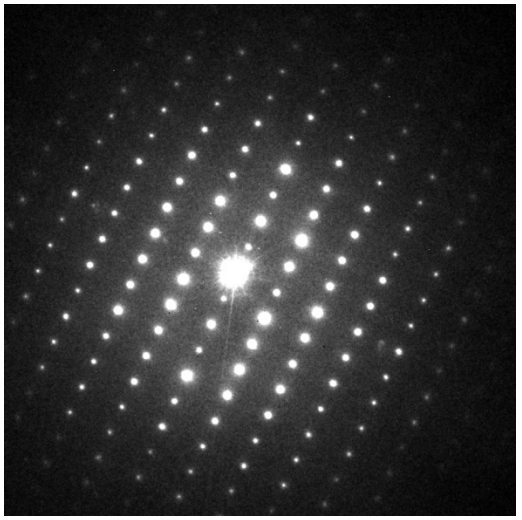
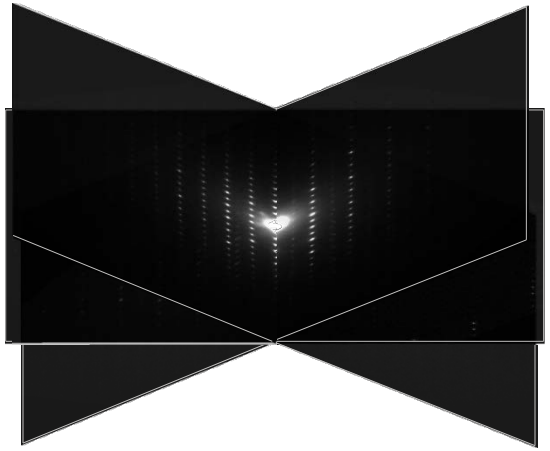
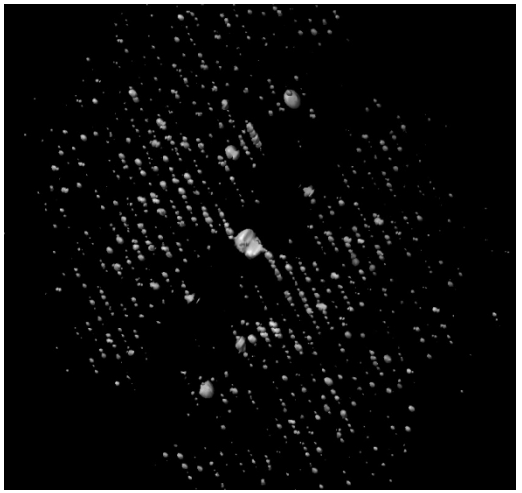
ADT Idea - 3D diffraction tomography

All previous electron diffraction attempts using TEM rely on in-zone (oriented) patterns

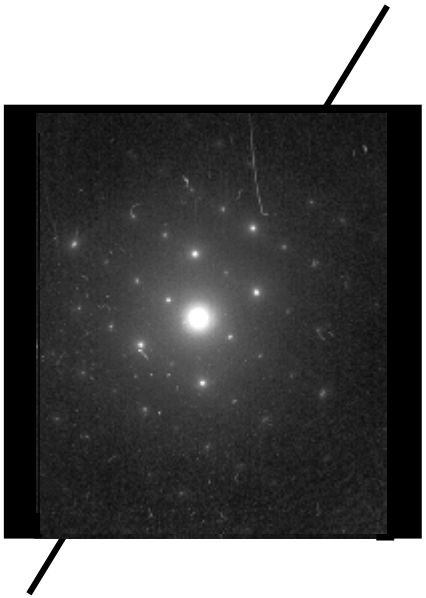


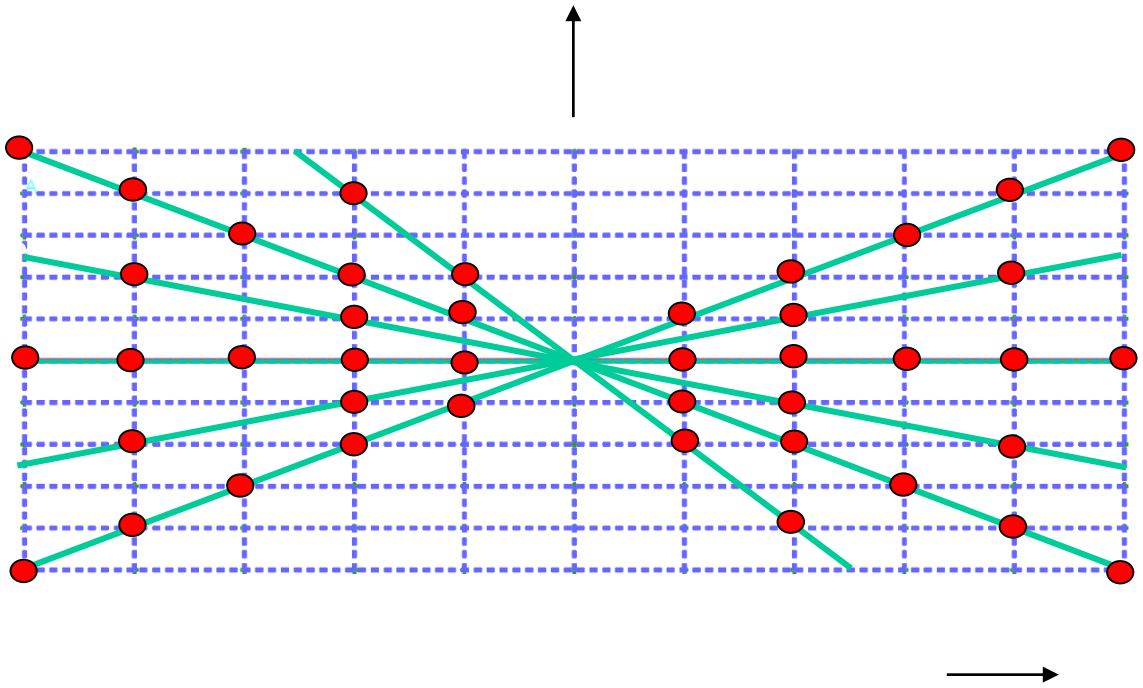




ADT approach: collection of full 3D reciprocal space starting from not oriented patterns

