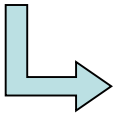
Basics of X-ray Diffraction

Dr. R. Bucher

What we do

We throw X-ray radiation at samples to determine structural information ….

Qualitative X-ray Diffraction



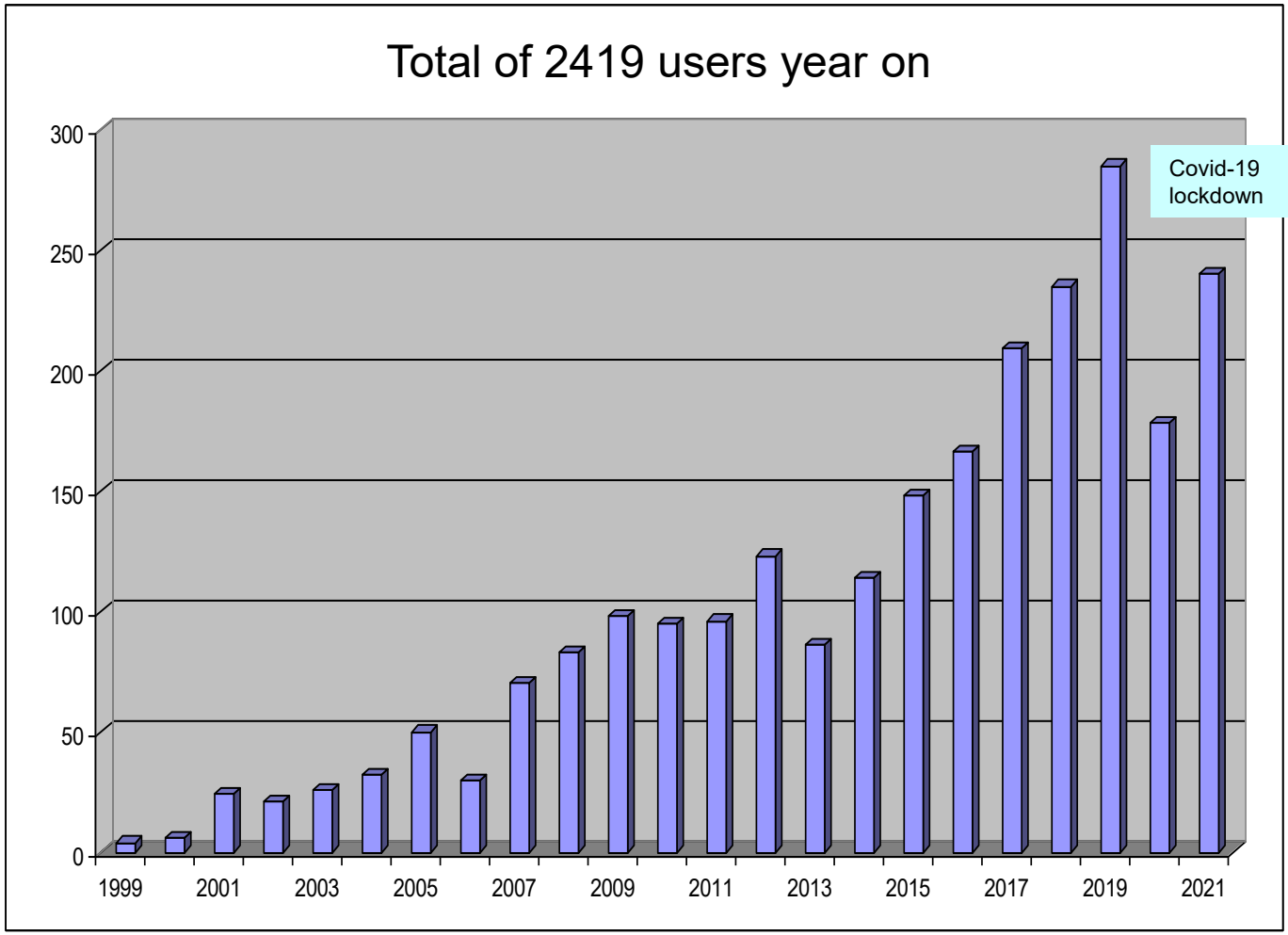
Determine phases (compounds) in specimen

Get information about their structure, cristallinity …

Provide **technical** and **scientific** support to user community

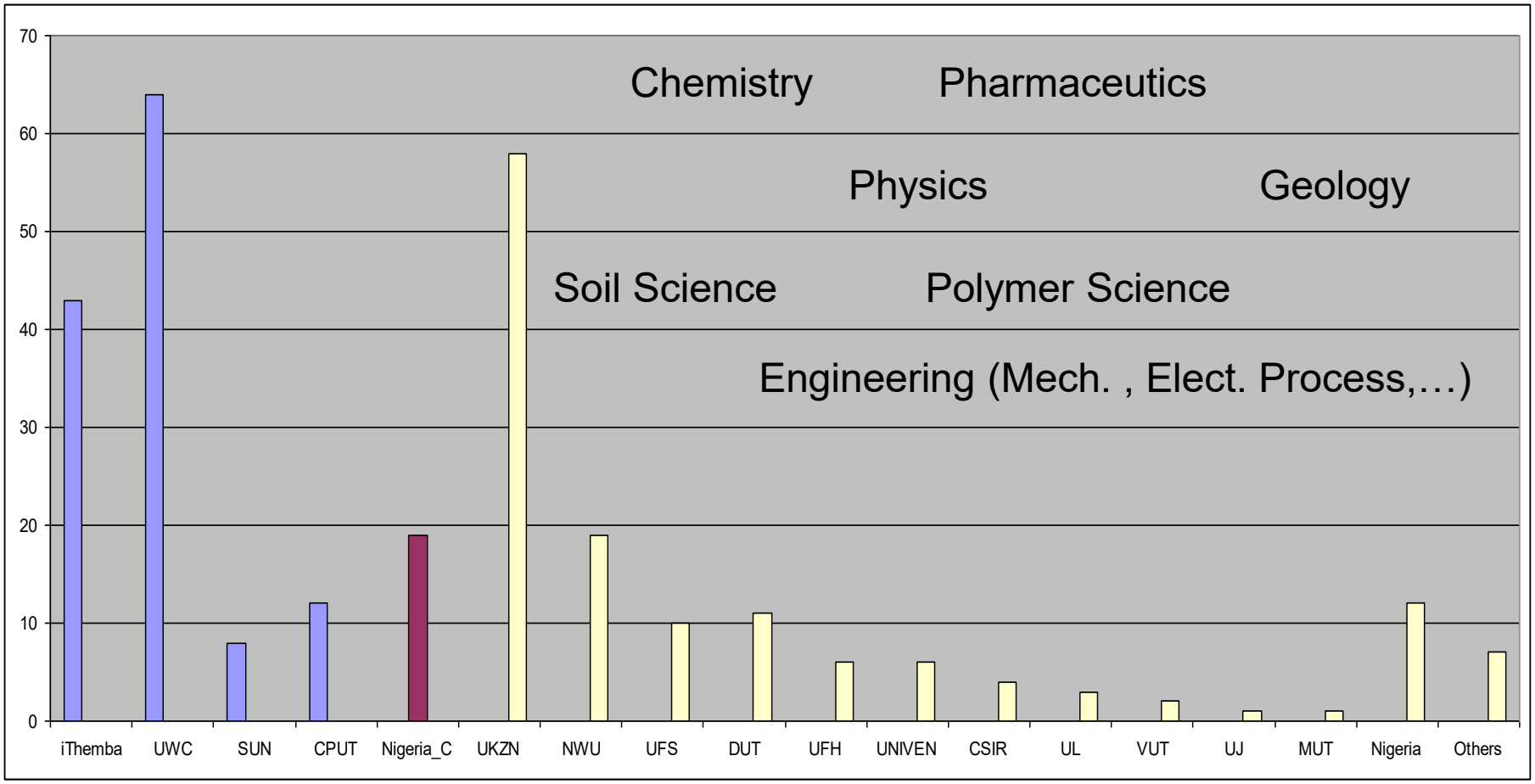
- Training on equipment
- Analysis of samples
- Discussion of results in the context of research projects

