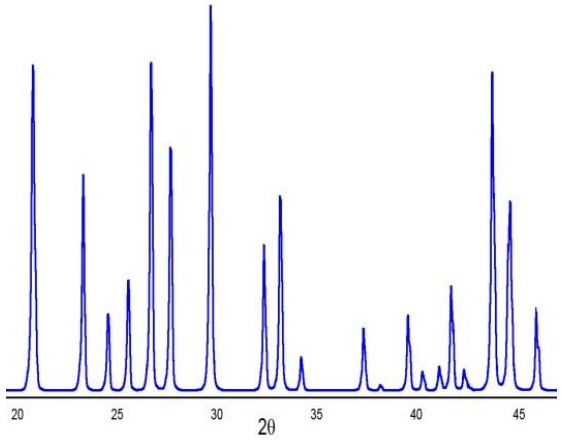
## Croucher summer courses

# PXRD and Electron crystallography for structure determination

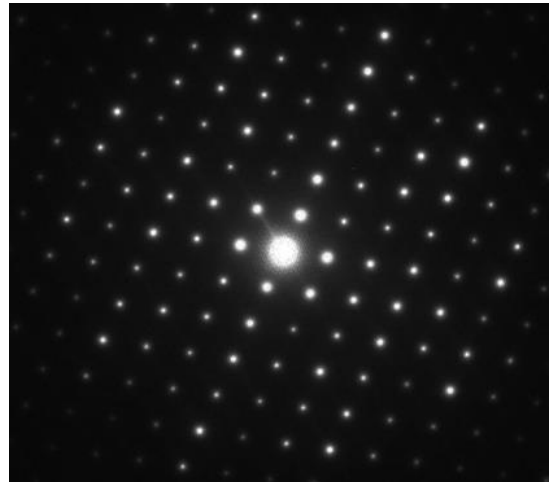



**Junliang Sun 孙俊良**

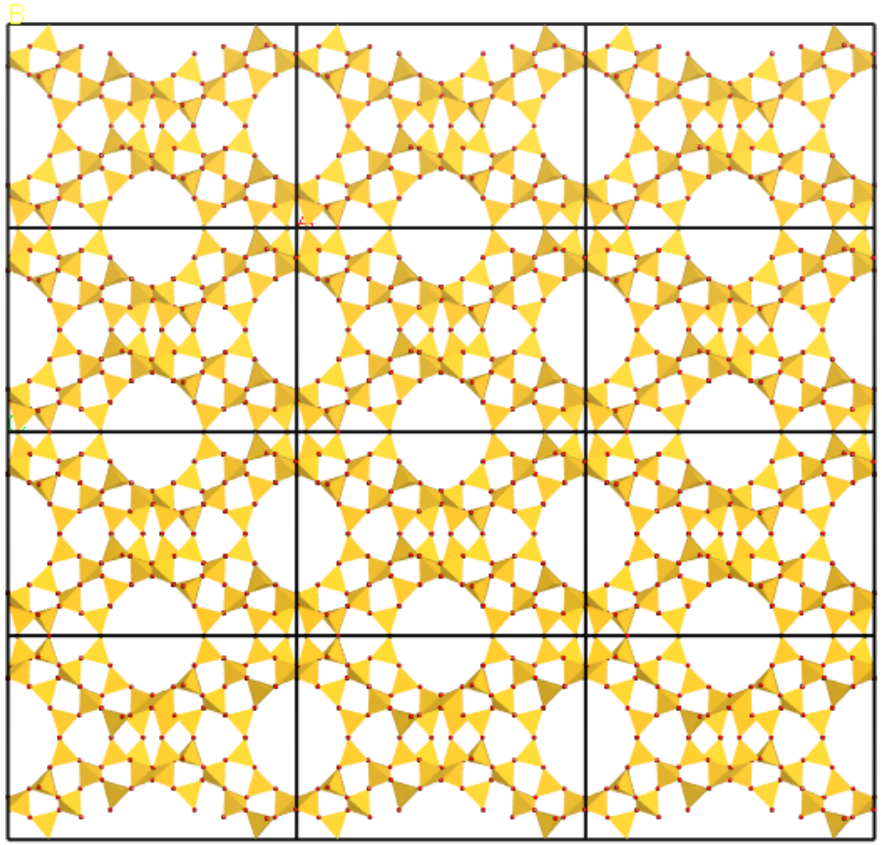
**Peking University**

junliang.sun@pku.edu.cn

**Hongkong 2024. 6. 19**



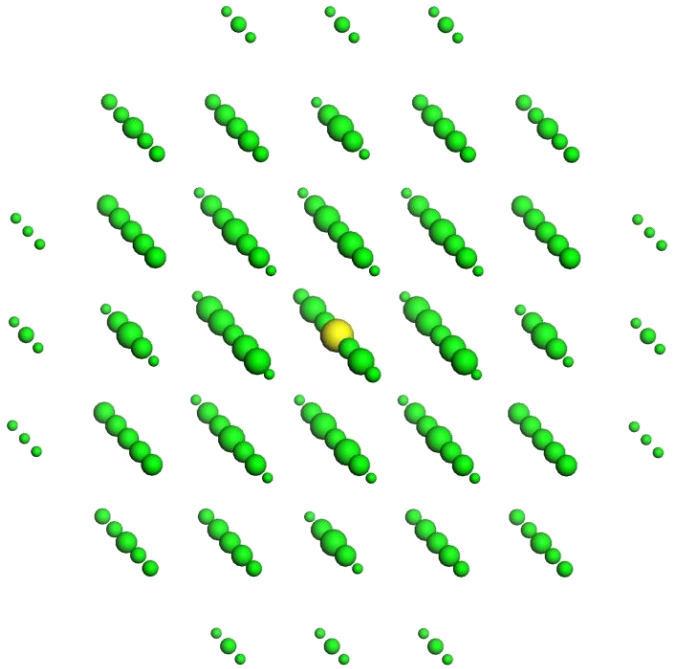
# Real space



Y-zeolite, *Fd*-3*m*

| Atom | X | Y | Z |
|---|---|---|---|
| Si | 0.9469 | 0.1251 | 0.0364 |

# Reciprocal Space

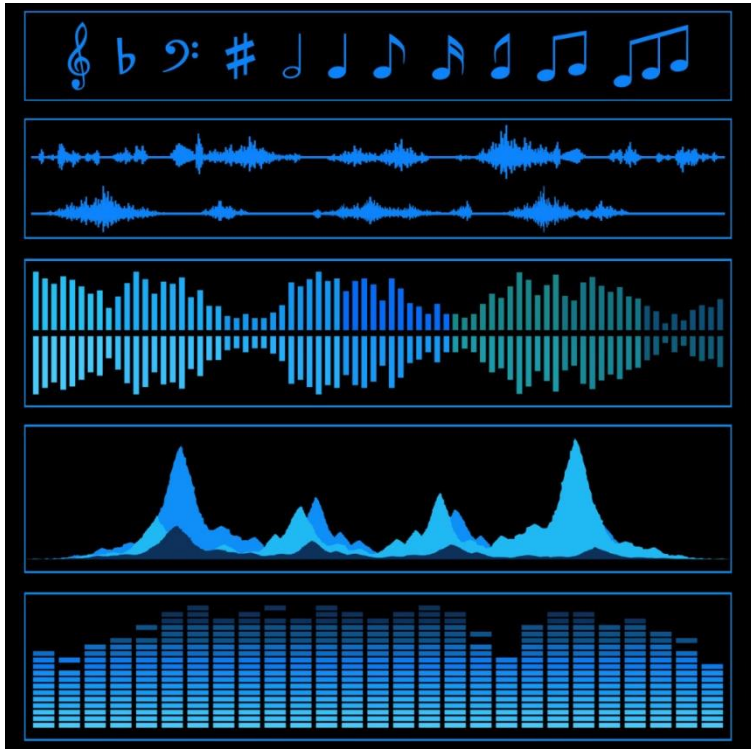


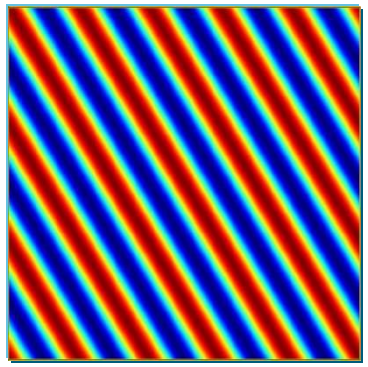
| h | k | l | $F_{hkl}$ | Pha |
|---|---|---|---|---|
| 1 | 1 | 1 | 100 | 0 |
| 2 | 2 | 0 | 12 | 0 |
| 3 | 1 | 1 | 6 | 180 |
| 3 | 3 | 2 | 10 | 0 |
| 5 | 1 | 1 | 4 | 0 |

. . .

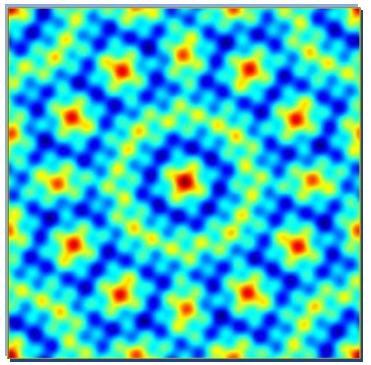
# 2D reciprocal space

| h | k | $F_{hk}$ | Pha |
|---|---|---|---|
| 0 | 6 | 100 | 0 |
| 3 | 5 | 91 | 0 |
| 5 | 3 | 90 | 0 |
| 14 | 8 | 86 | 0 |
| 5 | 9 | 80 | 0 |
| 8 | 14 | 79 | 0 |
| 14 | 14 | 79 | 0 |
| 8 | 8 | 78 | 0 |

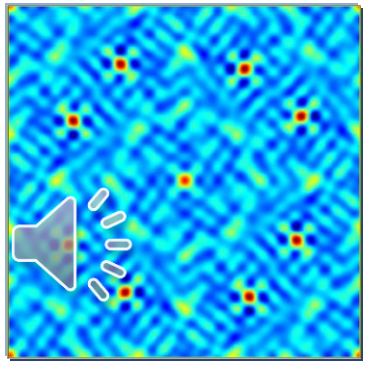




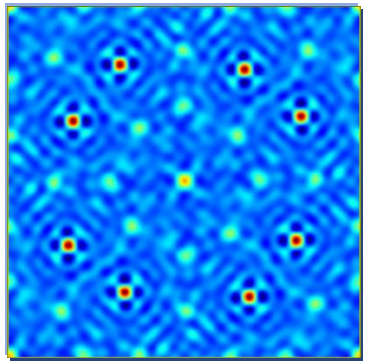
3 5



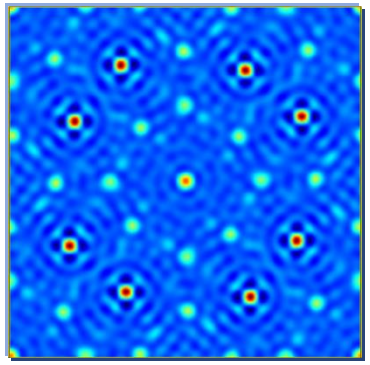
4 reflections (90%)



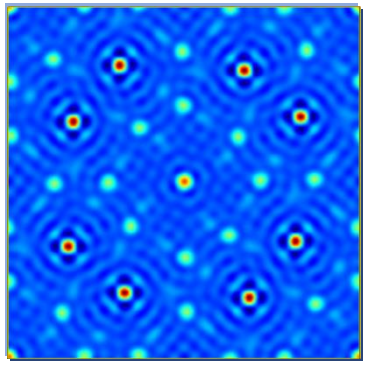
28 reflections(50%)



68 reflections(30%)



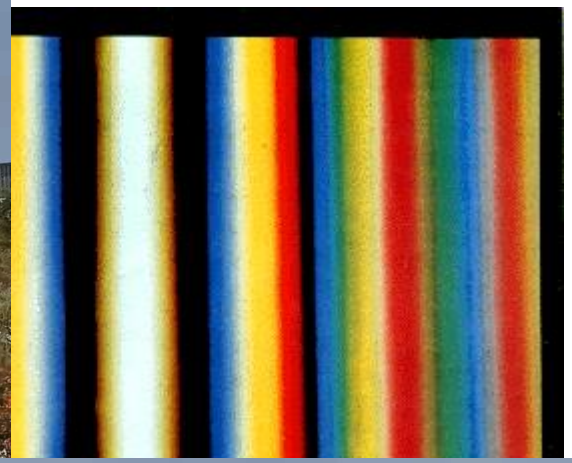
118 reflections(20%)

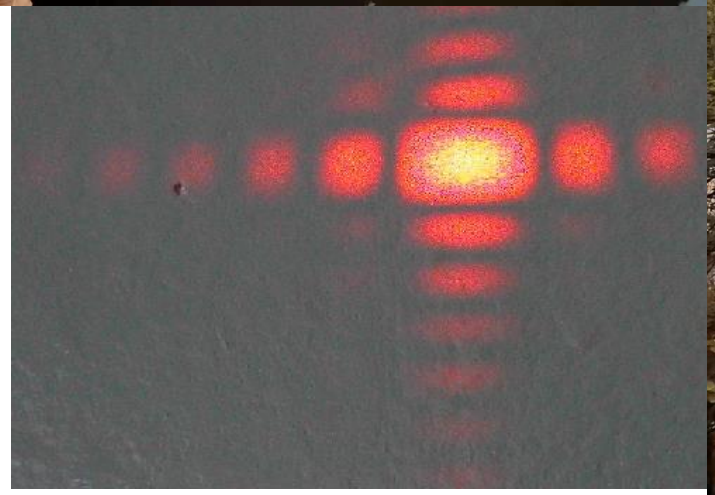


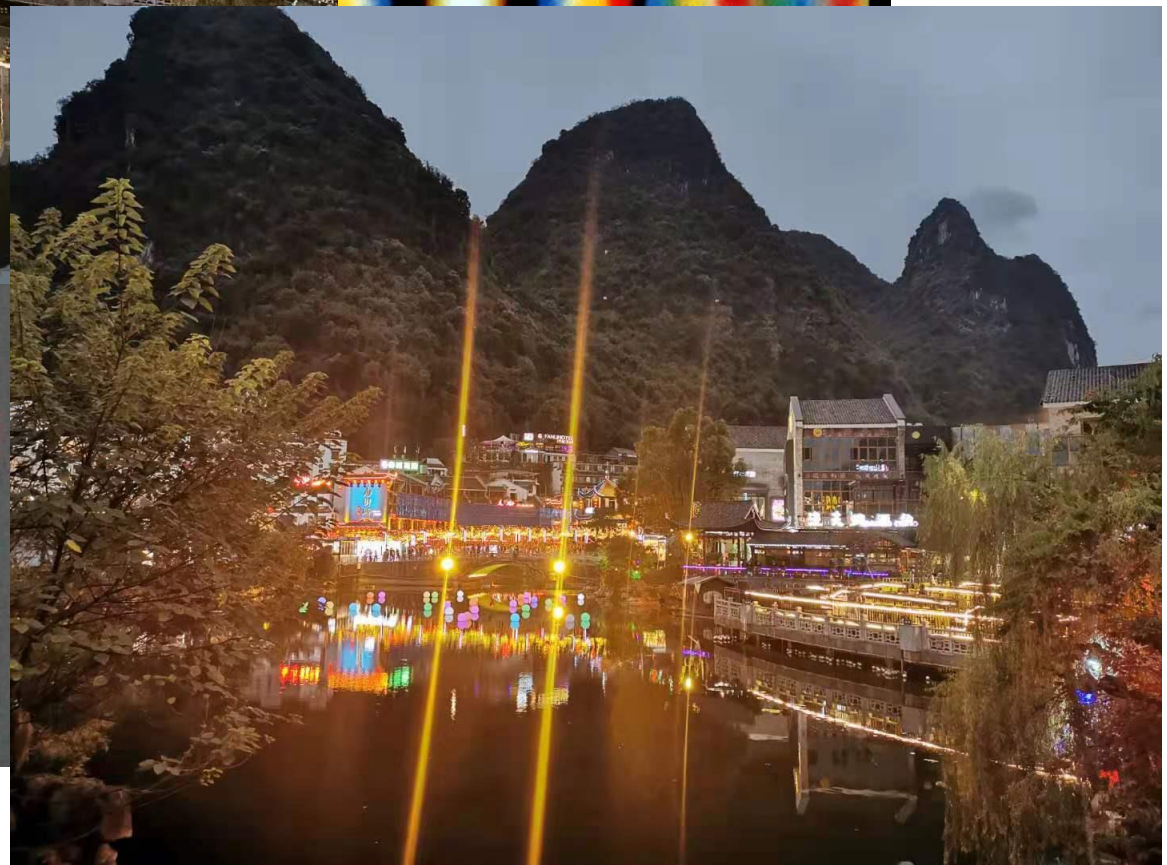
220 reflections

ffraction of grating









# Three different probes

## X-ray

- **1914** Physics, M. Von Laue
  *Diffraction of X-rays by crystals*

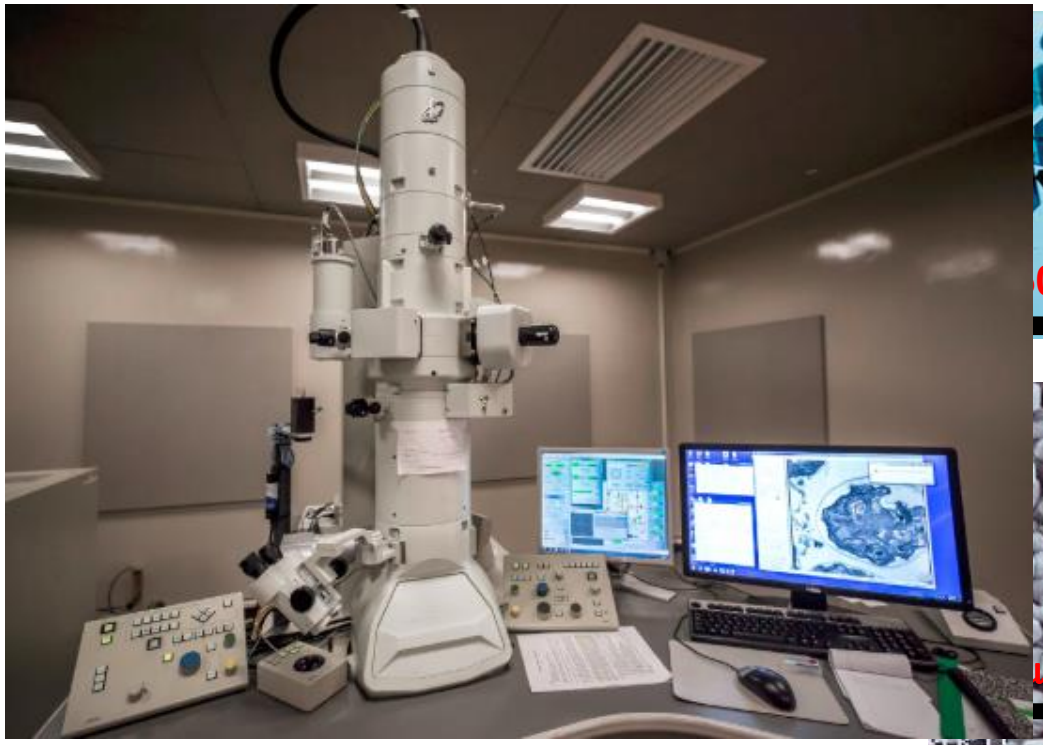
## Electron

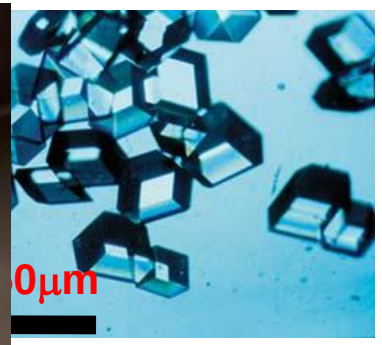
•**1937** Physics, C.J. Davisson and G. Thompson
*Diffraction of electrons by crystals*

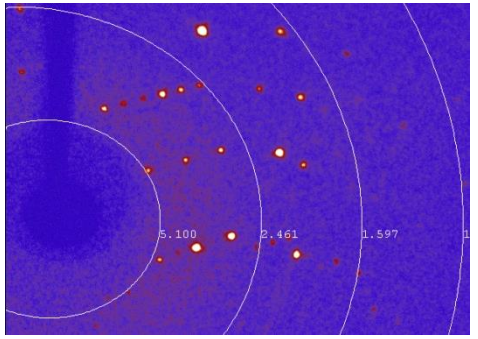
## Neutron

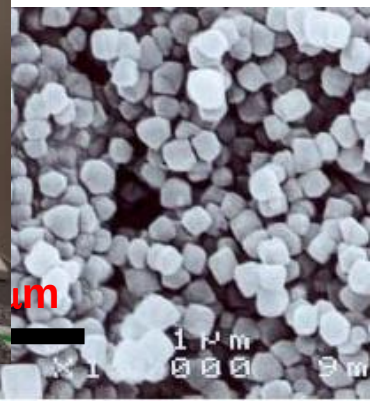
•**1994** Physics, C. Shull and N. Brockhouse
*Neutron diffraction*

