

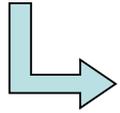
Basics of X-ray Diffraction

Dr. R. Bucher

What we do

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

Qualitative X-ray Diffraction



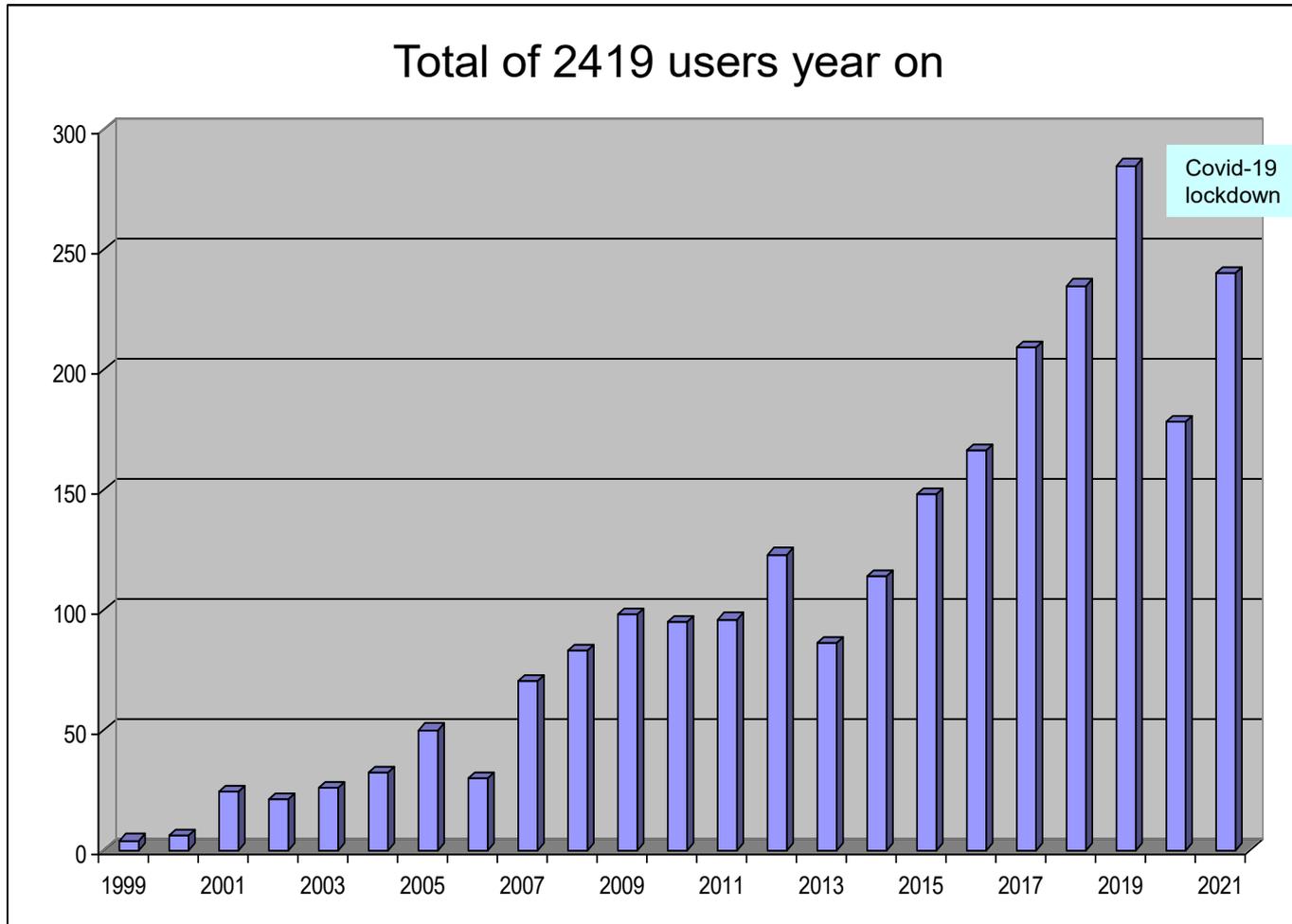
Determine phases (compounds) in specimen

Get information about their structure, cristallinity ...

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

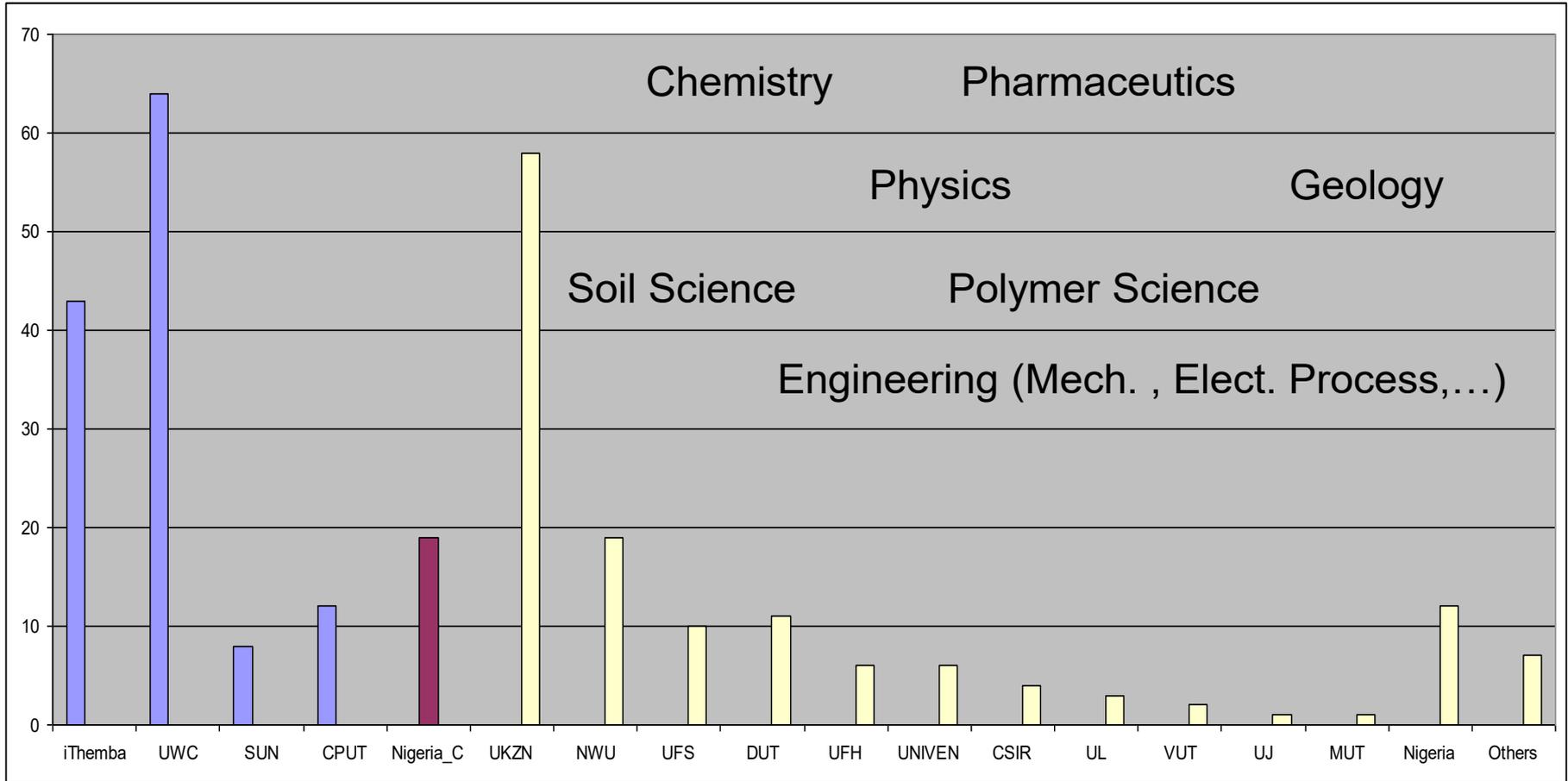
- Training on equipment
- Analysis of samples
- Discussion of results in the context of research projects