TEM :zone axis tilt series acquisition





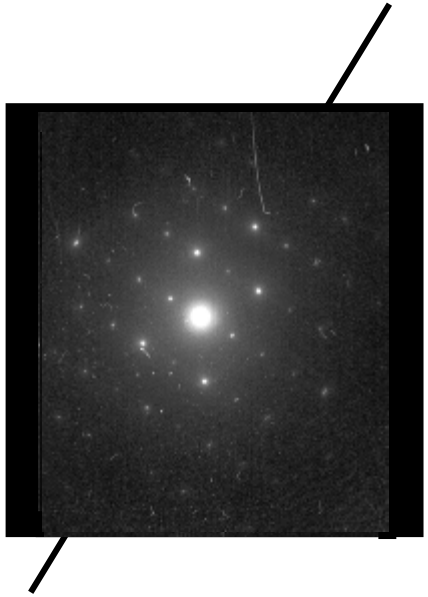
Courtesy : Prof. U Kolb UMainz

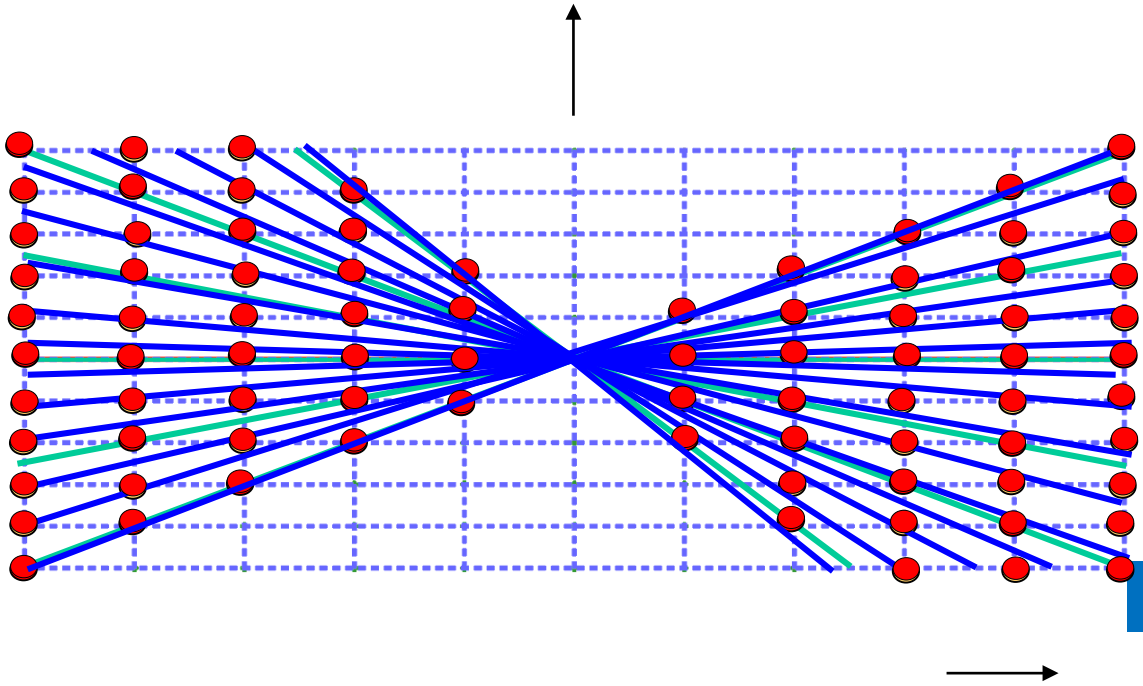
Problems of zone axis tilt series

- intensive training to get good tilts

- data collection is slow and tedious

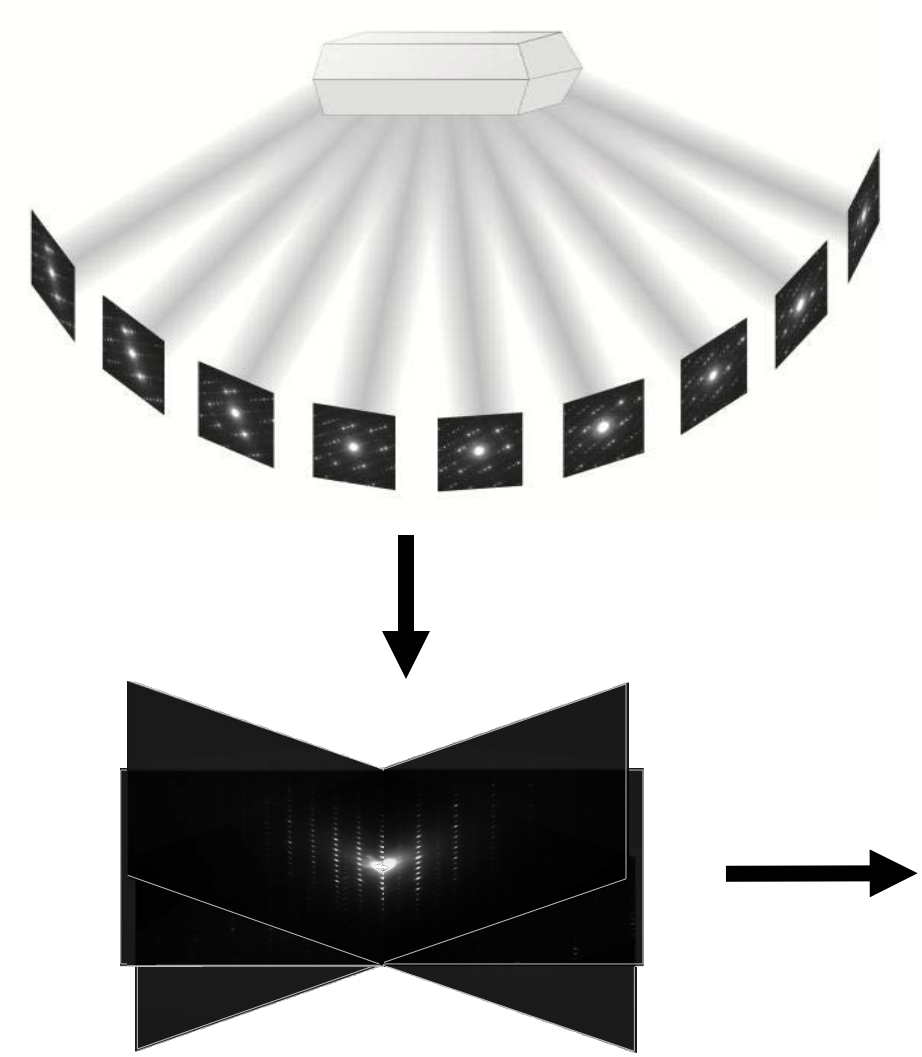
- you miss most of high indexed reflections, especially in the peripheral areas of the reciprocal space



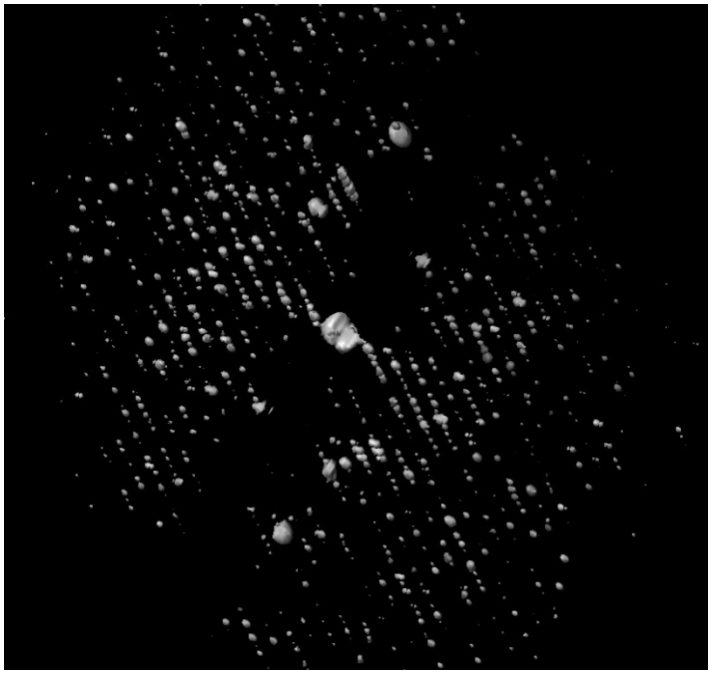


Courtesy : Prof. U Kolb UMainz

Data analysis – ADT3D



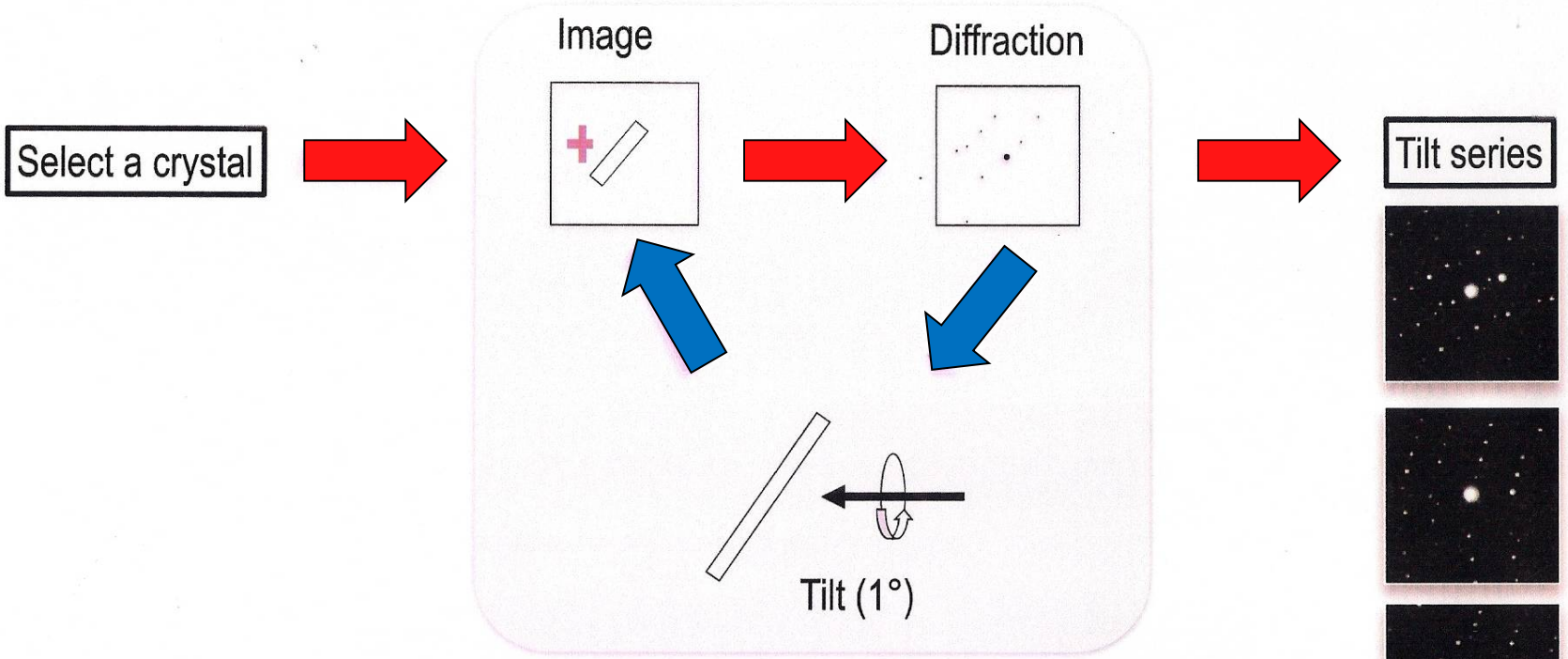
Data analysis by ADT3D
3D reconstrucution of diffraction space



diffraction tomography. Part II – Cell parameter determination. U. Kolb, T. Gorelik and M.T. Otten, *Ultramicroscopy*, **108**, 763-772 (2008).