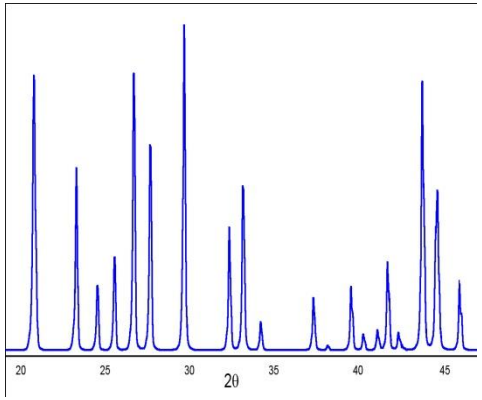
# Three structure determination methods



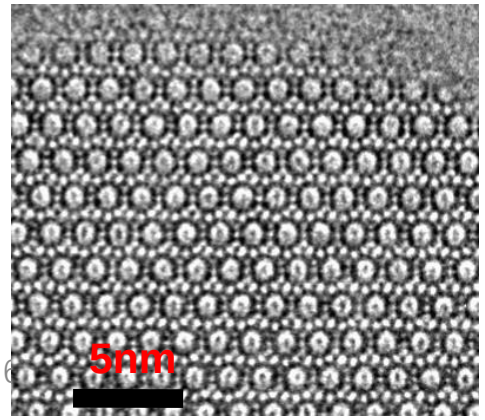


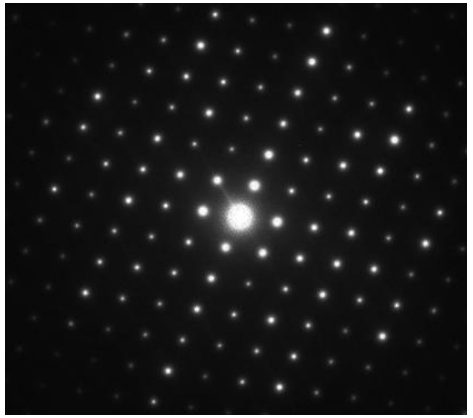



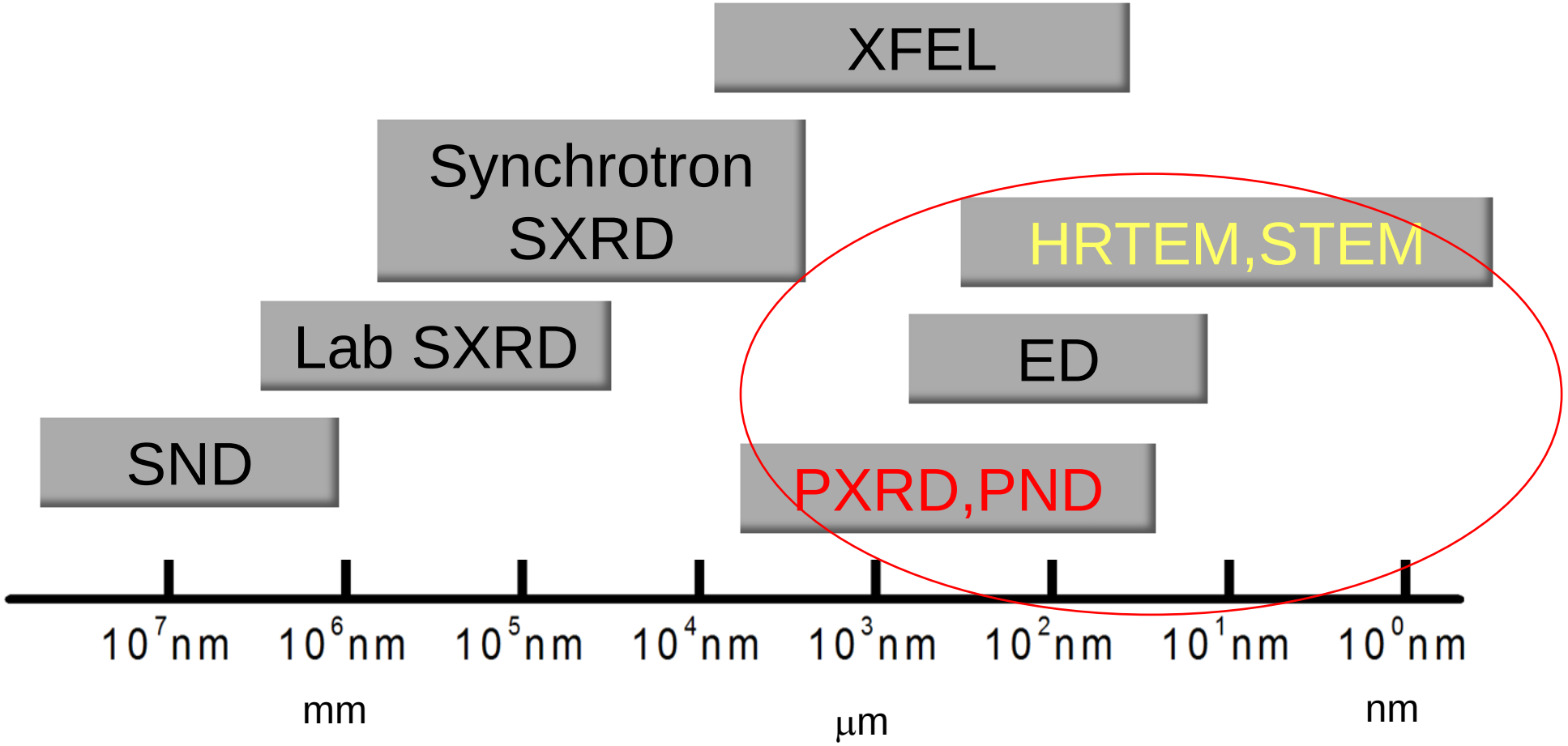




- Electron microscopy
  > a few unit cells
  (EM Images and
  ED patterns)



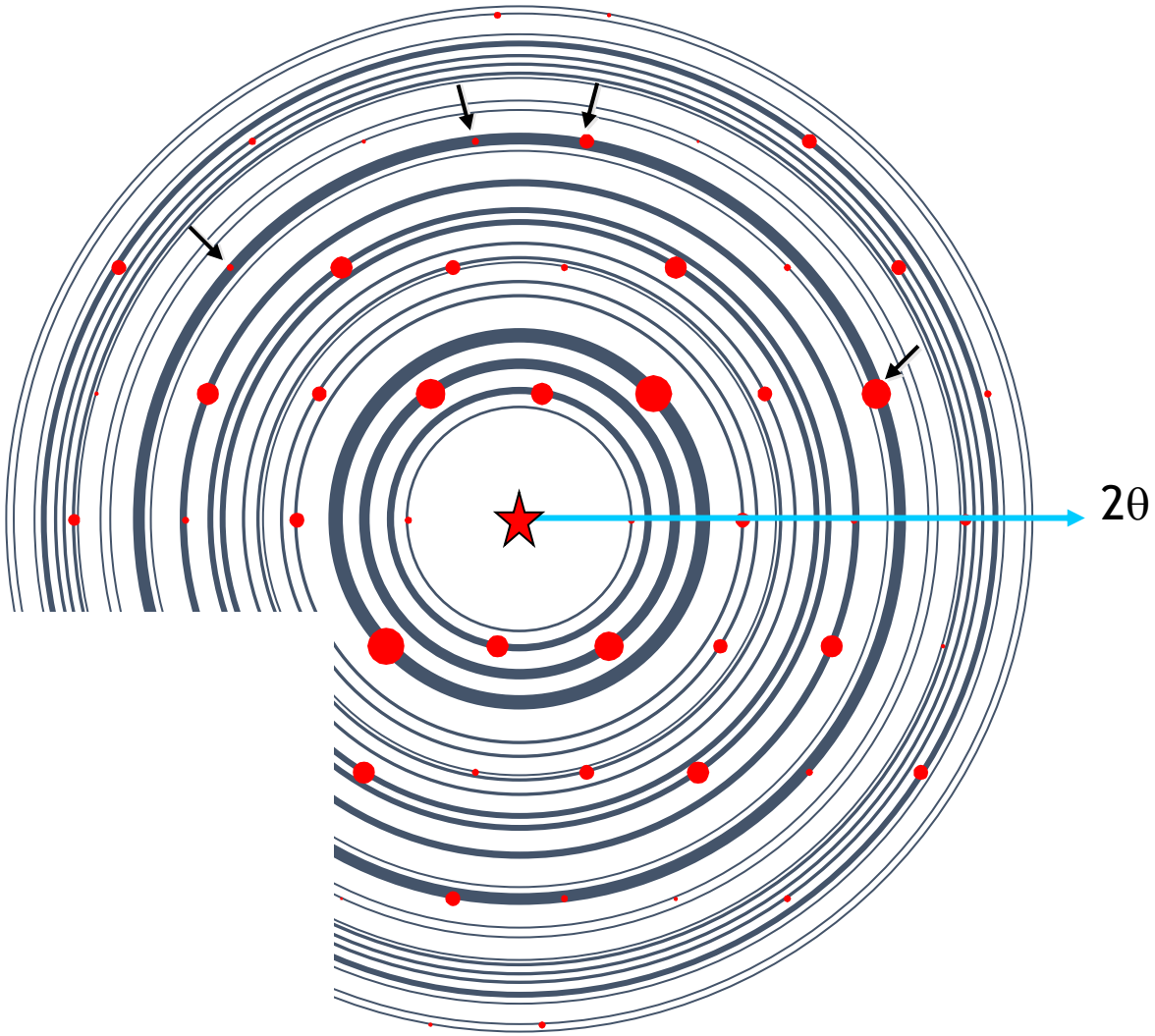



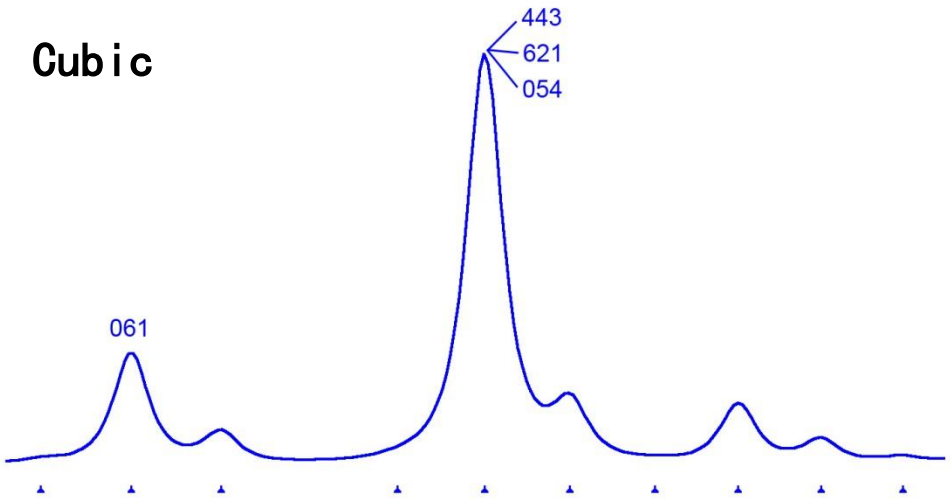



Crystal size limitation for different techniques

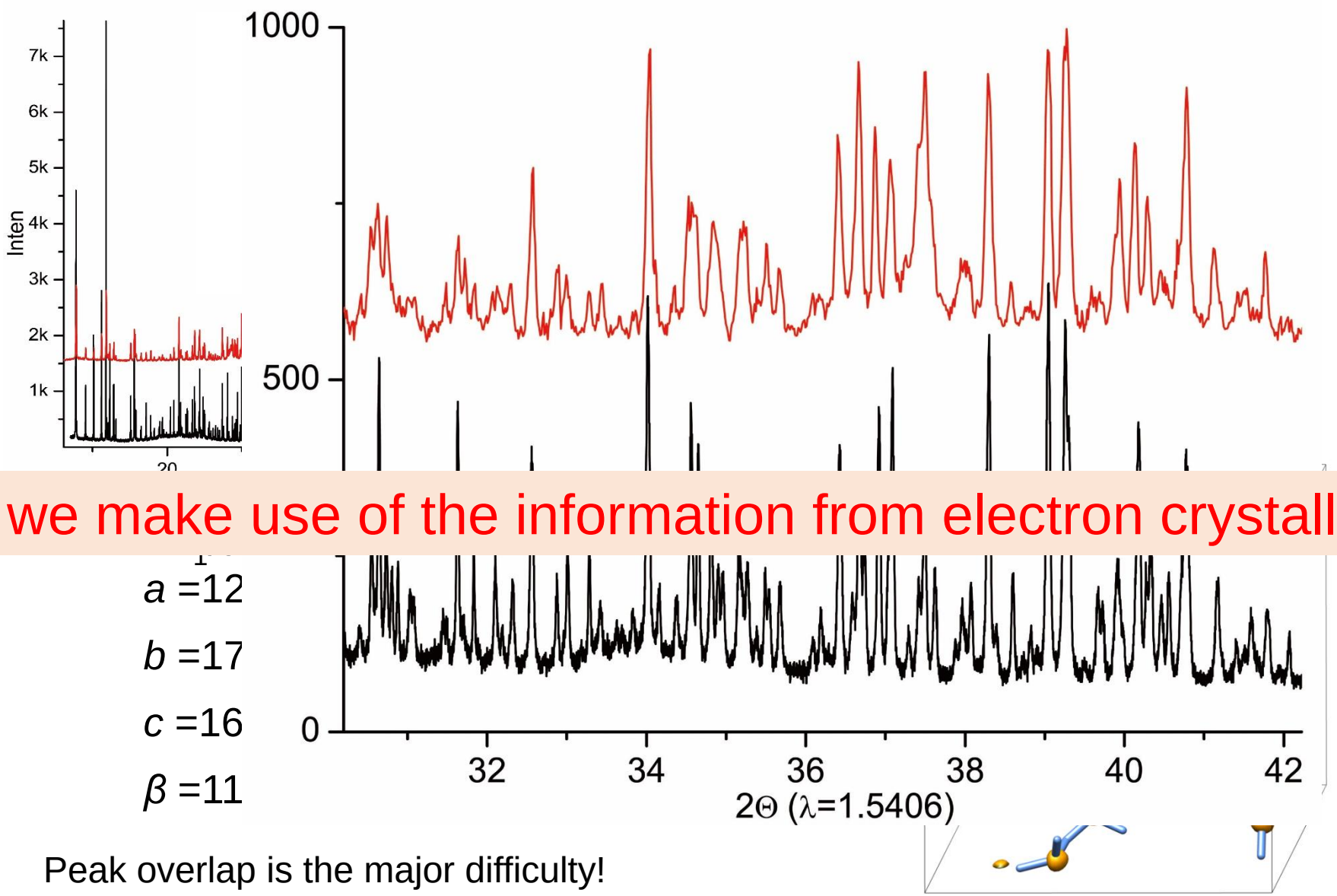
# Structure Solution by Powder XRD





Most complicated Germanates SU-74 by PXRD




Can we make use of the information from electron crystallography?

Peak overlap is the major difficulty!

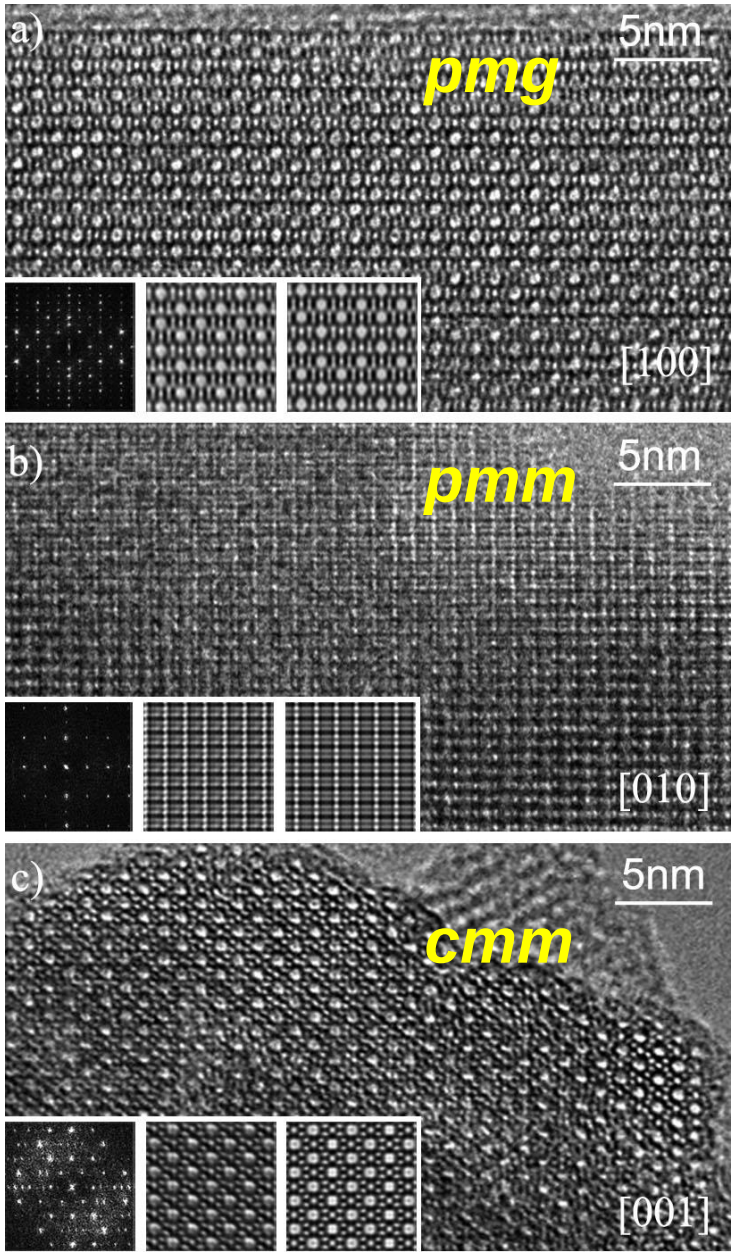
Inge et al. *Cryst. Growth Des.* **2012**, *12*, 4853

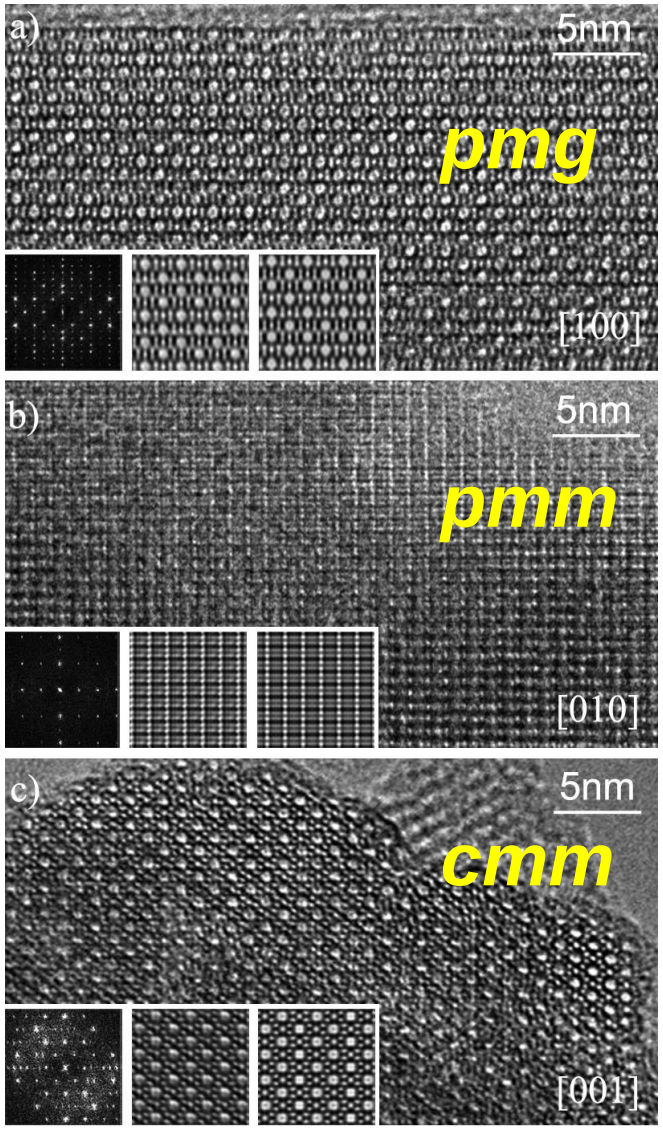
# Structure determination from images

**Reflection symbol:** *C-c-*

- *hkl*: *h*+*k* = 2*n*;
- 0*kl*: *k* = 2*n*;
- *h*0*l*: *h* = 2*n*, *l* = 2*n*;
- *hk*0: *h*+*k* = 2*n*;
- *h*00: *h* = 2*n*;
- 0*k*0: *k* = 2*n*;
- 00*l*: *l* = 2*n*.

| S. P. | [1 0 0] | [0 1 0] | [0 0 1] |
|---|---|---|---|
| $Cmc2_1$ | *pg* | *pm* (*m*⊥***a***) | *cmm* |
| *C*2*cm* | *pmg* | *pm* (*m*⊥***c***) | *cm* (*m*⊥***b***) |
| ***Cmcm*** | ***pmg*** | ***pmm*** | ***cmm*** |



