X-Ray Diffraction

Lecture note-5

Materi Perkuliahan

Pertemuan	Topik	Subtopik	Referensi
1	*Scanning Electron Microscopy (SEM)*		PPT: NTU lecture & MIT lecture Handbook: lihat SAP
2	*Transmission Electron Microscopy (TEM)*		Brent Fultz · James Howe, Transmission Electron Microscopy and Diffractometry of Materials, Springer 2008
3	*X-Ray Diffraction (XRD)-1*	Sinar-X: sumber dan sifat-sifatnya	Y. Waseda et. al. X-Ray Diffraction Crystallography
4	***X-Ray Diffraction (XRD)-2:* Overview Struktur kristal**	**Sel satuan,Bravais lattice Index Miller, d-spacing**	**Y. Waseda et. al. X-Ray Diffraction Crystallography**
5	*X-Ray Diffraction (XRD)-3: Interaksi Sinar-X dan Struktur kristal*	Fenomena difraksi, Hukum Bragg Fenomena scattering yang berpengaruh thd intesitas	Y. Waseda et. al. X-Ray Diffraction Crystallography
6	*X-Ray Diffraction (XRD)-4: Aplikasi difraksi*	Identifikasi senyawa dgn Hanawalt index. Membuat diagram fasa	Y. Waseda et. al. X-Ray Diffraction Crystallography
7	*X-Ray Diffraction (XRD)-5: Aplikasi Difraksi*	Pengenalan texture, pengukuran tegangan sisa	Y. Waseda et. al. X-Ray Diffraction Crystallography

Bragg's law is a simplistic model to understand what conditions are required for diffraction.

$$\lambda = 2d_{hkl} \sin \theta$$
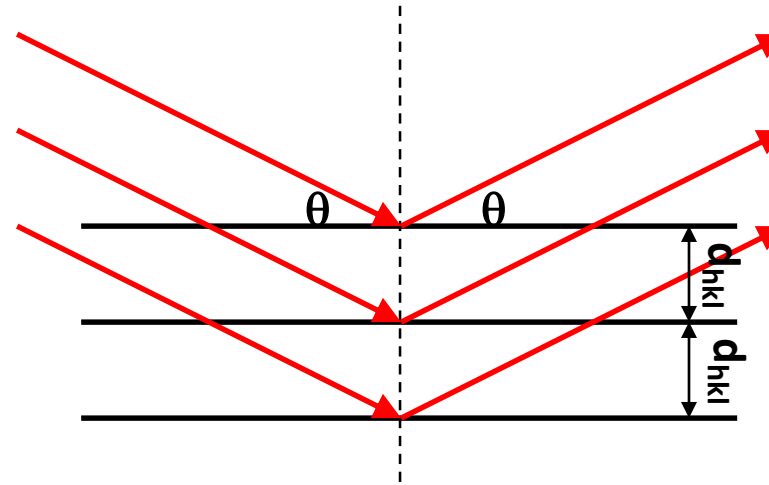
- For parallel planes of atoms, with a space d_{hkl} between the planes, constructive interference only occurs when Bragg's law is satisfied.
  - In our diffractometers, the X-ray wavelength λ is fixed.
  - Consequently, a family of planes produces a diffraction peak only at a specific angle θ.
  - Additionally, the plane normal must be parallel to the diffraction vector
    - Plane normal: the direction perpendicular to a plane of atoms
    - Diffraction vector: the vector that bisects the angle between the incident and diffracted beam
- **The space between diffracting planes of atoms determines peak positions.**
- **The peak intensity is determined by what atoms are in the diffracting plane.**

Jarak antar bidang pada sistem kristal

Table 3.1 Information of plane spacing for seven crystal systems

Cubic	$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$
Tetragonal	$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$
Hexagonal	$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2}$
Trigonal	$\frac{1}{d^2} = \frac{(h^2+k^2+l^2)\sin^2\alpha + 2(hk+kl+hl)(\cos^2\alpha - \cos\alpha)}{a^2(1-3\cos^2\alpha + 2\cos^3\alpha)}$
Orthorhombic	$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
Monoclinic	$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$
Triclinic	$\frac{1}{d^2} = \frac{1}{V^2}(S_{11}h^2 + S_{22}k^2 + S_{23}k^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl)$

On the triclinic system, V is the volume of a unit cell and the coefficients are given below.

$$S_{11} = b^2c^2\sin^2\alpha, \qquad S_{12} = abc^2(\cos\alpha\cos\beta - \cos\gamma),$$

$$S_{22} = a^2c^2\sin^2\beta, \qquad S_{23} = a^2bc(\cos\beta\cos\gamma - \cos\alpha),$$

$$S_{33} = a^2b^2\sin^2\gamma, \qquad S_{13} = ab^2c(\cos\gamma\cos\alpha - \cos\beta)$$

Penentuan Struktur: Sistem Kubik

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

- Analysis of diffraction data is to say "indexing pattern analysis."

- By combining the Bragg condition with the plane spacing for a cubic system, the diffraction peaks with the $\sin^2\theta$ values satisfy the following equation:

$$\frac{\sin^2\theta}{(h^2 + k^2 + l^2)} = \frac{\sin^2\theta}{S} = \frac{\lambda^2}{4a^2}, \quad \text{where } S = h^2 + k^2 + l^2$$

the sum of the square of plane indices, corresponding to the measured diffraction peaks is always an integer and $\lambda^2/4a^2$ is found a constant for any X-ray diffraction pattern.

Another method using the following equation:

$$\frac{4\sin^2\theta}{\lambda^2} = \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

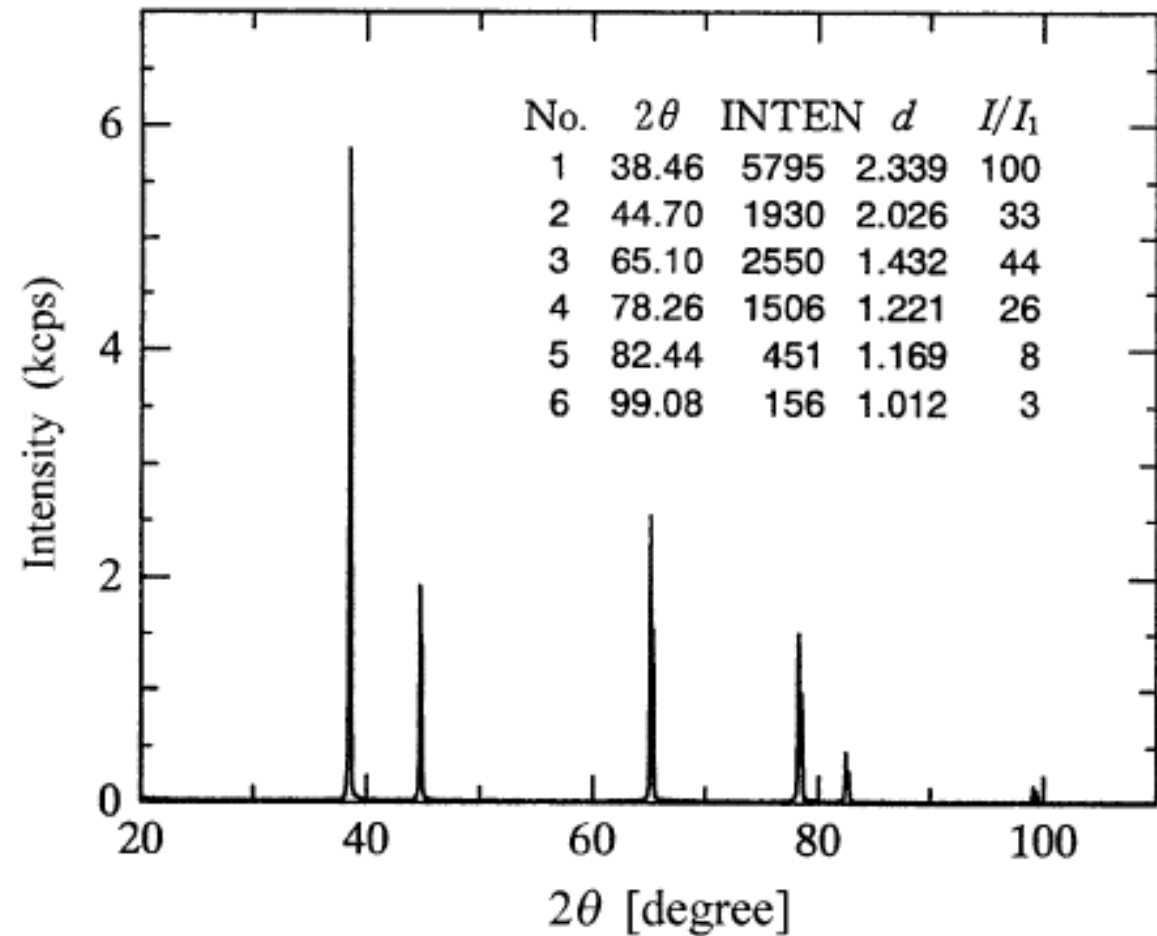# Penentuan Struktur: Sistem Kubik

No.	2θ	INTEN	d	I/I_1
1	38.46	5795	2.339	100
2	44.70	1930	2.026	33
3	65.10	2550	1.432	44
4	78.26	1506	1.221	26
5	82.44	451	1.169	8
6	99.08	156	1.012	3

Fig. 4.4 X-ray diffraction pattern of a metal sample with cubic structure obtained by Cu-Kα radiation

Fig. 4.5 Characteristic sequence of diffraction peaks of four common cubic lattice types together with a hexagonal close-packed lattice
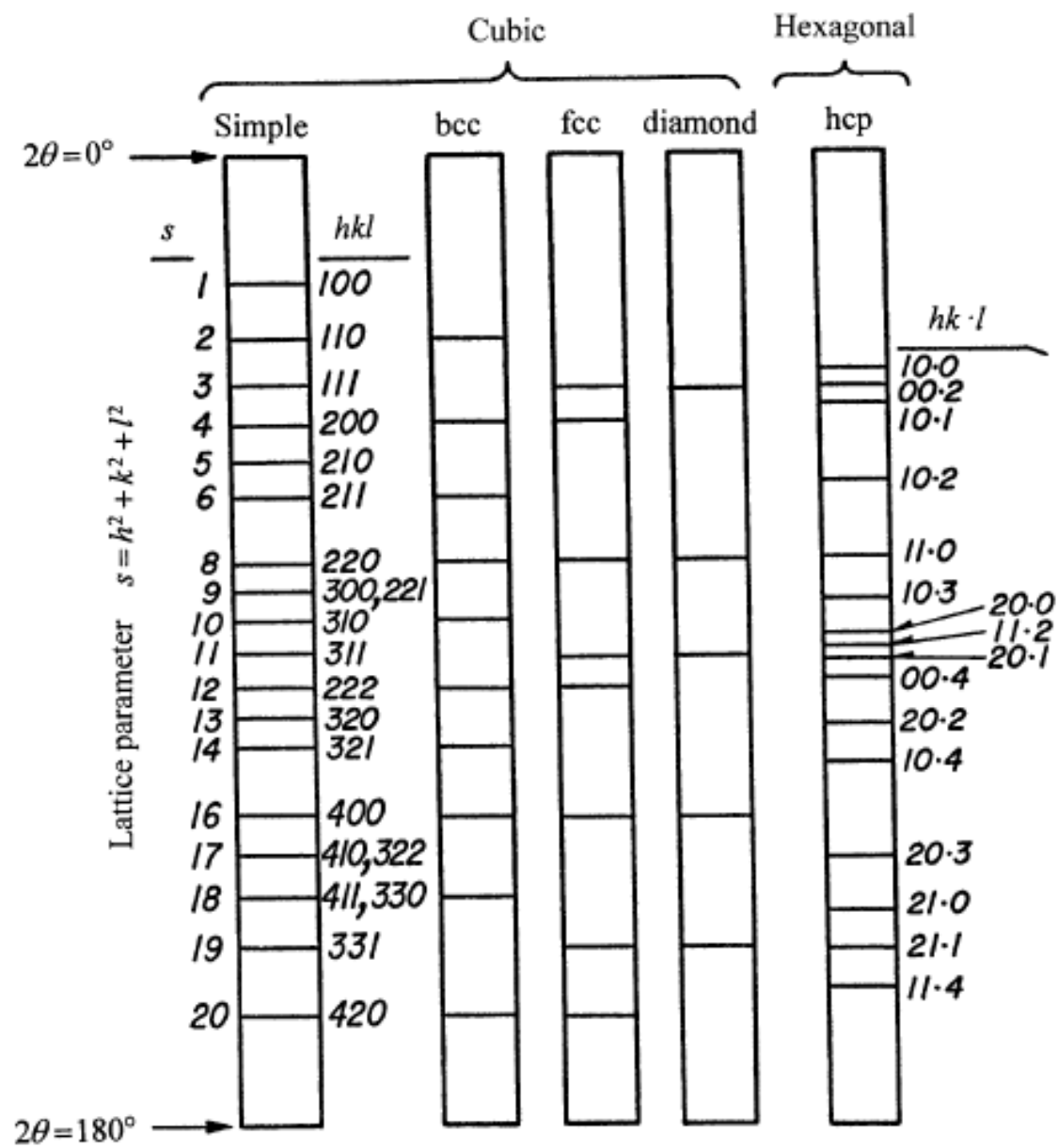
TABLE I. *Selection Rules for Diffraction Peaks in Cubic Systems*

Bravais Lattice	Reflections Present	Reflections Absent
Simple Cubic	All	None
Body-Centered Cubic	$(h+k+l)$ = even	$(h+k+l)$ = odd
Face-Centered Cubic	h,k,l unmixed (either all odd or all even)	h,k,l mixed

DIFRACTOMETER SINAR X

- X-ray source is generally fixed.

- Rotate sample and detector to adjust θ/2θ.

