

IUCr2017, Hyderabad, IN  
25-08-2017



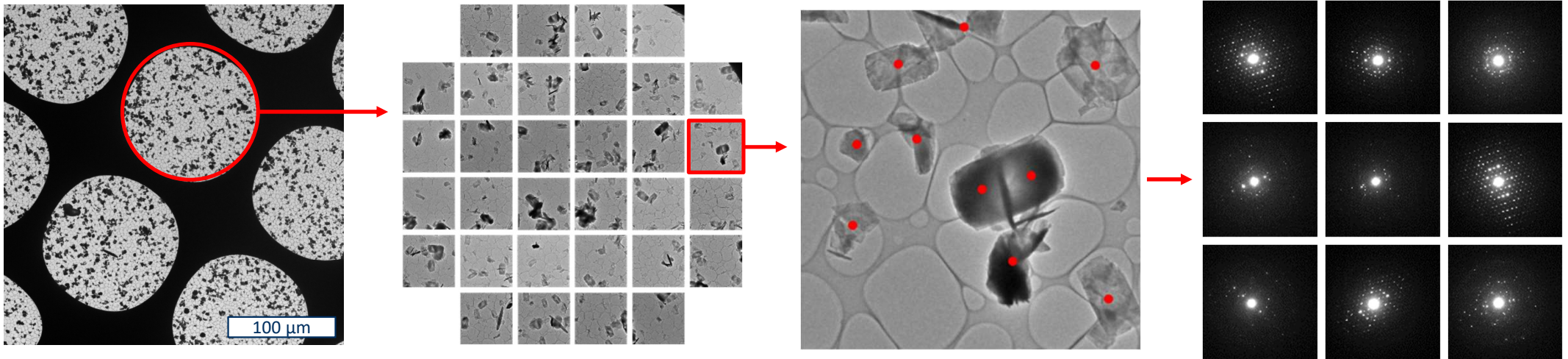
# Serial Electron Crystallography

Structure determination & phase analysis

Stef Smeets

Stockholm University

# Serial electron crystallography



Randomly oriented crystals

1 crystal = 1 diffraction pattern

Combine data from many crystals

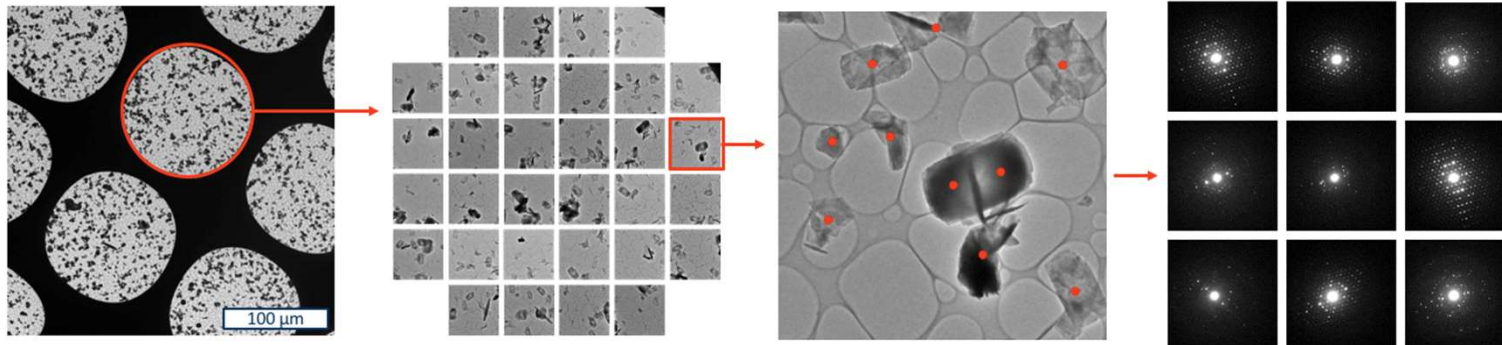
# Serial electron crystallography

## *Why use a TEM?*

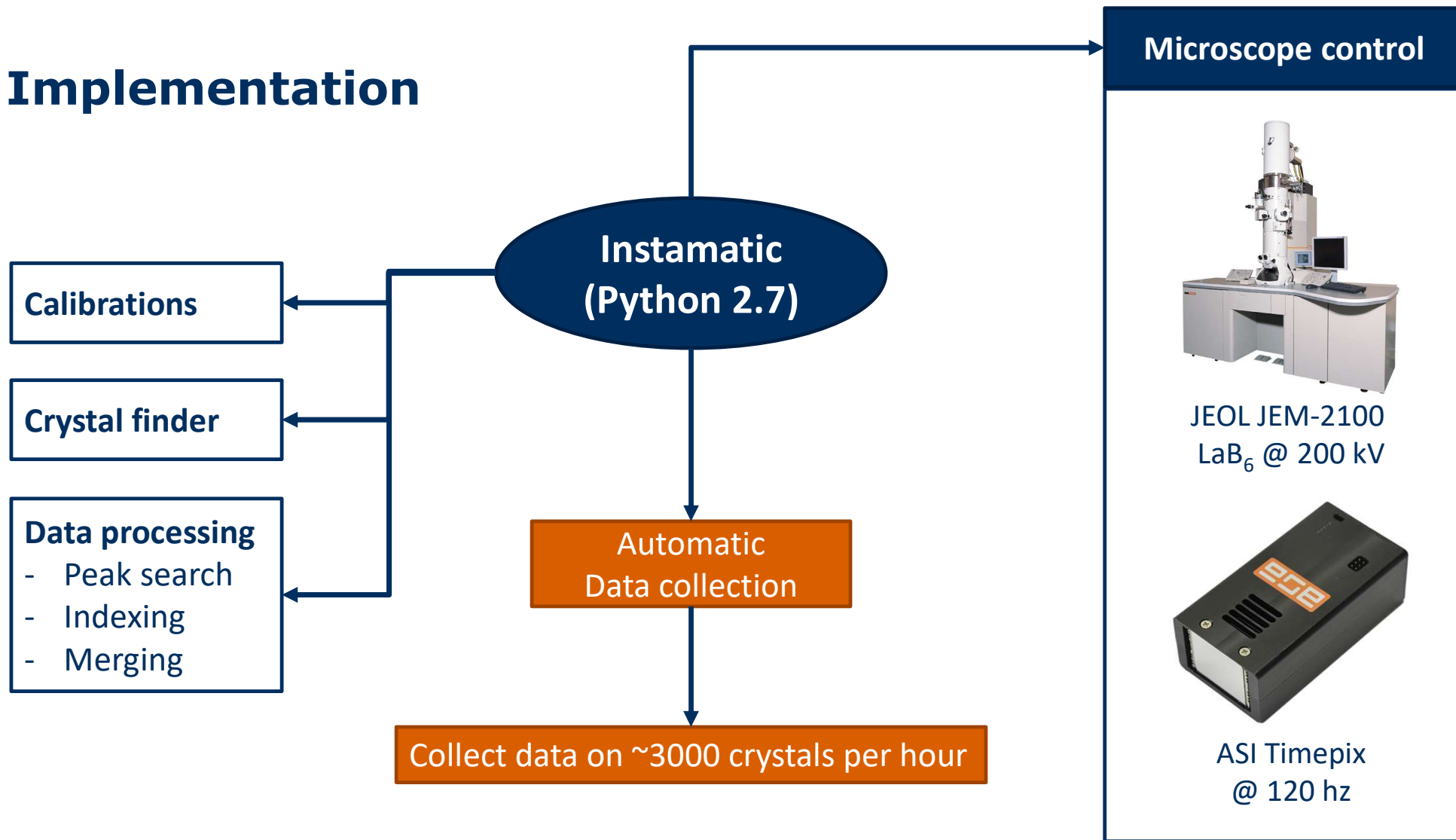
- Electron beam is very intense
- Crystals can be located from images
- TEMs can be programmed
- There is one in many labs