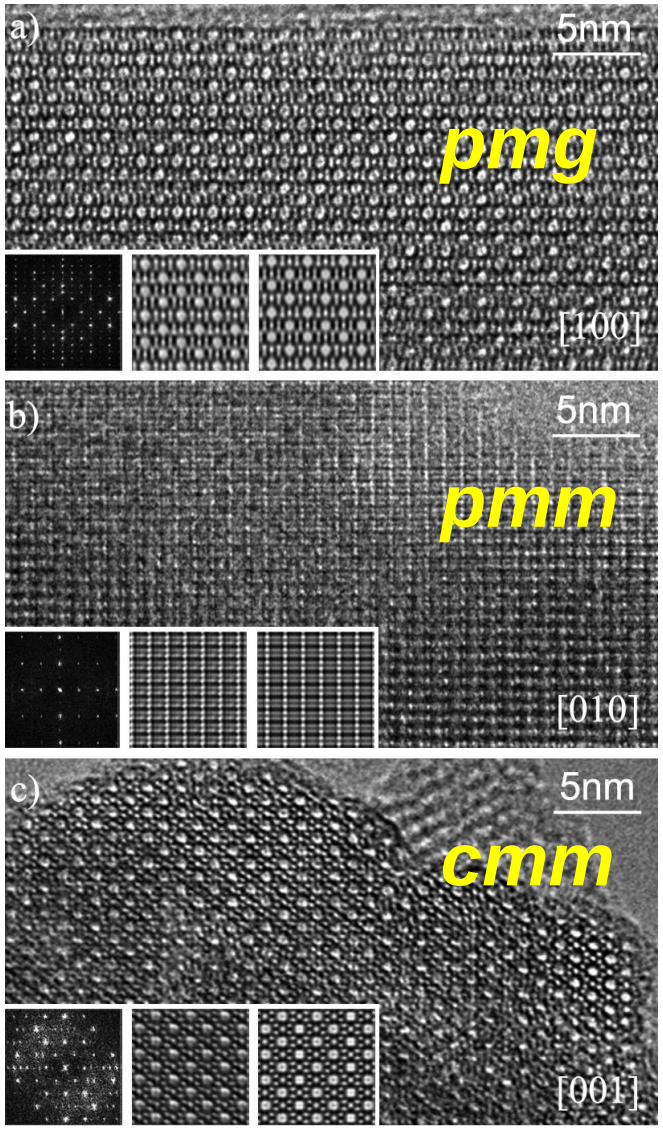



2D images

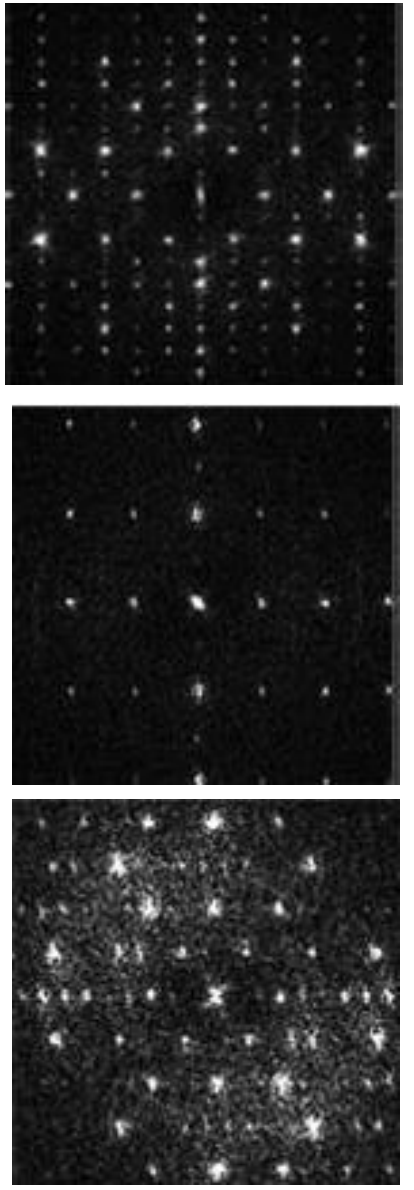


Project of 3D objects

Space group: *Cmcm*， $a$ = 14.3 Å, $b$ = 57.4 Å, $c$ = 20.1 Å




Fourier transform



2D images

2D reciprocal space

Space group: *Cmcm*， $a$ = 14.3 Å, $b$ = 57.4 Å, $c$ = 20.1 Å

| [100] | | | | | [010] | | | | | [001] | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| h | k | l | Amp | Pha | h | k | l | Amp | Pha | h | k | l | Amp | Pha |
| 0 | 0 | 2 | 6842 | 180 | 0 | 0 | 2 | 3011 | 180 | 0 | 4 | 0 | 1280 | 0 |
| 0 | 0 | 4 | 7000 | 0 | 0 | 0 | 4 | 3693 | 0 | 0 | 6 | 0 | 6638 | 0 |
| 0 | 0 | 6 | 2474 | 180 | 0 | 0 | 6 | 2997 | 180 | 0 | 8 | 0 | 1174 | 180 |
| 0 | 2 | 0 | 1201 | 0 | 0 | 0 | 12 | 105 | 0 | 0 | 10 | 0 | 661 | 180 |
| 0 | 2 | 1 | 238 | 0 | 2 | 0 | 0 | 4267 | 0 | 0 | 12 | 0 | 2814 | 0 |
| 0 | 2 | -1 | 238 | 180 | 2 | 0 | 2 | 674 | 0 | 0 | 14 | 0 | 1911 | 0 |
| 0 | 2 | 2 | 648 | 0 | 2 | 0 | -2 | 674 | 0 | 0 | 16 | 0 | 2400 | 180 |
| 0 | 2 | -2 | 648 | 0 | 2 | 0 | 4 | 123 | 180 | 0 | 22 | 0 | 448 | 180 |
| 0 | 2 | 3 | 923 | 180 | 2 | 0 | -4 | 123 | 180 | 0 | 24 | 0 | 439 | 180 |
| 0 | 2 | -3 | 923 | 0 | 2 | 0 | 6 | 178 | 180 | 1 | 1 | 0 | 687 | 180 |
| 0 | 2 | 4 | 524 | 180 | 2 | 0 | -6 | 178 | 180 | 1 | -1 | 0 | 687 | 180 |
| 0 | 2 | -4 | 524 | 180 | 2 | 0 | 8 | 278 | 0 | 1 | 3 | 0 | 7376 | 0 |
| 0 | 2 | 5 | 1019 | 180 | 2 | 0 | -8 | 278 | 0 | 1 | -3 | 0 | 7376 | 0 |
| 0 | 2 | -5 | 1019 | 0 | 2 | 0 | 10 | 147 | 0 | 1 | 7 | 0 | 1349 | 0 |
| 0 | 2 | 6 | 240 | 0 | 2 | 0 | -10 | 147 | 0 | 1 | -7 | 0 | 1349 | 0 |
| 0 | 2 | -6 | 240 | 0 | 4 | 0 | 0 | 10000 | 180 | 1 | 9 | 0 | 3533 | 0 |
| 0 | 2 | 7 | 224 | 180 | 4 | 0 | 2 | 1175 | 180 | 1 | -9 | 0 | 3533 | 0 |
| 0 | 2 | -7 | 224 | 0 | 4 | 0 | -2 | 1175 | 180 | 1 | 11 | 0 | 422 | 0 |
| 0 | 2 | 8 | 130 | 0 | 4 | 0 | 4 | 552 | 0 | 1 | -11 | 0 | 422 | 0 |
| 0 | 2 | -8 | 130 | 0 | 4 | 0 | -4 | 552 | 0 | 1 | 13 | 0 | 235 | 180 |
| 0 | 2 | 9 | 105 | 0 | 4 | 0 | 6 | 332 | 180 | 1 | -13 | 0 | 235 | 180 |
| 0 | 2 | -9 | 105 | 180 | 4 | 0 | -6 | 332 | 180 | 1 | 15 | 0 | 4702 | 180 |
| 0 | 2 | 10 | 87 | 180 | 4 | 0 | 8 | 172 | 180 | 1 | -15 | 0 | 4702 | 180 |
| 0 | 2 | -10 | 87 | 180 | 4 | 0 | -8 | 172 | 180 | 1 | 17 | 0 | 149 | 180 |
| 0 | 4 | 0 | 1120 | 0 | 4 | 0 | 10 | 86 | 180 | 1 | -17 | 0 | 149 | 180 |
| 0 | 4 | 1 | 6428 | 180 | 4 | 0 | -10 | 86 | 180 | 1 | 19 | 0 | 297 | 180 |
| 0 | 4 | -1 | 6428 | 0 | 4 | 0 | 12 | 81 | 0 | 1 | -19 | 0 | 297 | 180 |
| 0 | 4 | 2 | 382 | 180 | 4 | 0 | -12 | 81 | 0 | 1 | 21 | 0 | 283 | 180 |
| 0 | 4 | -2 | 382 | 180 | 6 | 0 | 0 | 651 | 180 | 1 | -21 | 0 | 283 | 180 |
| 0 | 4 | 3 | 6892 | 0 | 6 | 0 | 2 | 241 | 180 | 1 | 25 | 0 | 94 | 180 |

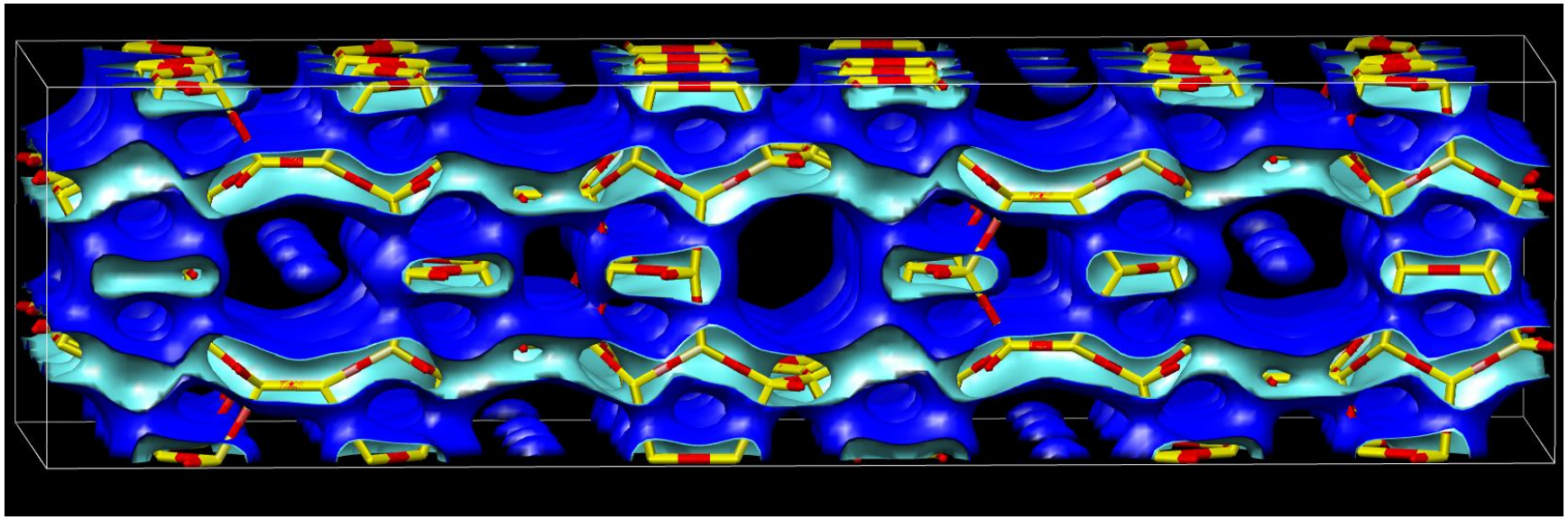
# 3D HKL file

| h | k | l | $A_{exp}$ | $\varphi_{exp}$ | $d$-val | $A_{cal}$ | $\varphi_{cal}$ |
|---|---|---|---|---|---|---|---|
| 4 | 0 | 0 | 10000 | 0 | 3.55 | 10000 | 0 |
| 0 | 4 | 5 | 6832 | 0 | 3.85 | 9587 | 0 |
| 3 | 9 | 0 | 6803 | 0 | 3.80 | 8490 | 0 |
| 2 | 0 | 0 | 6519 | 180 | 7.10 | 5481 | 180 |
| 2 | 6 | 0 | 6130 | 180 | 5.70 | 3973 | 180 |
| 0 | 6 | 0 | 5852 | 180 | 9.54 | 6400 | 180 |
| 0 | 0 | 4 | 5781 | 180 | 5.00 | 4474 | 180 |
| 0 | 4 | 3 | 4893 | 0 | 6.04 | 3351 | 0 |
| 0 | 0 | 2 | 4672 | 0 | 10.00 | 6184 | 0 |
| 1 | 3 | 0 | 4185 | 180 | 11.40 | 5342 | 180 |
| 1 | 15 | 0 | 3949 | 0 | 3.69 | 5153 | 0 |
| 0 | 4 | 1 | 3617 | 180 | 11.64 | 4337 | 180 |
| 0 | 0 | 6 | 2922 | 0 | 3.33 | 3193 | 0 |
| 0 | 8 | 0 | 2912 | 0 | 7.15 | 3264 | 0 |
| 0 | 8 | 2 | 2525 | 180 | 5.82 | 2196 | 180 |
| 1 | 7 | 0 | 2096 | 180 | 7.09 | 2170 | 180 |
| 0 | 12 | 0 | 2019 | 180 | 4.77 | 1614 | 180 |
| 0 | 12 | 3 | 1958 | 0 | 3.88 | 3917 | 0 |
| 4 | 0 | 2 | 1871 | 0 | 3.35 | 1637 | 0 |
| 2 | 8 | 0 | 1529 | 180 | 5.04 | 1534 | 180 |
| 1 | 9 | 0 | 1402 | 180 | 5.80 | 550 | 180 |
| 3 | 3 | 0 | 1301 | 0 | 4.60 | 1281 | 0 |
| 0 | 0 | 10 | 1274 | 180 | 2.00 | 8153 | 180 |
| 0 | 16 | 0 | 1246 | 0 | 3.58 | 3639 | 0 |
| 0 | 14 | 0 | 1212 | 180 | 4.09 | 1994 | 180 |
| 6 | 0 | 0 | 1179 | 0 | 2.37 | 1107 | 0 |

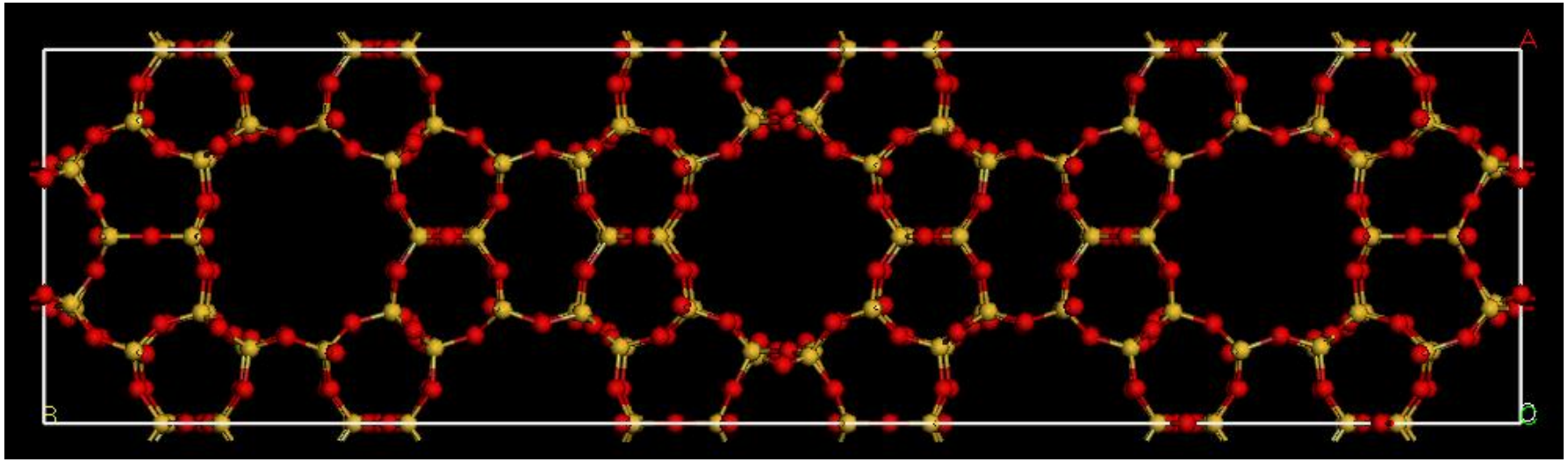
Continue....

| h | k | l | $A_{exp}$ | $\varphi_{exp}$ | $d$-val | $A_{cal}$ | $\varphi_{cal}$ |
|---|---|---|---|---|---|---|---|
| 0 | 10 | 0 | 1137 | 0 | 5.72 | 1294 | 0 |
| 4 | 6 | 0 | 1092 | 180 | 3.33 | 4512 | 180 |
| 2 | 10 | 0 | 1006 | 0 | 4.46 | 983 | 0 |
| 0 | 0 | 8 | 997 | 180 | 2.50 | 3662 | 180 |
| 0 | 10 | 3 | 889 | 180 | 4.34 | 1217 | 180 |
| 2 | 0 | 2 | 865 | 180 | 5.79 | 964 | 180 |
| 4 | 0 | 4 | 812 | 180 | 2.90 | 916 | 180 |
| 0 | 8 | 1 | 690 | 180 | 6.74 | 540 | 180 |
| 2 | 14 | 0 | 614 | 180 | 3.54 | 1187 | 180 |
| 0 | 6 | 5 | 570 | 0 | 3.69 | 1126 | 0 |
| 5 | 9 | 0 | 530 | 0 | 2.59 | 1877 | 180* |
| 0 | 8 | 3 | 516 | 0 | 4.88 | 378 | 0 |
| 0 | 2 | 5 | 504 | 0 | 3.96 | 620 | 0 |
| 8 | 0 | 0 | 479 | 180 | 1.78 | 925 | 0* |
| 0 | 2 | 2 | 464 | 0 | 9.44 | 563 | 0 |
| 0 | 10 | 1 | 462 | 0 | 5.50 | 980 | 0 |
| 0 | 6 | 2 | 453 | 180 | 6.90 | 625 | 180 |
| 0 | 12 | 1 | 448 | 180 | 4.64 | 823 | 180 |
| 4 | 0 | 6 | 441 | 0 | 2.43 | 784 | 0 |
| 3 | 13 | 0 | 434 | 0 | 3.22 | 2058 | 0 |
| 0 | 2 | 3 | 433 | 180 | 6.49 | 158 | 180 |
| 1 | 11 | 0 | 430 | 180 | 4.89 | 107 | 180 |
| 0 | 10 | 2 | 429 | 180 | 4.97 | 228 | 180 |
| 0 | 6 | 1 | 426 | 180 | 8.61 | 434 | 180 |
| 2 | 16 | 0 | 426 | 180 | 3.20 | 3565 | 180 |
| 1 | 13 | 0 | 423 | 0 | 4.21 | 674 | 0 |
| 3 | 21 | 0 | 401 | 0 | 2.36 | 2310 | 180* |