- On instruments such as our Bruker D8 and Philips MPD, the source and detector move while the sample remains stationary.
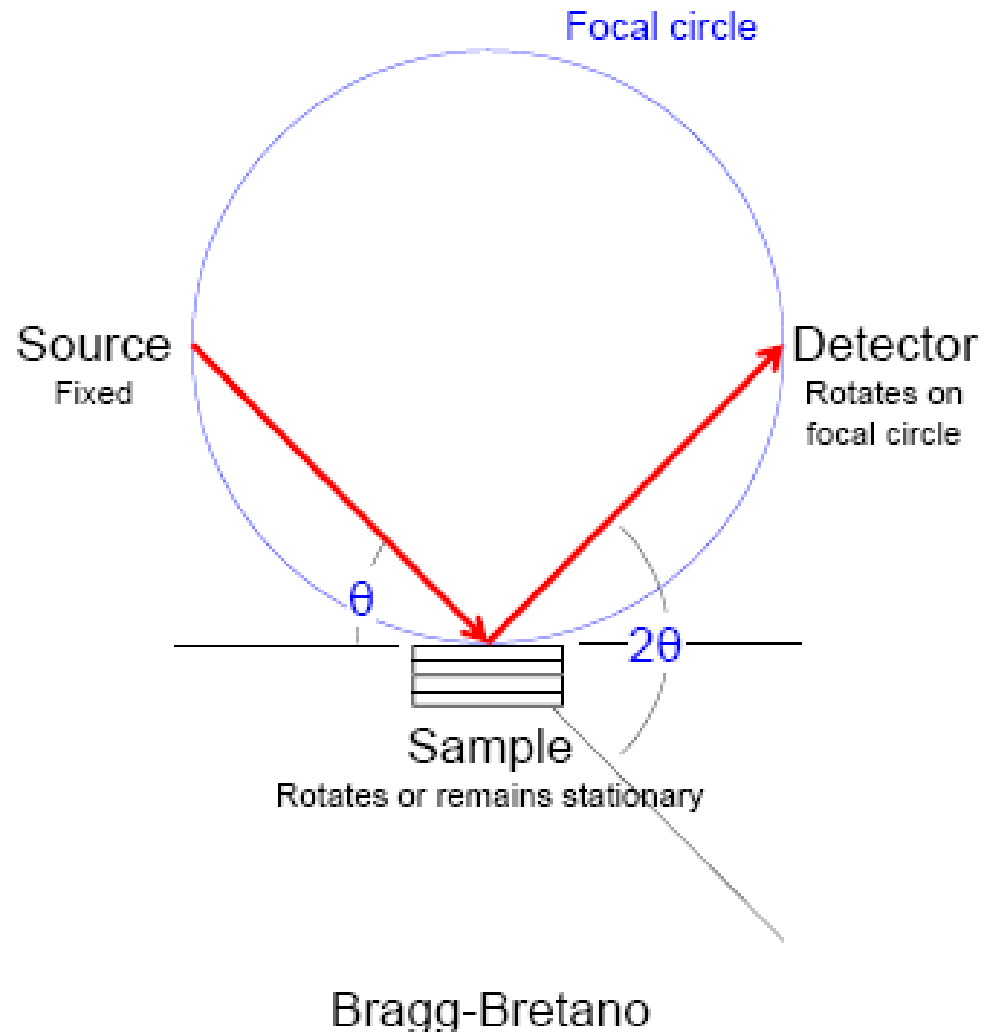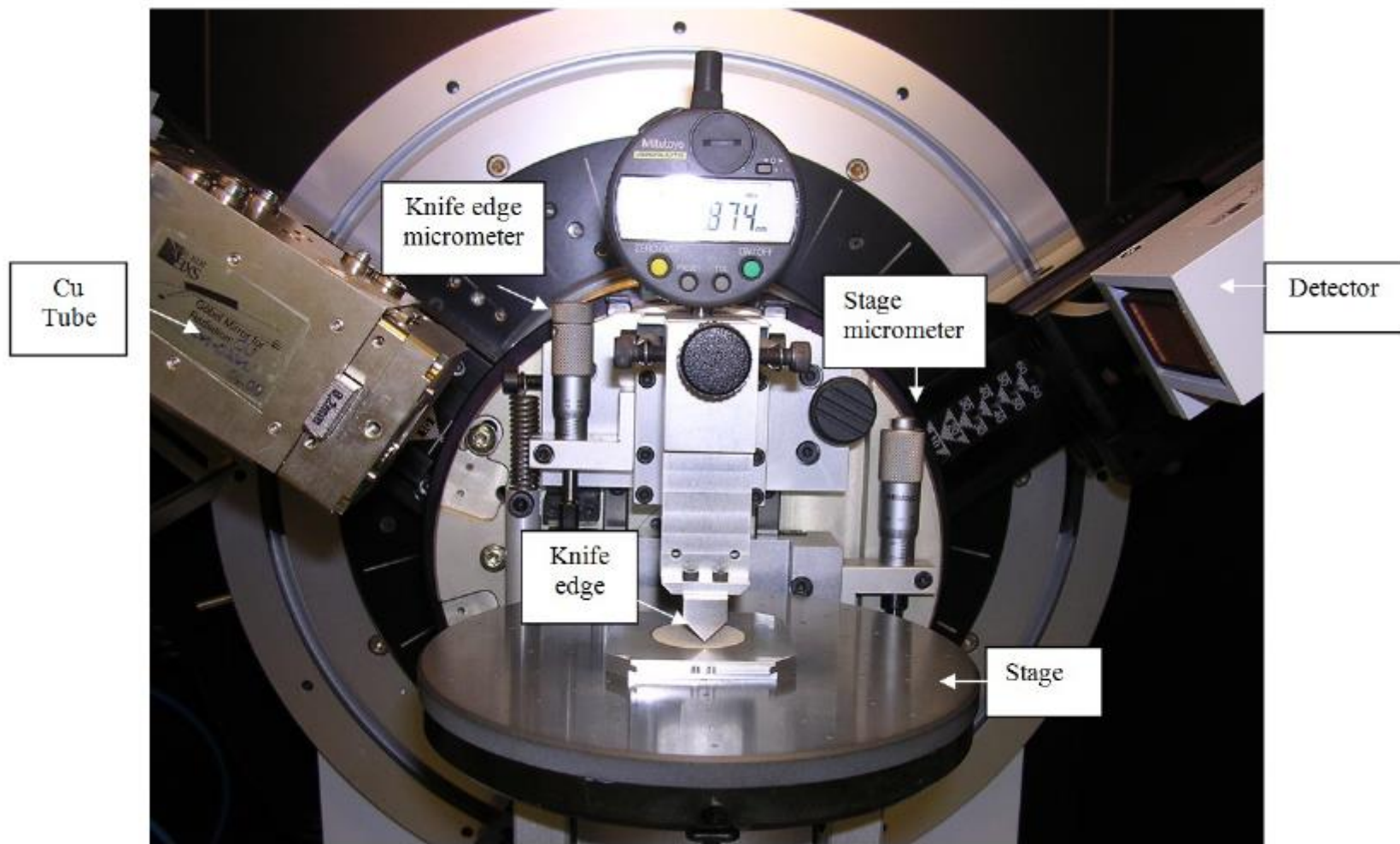
Focal circle

Source
Fixed

Detector
Rotates on
focal circle

θ

2θ

Sample
Rotates or remains stationary

Bragg-Bretano

An X-Ray Diffraction machine

KOMPONEN UTAMA MESIN XRD

1. sumber penghasil sinar X

2. optik primer ; mengatur sinar X yg akan menuju sample.

3. sample holder & stage ; tempat sample di simpan, holder bisa utk serbuk, bulk, film tipis.

4. optik sekunder; menerima sinar X yg di difraksikan sample.

5. detektor; mendeteksi sinar X yg didifraksikan sampel

The X-ray beam produced by the X-ray tube is divergent. Incident-beam optics are used to limit this divergence

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

- X Rays from an X-ray tube are:
  - divergent
  - contain multiple characteristic wavelengths as well as Bremmsstrahlung radiation
- neither of these conditions suit our ability to use X rays for analysis
  - the divergence means that instead of a single incident angle q, the sample is actually illuminated by photons with a range of incident angles.
  - the spectral contamination means that the sample does not diffract a single wavelength of radiation, but rather several wavelengths of radiation.
    - Consequently, a single set of crystallographic planes will produce several diffraction peaks instead of one diffraction peak.
- Optics are used to:
  - limit divergence of the X-ray beam
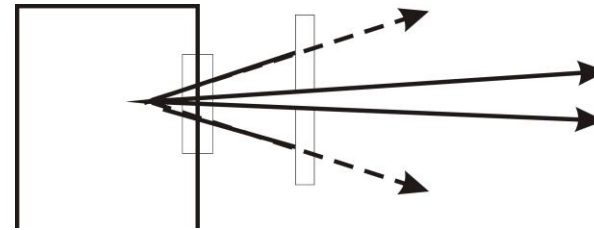 - refocus X rays into parallel paths
  - remove unwanted wavelengths

Bragg-Brentano Diffractometer

Detector

Kβ filter

Flat powder sample

X-ray tube
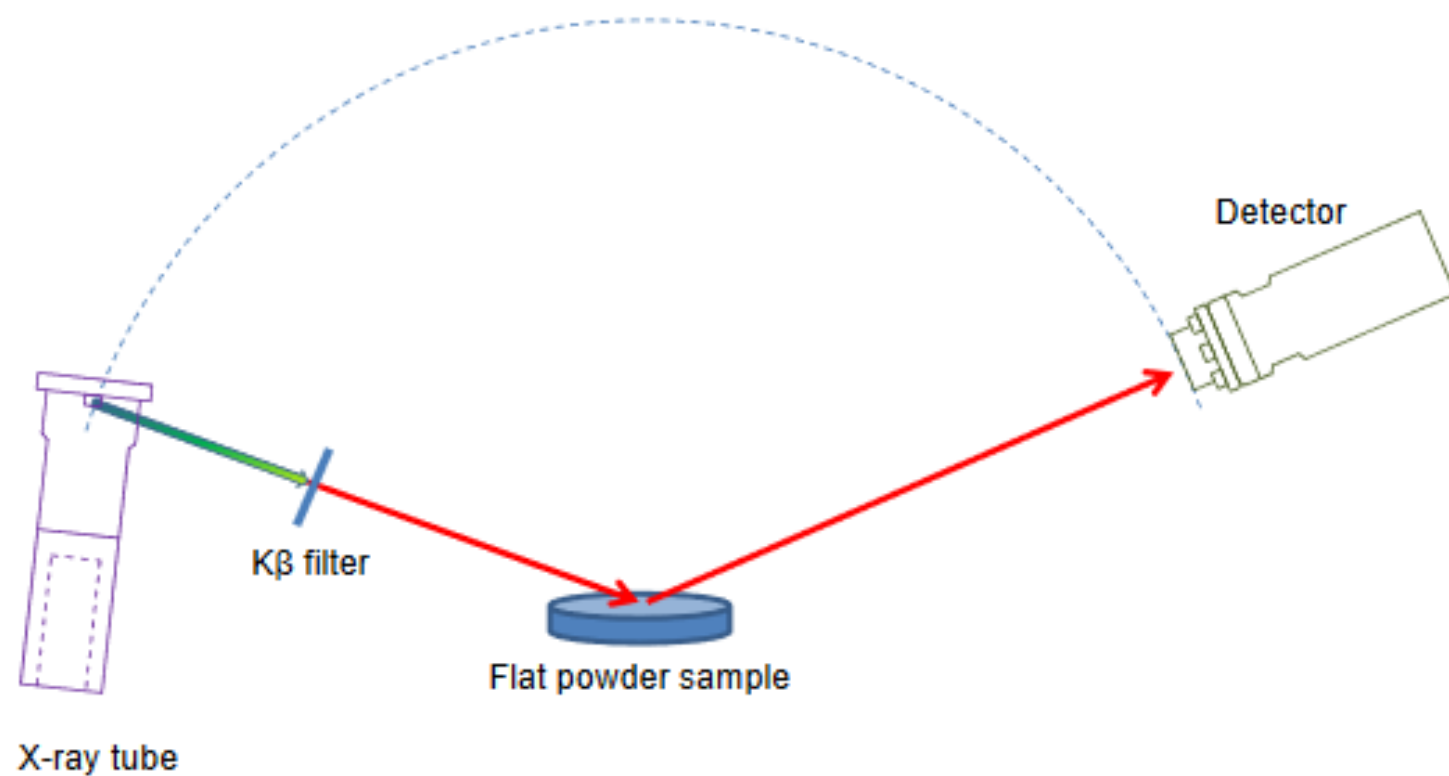
More optical elements are required
to control the beam pattern.

Divergence slits are used to limit the divergence of the incident X-ray beam.

- The slits block X-rays that have too great a divergence.

- The size of the divergence slit influences peak intensity and peak shapes.

- Narrow divergence slits:
  - reduce the intensity of the X-ray beam
  - reduce the length of the X-ray beam hitting the sample
  - produce sharper peaks
    - the instrumental resolution is improved so that closely spaced peaks can be resolved.

Other optics:

- limit divergence of the X-ray beam
  - Divergence limiting slits
  - Parallel plate collimators
  - Soller slits
- refocus X rays into parallel paths
  - "parallel-beam optics"
  - parabolic mirrors and capillary lenses
  - focusing mirrors and lenses
- remove unwanted wavelengths
  - monochromators
  - Kβ filters
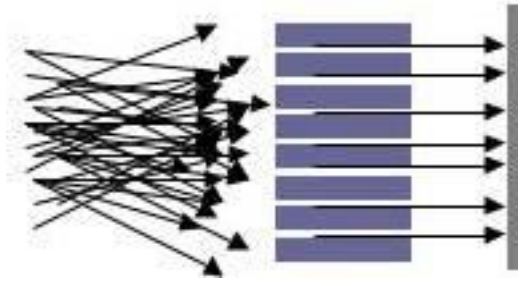
Parallel Plate Collimator & Soller Slits block divergent X-rays, but do not restrict beam size like a divergent slit
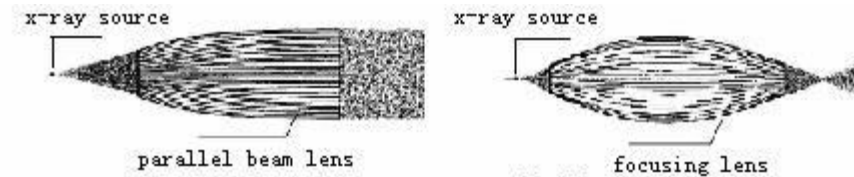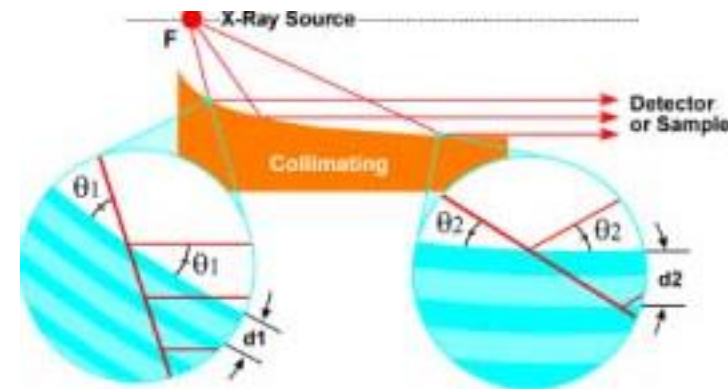

Göbel Mirrors and capillary lenses collect a large portion of the divergent beam and refocus it into a nearly parallel beam

Monochromators remove unwanted wavelengths of radiation from the incident or diffracted X-ray beam.

- Diffraction from a crystal monochromator can be used to select one wavelength of radiation and provide energy discrimination.

- An incident-beam monochromator might be used to select only Ka1 radiation for the tube source.

- A diffracted-beam monochromator, such as on the Rigaku RU300, may be used to remove fluoresced photons, Kb, or W-contimination photons from reaching the detector.
    - Without the RSM slit, the monochromator removes ~75% of unwanted wavelengths of radiation.
    - When the RSM slit is used, over 99% of the unwanted wavelengths of radiation can be removed from the beam.
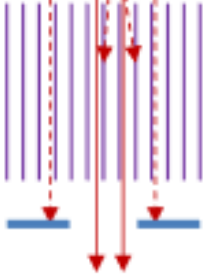
Beam Divergence

Limiting vertical divergence
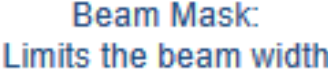with a «divergence slit» (DS)
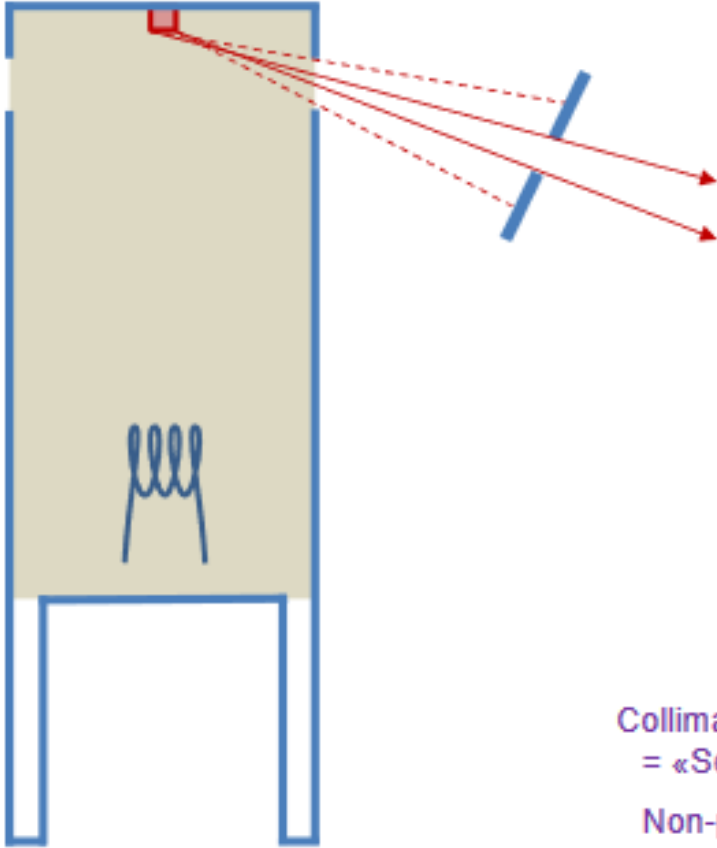
Limiting horizontal divergence
with a «Collimator»
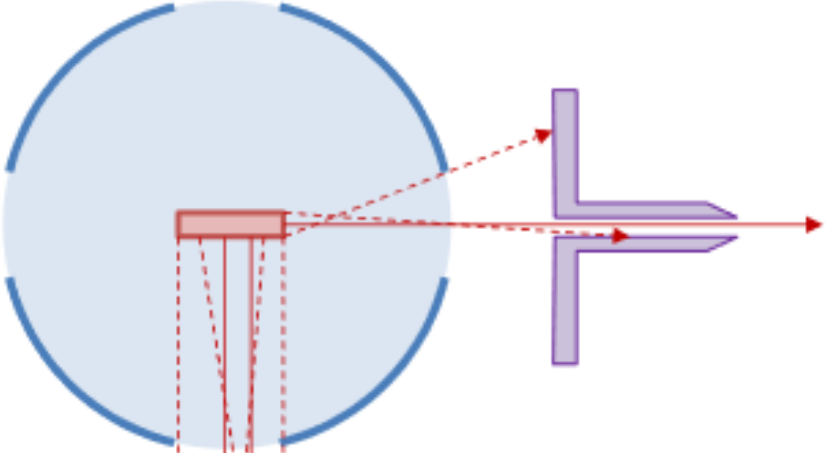
Collimator for Line focus
= «Soller Slits» (SS):