## *Advantages*

- Beam damage is avoided
- Simple alignment
- No rotation needed
- Fully automatic data collection



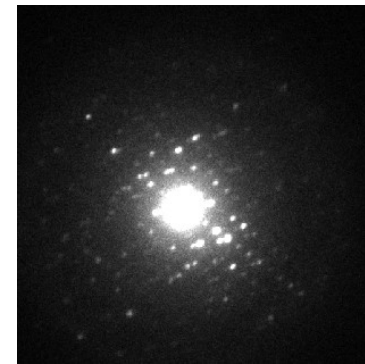
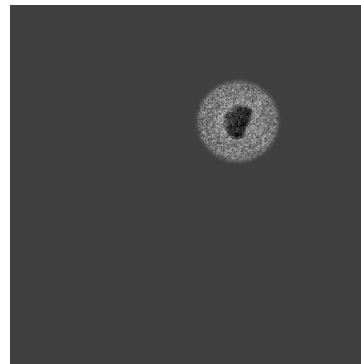
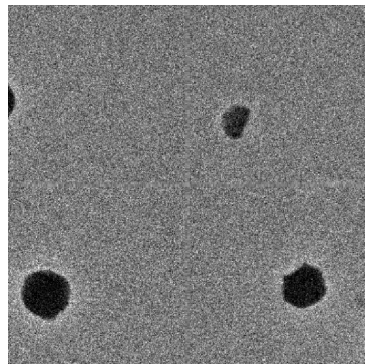
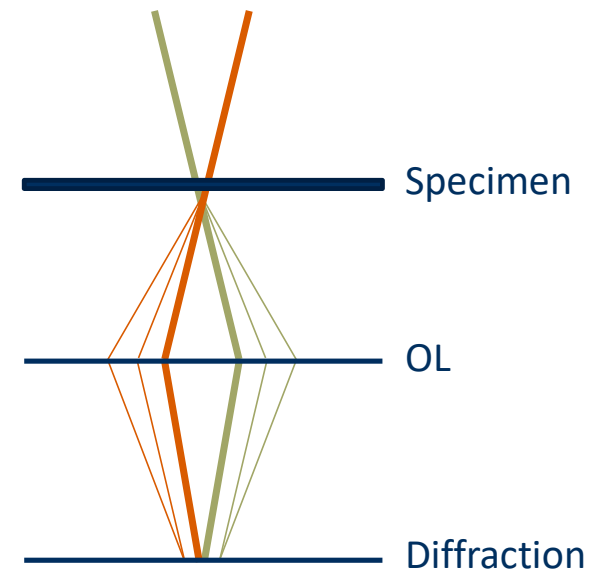
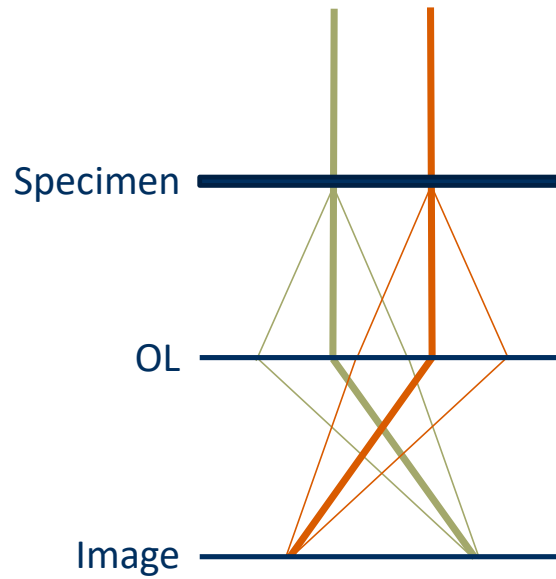
# Implementation



Imaging mode

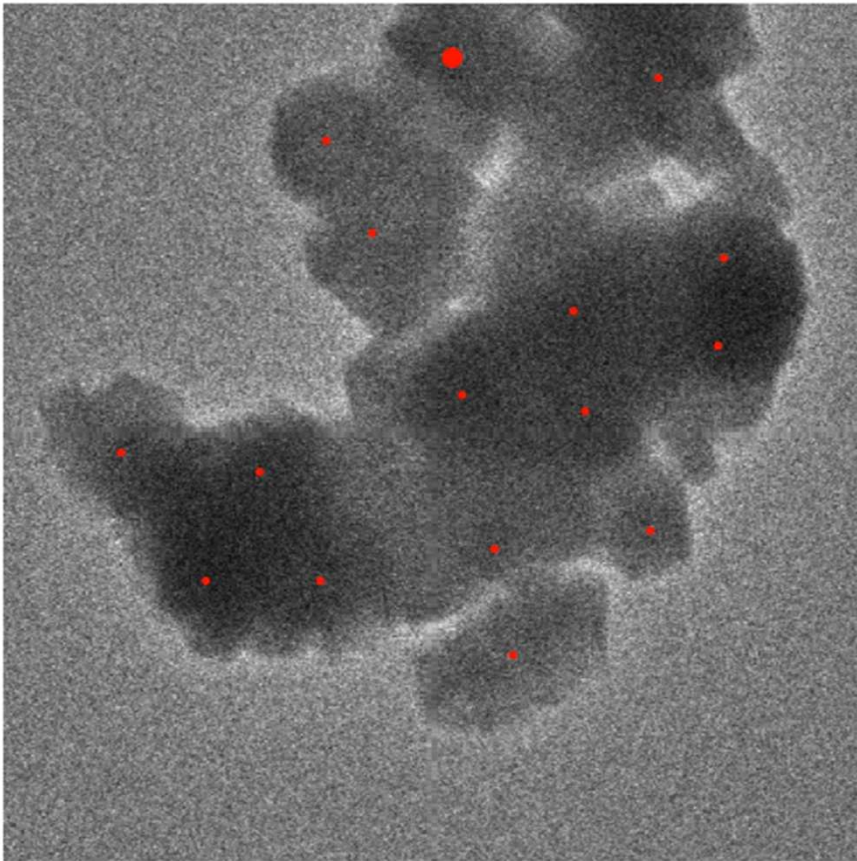


Diffraction mode  
(convergent beam)

