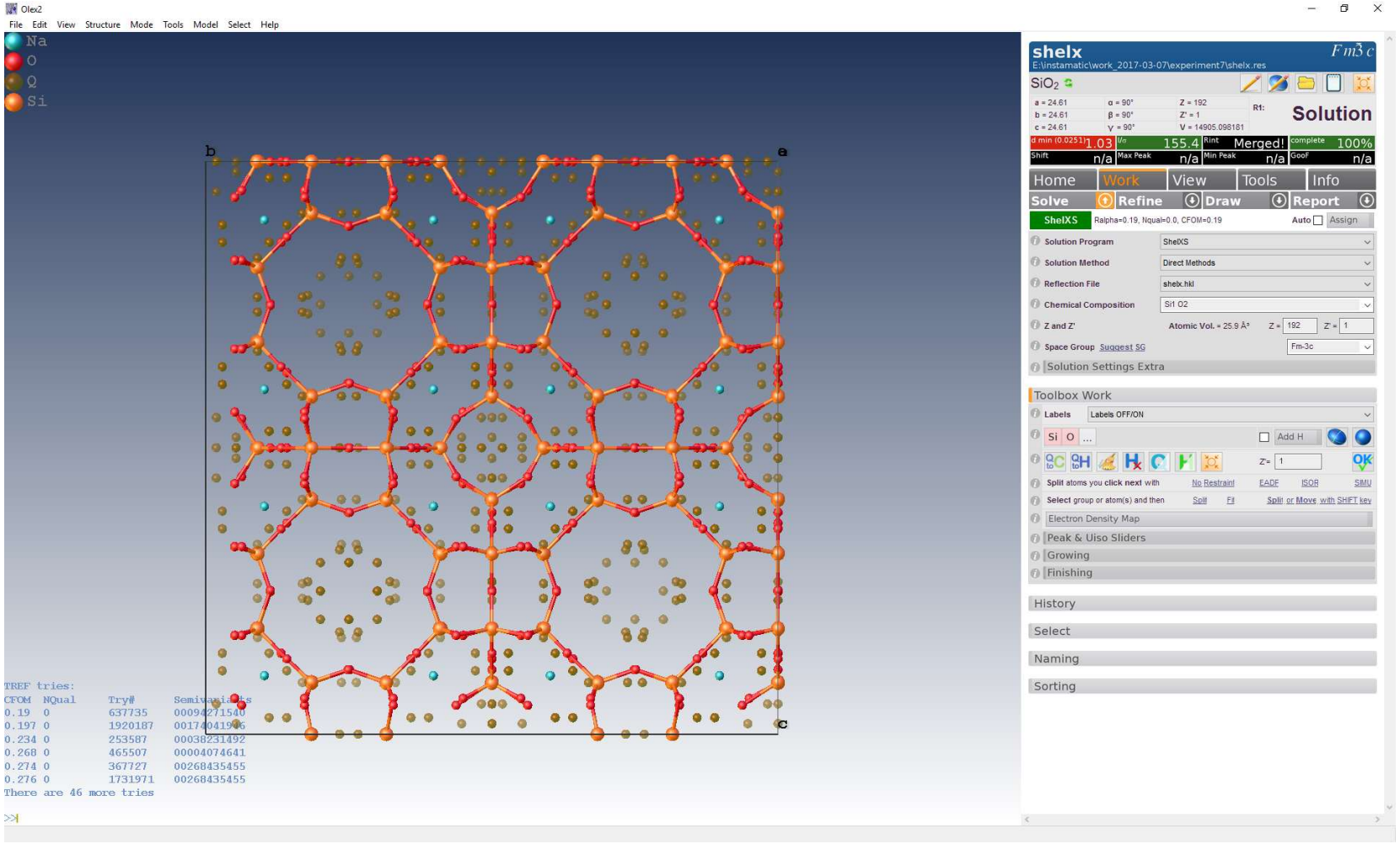
SerialMerge – rank-based merging

- Avoid scaling
- Avoid modelling intensities
- Robust with low quality data



S. Smeets & W. Wan, *J. Appl. Cryst.* (2017). **50**, 885-892
www.github.com/stefsmeets/serialmerge

Structure determination



Zeolite A

$Fm\bar{3}c$

$a = 24.61$ Å

$Si_{96}Al_{96}O_{384}$

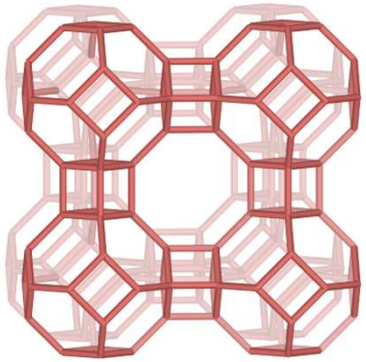
$Z = 192$

200 frames

Reflections

Total:	19804
Unique:	227
d_{min}:	1.03 Å
Compl.:	100%

Structures solved



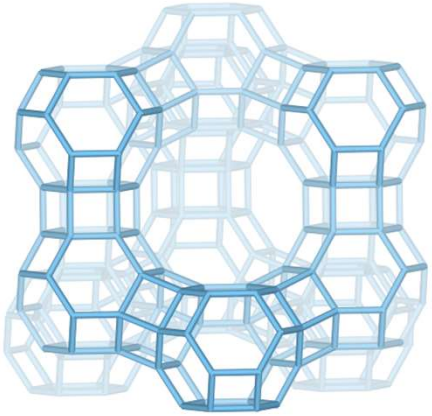
Zeolite A

$Fm\bar{3}c$

$a = 24.61$ Å

$Si_{96}Al_{96}O_{384}$

$Z = 192$



Zeolite Y