The XRD Lab over the past 22 years



1358 different users over the 22 years period

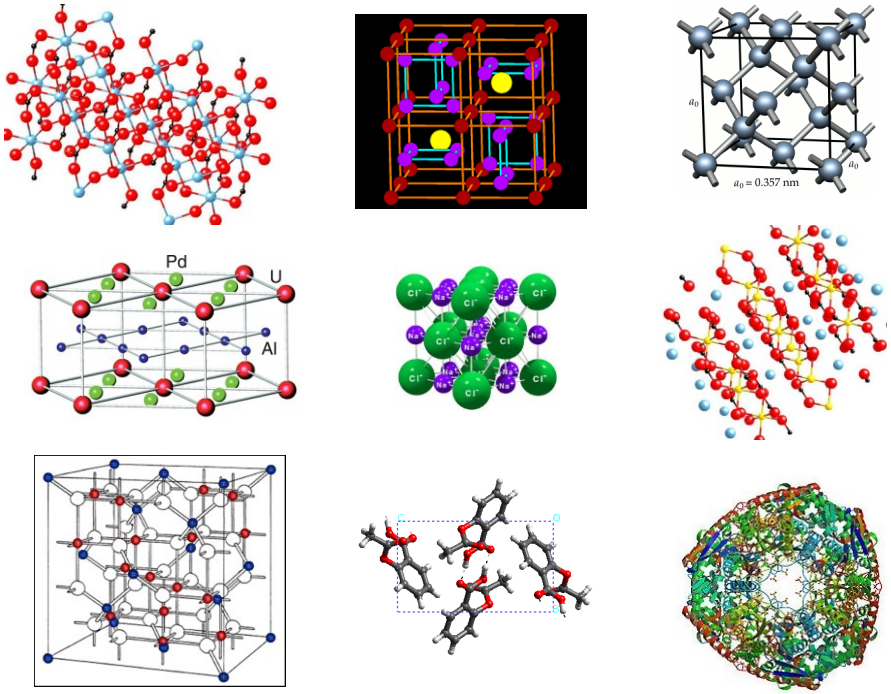
2019: **285 users** with **4800 samples** analysed



Others: FUT, MUT, NMU, UJ, UL, UNIZUL,UP, VUT, Wits, …

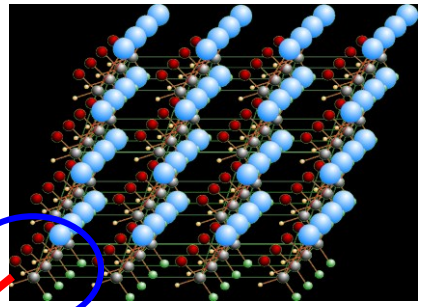
Crystal structure

Complicated … well over half a million structures known so far.

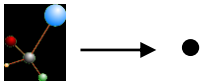


We need to simplify …

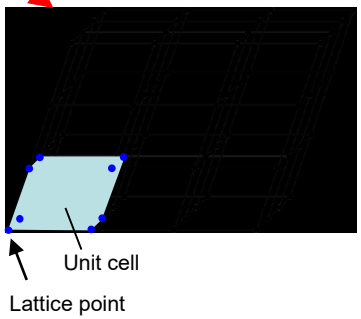
The backbone of crystal structures



Basis : smallest possible cluster of atoms that is repeated periodically in space



Loss of chemical information



Unit cell : translated block of the crystal structure

7 Crystal classes

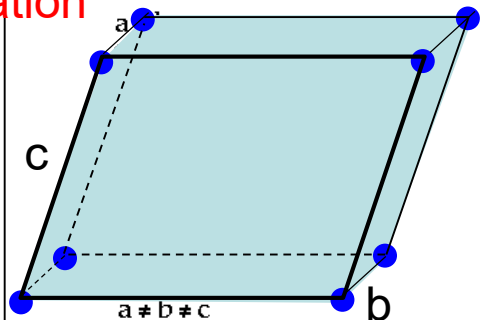
14 different Point lattices

Point lattice

CUBIC
$a = b = c$
$\alpha = \beta = \gamma = 90°$

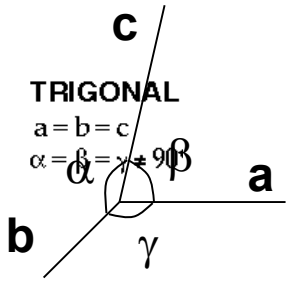
TETRAGONAL
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