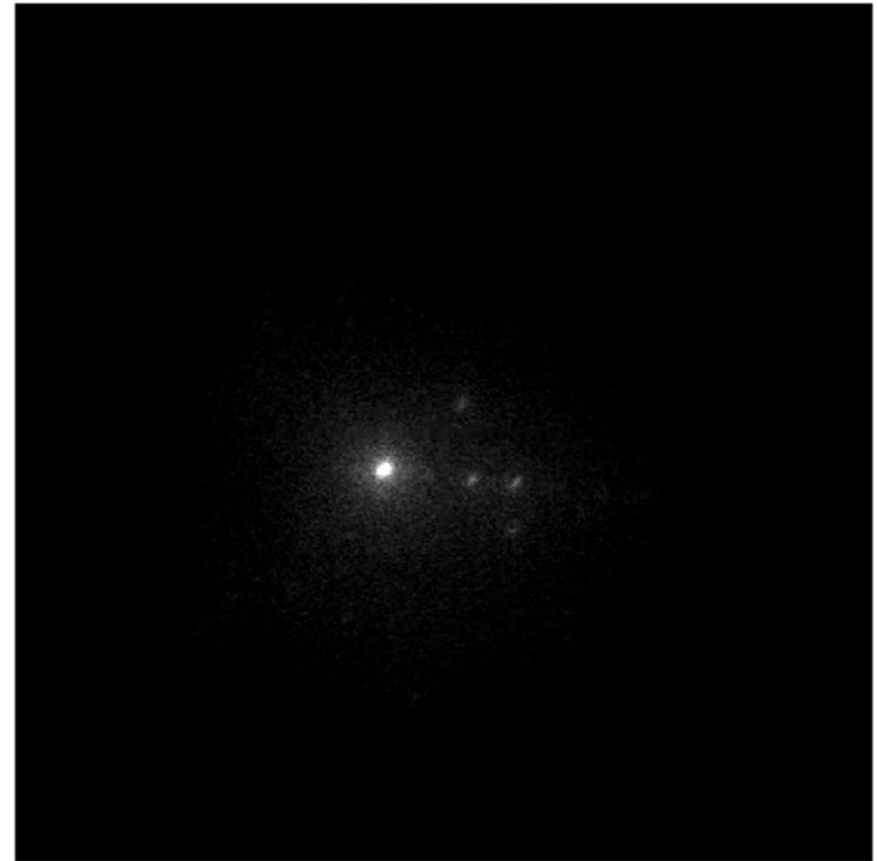


## Data collection (Zeolite Y)

images\image\_0000.h5



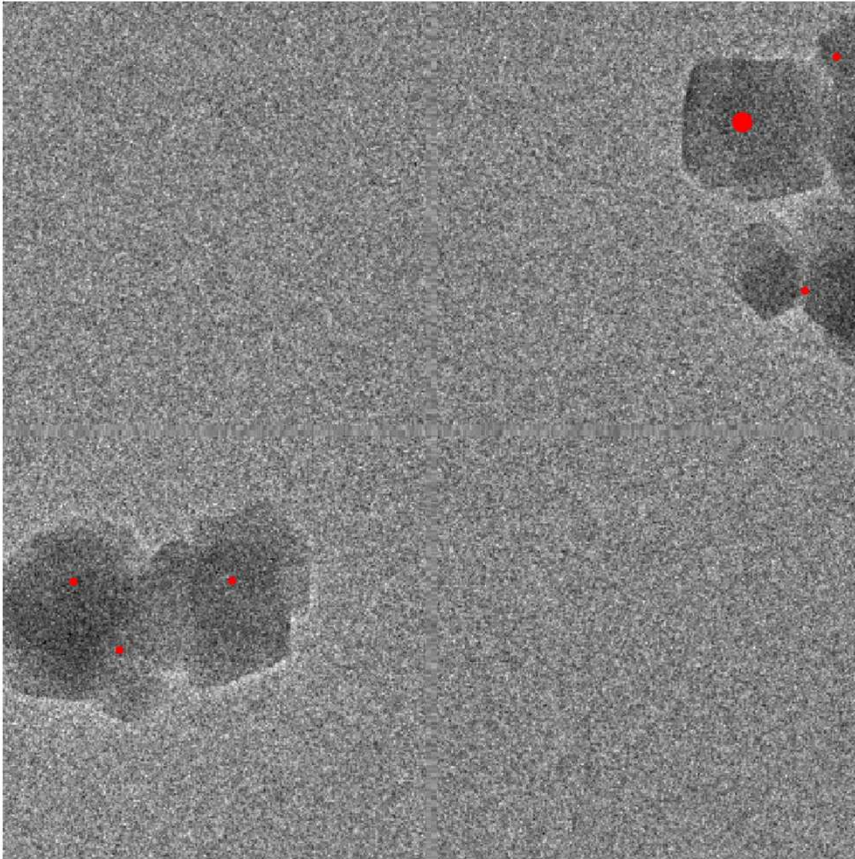
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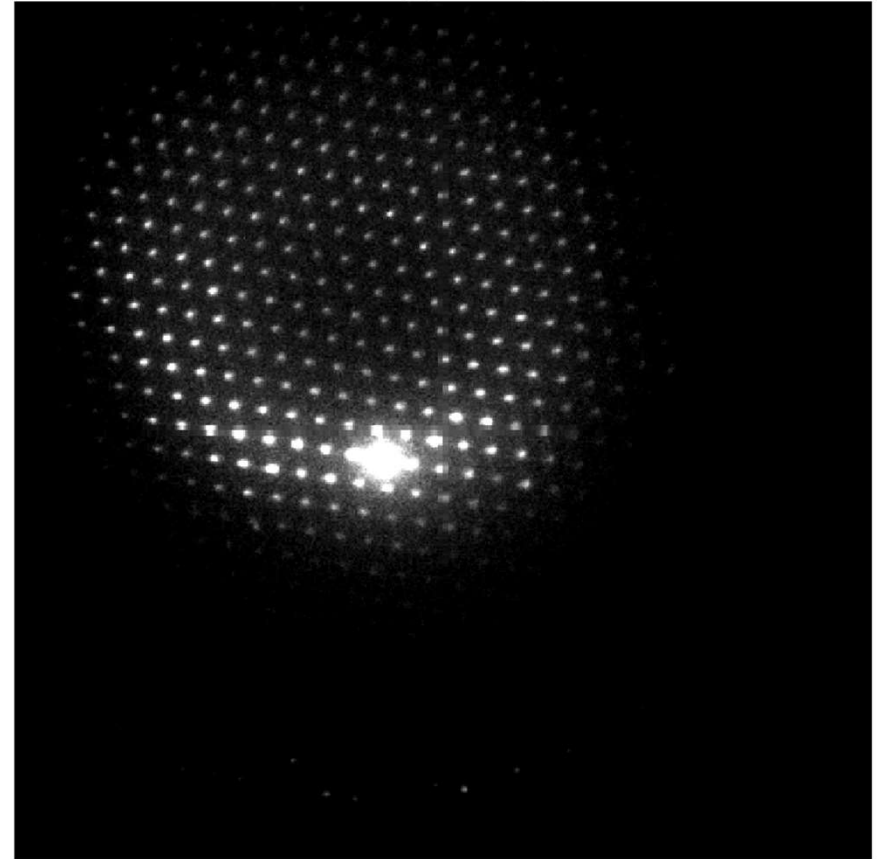


