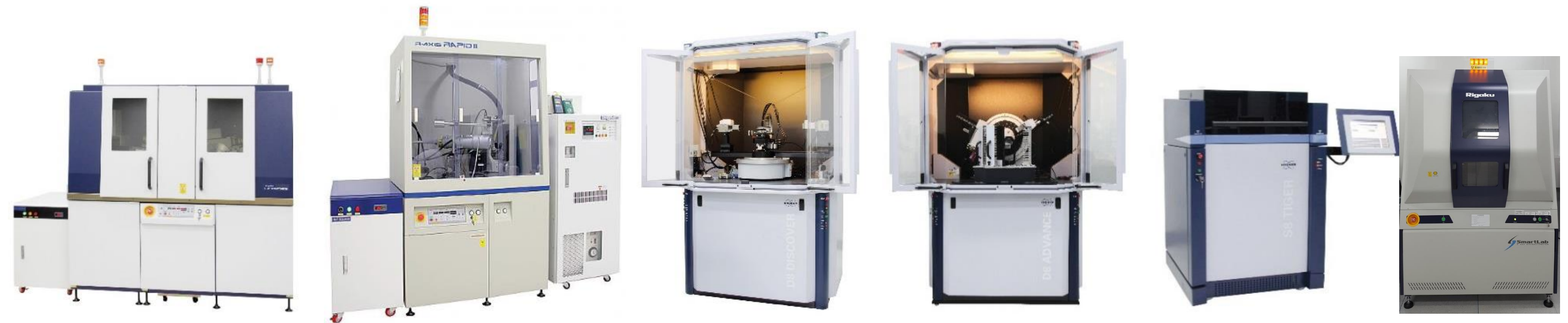


# 고출력 분말 X선 회절 분석 자율 사용자 교육

Nov, 10<sup>th</sup> 2017



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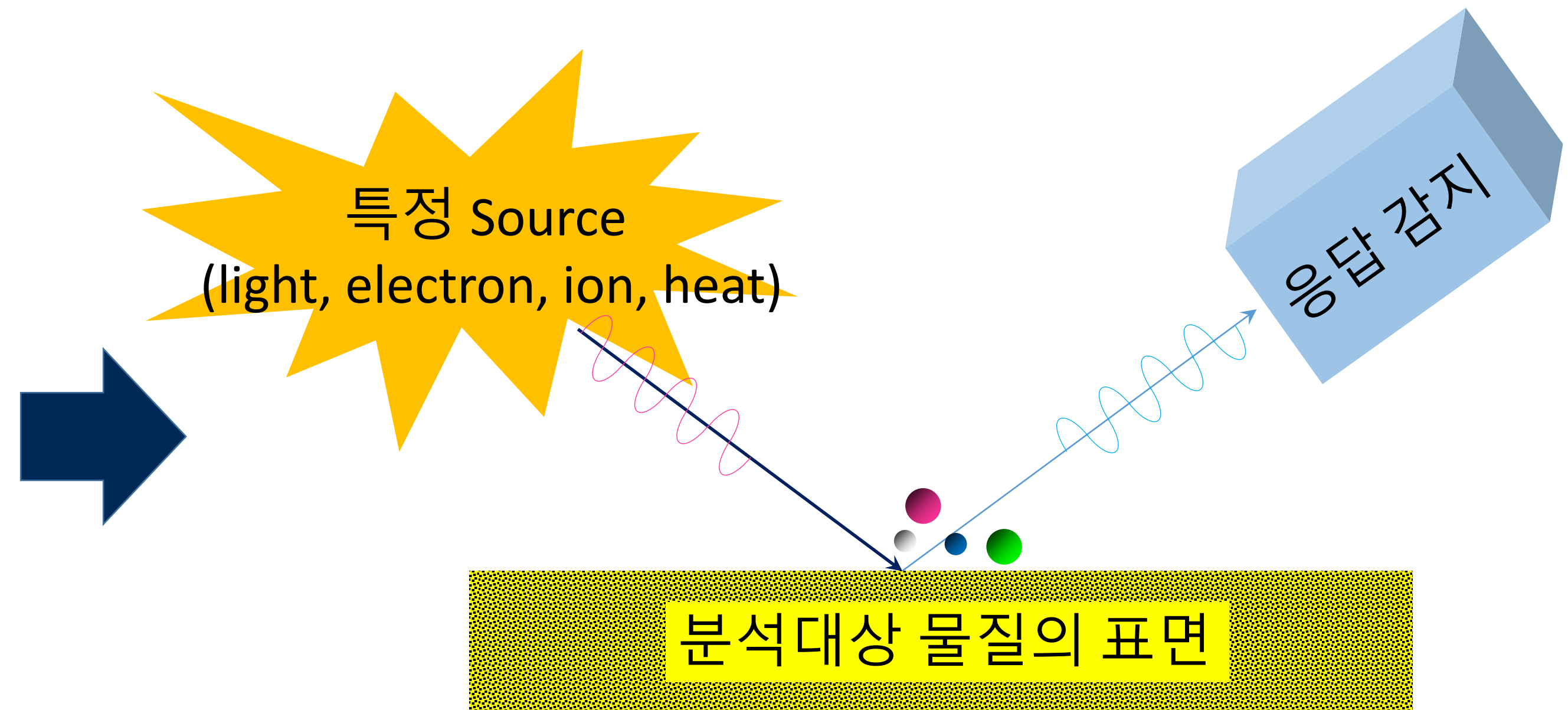
# CONTENTS

|                 |    |                       |    |
|-----------------|----|-----------------------|----|
| 1. Introduction | 03 | 4. Application        | 41 |
| 2. Basic Theory | 14 | 5. Sample Preparation | 51 |
| 3. Hardware     | 31 | 6. Caution for use    | 55 |