ORTHORHOMBIC



$a \neq b \neq c$
$\alpha = \gamma = 90°$
$\beta \neq 120°$

TRIGONAL
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$

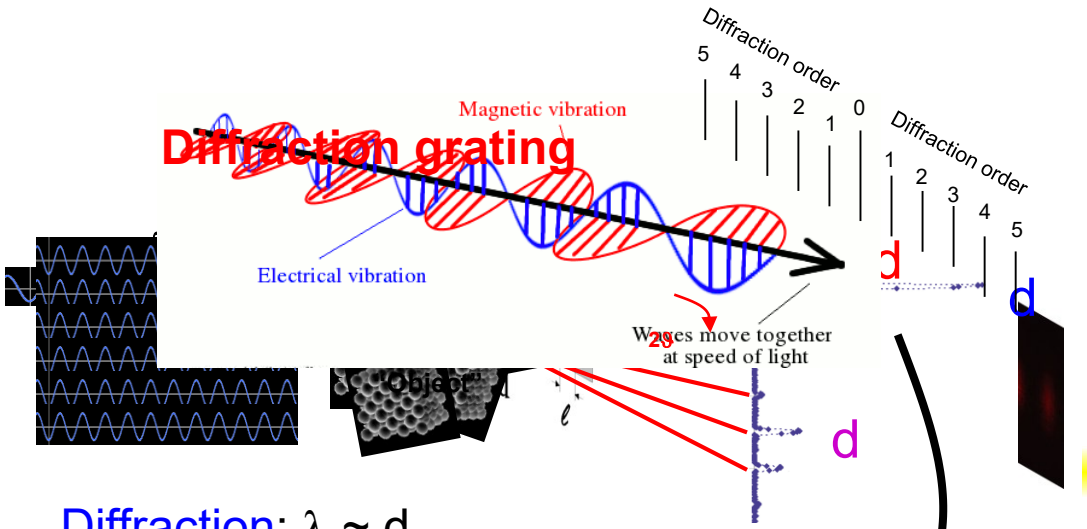


TRICLINIC
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

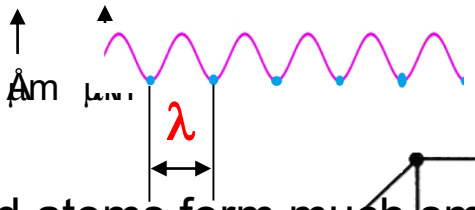
a,b,c, α,β,γ : **lattice constants**

The electromagnetic spectrum

X-ray Diffraction is the study of the crystalline structure of point lattice



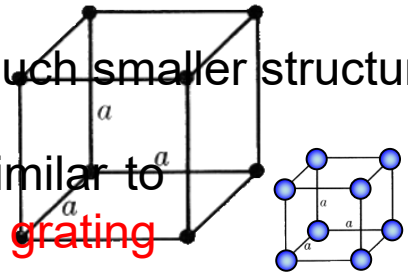
Diffraction: $\lambda \sim d$



Crystallized atoms form much smaller structures

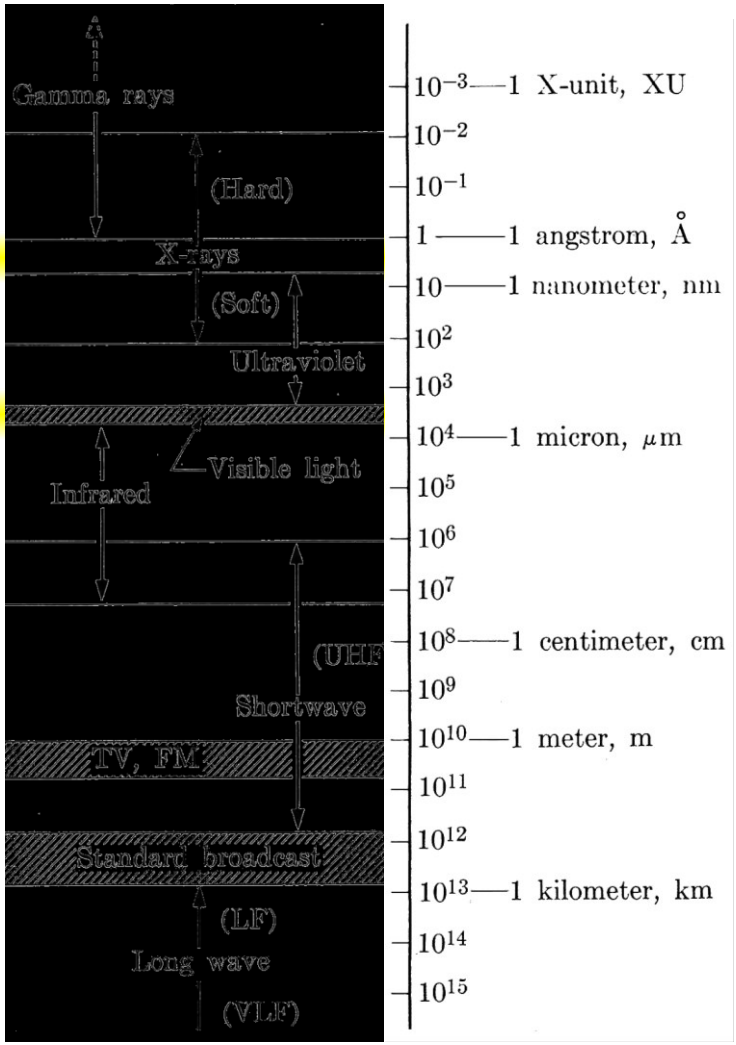
Structural "Fingerprint"

Lattice constant a similar to an atomic diffraction grating



Relation between peaks "d" and the point lattice

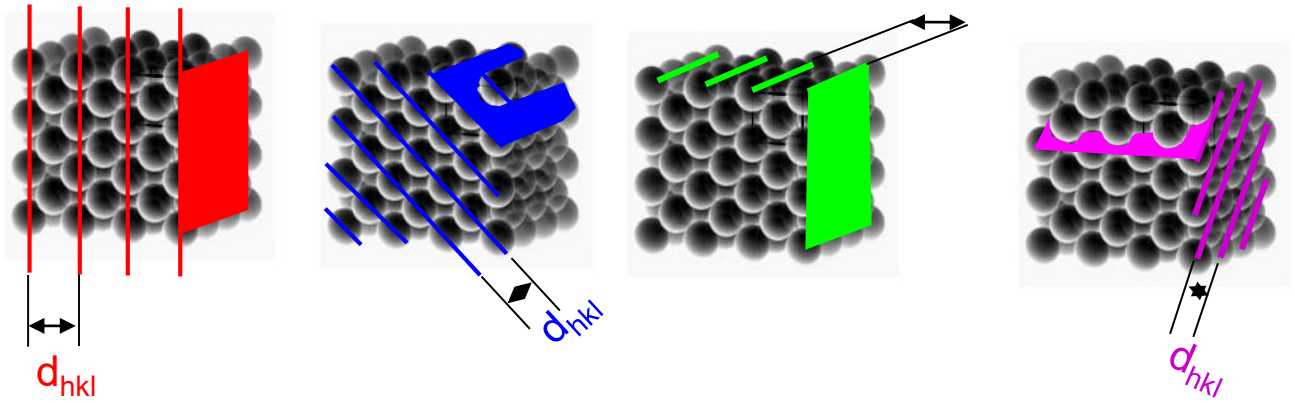
Wavelength [1Å = 10^{-10}m]



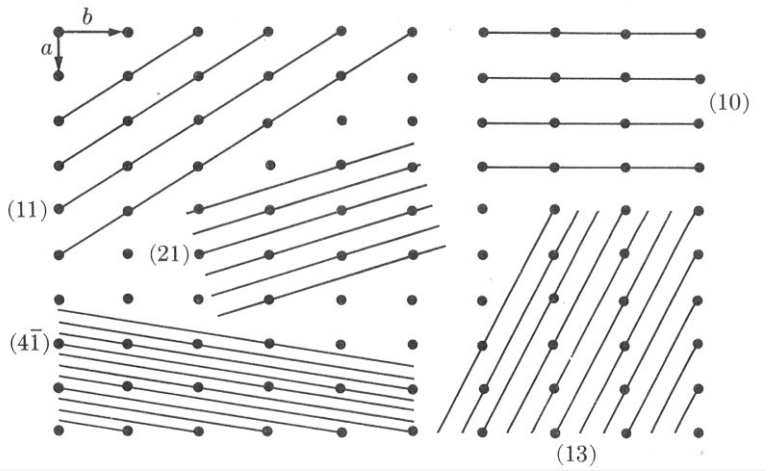
Concept of **sets of parallel planes** (diffraction gratings)

They describe the periodicity of point lattices

3D crystals



2D crystals

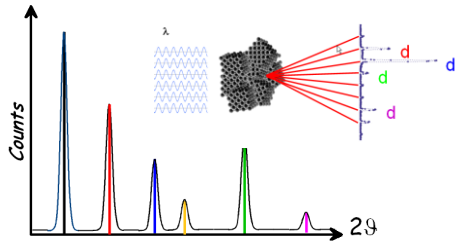


$$\text{point lattice} = \{ d_{hkl} \mid h,k,l \in \square \}$$

Cubic:

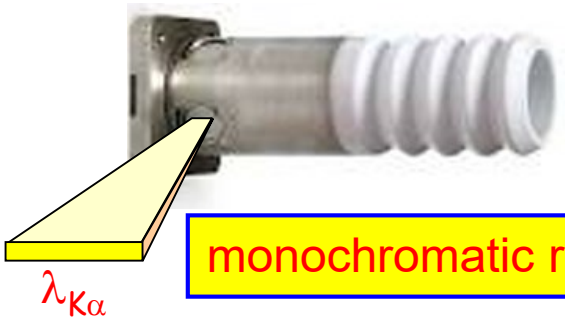
$d_{100} > d_{110} > d_{111} > d_{200} > d_{210}$ ....