## Data collection 1/4

images\image\_0255.h5

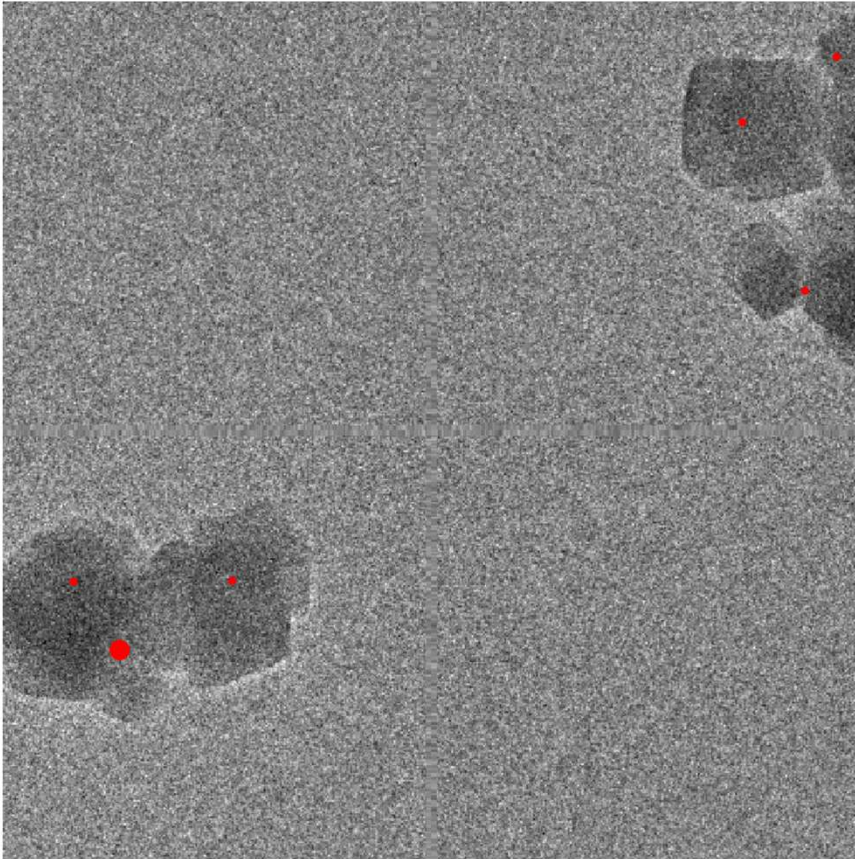


data\image\_0255\_0001.h5

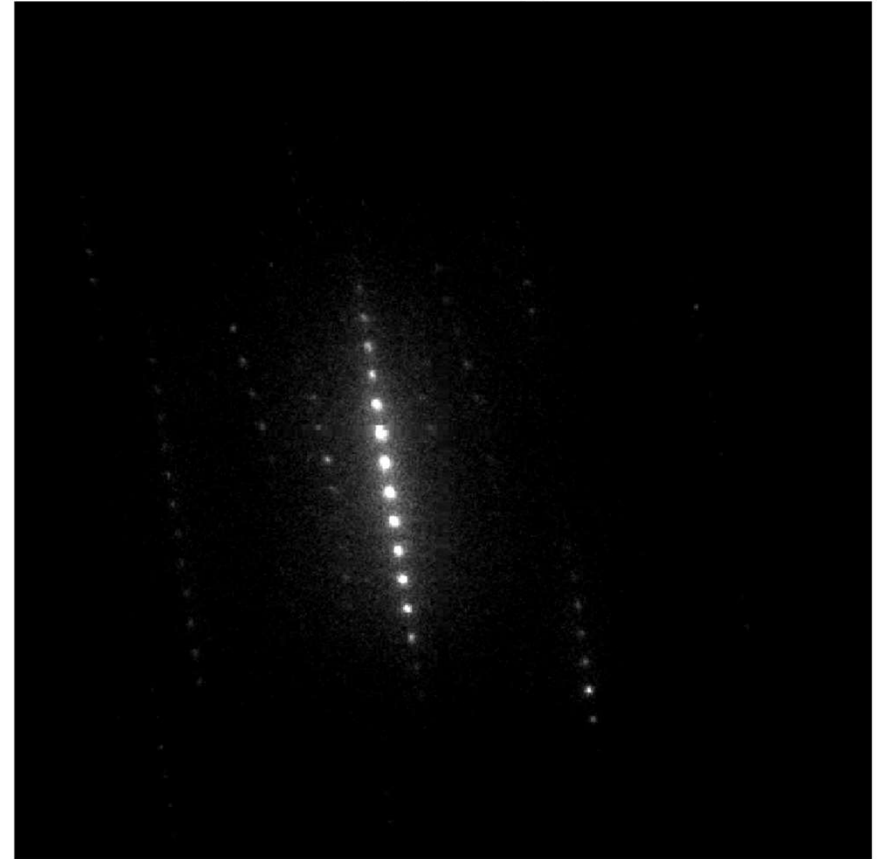


## Data collection 2/4

images\image\_0255.h5



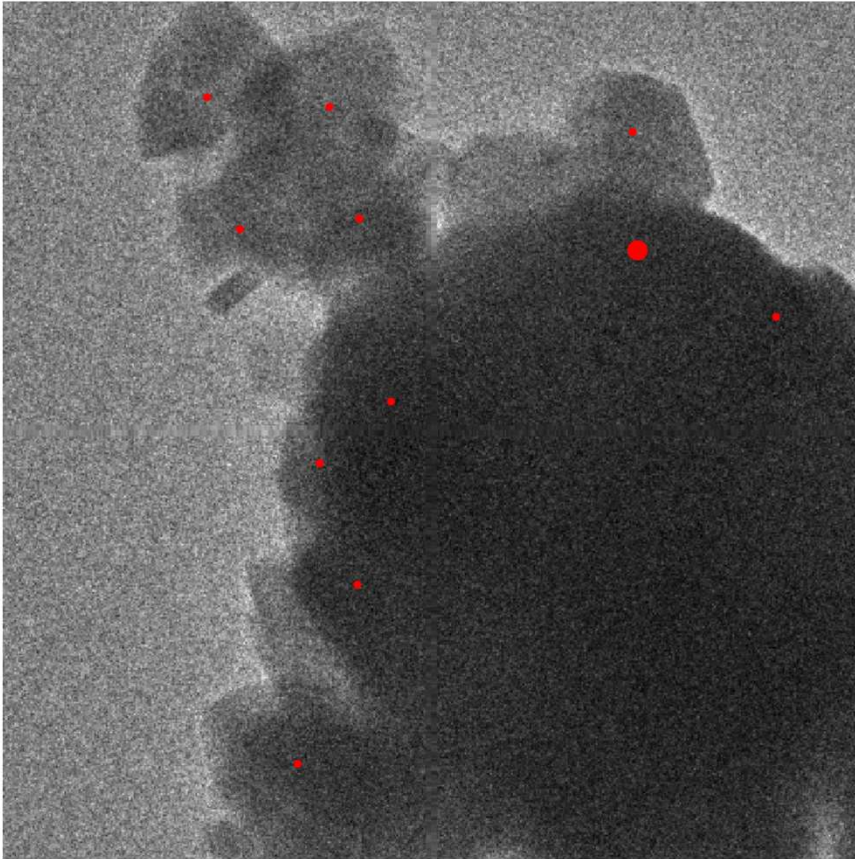
data\image\_0255\_0005.h5



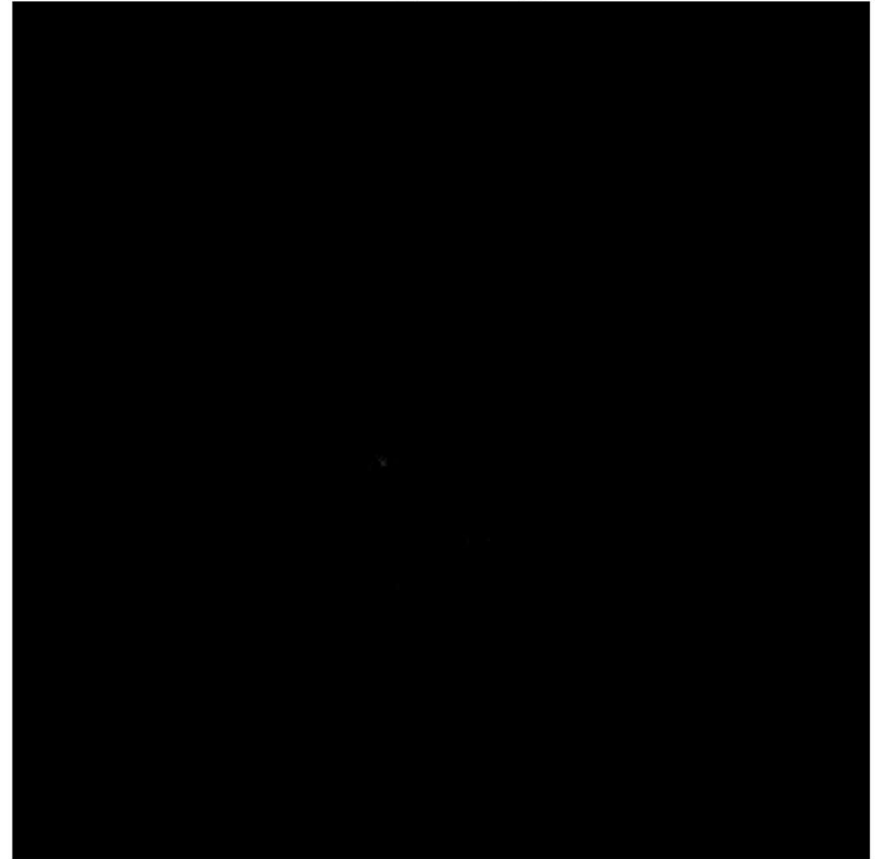