Non-parallel rays are
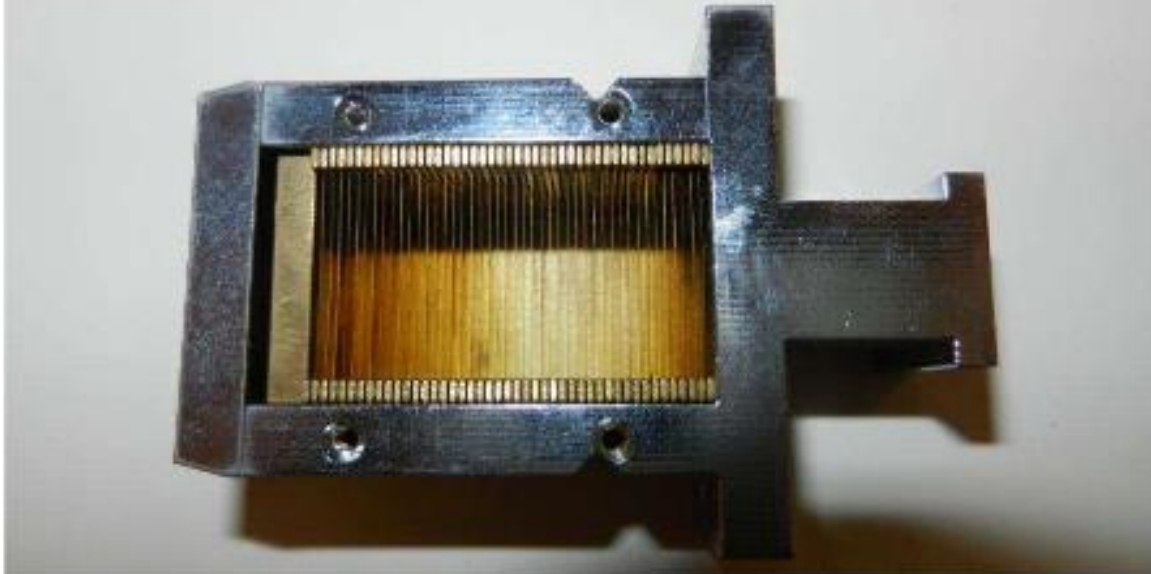blocked by lamellae

Beam Mask:
Limits the beam width

Beam Divergence

Divergence Slit

Soller Slit

Beam Masks
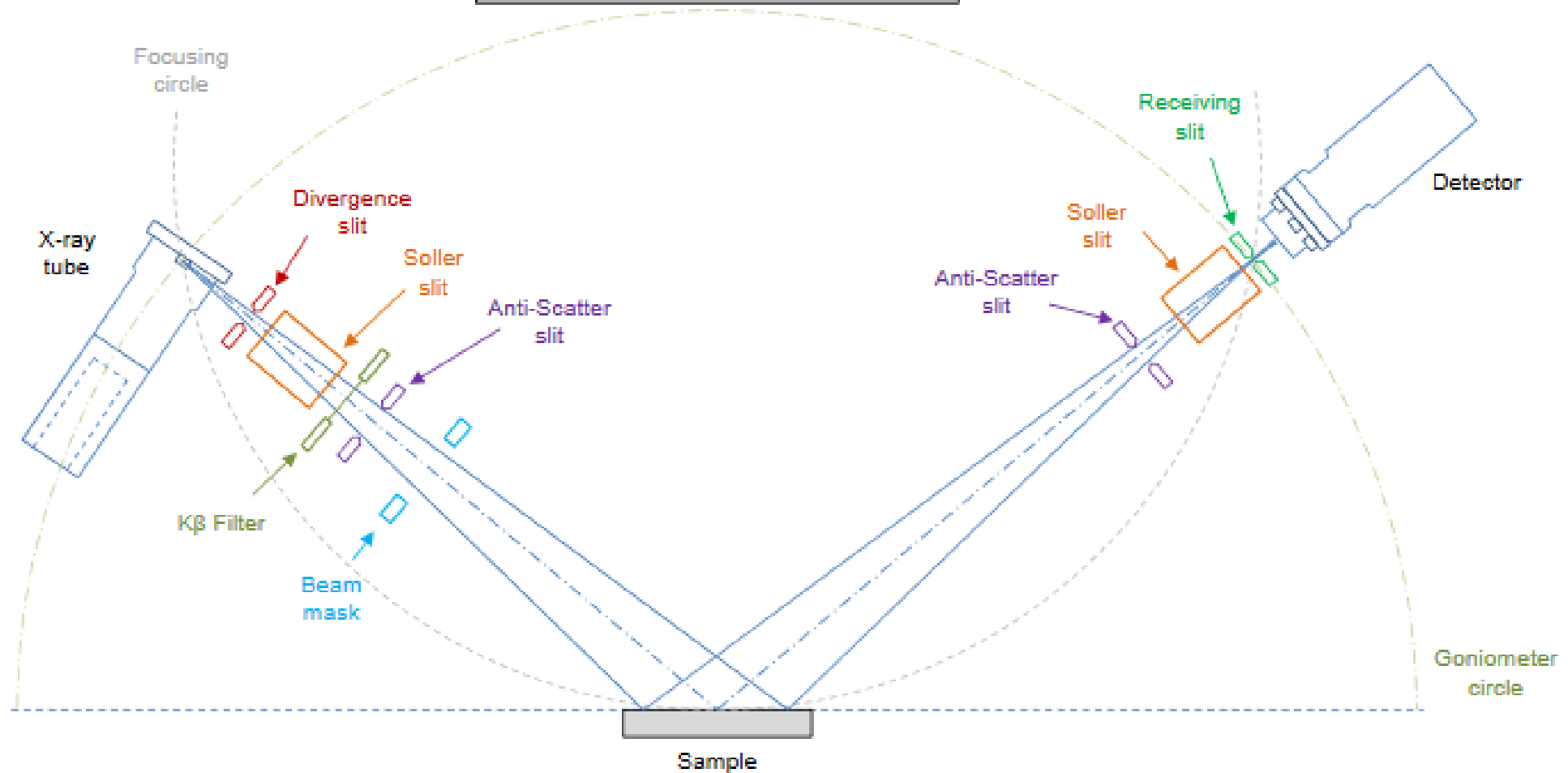
Primary Optics – Soller Slits
Axial Divergence

Functions :
Primary Optics – Divergence Slit

5° 3°

- Limits height divergence, thus controls illuminated sample surface

- Reduces height divergence thereby narrows peak shape

X-Ray beam

Specimen
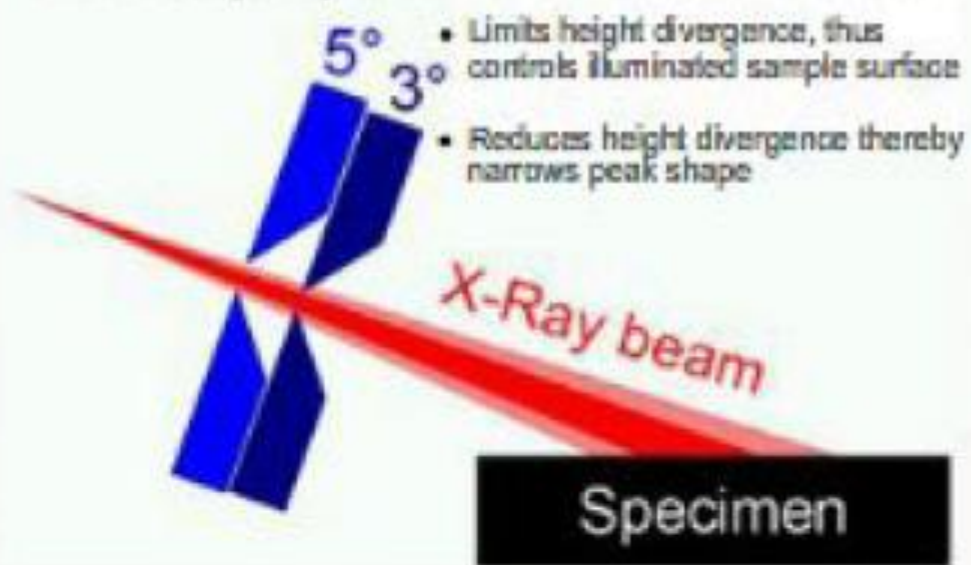
Primary Optics – Soller Slits
Peak Asymmetry

Reflection at $2\Theta = 18°$
no soller slits

6° soller slits
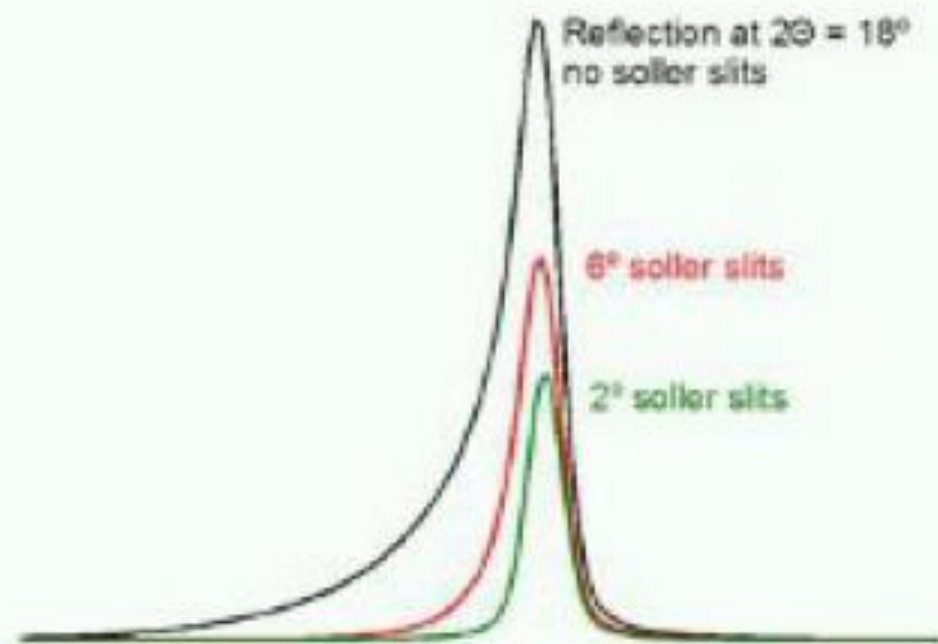
2° soller slits

Optimum Settings: Divergence Slit
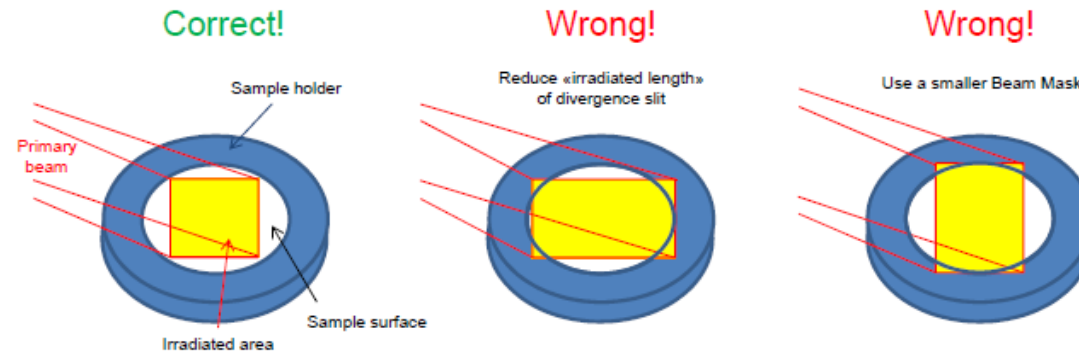
Optical Element	Effect	Too Small	Too Large
Divergence Slit	Adjusts beam length on the sample	Loss of intensity	Beam spills over sample
Soller Slit	Reduces peak asymmetry	Loss of intensity, Better resolution	More asymmetry, Less resolution
Anti-Scatter Slit	Reduces background signal	Loss of intensity	High background
Beam Mask	Adjusts beam width on the sample	Loss of intensity	Beam spills over sample
~~Receiving Slit~~	~~Adjusts peak width / resolution~~	~~Loss of intensity, Better resolution~~	~~Loss of resolution, Higher intensity~~
Kβ Filter	Reduces Kβ peaks	-	-
Graphite Monochromator	Eliminates Kβ peaks	-	-

Detectors

- point detectors
  - observe one point of space at a time
    - slow, but compatible with most/all optics
  - scintillation and gas proportional detectors count all photons, within an energy window, that hit them
  - Si(Li) detectors can electronically analyze or filter wavelengths
- position sensitive detectors
  - linear PSDs observe all photons scattered along a line from 2 to 10° long
  - 2D area detectors observe all photons scattered along a conic section
  - gas proportional (gas on wire; microgap anodes)
    - limited resolution, issues with deadtime and saturation
  - CCD
    - limited in size, expensive
  - solid state real-time multiple semiconductor strips
    - high speed with high resolution, robust

- selain tampilan kurva intensitas vs 2θ (point detector) , pola difraksi sinar x juga bisa ditampilkan dalam bentuk titik (line detector).
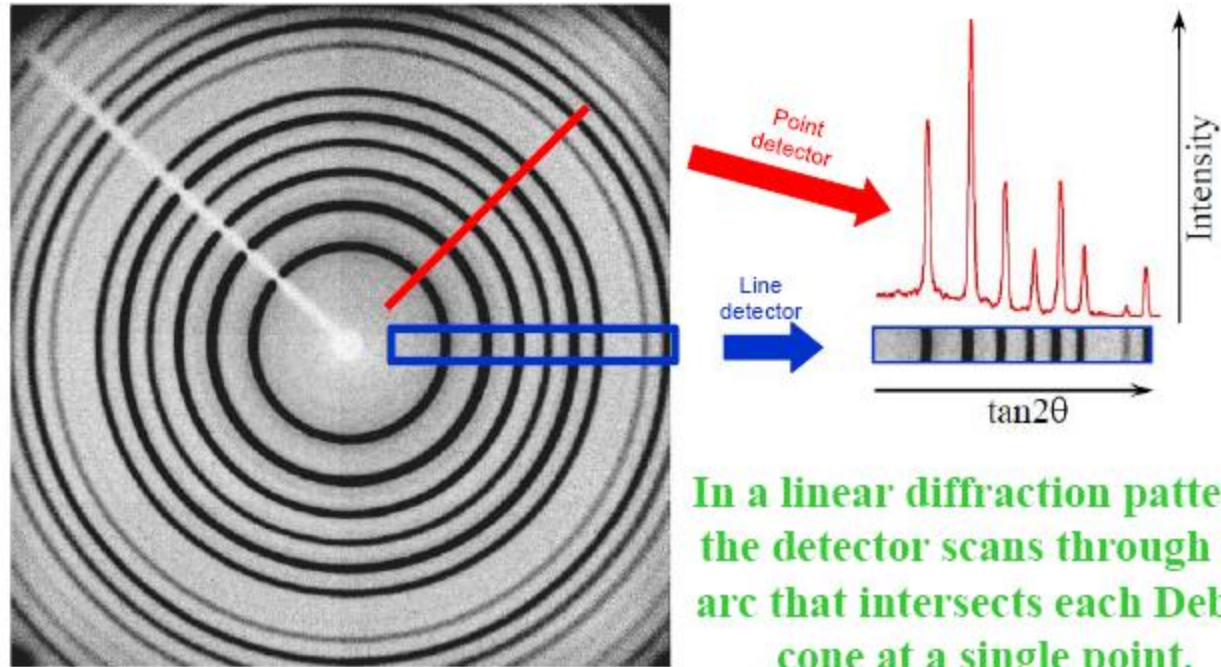
Figure 8.4

PARAMETER PADA MESIN XRD

- scan range; sudut scan awal dan akhir (mis; dari 10 ke 80°)
- scan speed; kecepatan scan, semakin lambat semakin baik pola difraksi yg dihasilkan.
- power, terdiri dari tegangan dan arus, biasanya 40 kv, 30 ma.
- step width
- slit width, mengatur intensitas dan resolusi sinar x

The diffraction pattern consists of a record of photon intensity versus detector angle 2θ.