Structural fingerprint of the point lattice



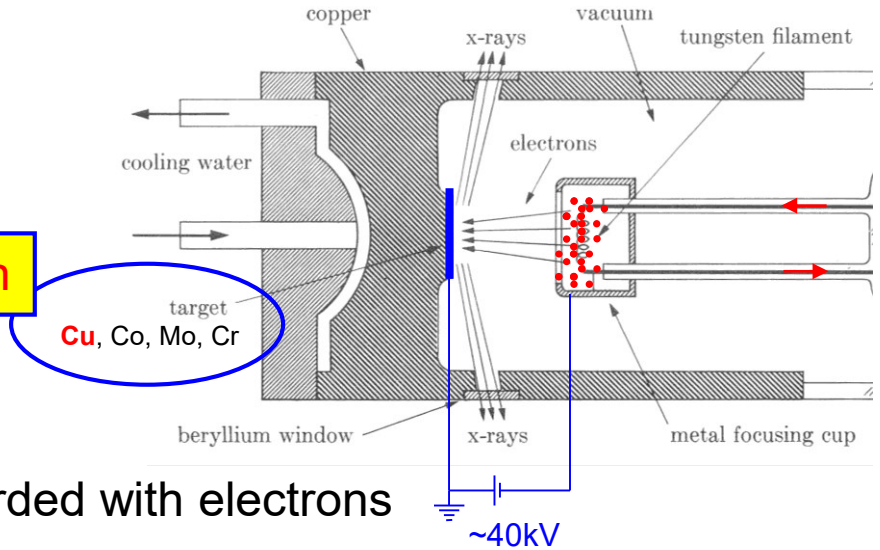
⇨ We need X-rays

Generation of X-rays



$\lambda_{K\alpha}$

monochromatic radiation

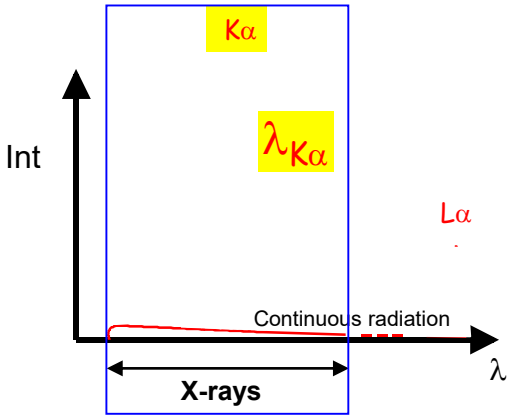


Target: produces X-rays when bombarded with electrons

$$E_{el.}^{pot} = eU = E_{el.}^{kin} = \gamma\left(m - m_0\right)c^2$$

eU > threshold value for ionization energy

Characteristic radiation

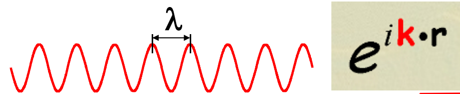


XRD: only strongest Kα line wanted (wavelength $\lambda_{K\alpha}$)

⇨ filter out Kβ

Bragg's law

- **Monochromatic** radiation: Cu-Kα_1



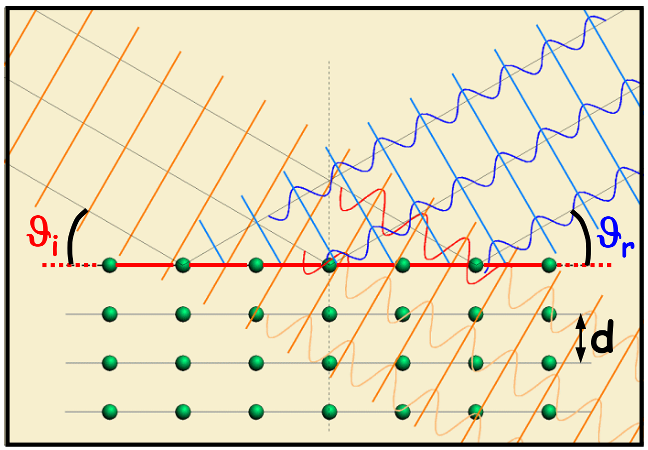
- **Single crystal** (1 grain of polycrystalline sample)

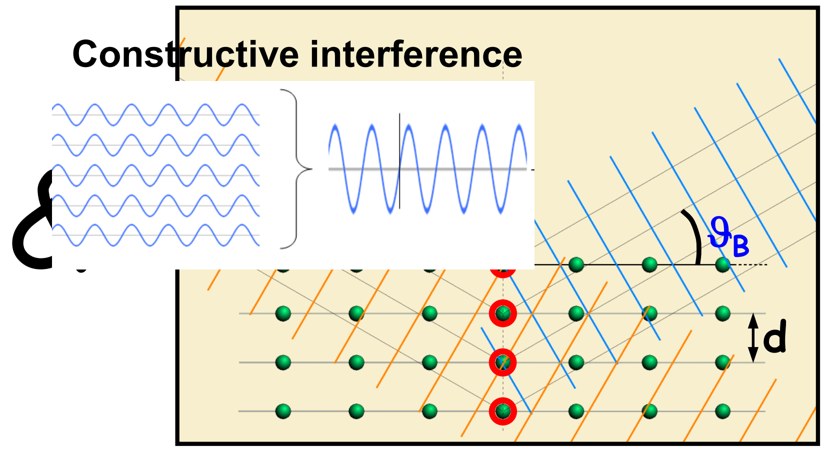
Specular reflection

Incident angle = reflected angle

Bragg angle ϑ_B

$\vartheta_i = \vartheta_r = \vartheta_B$





- For constructive interference for all atoms within the same plane
- For given λ and d
- But not between different planes: f(λ,d,ϑ)

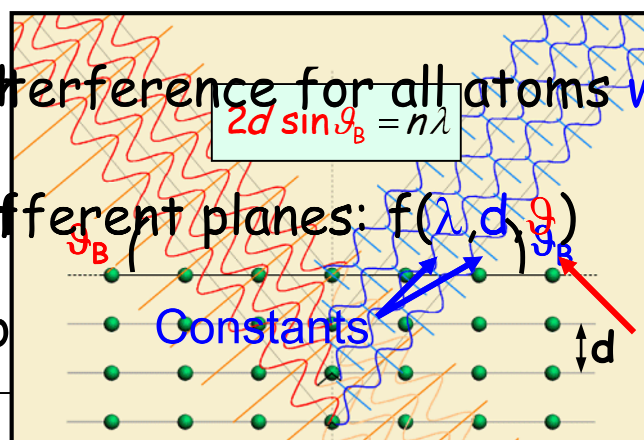
↳ Constructive interference different planes

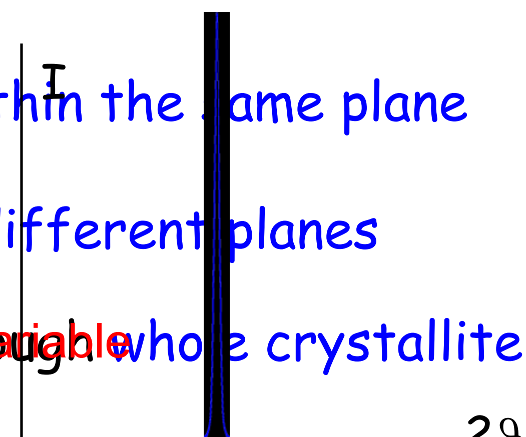
↳ Constructive interference through whole crystallite