# Introduction

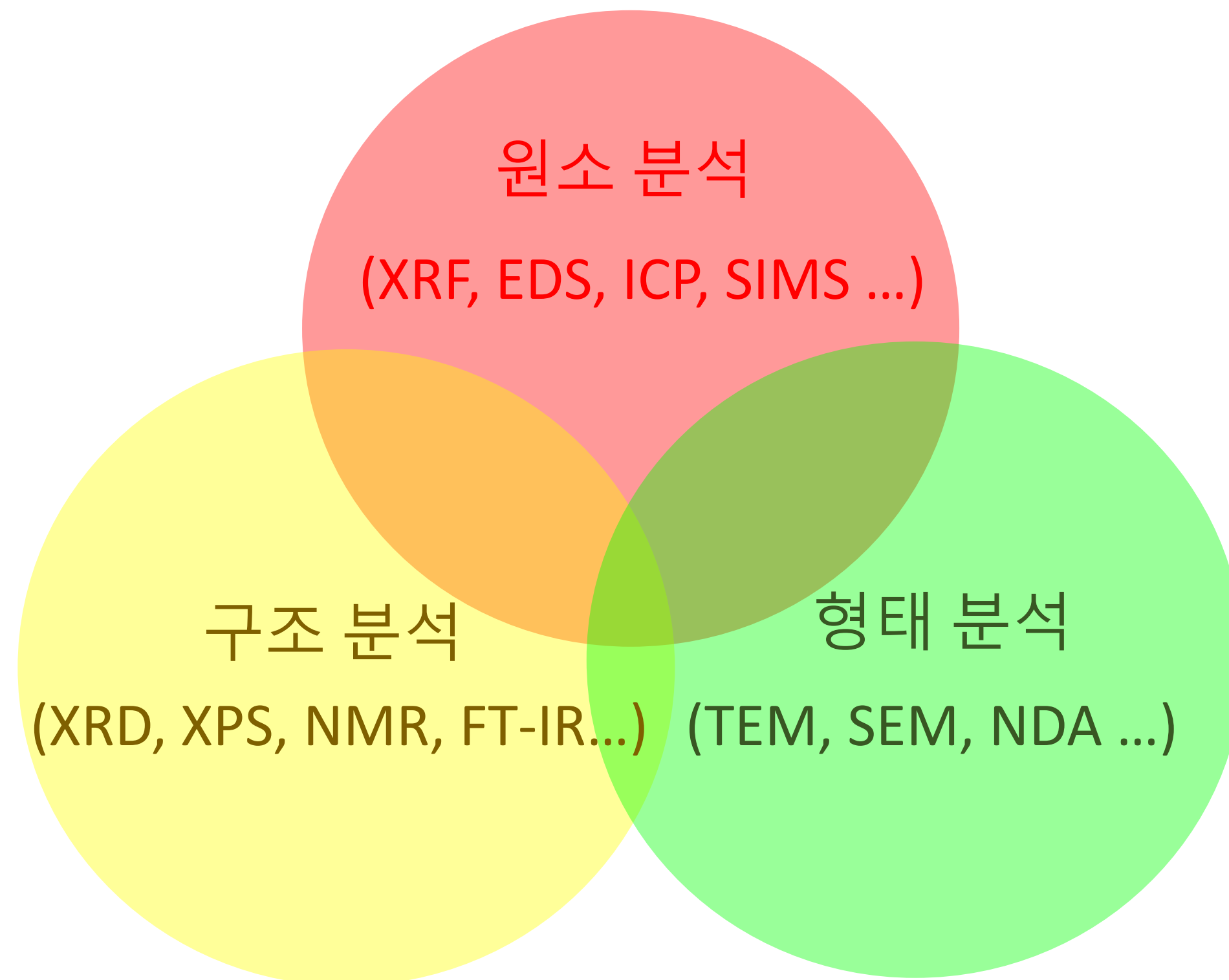
## 분석 기술이란

어느 물질에 대하여 외부로부터 변화를 주어 발생하는 응답 특성을 해석하는 작업



분석 기술의 성격

- 시료 준비 및 데이터 해석이 기술의 핵심
- 분석 결과에 대한 정확도와 재현성 확보
- 문제 해결 능력이 요구



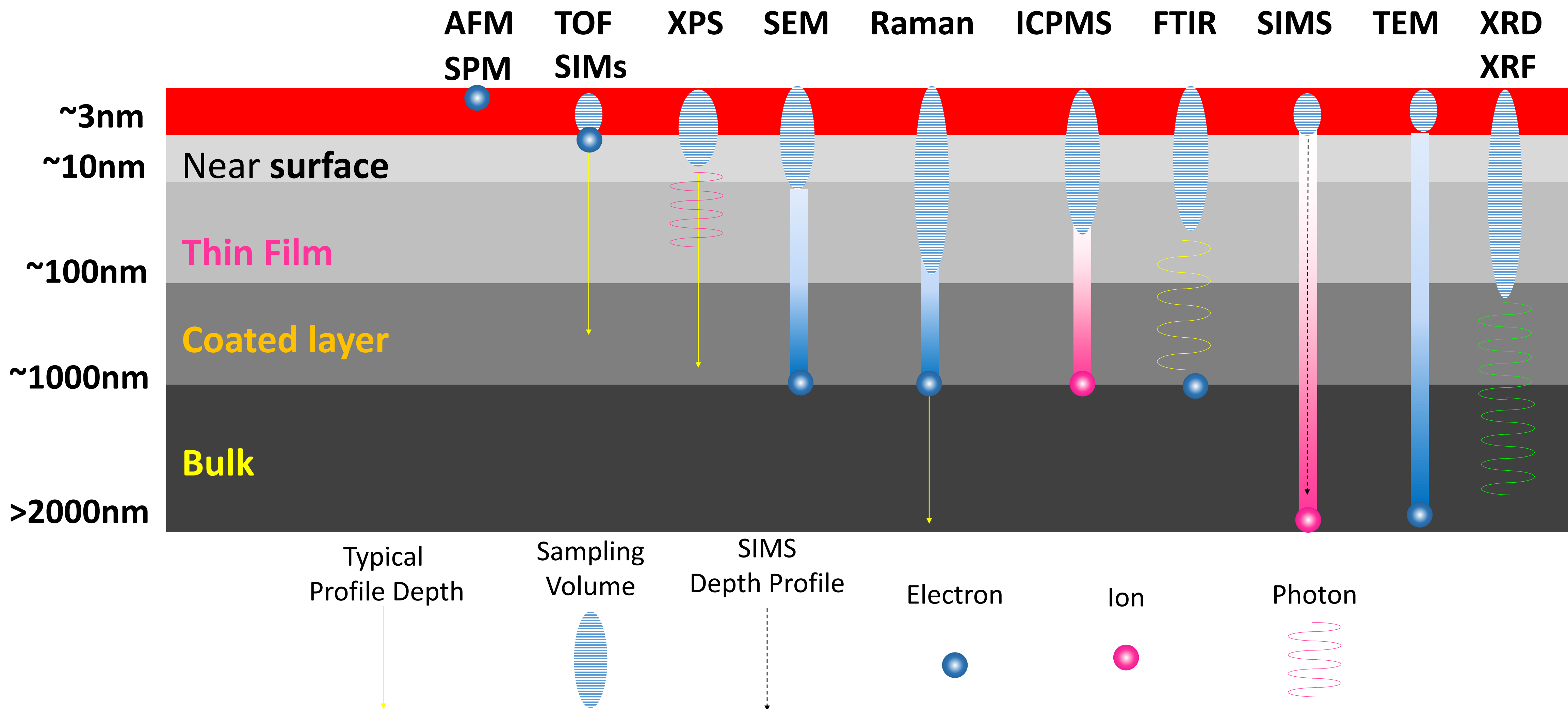
XRD  
(X-ray Diffractometer)