The XRD Lab over the past 22 years



1358 different users over the 22 years period

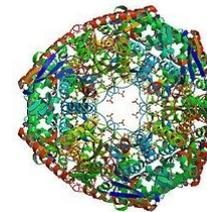
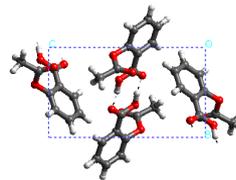
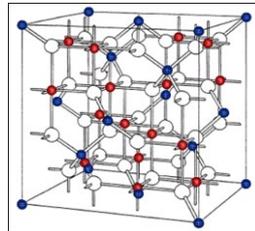
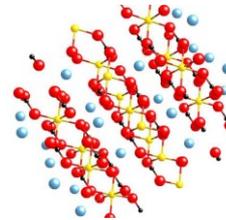
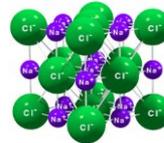
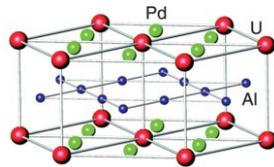
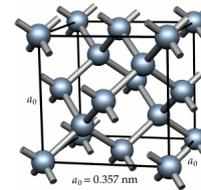
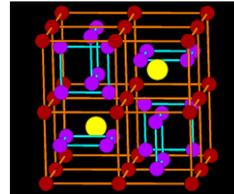
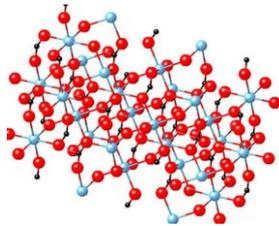
2019: **285 users** with **4800 samples** analysed



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

Crystal structure

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

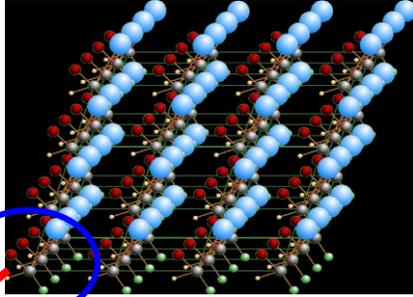


We need to simplify ...

The backbone of crystal structures

7 Crystal classes

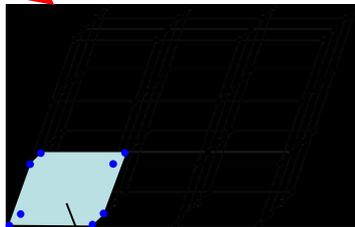
14 different Point lattices



Basis : smallest possible cluster **Unit cell** translated block of the crystal structure



Loss of chemical information



Unit cell
Lattice point

Point lattice

CUBIC

$$a = b = c$$

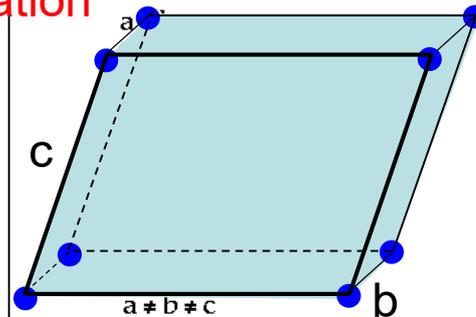
$$\alpha = \beta = \gamma = 90^\circ$$

TETRAGONAL

$$a = b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

ORTHORHOMBIC



$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

TRICLINIC

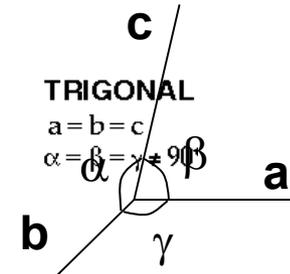
$$a \neq b \neq c$$

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$

TRIGONAL

$$a = b = c$$

$$\alpha = \beta = \gamma \neq 90^\circ$$

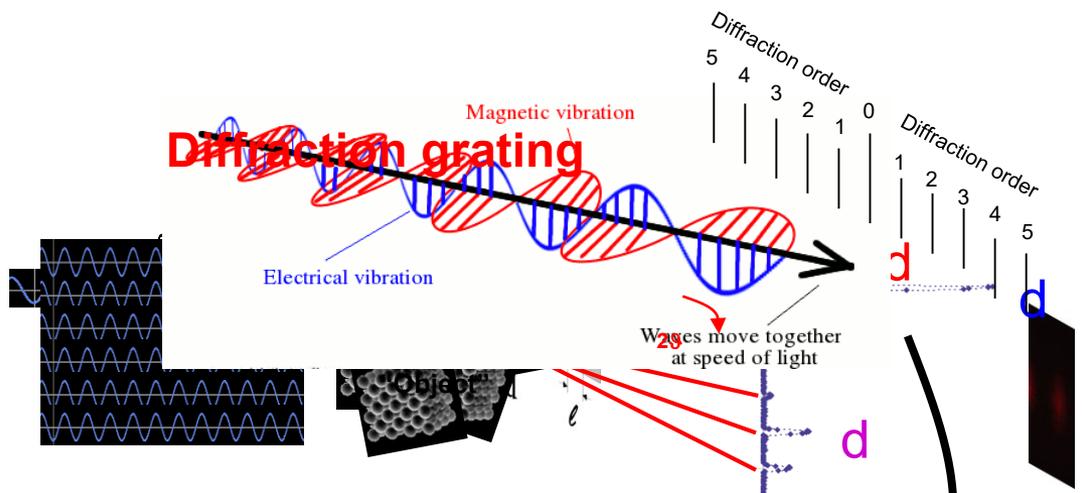


$a, b, c, \alpha, \beta, \gamma$: **lattice constants**

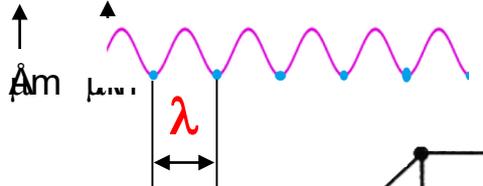
The electromagnetic spectrum

Diffraction is the light structure of point lattice

Wavelength
[1Å = 10⁻¹⁰m]



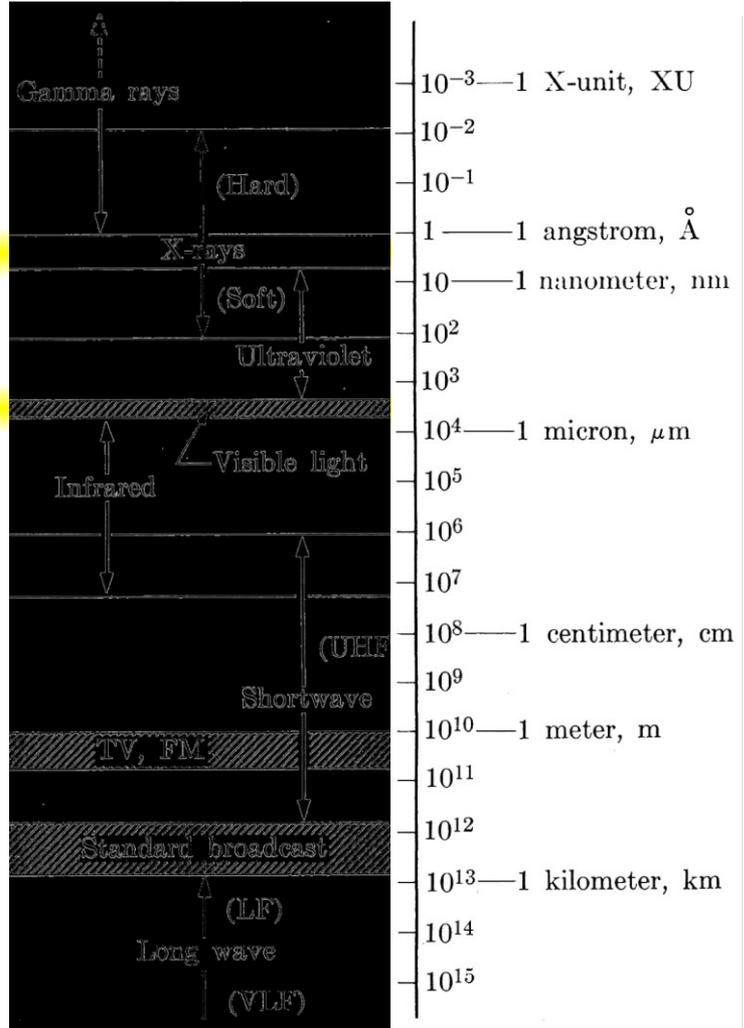
Diffraction: $\lambda \sim d$



Crystallized atoms form much smaller structures

Structural "Fingerprint" Lattice constant a similar to an atomic diffraction grating