# 3D potential map

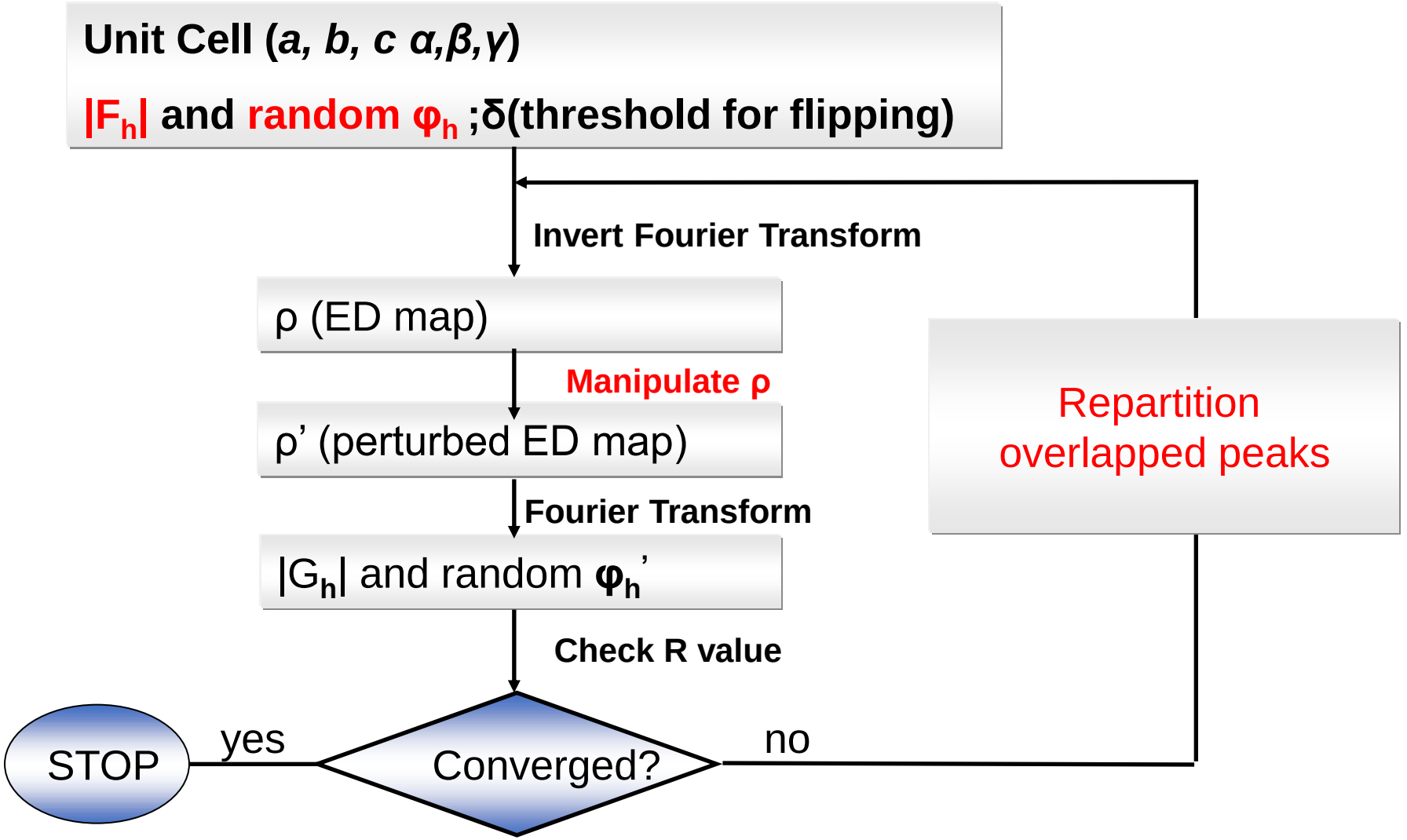


## After energy optimization

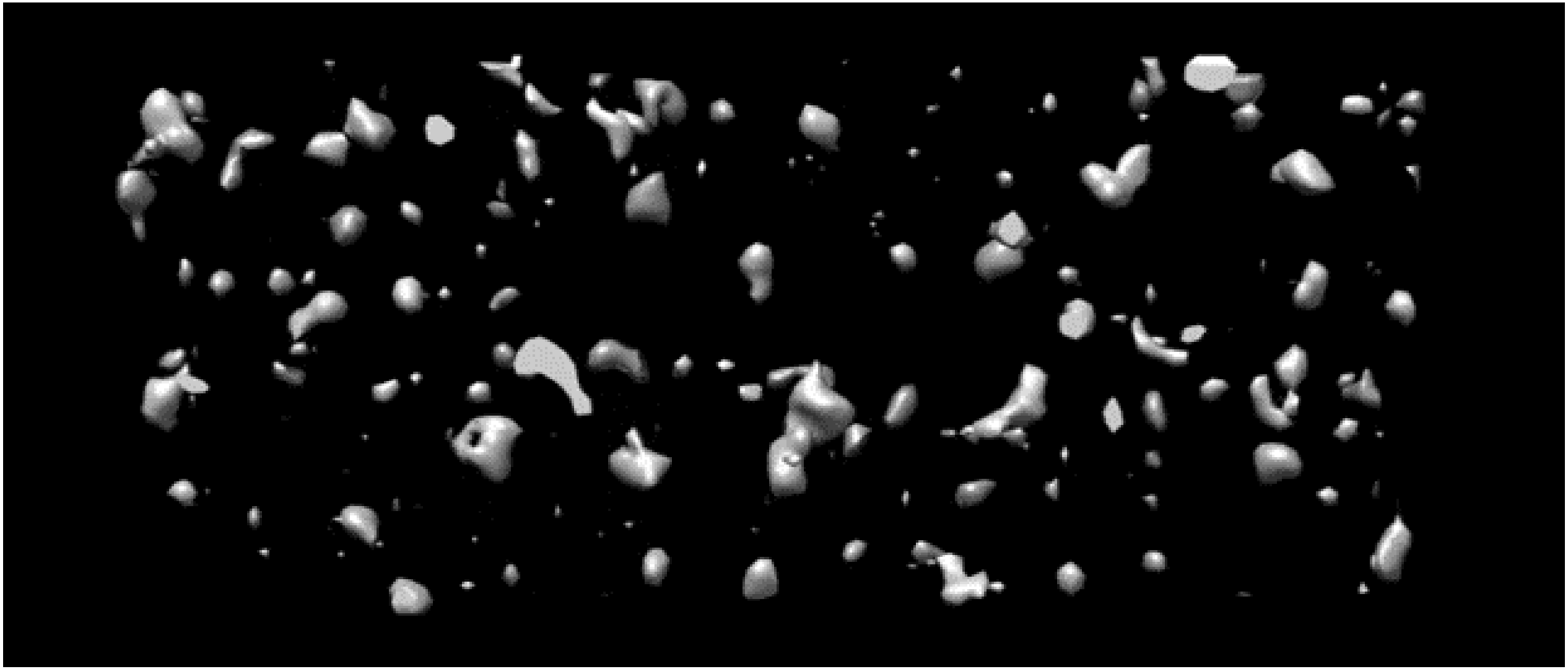



Average deviation of Si： 0.1Å

# Modified Charge Flipping

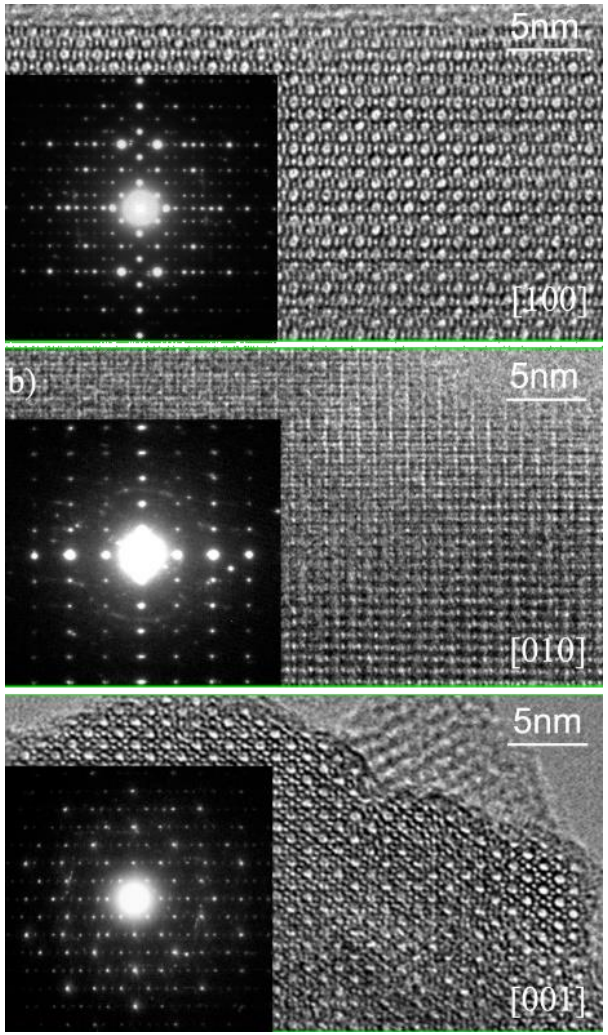


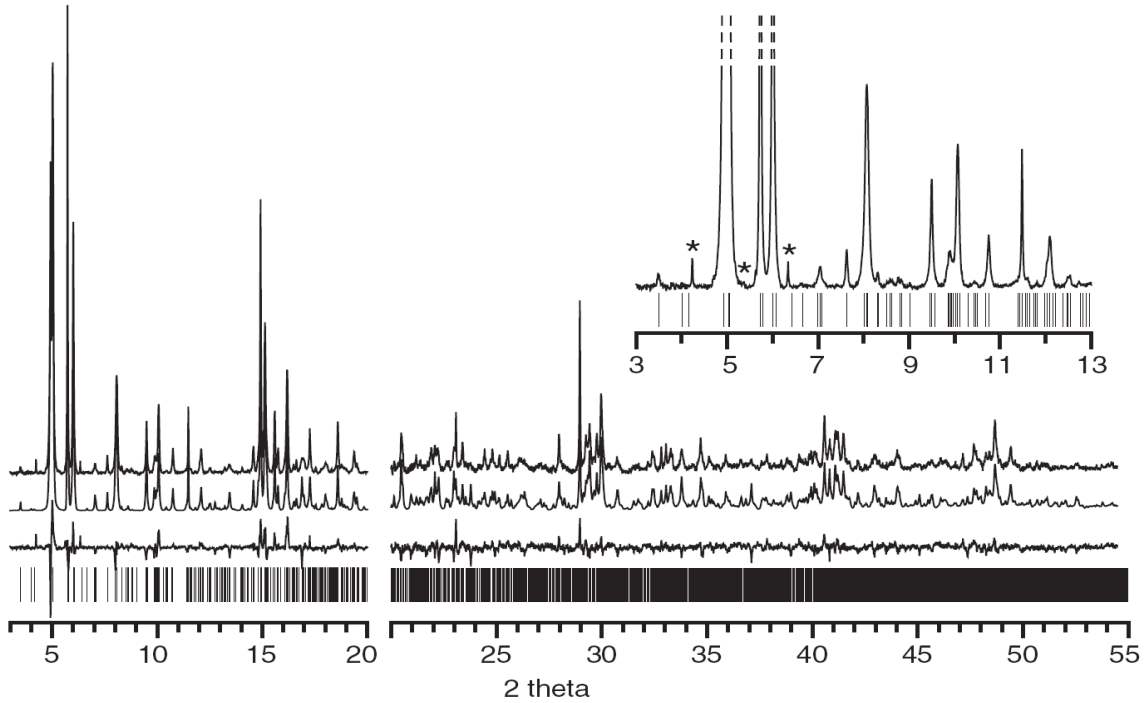

$\delta = K_{ed}\sigma(\rho), \quad 0.9<K_{ed}<1.3$

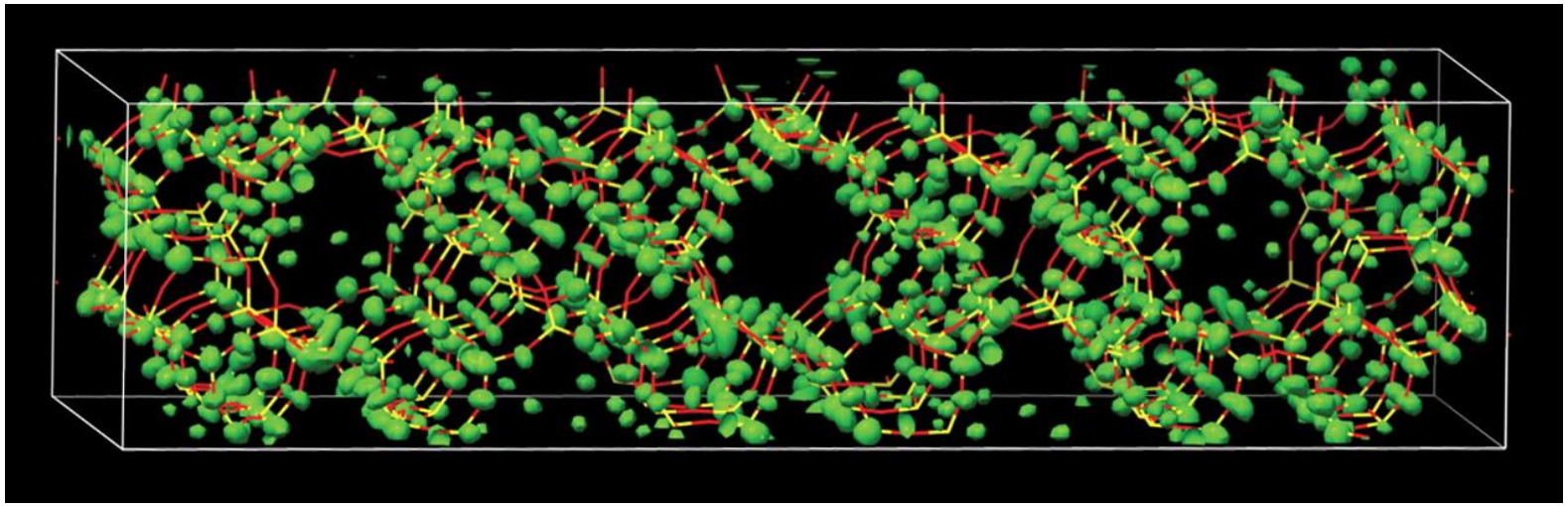


# Phases from HRTEM images assist PXRD structure determination

IM-5 zeolites

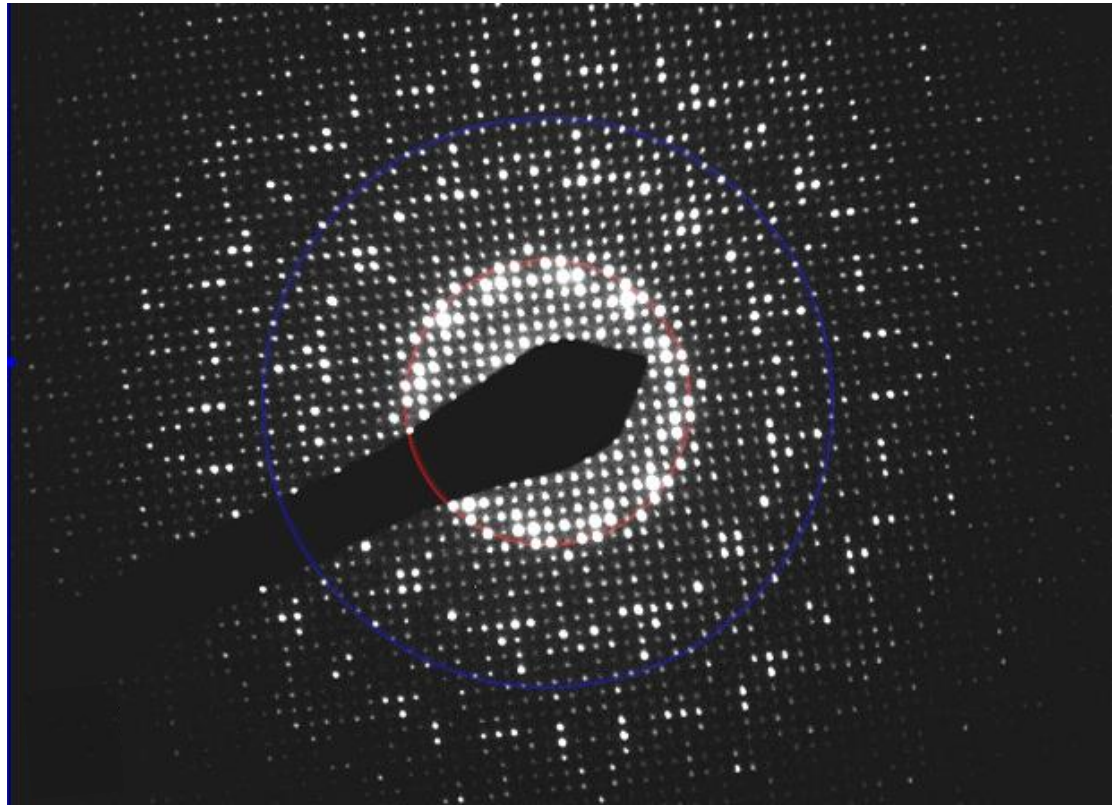


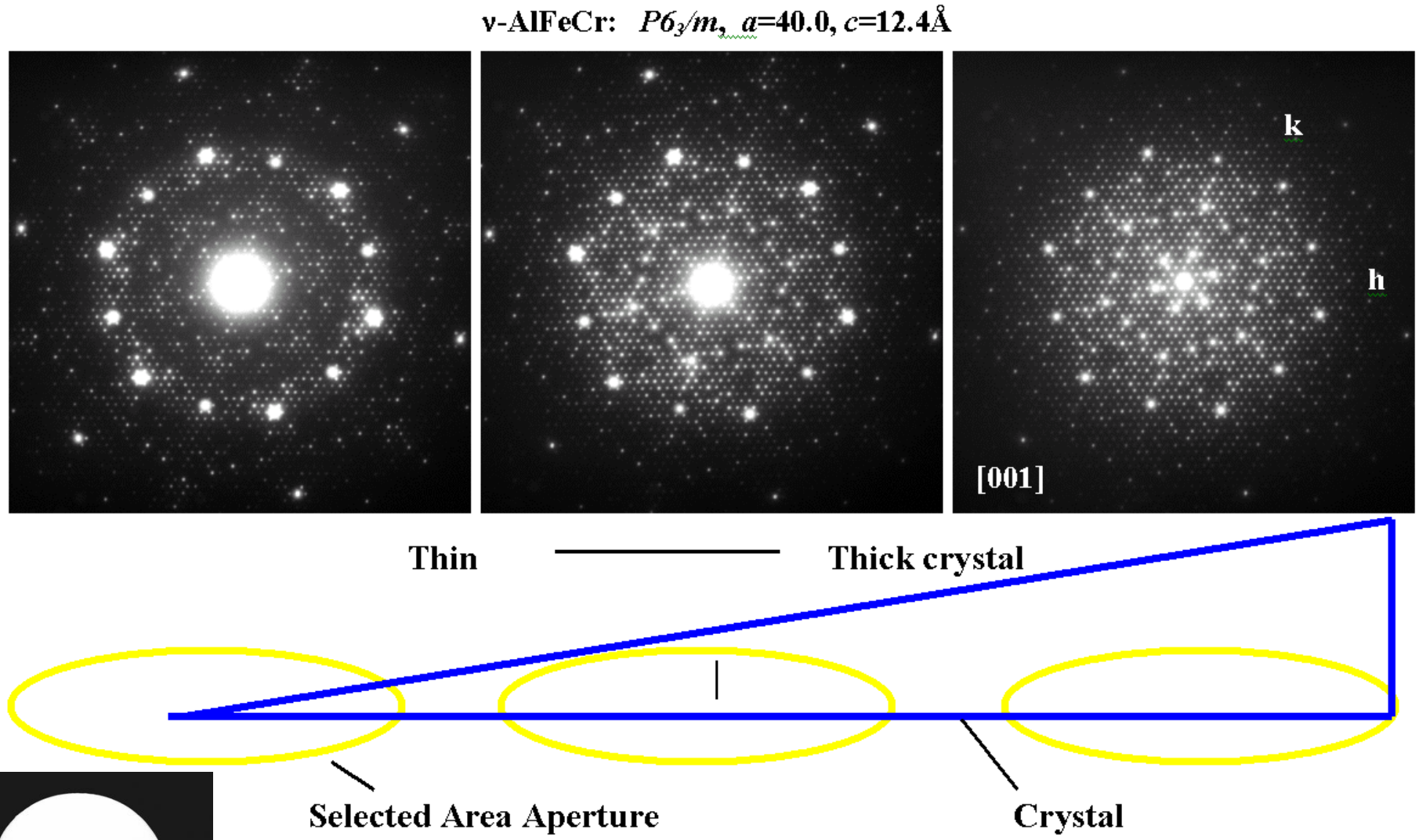



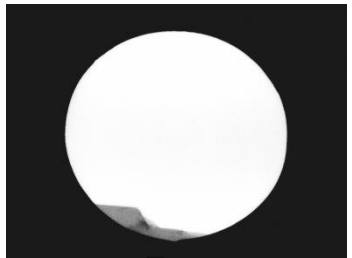
Baerlocher, Gramm, Zou et al. *Science*, **2007**, *315*, 1113

# Make use of electron diffraction



# Dynamical effects make intensity less accurate

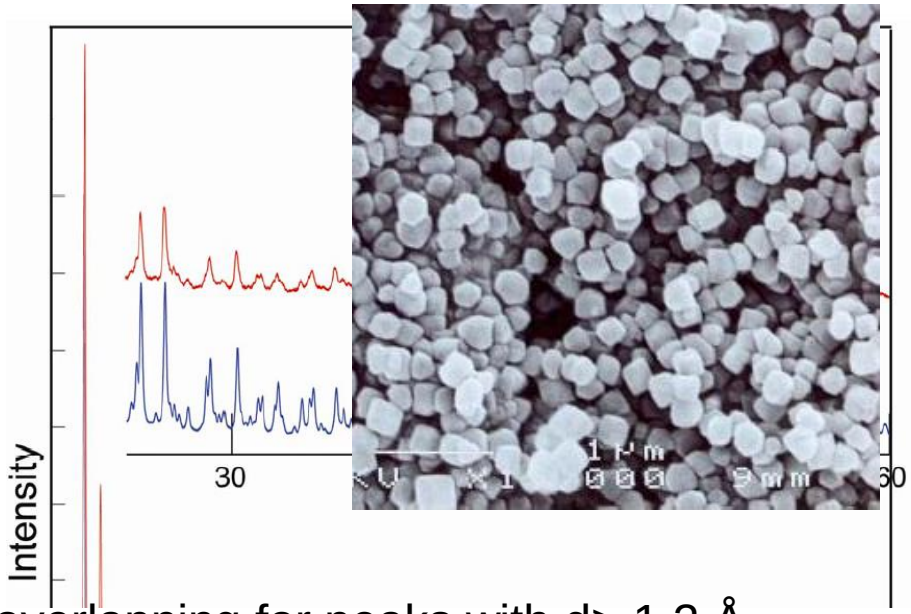


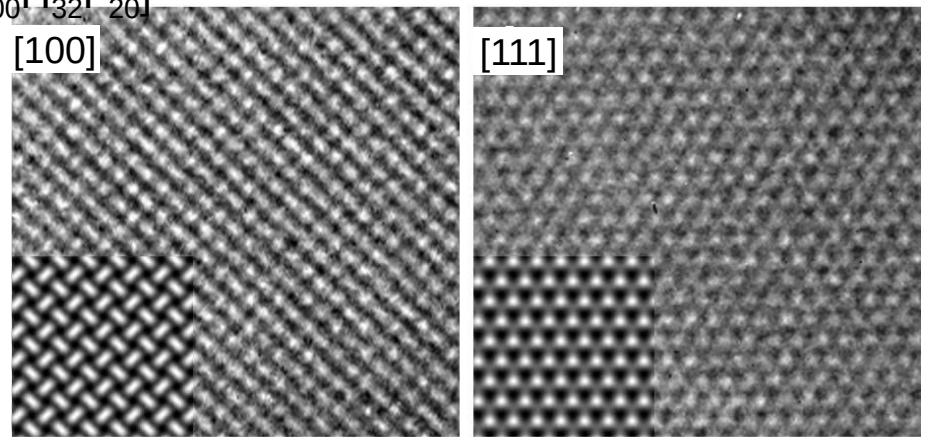



Less dynamical effects from thinner area

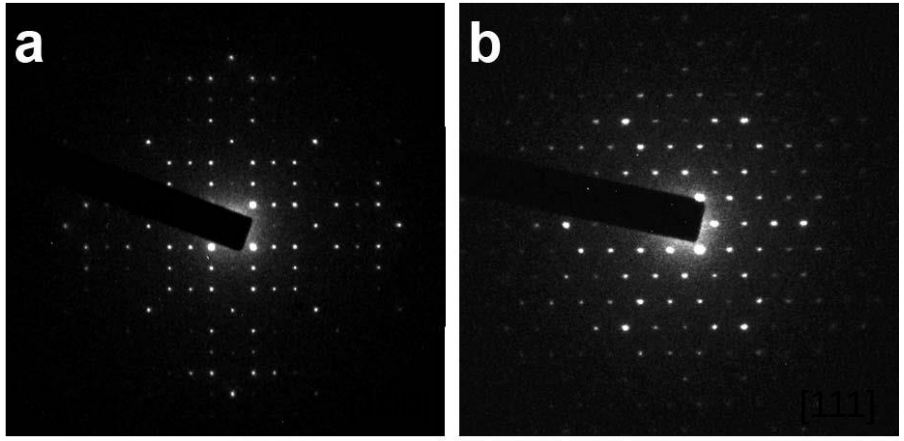
# ITQ-37, mesoporous chiral zeolite

$|(C_{22}N_2H_{40})_{10.5}(H_2O)_x|[Ge_{80}Si_{112}O_{400}H_{32}F_{20}]$




HRTEM images along [100] and [111]




SAED along [100] and [111]

- 94% overlapping for peaks with d> 1.2 Å
- Broadening by small crystal size (~100nm)
- Low resolution due to disordered guests
- Electron beam sensitivity

**Use ED to partition the overlapping peaks**

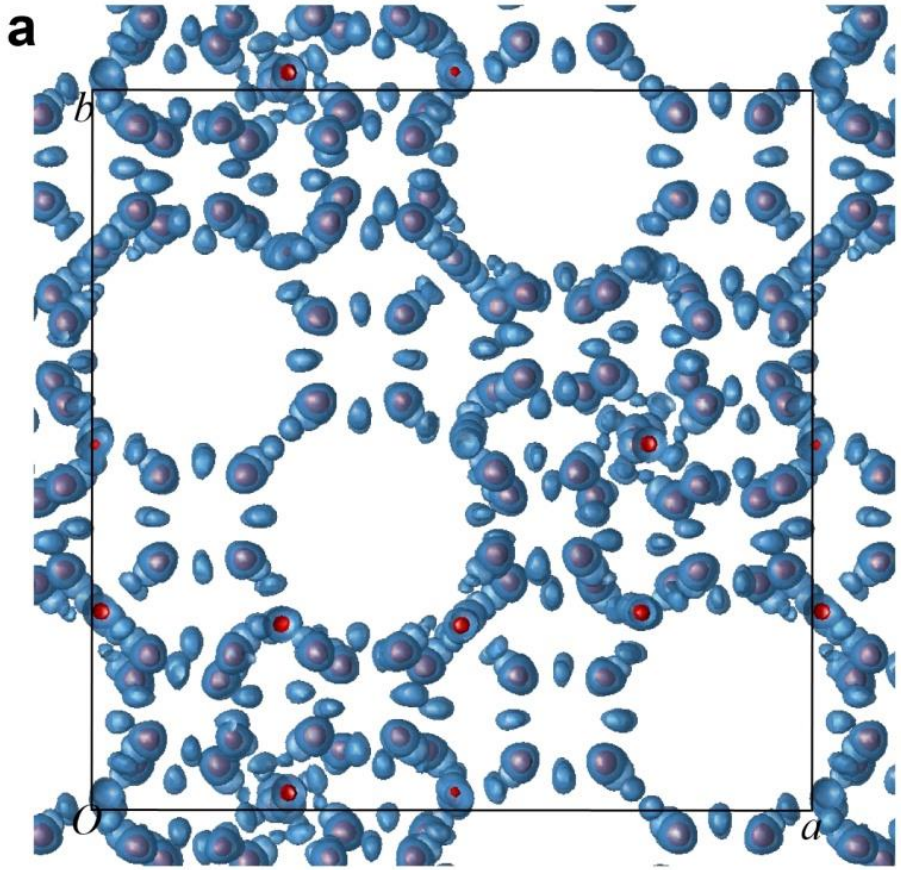
6.5 Å

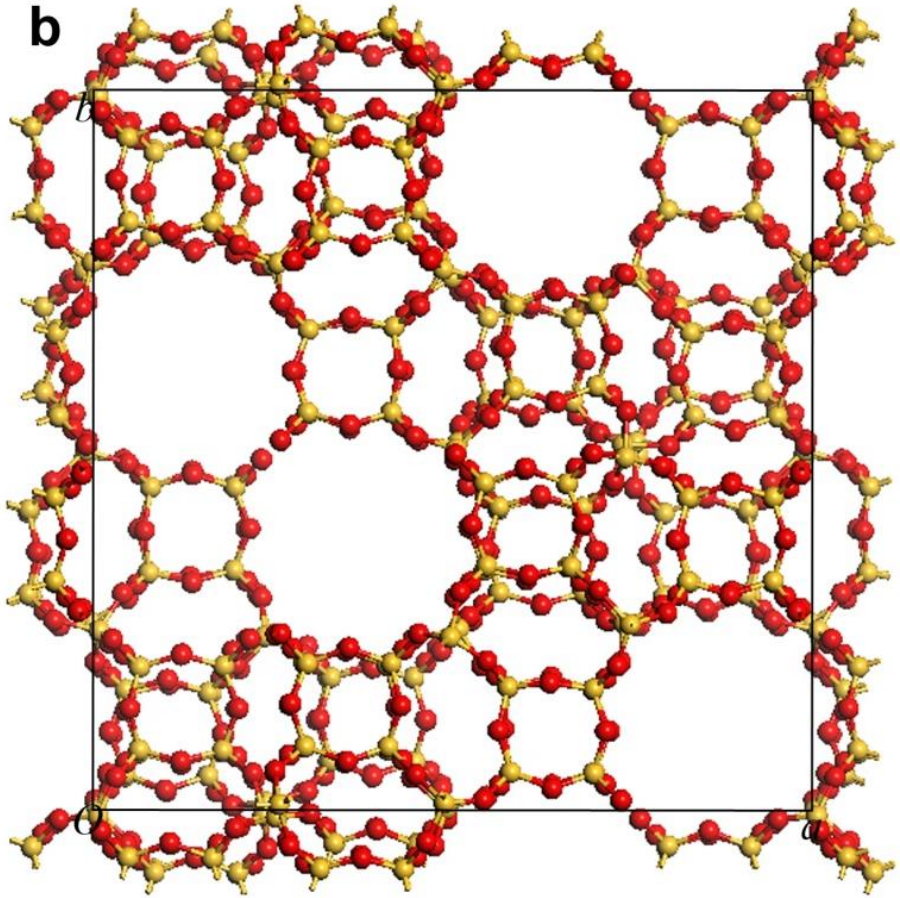
Sun,Corma*, Zou* et al *Nature* **2009** , *458*, 1154