$$2d\sin\vartheta_B = n\lambda$$

Constants

Variable





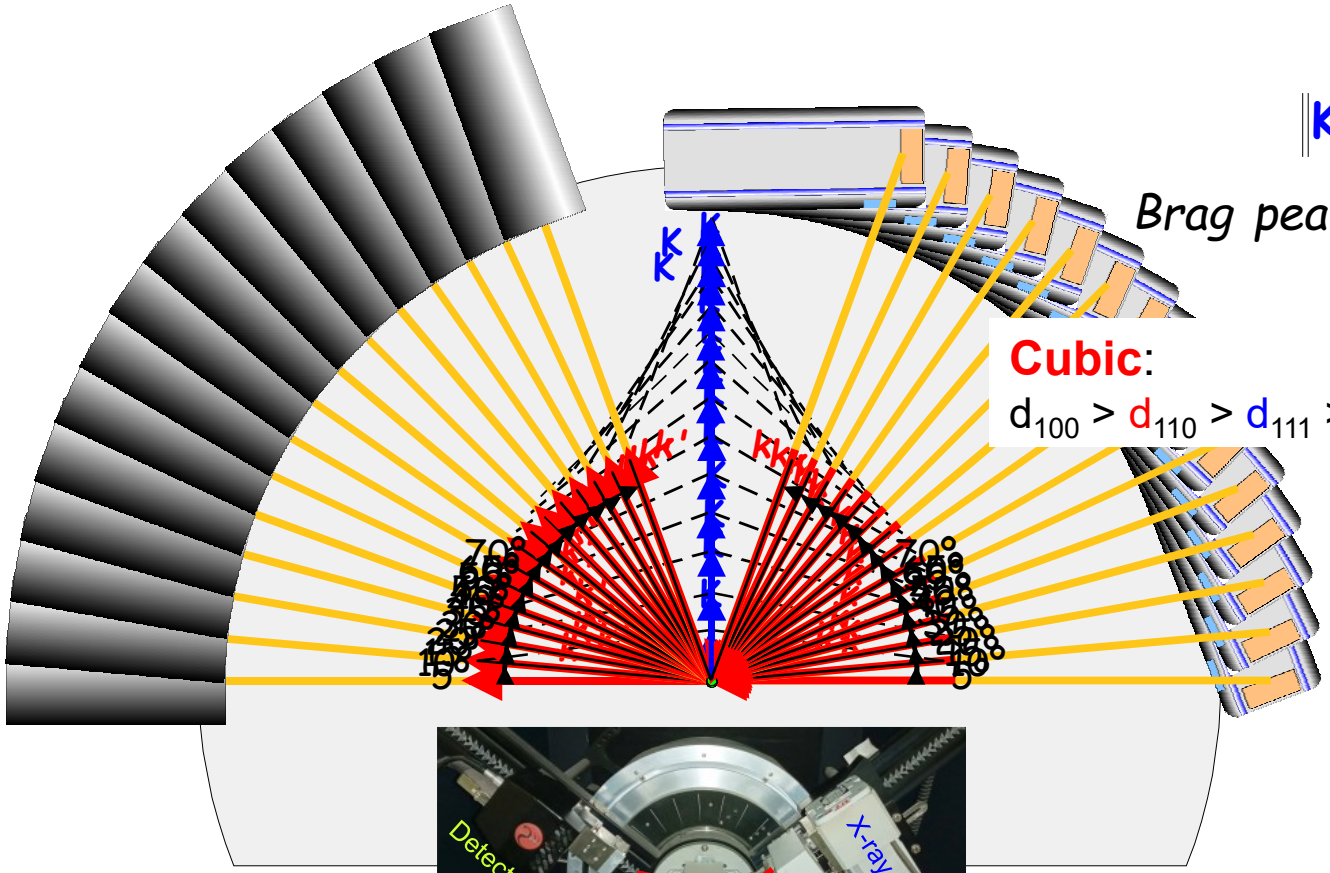
The XRD Diffractometer

Monochromatic radiation: Kα

Elastic scattering process $|\mathbf{k}| = |\mathbf{k}'| = \frac{2\pi}{\lambda_{K\alpha}}$

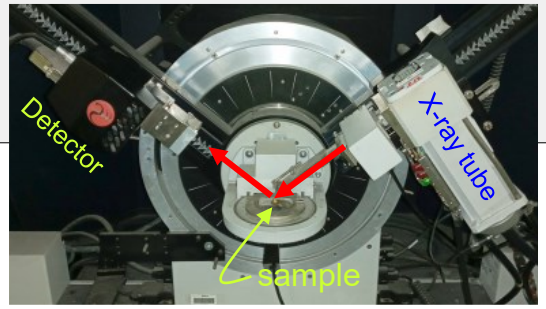
$|\mathbf{K}| = \frac{2\pi}{D}$

Brag peaks for $D = d_{hkl}$



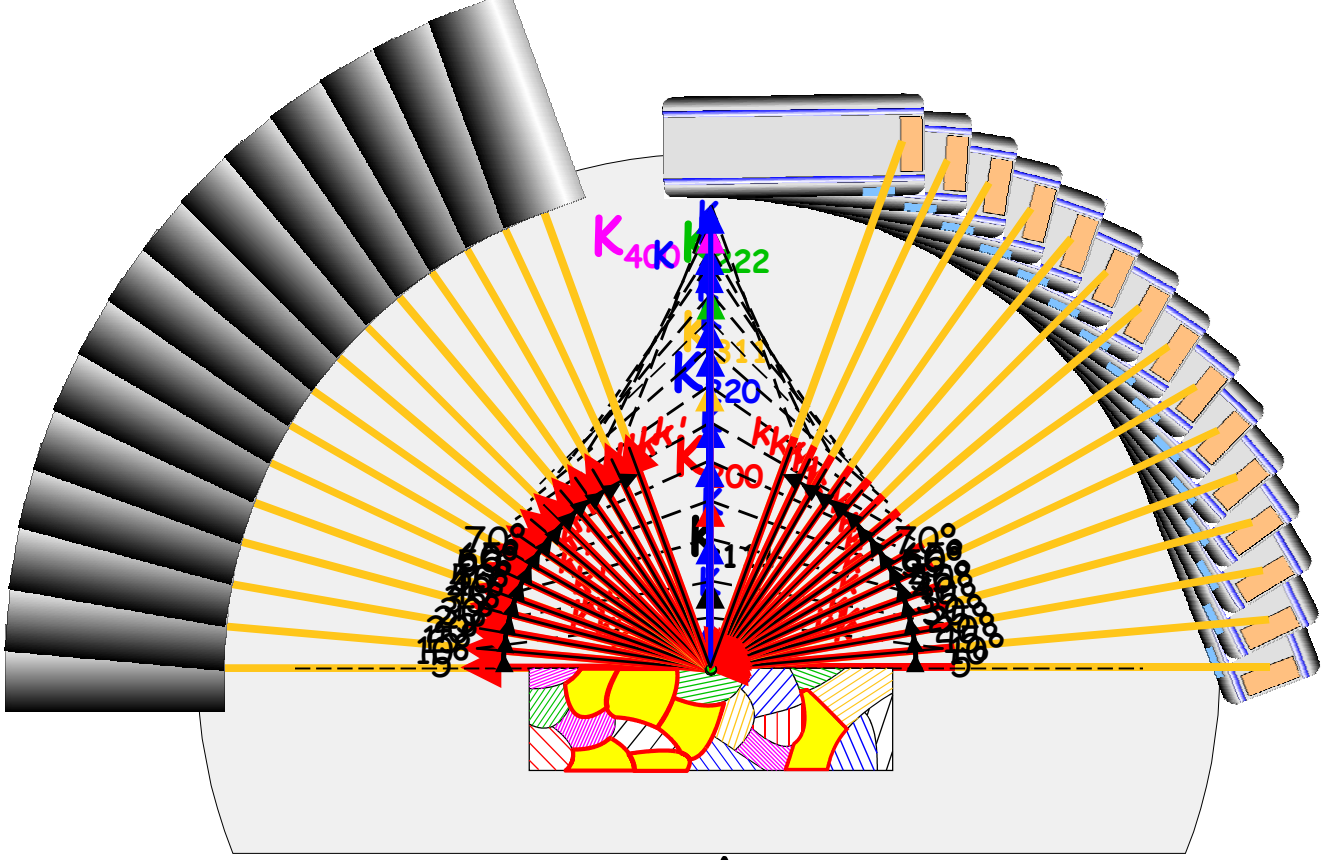
Cubic:

$d_{100} > d_{110} > d_{111} > d_{200} > d_{210}$ ....