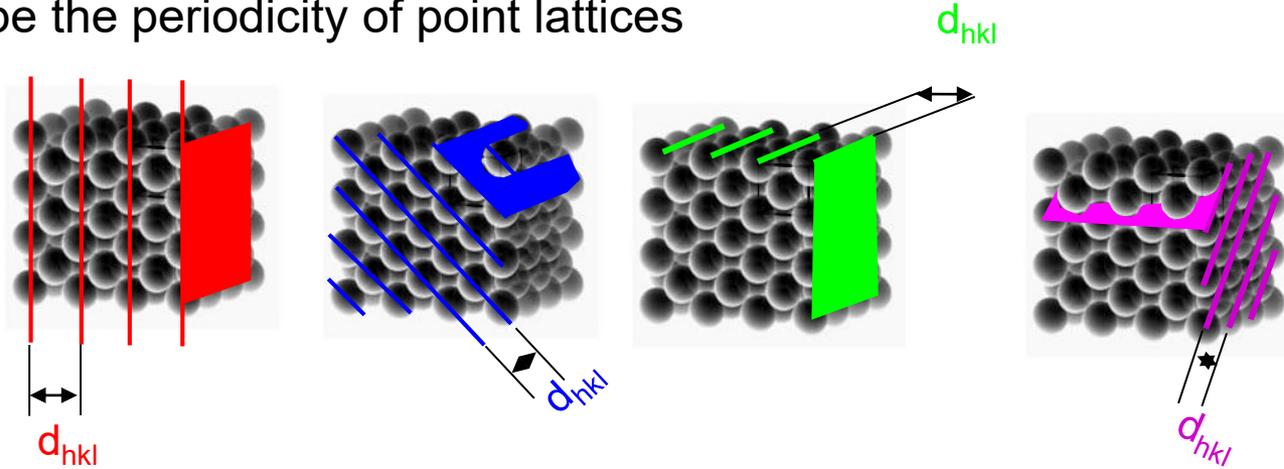
Relation between peaks d and the crystal lattice



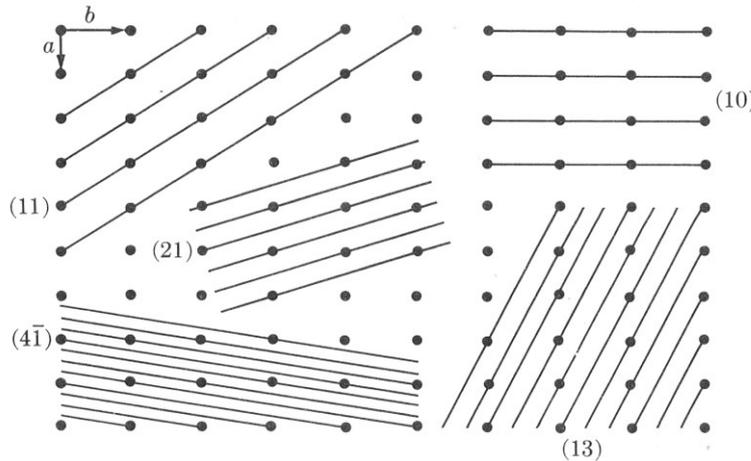
Concept of **sets of parallel planes** (diffraction gratings)

They describe the periodicity of point lattices

3D crystals



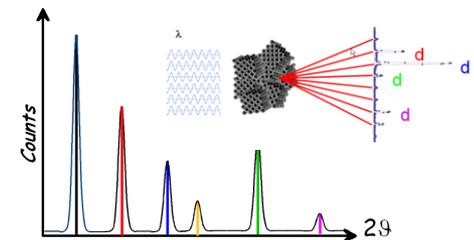
2D crystals



Cubic:

$$d_{100} > d_{110} > d_{111} > d_{200} > d_{210} \dots$$

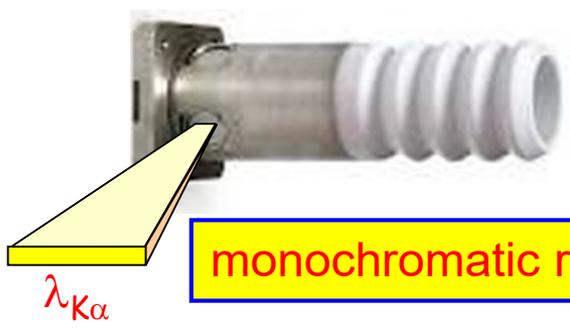
Structural fingerprint of the point lattice



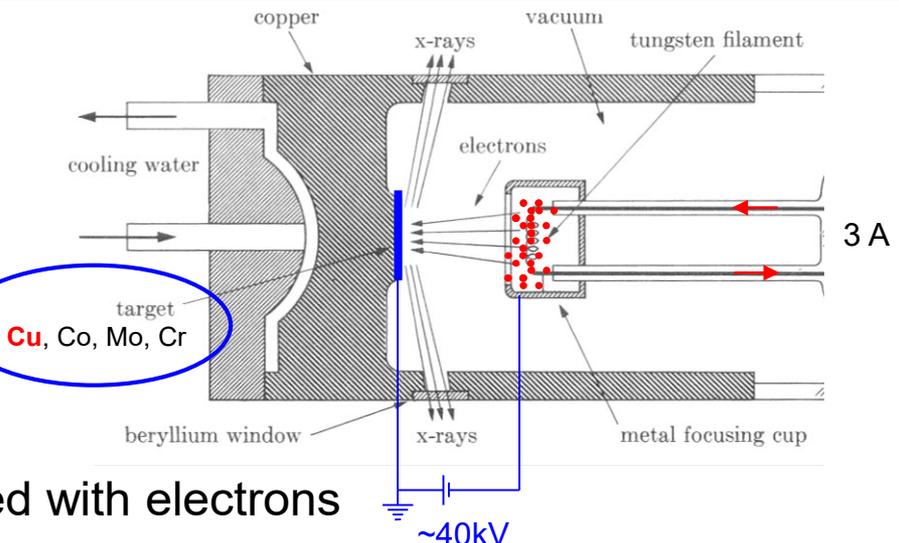
➡ We need X-rays

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

Generation of X-rays



monochromatic radiation



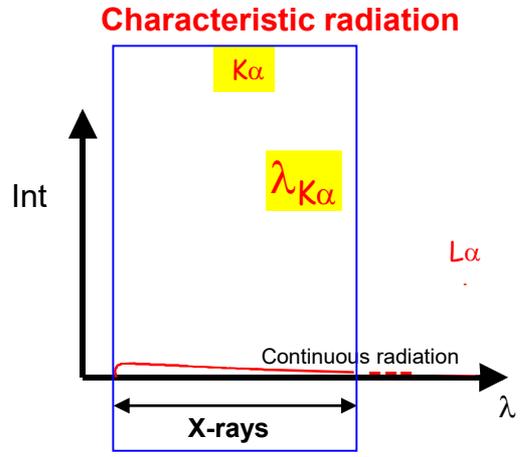
Target: produces X-rays when bombarded with electrons