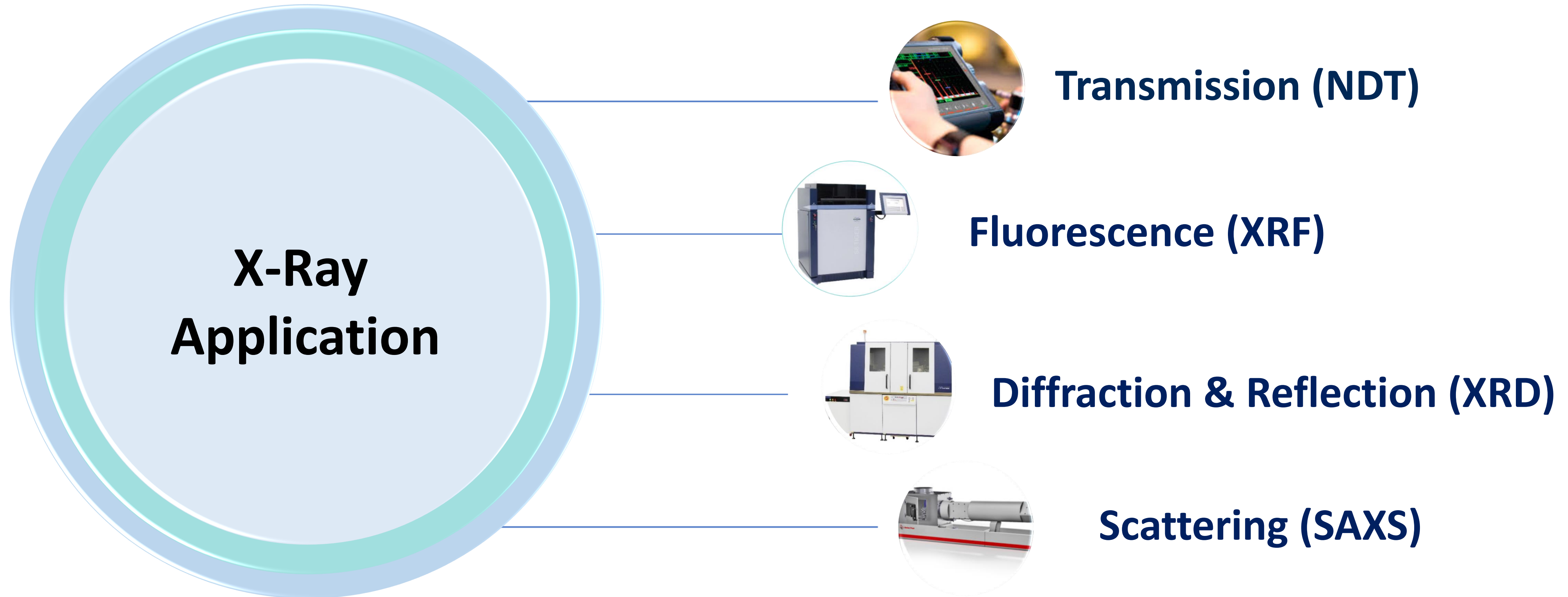
결정구조 분석  
(Crystal Structure Analysis)  
 $\text{LiCoO}_2$ ,  $\text{Fe}_3\text{O}_4$ , GaN

XRF  
(X-ray Fluorescence)

