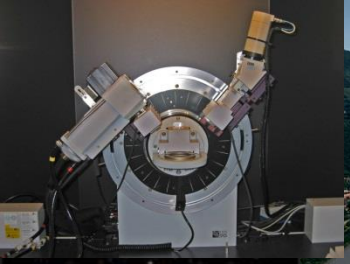
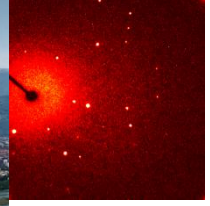
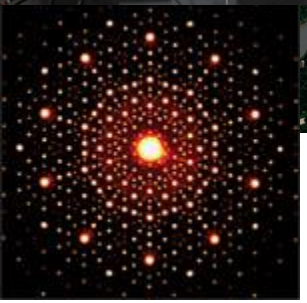
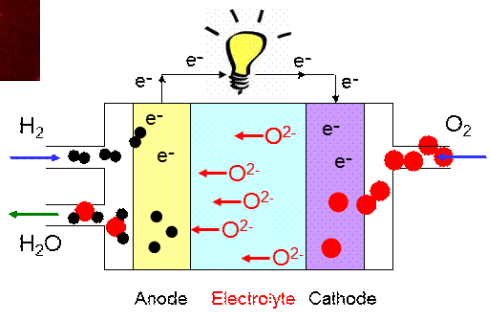
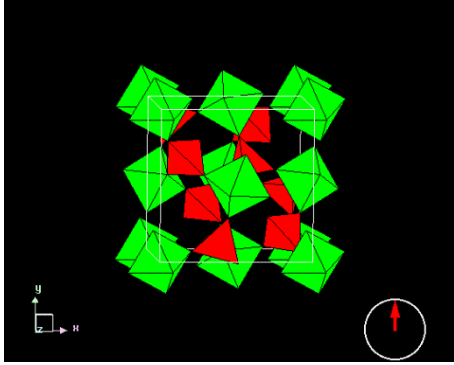
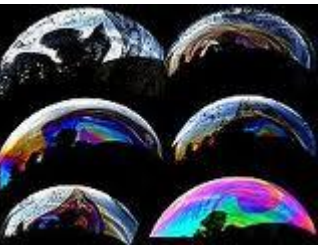
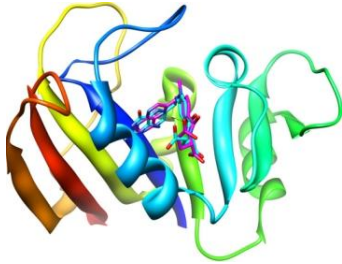




Nove fizickohemijske metode

Metode zasnovane na sinhrotronskom zracenju (Difrakcione metode)

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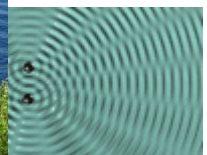


Metode zasnovane na sinhrotronskom zracenju (Difrakcione metode)

- Plan predavanja:
  - Difrakcione metode strukturne karakterizacije materijala
  - Eksperimentalni aspekti difrakcije sinhrotronskog X-zracenja
  - Oblasti primene difrakcije sinhrotronskog X-zracenja
  - Prednosti (i mane) u odnosu na laboratorijski XRD
  - Primeri studija neorganskih funkcionalnih materijala
- Preporuceni prag znanja:
  - Osnovne kristalografske definicije
  - Kristalografska simetrija, prostorne grupe
  - Difrakcija kao fizicka pojava
  - Bragg-ov zakon
  - Rasejanje sa jedinicne celije: strukturni faktor

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Why Study Structures of Solids?

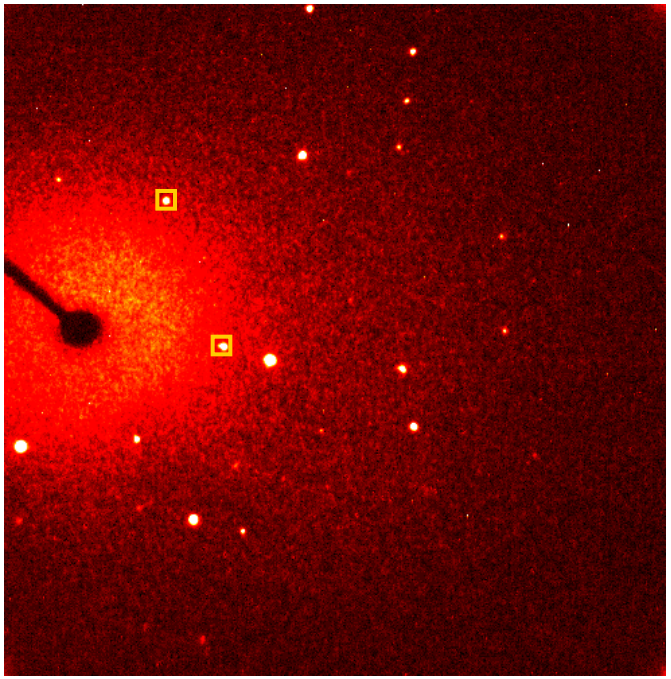
- Proof of molecular structure
  - Quick analytical tool for the synthetic chemist
    - What molecule have I made?
- Determination of crystal structure
  - Task for the crystallographer
    - How are the atoms/molecules in this solid arranged in 3D?
- Insight into structure-property relationships
  - Key characterisation method for the materials chemist
    - Why is my material an ionic conductor?
    - Why does my material exhibit negative thermal expansion?
    - How can I make a better superconductor?