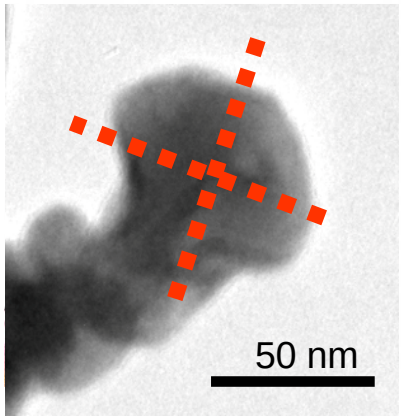
Technique

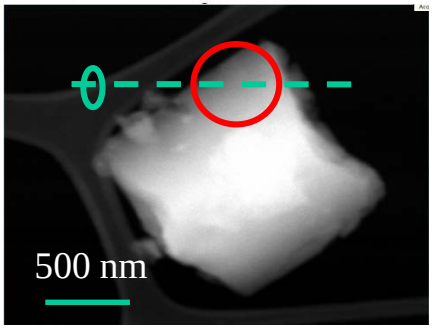
3D sampling of reciprocal space



Arbitrary axis: Less dynamical effects,
More reflections
Easier to learn

Data collection: Any TEM using SAED or NED,
~30° for unit cell parameter
≥ 100° for structure solution

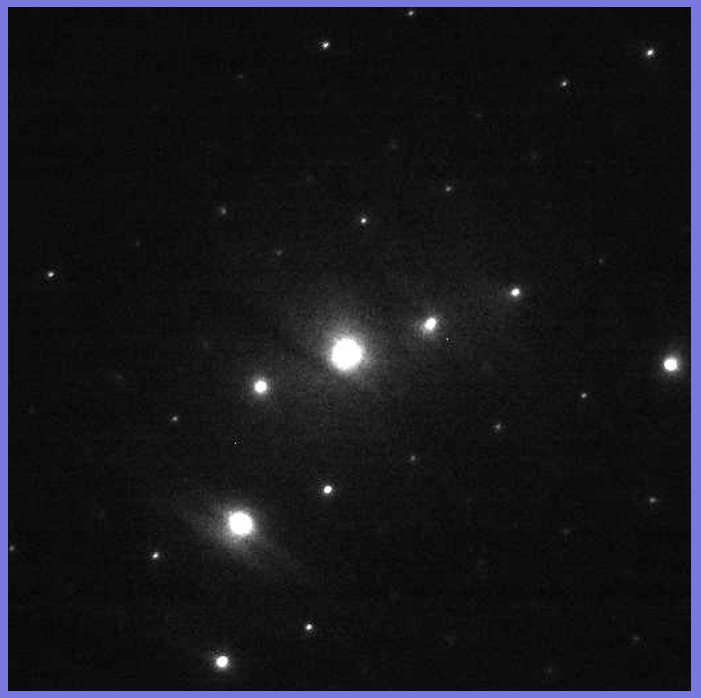


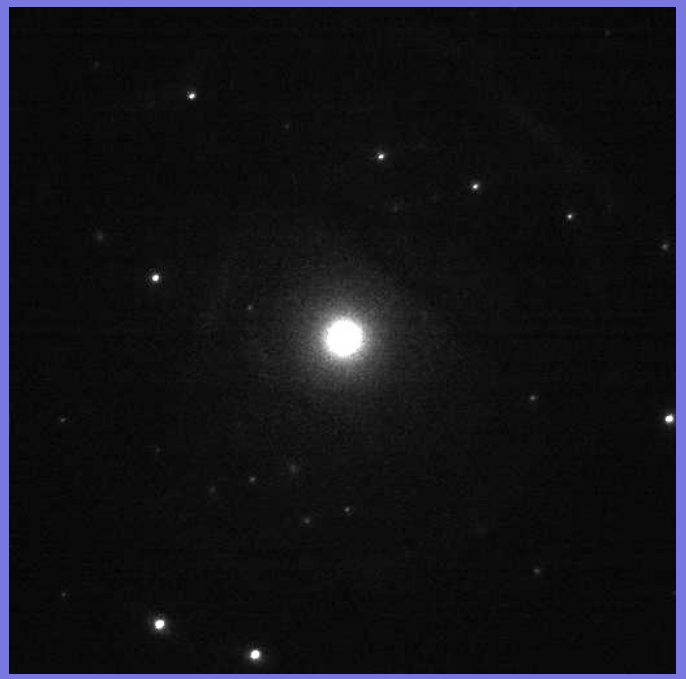


3D sampling of reciprocal space

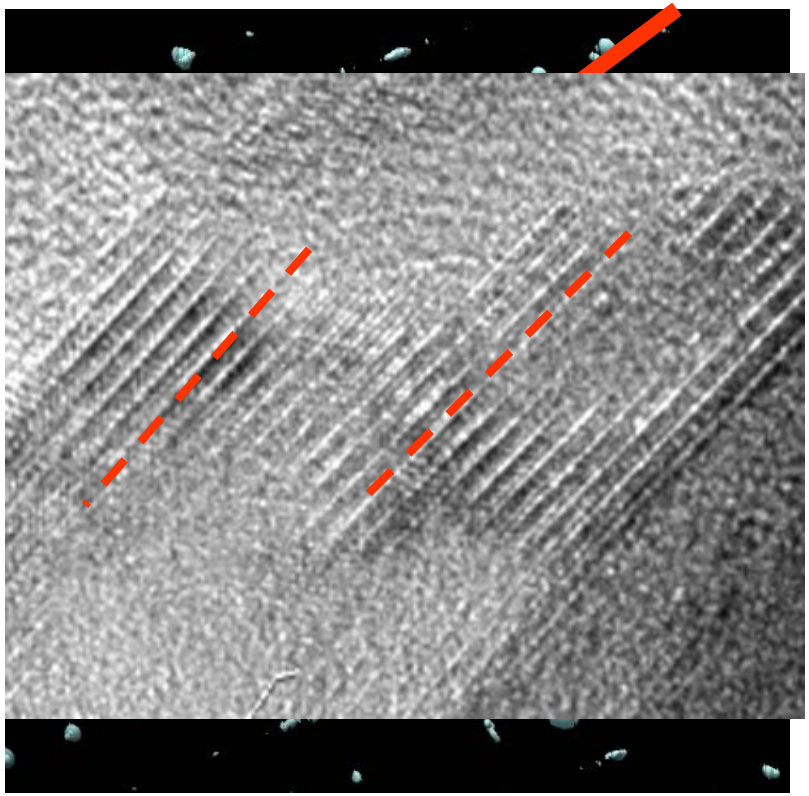
Tilt angle ±30° (max. ±70°)