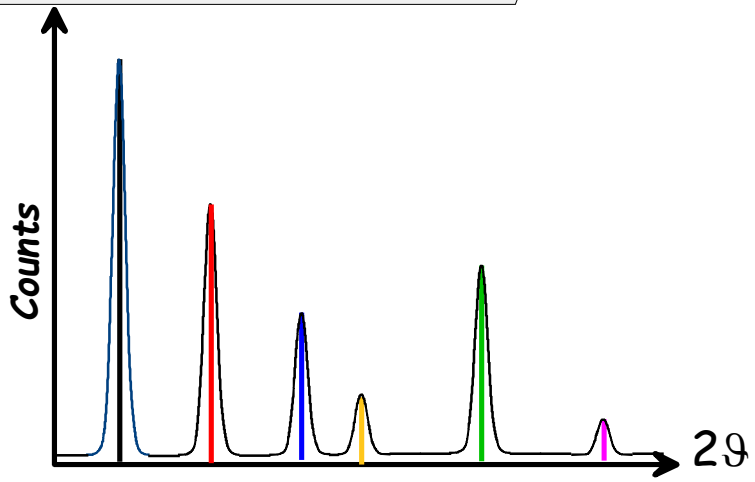
$\mathbf{K}$ = Scattering vector = $\mathbf{k}' - \mathbf{k}$

$|\mathbf{K}| = 0 \rightarrow \max$

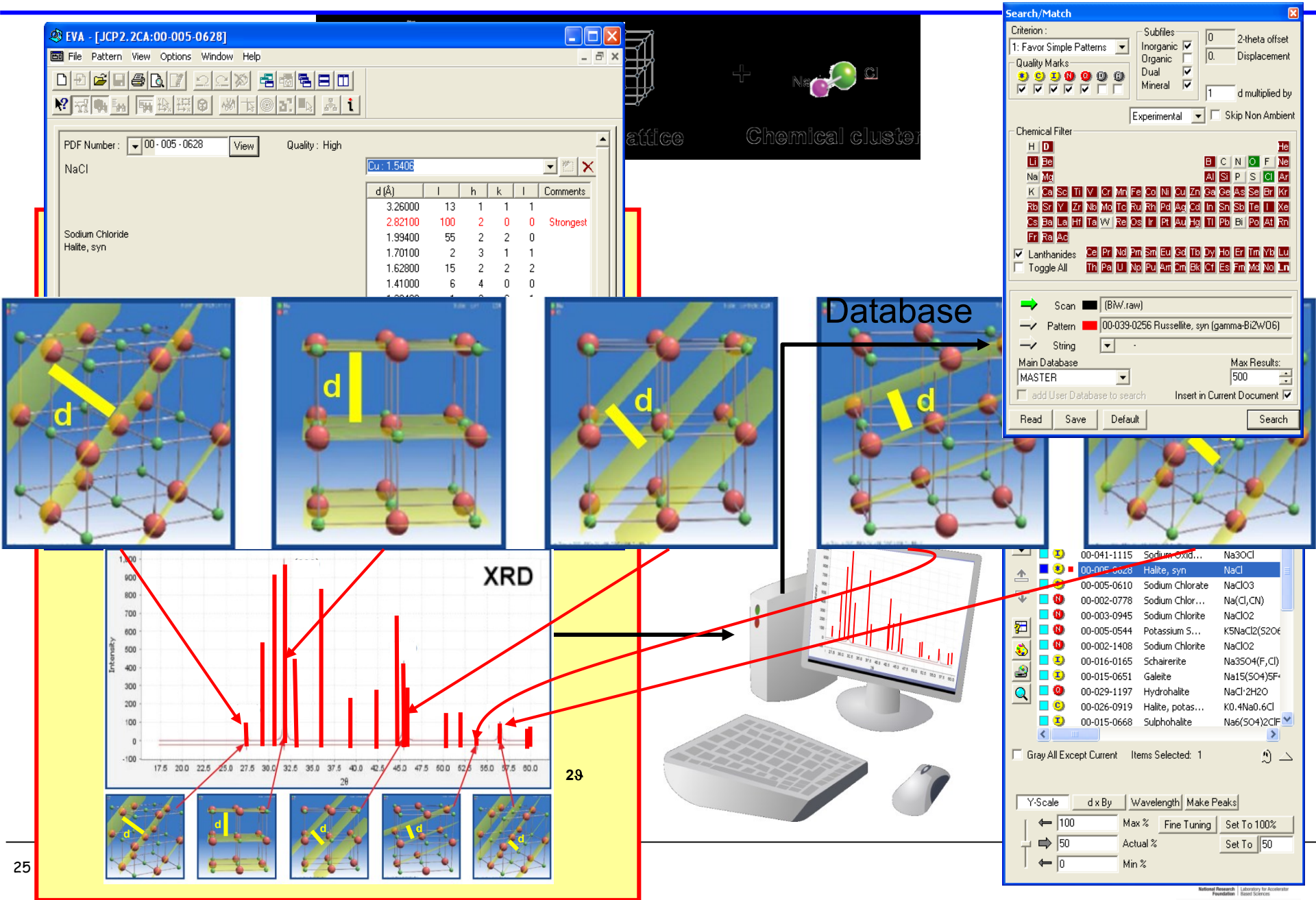


Polycrystalline sample

- Very small grains ~ 2-10 μm
- Random oriented



Analysis procedure

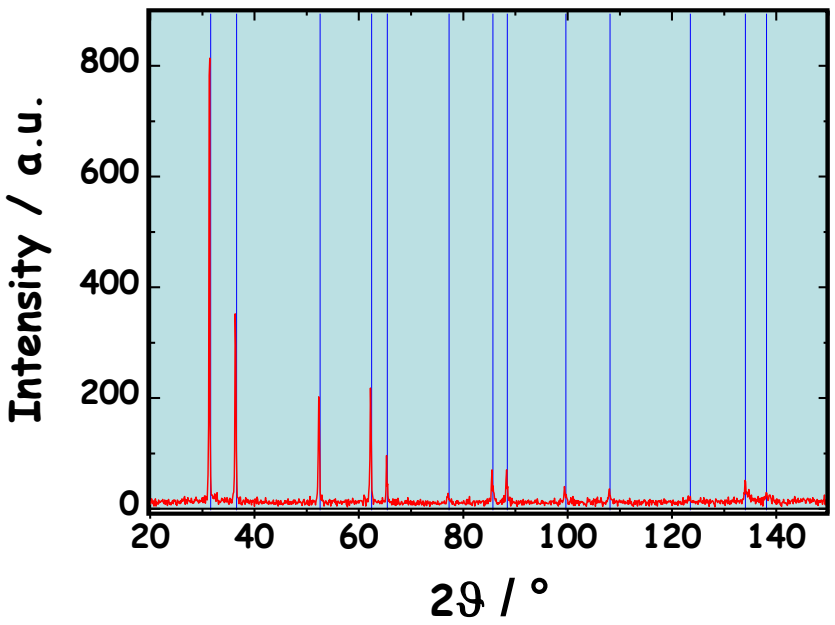


Some examples

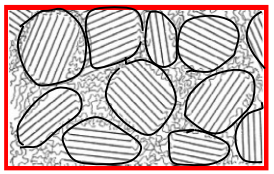
Metals:

Lead (Pb)

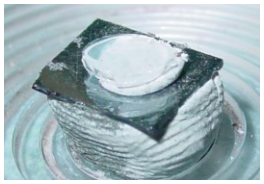
a = b = c = 8.54 Å (fcc)