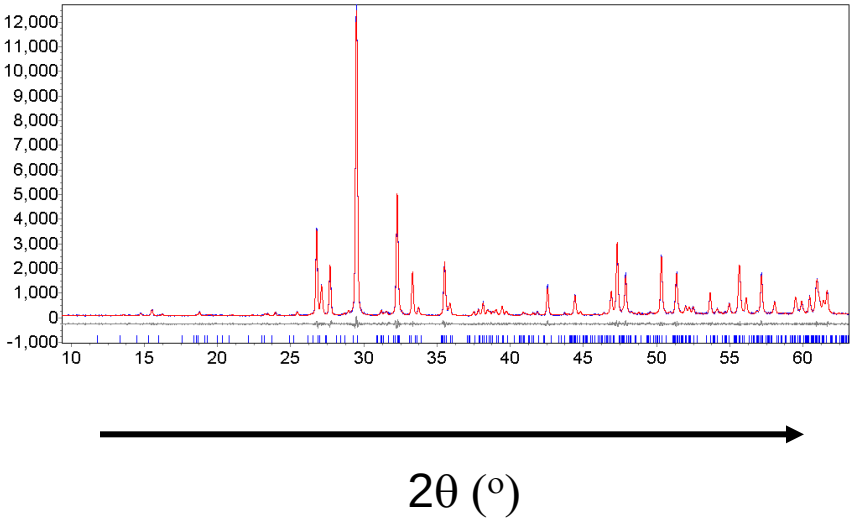
Diffraction Patterns

- Experimentally observed diffraction patterns

Single crystal diffraction

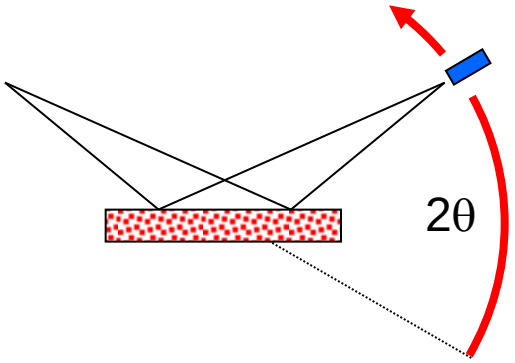
Powder diffraction



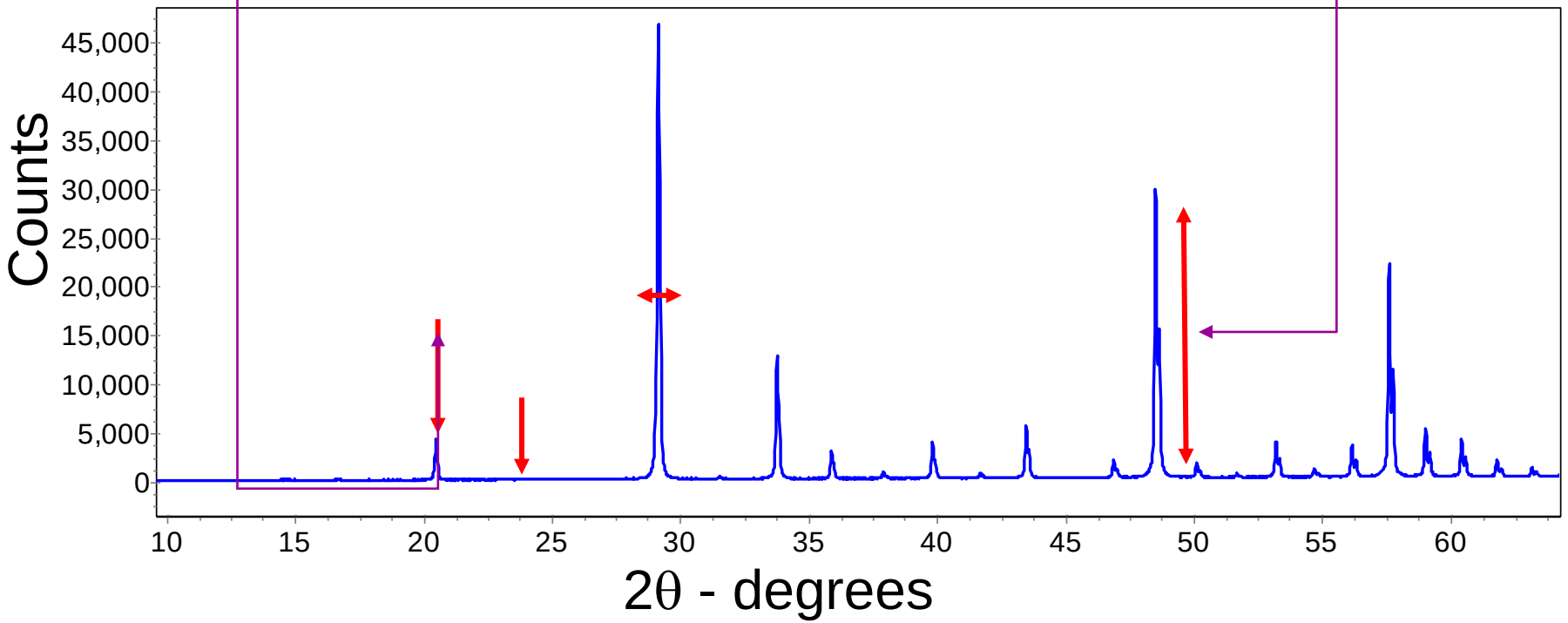


Information in a Powder Pattern

1. Peak positions determined by size and shape of unit cell – internal structure

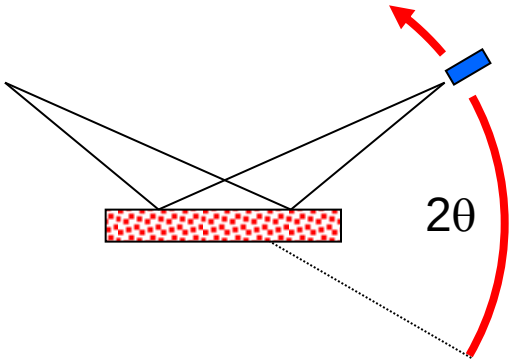


2. Peak Intensities determined by where atoms sit in unit cell – internal structure

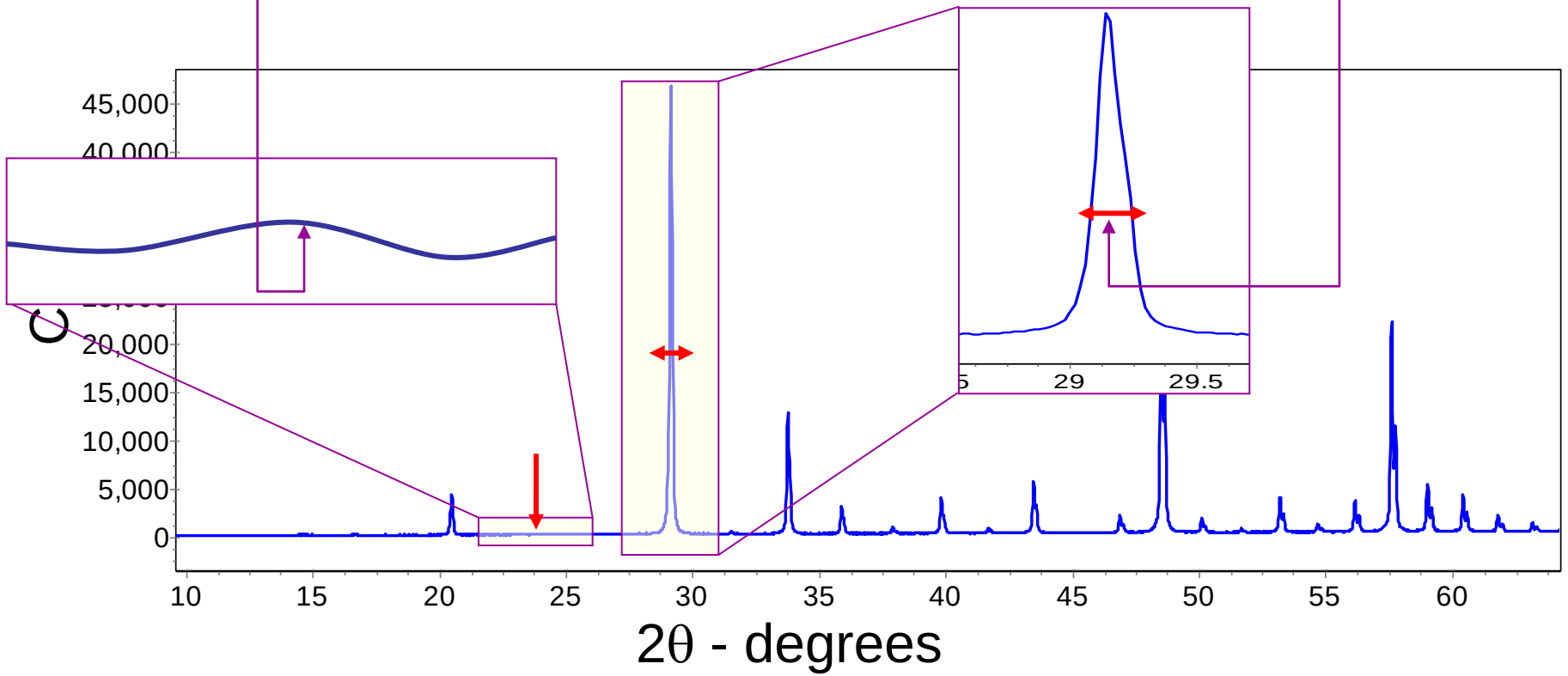


Information in a Powder Pattern

4. Background oscillations may contain information about short range order in material

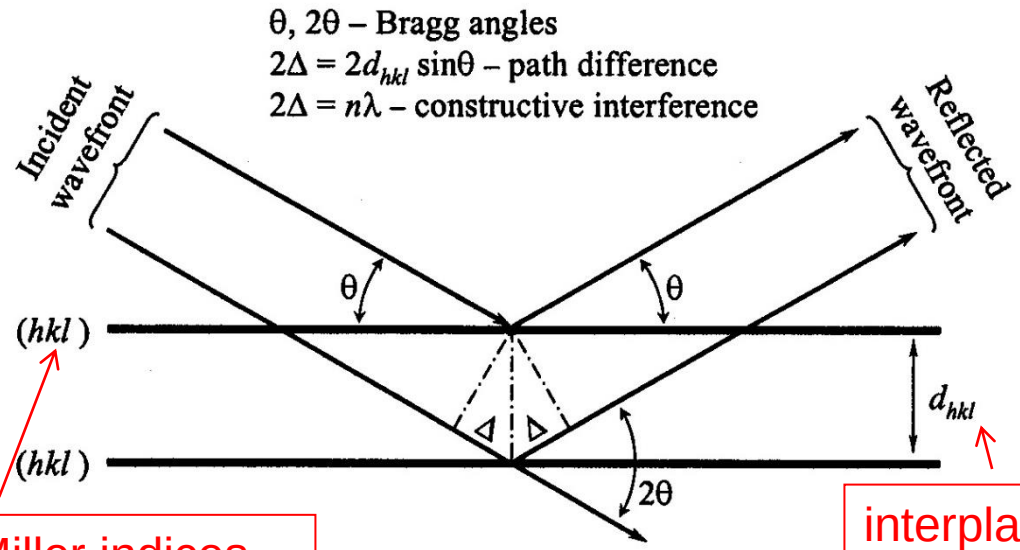


3. Peak widths determined by size/strain of crystallites - microstructure.



Bragg's Law

- Simplistic, but useful view of diffraction
  - Atoms arranged in parallel planes in a crystal
  - Incident X-rays reflected off the planes
  - Peaks in diffraction patterns referred to as "reflections"



$2\Delta = n\lambda$

(n=order of diffraction*)

$2d_{hkl}\sin\theta = \lambda$

Miller indices

interplanar spacing, d-spacing

*n=1, because n^{th} order diffraction from (hkl) planes with spacing d can be treated as 1^{st} order diffraction from (nh, nk, nl) planes with spacing d/n

d-spacings and Cell Parameters

- d-spacings in crystals are related to the unit cell parameters a, b and c
- For orthogonal crystal systems:

$$\frac{1}{d_{hkl}^{\,2}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

- Applications:
  - From known unit cell parameters, we can predict diffraction patterns (peak positions)
  - From experimentally observed peak positions, we can determine unit cell parameters

Scattering of X-rays by the Unit Cell

- Peak intensities, I_{hkl}: $I_{hkl} \propto |F_{hkl}|^2$
  - $|F_{hkl}|$ ~ the collective scattering power of the atoms in the unit cell
  - Other factors: absorption, thermal vibrations, site occupancies, …

- Structure factor, F_{hkl}

$$F_{hkl} = \sum_{1}^{N} f_n e^{2\pi i(hx_n + ky_n + lz_n)}$$

Electronic property of the atom
Information about atom types

Structural property of the unit cell
Information about atomic positions

- F_{hkl} is a complex number: $F_{hkl} = |F_{hkl}| e^{i\phi_{hkl}}$

*x_n, y_n *and* z_n are atomic fractional coordinates: $x_n = x/a$, $y_n = y/b$, $z_n = z/c$

Structure Determination: Typical Output

- Table of determined (refined) structural parameters

Table 1. Structural Parameters for $Bi_8La_{10}O_{27}$ at Room Temperature: a = 12.0640(3) Å, b = 16.3564(4) Å, c = 4.09871(6) Å, and V = 808.77(4) Å^3

atom[a]	site	x	y	z	occ	U_{eq} (Å^2)
Bi1	4e	0.3110(1)	0	0	1	0.009
Bi2	4g	0	0.3310(1)	0	1	0.010
La1	8n	0.3417(2)	0.3257(1)	0	1	0.013
La2	2a	0	0	0	1	0.018
O1	4h	0	0.0888(5)	0.5	1	0.005
O2	4h	0	0.2759(3)	0.5	1	0.016
O3	8n	0.1894(5)	0.0879(3)	0	1	0.024
O4	8n	0.1523(3)	0.2638(3)	0	1	0.010
O5	8n	0.186(1)	0.458(1)	0	0.349(5)	0.036(2)[b]
O6	4h	0	0.32(1)	0.5	0.08(1)	0.036(2)[b]

unit cell parameters

atomic coordinates

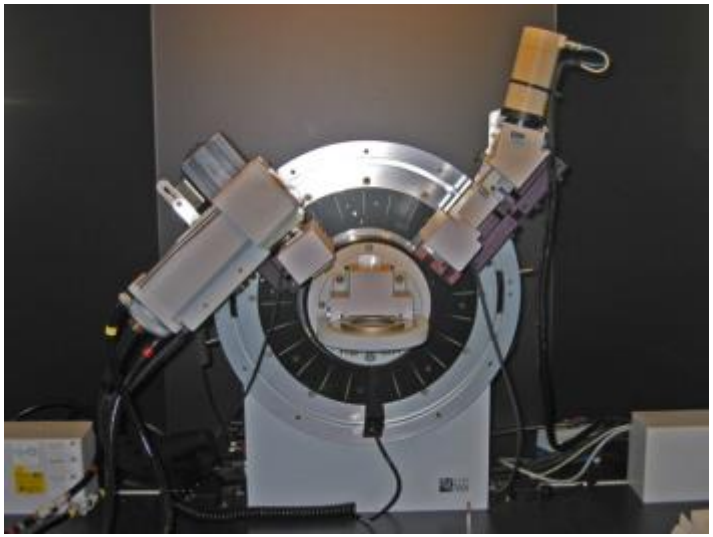
atomic displacement parameters (ADPs), or thermal parameters

atomic site occupancies

- From these parameters, conclusions about the atomic connectivity and coordination environments (bond lengths and angles) can be drawn

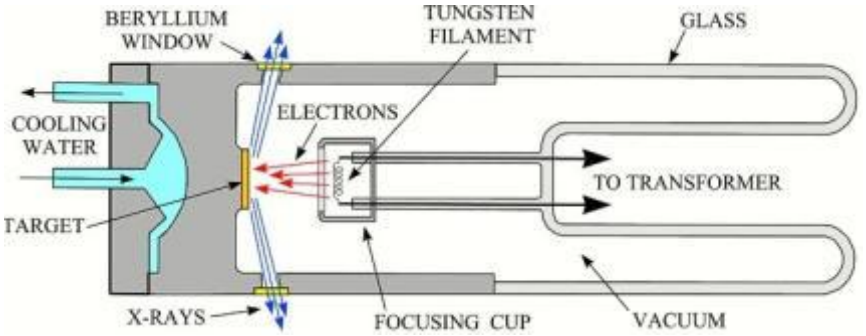
Experimental Aspects

Source	Sample	Detector
X-rays Neutrons	Single crystal Powder	Point detectors 2D detectors

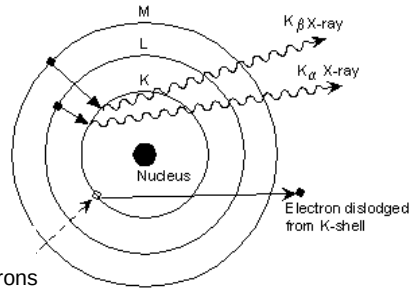


Laboratory X-ray Diffraction

- Laboratory source: X-ray tube

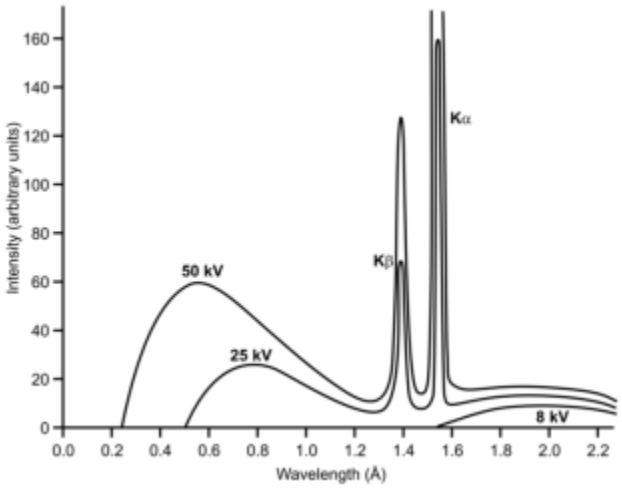


- Electrons accelerated from a filament (W) into a metal target (Cu, Mo)
  - continuous spectrum (bremsstrahlung)
  - characteristic X-rays (electronic transitions)



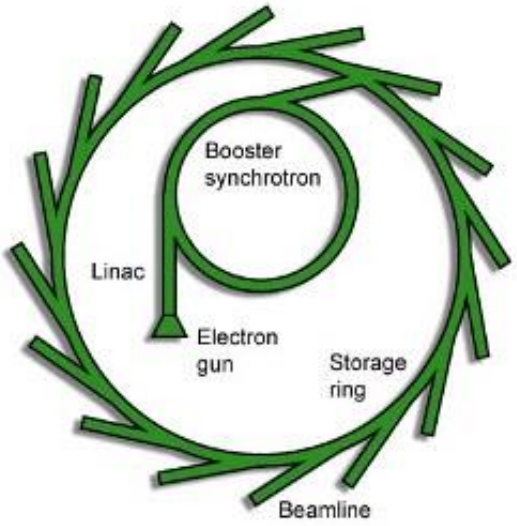
Cu Kα: 1.54184 Å

Mo Kα: 0.711445 Å



Synchrotron X-ray Diffraction (SXRD)

- Synchrotron radiation
  - Electrons moving at relativistic speed along a curved path