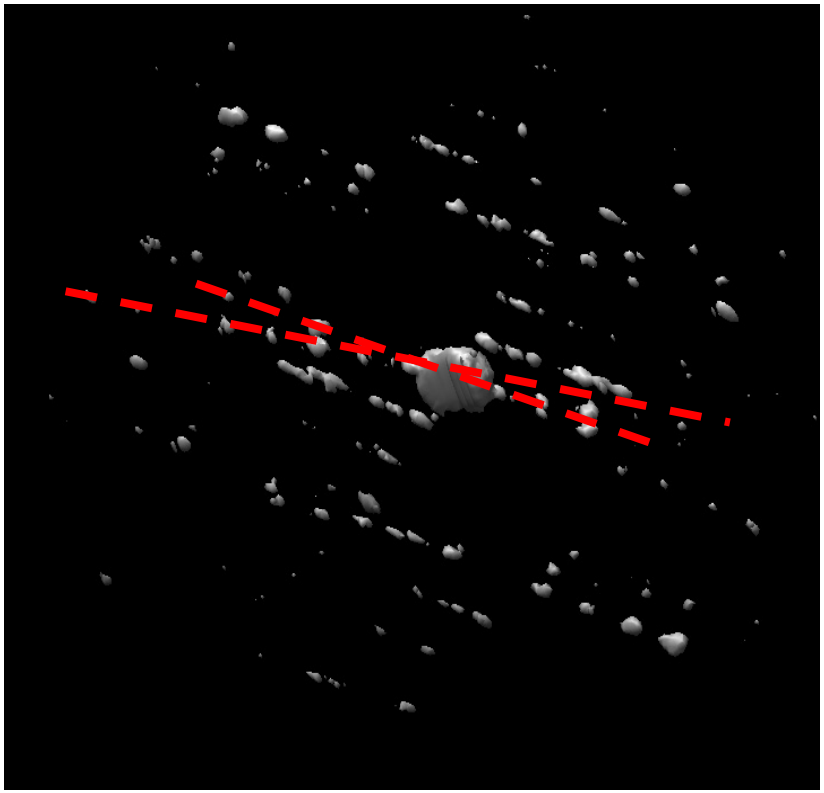
In steps of 1°





Disorder & Polycrystallinity





DISORDER

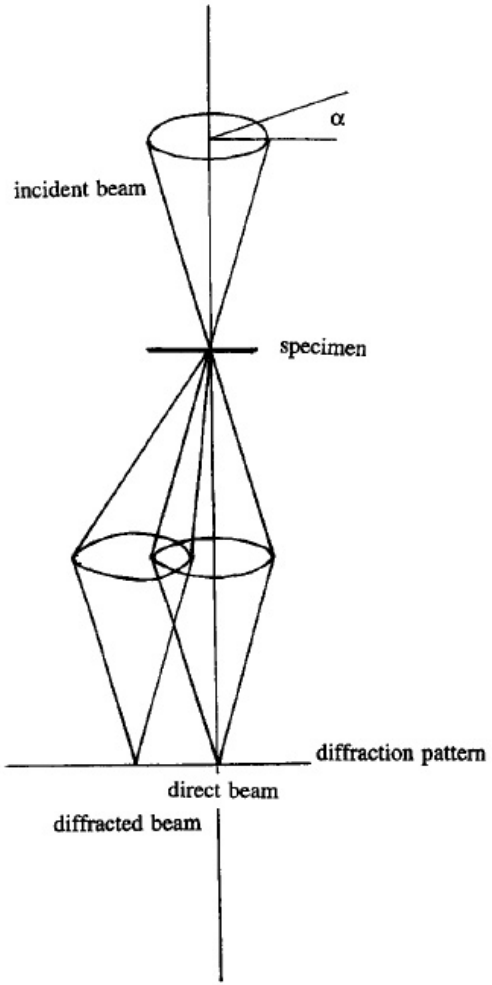
$0kl$: k = 2N+1

POLYCRYSTALS

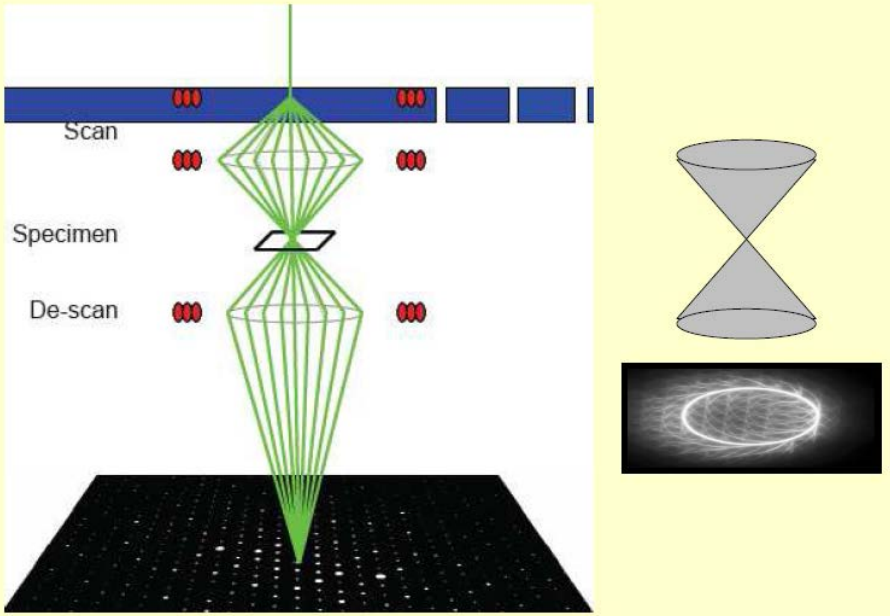
c* tilted ~ 3˚

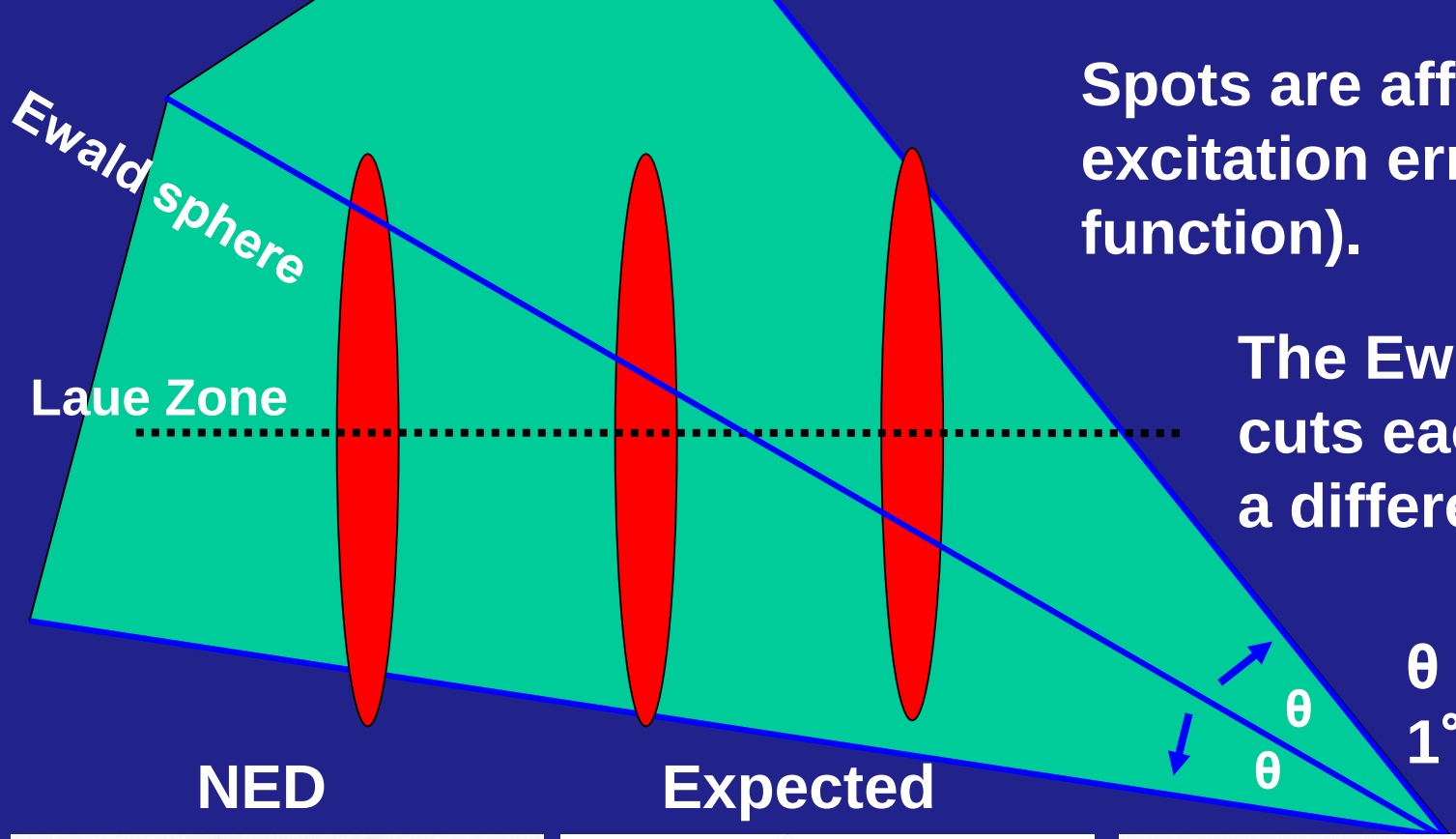
Results

Precession Electron Diffraction (PED)



Scan and descan **the beam to have stationary pattern**





Spots are affected by excitation error (spike function).

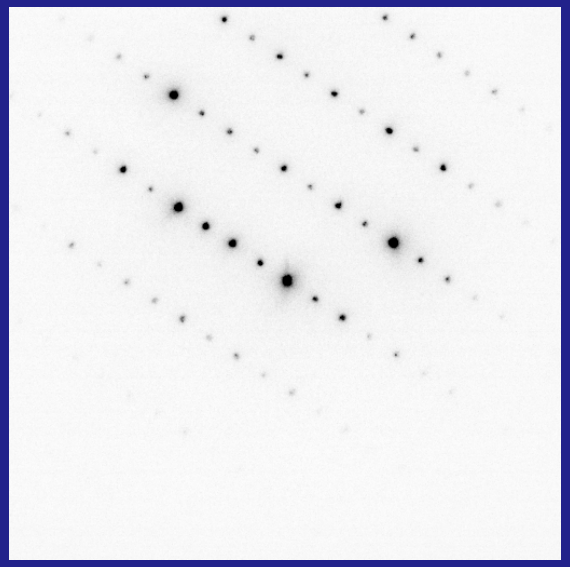
The Ewald sphere cuts each spot in a different way.