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

eU ~~is the~~ ~~horizontal~~ ~~line~~ ~~energy~~

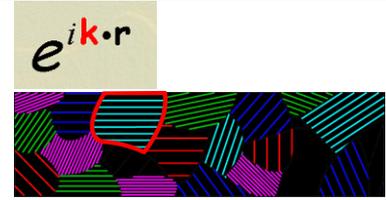
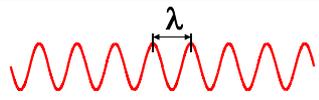
XRD: only strongest $K\alpha$ line wanted (wavelength $\lambda_{K\alpha}$)

→ filter out $K\beta$



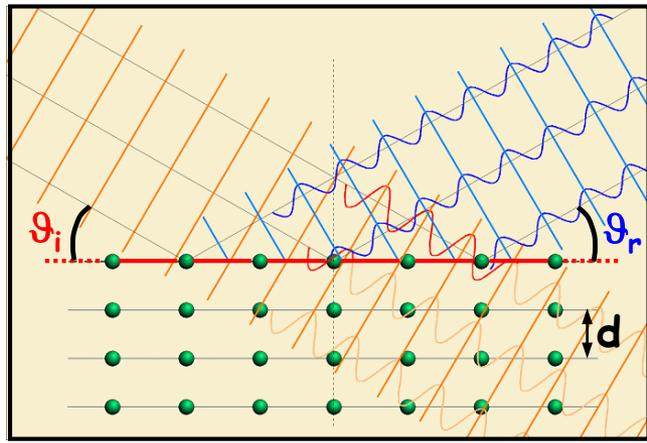
Bragg's law

- Monochromatic radiation: Cu-K α_1
- Single crystal (1 grain of polycrystalline sample)



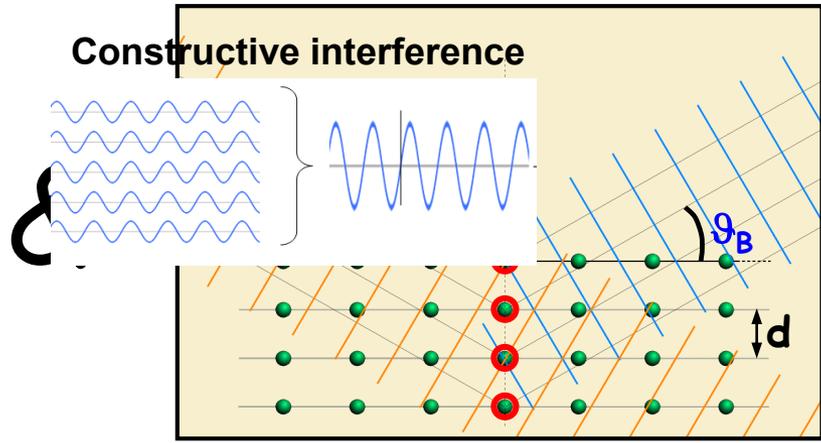
Specular reflection

Incident angle = reflected angle



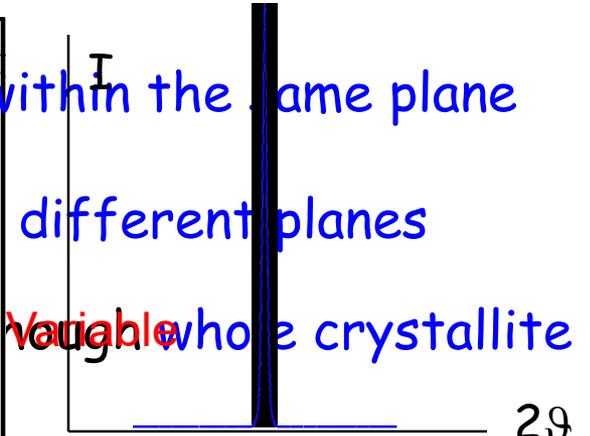
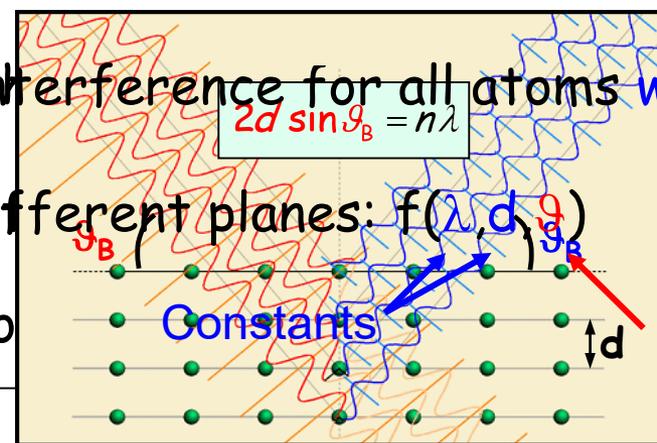
Bragg angle ϑ_B