## Data collection 3/4

images\image\_0333.h5

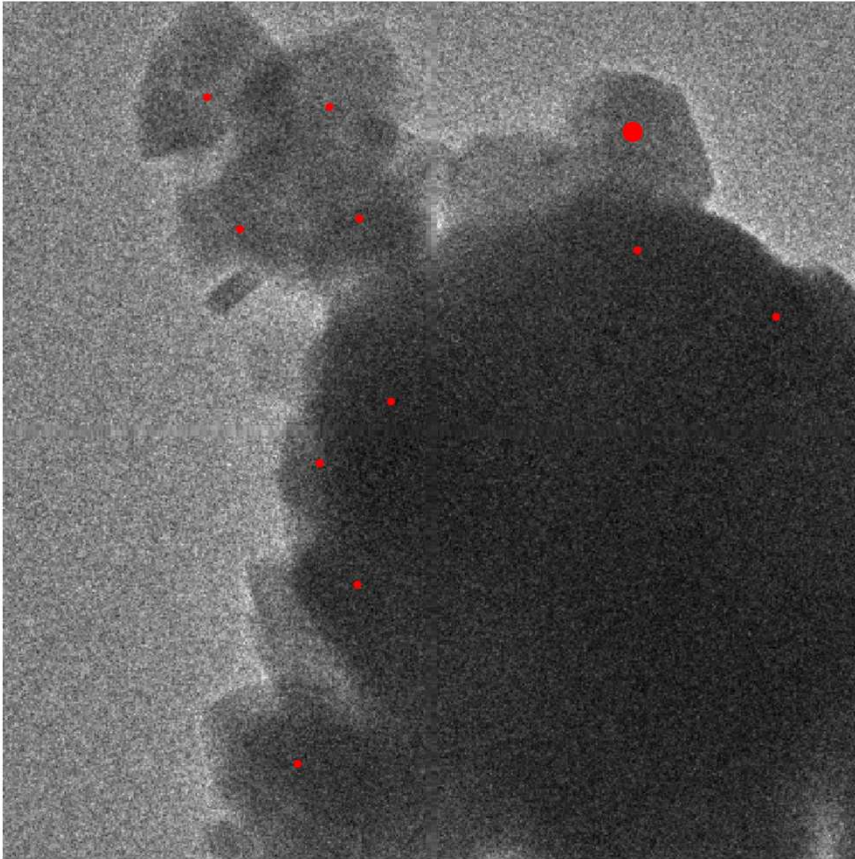


data\image\_0333\_0006.h5

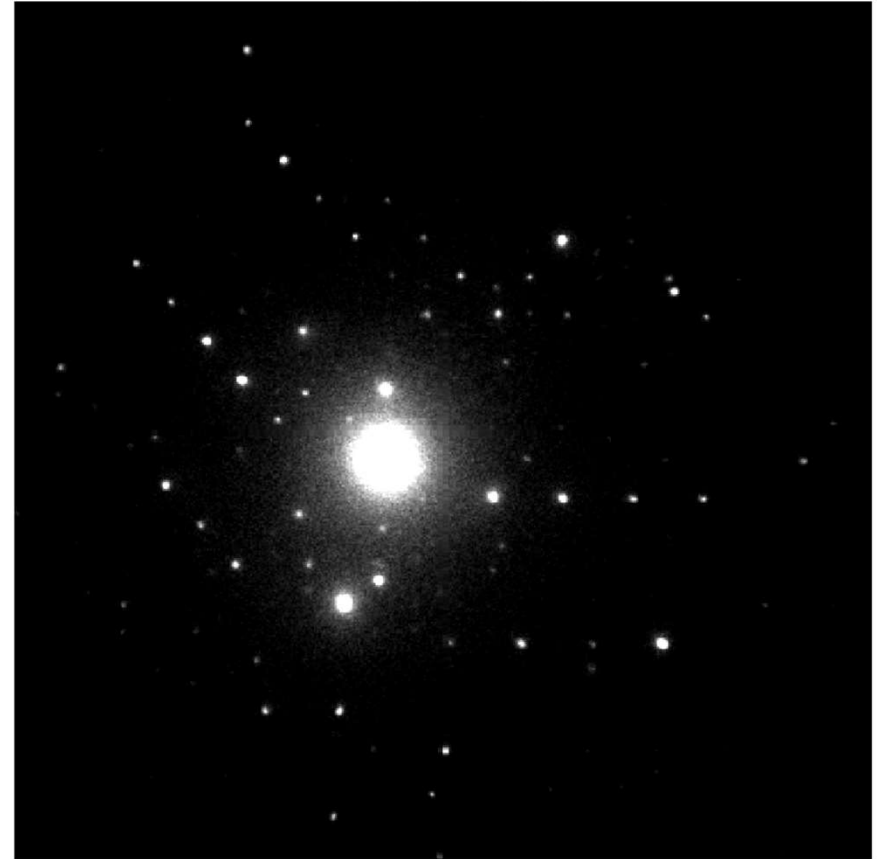


## Data collection 4/4

images\image\_0333.h5

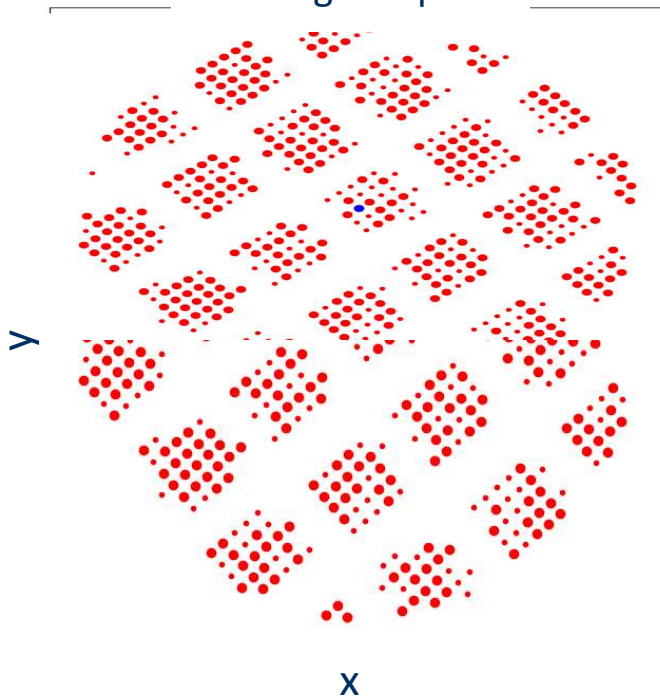


data\image\_0333\_0005.h5



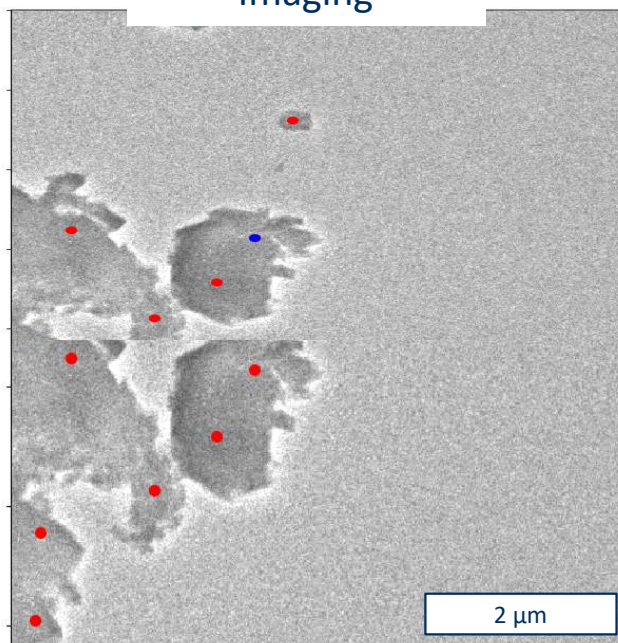
# Data collection (zeolite A)