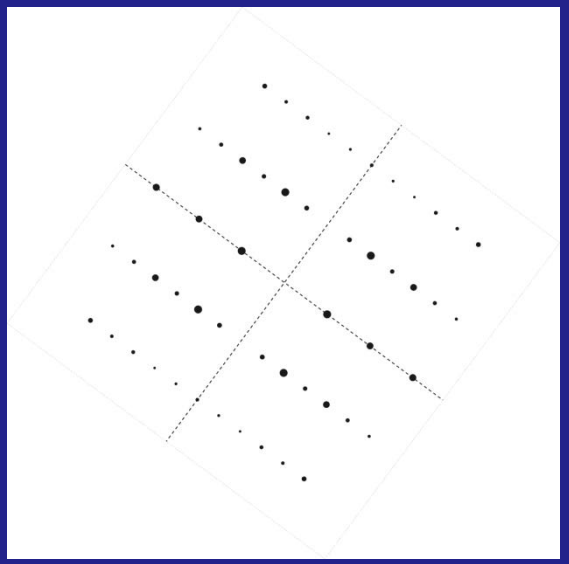
θ = 1°

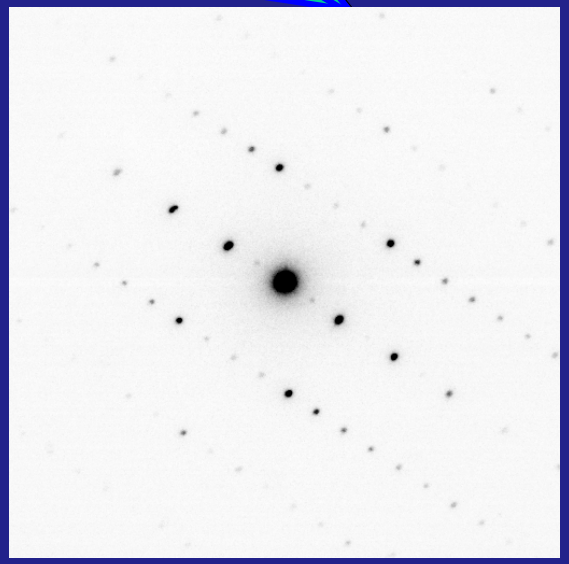
NED

Expected

PED

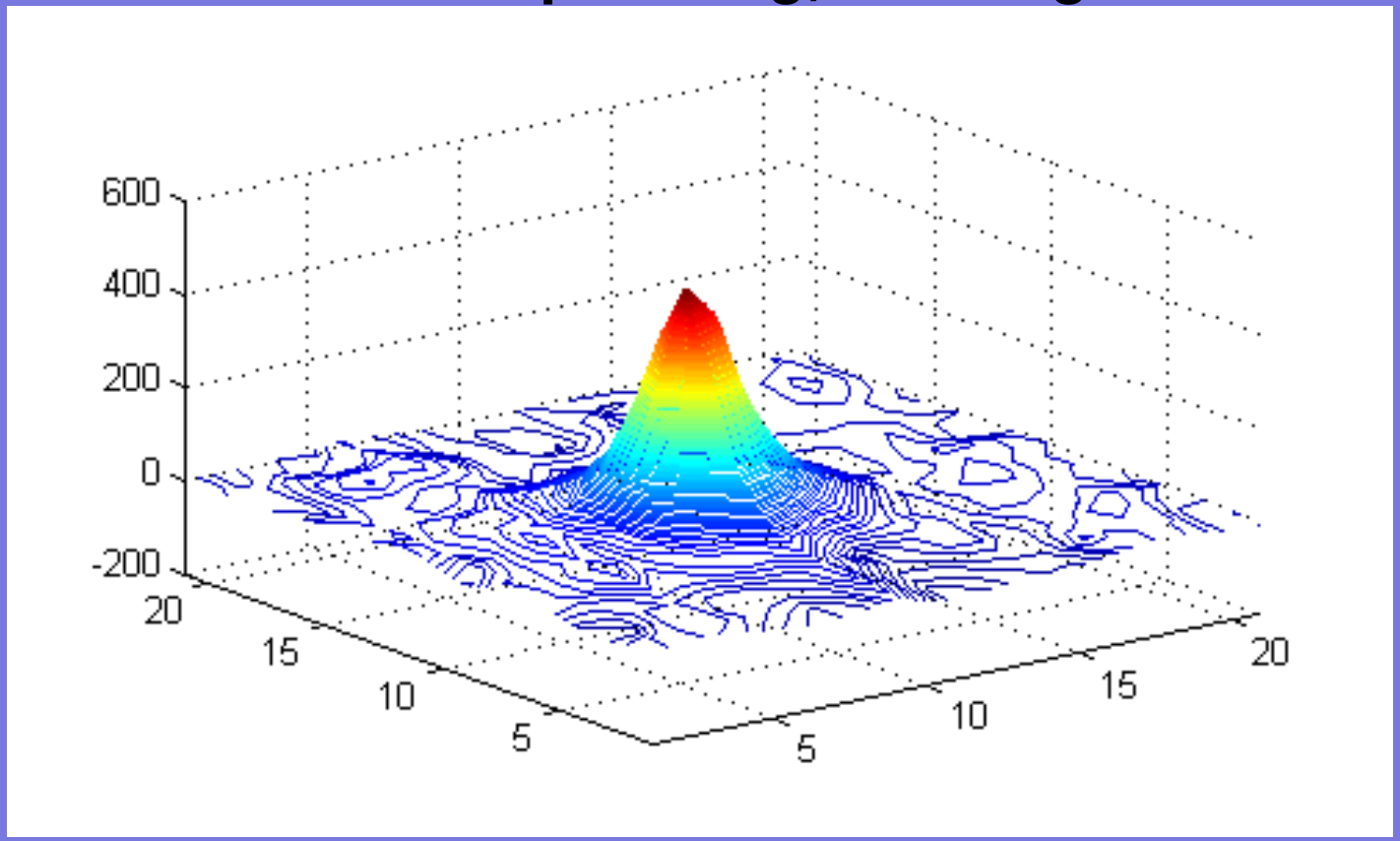




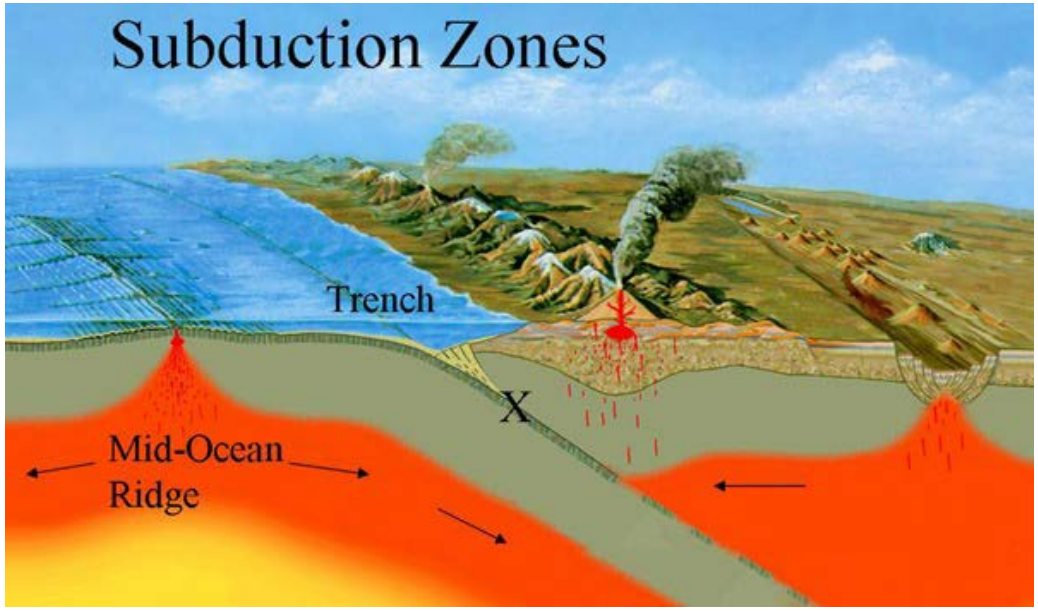


Intensity determination

- Determination of the area for integration
- Fine background subtraction
- Integration of the peak
- …outlook: shape fitting, 3D integration



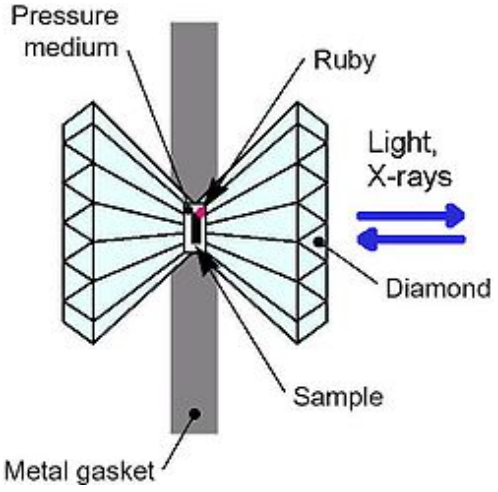
HP phases : HAPY



Subduction of hydrated ultramafic rocks brings water into upper mantle

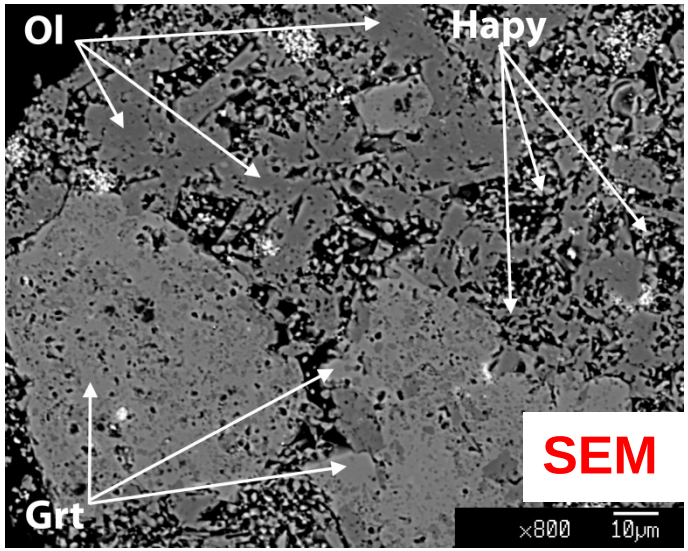
Releasing of water could explain partial melting of mantle wedge: volcanism, seismicity