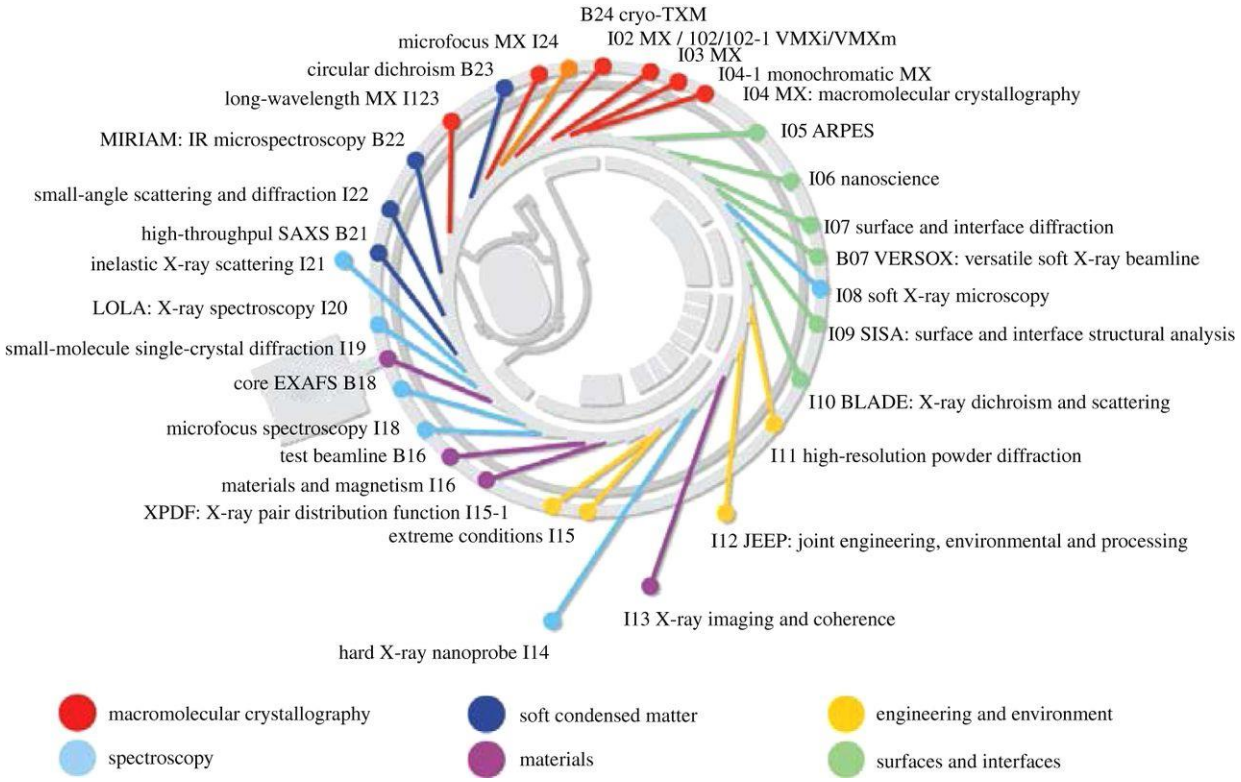
- Advantages over lab sources
  1. Tunable λ
  2. High intensity
  3. Highly monochromatic λ and highly collimated beam

- Disadvantages
  1. Access: proposal, delay, limited beam time, no opportunity to repeat
  2. Lack of control over options and conditions

Synchrotron X-ray Diffraction (SXRD)

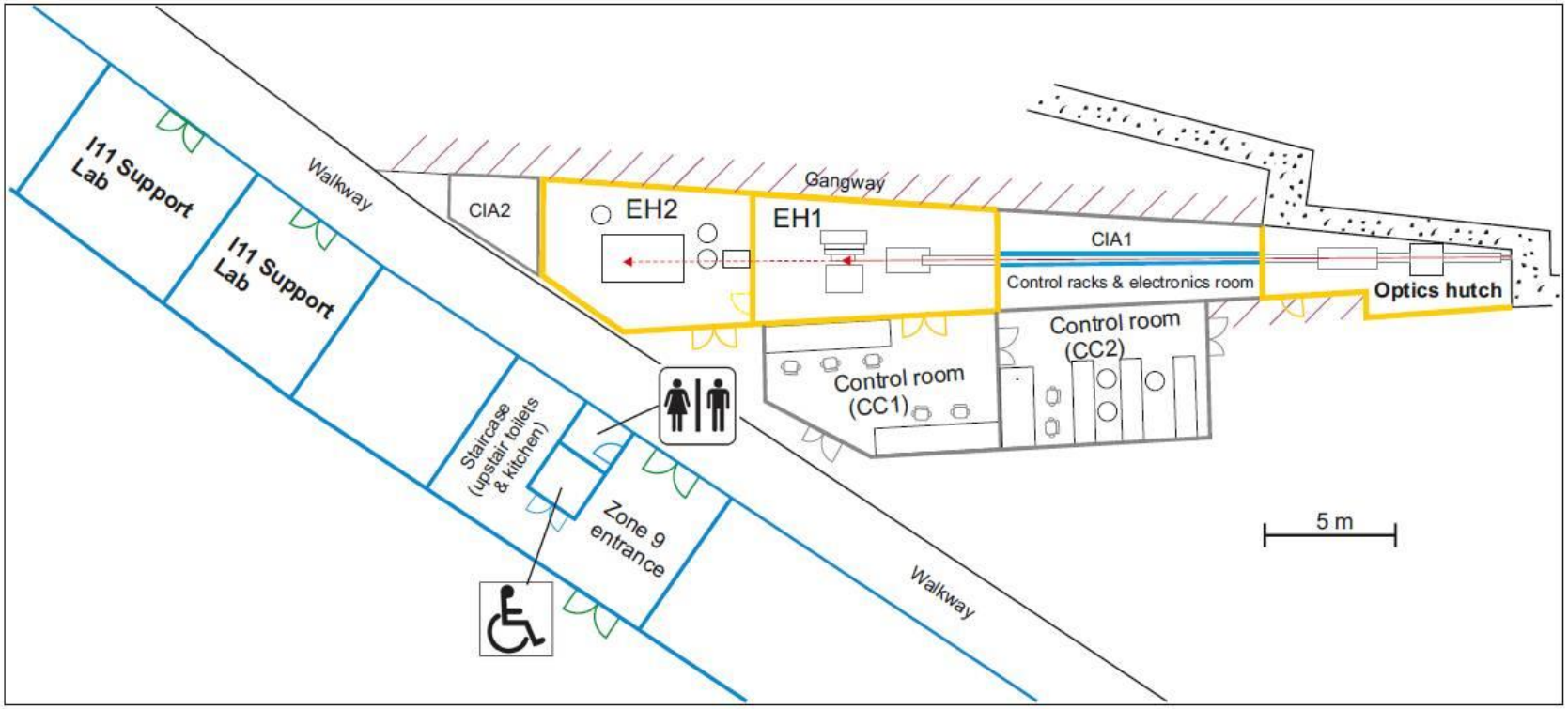
Synchrotron X-ray Diffraction (SXRD)

- Diamond Light Source, UK



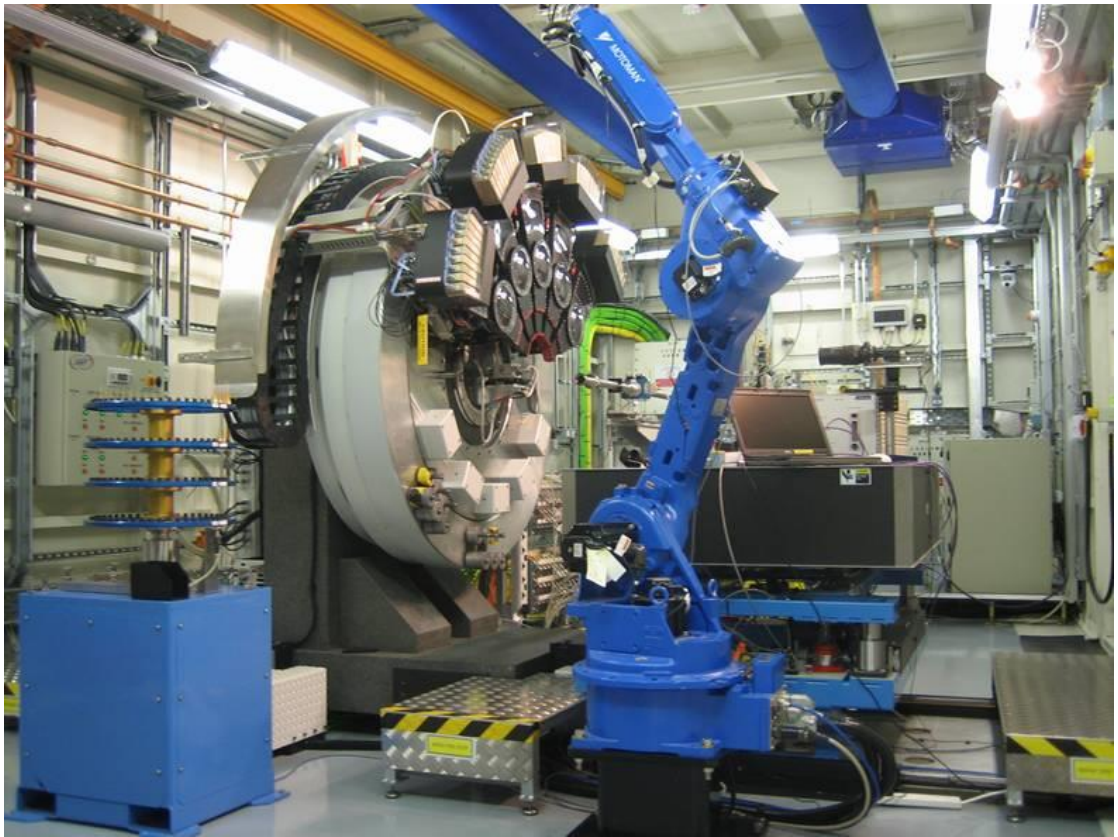
Synchrotron X-ray Diffraction (SXRD)

- Powder diffraction beamline I11, Diamond Light Source, UK
  - Layout and area plan



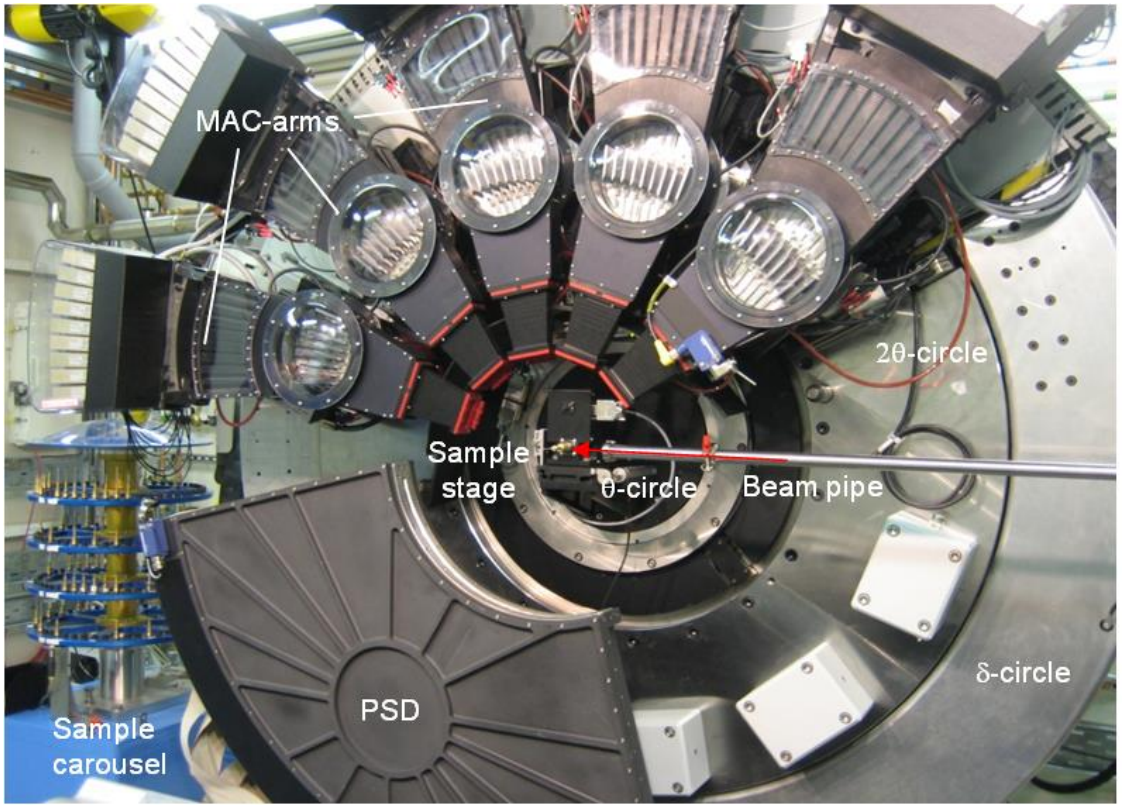
Synchrotron X-ray Diffraction (SXRD)