# ITQ-37

0.7e/Å$^3$ in Blue

2.7e/Å$^3$ in red



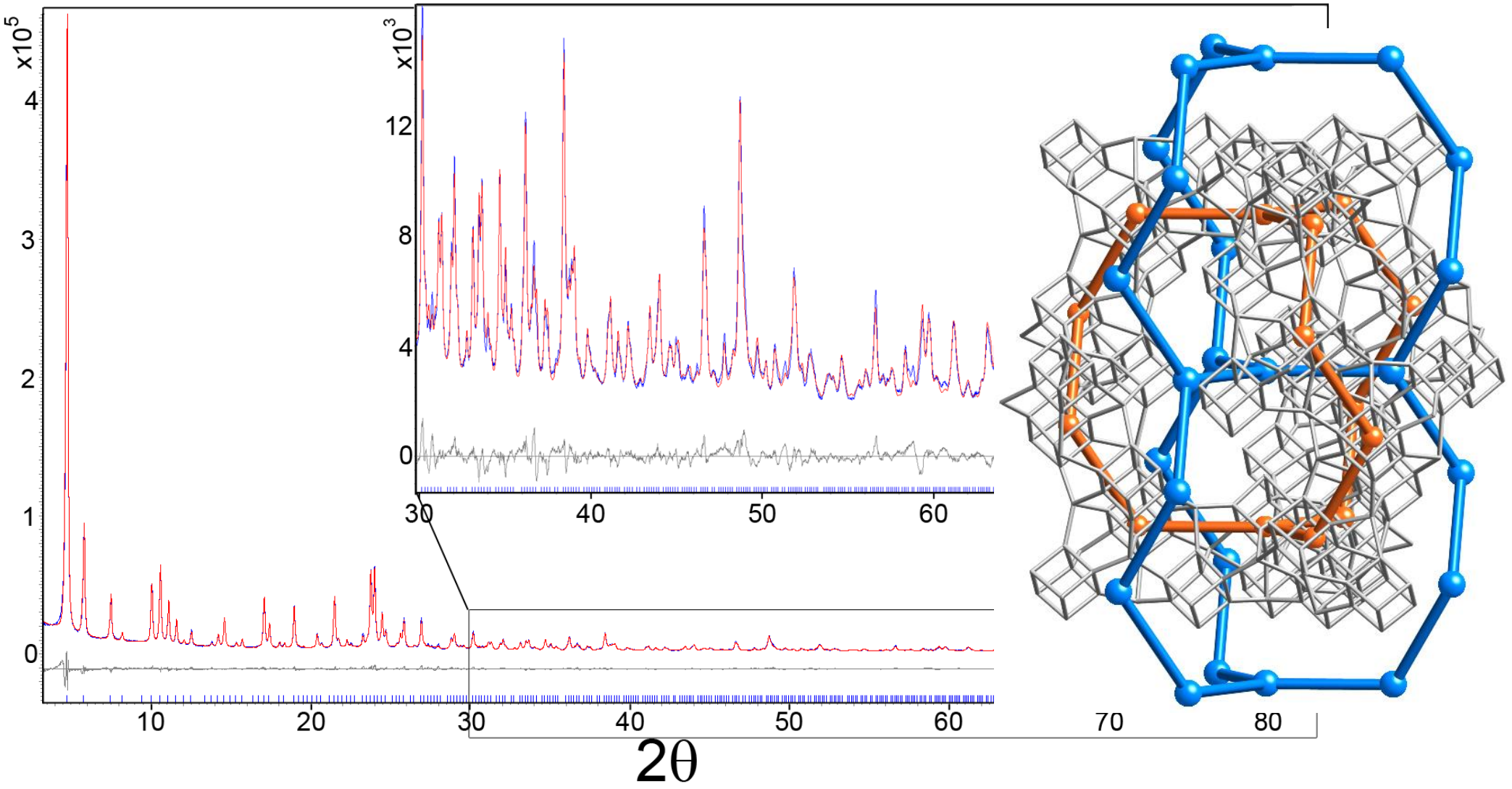




**Electron density from charge flipping**

**Structure model**



22



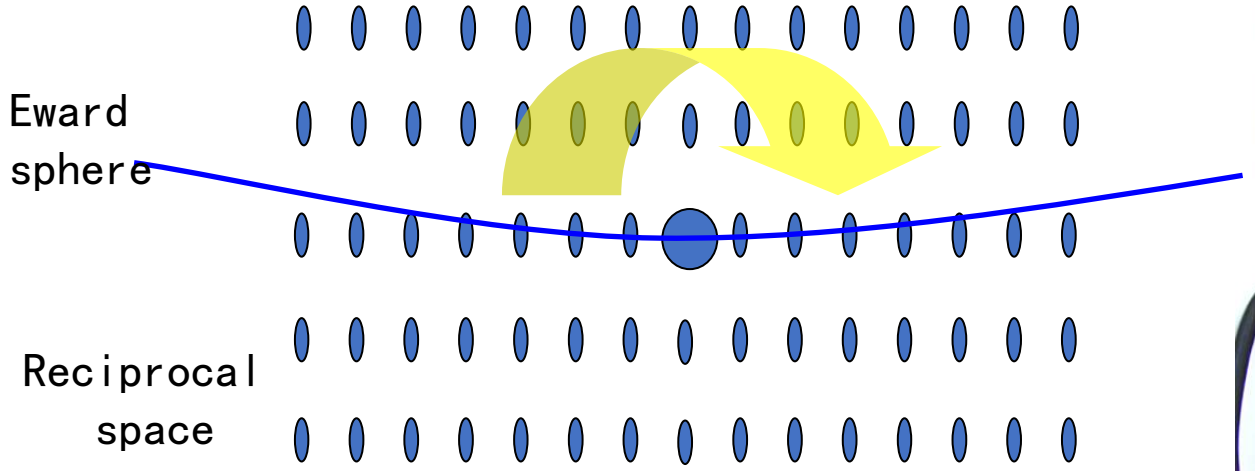

$R_p$=0.0380 $R_{wp}$=0.0500 $R_{exp}$=0.0115 $R_1$=0.0116

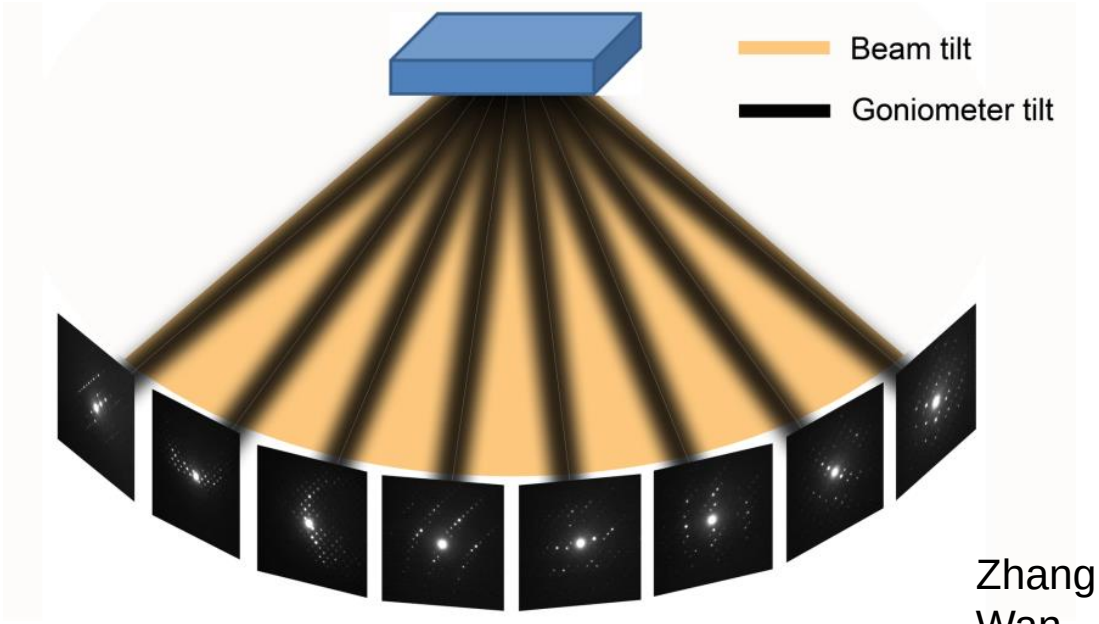


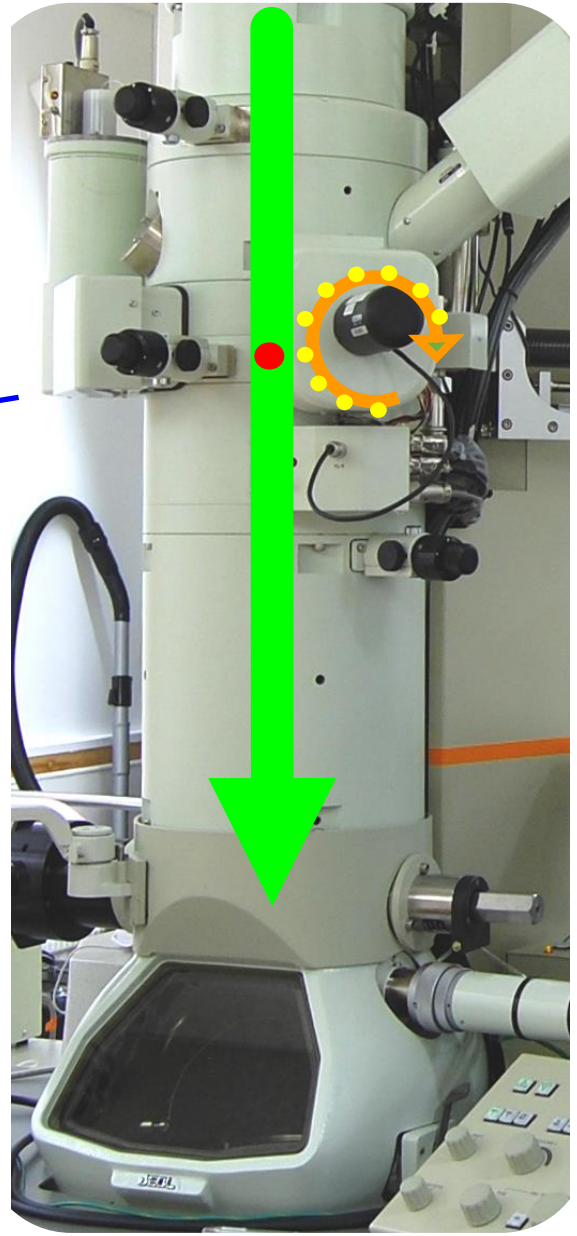
23

# Rotation electron diffraction(RED)

Single crystal ED on nano-crystals



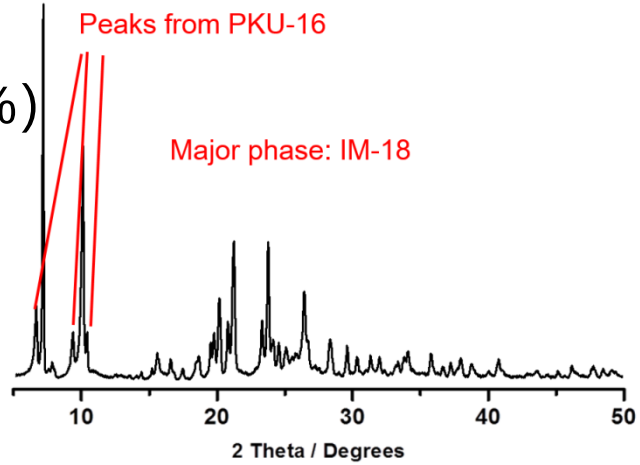



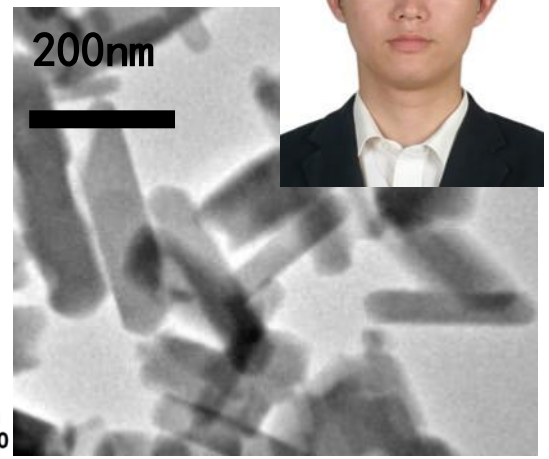
Zhang et al. *Z. Kristallogr.*, **2010**, *225*, 94
Wan, et al. *J. Appl. Cryst.*, **2013**, *46*, 1863

# Advantage

- Fast data collection(< 1h)
- High intensity accuracy(30%)
- Small crystal size(50nm)
- High completeness(80%)
- Low requirements for operators and hardware