MgO-Al_2O_3-SiO_2-H_2O (MASH) system is a model for ultramafic rocks subduction



Materials

HP phases : HAPY

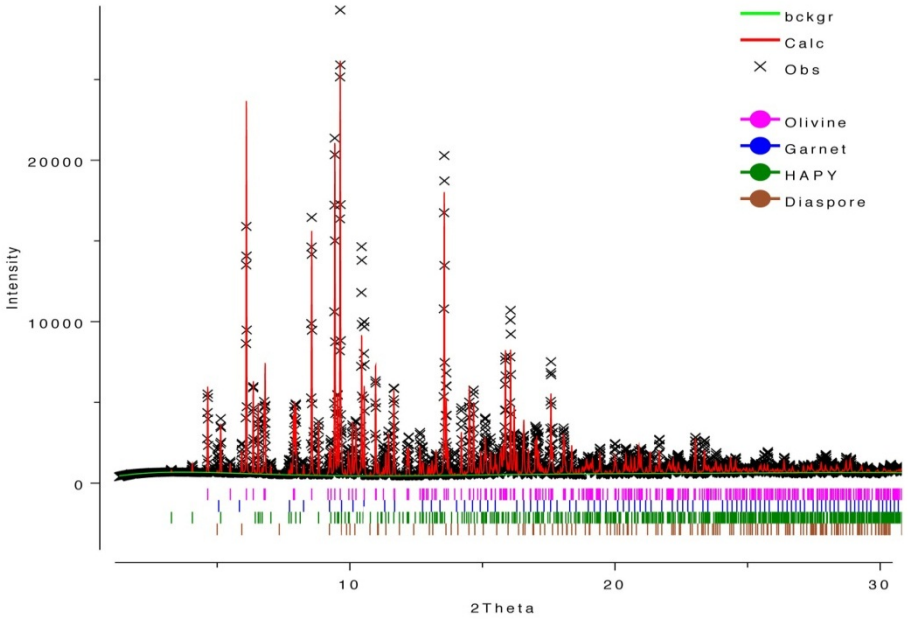


A new phase was detected in two experiments: 700ºC, 5.2 GPa and 720ºC, 5.4 GPa

Fosterite and pyrope main phases; extra peaks from the new nanocrystalline phase

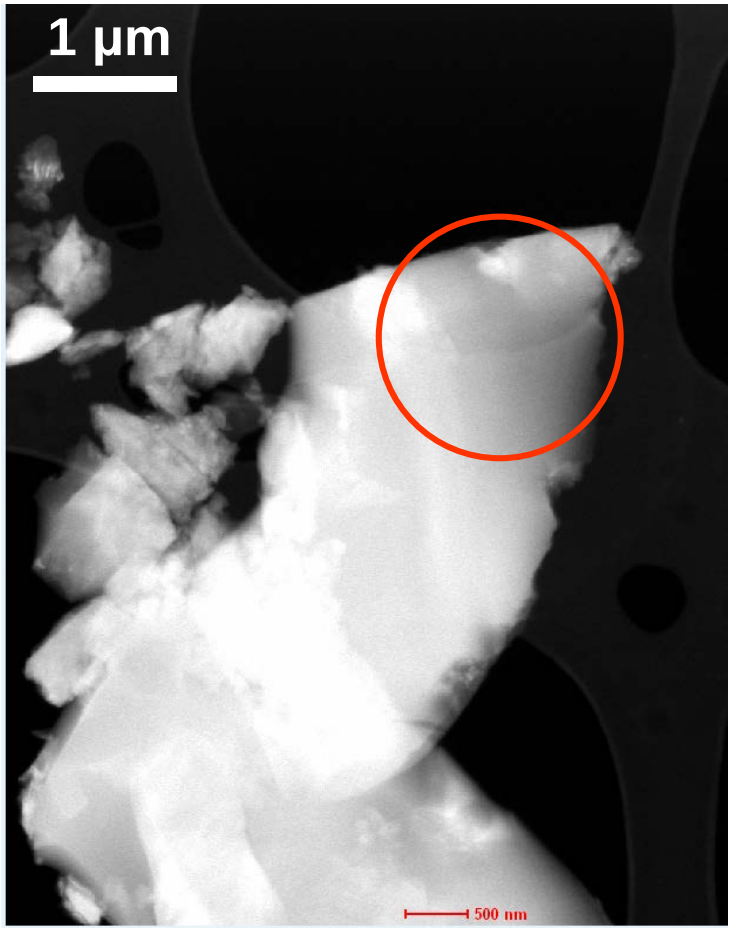
TEM-EDX: Mg:Al:Si ratio close to 2:2:1

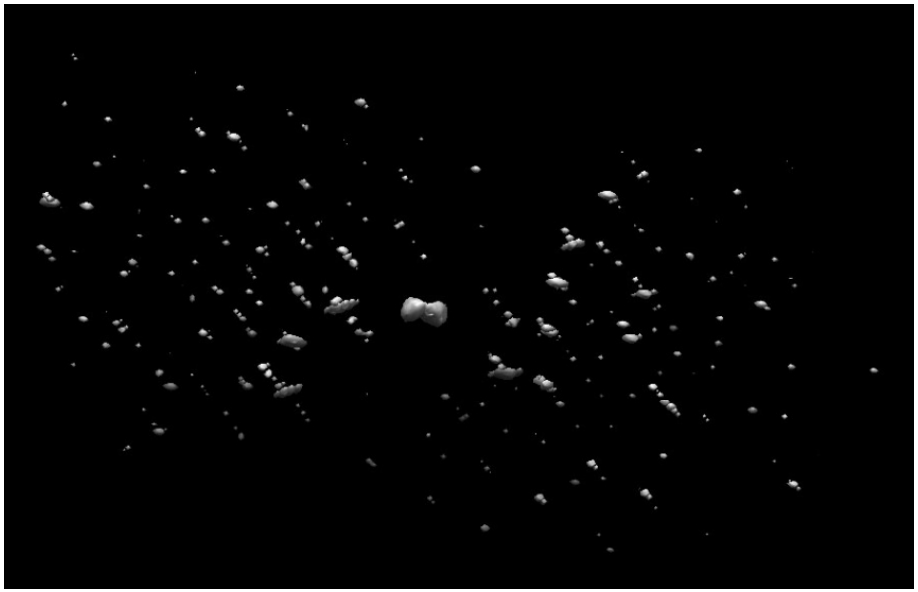
SAED: C-centred monoclinic cell; a=9.9Å, b=11.8 Å, c=5.1Å, β=110˚



Materials

HP phases : HAPY



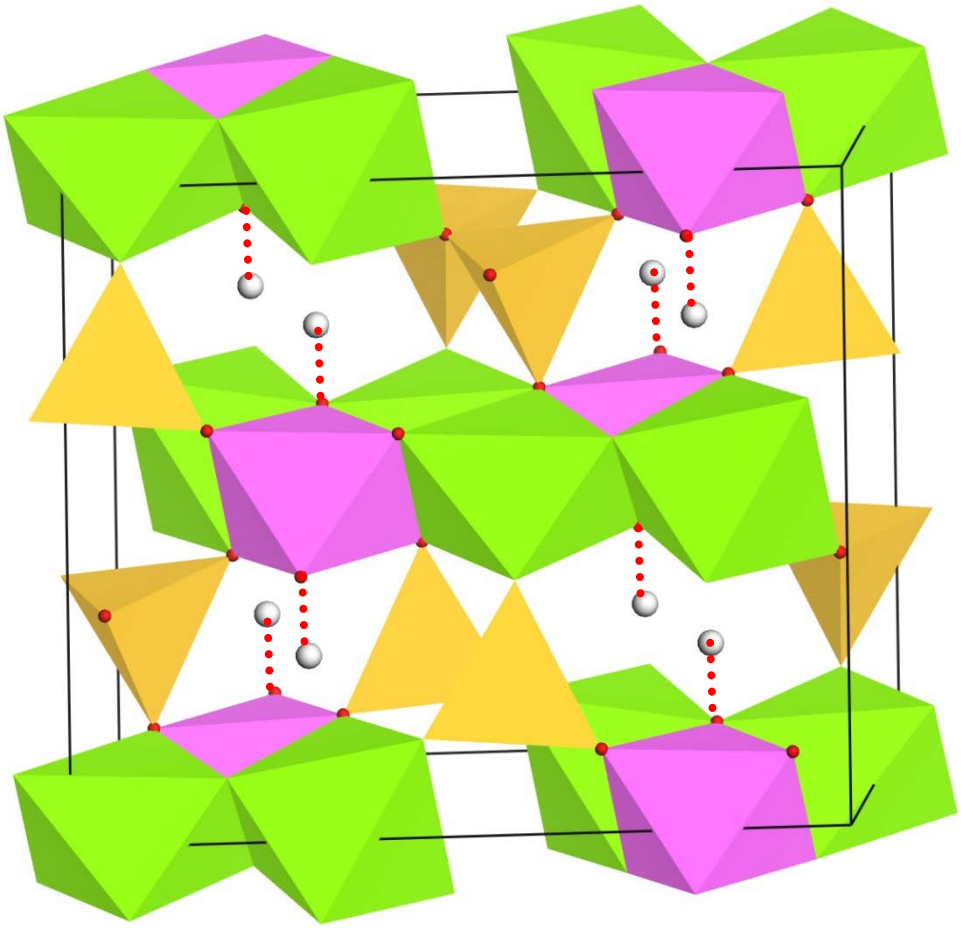


60° /+60° tilt

1656 collected reflections
255 independent reflections
86% completeness
1.0 Å resolution