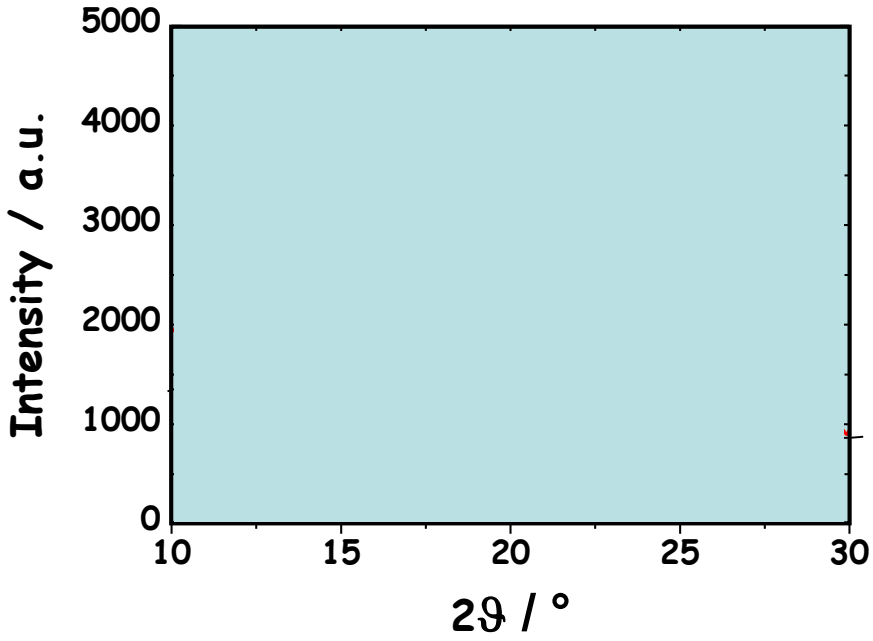
Polymers:



Polypropylene

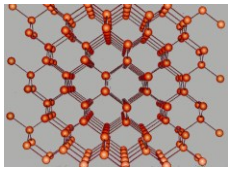


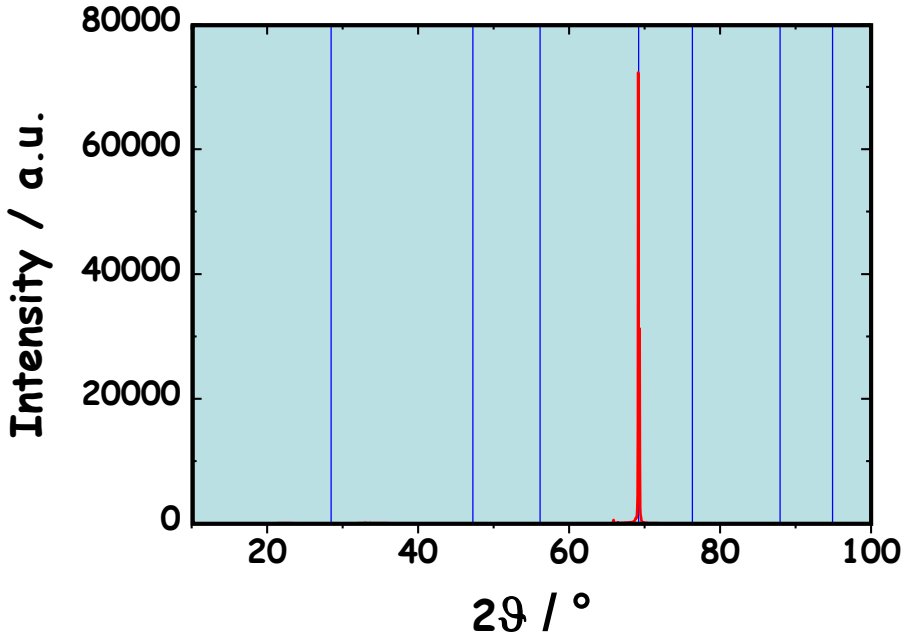
a = 8.54 Å b = 9.93 Å c = 42.41 Å



Single crystal:

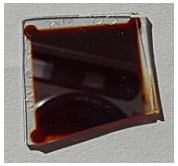
<100> Silicon wafer

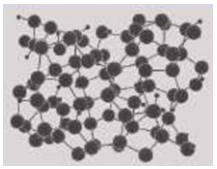




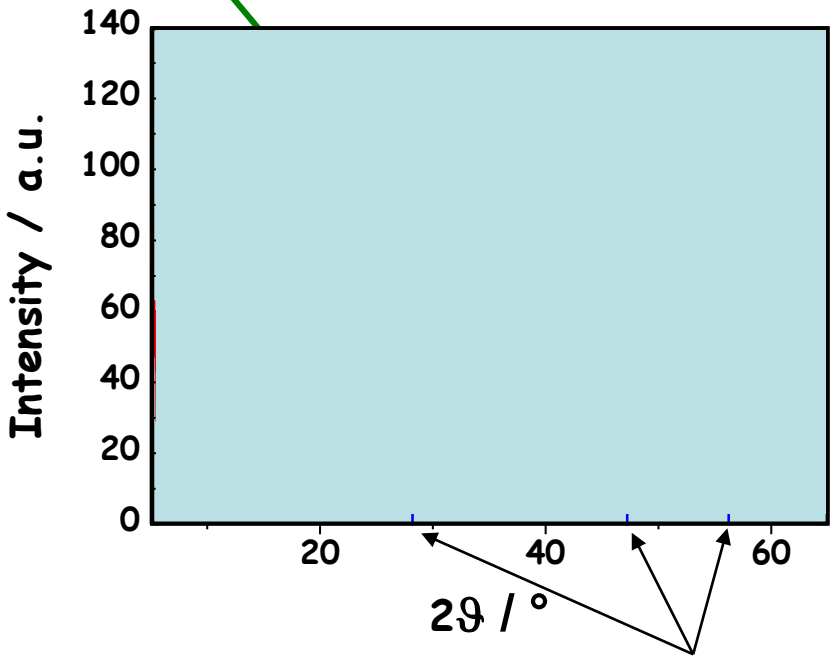
Amorphous material:

α-Silicon on amorphous glass





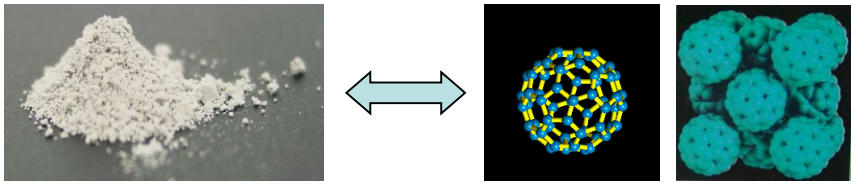
Diffuse maxima:
short-range order of nearest neighbors