- The position, intensity, width, and shape of the observed diffraction peaks tells us about the crystal structure and, in some cases, microstructure of the sample.
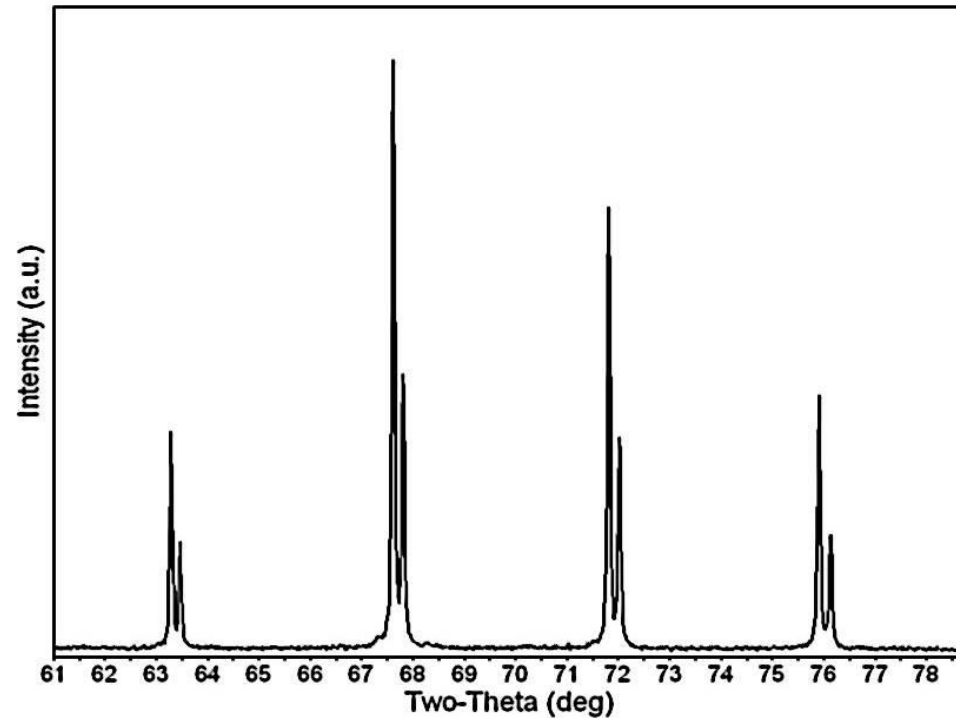
A single crystal specimen in a Bragg-Brentano diffractometer would produce only one family of peaks in the diffraction pattern.
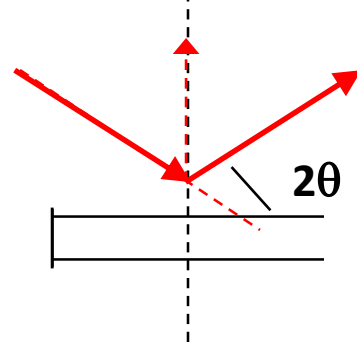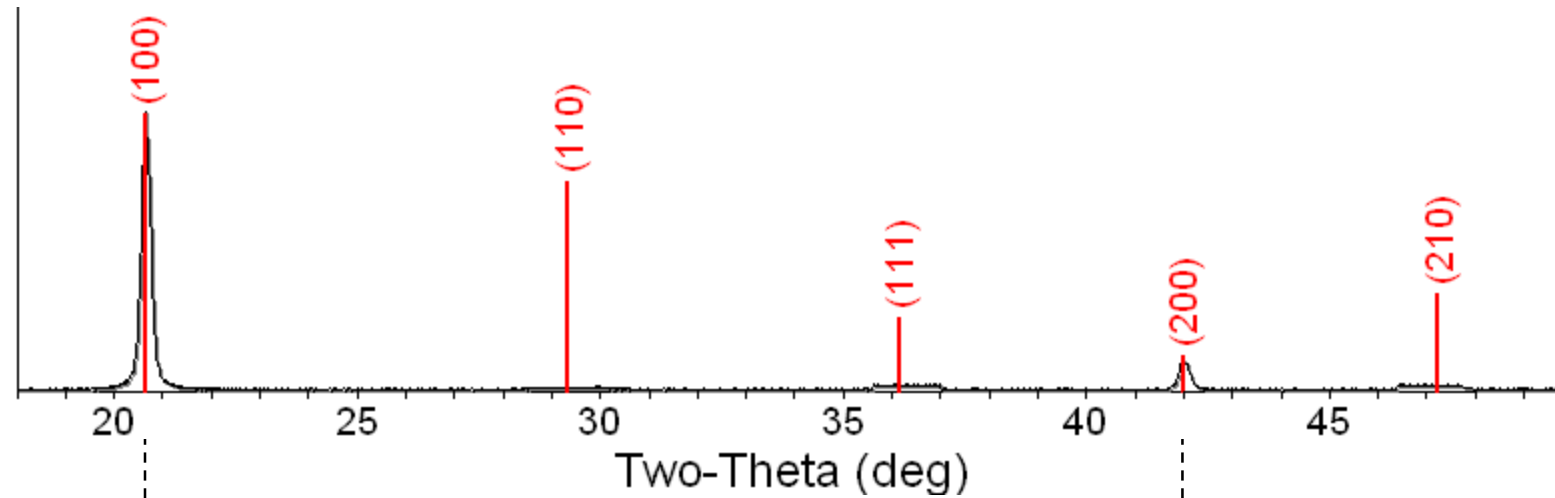
At 20.6 °2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.
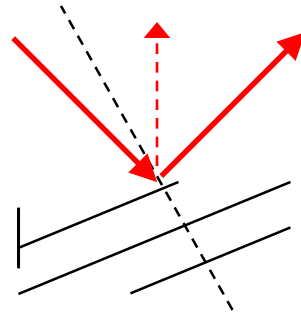
The (110) planes would diffract at 29.3 °2θ; however, they are not properly aligned to produce a diffraction peak (the perpendicular to those planes does not bisect the incident and diffracted beams). Only background is observed.
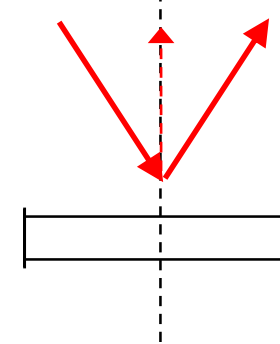
The (200) planes are parallel to the (100) planes. Therefore, they also diffract for this crystal. Since d_{200} is ½ d_{100}, they appear at 42 °2θ.

A polycrystalline sample should contain thousands of crystallites.
All diffraction peaks should be observed.
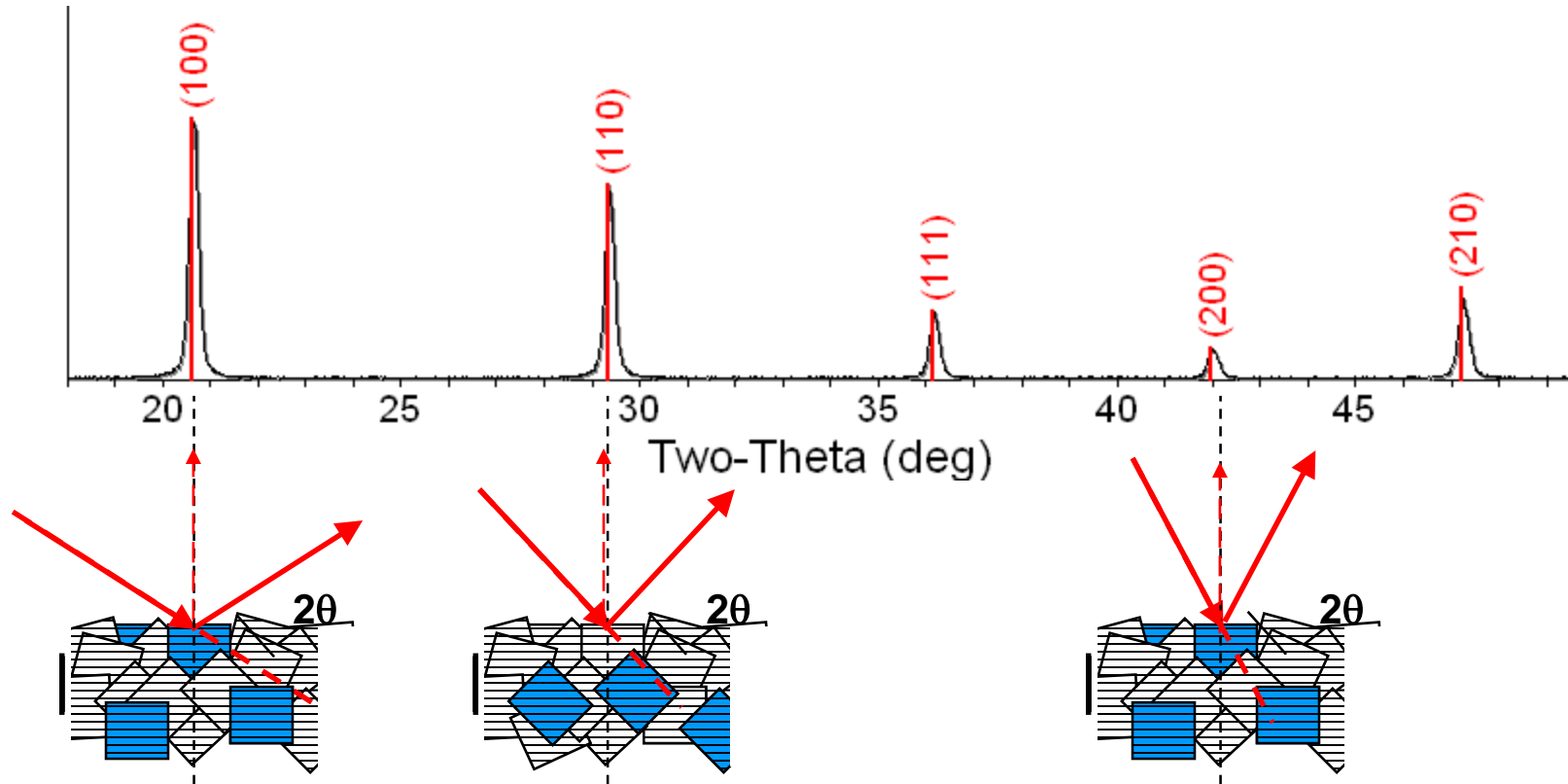
- For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract (the plane perpendicular bisects the incident and diffracted beams).

INTERPRETASI POLA DIFRAKSI

- umumnya pola difraksi ditampilkan dalam grafik intensitas vs 2θ.

- untuk analisis, pola difraksi lebih baik di laporkan dalam grafik/tabel intensitas relatif vs d_{hkl}.

- d_{hkl} bisa di hitung dari data 2θ dengan menggunakan hukum bragg.

- intensitas relatif di hitung dgn cara membagi intensitas absolut oleh intensitas maksimum.

- data d_{hkl} dan intensitas relatif yg dihitung, kemudian diurutkan berdasarkan nilai intensitas yg tertinggi.

Raw Data

Position [°2θ]	Intensity [cts]
25.2000	372.0000
25.2400	460.0000
25.2800	576.0000
25.3200	752.0000
25.3600	1088.0000
25.4000	1488.0000
25.4400	1892.0000
25.4800	2104.0000
25.5200	1720.0000
25.5600	1216.0000
25.6000	732.0000
25.6400	456.0000
25.6800	380.0000
25.7200	328.0000

[DEMO08.MDI] Demo08: Corundum

00-010-0173> Corundum - Al_2O_3

Intensity(Counts) vs Two-Theta (deg)
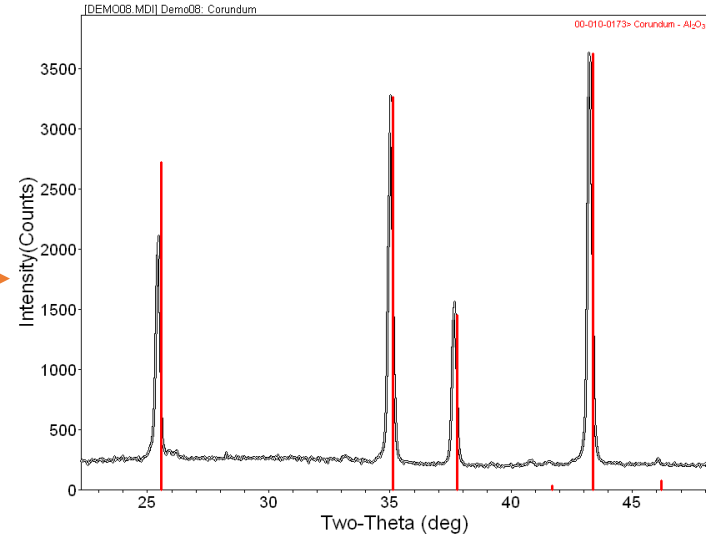
Reduced dI list

hkl	d_{hkl} (Å)	Relative Intensity (%)
{012}	3.4935	49.8
{104}	2.5583	85.8
{110}	2.3852	36.1
{006}	2.1701	1.9
{113}	2.0903	100.0
{202}	1.9680	1.4

What can we do with XRD?

- Identify phase composition
- Measure unit cell lattice parameters
- Estimate crystallite size, microstrain, and defect concentration
- Measure residual stress
- Measure texture and/or epitaxy
- Evaluate thin film quality
- Measure multilayer thin film thickness, roughness, and density
- Determine orientation of single crystals
- Solve or refine crystal structures
- Analyze ordered meso- and nanostructures

Mengapa menggunakan XRD?

- Powder XRD is a rapid method that can be used to routinely assess the nature of a sample.

- Can be used for **qualitative phase ID** – What is in the sample?

  And **quantitative phase analysis**. How much is in the sample?

- Each crystalline phase has a unique powder diffraction pattern

- You can distinguish between mixtures and compounds as the diffraction method is sensitive to structure not just composition

- The powder pattern for the spinel $MgAl_2O_4$ looks different from the powder pattern of a MgO, Al_2O_3 mixture

- You can distinguish between different polymorphic forms of the same compound

The diffraction pattern of every phase is a unique 'fingerprint'
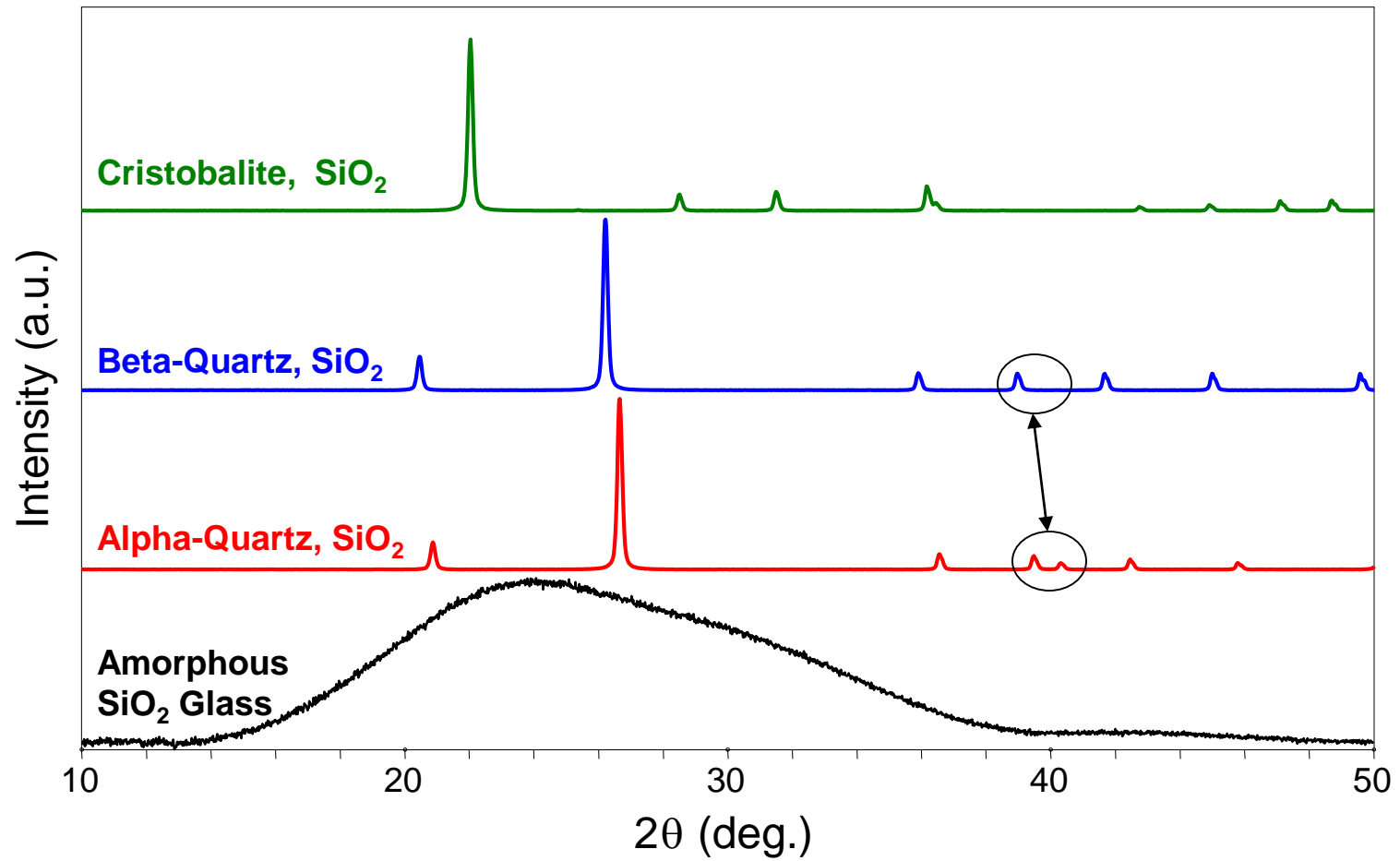
Phase ID is often used for Quality Control and Analyses of Processes

- what did I make?

- did I make what I was trying to make?

- are my raw materials pure?