$Fd\bar{3}m$

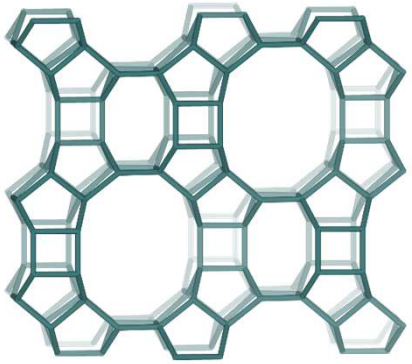
$a = 24.74$ Å

$Si_{192}O_{384}$

$Z = 192$

Direct methods

ShelXS



Mordenite

$Cmcm$

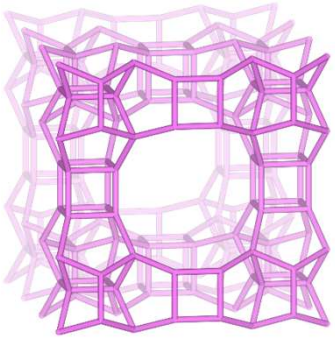
$a = 18.11$ Å

$b = 20.53$ Å

$c = 7.53$ Å

$Si_{40}Al_8O_{96}$

$Z = 16$



Ge-BEC

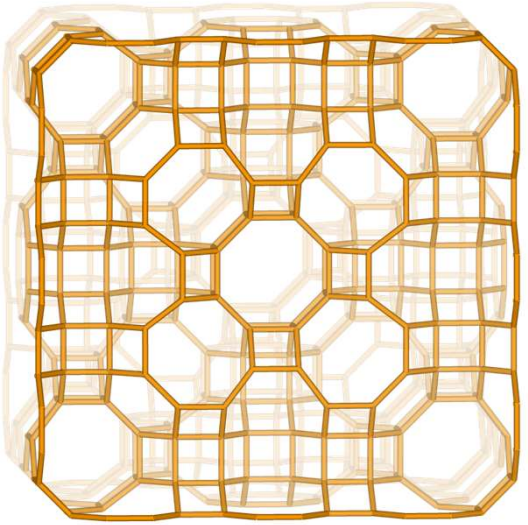
$P4_2/mmc$

$a = 12.82$ Å

$c = 13.35$ Å

$Si/Ge_{32}O_{64}$

$Z = 16$



Paulingite

$Im\bar{3}m$

$a = 35.08$ Å

$Si_{672}O_{1344}$

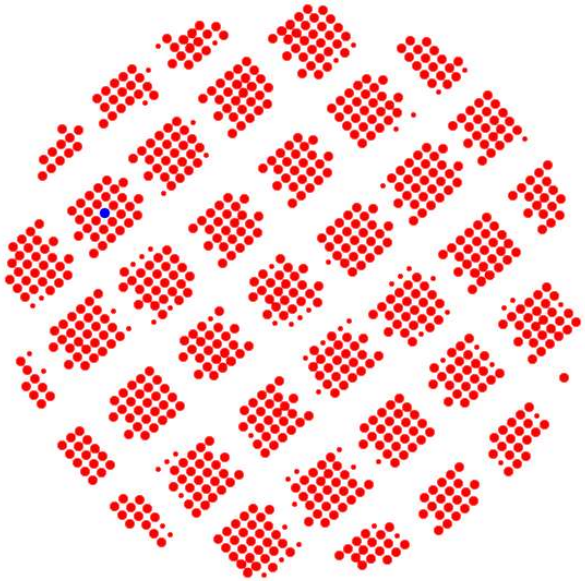
$Z = 96$

Dual-space methods

FOCUS

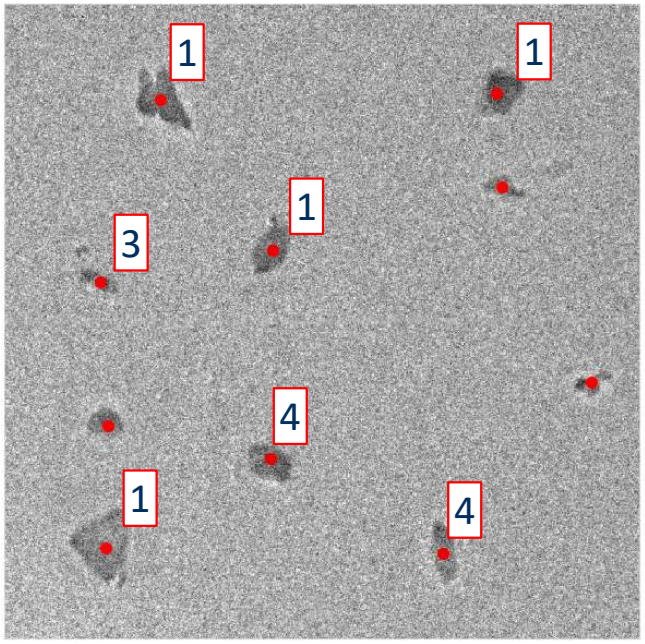
Phase analysis (Ni-Se-O-Cl)

Stage map

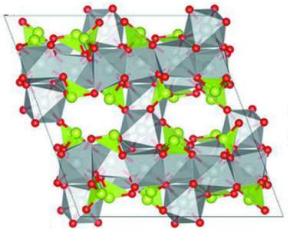


400 x 400 µm
925 images
6171 patterns
~90 minutes

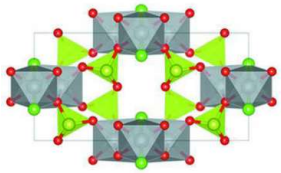
Identify crystals



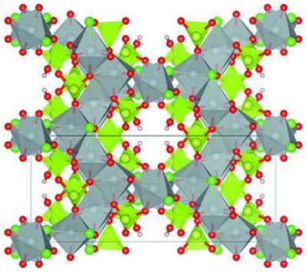
1



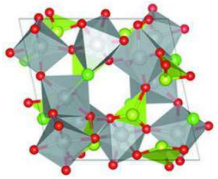
2



4



3



Conclusions

- Use electrons for structure determination of polycrystalline materials
- Use XRPD for structure completion and fine details
- Flexibility of simulated annealing is ideal for structure completion

- Serial ED data can be collected routinely & automatically
  - Applications
    - Structure determination (of beam-sensitive materials)
    - Crystal identification (screening, phase analysis, polymorphism)