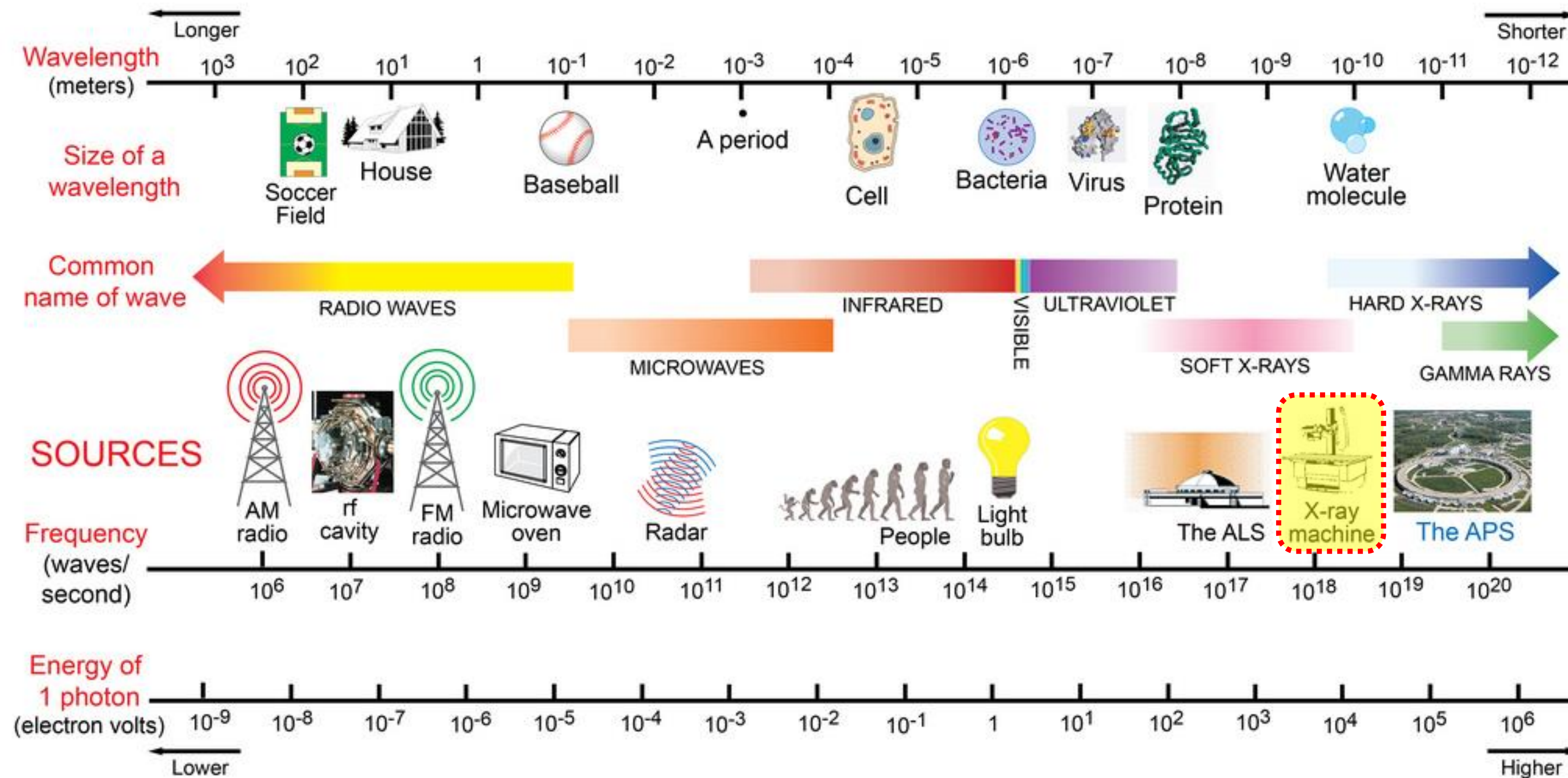
원소 분석  
(Element Analysis)  
Si, Al, Fe, Ni, Cu ...