In the example below, the nanocrystalline Y_2O_3 did not match the reference pattern for yttria
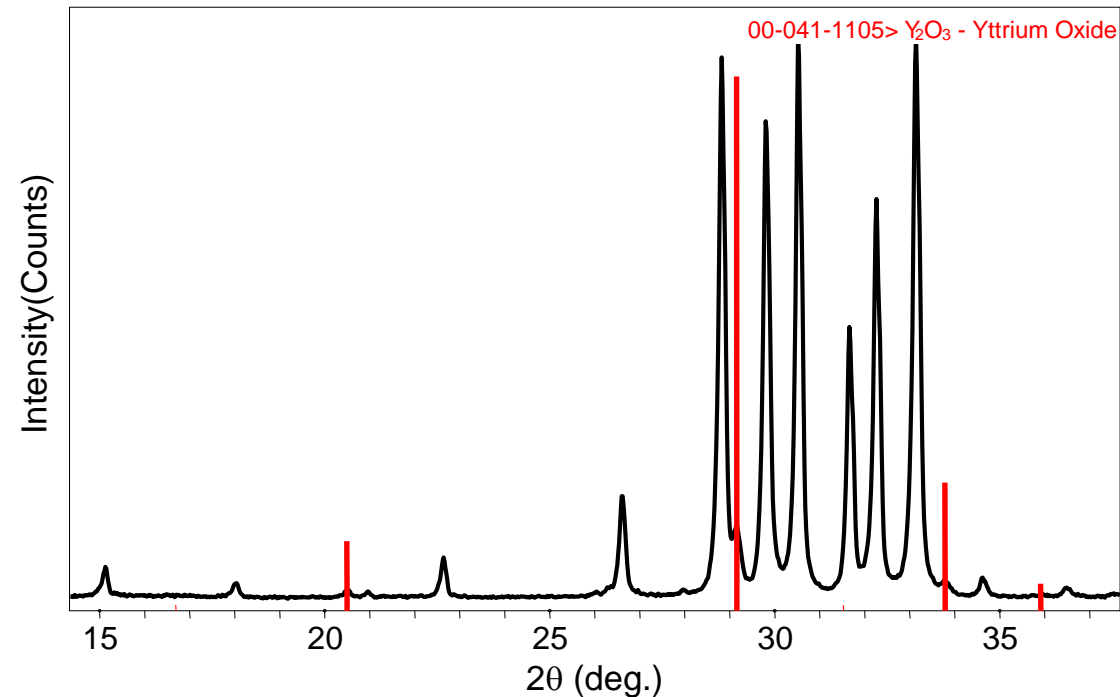
Not only can the PDF provide phase matching, but it can also be a useful data-mining source

- the sample contained a large fraction of monoclinic Y_2O_3

- the PDF card pointed to a reference describing this as a metastable phase previously observed only in thin films of Y_2O_3

B. Chivas and T.F. Morse, Boston University
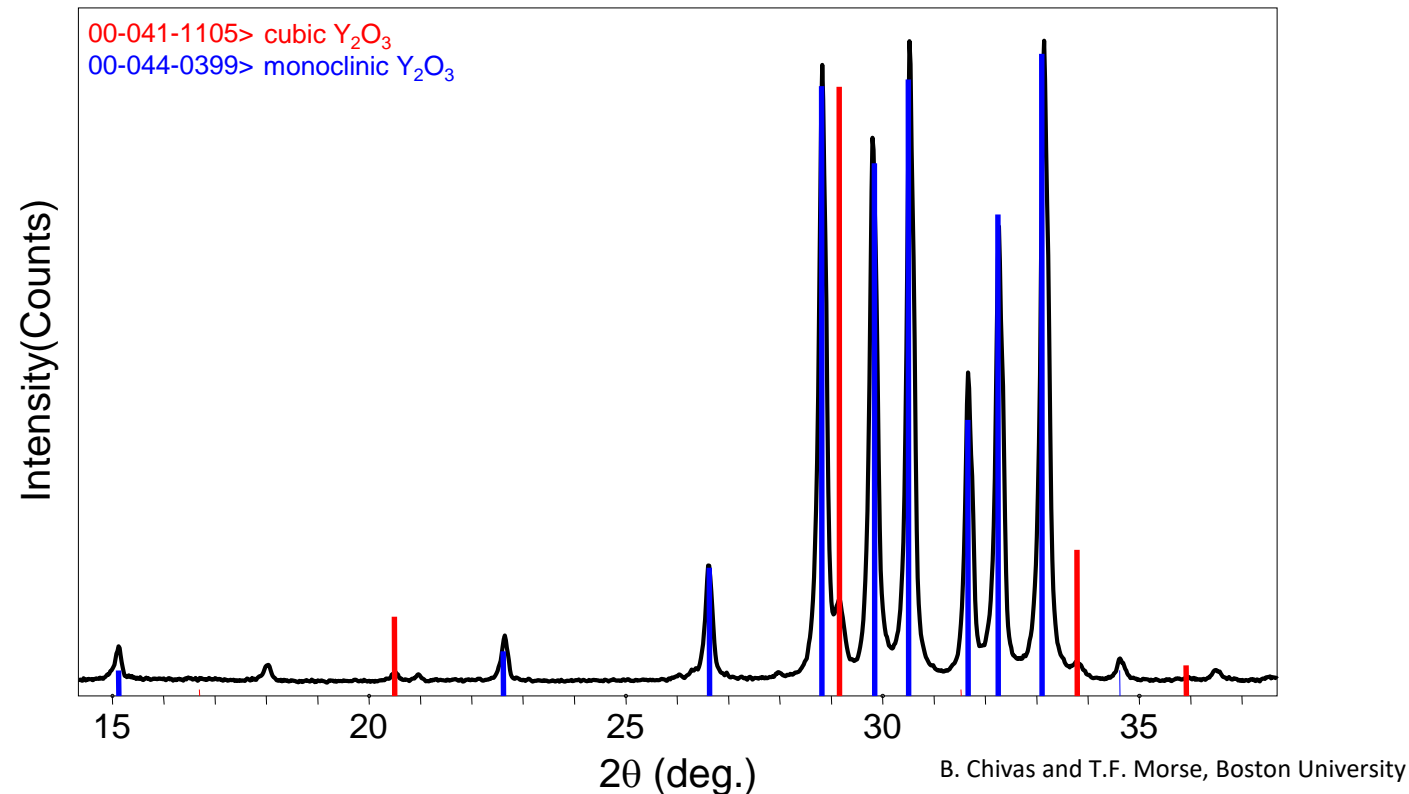
We can use these phase analysis techniques to study reactions *ex situ*

- we revisit the sample of nanocrystalline Y_2O_3, now comparing the results of annealing the original sample

- we see that annealing converted all of the monoclinic Y_2O_3 into cubic Y_2O_3
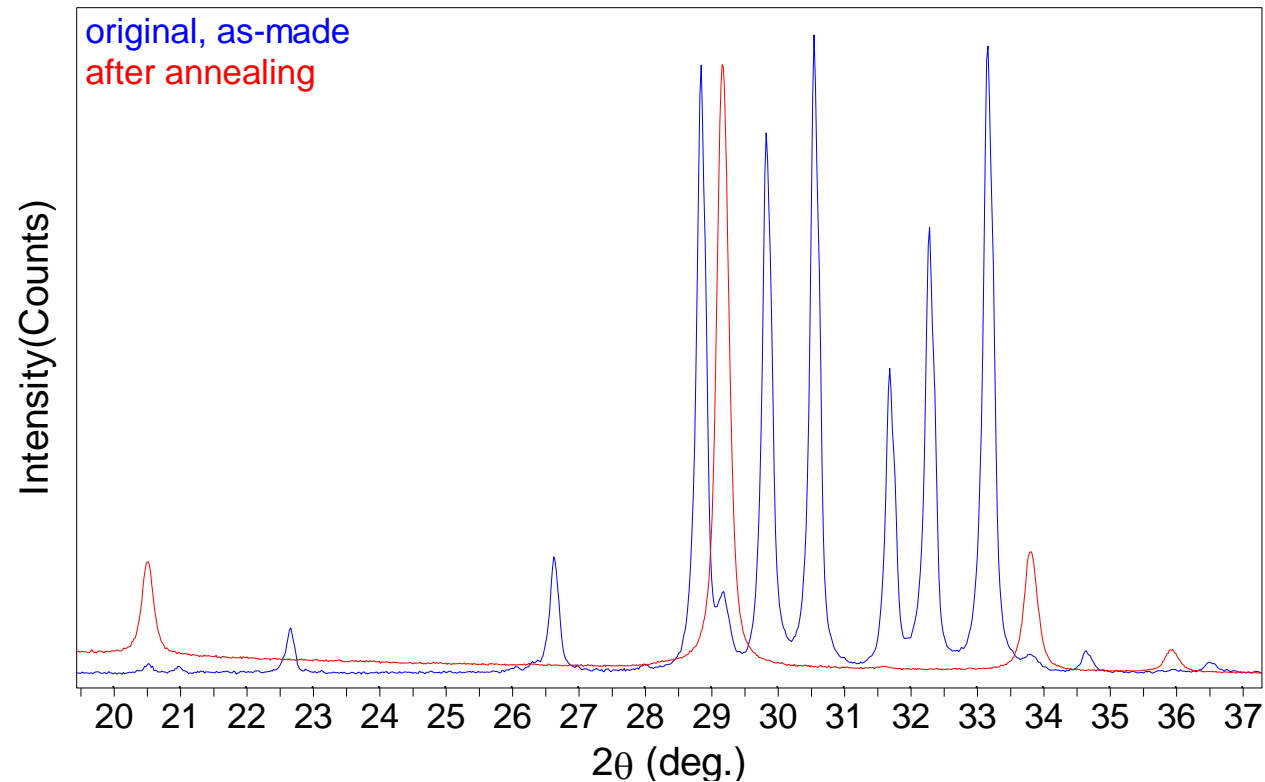
Powder patterns for different substances

◆ Can distinguish between the same compound with different structures and different compounds with the same structure
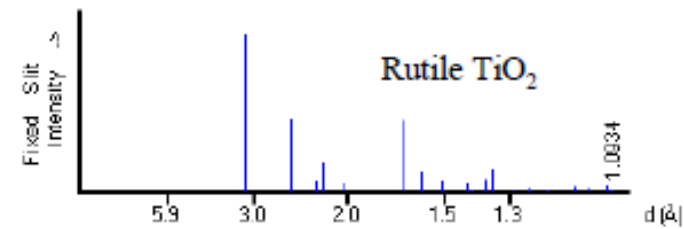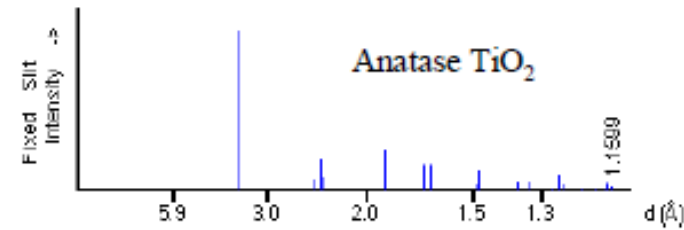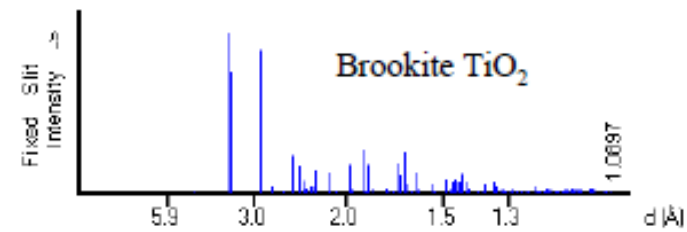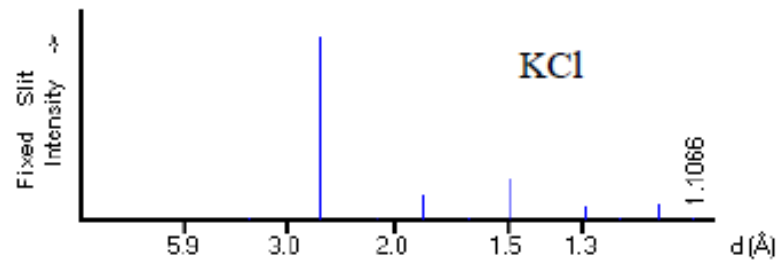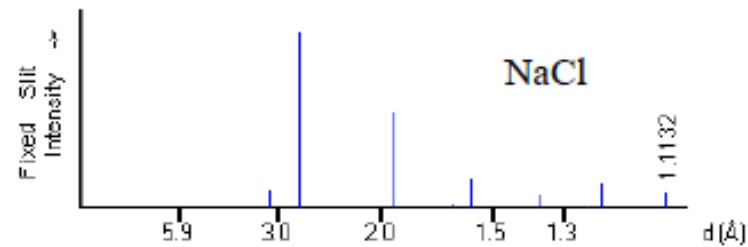
XRD can discern between isostructural compounds as well as between polymorphs

- we can map differences in electron density because X-rays scatter proportionally to Z^2

- the cubic phases of $CaTiO_3$ and $SrTiO_3$ have identical crystal structures, with the A cation replaced by Ca or Sr respectively
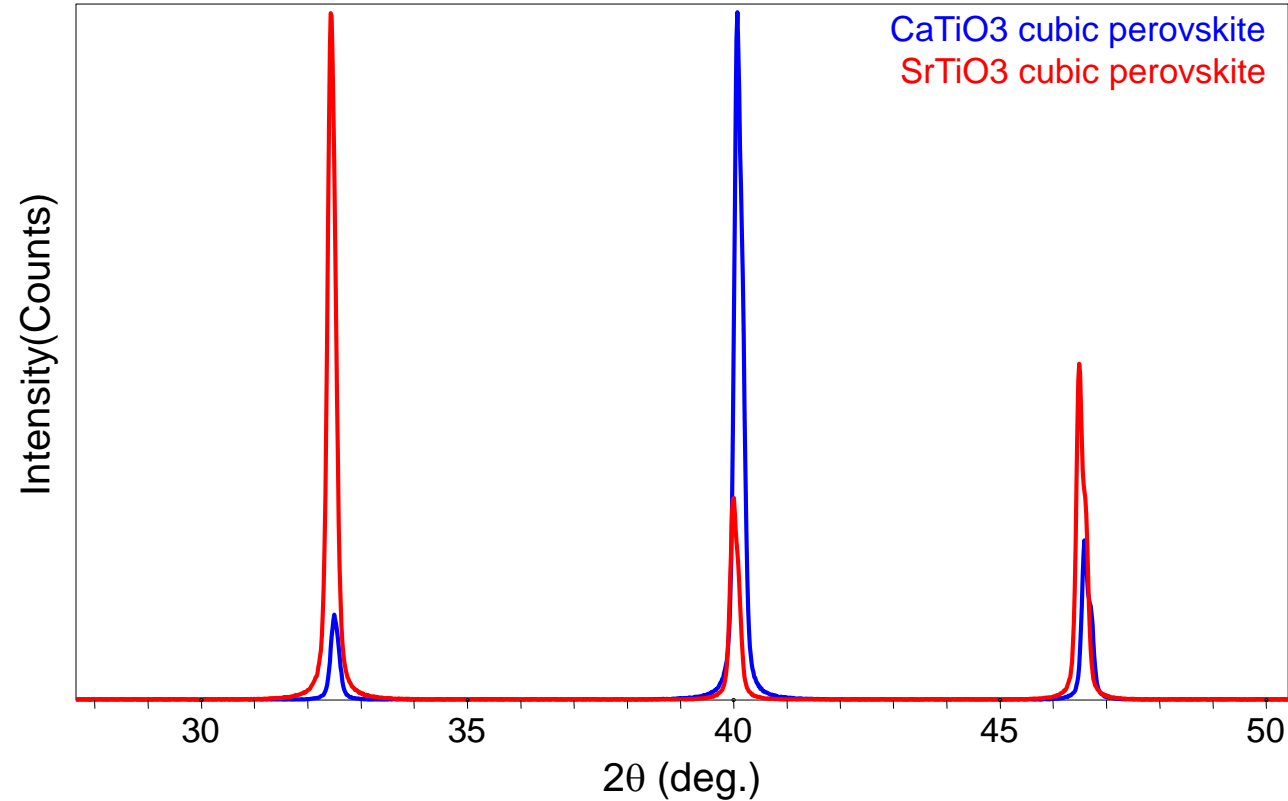
−*the cubic phase of CaTiO3 is not normally stable at RT− we stabilized this phase by quenching the sample

Identifikasi Fasa

- Using powder X-ray diffraction for phase identification
- – this can be done by calculating the unit cell and then search the NIST crystal data database for known compounds with the same or similar unit cells
  - Not very easy to do, but does not require that compound is in the ICDD powder diffraction file
- – usually done by comparing the measured pattern against the ICDD/JCPDS powder diffraction file data base.
- This contains powder patterns for a very large number of compounds.

Langkah2 Identifikasi Fasa

- Collect the XRD pattern over a range that is suitable for the material we are studying
  - typically 20 to 70 °2θ for inorganic specimens
  - typically 5 to 40 °2θ for organic specimens
  - data collection time ranges from 5 min to 1 hour for our instruments
    - in the "real world", these times are typically 30 min to 2 hours
- Compare the experimental data to a reference database of powder diffraction patterns
  - Subscribe to the **Powder Diffraction File**
    - 172,360 inorganic diffraction patterns
    - 107,507 inorganic crystal structures
    - 30,728 organic diffraction patterns
  - We also have the Cambridge Structural Database
    - ~400,000 organic crystal structures

A PDF card

Quality mark. * indicates high quality data, i – indicates reasonable data , o - indicates low reliability

Note intensity is normalized so that the strongest peak has a value of 100

d-spacings are used, rather than angles, as the angles depend upon the wavelength used for the measurements

5 – 6 2 8

d	2.82	1.99	1.63	3.26	NaCl		★
I/I_1	100	55	15	13	Sodium Chloride	(Halite)	

Rad. CuKα₁ λ 1.5405 Filter Ni Dia.
Cut off I/I₁ Diffractometer I/I cor.
Ref. Swanson and Fuyat, NBS Circular 539, Vol. 2, 41 (1953)

Sys. Cubic S.G. Fm3m (225)
a₀ 5.6402 b₀ c₀ A C
α β γ Z 4 Dx 2.164
Ref. Ibid.