## Zeolite: PKU-16

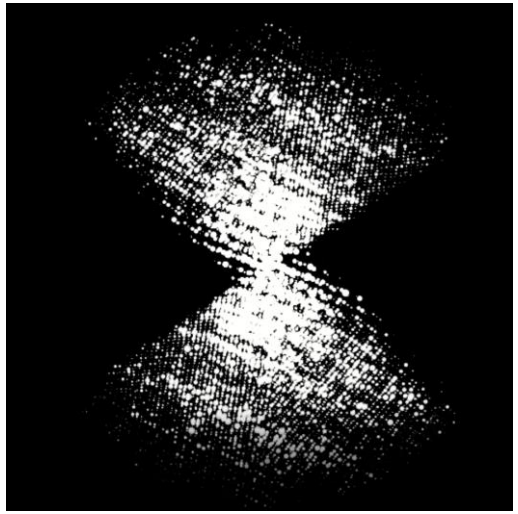


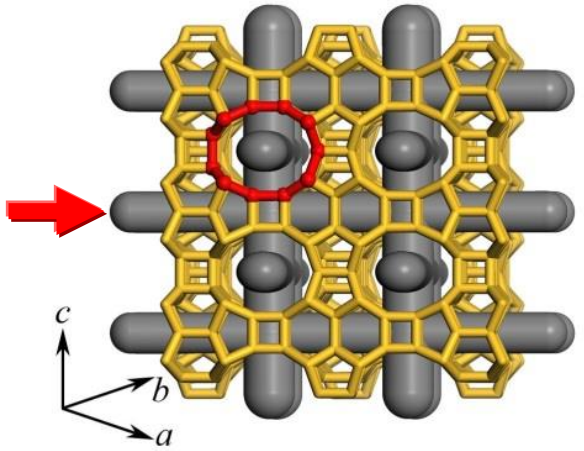











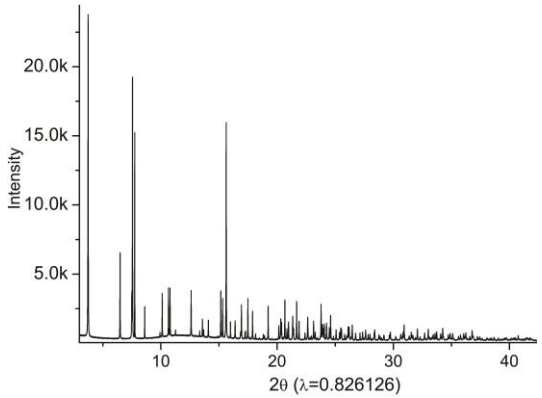


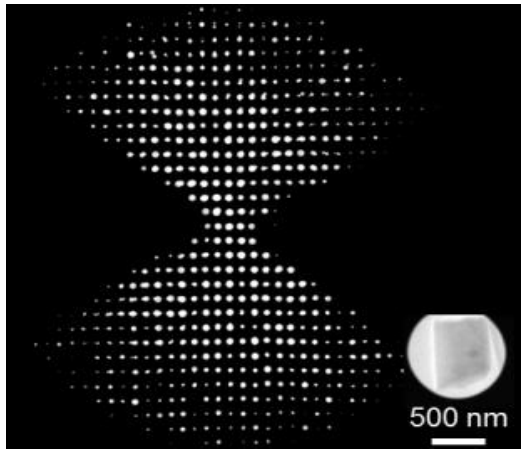

$P4_2/mnm$: $a$=19.1 Å, $c$=11.7 Å

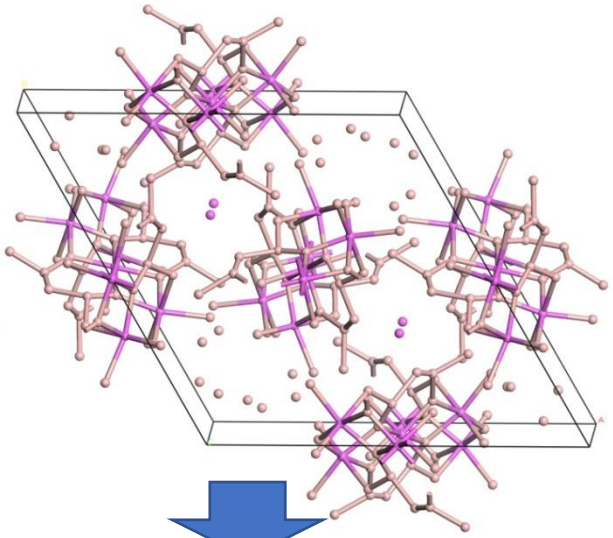
RED：$R_1$=0.26；PXRD：$R_{wp}$=0.07

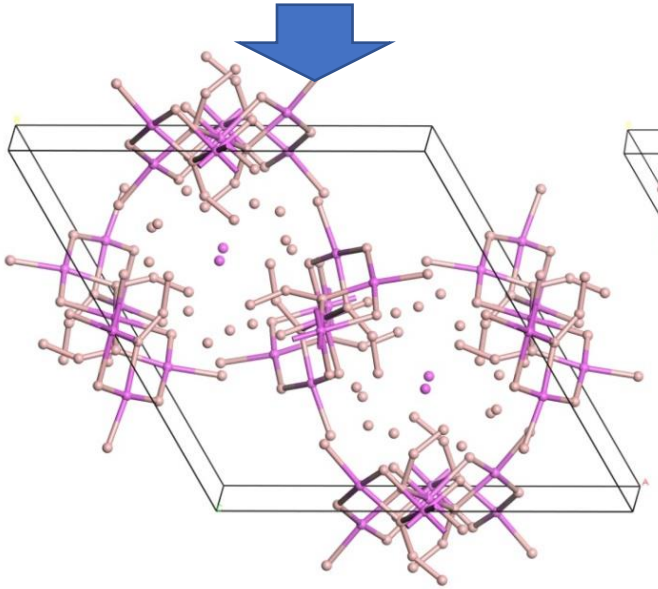
*Angew. Chem.* **2014**, *53* 5868

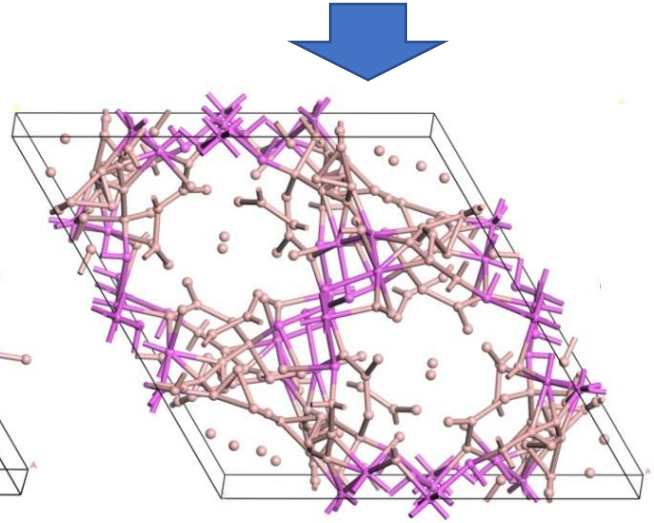
# Combine PXRD and 3D ED for PKU-3

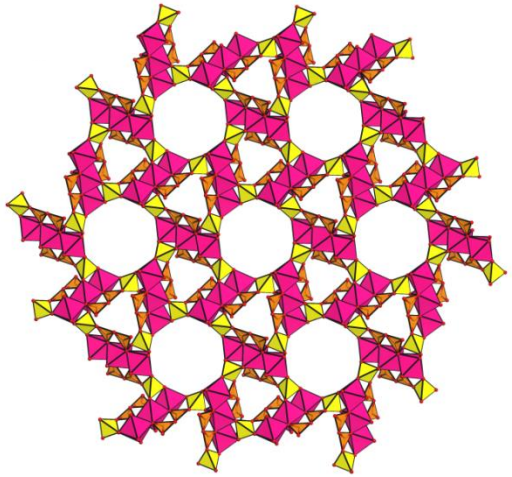








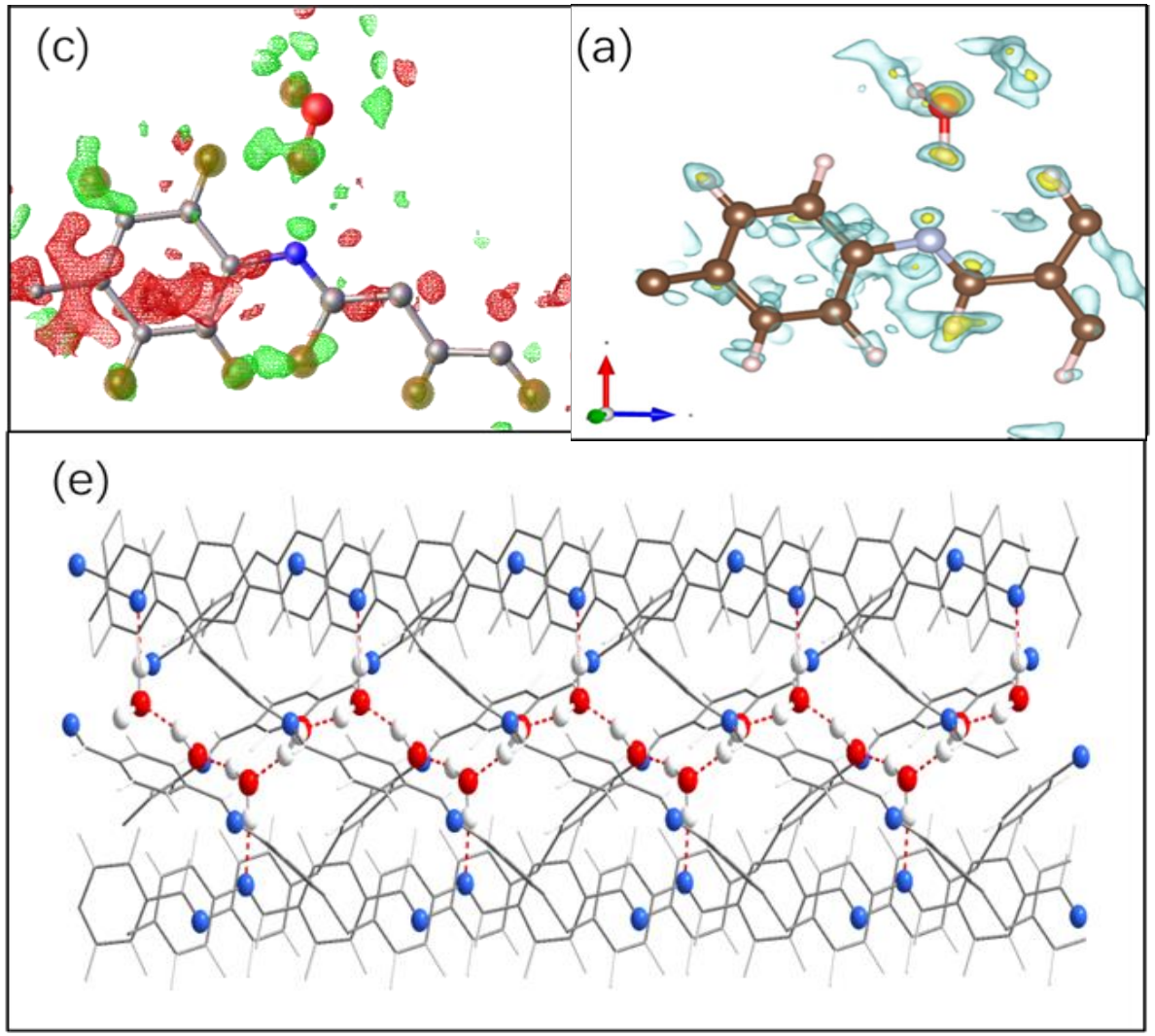


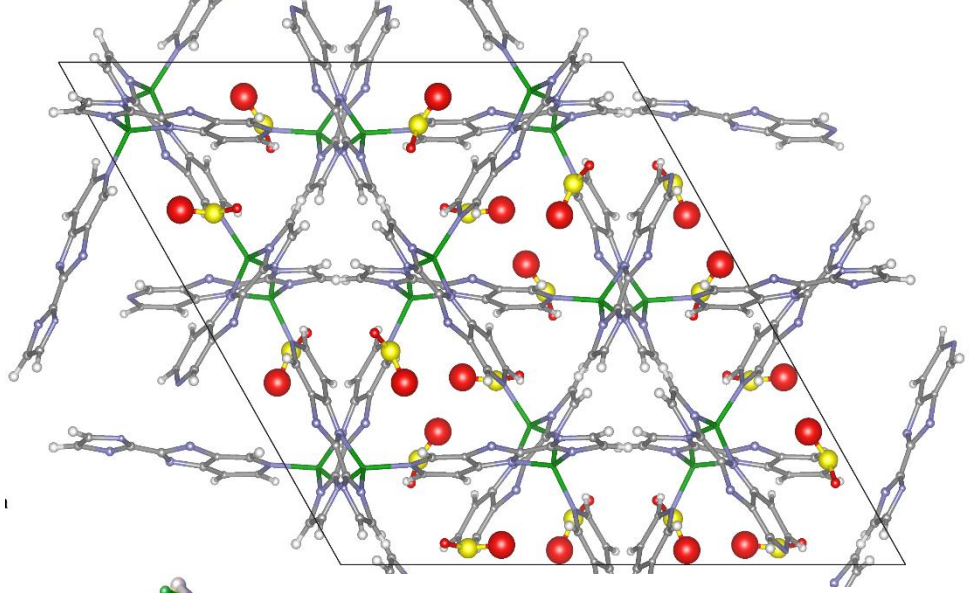
*P*-3*c*1: *a*=14.7 Å, *c*=12.4 Å

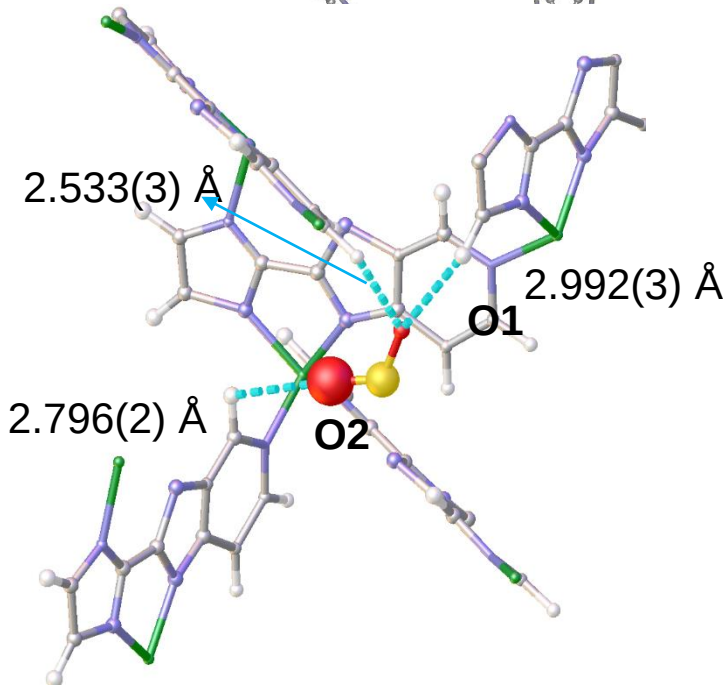
$H_{24.3}Al_9B_{18}O_{51}\cdot Cl_{3.3}\cdot 6.8H_2O$

PXRD: $R_{wp}$=0.0623, $R_p$=0.0471

Chen et al. *J. Am. Chem. Soc.* 2015, 137, 7074






## Location H atoms

## Location guest gas molecules

*Angew. Chem.* 2023, e202305985

ACCOUNTS of chemical research

Article

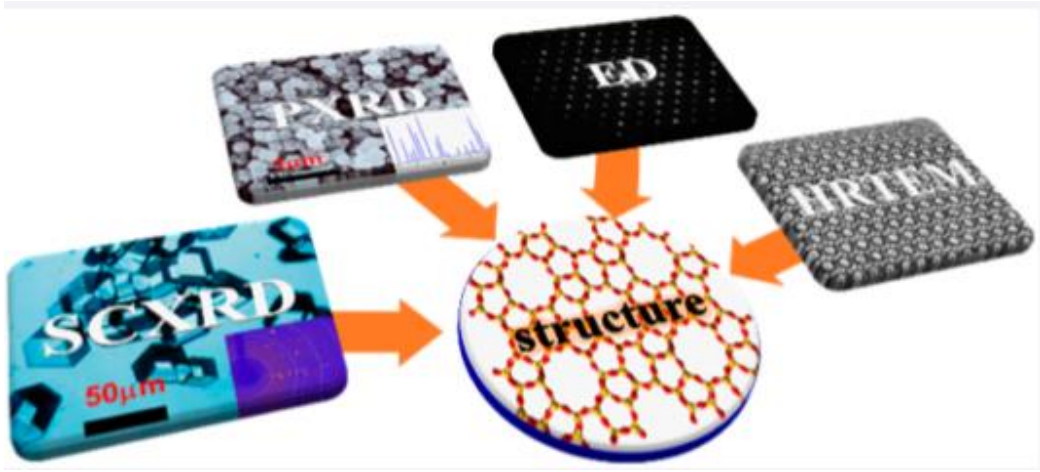
pubs.acs.org/accounts

# Application of X-ray Diffraction and Electron Crystallography for Solving Complex Structure Problems

Jian Li and Junliang Sun*

College of Chemistry and Molecular Engineering, Peking University, Yiheyuan Road 5, Beijing 100871, China

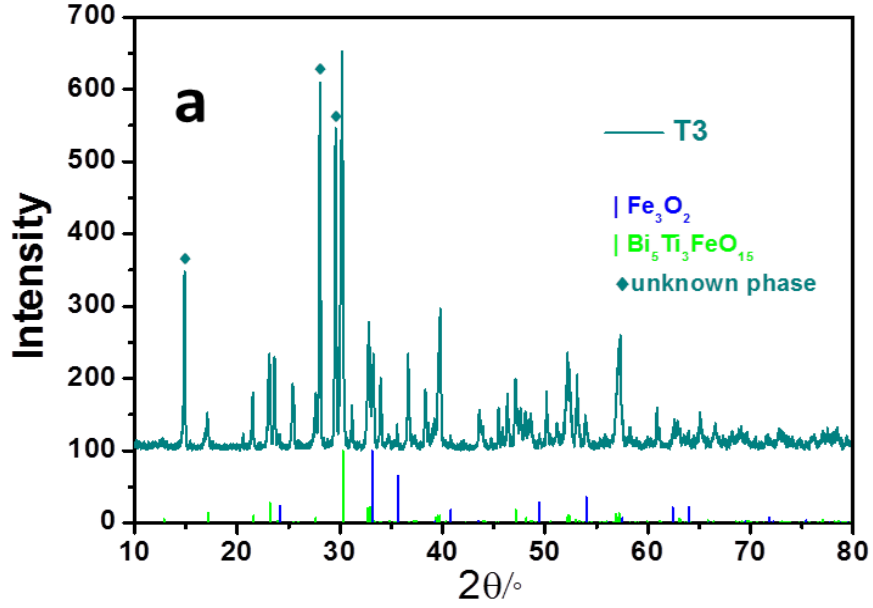
1. Peak overlapping
2. Impurity
3. Pseudo-symmetry
4. Disordered framework
5. Disordered guests
6. Hydrogen positions
7. Chirality
8. Incommensurate structures
9. …