Stage map



200 x 200  $\mu\text{m}$   
484 images  
35 minutes

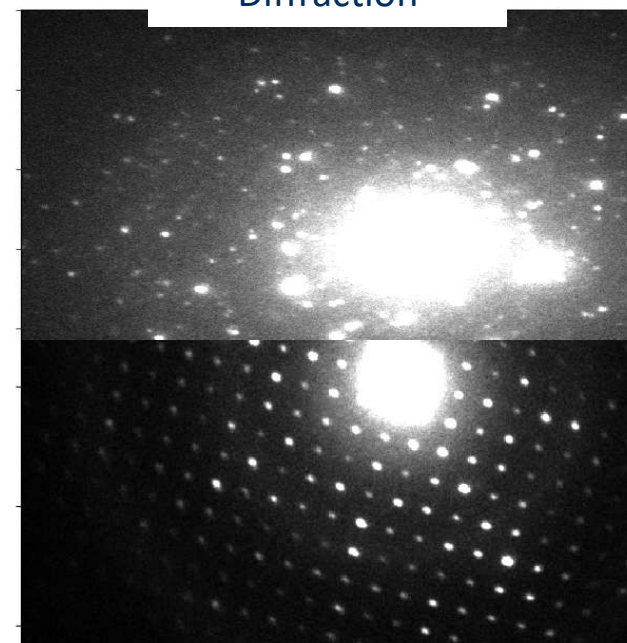
Imaging



Locate crystals

● Probe size  $\sim 500$  nm

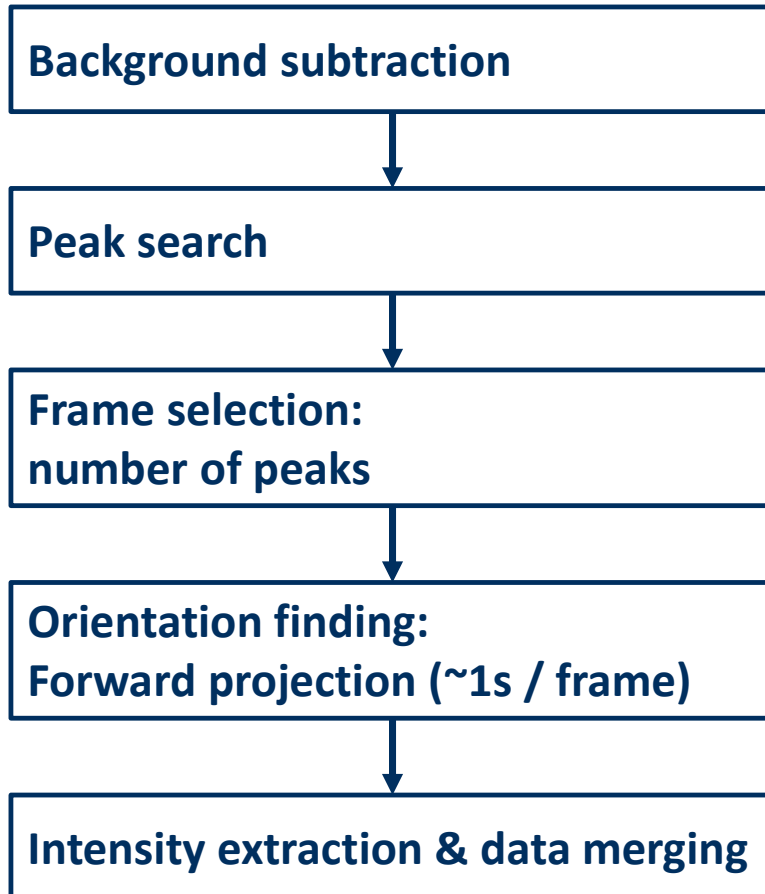
Diffraction



Collect data

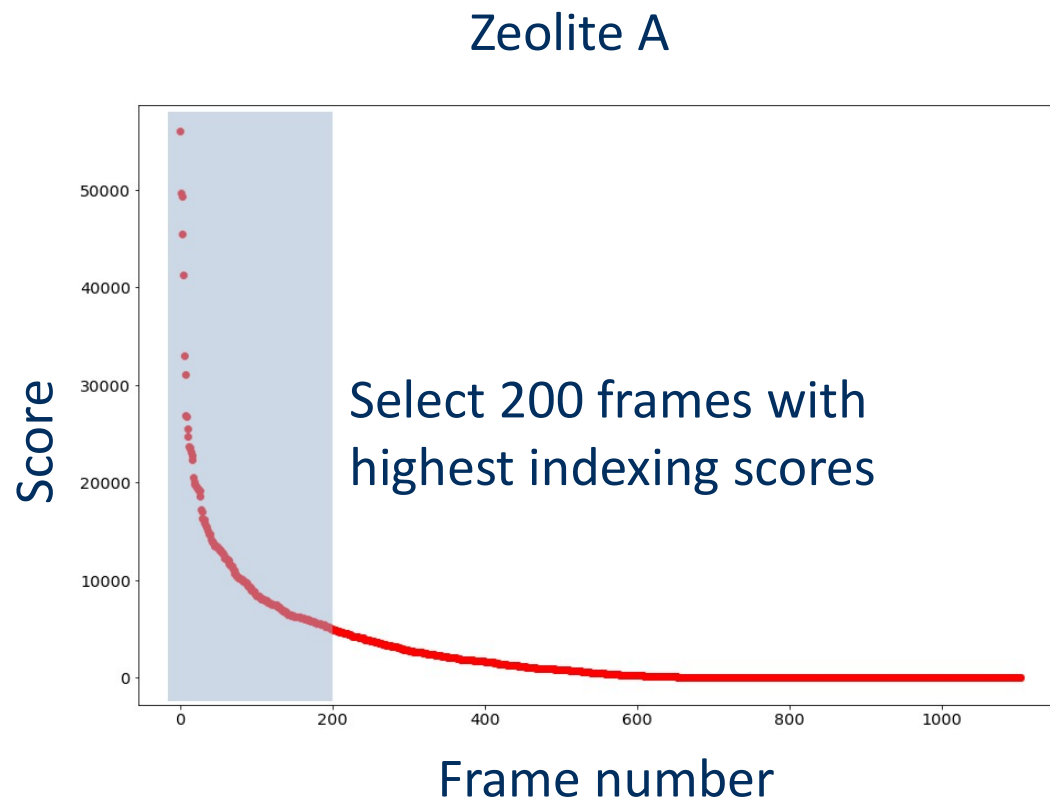
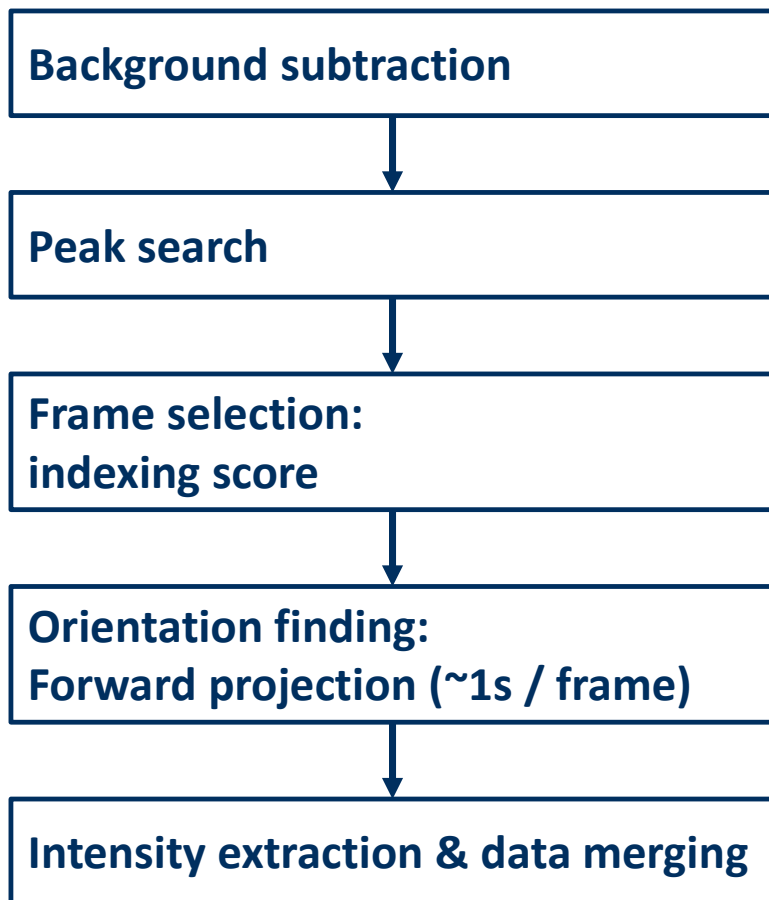
Total: 1107 patterns