εa nωβ 1.542 εy Sign
2V D mp Color Colorless
Ref. Ibid.

An ACS reagent grade sample recrystallized twice from hydrochloric acid.
X-ray pattern at 26°C.
Merck Index, 8th Ed., p. 956.

PDRM M-2

d A	I/I_1	hkl	d A	I/I_1	hkl
3.258	13	111			
2.821	100	200			
1.994	55	220			
1.701	2	311			
1.628	15	222			
1.410	6	400			
1.294	1	331			
1.261	11	420			
1.1515	7	422			
1.0855	1	511			
0.9969	2	440			
.9533	1	531			
.9401	3	600			
.8917	4	620			
.8601	1	533			
.8503	3	622			
.8141	2	444			

◆ Each entry is associated with a card number, the name and composition of the phase, the conditions for the data collection, a reference to the source of the information, crystallographic data, physical data, sample preparation information, a quality mark, and a list of d-spacings and intensities

Index untuk PDF

- There are several different types of indices available for the powder diffraction file in addition to software for doing computer searches

- – **Alphabetical index** gives card number of a given composition, or mineral name

- – **Hanawalt and other search indices** can be used to find a card that matches a diffraction pattern that you have measured

Indeks Hanawalt

- The Hanawalt index can be used to identify components in your sample **based on the d-spacings of the three most intense lines** arising from a phase.

- Index is organized by d-spacing of the strongest lines

  » Index contains 8 strongest lines for each phase, but search itself is initially based on only the three strongest

  » As this index makes use of intensity information, the search procedure can be impaired if the intensities that you measure are different from those in the PDF due to absorption, changes in wavelength, preferred orientation etc.

TABLE 9.2   PORTION OF THE ICDD HANAWALT SEARCH MANUAL*

QM	Strongest reflections								PSC	Chemical formula	Mineral name; common name	PDF #	I/I$_c$
*	2.82$_x$	1.99$_3$	3.99$_2$	1.63$_2$	1.41$_1$	1.26$_1$	1.07$_1$	1.78$_1$	cP5	Ca$_{0.6}$Sr$_{0.4}$NbO$_3$		47-35	7.05
	2.82$_x$	1.99$_9$	3.26$_8$	1.63$_7$	1.41$_1$	1.26$_1$	1.15$_1$	1.73$_1$	cF8	PdO		46-1211	
*	2.82$_9$	1.99$_x$	2.30$_6$	1.41$_4$	1.63$_2$	0.89$_1$	1.20$_1$	1.15$_1$	cP5	KMgF$_3$		18-1033	0.90
*	2.82$_x$	1.99$_6$	1.63$_2$	3.26$_1$	1.26$_1$	1.15$_1$	0.94$_1$	0.89$_1$	cF8	NaCl	Halite, syn	5-628	
C	2.82$_x$	1.99$_x$	1.99$_8$	1.26$_3$	1.63$_2$	1.15$_2$	0.94$_1$	1.41$_1$	cP2	BePd		18-428	

Prosedur menentukan fasa

- Locate d-spacing group for most intense line
- In second column, find best match to the d-spacing of the second strongest line (agreement should be ±0.01 Å
- Look in column three to find match for third line
- Compare relative intensities of the strongest lines for you best match and for you data
- If things look good, compare all lines on PDF card with what you observed. All lines that are on the PDF card should appear in you pattern and the relative intensities should be similar
- – Note agreement of d-spacings for high angle lines should be better than those at low angle as they are in general measured more accurately

NaCl example

d-spacings and intensities from unknown

d(Å)	I/I₁	d(Å)	I/I₁
3.25	10	1.00	20
2.82	100	0.95	5
2.18	5	0.94	20
1.99	60	0.89	20
1.71	5	0.86	5
1.63	30	0.85	20
1.42	20	0.82	10
1.25	30	0.79	10
1.15	30	0.78	20
1.09	5		

Three strongest lines: $d_1 = 2.82$, $d_2 = 1.99$ and $d_3 = 1.63$Å

TABLE 9.2 PORTION OF THE ICDD HANAWALT SEARCH MANUAL*

QM	Strongest reflections								PSC	Chemical formula	Mineral name; common name	PDF #	I/I_c
*	2.82_x	1.99_3	3.99_2	1.63_2	1.41_1	1.26_1	1.07_1	1.78_1	cP5	$Ca_{0.6}Sr_{0.4}NbO_3$		47-35	7.05
	2.82_x	1.99_0	3.26_8	1.63_7	1.41_1	1.26_1	1.15_1	1.73_1	cF8	PdO		46-1211	
*	2.82_3	1.99_x	2.30_6	1.41_4	1.63_2	0.89_1	1.20_1	1.15_1	cP5	$KMgF_3$		18-1033	0.90
*	2.82_x	1.99_x	1.63_2	3.26_1	1.26_1	1.15_1	0.94_1	0.89_1	cF8	NaCl	Halite, syn	5-628	
C	2.82_x	1.99_x	1.99_8	1.26_3	1.63_2	1.15_2	0.94_1	1.41_1	cP2	BePd		18-428	

Note subscripts after d-spacing relate to intensity. X is 100% line, 7 represent 70% etc.

d	2.82	1.99	1.63	3.26	NaCl	★
I/I₁	100	55	15	13	Sodium Chloride	(Halite)

Rad. CuKα₁ λ 1.5405 Filter Ni Dia.
Cut off I/I₁ Diffractometer I/I cor.
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a₀ 5.6402 b₀ c₀ A C
α β γ Z 4 Dx 2.164
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εα nωβ 1.542 εγ Sign
2V D mp Color Colorless
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An ACS reagent grade sample recrystallized twice from hydrochloric acid.
X-ray pattern at 26°C.
Merck Index, 8th Ed., p. 956.

d A	I/I₁	hkl	d A	I/I₁	hkl
3.258	13	111			
2.821	100	200			
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1.628	15	222			
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1.294	1	331			
1.261	11	420			
1.1515	7	422			
1.0855	1	511			
0.9969	2	440			
.9533	1	531			
.9401	3	600			
.8917	4	620			
.8601	1	533			
.8503	3	622			
.8141	2	444			

When is a match a match?

- **If you sample is a pure phase**, every line that you recorded should match well with one on the PDF card

  – However, you may have a second phase in your sample

  – You may have some kb lines in you pattern

  – The PDF card may not have any high angle lines on it

  – A line may be very weak

  – Intensity differences may arise due to absorption, wavelength differences, preferred orientation etc.

Identification of components in a mix

- Identification of components in a mixture can be difficult as the three strongest lines in your powder pattern may not all come from the same phase.

- – Need to examine different combinations of strong lines when using the Hanawalt index until a phase is tentatively identified. One one component is identified, ignore the lines from that phase a look for a match to the remaining lines

Cu and Cu$_2$O example

Pattern for unknown mixture

d(Å)	I/I$_1$	d(Å)	I/I$_1$
3.01	5	1.22	4
2.47	72	1.08*	20
2.13	28	1.04*	3
2.09*	100	0.98	5
1.80*	52	0.91*	4
1.50	20	0.83*	8
1.29	9	0.81*	10
1.28*	18		

First and third strongest line match copper

TABLE 9.4   PATTERN OF COPPER

d(Å)	I/I$_1$
2.088	100
1.808	46
1.278	20
1.0900	17
1.0436	5
0.9038	3
0.8293	9
0.8083	8

	Remainder of pattern of unknown		Pattern of Cu$_2$O	
	I/I$_1$			
d(Å)	Observed	Normalized	d(Å)	I/I$_1$
3.01	5	7	3.020	9
2.47	72	100	2.465	100
2.13	28	39	2.135	37
			1.743	1
1.50	20	28	1.510	27
1.29	9	13	1.287	17
1.22	4	6	1.233	4
			1.0674	2
0.98	5	7	0.9795	4
			0.9548	3
			0.8715	3
			0.8216	3

Remaining lines after rescaling can be identified as Cu$_2$O

Andi menemukan sebuah botol berlabel "standar metal" yang mengandung serbuk logam. Kemudian andi melakukan analisa dengan difraksi sinar X, sampai dengan sudut (2θ) 97° menggunakan sinar x dengan panjang gelombang 1.542Å. Hasil dari analisa XRD yang dilakukan andi adalah sbb: 2θ (derajat) dan Intensitas (intensitas dalam count/second)

2θ:	36.30	39.08	43.33	54.35	70.09	70.74	77.13	82.18	83.89	86.66	90.00	95.01
I:	4750	3975	9450	2820	2340	1890	70	1985	575	1510	200	475

Pertanyaan :
Identifikasi sampel yang dimaksud dan berikan komentar atas hasil yang diperoleh

				File No.
* Aluminum :	Al	2.34_x	2.02_5	1.22_2	**4- 787**
* Chromium :/Chromium syn	Cr (2B)	2.04_x	1.18_3	1.44_2	**6- 694**
* Cobalt :	Co (4F)	2.05_x	1.77_4	1.25_3	**15- 806**
* Copper :/Copper syn	Cu	2.09_x	1.81_5	1.28_2	**4- 836**
* Gold :/Gold syn	Au	2.36_x	2.04_5	1.23_4	**4- 784**
* Iron :/Iron syn	α-Fe (2B)	2.03_x	1.17_3	1.43_2	**6- 696**
* Lead :/Lead syn	Pb	2.86_x	2.48_5	1.49_3	**4- 686**
* Nickel :/Nickel syn	Ni	2.03_x	1.76_4	1.25_2	**4- 850**
* Silver :/Silver syn	Ag	2.36_x	2.04_4	1.23_3	**4- 783**
* Tin :/Tin syn	Sn	2.92_x	2.79_9	2.02_7	**4- 673**
* Titanium :	Ti	2.24_x	2.56_3	2.34_3	**5- 682**
* Zinc :/Zinc syn	Zn	2.09_x	2.47_5	2.31_4	**4- 831**

Computerized search match

- Identification of components in a mix is often done using computerized matching algorithms. They are not fool proof. The results depend on the data quality, the data base quality and the criteria used in the search

- – Matches are usually ranked using a figure of merit

- – Large figure of merit would indicate a good match using the definition below

Problems

- Phase in your sample may not be in PDF

- – Not common, but you have a big problem!

- Intensities in your pattern may be poor due to grainy sample, preferred orientation etc

- – Try multiple packings of sample. If you see intensity variations consider using a different sample preparation method or grinding the sample.

- Positions in you pattern may be wrong

- – Collect your data with an internal standard present so that you can correct any angular errors

- Your sample is a solid solution with a composition that does not correspond to a pattern in the database. Some software will contract or expand a lattice during the search match procedure to try and find matches in cases like this

- Data base pattern may be of poor quality

- untuk sistem dengan banyak fasa / multi senyawa, maka cara manual akan sulit dilakukan.

- biasanya analisa dibantu dengan software ; misal jade, topaz, xpowder, match, pcpdfwin, dst..

- software tsb harus dilengkapi dengan database xrd yg lengkap, misal pdf2 atau pdf4. harga database tsb sangat mahal, dan tiap tahun biasanya diupdate.
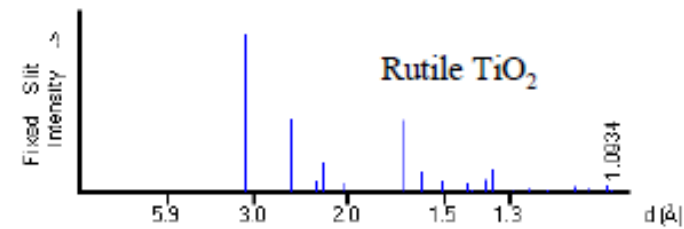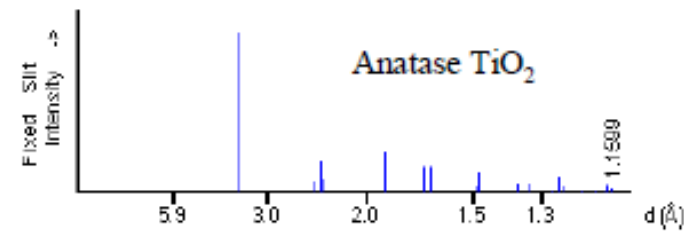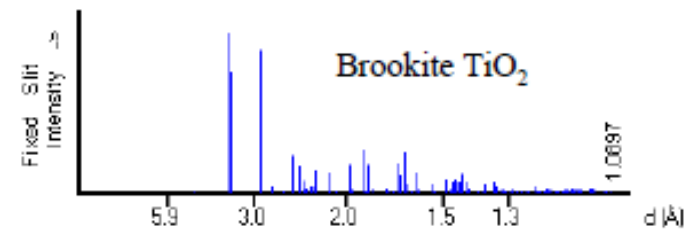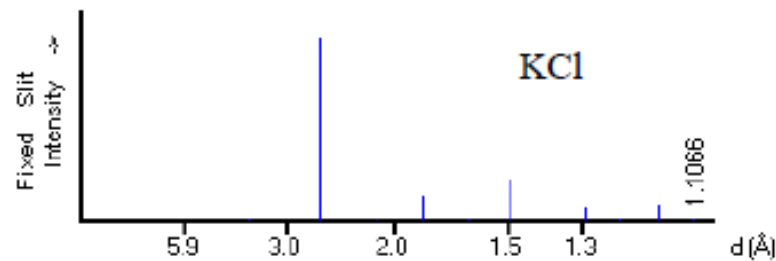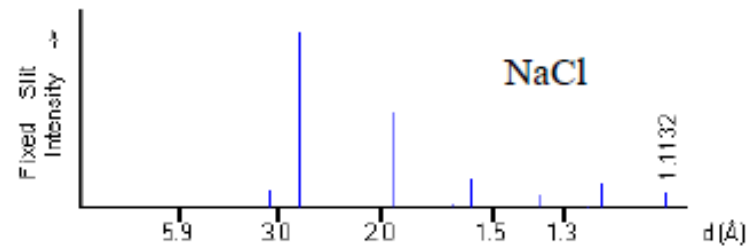
APLIKASI XRD

The diffraction pattern of every phase is a unique 'fingerprint'
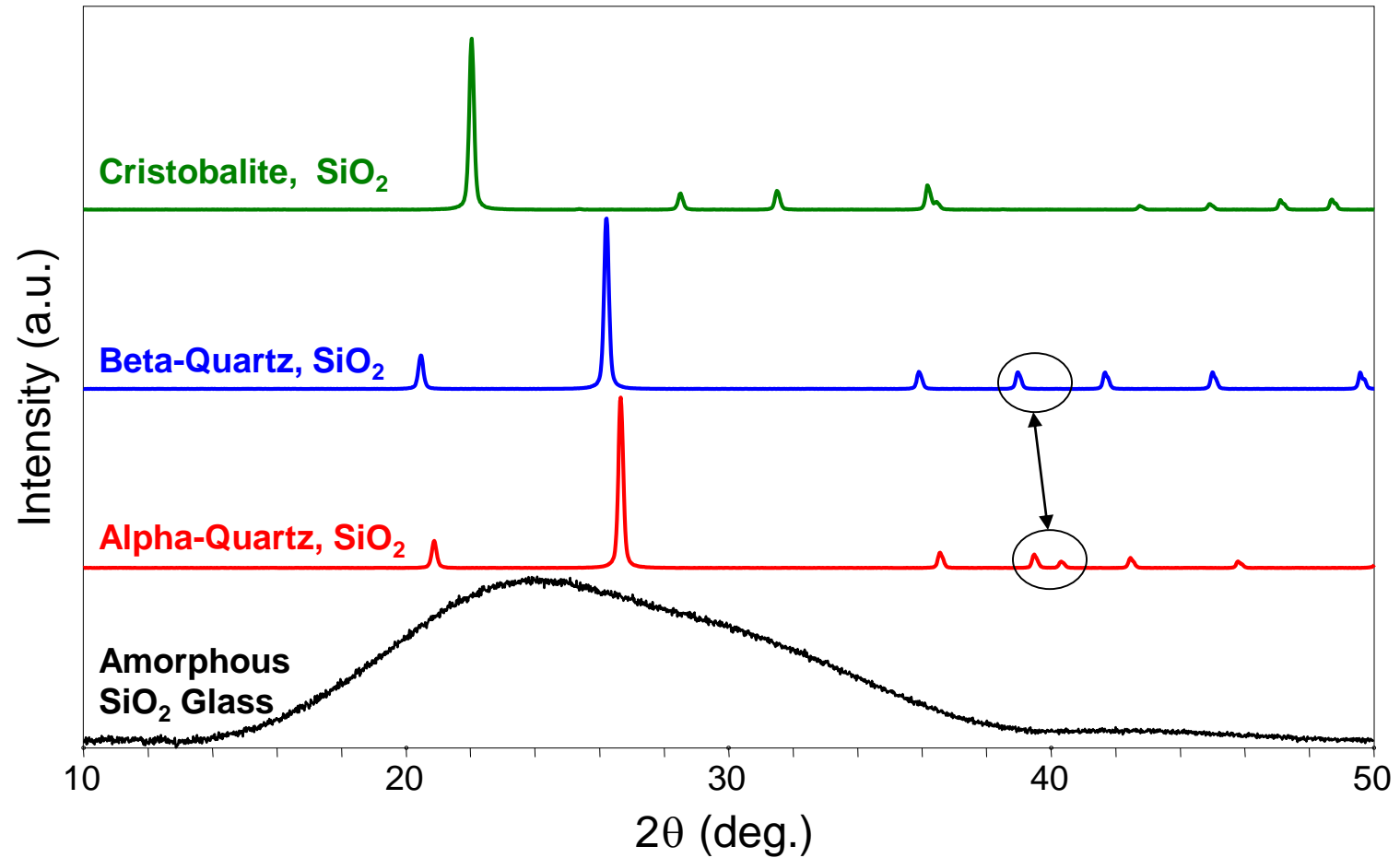
Powder patterns for different substances