Materials

HP phases HAPY



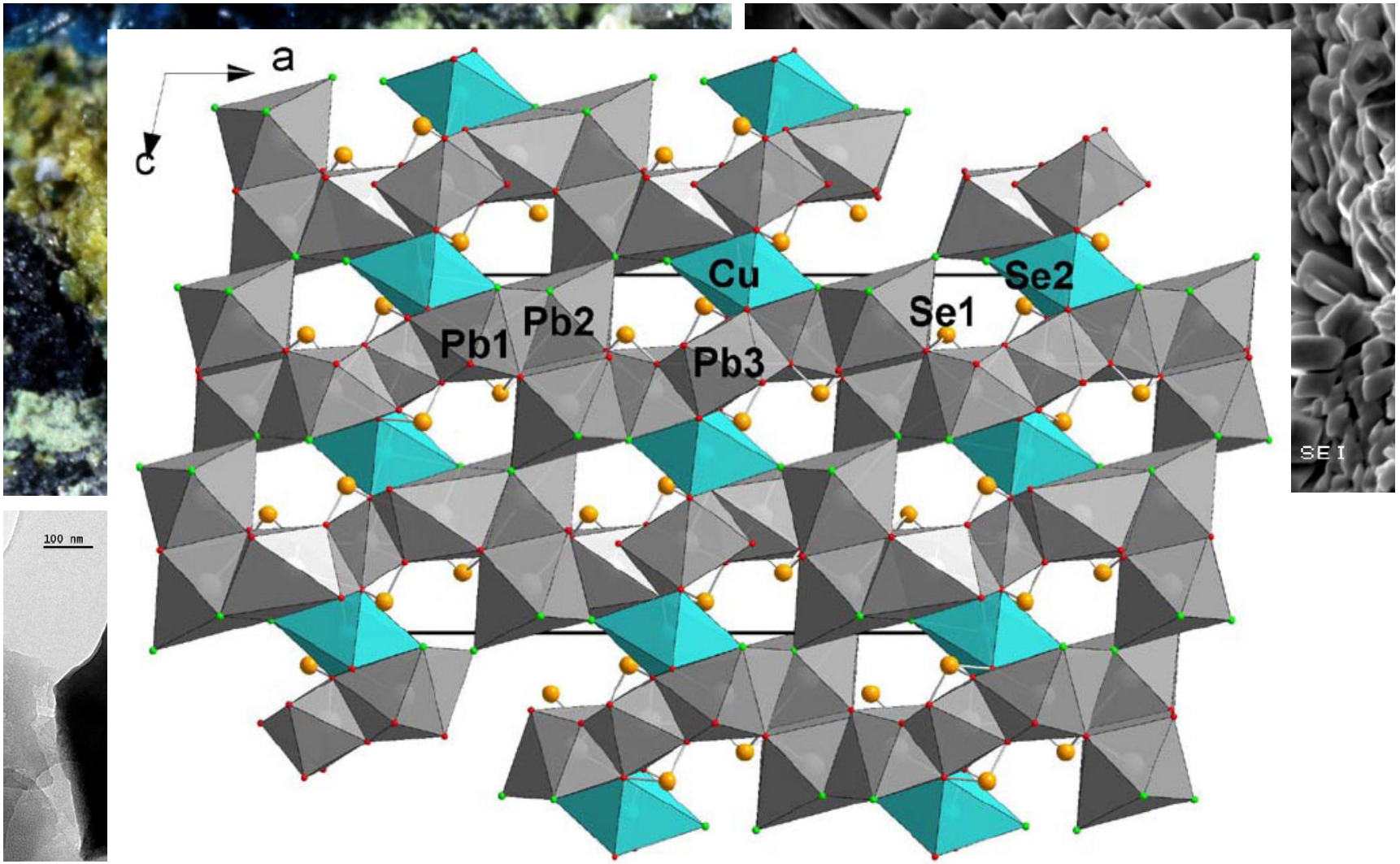
$Mg_2Al(OH)_2AlSiO_6$

HAPY (Hydrous Aluminum bearing PYroxene)

Pyroxene with an extra-cation in the octahedral layer

One octahedral vertex must be occupied by an hydroxil group

Manual acquisition : Sarrabusite mineral

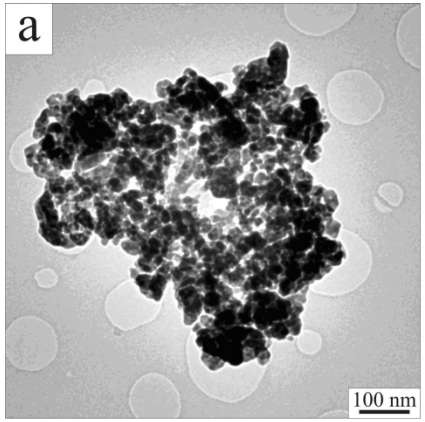


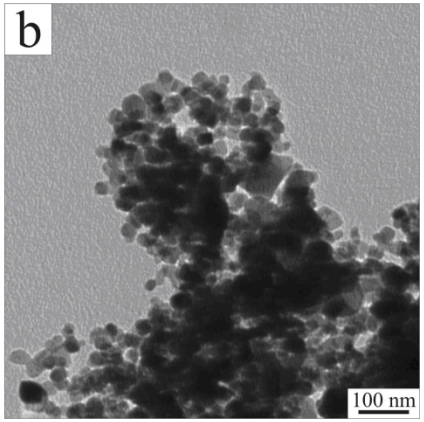
manual

electron diffraction tomography. M. Gemmi, I. Campostrini, F. Demartin, T. Gorelik, C.M. Gremaccioli, *Acta Crystallogr. A*, in print.

Materials

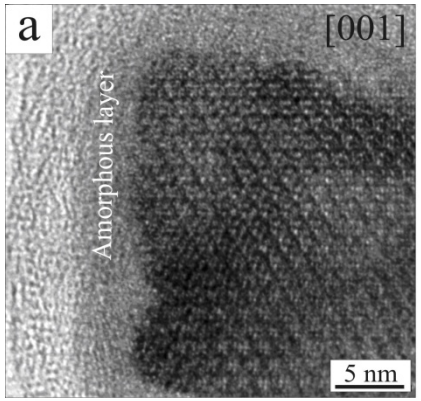
Multiphasic nanoparticles : $Zn_{1+\delta}Sb$

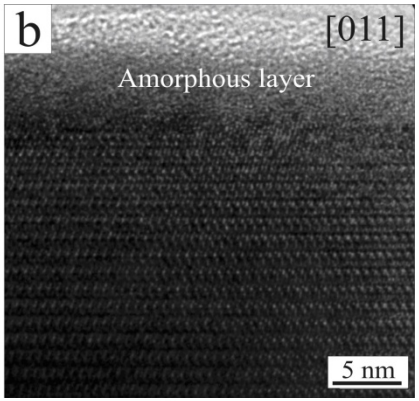


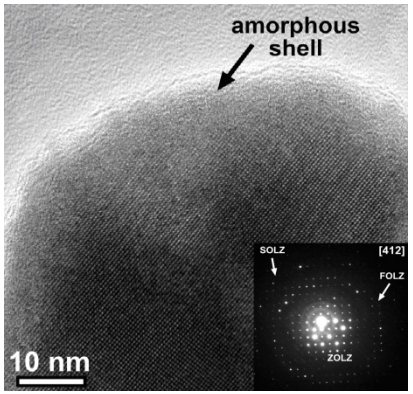


LRTEM: aggregates of particles (up to 50 nm)

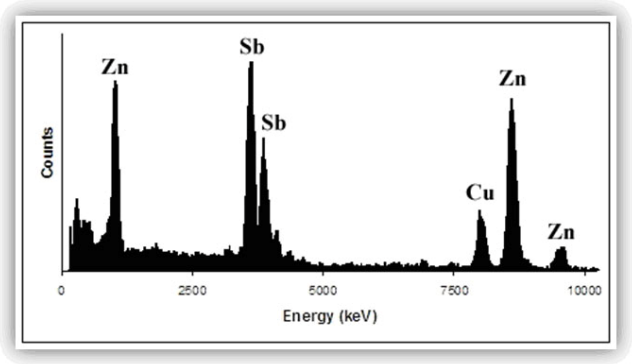
particles are mostly crystalline and single-crystal