# Depth & Volume of Analysis



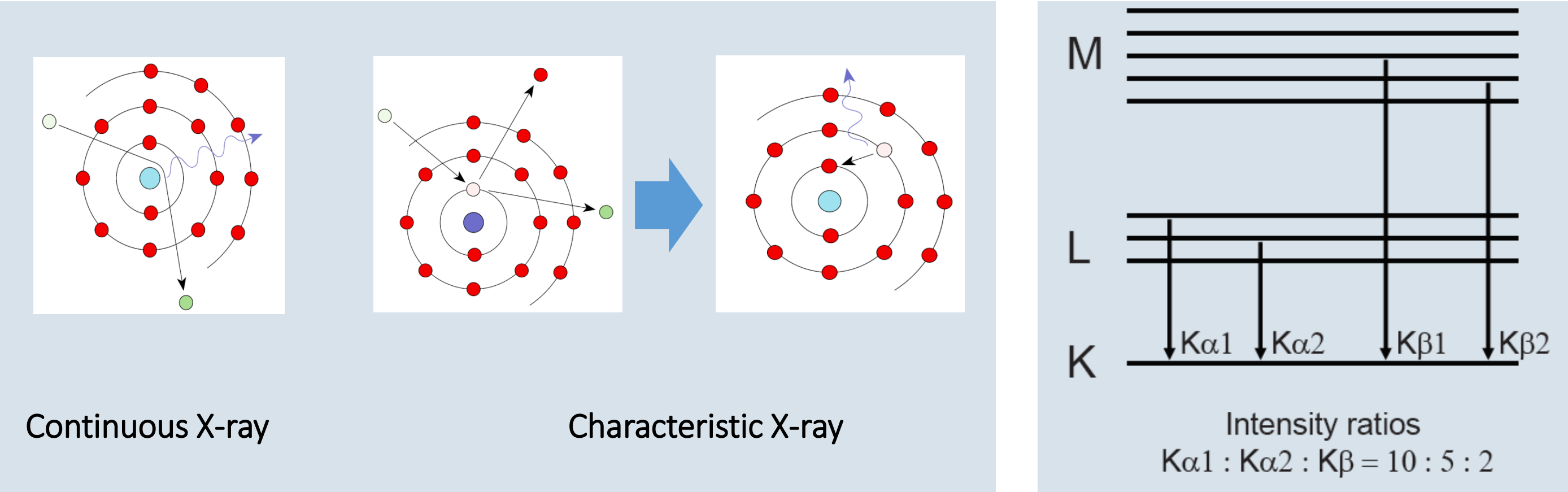
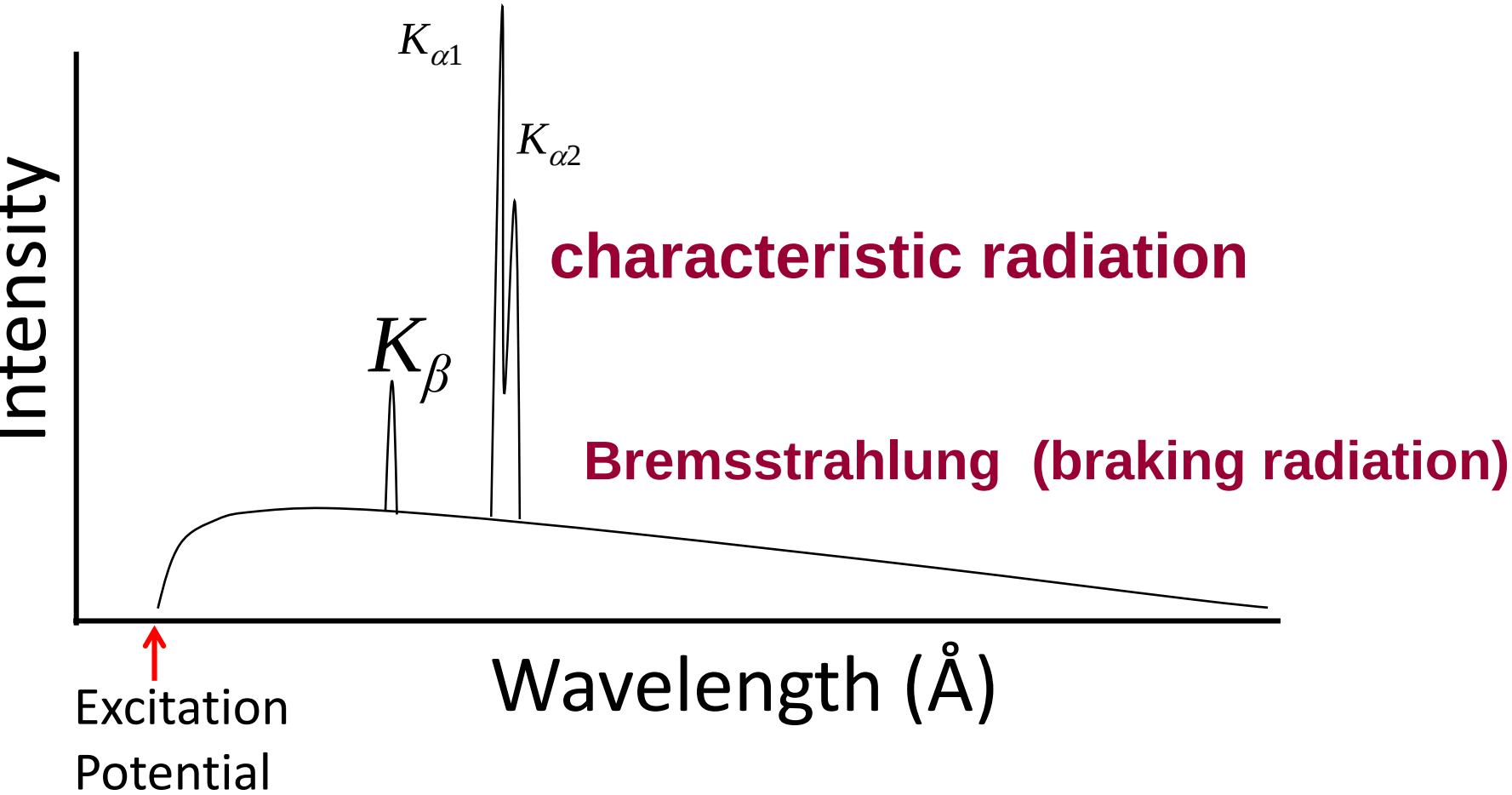