◆ Can distinguish between the same compound with different structures and different compounds with the same structure

SELAIN IDENTIFIKASI FASA, BISA JUGA MENENTUKAN BERAPA BANYAK FASA YG ADA (KURANG AKURAT)

Red Paint Pigment Mixture

28 wt% Hematite, Fe_2O_3

21 wt% Anatase, TiO_2

51 wt% Rutile, TiO_2
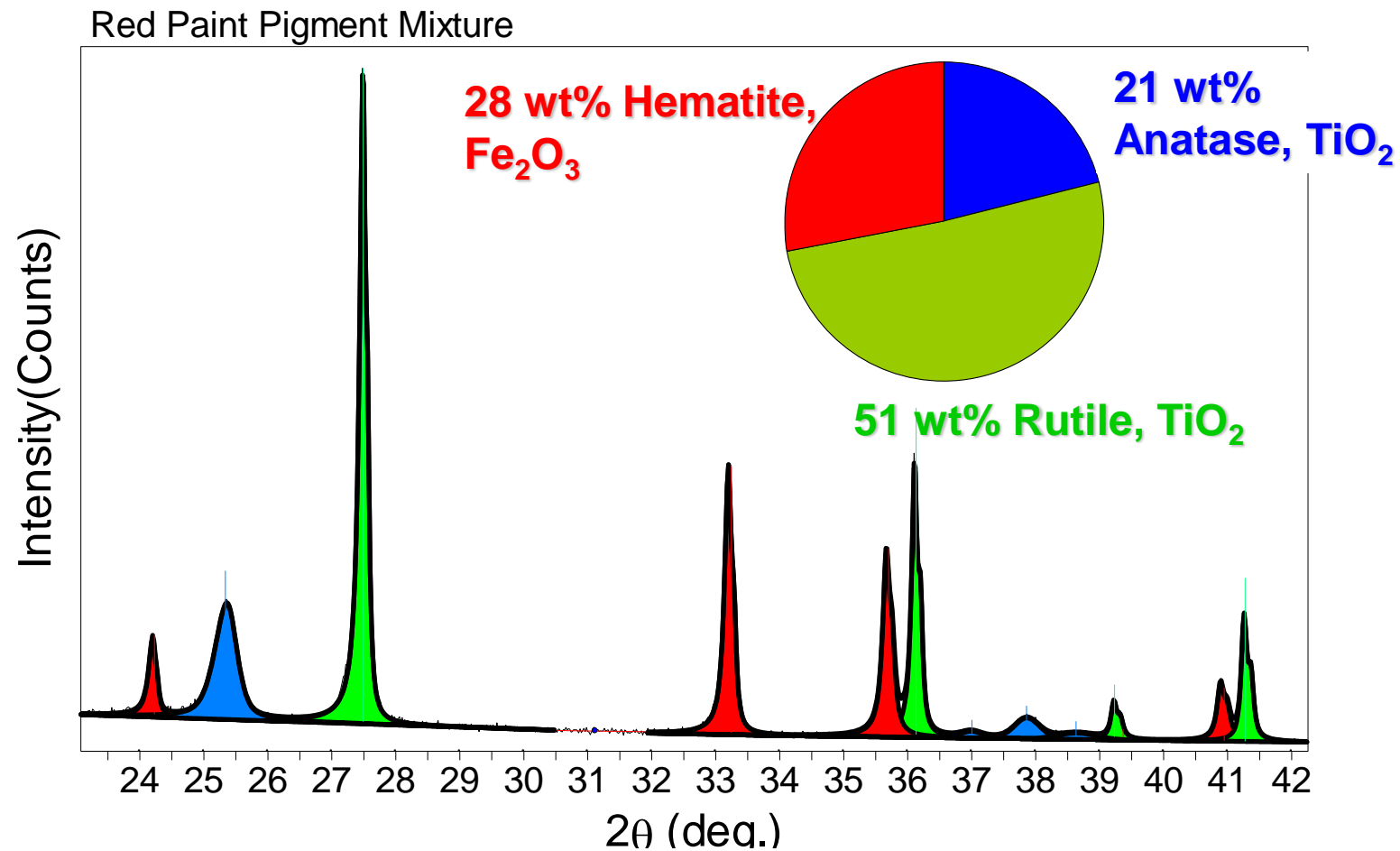
The Scherrer Equation was published in 1918

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

- **Peak width (B) is inversely proportional to crystallite size (L)**

- P. Scherrer, "Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen," *Nachr. Ges. Wiss. Göttingen* **26** (1918) pp 98-100.

- J.I. Langford and A.J.C. Wilson, "Scherrer after Sixty Years: A Survey and Some New Results in the Determination of Crystallite Size," *J. Appl. Cryst.* **11** (1978) pp 102-113.

Many factors may contribute to the observed peak profile

- Instrumental Peak Profile

- Crystallite Size

- Microstrain
  - Non-uniform Lattice Distortions
  - Faulting
  - Dislocations
  - Antiphase Domain Boundaries
  - Grain Surface Relaxation

- Solid Solution Inhomogeneity

- Temperature Factors

- ***The peak profile is a convolution of the profiles from all of these contributions***

Crystallite Size Broadening

$$B(2\theta) = \frac{0.94\lambda}{L\cos\theta}$$

- Peak Width B(2θ) varies inversely with crystallite size

- The constant of proportionality, K (the Scherrer constant) depends on the how the width is determined, the shape of the crystal, and the size distribution
  - the most common values for K are 0.94 (for FWHM of spherical crystals with cubic symmetry), 0.89 (for integral breadth of spherical crystals with cubic symmetry, and 1 (because 0.94 and 0.89 both round up to 1).
  - K actually varies from 0.62 to 2.08
  - For an excellent discussion of K, refer to JI Langford and AJC Wilson, "Scherrer after sixty years: A survey and some new results in the determination of crystallite size," *J. Appl. Cryst.* **11** (1978) p102-113.
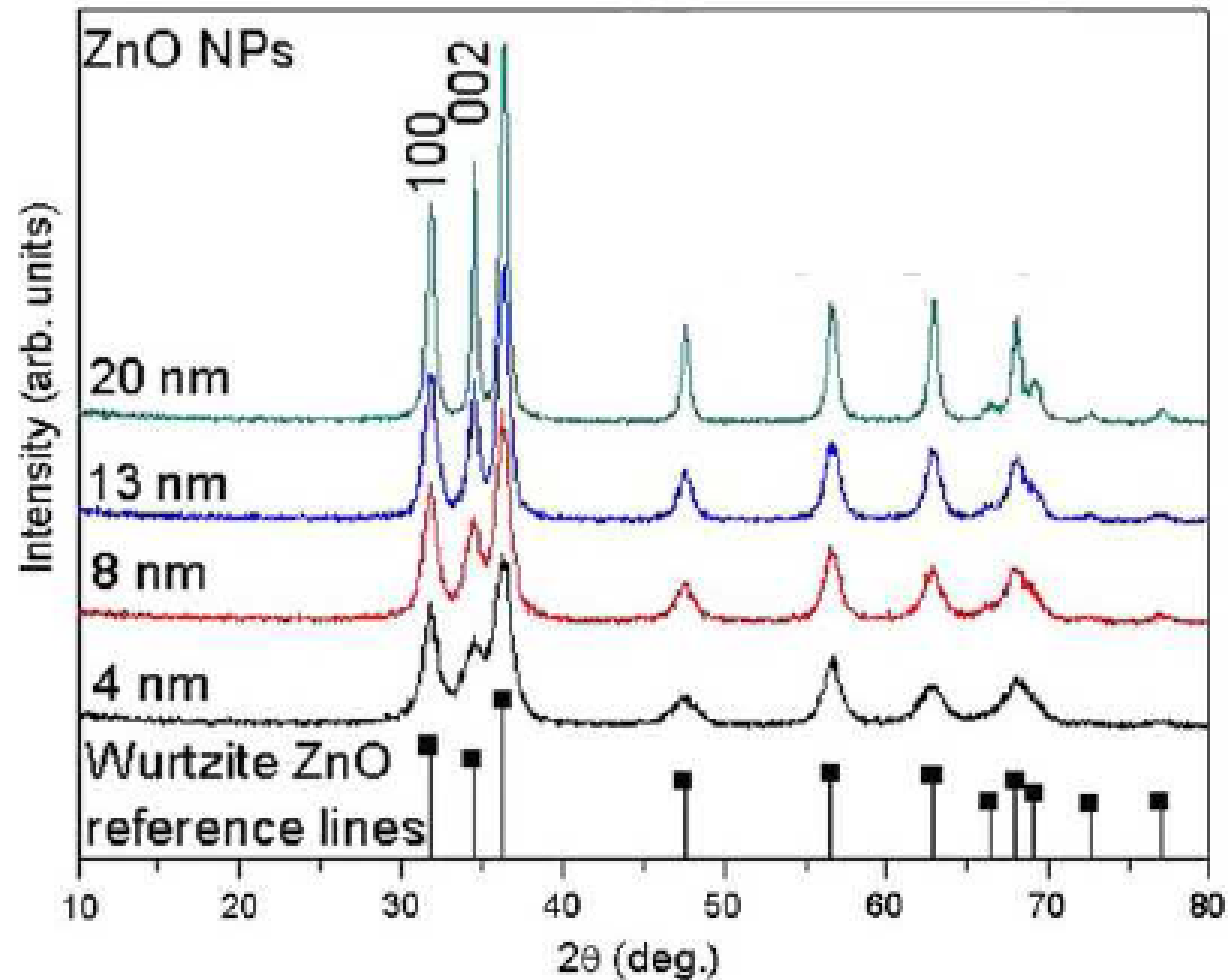
X-ray diffraction scans of powder samples of various sizes of ZnO nanoparticles recorded in air at room temperature. The X-ray source used was Cu Kα with wavelength λ = 1.5418 Å. The peak widths are inversely related to the crystallite sizes according to the Scherrer relation, enabling the XRD patterns to demonstrate the change in particle size. The stick pattern from reference data for wurtzite ZnO is shown along the x-axis (represented by the solid squares).

The Scherrer Constant, K

$$B(2\theta) = \frac{K\lambda}{L\cos\theta} \qquad\qquad B(2\theta) = \frac{0.94\lambda}{L\cos\theta}$$

- The constant of proportionality, K (the Scherrer constant) depends on the how the width is determined, the shape of the crystal, and the size distribution
  - the most common values for K are:
    - 0.94 for FWHM of spherical crystals with cubic symmetry
    - 0.89 for integral breadth of spherical crystals w/ cubic symmetry
    - 1, because 0.94 and 0.89 both round up to 1
  - K actually varies from 0.62 to 2.08
- For an excellent discussion of K, refer to JI Langford and AJC Wilson, "Scherrer after sixty years: A survey and some new results in the determination of crystallite size," *J. Appl. Cryst.* **11** (1978) p102-113.

Methods used to Define Peak Width

- Full Width at Half Maximum (FWHM)
  - the width of the diffraction peak, in radians, at a height half-way between background and the peak maximum

- Integral Breadth
  - the total area under the peak divided by the peak height
  - the width of a rectangle having the same area and the same height as the peak
  - requires very careful evaluation of the tails of the peak and the background
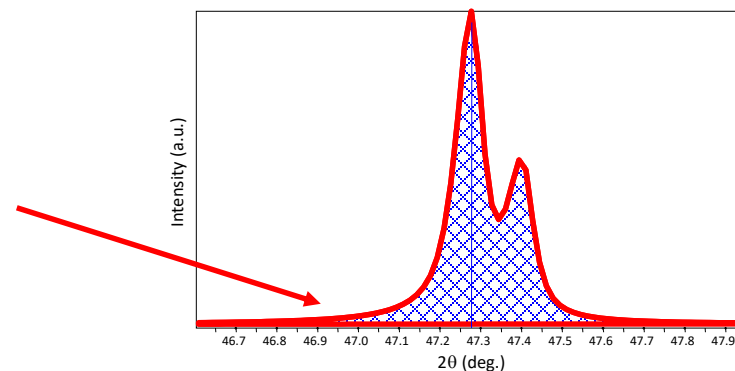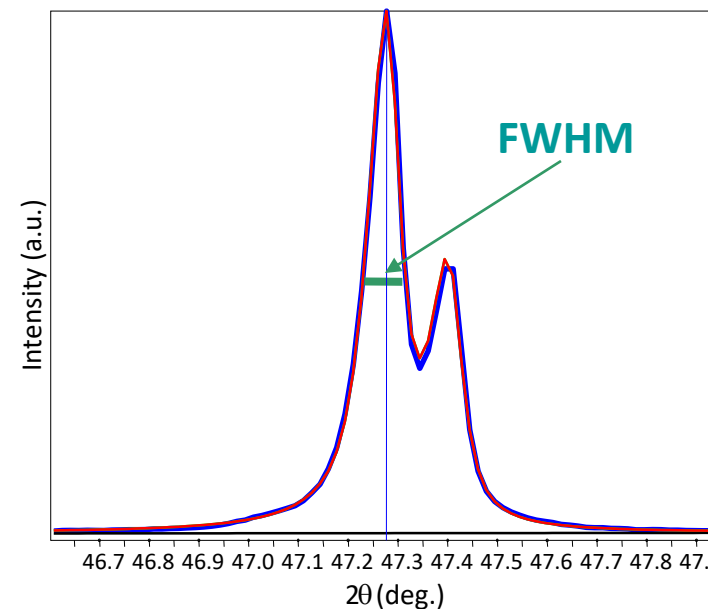
Remember, Crystallite Size is Different than Particle Size

- A particle may be made up of several different crystallites
- Crystallite size often matches grain size, but there are exceptions

Scherrer Method

- Predicts the size of crystallites based on the width of the diffraction peak.
- Diffraction peaks are a result of constructive interference of X-rays reflected by crystal planes. The more planes the sharper the peak so the smaller the crystallite size the broader the diffraction peak.
- Large particles might contain several crystallites. Nanometer-sized particles often contain only one crystallite.
- Provides a lower bound on the particle size since additional factors can contribute to the width of a diffraction peak.

$$\text{Particle diameter} = \frac{\lambda}{\sin(\Delta\theta)\cos(2\theta)}$$

λ is the X-ray wavelength, $\Delta\theta$ is the peak-width at half-height and 2θ is the peak location.

Examples: Particle Size Calculation
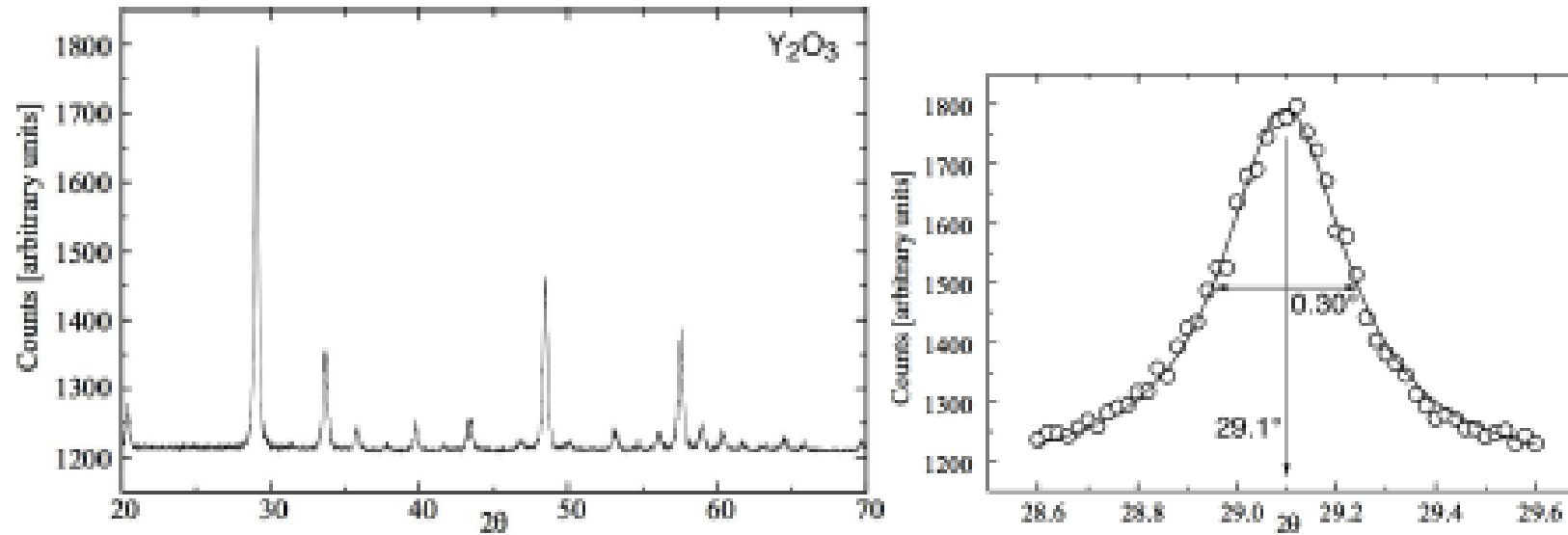
$$\text{Particle diameter} = \frac{\lambda}{\sin(\Delta\theta)\cos(2\theta)} = \frac{0.15418 \text{ nm}}{\sin(0.30°) \, \cos(29.1°)} = 34 \text{ nm}$$

λ is the X-ray wavelength for Cu K_α, $\Delta\theta$ is the peak-width at half-height and 2θ is the peak location.