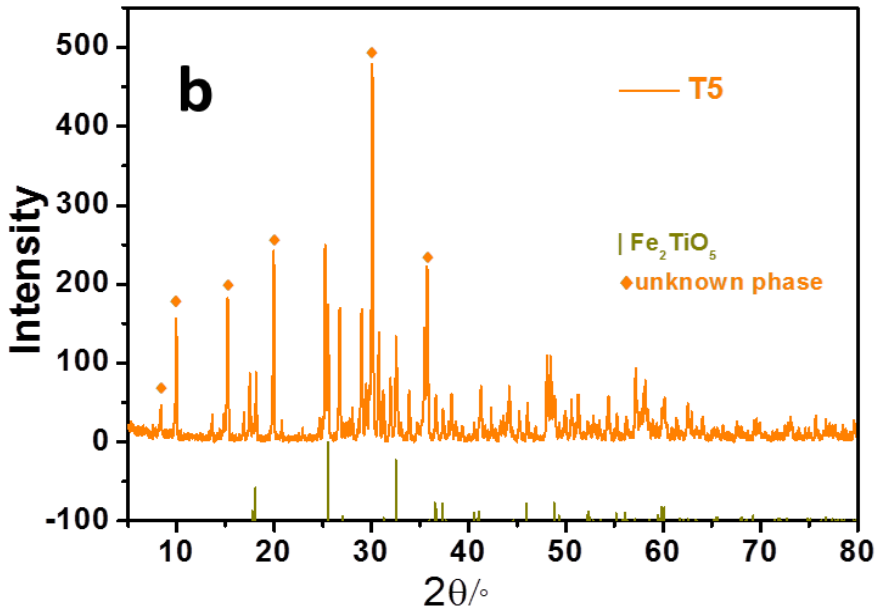


# Find new phases from impurity

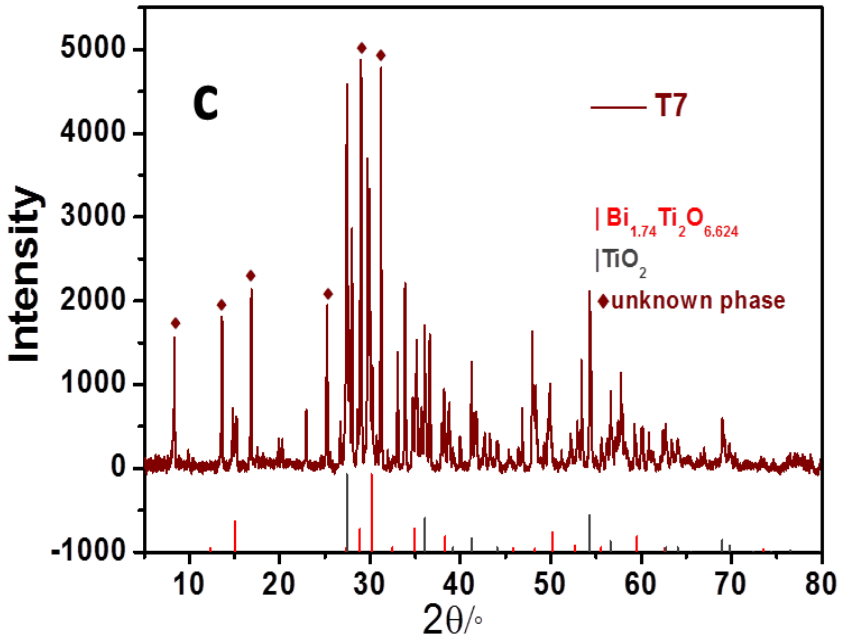



Bi-Fe-Ti-O system

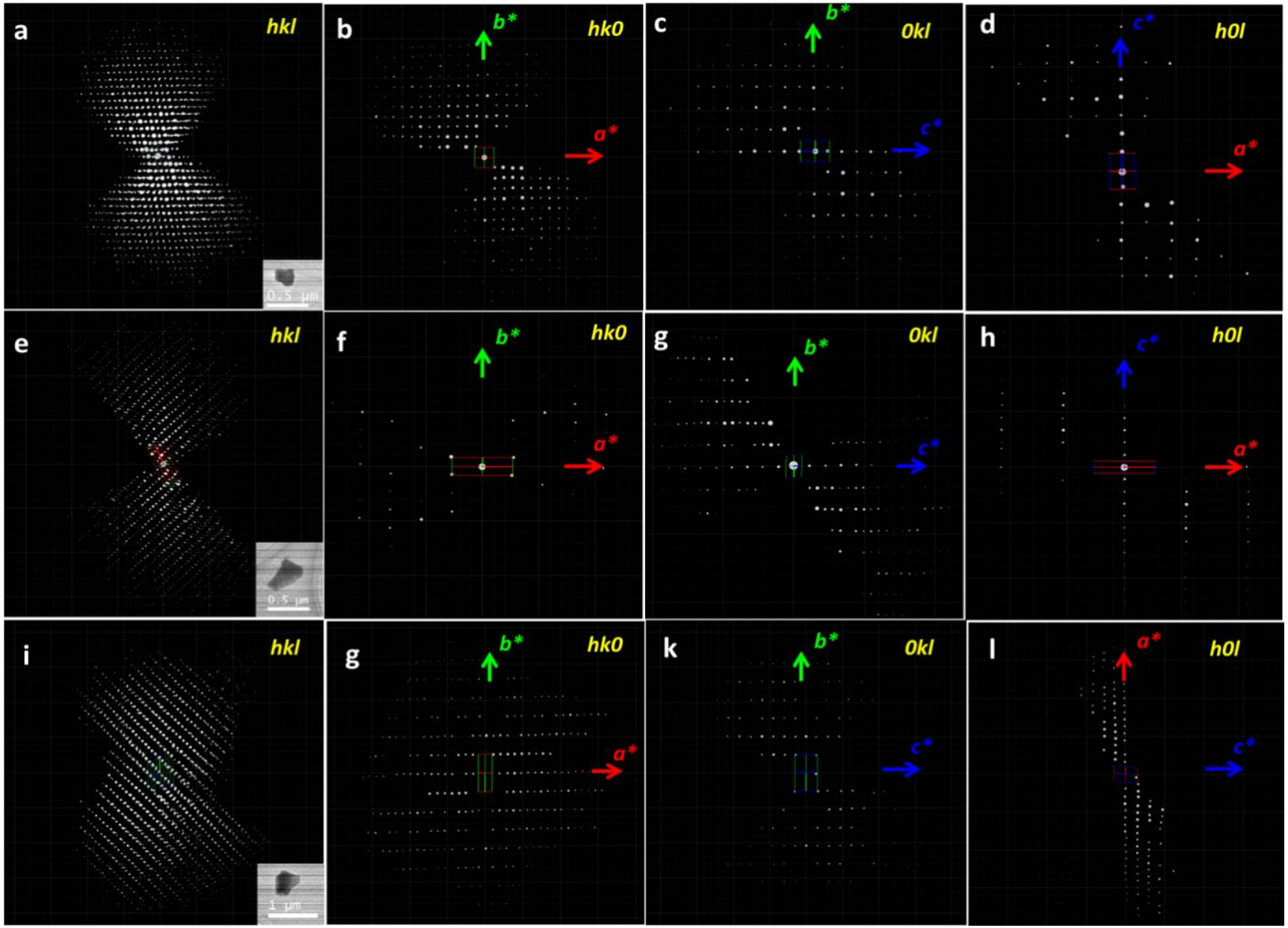


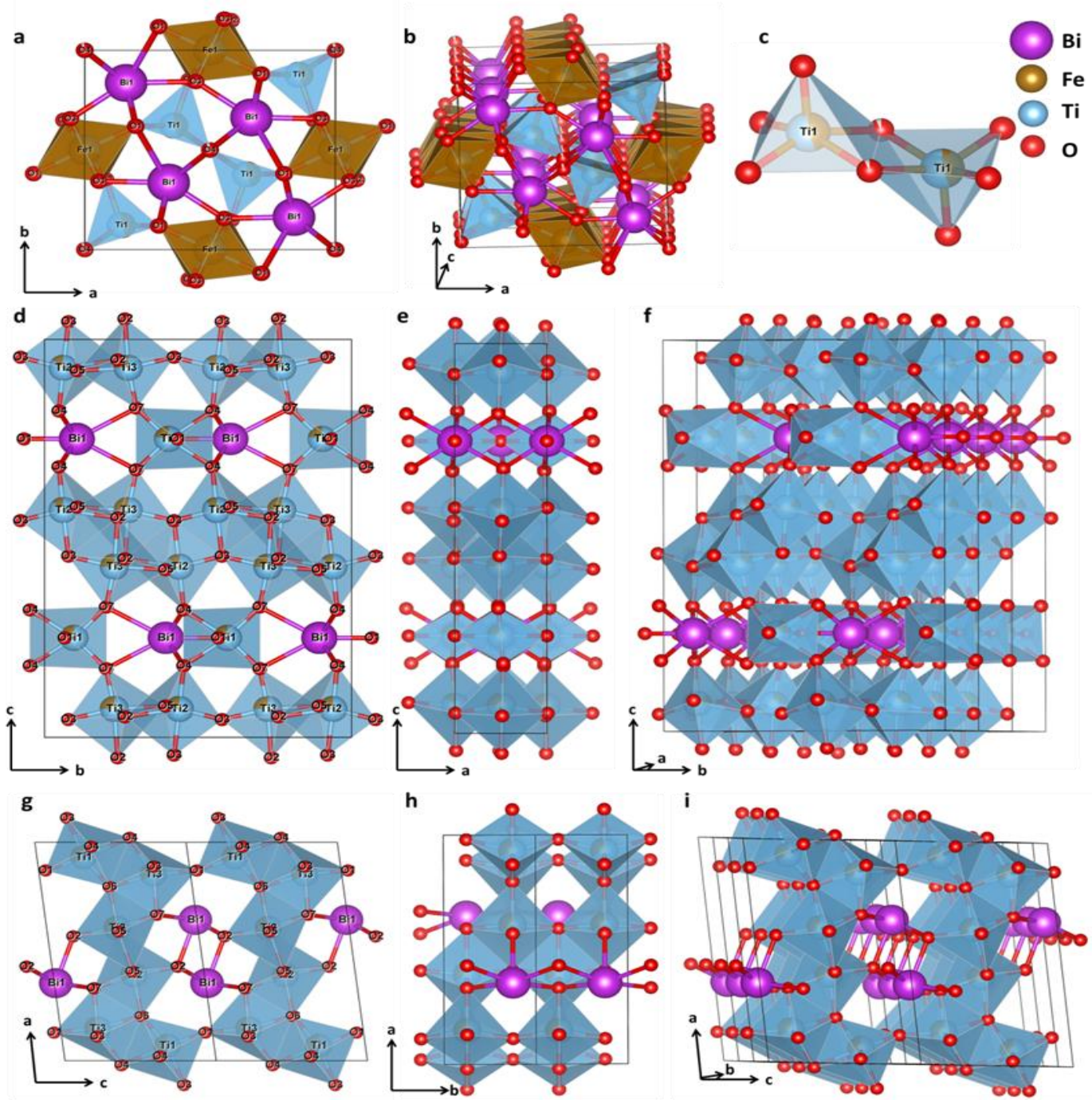



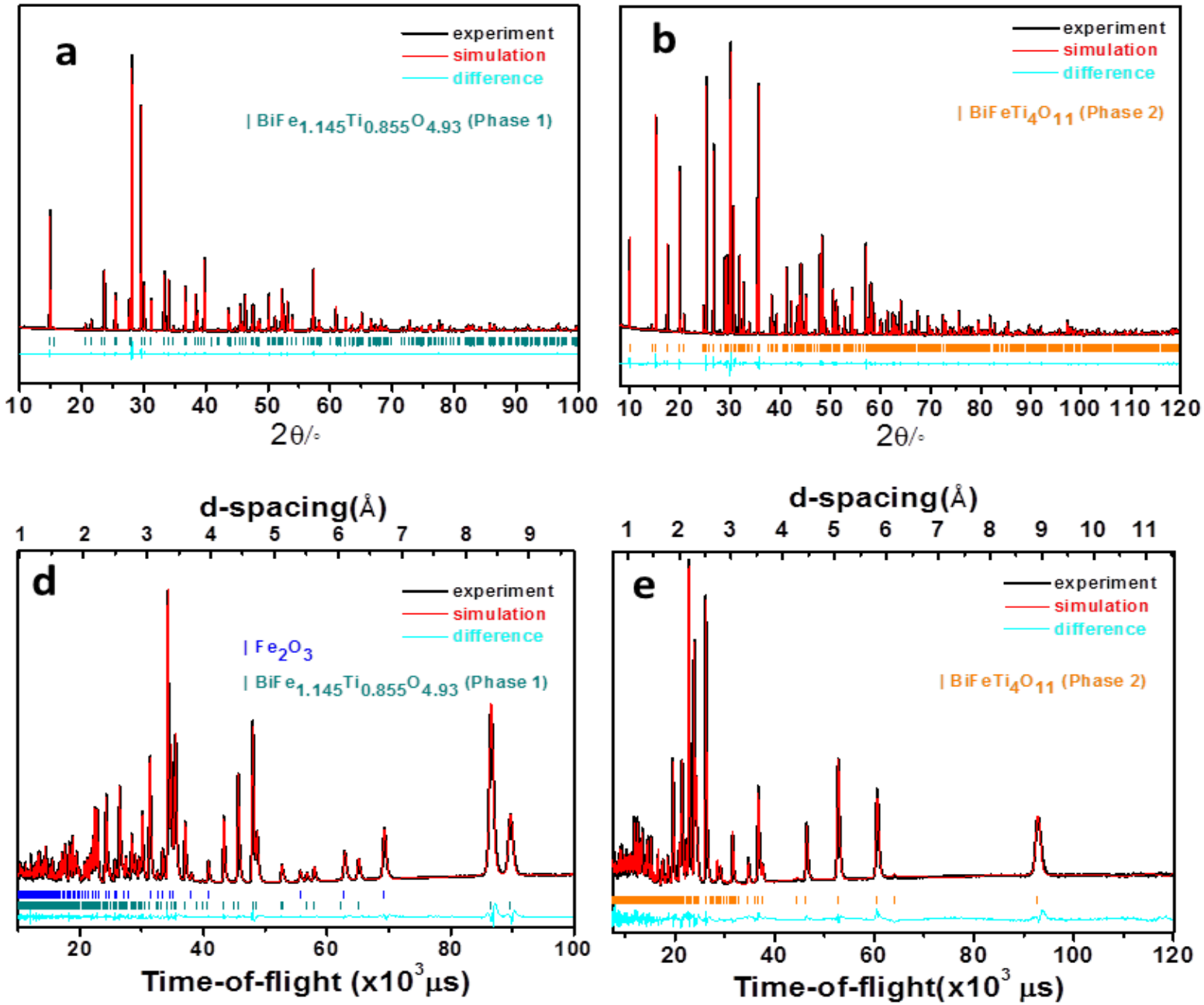

**T3、T5、T7 include three unknown phases**




J. Am. Chem. Soc. **2019**, *141*,4990

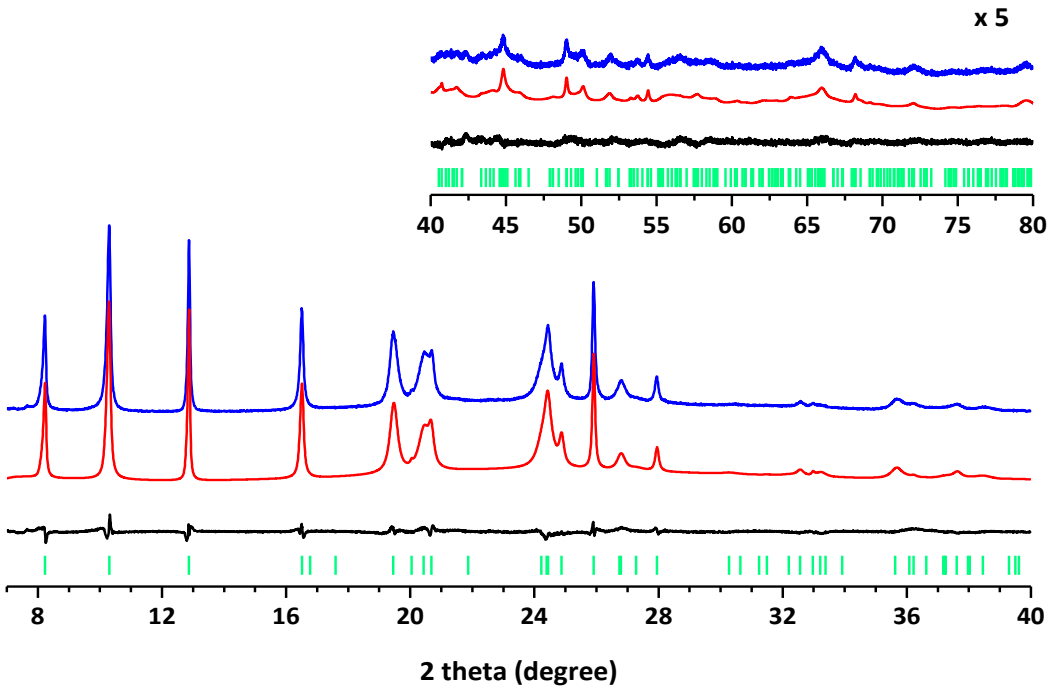

a
hkl
b
b*
hk0
a*
c
b*
0kl
c*
d
c*
h0l
a*
e
hkl
0.5 μm
f
b*
hk0
a*
g
b*
0kl
c*
h
c*
h0l
a*
i
hkl
1 μm
g
b*
hk0
a*
k
b*
0kl
c*
l
a*
h0l
c*


a
b
c
d
e
f
g
h
i
Bi
Fe
Ti
O

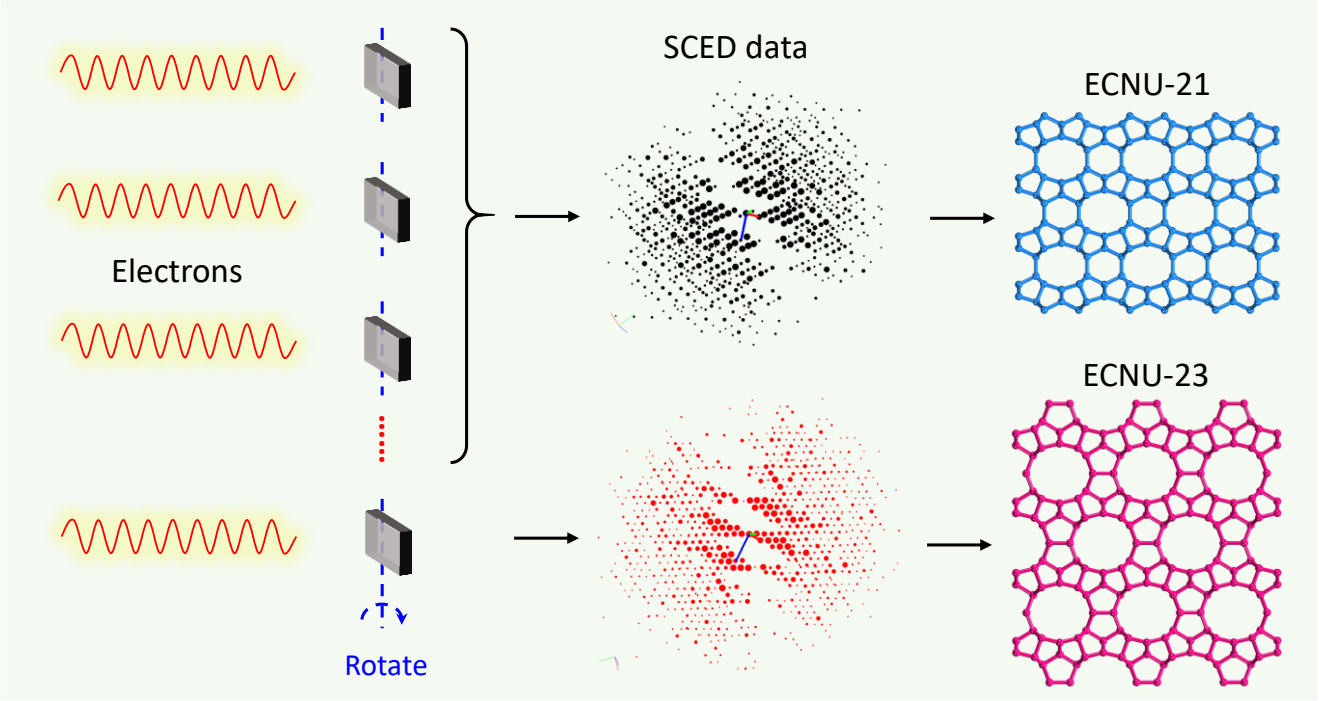

a
experiment
simulation
difference
| BiFe1.145Ti0.855O4.93 (Phase 1)
10 20 30 40 50 60 70 80 90 100
2θ/◦
b
experiment
simulation
difference
| BiFeTi4O11 (Phase 2)
10 20 30 40 50 60 70 80 90 100 110 120
2θ/◦
d-spacing(Å)
1 2 3 4 5 6 7 8 9
d
experiment
simulation
difference
| Fe2O3
| BiFe1.145Ti0.855O4.93 (Phase 1)
20 40 60 80 100
Time-of-flight (x10^3 μs)
d-spacing(Å)
1 2 3 4 5 6 7 8 9 10 11
e
experiment
simulation
difference
| BiFeTi4O11 (Phase 2)
20 40 60 80 100 120
Time-of-flight(x10^3 μs)

# Finding new phases from a “pure” sample

ECNU-23 zeolite from ECNU-21




**PXRD shows a pure ECNU-21 sample**

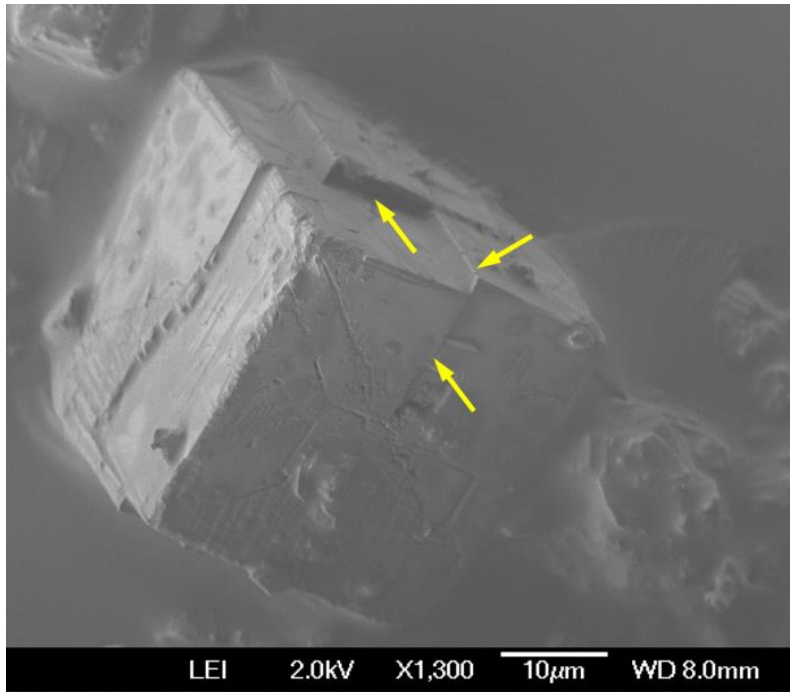


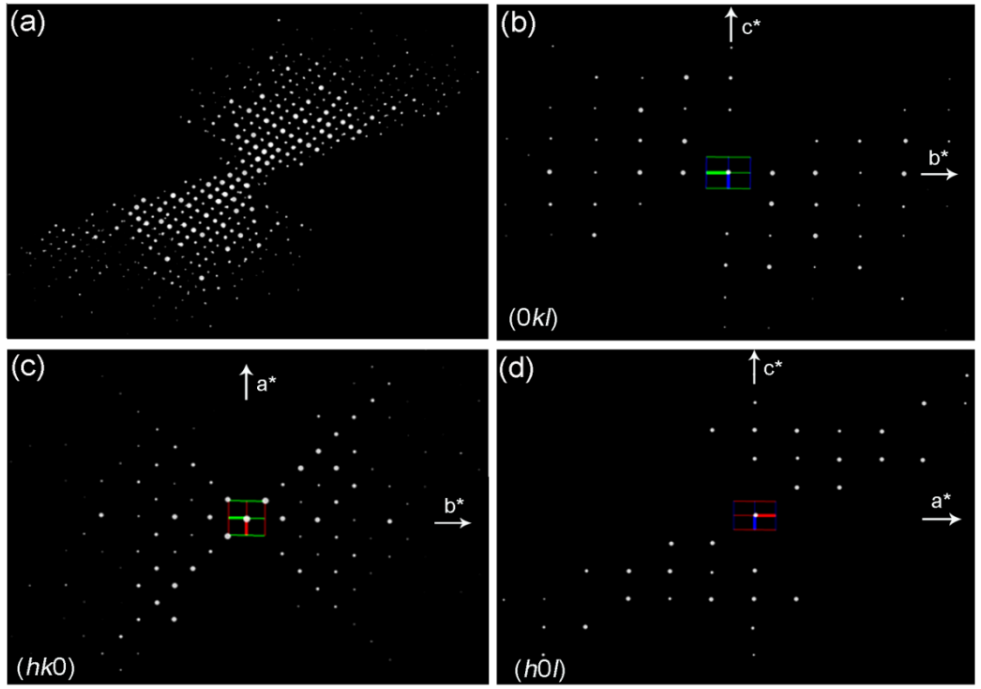

**Find a new zeolite ECNU-23 by accident**

Xu*, Han*, Sun*, Wu* et al. *Angew. Chem. Int. Ed.* **2020**, 59, 1166

# Psudo-symmetry

## Zeolite PKU-14



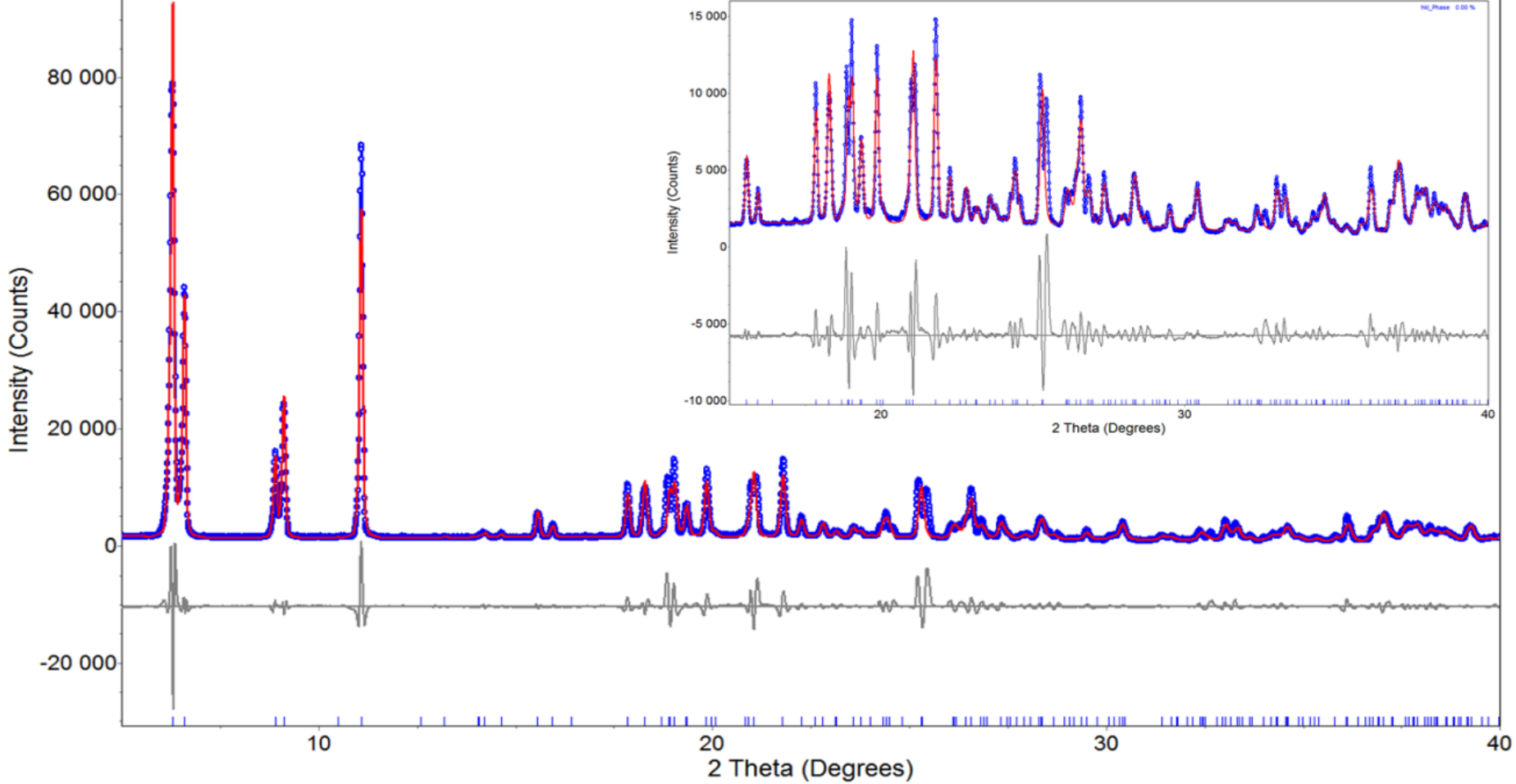



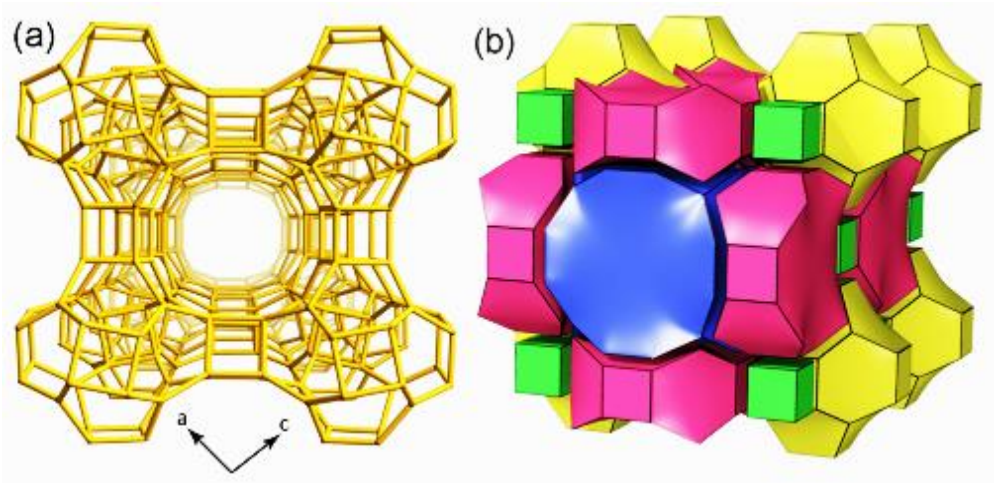

Cubic?