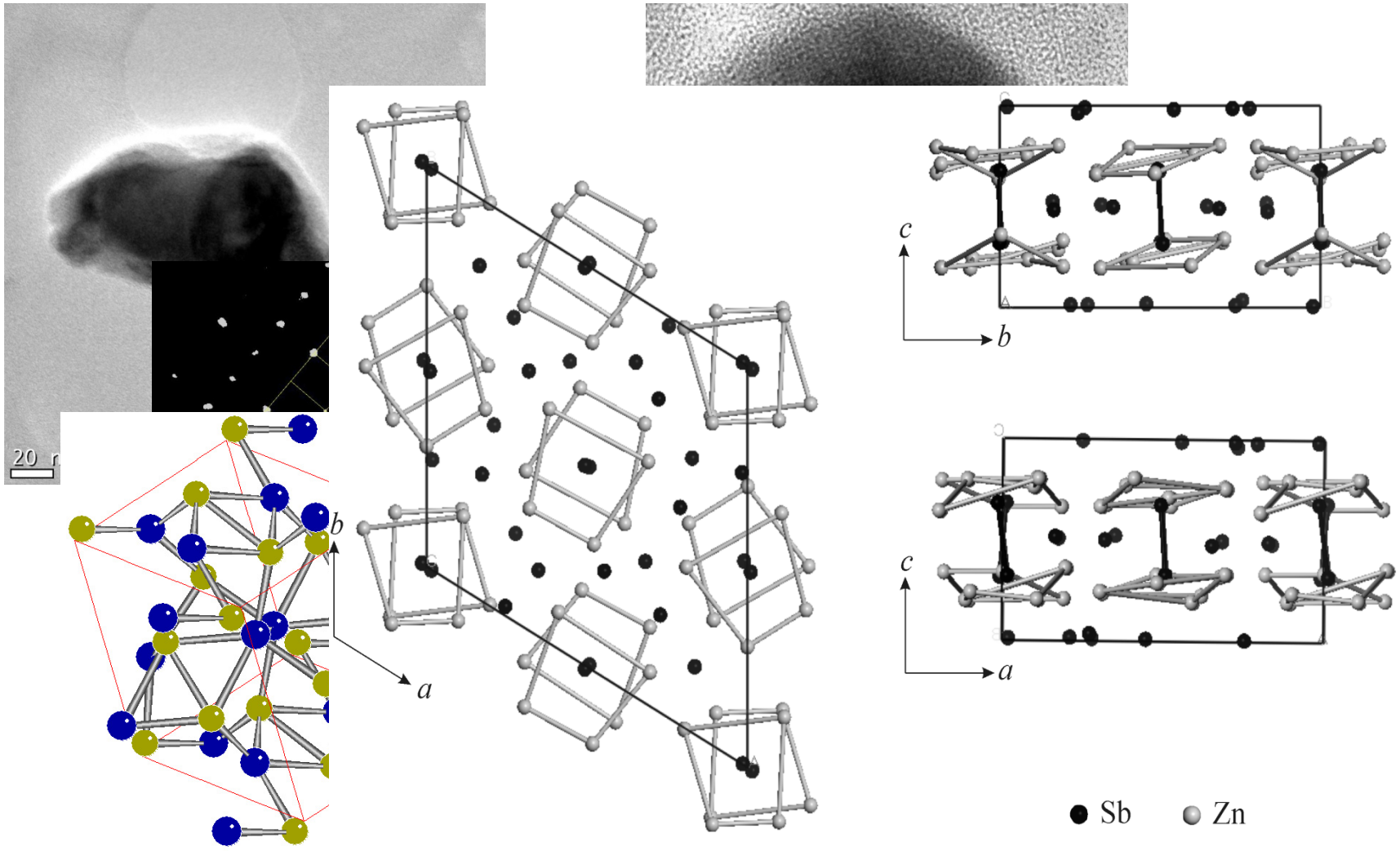
HRTEM and conventional ED: cell parameters do not fit with previous reported structures



EDX:
composition close to Zn:SB

Materials

Multiphasic nanoparticles : $Zn_{1+\delta}Sb$

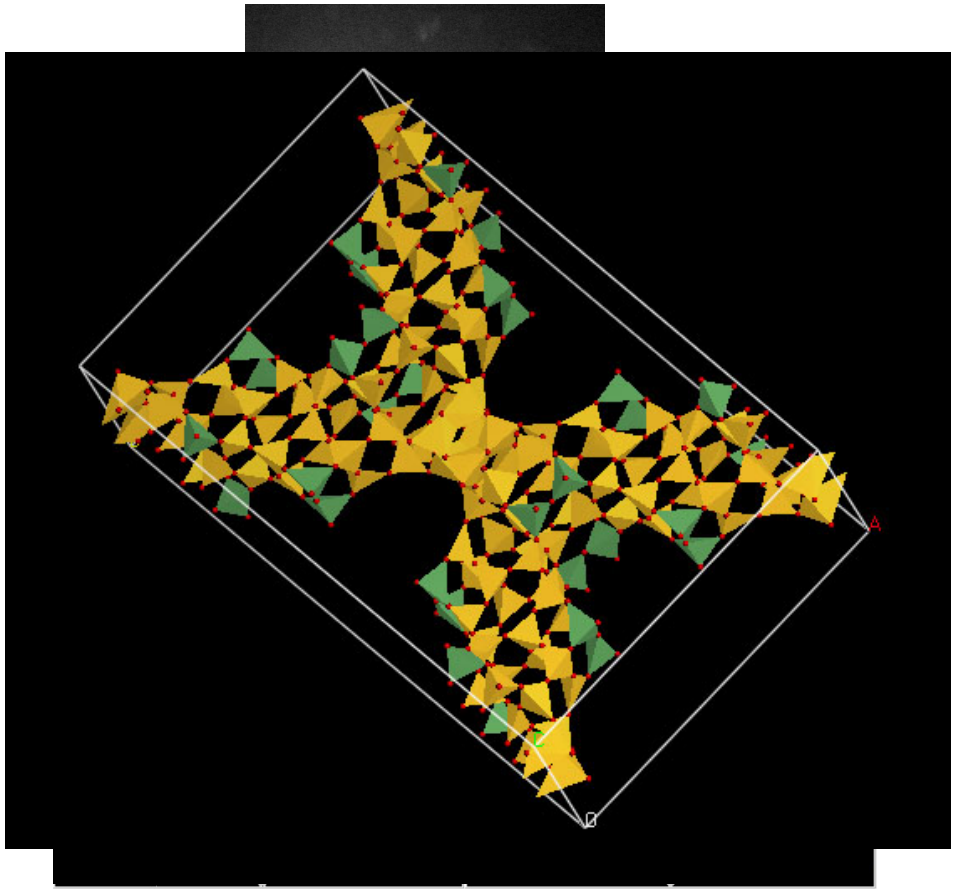


Solution Synthesis of a New Thermoelectric $Zn_{1+x}Sb$ Nanophase and Its Structure Determination Using Automated Electron Diffraction Tomography. C.S. Birkel, E. Mugnaioli, T. Gorelik, U. Kolb, M. Panthöfer, W. Tremel, *J. Am. Chem. Soc.*, **132**, 9881-9889 (2010).

Materials

Beam sensitive materials : Zeolites

Extremely beam sensitive materials: data collected with a cryo-holder; beam slightly shifted during the acquisition



Space group: Cmmm;

a=29.1Å, b=41.9Å, c=12.8Å; V=14040 Å^3

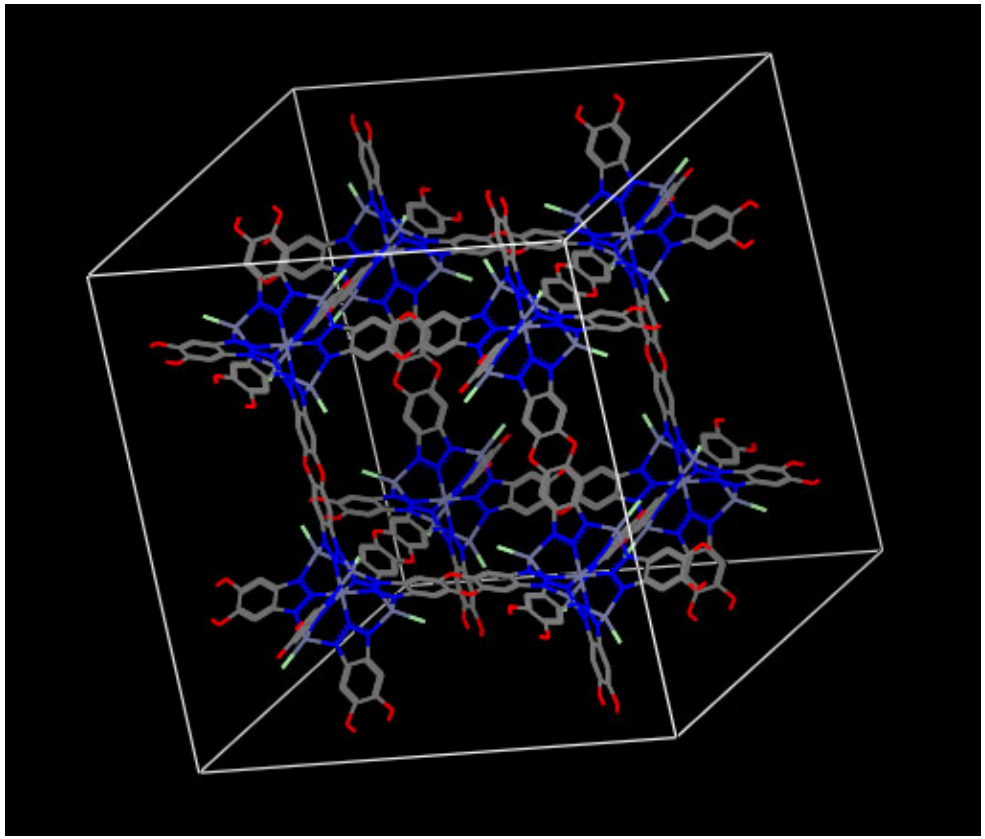
Normally zeolites don't need cryo-conditions, but this sample is extremely beam sensitive due to the presence of **organic templates**

Synthesis and Structure Determination of the Hierarchical Meso-Microporous Zeolite ITQ-43. J. Jiang, J.L. Jorda, J. Yu, L.A. Baumes, E. Mugnaioli, M.J. Diaz-Cabanas, U. Kolb, A. Corma, *Science*, **333**, 1131-1134 (2011).

Materials

Beam sensitive materials : MOFs

materials: data collected with a cryo-holder; beam slightly shifted during the acquisition



Space group: Fm3m;
a=32.0Å; V= 32770Å^3

Only 66° tilt

Cubic symmetry: delivers all reflections 100% completeness

Elucidating Gating Effects for Hydrogen Sorption in MFU-4 Type Triazolate-Based Metal-Organic Frameworks Featuring Different Pore Sizes. D. Denysenko, M. Grzywa, M. Tonigold, B. Streppel, I. Krkljus, M. Hirscher, E. Mugnaioli, U. Kolb, J. Hanss, D. Volkmer, *Chem. Eur. J.*, **17**, 1837-1848 (2011).