- Powder diffraction beamline I11, Diamond Light Source, UK
  - Experimental hutch 1 (EH1): the diffractometer



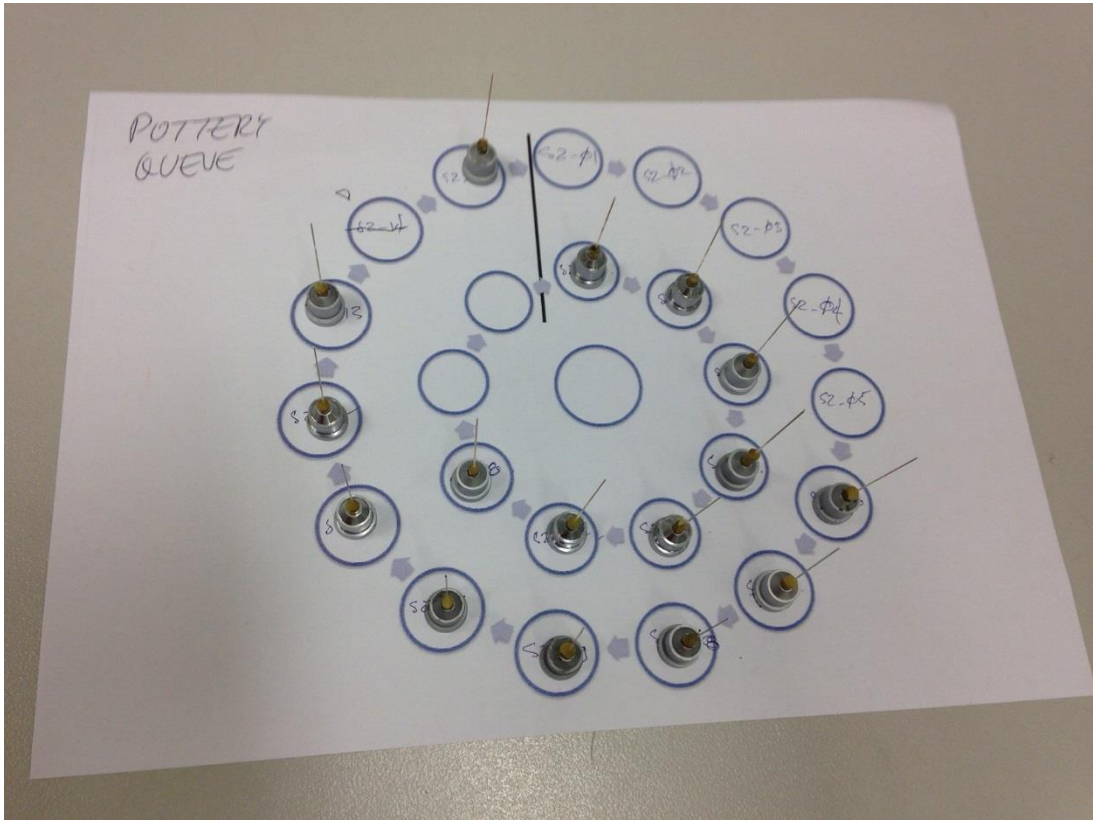
Synchrotron X-ray Diffraction (SXRD)

- Powder diffraction beamline I11, Diamond Light Source, UK
  - Sample stage and detectors



Synchrotron X-ray Diffraction (SXRD)

- Powder diffraction beamline I11, Diamond Light Source, UK
  - Prepared samples in capillaries

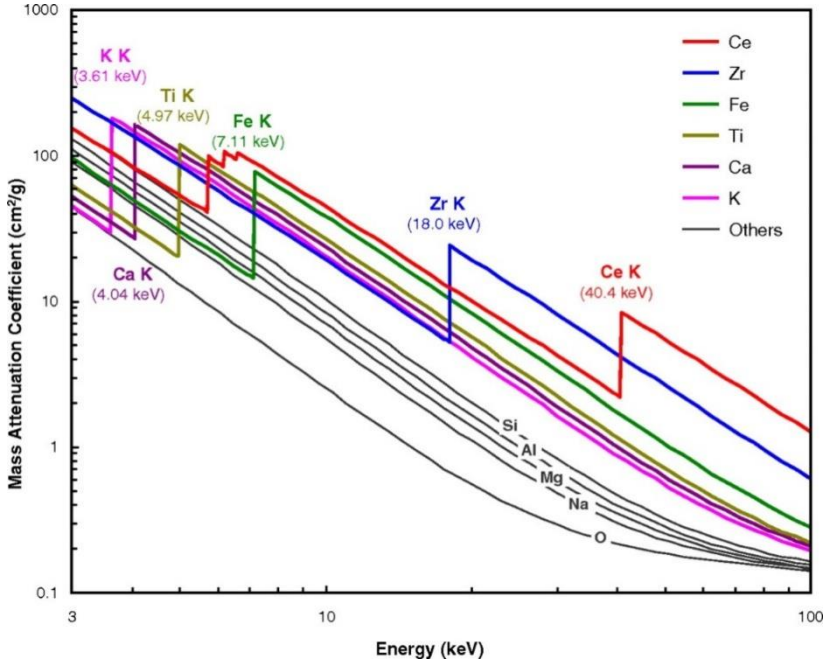


SXRD: Tunable Wavelength

- Flux vs. energy
  - I11 at Diamond: 6-25 keV (0.4-2.1 Å), optimised at 15 keV

$I_x \propto I_o\, e^{-\mu x}$ $\quad\quad$ $\mu = f(E)$

- Optimising absorption
  1. Minimising absorption (hard X-rays)
  2. Experiments away from absorption edges
  3. Experiments at absorption edges



- Applications of resonant (anomalous) scattering
  - Macromolecular xtl: multiple anomalous diffraction (MAD) phasing
  - Physics: exotic magnetism (skyrmions)

SXRD: Tunable Wavelength

- Example 1: Minimising absorption
  - Choose λ and capillary size so that: μ*r < 1.5
  - What capillary size would you use to measure Bi_2O_3 with λ = 0.410 Å and 0.825 Å?

Information: Bi_2O_3 density 8.9 g/cm^3; powder packing density 60%; RMM (Bi_2O_3) = 466.0; mass absorption coefficients for λ = 0.41 Å: Bi 31.520 cm^2/g, O 0.378 cm^2/g; for λ = 0.825 Å: Bi 116.000 cm^2/g, O 1.836 cm^2/g.

lambda (A)	Bi mu/rho	O mu/rho	MW (Bi2O3)	Bi w frac	O w frac	Bi2O3 mu/rho	Bi2O3 rho	packed rho	Bi2O3 mu (cm-1)	d cap (mm)	r cap (cm)	mu*r
0.41	31.520	0.378	466.0	0.897	0.103	28.310	8.900	5.340	151.173	0.500	0.025	3.78
										0.400	0.020	3.02
										0.300	0.015	2.27
										0.200	0.010	1.51
										0.100	0.005	0.76

lambda (A)	Bi mu/rho	O mu/rho	MW (Bi2O3)	Bi w frac	O w frac	Bi2O3 mu/rho	Bi2O3 rho	packed rho	Bi2O3 mu (cm-1)	d cap (mm)	r cap (cm)	mu*r
0.825	116.000	1.836	466.0	0.897	0.103	104.231	8.900	5.340	556.592	0.500	0.025	13.91
										0.400	0.020	11.13
										0.300	0.015	8.35
										0.200	0.010	5.57
										0.100	0.005	2.78

SXRD: Intensity

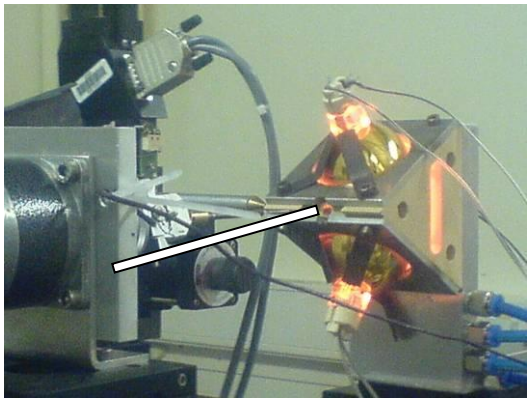
- Intensity ~10^3 lab X-ray source
  - Small samples
  - Rapid data collections
  - Excellent statistics
  - In-situ experiments, complex sample environments

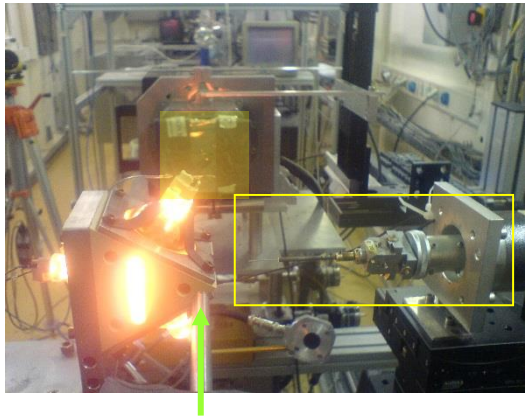
- Example 2: $ZrMo_2O_8$ ultra-rapid synthesis/in-situ SXRD
  - Negative thermal expansion (NTE) material
  - Cubic γ-$ZrMo_2O_8$ shows smooth NTE ($\alpha = -8 \times 10^{-6}$ K^{-1}) over a wide temperature range
  - Previously produced under kinetic control (e.g. dehydration of $ZrMo_2O_7(OH)_2 \cdot 2H_2O$)
  - Metastable

JSO Evans et al., *JACS*, 131, 48, 17560, 2009.

SXRD: Intensity

- Example 2: $ZrMo_2O_8$ ultra-rapid synthesis/in-situ SXRD
  - Beamline ID11 at ESRF, Grenoble
  - λ = 0.19902(2) Å
  - Stoichiometric amounts of ZrO_2 and MoO_3 packed into Pt capillaries (0.57 mm diameter, 0.04 mm wall thickness)

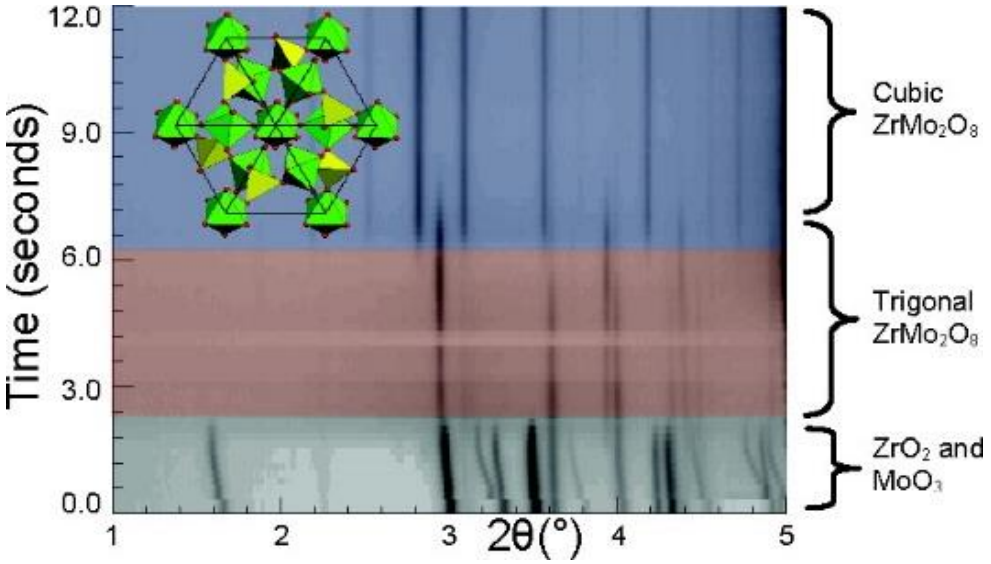




JSO Evans et al., *JACS*, 131, 48, 17560, 2009.