# Data processing





# Data processing



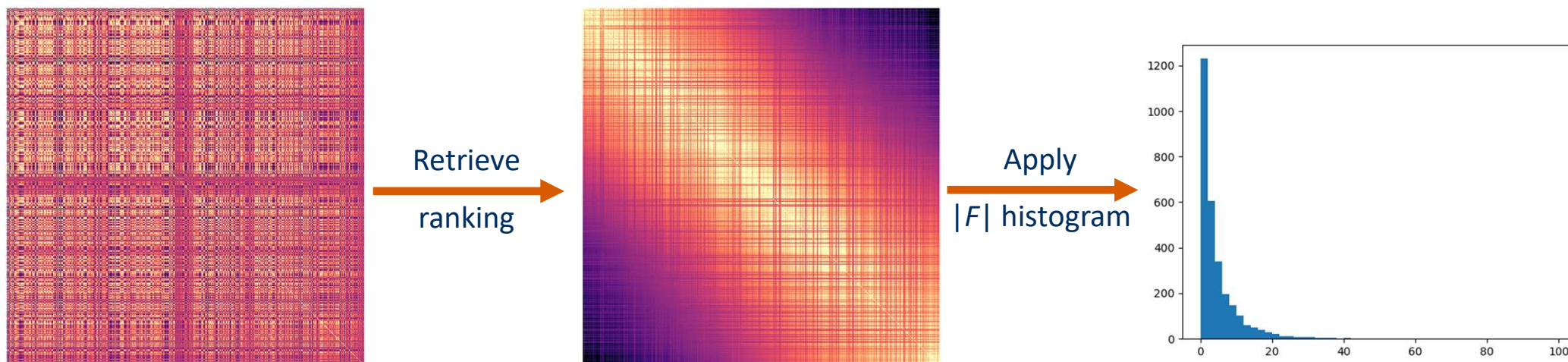
# Data Merging

## 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](http://www.github.com/stefsmeets/serialmerge)

# Structure determination

**shelx**  
 E:\instamatic\work\_2017-03-07\experiment7\shelx.res  
 $\text{SiO}_2$   $Fm\bar{3}c$   
 a = 24.61 Å  $\alpha = 90^\circ$  Z = 192 Rt:  
 b = 24.61 Å  $\beta = 90^\circ$  Z' = 1  
 c = 24.61 Å  $\gamma = 90^\circ$  V = 14905.098181  
**Solution**  
 $d_{\min}$  0.02511 0.03  $I_{\text{int}}$  155.4  $I_{\text{int}}$  Merged complete 100%  
 Shift n/a Max Peak n/a Min Peak n/a Goof n/a  
 Home Work View Tools Info  
 Solve Refine Draw Report  
 ShelXS  $R_{\text{alpha}}=0.19$ ,  $N_{\text{qual}}=0.0$ ,  $\text{CFOM}=0.19$  Auto Assign  
 Solution Program: ShelXS  
 Solution Method: Direct Methods  
 Reflection File: shelx.hkl  
 Chemical Composition:  $\text{Si}_2\text{O}_7$   
 Z and Z': Atomic Vol. = 25.9 Å<sup>3</sup> Z = 192 Z' = 1  
 Space Group: Suggest SG  $Fm\bar{3}c$   
 Solution Settings Extra  
 Toolbox Work  
 Labels Labels OFF/ON  
 Si O ... Add H  
 Split atoms you click next with: No Restraint EADE ISOR SMU  
 Select group or atom(s) and then: Split FI Split or Move with SHIF key  
 Electron Density Map  
 Peak & Uiso Sliders  
 Growing  
 Finishing  
 History  
 Select  
 Naming  
 Sorting

```

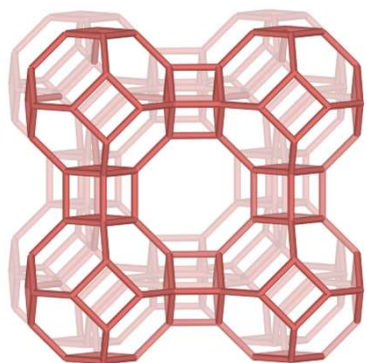
TREF tries:
CFOM NQual Try# Semiivariates
0.19 0 637735 00094271540
0.197 0 1920187 00174041946
0.234 0 253587 00038231492
0.268 0 465507 00004074641
0.274 0 367727 00268435455
0.276 0 1731971 00268435455
There are 46 more tries
  
```

**Zeolite A**  
 $Fm\bar{3}c$   
 $a = 24.61 \text{ \AA}$   
 $\text{Si}_{96}\text{Al}_{96}\text{O}_{384}$   
 $Z = 192$

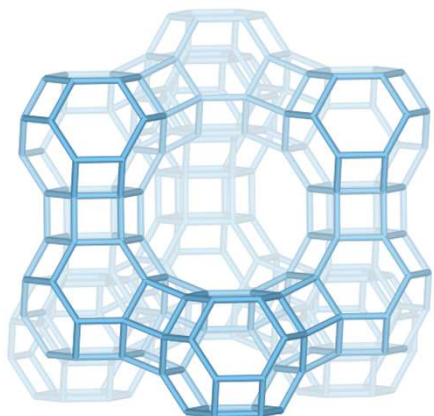
200 frames

**Reflections**  
 Total: 19804  
 Unique: 227  
 $d_{\min}$ : 1.03 Å  
 Compl.: 100%

# Structures solved

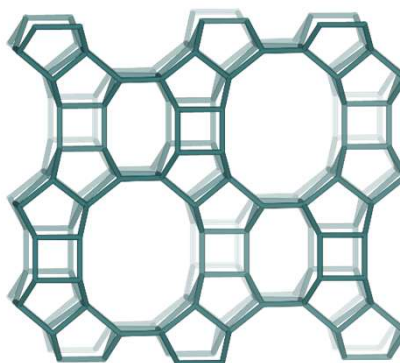


Zeolite A  
 $Fm\bar{3}c$   
 $a = 24.61 \text{ \AA}$   
 $\text{Si}_{96}\text{Al}_{96}\text{O}_{384}$   
 $Z = 192$