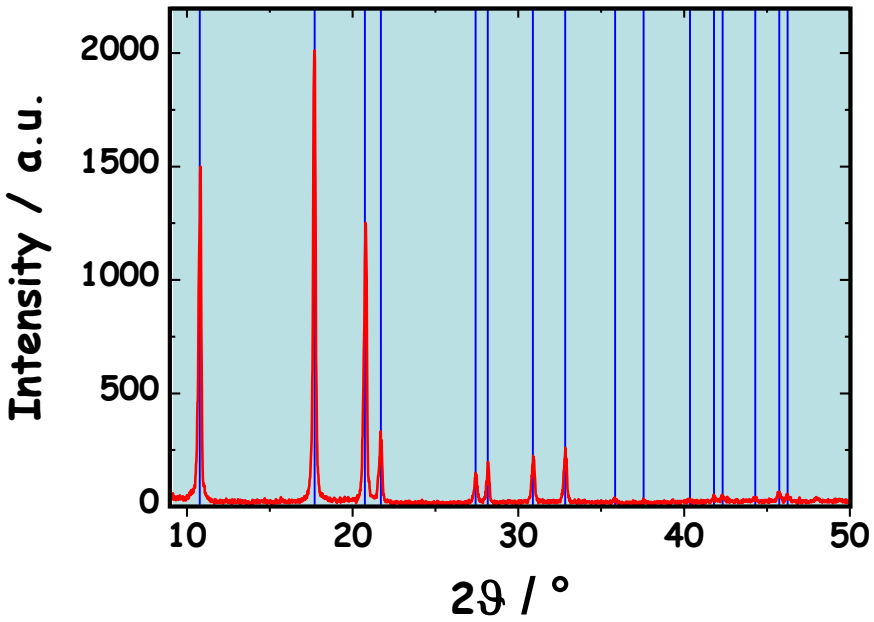
Annealing: phase transition to **polycrystalline** Si

Nanostructures:

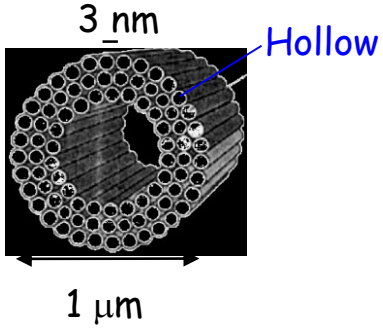
C60 - Buckminsterfullerene

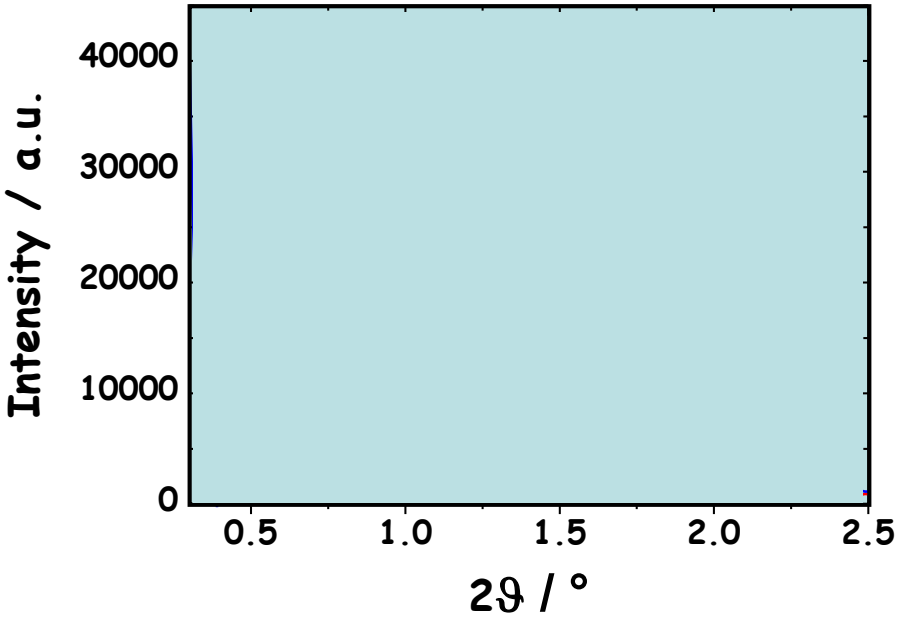


fcc



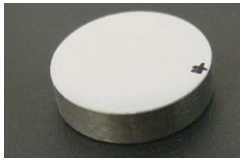
Fuel cells - mesoporous silica

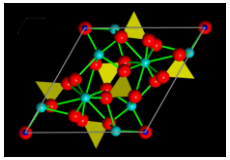




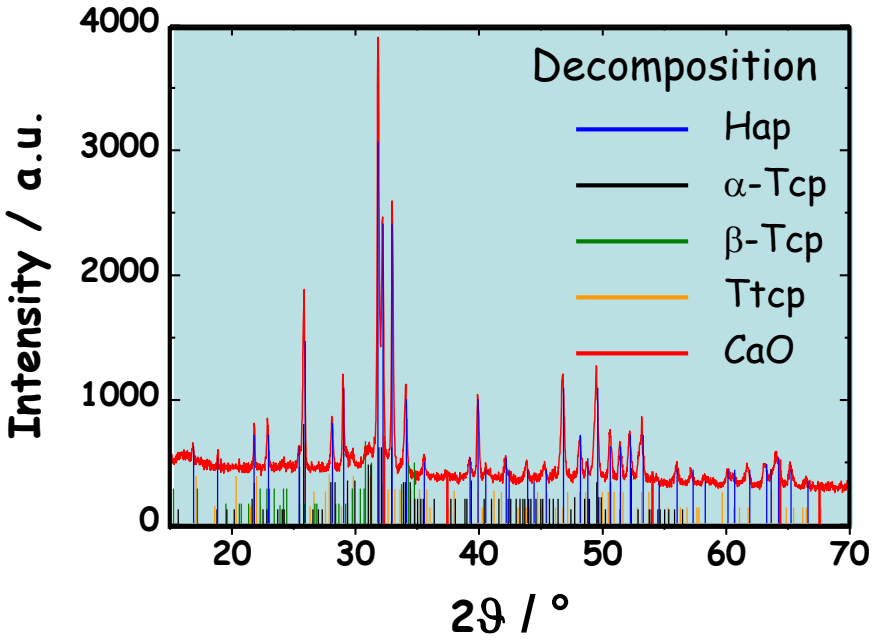
Multiphase compounds:

Hap Bio-coating





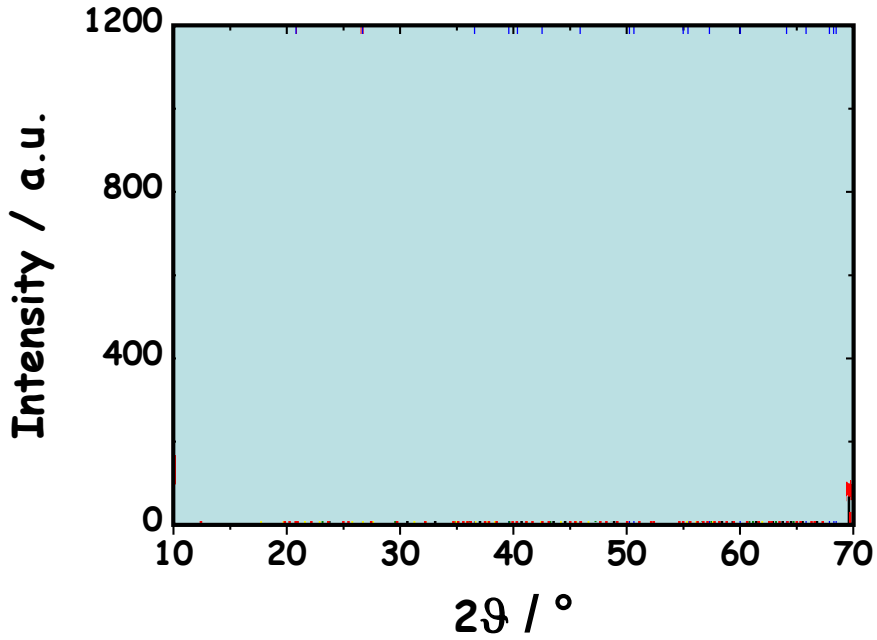
$Ca_{10}(PO_4)_6(OH)_2$



Geology

Core sample, bore hole EAA1

Bredasdorp, offshore RSA



XRD not limited to qualitative phase analysis

… X-ray optics dependent