SXRD: Intensity

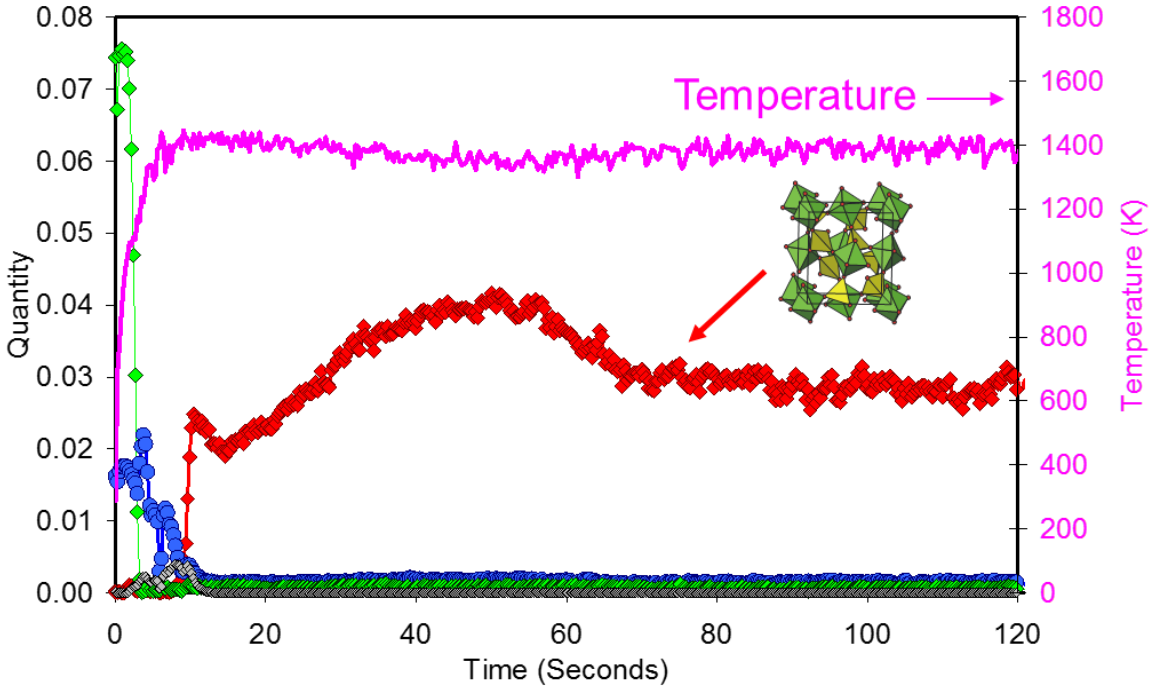
- Example 2: $ZrMo_2O_8$ ultra-rapid synthesis/in-situ SXRD
  - 0.25 s data collections; 480 patterns in 120 s



JSO Evans et al., *JACS*, 131, 48, 17560, 2009.

SXRD: Intensity

- Example 2: $ZrMo_2O_8$ ultra-rapid synthesis/in-situ SXRD
  - Cubic γ-$ZrMo_2O_8$ formed directly from oxides at 1400 K
  - Can be quenched to room temperature
  - Insight into the reaction pathways from quantitative analysis by Rietveld refinement (5 phases)



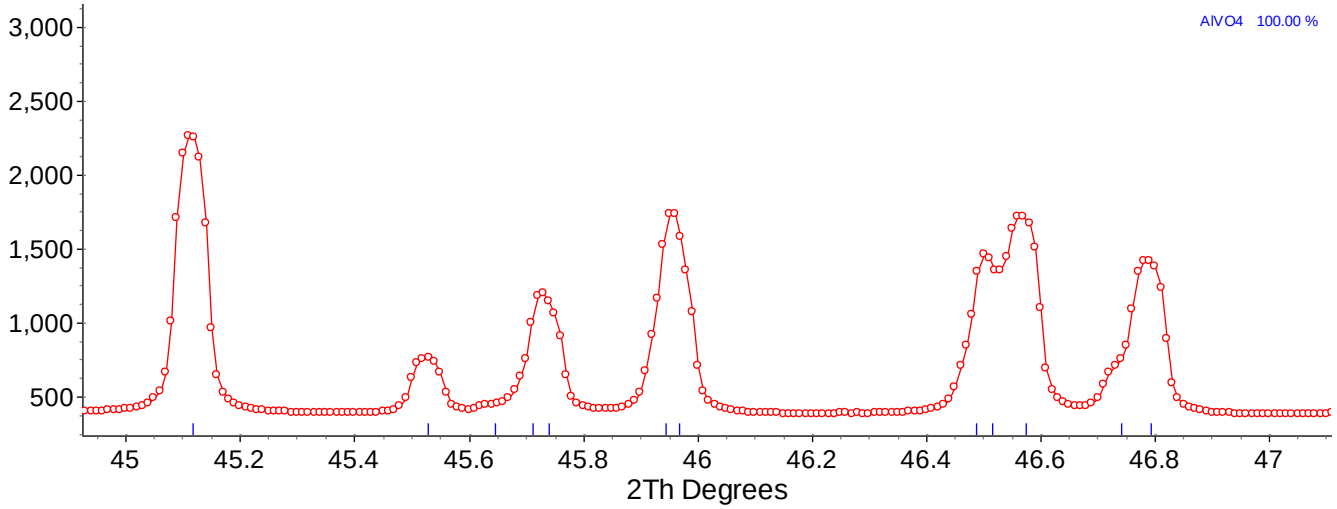
JSO Evans et al., *JACS*, 131, 48, 17560, 2009.

SXRD: High Resolution

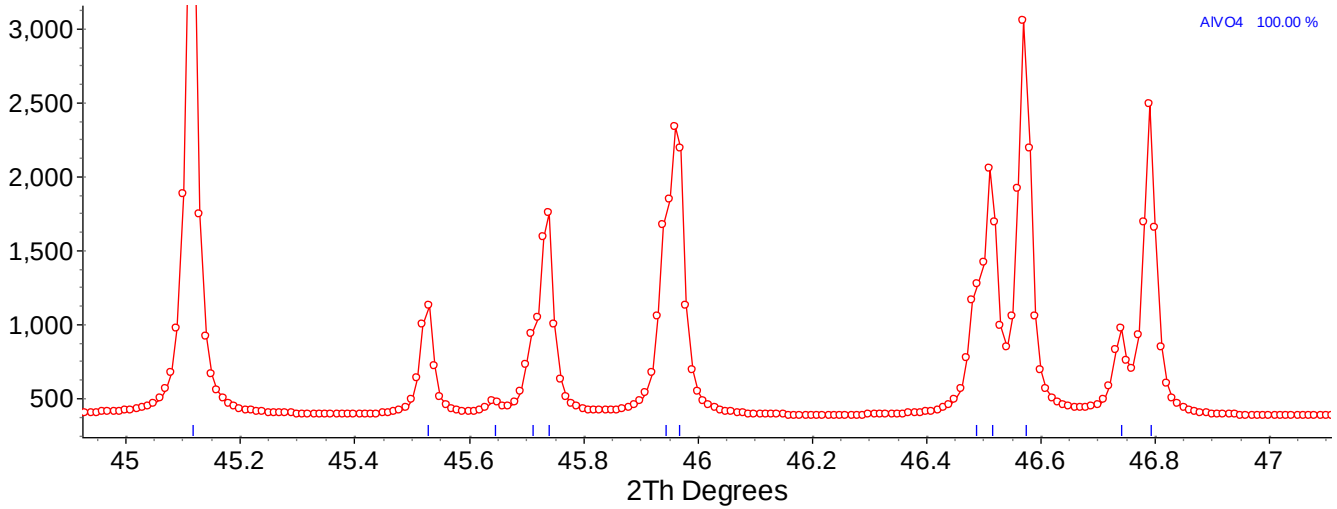
- Resolution: $\Delta d/d$
- Highly monochromatic λ and highly collimated beam
  - Narrow instrumental peak shape
  - Best resolution instruments: $\Delta d/d \sim 10^{-4}$
- Peak widths depend on:
  - Source
  - Instrument (optics)
  - Sample