Tetragonal: *I*4/mcm

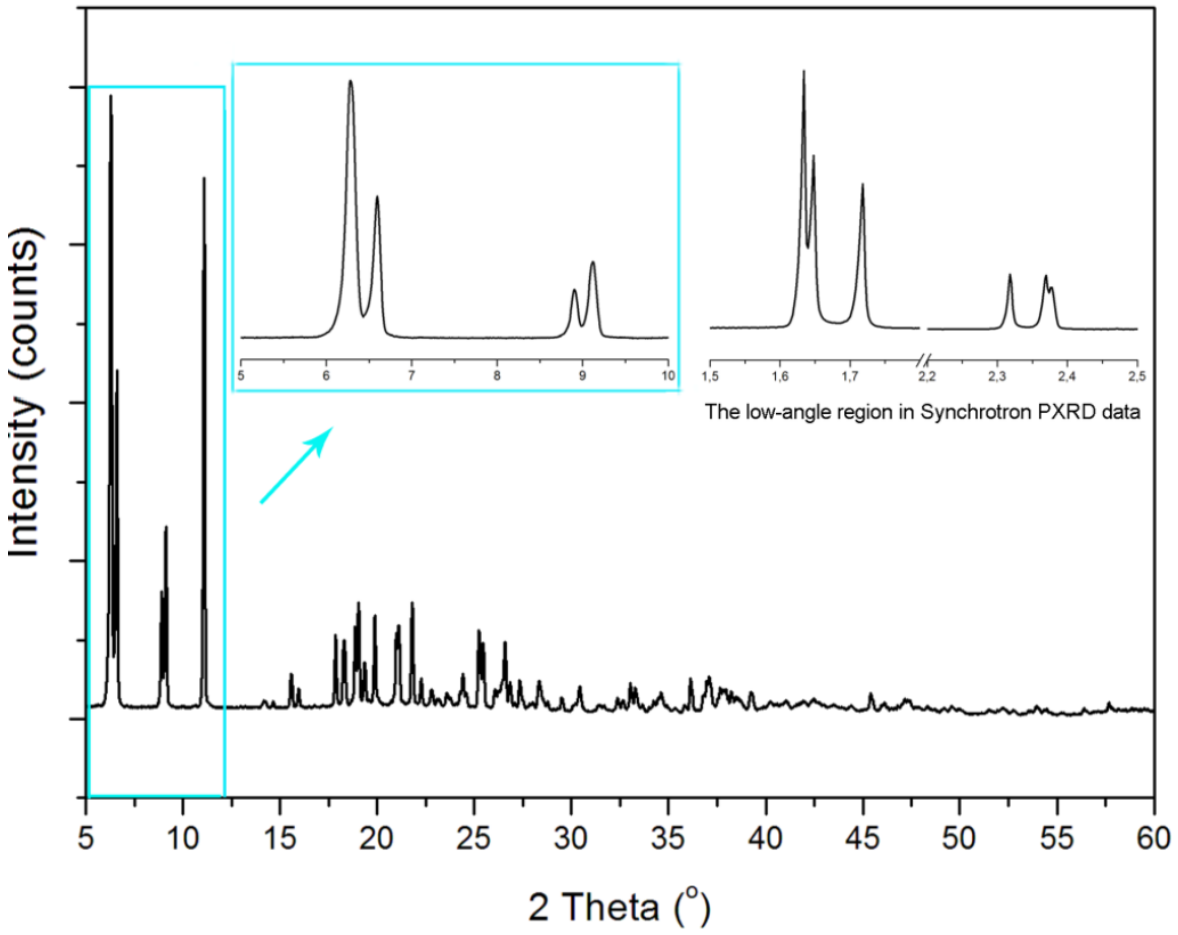
19.8 Å, 26. 8 Å

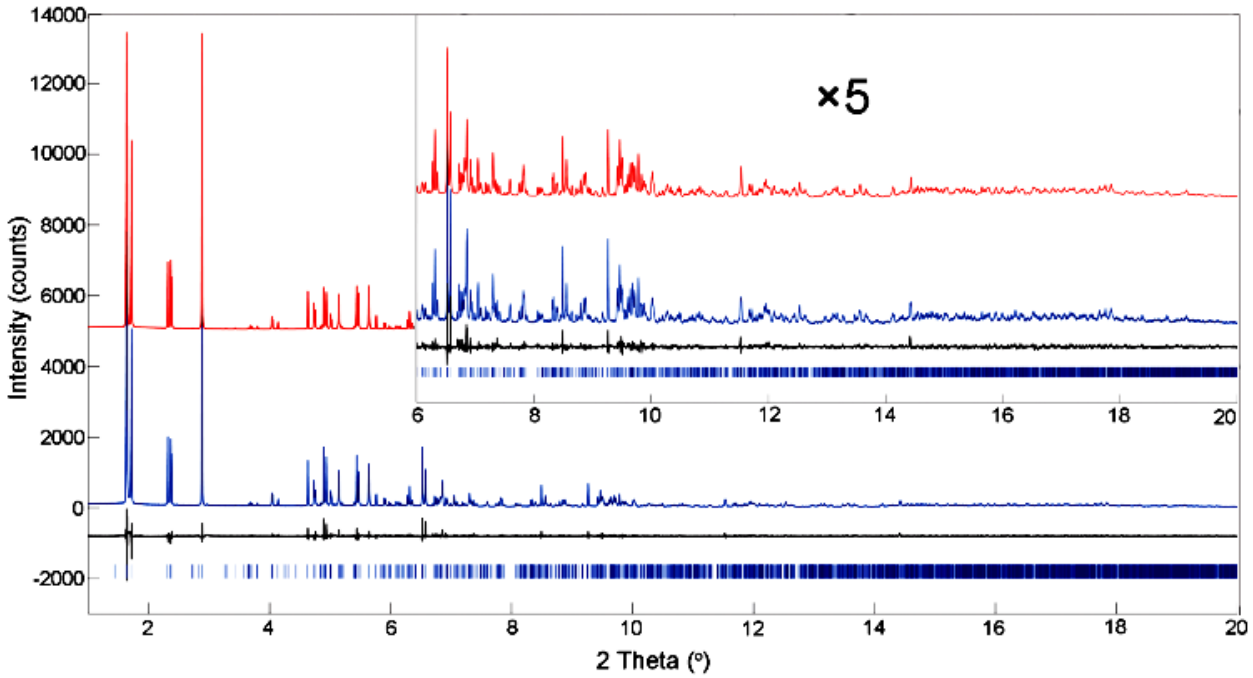
Liang et. al. *Chem. Eur. J.* **2014**, 20,16097




Framework structure from the data in $K_{a1}$ system through simulated annealing



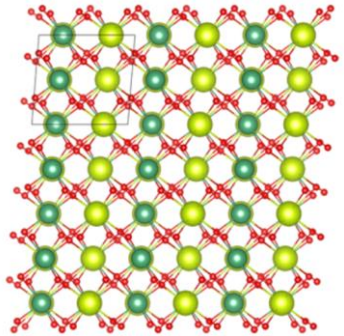

**Monoclinic: *I2/m***

**19.8075(7) Å, 26.7538(7) Å,19.8127(7) Å**

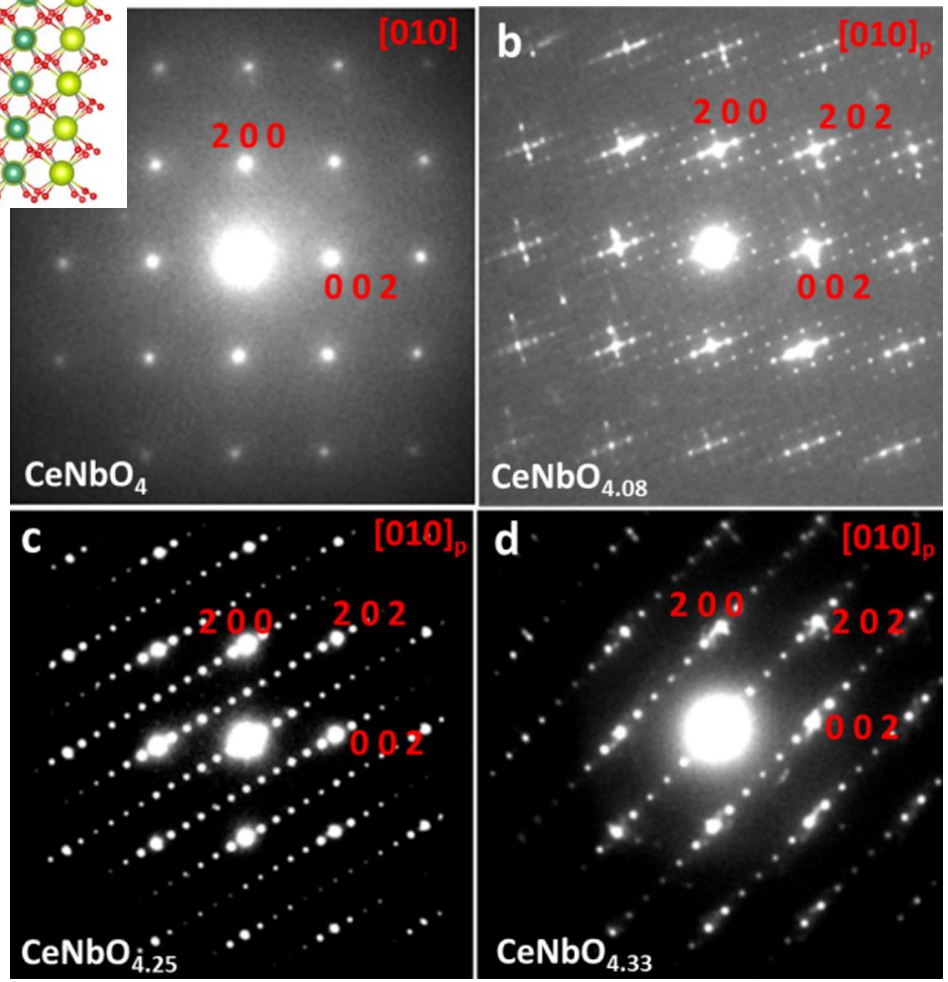
**90.4810(5)°**

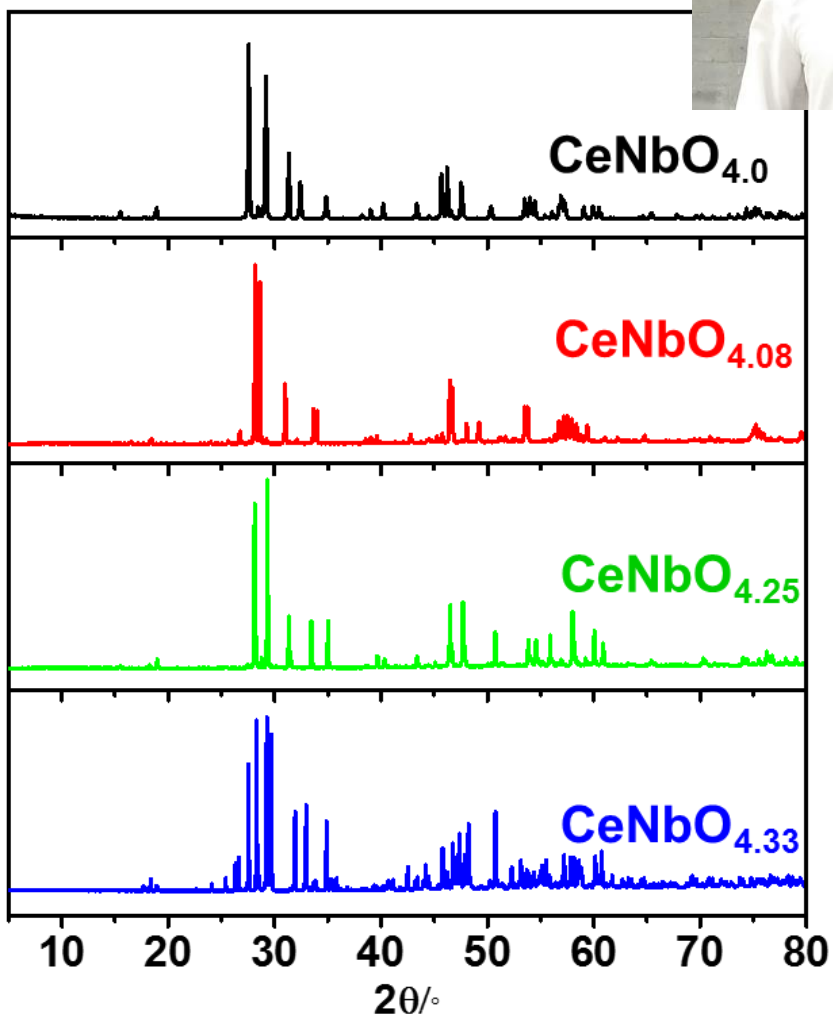
$(110)_{tetragonal}$ is split into two peaks $(110)_{Monoclinic}$ and $(1\text{-}10)_{Monoclinic}$.

# Incommensurate structures



## Ion conductor $CeNbO_{4+x}$



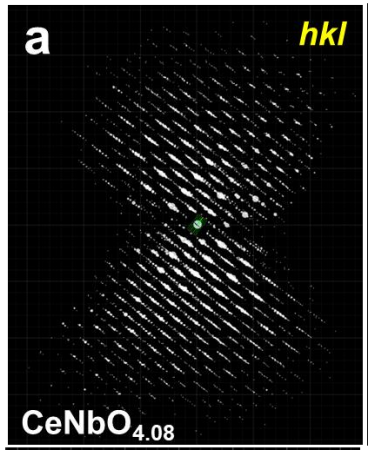



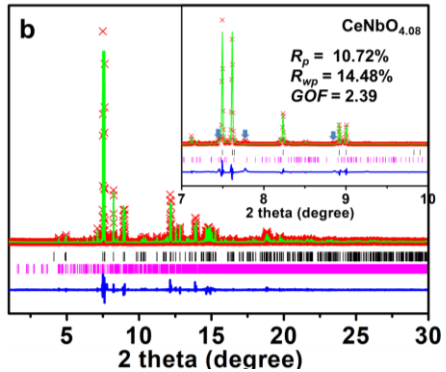


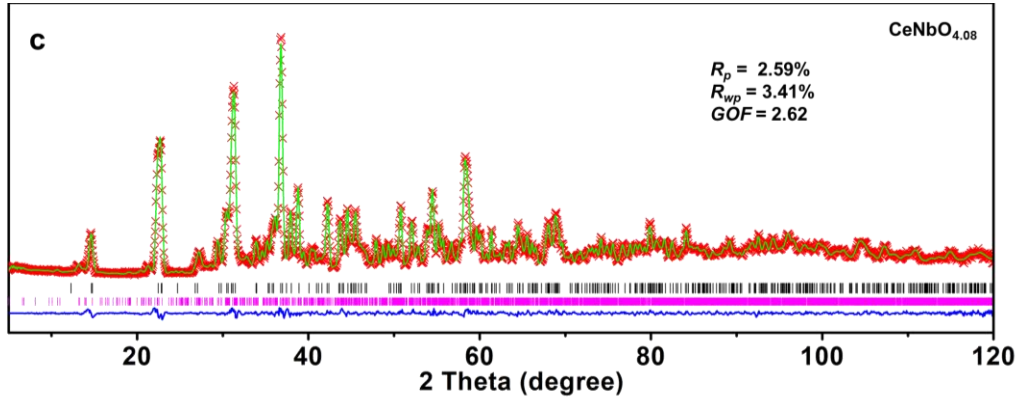


## Pseudo tetragonal

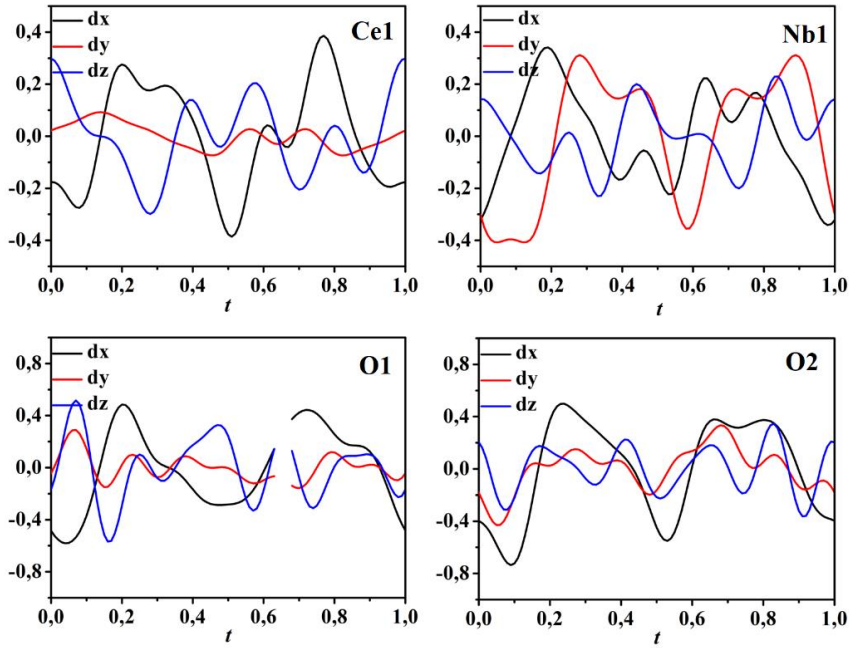
*Xiaojun Kuang* Junliang Sun* et al Nat. Commun.* **2020**, 11, 4751



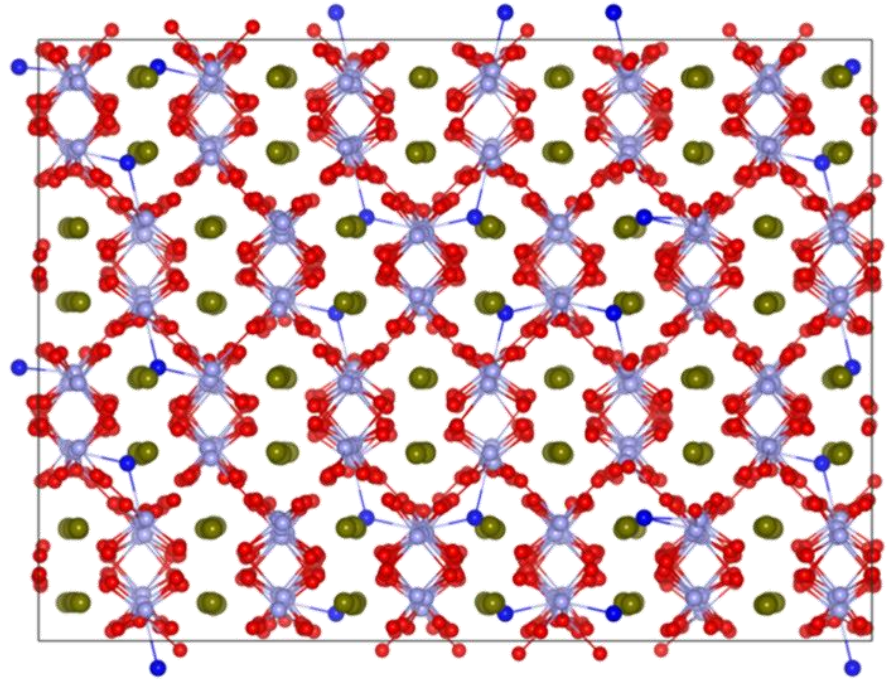




3D electron diffraction  powder X-ray diffraction  Neutron diffraction

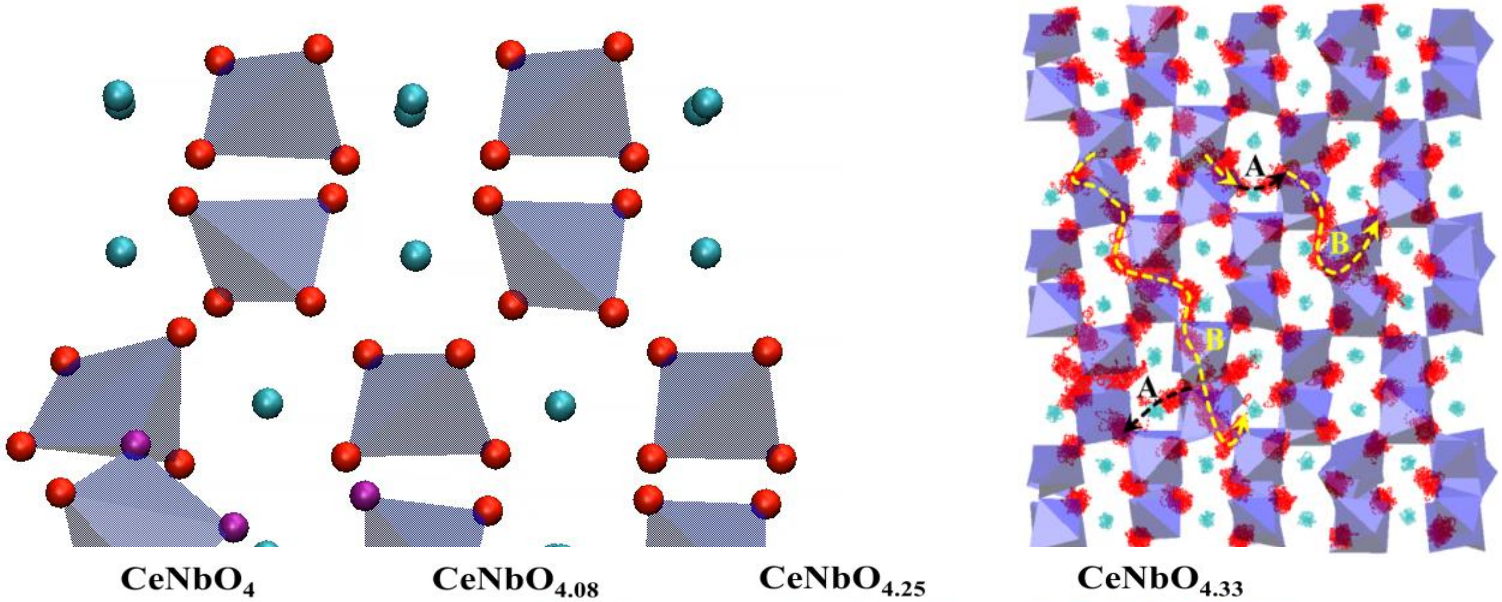



Modulation of atomic positions

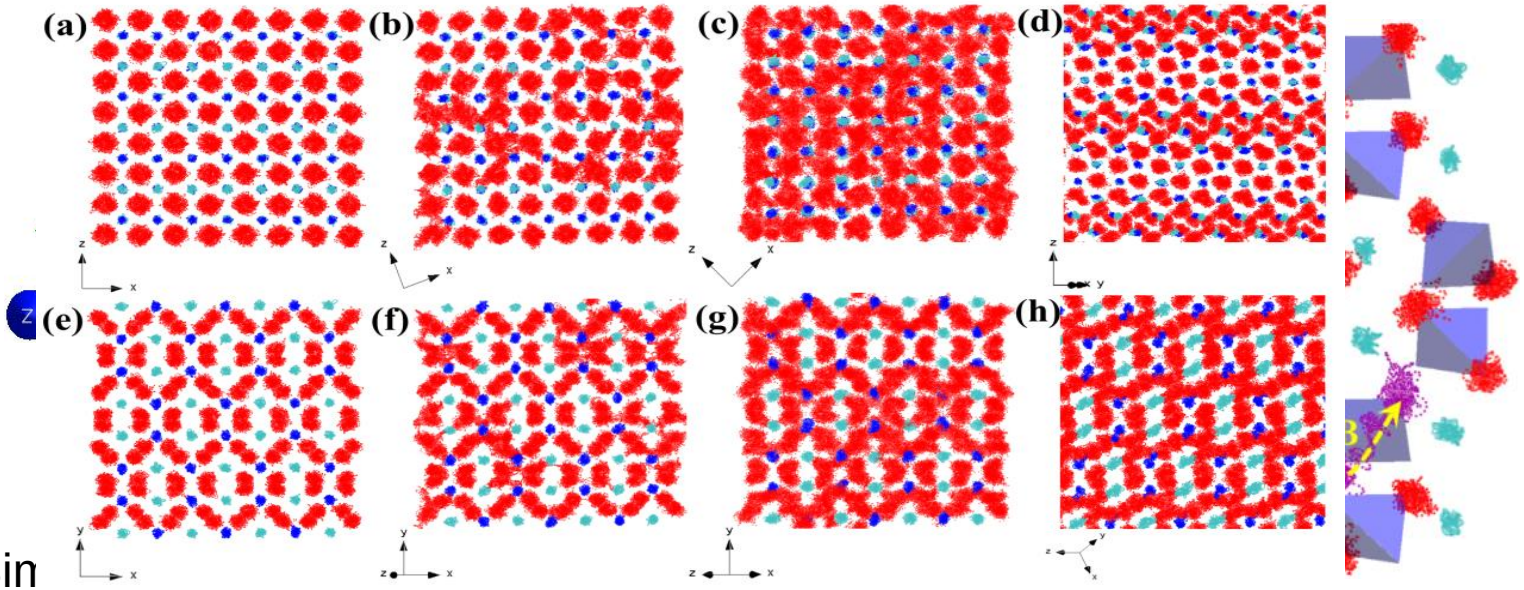


Superstructure of CeNbO4.08
blue spheres are additional oxygen

# Transportation mechanism of oxygen ions




$CeNbO_4$ $CeNbO_{4.08}$ $CeNbO_{4.25}$ $CeNbO_{4.33}$




Sin

# Comparison of different techniques

| | SXRD | PXRD | 3D ED |
|---|---|---|---|
| Size limit | Tens of μm | Tens of nm | Tens of nm |
| Crystal quality | High | High | Low |
| Purity | Low | High | Low |
| Crystal quantity | Media | Large | Low |
| Collection speed | Media | fast | Slow-> fast |
| Collection difficult | Low | Low | High -> Low |
| Independent data points | Abundant | Low | Abundant |
| Structure solution | Easy | Difficult | Difficult -> media |
| Refinement | Reliable | Media | Unreliable -> reliable |