$$\vartheta_i = \vartheta_r = \vartheta_B$$



➤ For given λ and d interference for all atoms within the same plane

➤ But **not** for different planes: $f(\lambda, d, \vartheta_B)$



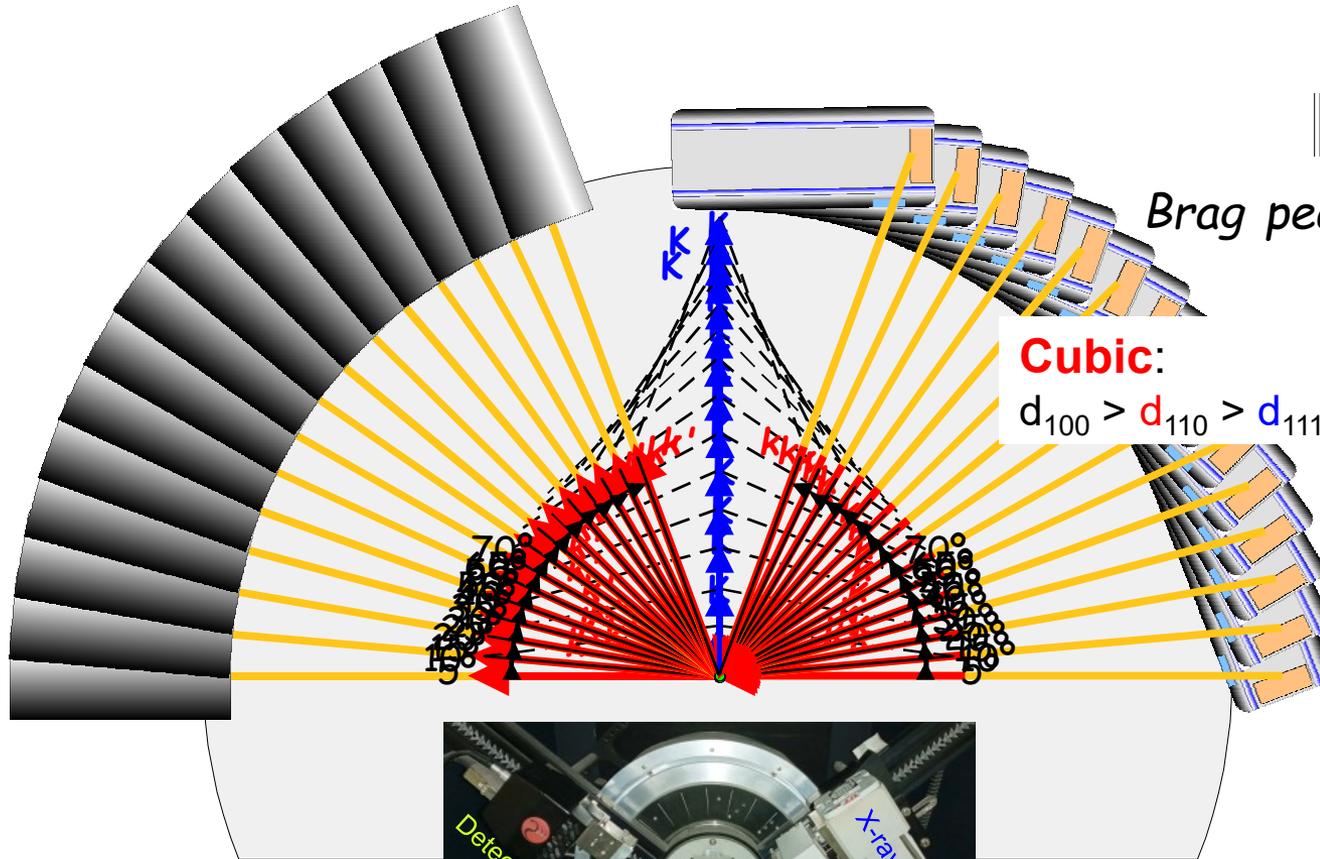
The XRD Diffractometer

Monochromatic radiation: $K\alpha$

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

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

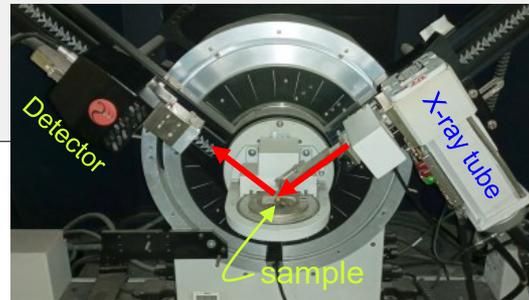
Bragg peaks for $D = d_{hkl}$



Cubic:

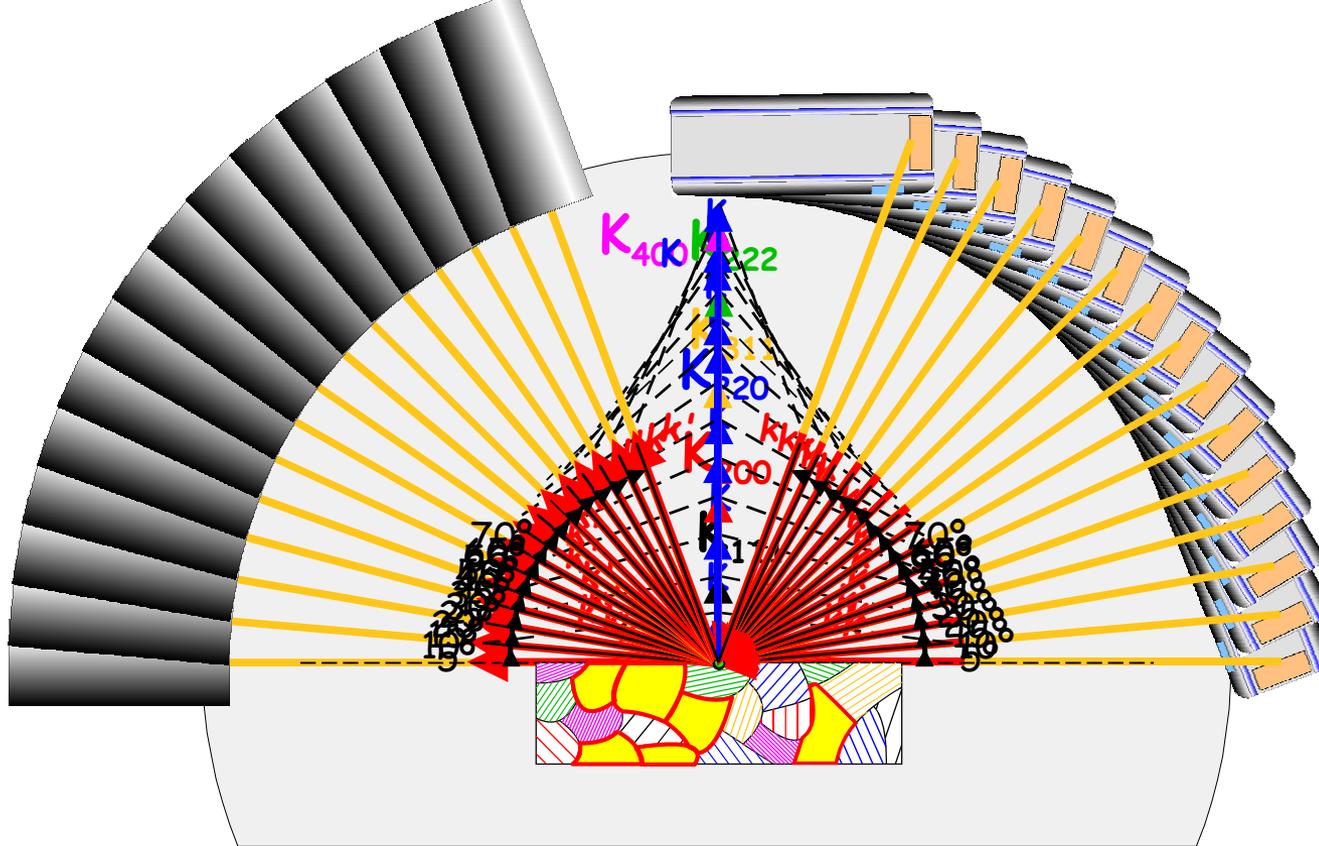
$$d_{100} > d_{110} > d_{111} > d_{200} > d_{210} \dots$$

Detector



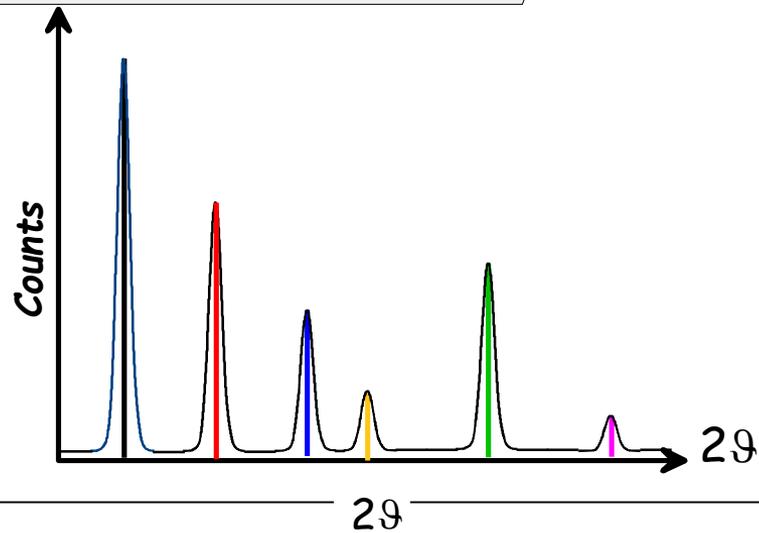
$\mathbf{K} = \text{Scattering vector} = \mathbf{k}' - \mathbf{k}$

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



Polycrystalline sample

- Very small grains $\sim 2\text{-}10\ \mu\text{m}$
- Random oriented



Analysis procedure

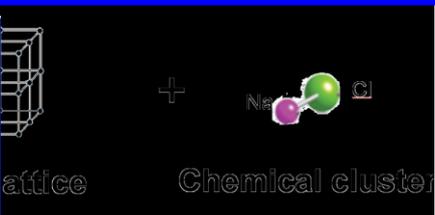
EVA - [JCP2.2CA:00-005-0628]

PDF Number: 00-005-0628 Quality: High

NaCl

Sodium Chloride
Halite, syn

d (Å)	I	h	k	l	Comments
3.26000	13	1	1	1	
2.82100	100	2	0	0	Strongest
1.99400	55	2	2	0	
1.70100	2	3	1	1	
1.62800	15	2	2	2	
1.41000	6	4	0	0	