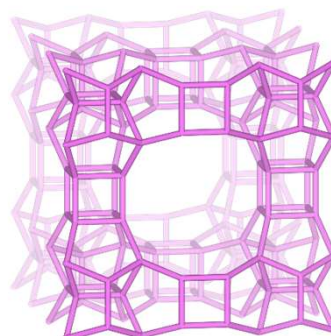


Zeolite Y  
 $Fd\bar{3}m$   
 $a = 24.74 \text{ \AA}$   
 $\text{Si}_{192}\text{O}_{384}$   
 $Z = 192$

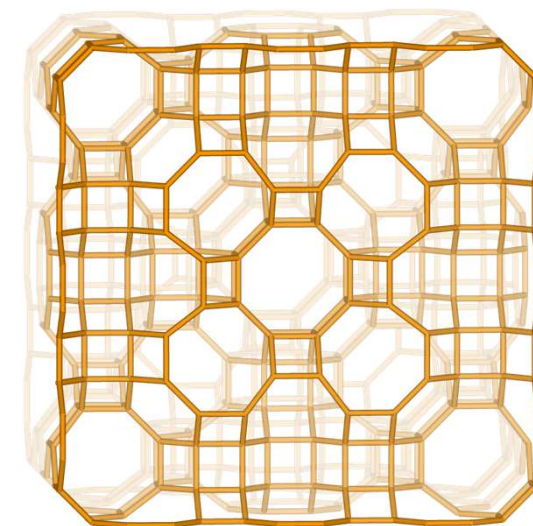
Direct methods  
ShelXS



Mordenite  
 $Cmcm$   
 $a = 18.11 \text{ \AA}$   
 $b = 20.53 \text{ \AA}$   
 $c = 7.53 \text{ \AA}$   
 $\text{Si}_{40}\text{Al}_8\text{O}_{96}$   
 $Z = 16$



Ge-BEC  
 $P4_2/mmc$   
 $a = 12.82 \text{ \AA}$   
 $c = 13.35 \text{ \AA}$   
 $\text{Si/Ge}_{32}\text{O}_{64}$   
 $Z = 16$



Paulingite  
 $Im\bar{3}m$   
 $a = 35.08 \text{ \AA}$   
 $\text{Si}_{672}\text{O}_{1344}$   
 $Z = 96$

Dual-space methods  
FOCUS

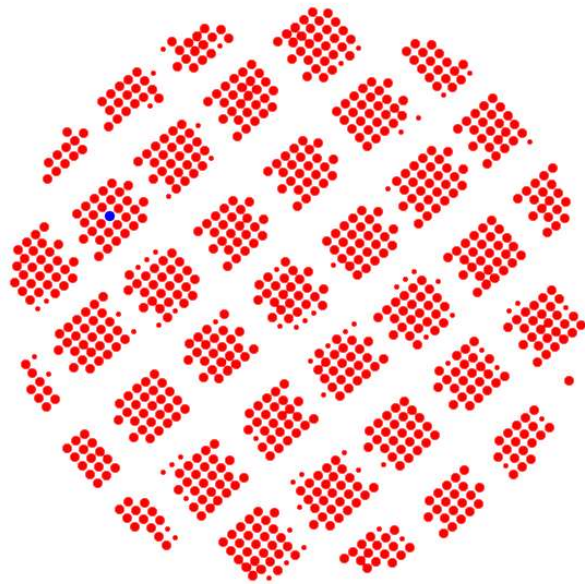


## Structures solved

	Time (min)	Patterns total	Patterns merged	Refs. total	Refs. unique	Compl. (%)	$d_{\min}$ (Å)	Method
<b>Zeolite A</b>	35	1107	200	19804	227	100	1.0	ShelXS
<b>Zeolite Y</b>	80	2506	99	7569	387	100	1.0	ShelXS
<b>Mordenite</b>	25	694	62	2882	603	(72)	1.0	FOCUS
<b>Ge-BEC</b>	100	6520	232	26144	481	(71)	1.0	FOCUS
<b>Paulingite</b>	40	780	83	9247	813	87	1.35	FOCUS

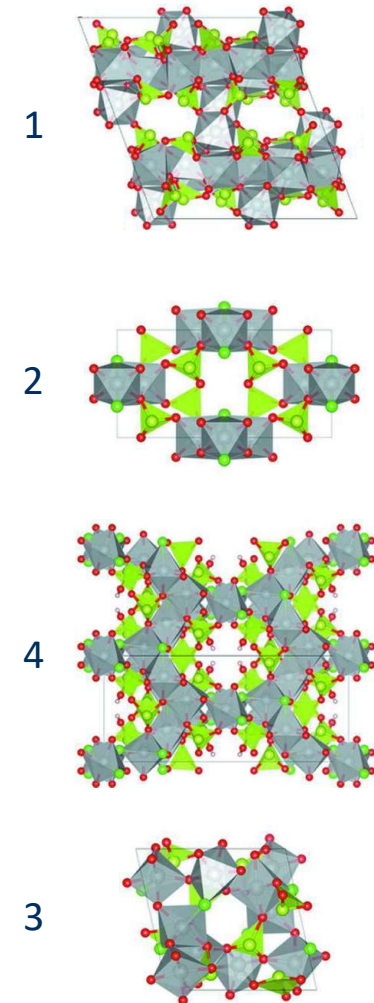
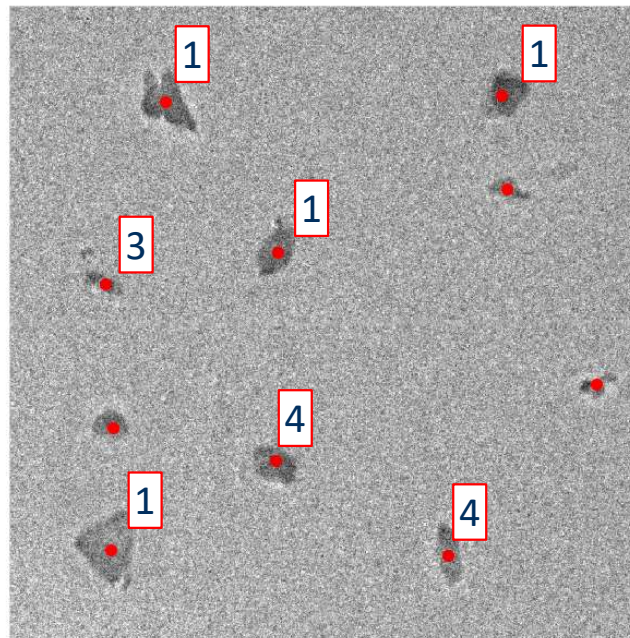
# Phase analysis (Ni-Se-O-Cl)

Stage map



400 x 400  $\mu\text{m}$   
925 images  
6171 patterns  
~90 minutes

Identify crystals



## Conclusions

- Serial ED data can be collected routinely & automatically
- SerialMerge algorithm can effectively merge serial ED data
- 100-200 diffraction patterns are enough for structure determination

## *Applications*

- Structure determination (of beam-sensitive materials)
- Crystal identification
  - Screening
  - Quantitative phase analysis
  - Polymorphism