# What is X-ray?



“ Wave or Particle of energy called photon with short wave length ( $0.5 \sim 2.5 \text{ \AA}$ ) ”

# What is X-ray?



| Cu Anode          | Wavelength | Mo Anode          | Wavelength | Cr Anode          | Wavelength | Co Anode          | Wavelength |
|-------------------|------------|-------------------|------------|-------------------|------------|-------------------|------------|
| Cu $K_{\alpha 1}$ | 1.540598 Å | Mo $K_{\alpha 1}$ | 0.709319 Å | Cr $K_{\alpha 1}$ | 2.289760 Å | Co $K_{\alpha 1}$ | 1.789010 Å |
| Cu $K_{\alpha 2}$ | 1.544426 Å | Mo $K_{\alpha 2}$ | 0.713609 Å | Cr $K_{\alpha 2}$ | 2.293663 Å | Co $K_{\alpha 2}$ | 1.792900 Å |
| Cu $K_{\beta}$    | 1.392250 Å | Mo $K_{\beta}$    | 0.632305 Å | Cr $K_{\beta}$    | 2.084920 Å | Co $K_{\beta}$    | 1.620830 Å |

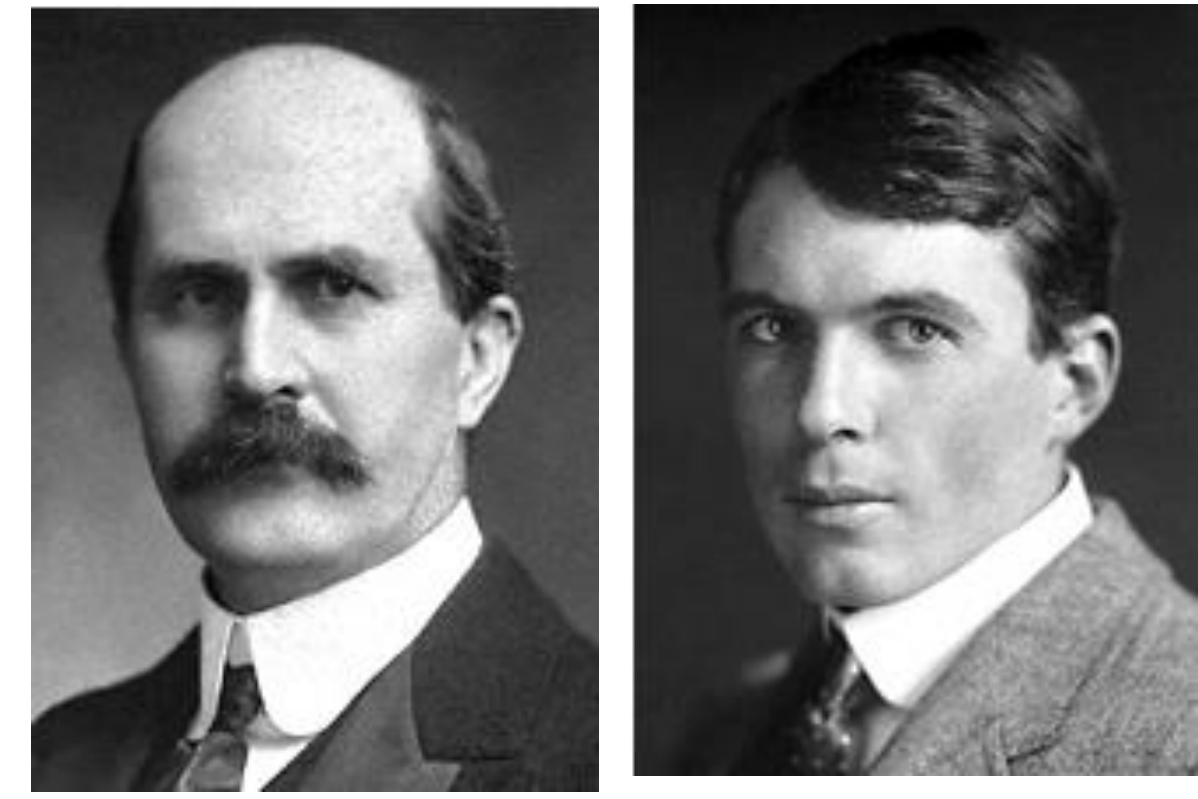
# History of X-ray



1895년 Rontgen, X-ray 발견



1912년 Laue, 회절 현상

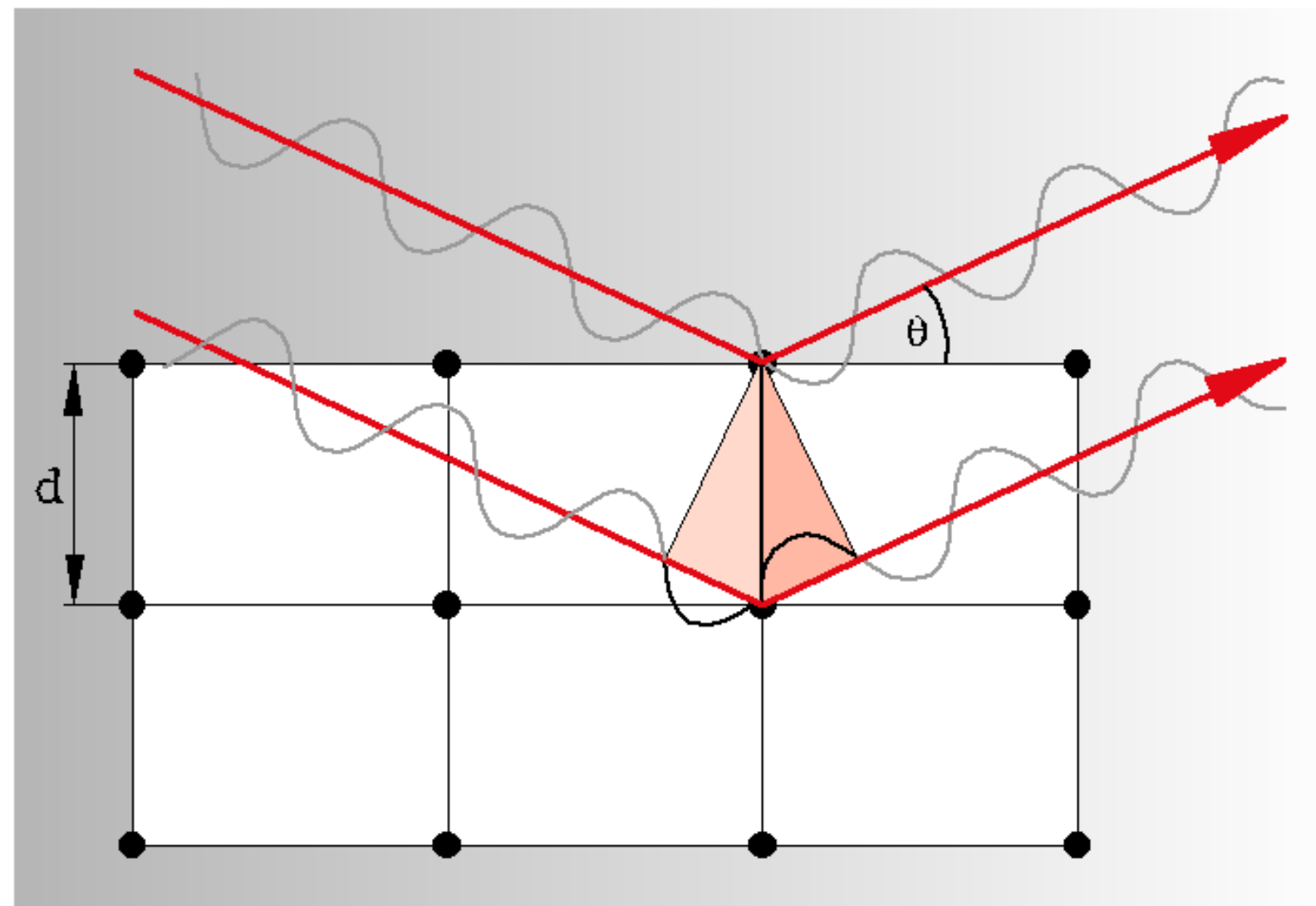


1913년 Bragg, Bragg 법칙

# What is Diffraction?

“ 원자간 거리가  $d$ 인 임의의 결정에 파장  $\lambda$ 인 X-선을 입사각  $\theta$ 로 조사하면, X-선은 원자에 의해 모든 방향으로 산란된다.