Estimation of Residual Stress

- **Definition: Stresses that remain in material or** body without application of an external load (applied force, displacement of thermal gradient).

- **Origin: Usually originates during manufacturing** and processing of materials due to heterogeneous plastic deformations, thermal contractions and phase transformations.

Origin of Residual Stress

- Mechanical
- Thermal
- Chemical

Mechanically Generated

- Occurs due to manufacturing process that produce non-uniform plastic deformation.

- May develop naturally during processing or treatment or may be introduced deliberately to develop a particular stress profile in a component.

- Operations that produce "undesirable" surface tensile stresses or residual stress gradients are rod or wire drawing, welding, machining (turning, milling) and grinding.

- Compressive residual stresses can be introduced by shot peening, autofrettage of pressure vessels, toughening of glass or cold expansion of holes

Thermally Generated

- **Macroscopically: Occurs as a result of** non-uniform heating or cooling operations

- **Microscopic level: Can also develop in a** material during manufacture and processing as a consequence of Coefficient of thermal expansion mismatch between different phases or constituents.

Chemically Generated

- Develops due to volume changes associated with chemical reactions, precipitation or phase transformations.

- Chemical surface treatments and coatings can lead to the generation of substantial residual stress gradients in the surface layers of components.

- For example, nitriding produces compressive stress in the diffusion region due to expansion of the lattice and precipitation of nitrides.

Residual stress

- Residual stress causes small changes in d and shifts the diffraction angle.

- Residual stresses are determined from the diffraction data by calculating the residual strain from the diffraction peak positions.

Measuring peak positions at different tilts allows us to quantify residual strains

- Measuring the same diffraction peak at different tilts allows us to measure the d-spacing between planes (hkl) at different orientations within the physical sample

- With no strain, (hkl) planes have a d-spacing d_0

- With a uniaxial in-plane stress, planes (hkl) that are parallel to the sample surface (tilt=0°) have a d_{hkl} distorted by Poisson's ratio

- With the same uniaxial in-plane stress, planes (hkl) that are tilted with respect to the sample surface are strained by a greater amount determined by Young's modulus and Poisson's ratio
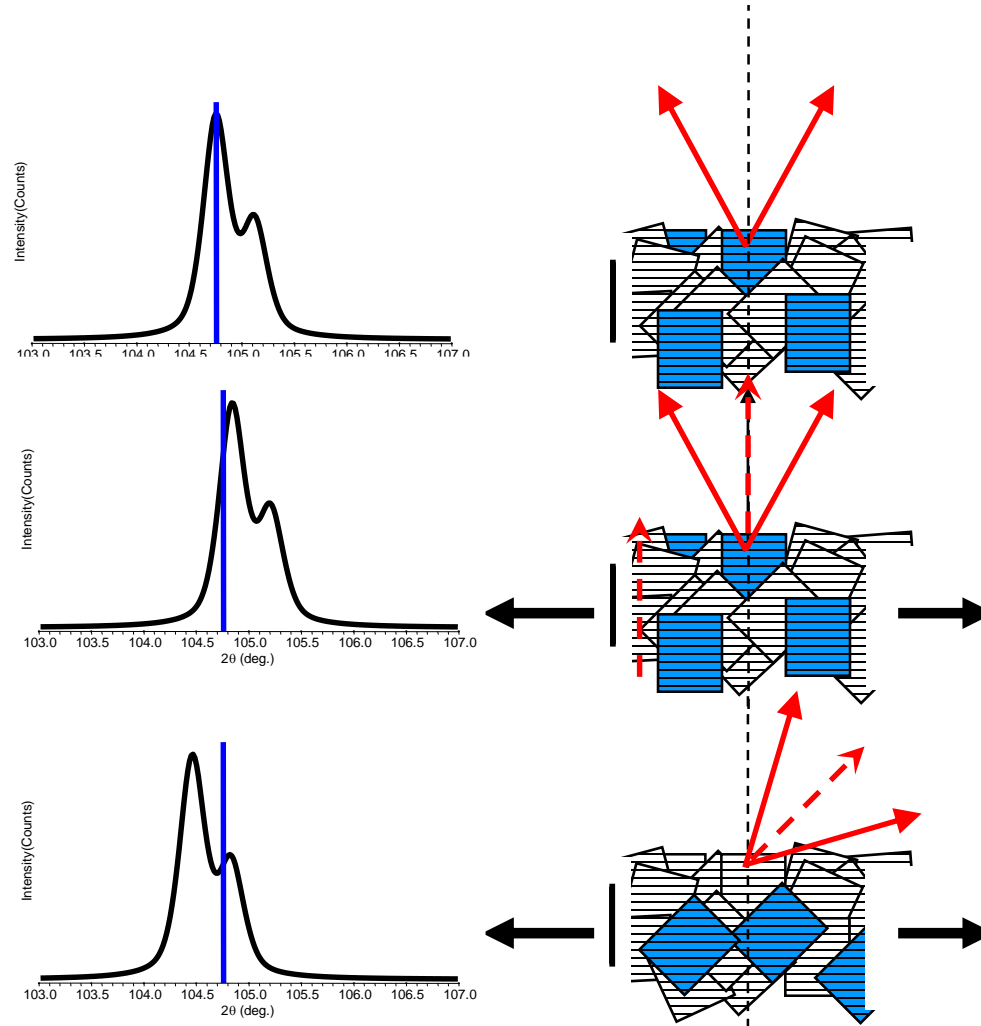
Estimation by XRD

- One of the most widely used non-destructive techniques for residual stress measurement.

- Residual stress in the material causes the interplanar spacing of the material to change.

- Changes in the interplanar spacing "d" can be used with the Bragg's equation to detect elastic strain "ε" through a change in the Bragg scattering angle Δθ

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

giving

$$\varepsilon = \frac{\Delta d}{d} = -\cot \theta \, \Delta \theta$$

Accurate determination of stress free spacing "d_0" is required

- Stress is evaluated from strain values using Young's modulus, Poisson ratio and taking into consideration Elastic Anisotropy of the material.

- Typically single peak, available at highest value of 2θ, is used for analysis.

- Diffraction is selective and hence biased towards a particular sets of grains.

- The peak shift sample both Type I and average Type II stresses, while Type III stresses give peak broadening.

Instrumentation

- Parallel X-ray Beam
- Goniometer capable of rotation and tilt
- ψ- tilting is performed either in **iso-inclination mode or sideinclination** mode
- **Side-inclination is preferred because :**
    - The effect of misalignments of the sample height on the stress result is less pronounced
    - The range of tilt angles is not restricted by small Bragg Angles
    - The measurements on samples with concave surface are less hindered by shading effects
- Stress free sample of the material under investigation is needed

Residual stresses are determined from the diffraction data by calculating the strain from the diffraction peak positions.
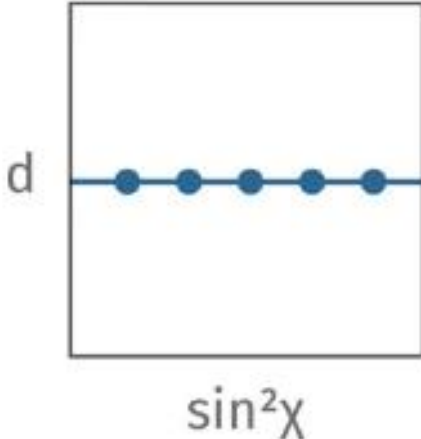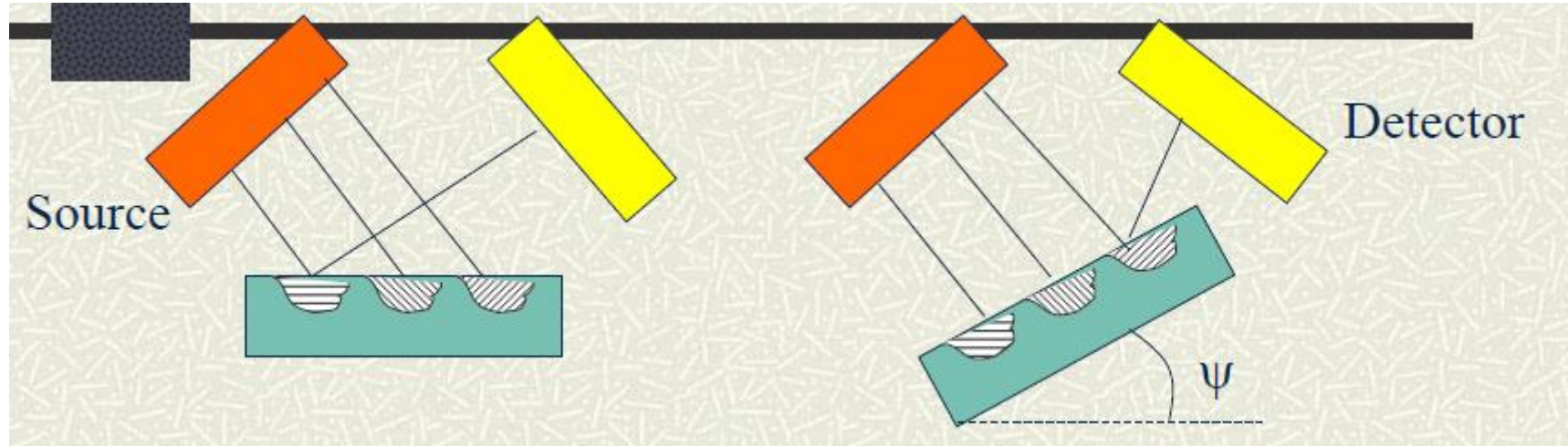
COMPRESSIVE STRESS

d

$\sin^2\chi$

**TENSILE STRESS**

d

$\sin^2\chi$

NO STRESS

d

$\sin^2\chi$
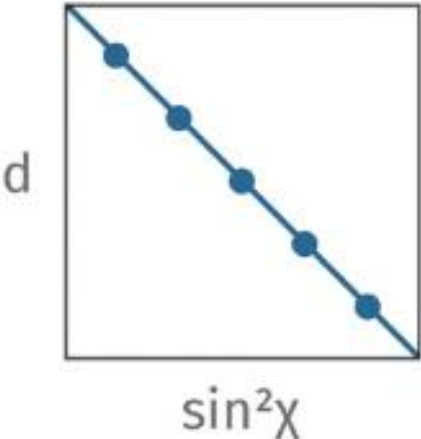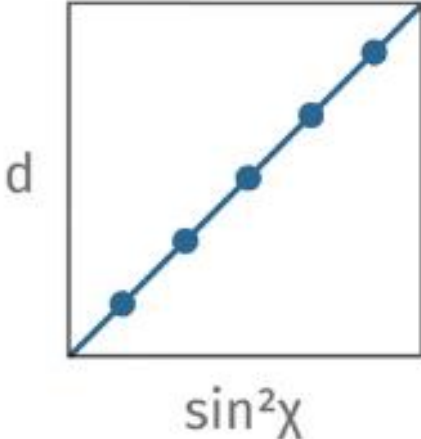
X=tilt angles

# Resolving Multi-axial Stresses

Source

Detector

ψ

When the *sample is level, only one set of planes diffract. But when the sample is tilted, a different sets of crystallites diffract. Thus each* set of crystallites resolve a different directional component of the stress to which the sample is subjected. If the sample is compressed from the sides, the lattice spacing of crystallites oriented parallel to the surface will increase more than those oriented at an angle to the surface. *The peak position will shift during tilting, since crystallites* are subjected to different magnitude of stress
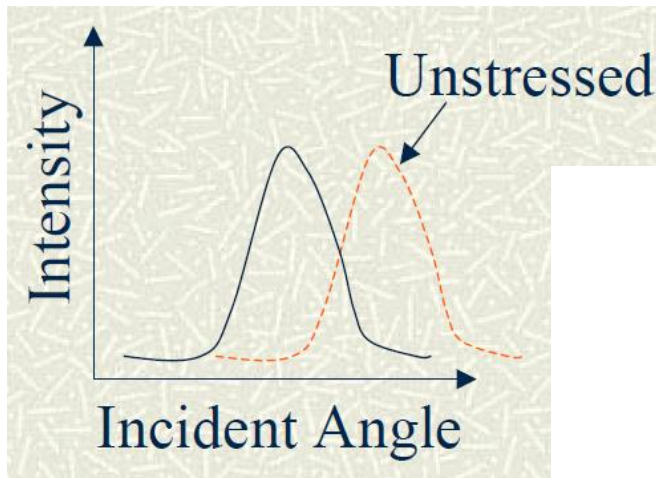
Residual Stress by X-ray Diffraction Techniques

Unstressed

Source

Detector
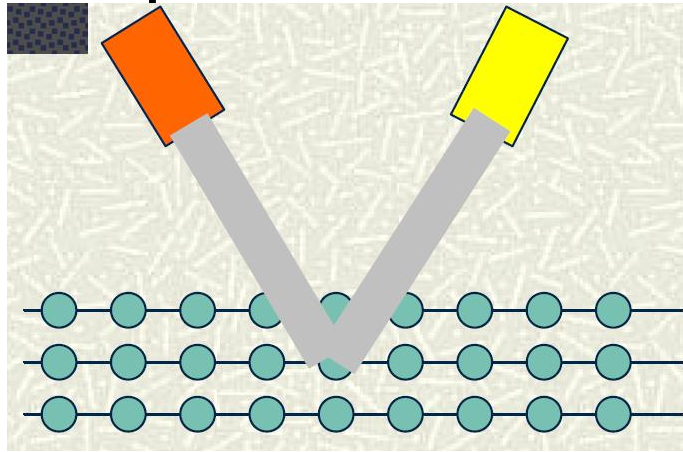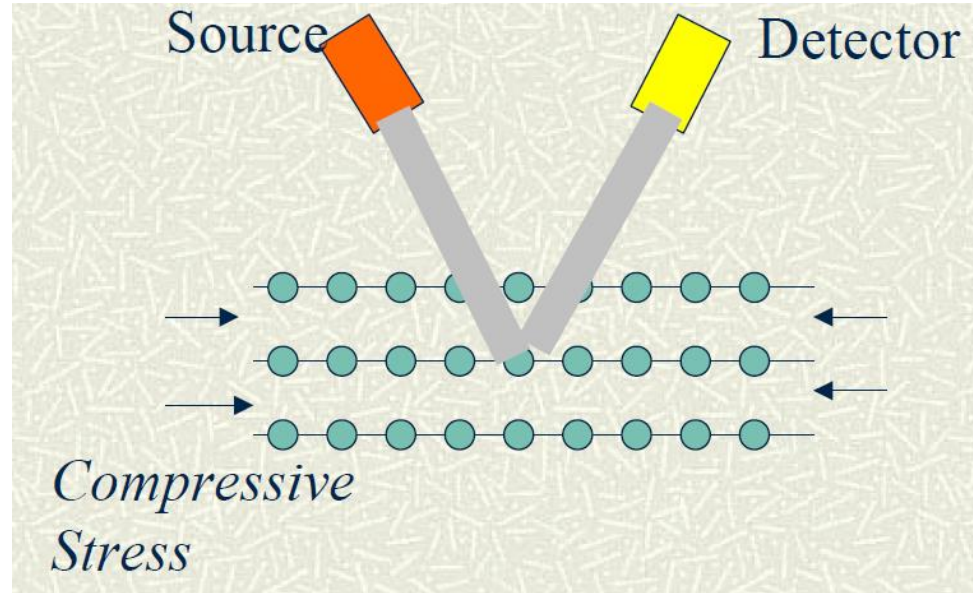
Compressive Stress

The compressive stress spreads apart the planes of atoms parallel to the surface (and perpendicular to the stress), which results in diffraction peaks at lower angles of incidence

Strain-Sin² ψ Curves