$$Y(2\theta) = (\text{Source} \otimes \text{Instrument}) \otimes \text{Sample}$$

High vs Medium Resolution

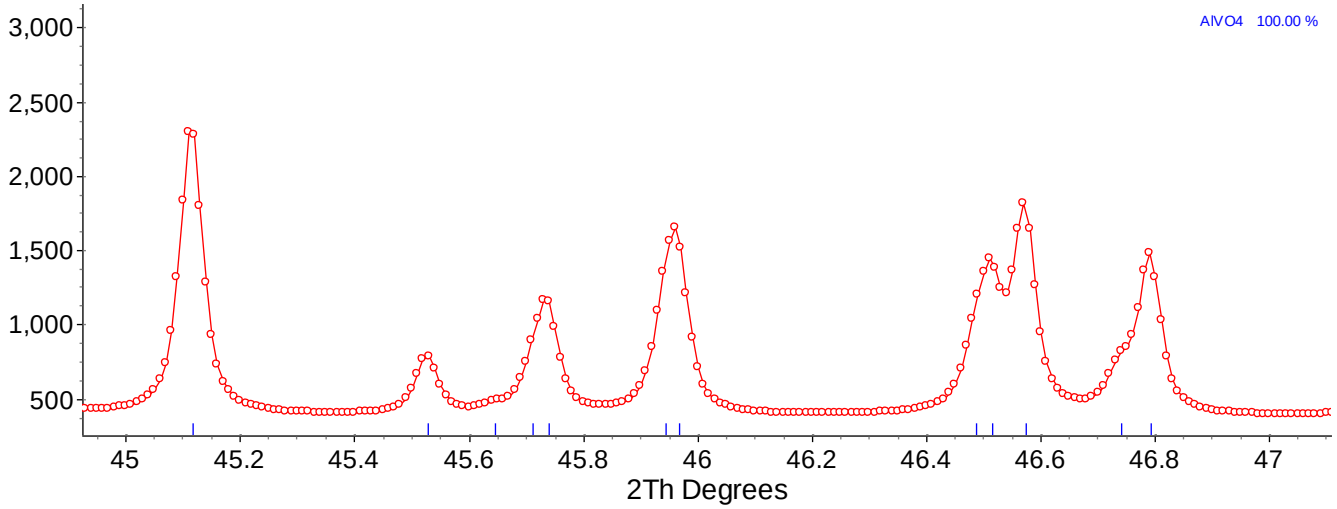


0.20 mm detector slit



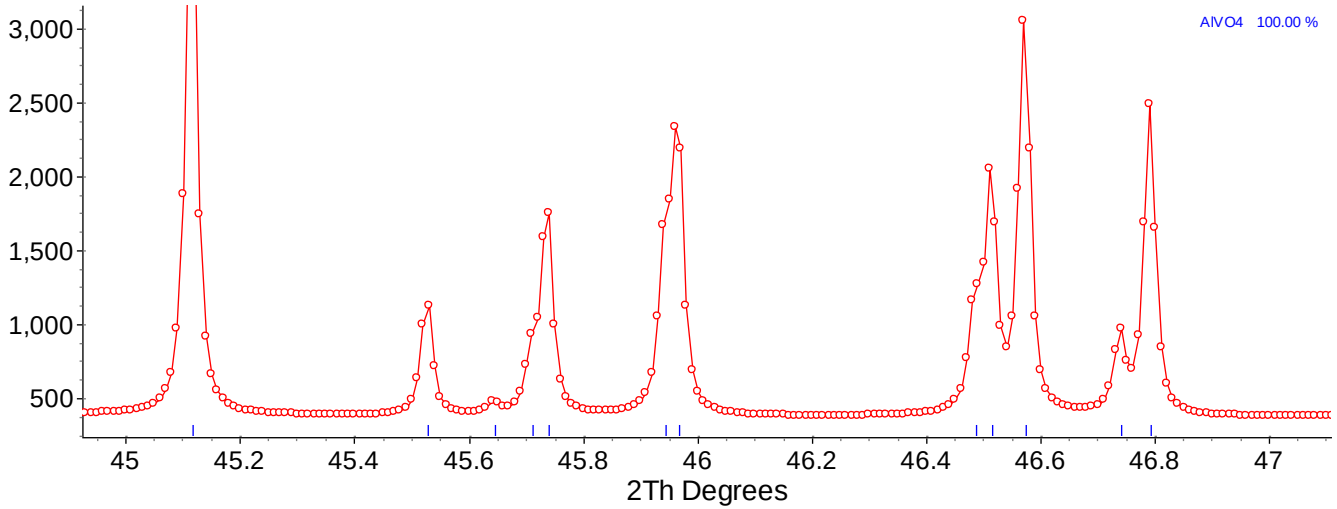
0.05 mm detector slit

Large vs Small Domains



500 nm domains

0.05 mm detector slit

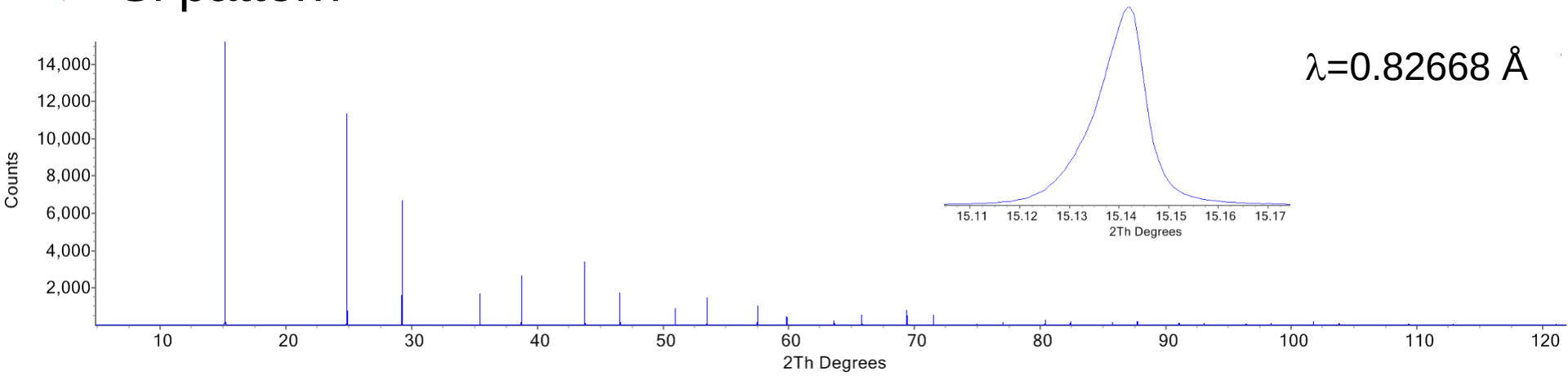


“infinite” domains

0.05 mm detector slit

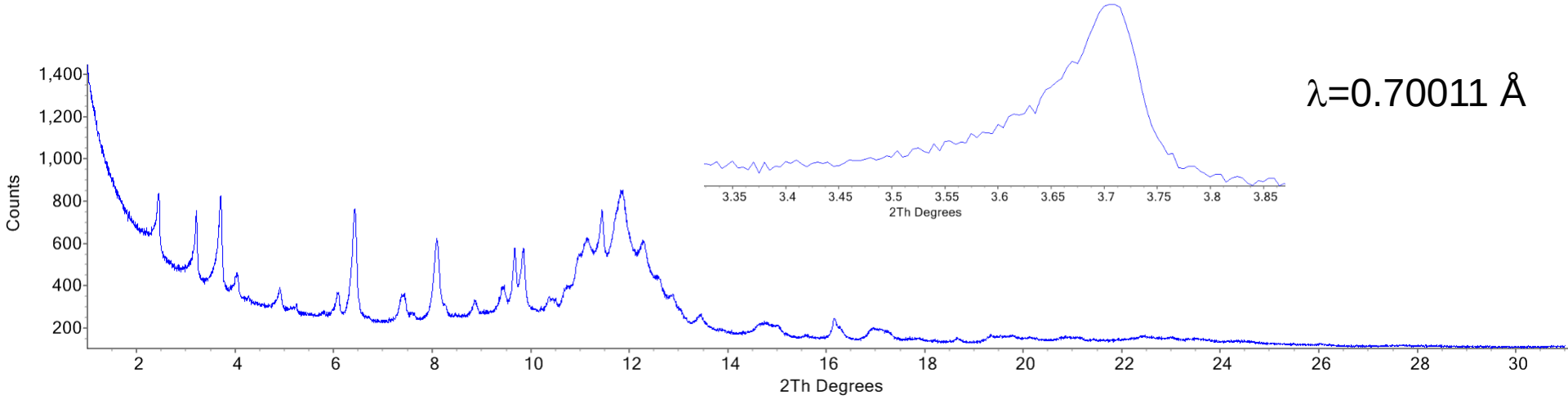
SXRD: High Resolution

- Si pattern



λ=0.82668 Å

- Mechanochemically prepared small organic



λ=0.70011 Å

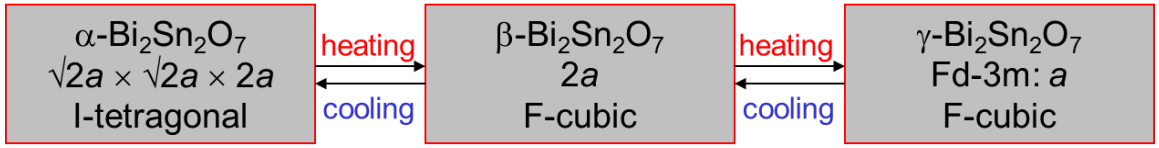
SXRD: High Resolution

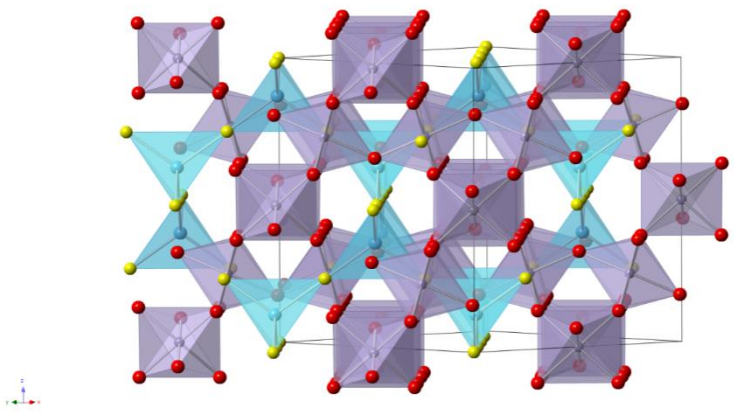
- Example 3: Analysis of Egyptian eye make-up (2000 BC)
- Lab XRD suggested:
  - Galena (PbS) and cerussite ($PbCO_3$) – naturally occuring
  - Laurionite (PbOHCl) and phosgenite ($Pb_2Cl_2CO_3$) – very rare in nature
- High-resolution synchrotron XRD used for quantification
  - Laurionite and phosgenite up to 75%
- SEM used for particle morphology analysis
  - Particle morphology consistent with wet chemistry production
- Wet chemistry products
  - Purified (PbO, NaCl, $Na_2CO_3)_{aq.}$
  - Multiple solution reactions, filtrations, pH control
- Conclusion: Egyptians used wet chemistry ~2000 BC
  - Chemical technology in Ancient Egypt very sophisticated

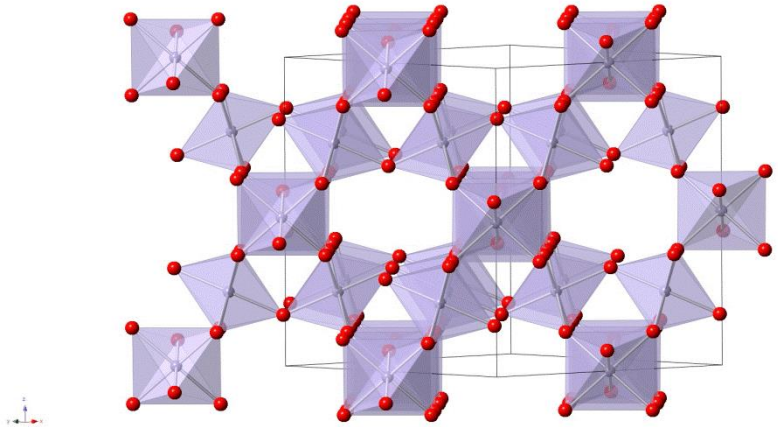
Walter et al., *Nature*, 397, 483, 1999.

SXRD: High Resolution

- Example 4: $Bi_2Sn_2O_7$ structure solution
  - Phase diagram (old)







Cubic γ-$Bi_2Sn_2O_7$

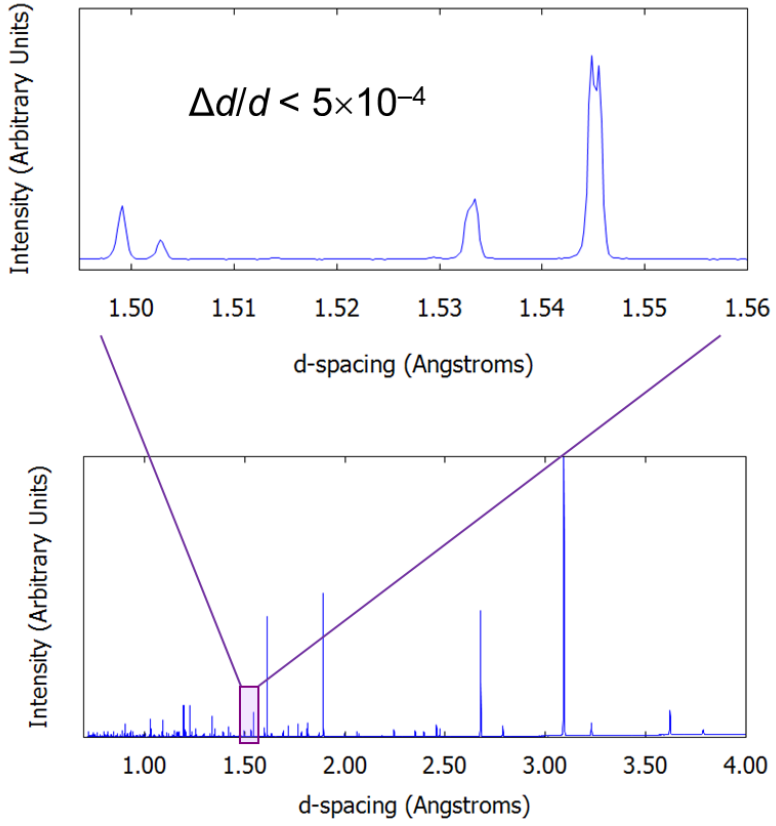
Fd-3*m*
a = 10.72 Å

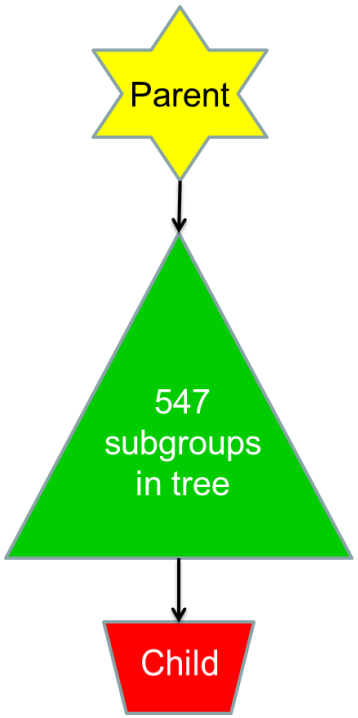
Interpenetrating Sn_2O_6 and Bi_2O' frameworks

IR Evans, JSO Evans et al., *JACS*, 138, 25, 8031, 2016.

SXRD: High Resolution

- Example 4: $Bi_2Sn_2O_7$ structure solution
  - Beamline I11, Diamond Light Source, UK
  - β-$Bi_2Sn_2O_7$ is not cubic
  - Very important for the structure solution methodology used
  - Exhaustive symmetry descent approach