이때 산란된 X-선의 경로 차가 입사 X-선 파장의 정수 배로 된 X-선은 간섭효과에 의해 강해진다. 이 현상을 회절현상이라 부른다. ”



$$\text{Bragg's Law } n\lambda = 2d \sin \theta$$

| 장비  | Known     | Measure  | Calculated |
|-----|-----------|----------|------------|
| XRD | $\lambda$ | $\theta$ | $d$        |
| XRF | $d$       | $\theta$ | $\lambda$  |

## Why X-ray Diffraction?

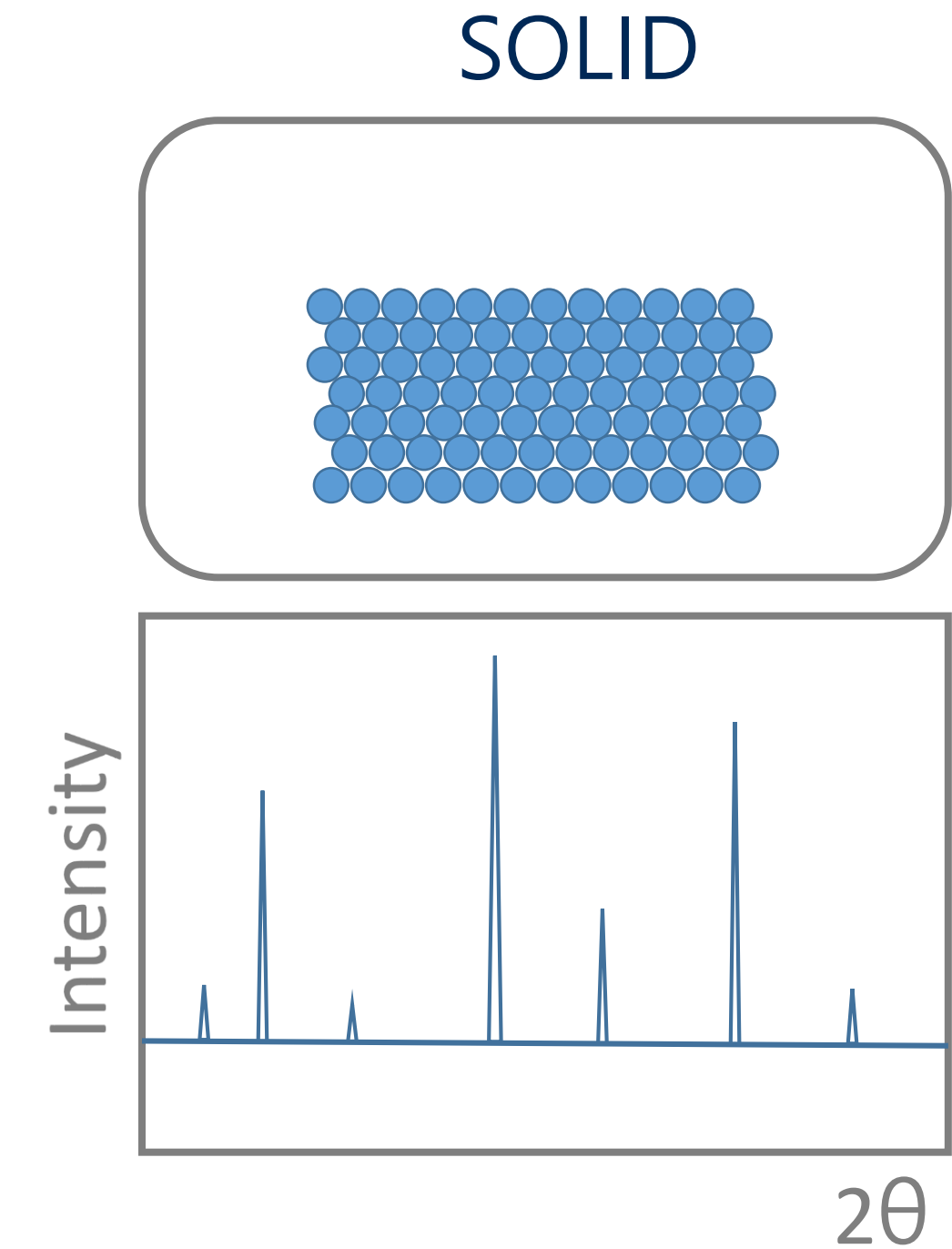