Search/Match

Criterion: 1: Favor Simple Patterns

Quality Marks: Organic Mineral

Subfiles: 0 2-theta offset 0 Displacement 1 d multiplied by

Chemical Filter

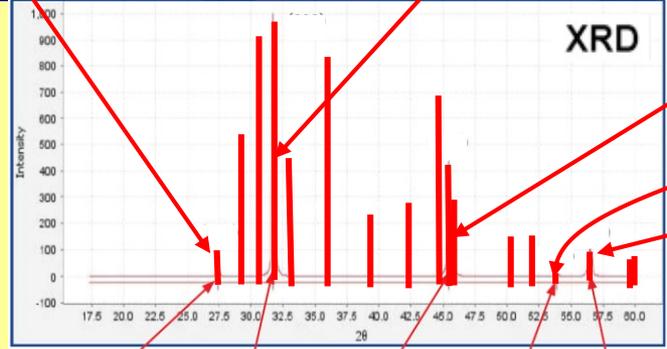
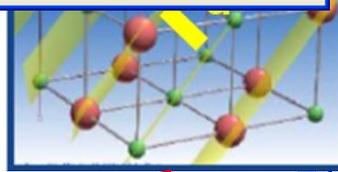
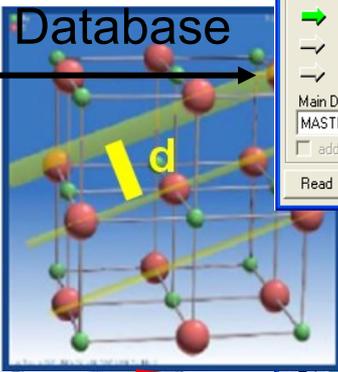
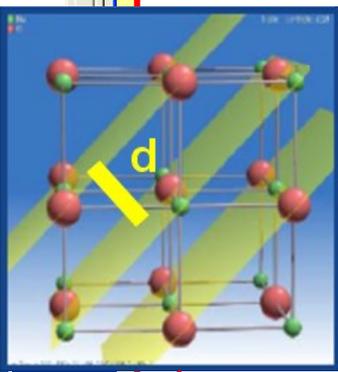
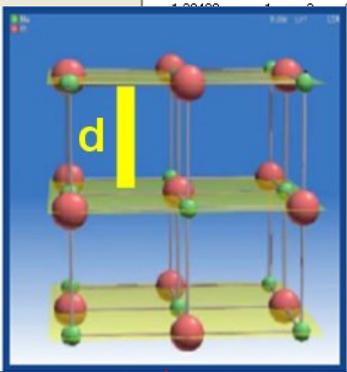
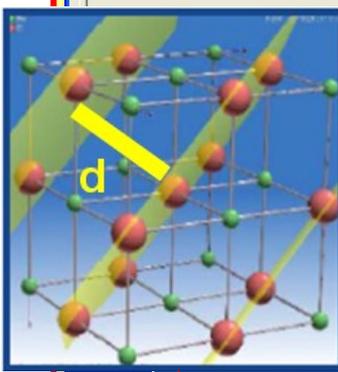
Lanthanides Toggle All

Scan (BW.raw)

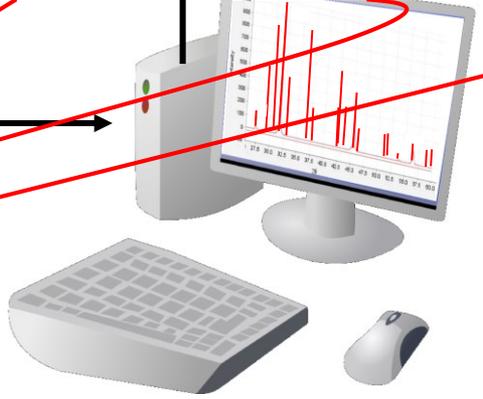
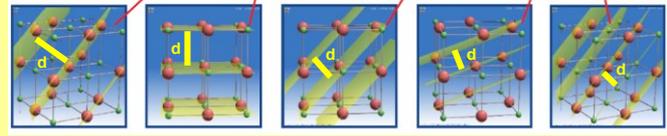
Pattern: 00-039-0256 Russellite, syn (gamma-Bi2W06)

Main Database: MASTER Max Results: 500

Read Save Default Search



29



	00-041-1115	Sodium Oxid...	Na3OCl
	00-005-0628	Halite, syn	NaCl
	00-005-0610	Sodium Chlorate	NaClO3
	00-002-0778	Sodium Chlor...	Na(Cl,CN)
	00-003-0945	Sodium Chlorite	NaClO2
	00-005-0544	Potassium S...	K5NaCl2(S2O6)
	00-002-1408	Sodium Chlorite	NaClO2
	00-016-0165	Schairerite	Na3SO4(F,Cl)
	00-015-0651	Gaiteite	Na15(SO4)5F-
	00-029-1197	Hydrohalite	NaCl·2H2O
	00-026-0919	Halite, potas...	K0.4Na0.6Cl
	00-015-0668	Sulphohalite	Na6(SO4)2ClF

Gray All Except Current Items Selected: 1

Y-Scale d x By Wavelength Make Peaks

← 100 Max % Fine Tuning Set To 100%

→ 50 Actual % Set To 50

← 0 Min %

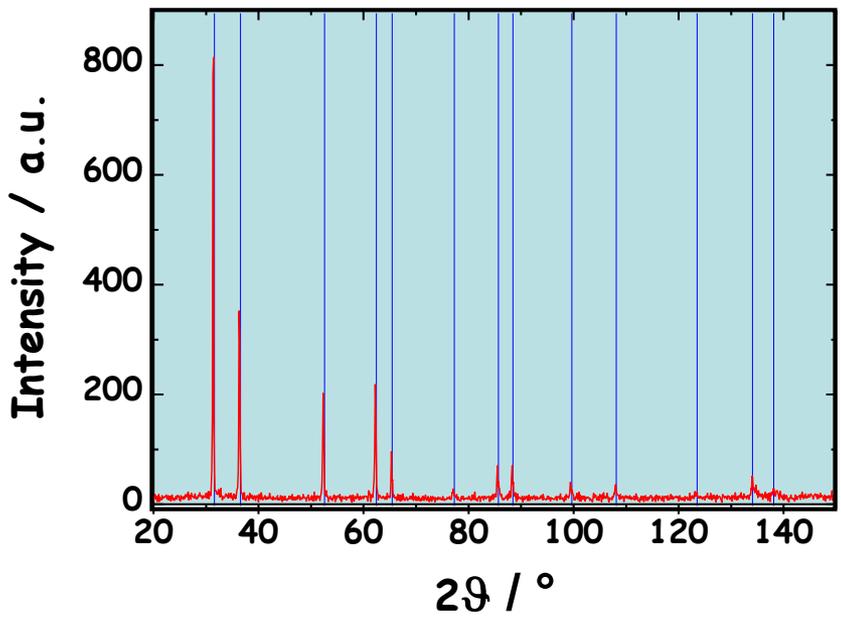
Some examples

Metals:

Lead (Pb)

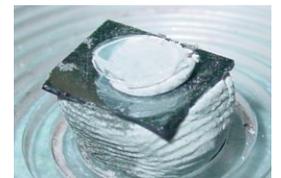
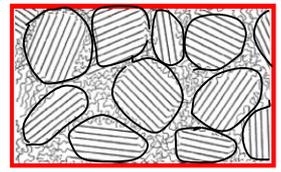


$$a = b = c = 8.54 \text{ \AA} \text{ (fcc)}$$

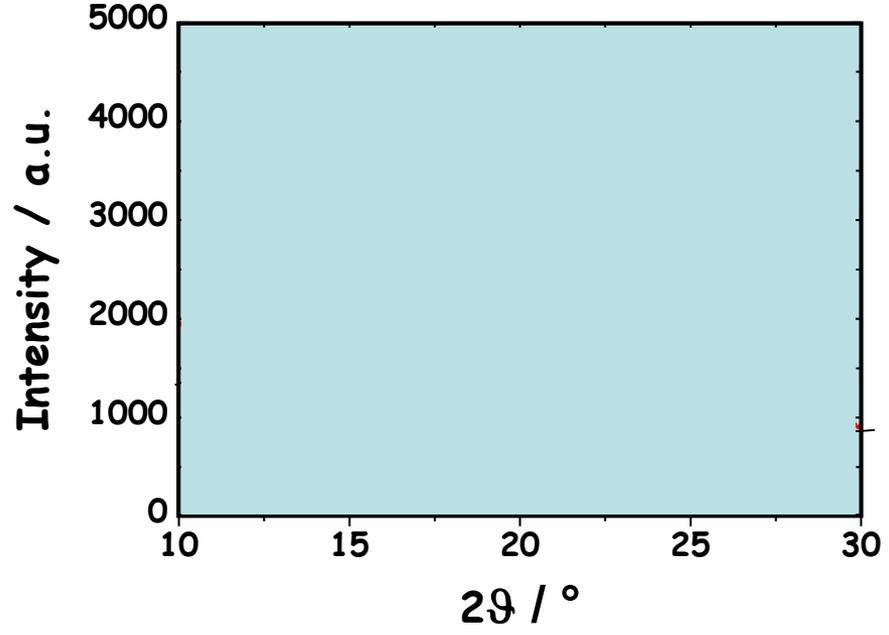


Polymers:

Polypropylene

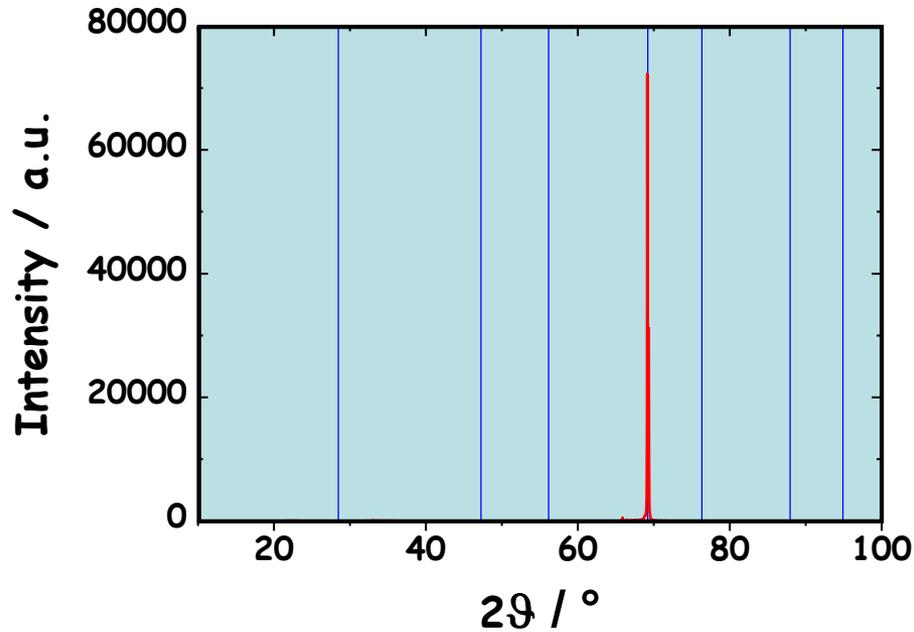
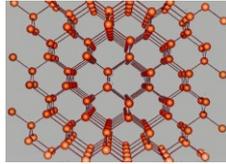


$$a = 8.54 \text{ \AA} \quad b = 9.93 \text{ \AA} \quad c = 42.41 \text{ \AA}$$



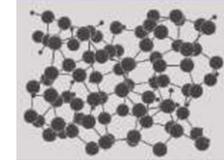
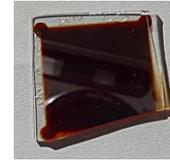
Single crystal:

<100> Silicon wafer

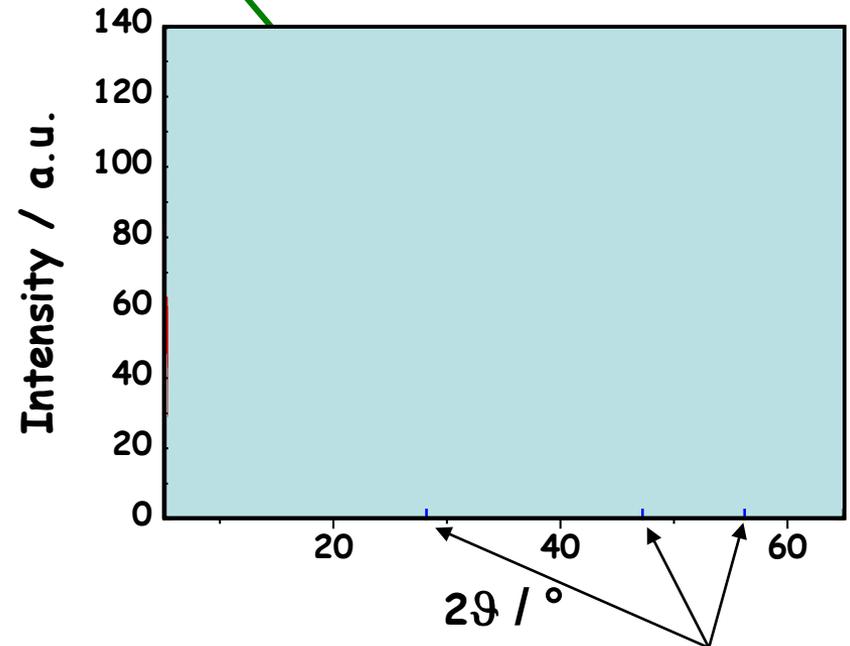


Amorphous material:

α-Silicon on amorphous glass



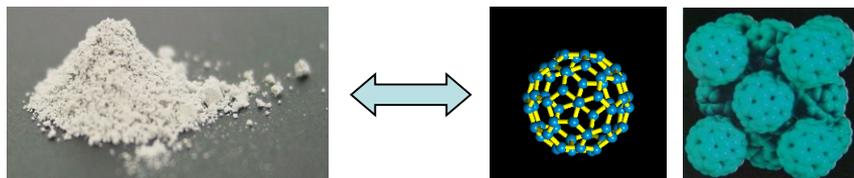
Diffuse maxima:
short-range order of nearest neighbors



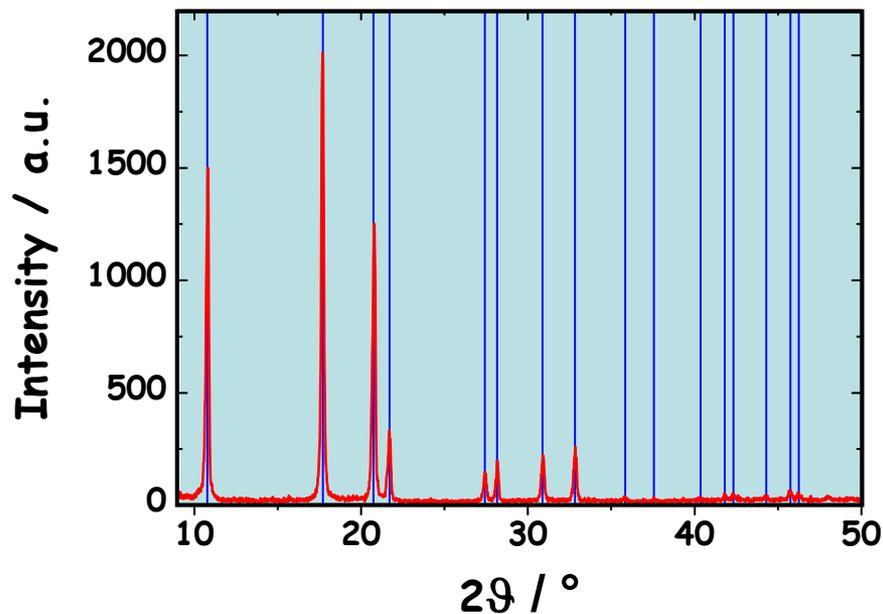
Annealing: phase transition to polycrystalline Si