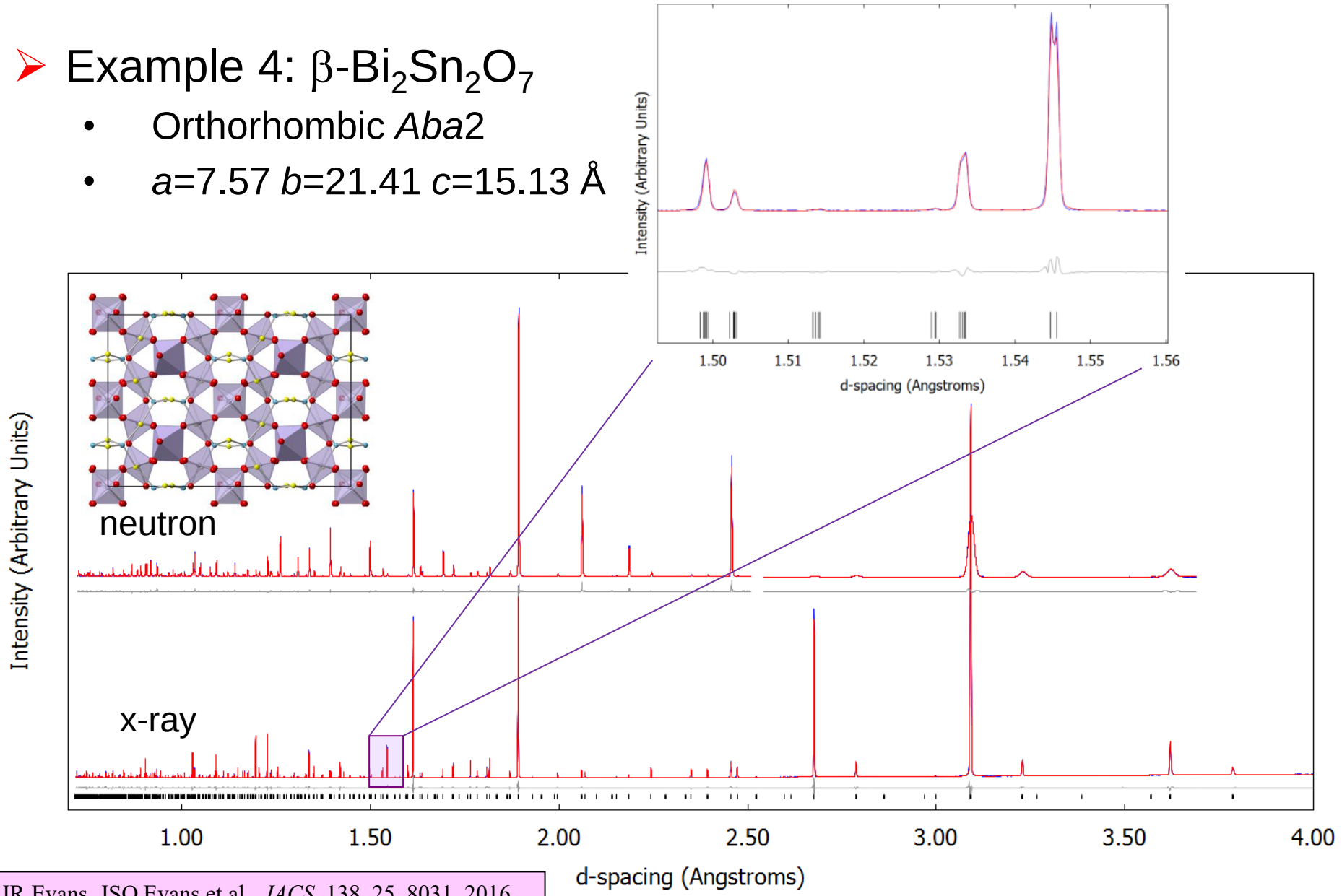
Fd-3m γ parent

P1 $\sqrt{2}a \times \sqrt{2}a \times 2a$ child

IR Evans, JSO Evans et al., *JACS*, 138, 25, 8031, 2016.

SXRD: High Resolution

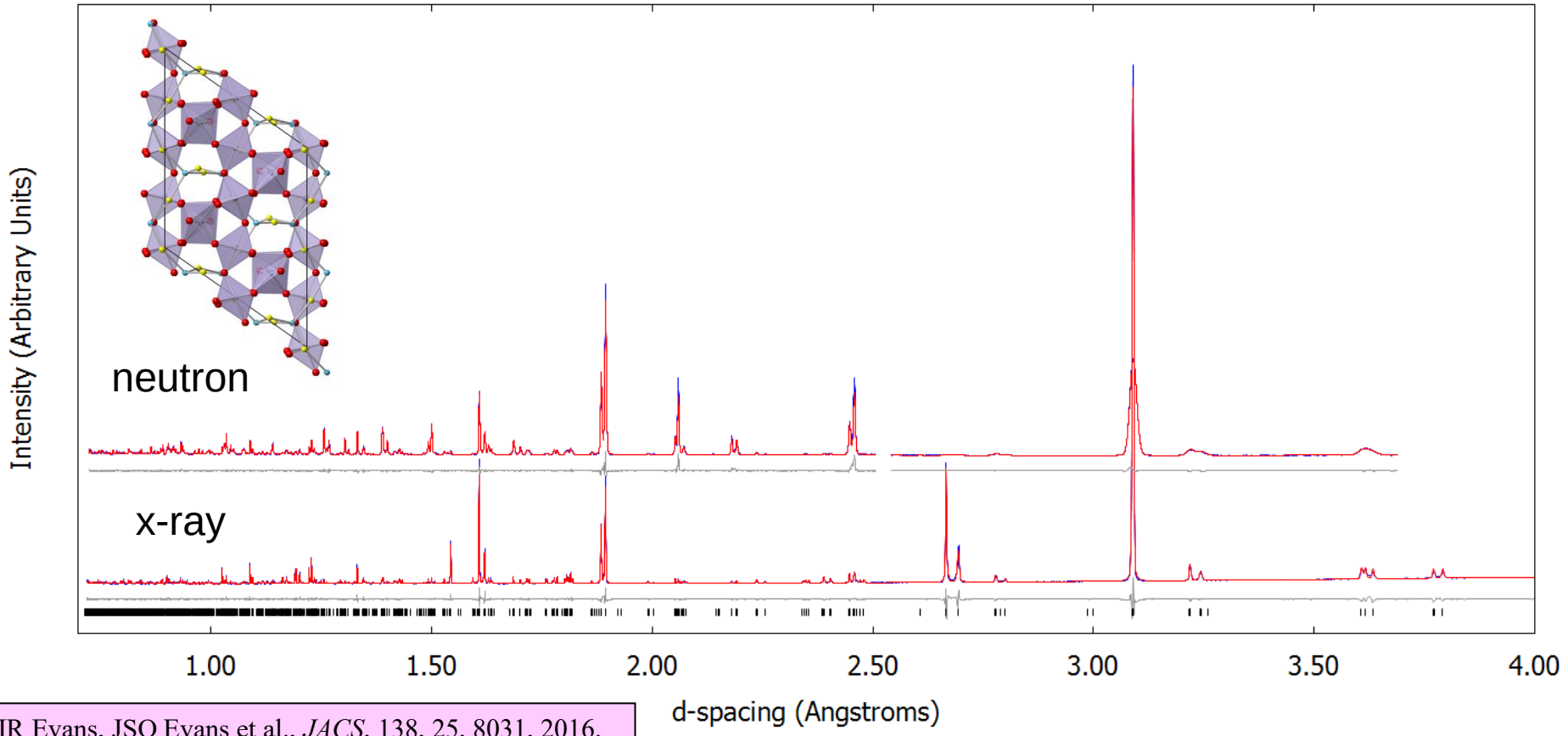
- Example 4: β-$Bi_2Sn_2O_7$
  - Orthorhombic *Aba*2
  - *a*=7.57 *b*=21.41 *c*=15.13 Å



IR Evans, JSO Evans et al., *JACS*, 138, 25, 8031, 2016.

SXRD: High Resolution

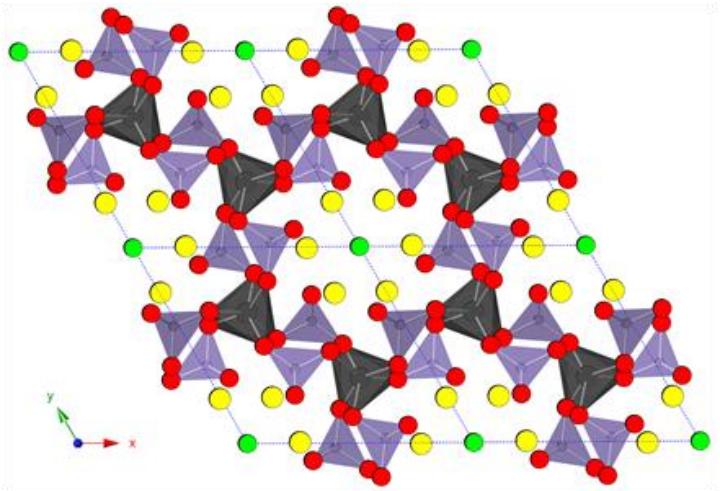
- Example 4: α-$Bi_2Sn_2O_7$
  - Monoclinic *Cc*
  - *a*=7.57 *b*=21.41 *c*=15.13 Å β=125°



IR Evans, JSO Evans et al., *JACS*, 138, 25, 8031, 2016.

SXRD: High Resolution

- Example 5: $Bi_2La_8(GeO_4)_6O_3$
  - Oxide ion conductor
  - Apatite structure type (normally hexagonal)
  - $Bi_2La_8(GeO_4)_6O_3$ triclinic at room temperature

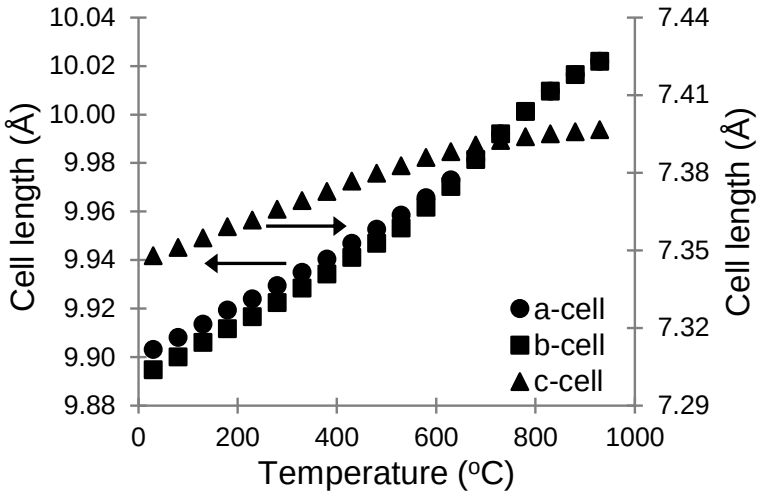


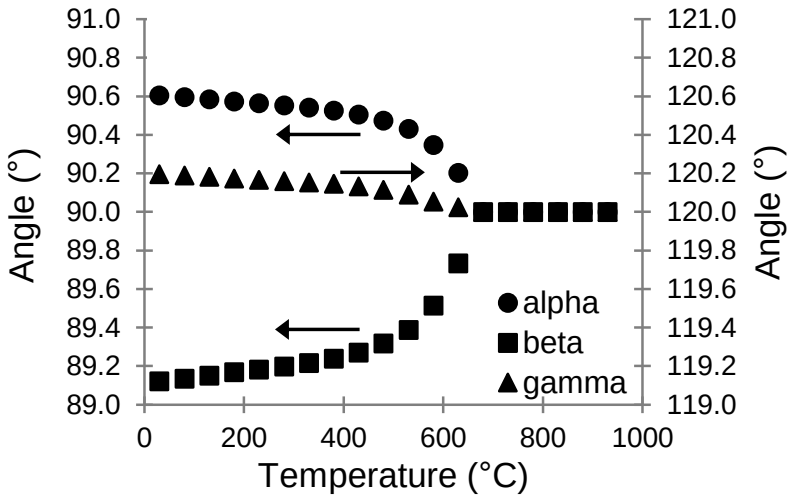
  - Very small unit cell distortions:
    a = 9.90376(10) Å, b = 9.89598(12) Å, c = 7.34622(7) Å
    α = 90.5638(9)°, β = 89.2007(8)°, γ = 120.1412(7)°,

IR Evans et al., *Advanced Functional Materials*, 27, 1605625, 2017.

SXRD: High Resolution

- Example 5: $Bi_2La_8(GeO_4)_6O_3$
  - High-resolution PD beamline, Australian Synchrotron, Melbourne
  - Phase transition to hexagonal above 700°C
  - Unit cell parameters extracted by Rietveld fitting of the data



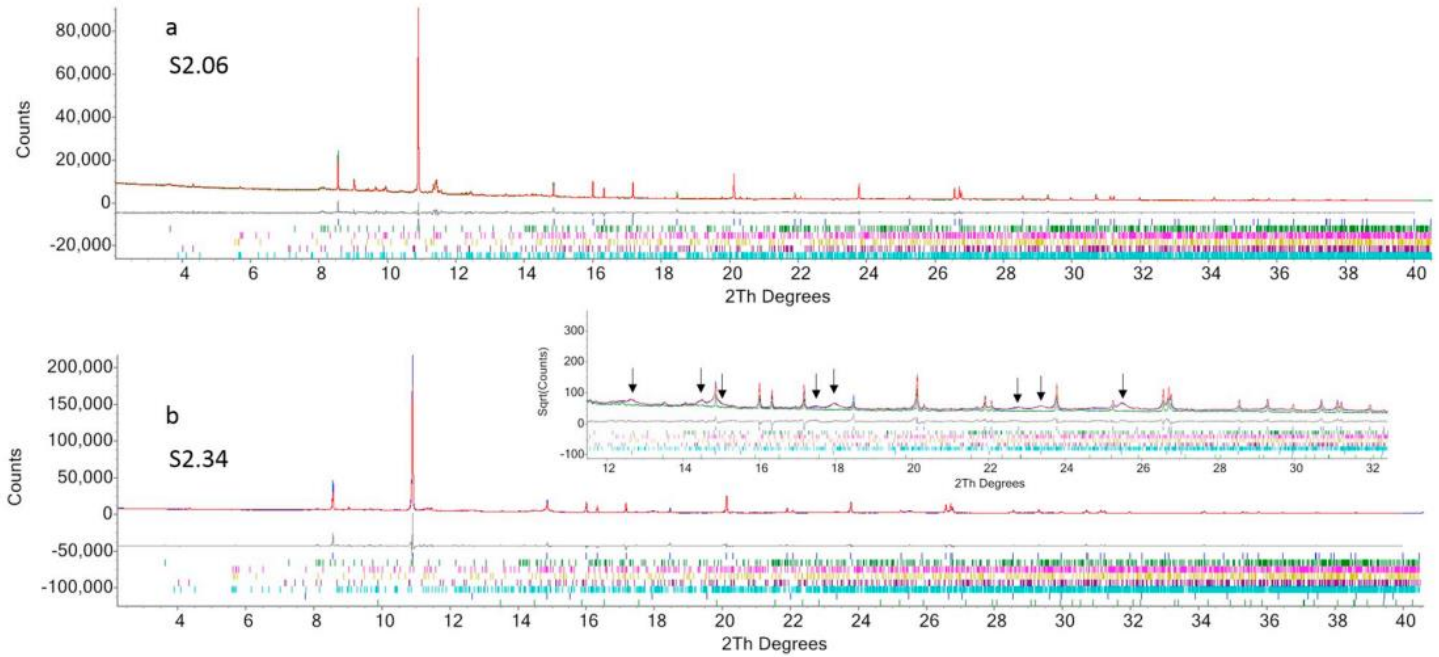


IR Evans et al., *Advanced Functional Materials*, 27, 1605625, 2017.

SXRD: High Intensity and Resolution

- Archaeological pottery (Studenica Monastery)
  - High-resolution PD beamline, Australian Synchrotron, Melbourne

Microchemical Journal 146 (2019) 557–567



S Stojanovic, IR Evans, L Damjanovic-Vasilic et al., *Microchemical Journal*, 146, 557, 2019.

SXRD: High Intensity and Resolution

- Archaeological pottery (Studenica Monastery)
  - High-resolution PD beamline, Australian Synchrotron, Melbourne

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Raman spectroscopy
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Multivariate statistical analysis

ABSTRACT

A collection of 63 pottery shards excavated at the Studenica Monastery, Serbia, originating from two distinct cultural strata (late 12th until the late 13th century, and the 14th and the first half of 15th century) was subject of this work. Mineralogical and chemical composition of body and glaze and production technology of investigated pottery were determined combining optical microscopy, inductively coupled plasma-optical emission and wavelength dispersive X-ray fluorescence spectrometry, Fourier transform infrared and micro-Raman spectroscopy, high-resolution synchrotron powder X-ray diffraction and multivariate statistical analysis. In addition, clay rod with traces of glaze from the kiln found within the Monastery complex was investigated. The firing temperature was estimated at 600–700 °C for the most of cookware and at 800–1000 °C for tableware. Pottery, made of non-calcareous clay, was covered with transparent lead based glaze and copper and iron were used as colorants. Combining results of all used techniques no significant differences in mineralogical and chemical composition among samples from two cultural strata were identified indicating continuous pottery production process from 13th until 15th century in Studenica.

S Stojanovic, IR Evans, L Damjanovic-Vasilic et al., *Microchemical Journal*, 146, 557, 2019.

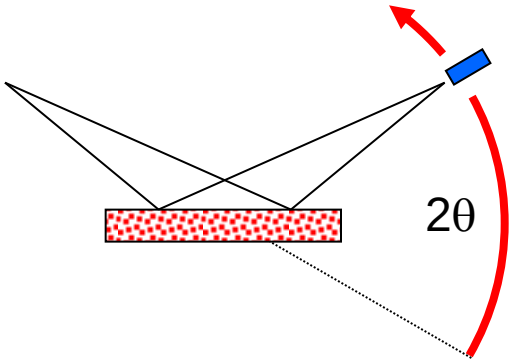
Synchrotron X-ray Diffraction (SXRD)

- Advantages over lab sources
  1. Tunable λ
  2. High intensity
  3. Highly monochromatic λ and highly collimated beam

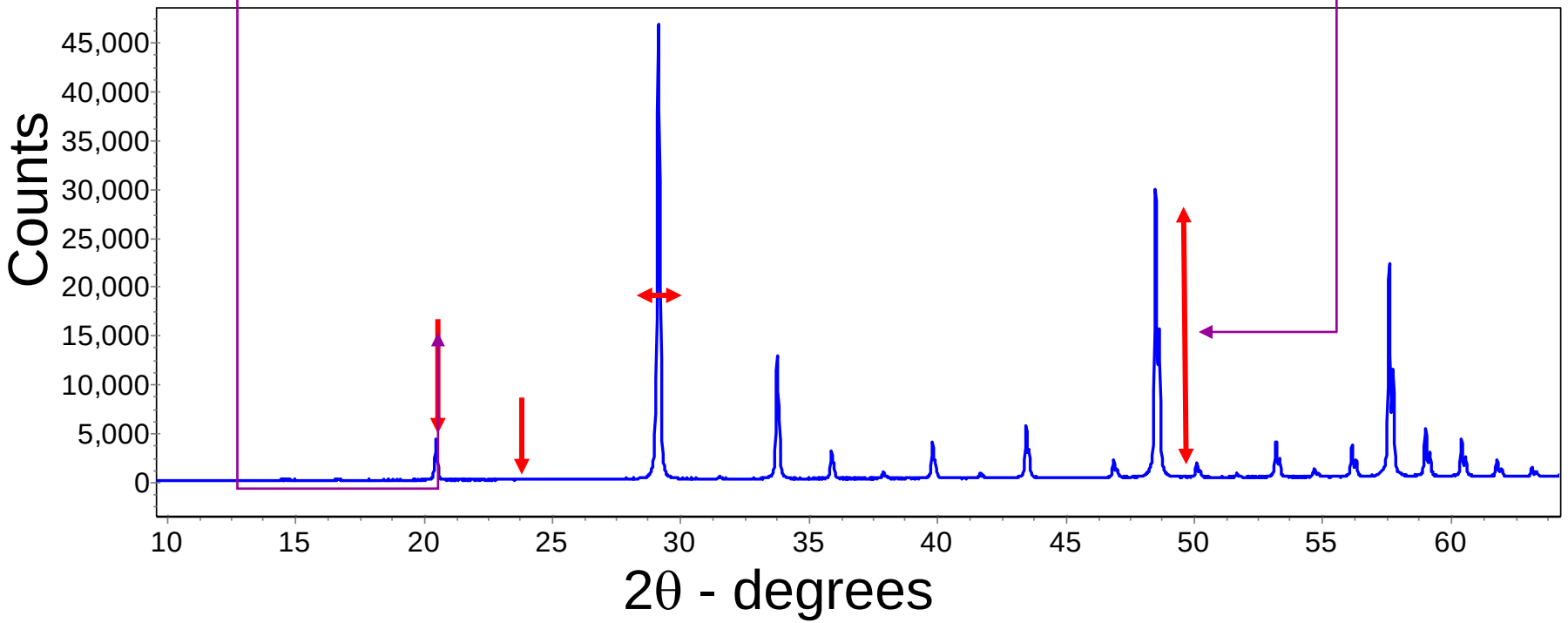
- Disadvantages
  1. Access: proposal, delay, limited beam time, no opportunity to repeat
  2. Lack of control over options and conditions

Information in a Powder Pattern

1. Peak positions determined by size and shape of unit cell – internal structure

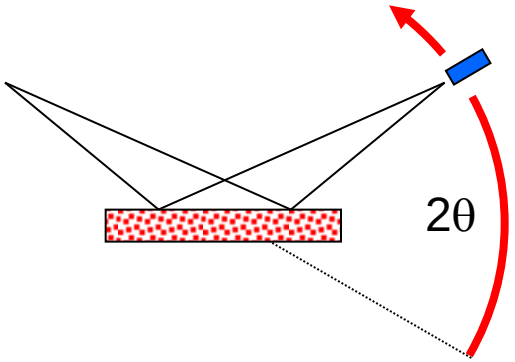


2. Peak Intensities determined by where atoms sit in unit cell – internal structure

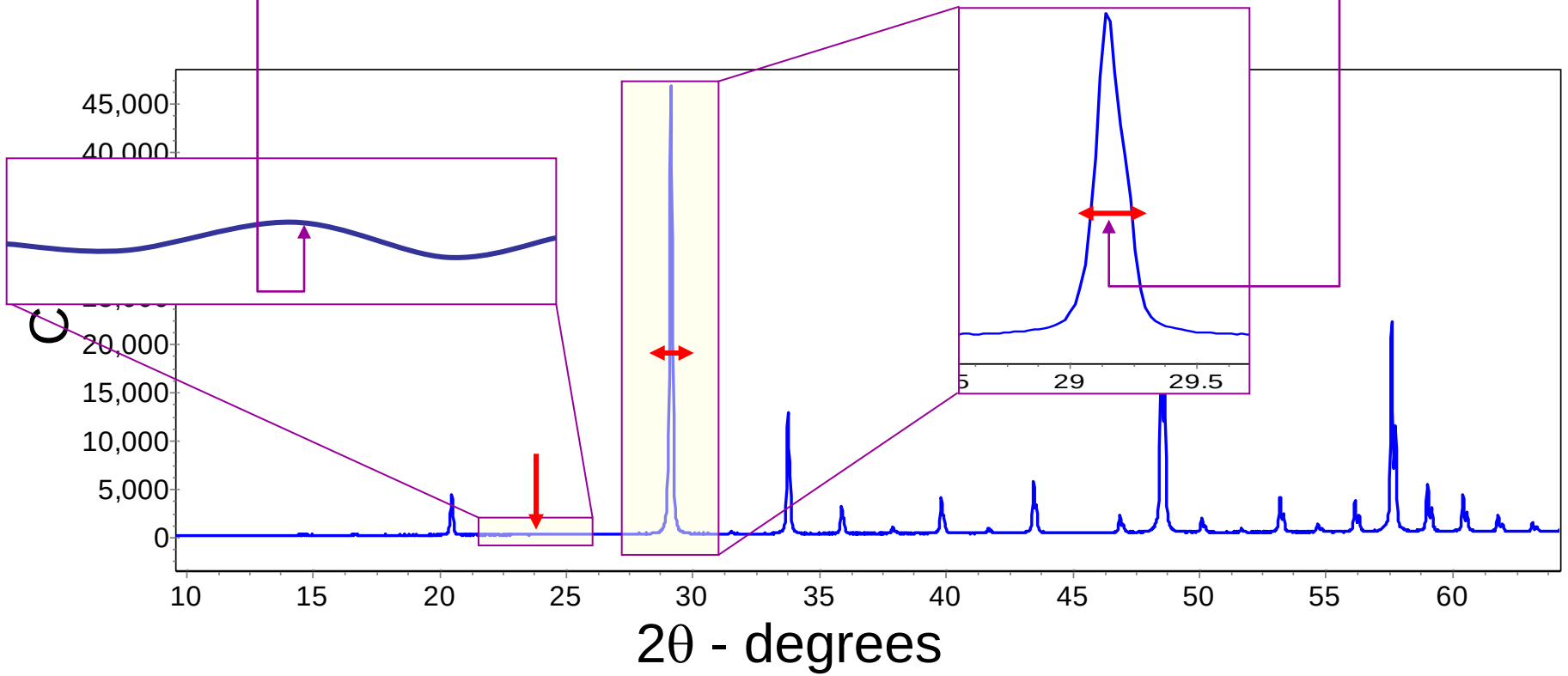


Information in a Powder Pattern

4. Background oscillations may contain information about short range order in material



3. Peak widths determined by size/strain of crystallites - microstructure.



Structure Determination: Typical Output

- Table of determined (refined) structural parameters

Table 1. Structural Parameters for $Bi_8La_{10}O_{27}$ at Room Temperature: a = 12.0640(3) Å, b = 16.3564(4) Å, c = 4.09871(6) Å, and V = 808.77(4) Å^3

atom[a]	site	x	y	z	occ	U_{eq} (Å^2)
Bi1	4e	0.3110(1)	0	0	1	0.009
Bi2	4g	0	0.3310(1)	0	1	0.010
La1	8n	0.3417(2)	0.3257(1)	0	1	0.013
La2	2a	0	0	0	1	0.018
O1	4h	0	0.0888(5)	0.5	1	0.005
O2	4h	0	0.2759(3)	0.5	1	0.016
O3	8n	0.1894(5)	0.0879(3)	0	1	0.024
O4	8n	0.1523(3)	0.2638(3)	0	1	0.010
O5	8n	0.186(1)	0.458(1)	0	0.349(5)	0.036(2)[b]
O6	4h	0	0.32(1)	0.5	0.08(1)	0.036(2)[b]

unit cell parameters

atomic coordinates

atomic displacement parameters (ADPs), or thermal parameters

atomic site occupancies

- From these parameters, conclusions about the atomic connectivity and coordination environments (bond lengths and angles) can be drawn