Nanostructures:

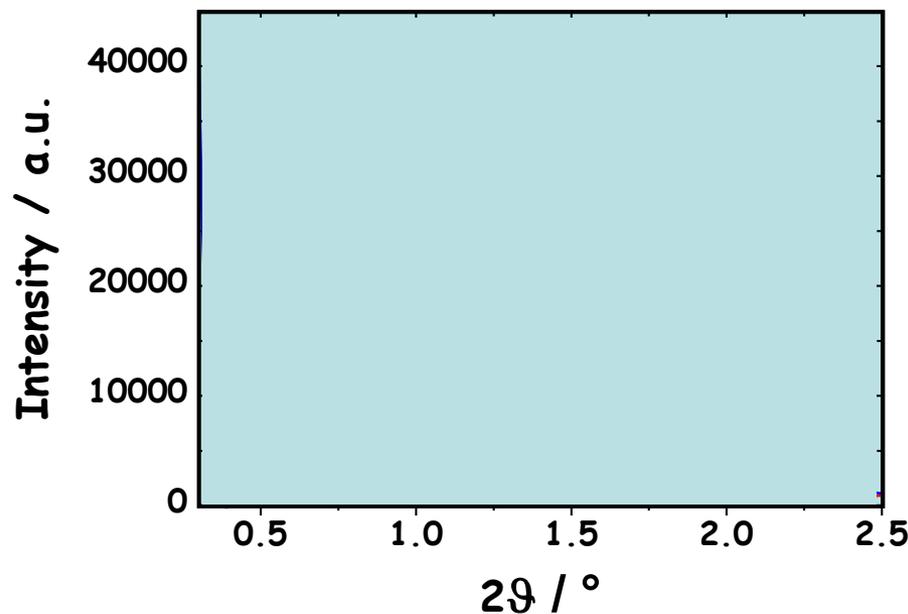
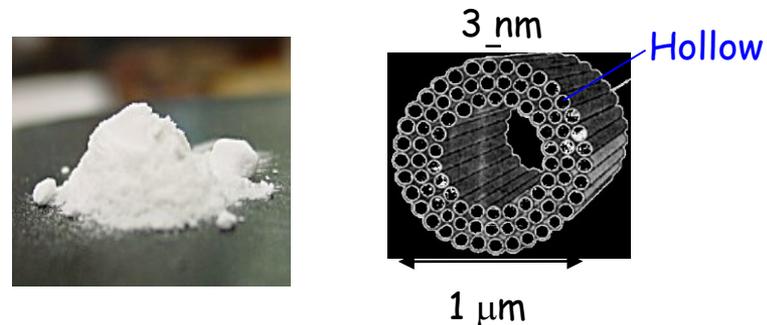
C60 - Buckminsterfullerene



fcc

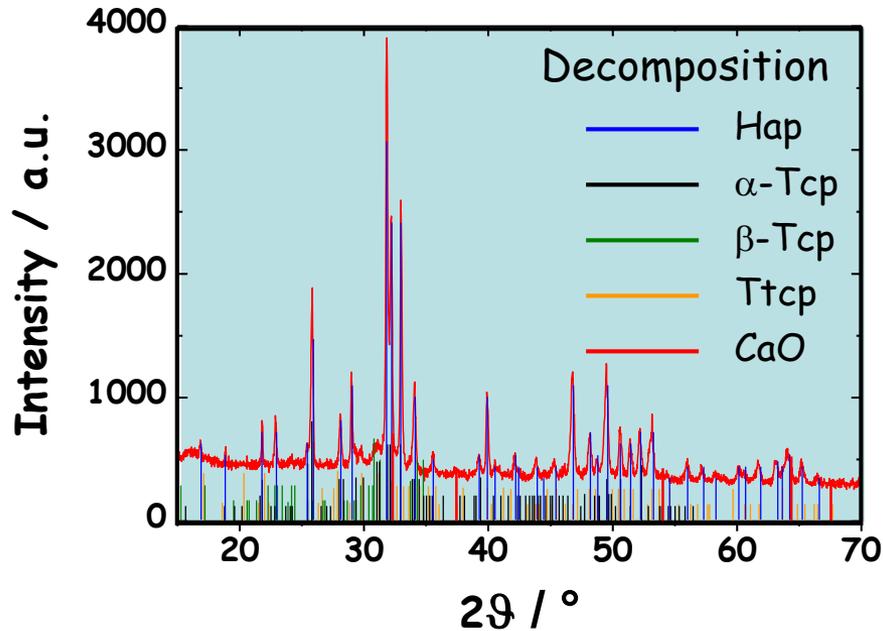
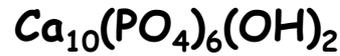
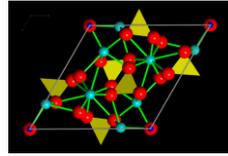
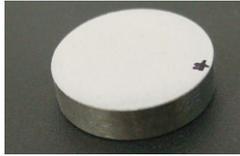


Fuel cells - mesoporous silica



Multiphase compounds:

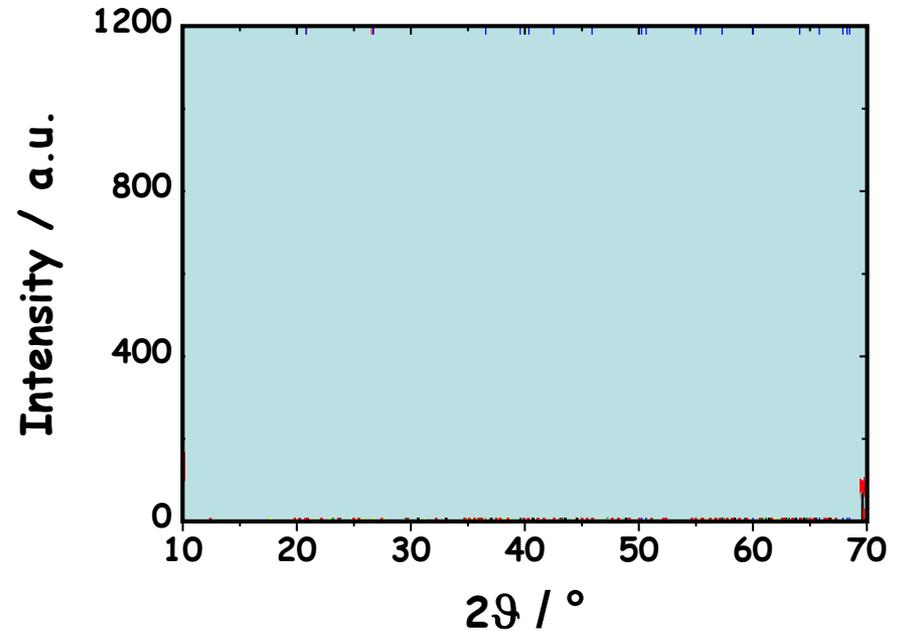
Hap Bio-coating



Geology

Core sample, bore hole EAA1

Bredasdorp, offshore RSA



XRD not limited to qualitative phase analysis

... X-ray optics dependent

Ultra fast reciprocal space maps
for epitaxial layer analysis

Non-ambient X-ray analysis
for *in situ* studies of advanced materials

Grazing incidence XRD
for surface analysis and depth profiling

Phase identification and quantification
to determine composition or monitor purity

Grazing incidence small-angle X-ray scattering
for characterization of nanostructure on surfaces

Small-angle X-ray scattering
for particle size analysis

X-ray reflectometry
to determine thin film thickness and roughness

Ultra small-angle X-ray scattering
for accessing very large d-spacings

Hard radiation applications
e.g. for *in operando* studies of batteries

Pole figures
for texture analysis

Residual stress
for component and failure analysis

Advanced SAXS/WAXS
for nanostructure analysis

Transmission XRD
for characterization of organic materials

2D XRD
for microstructural analysis

Computed tomography
for investigating the internal structure of objects

Pain distribution function
for studying the local atomic structure of disordered materials