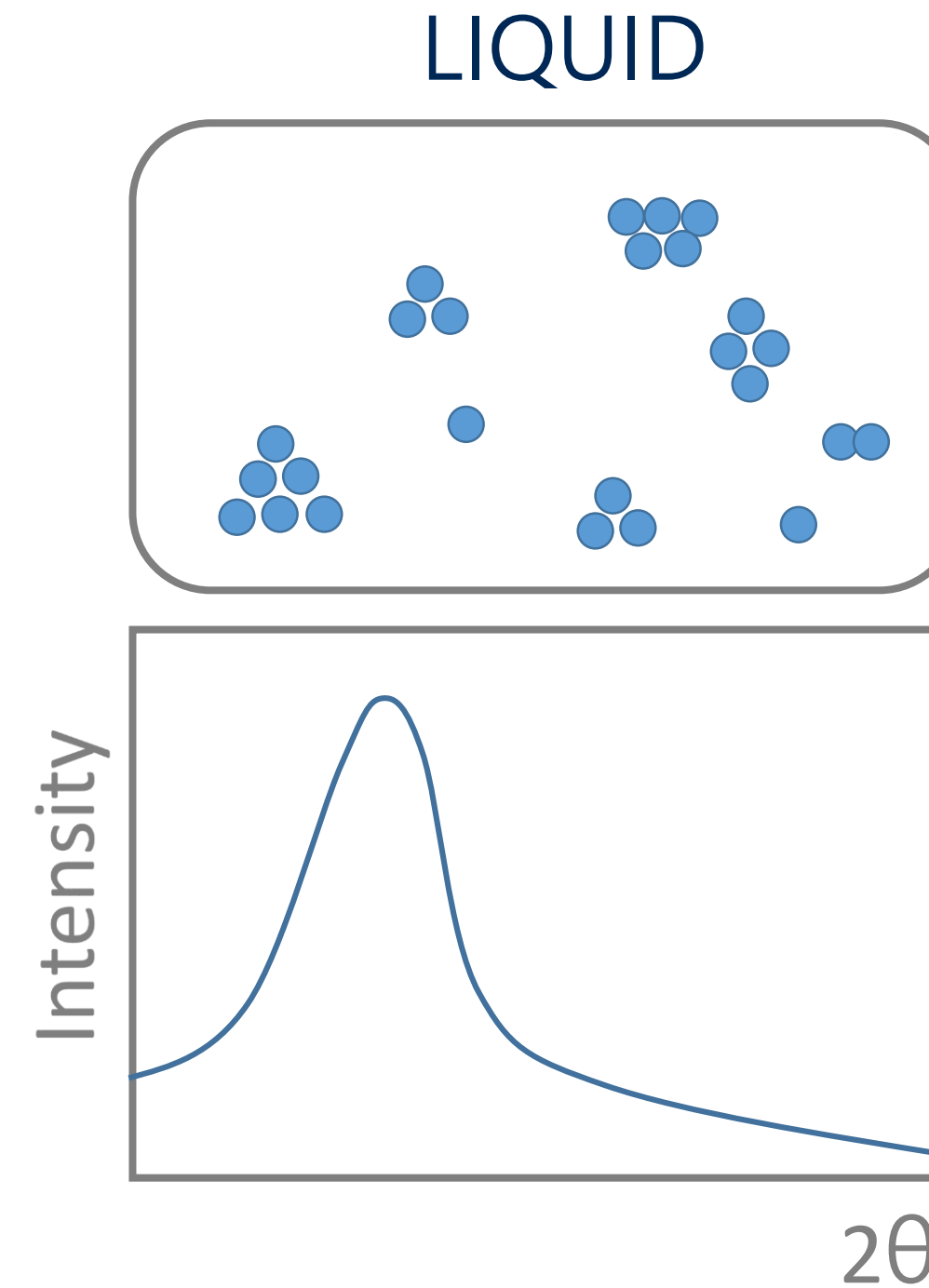
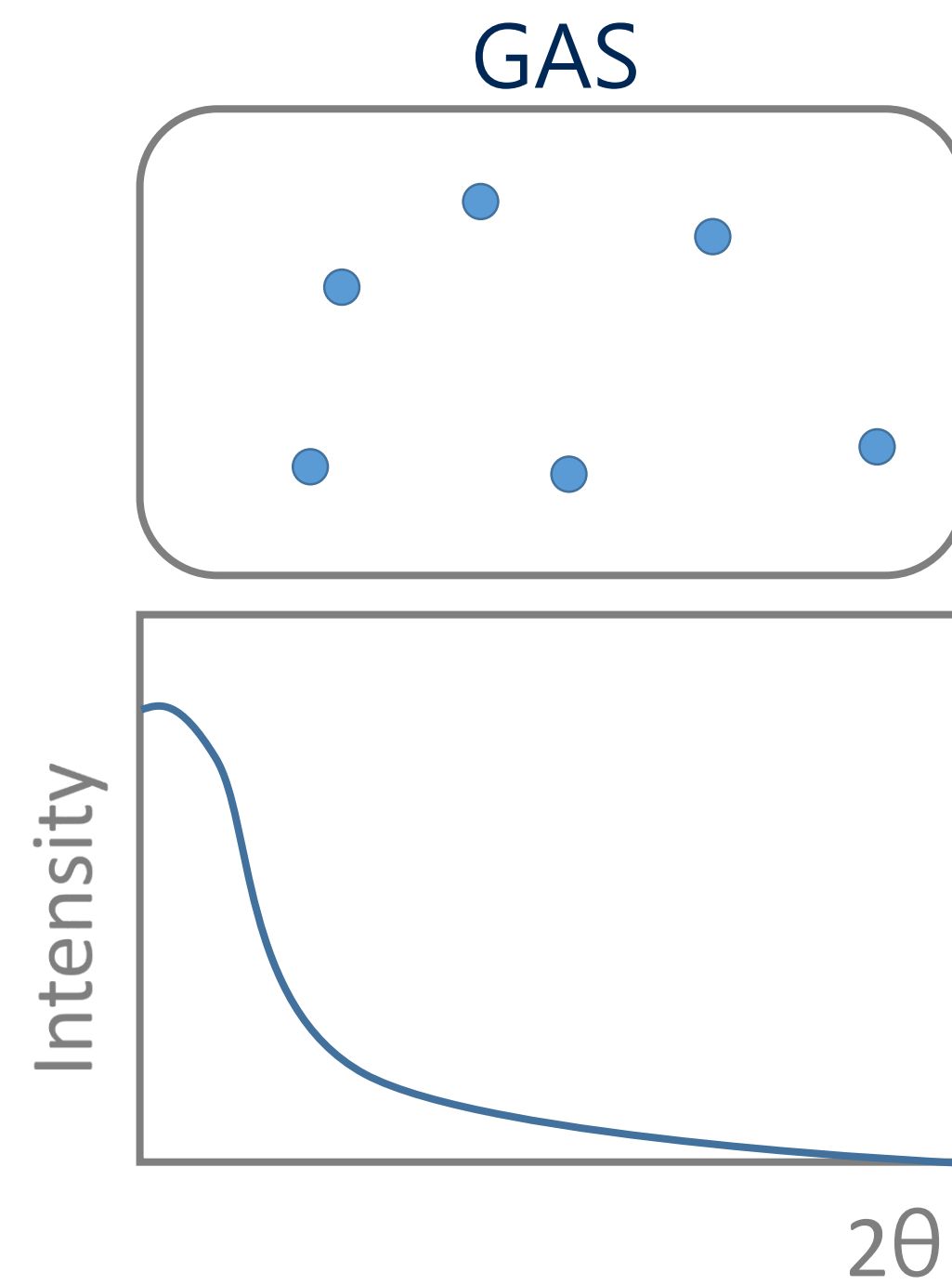
“ X선 회절의 강도와 진행 방향은 물질을 구성하고 있는 원자의 배열과 밀접한 관련이 있다.  
이러한 특성을 이용하여 물질의 결정 구조나 배열 상태를 알 수 있다. ”

## X-ray Diffractometer?

“ X선을 시료에 조사하여 회절되는 X선을 검출하여, x축으로 회절 방향과 y축으로 회절 강도의 데이터를 얻는 분석 장비”

# X-Ray Diffraction of the State

13

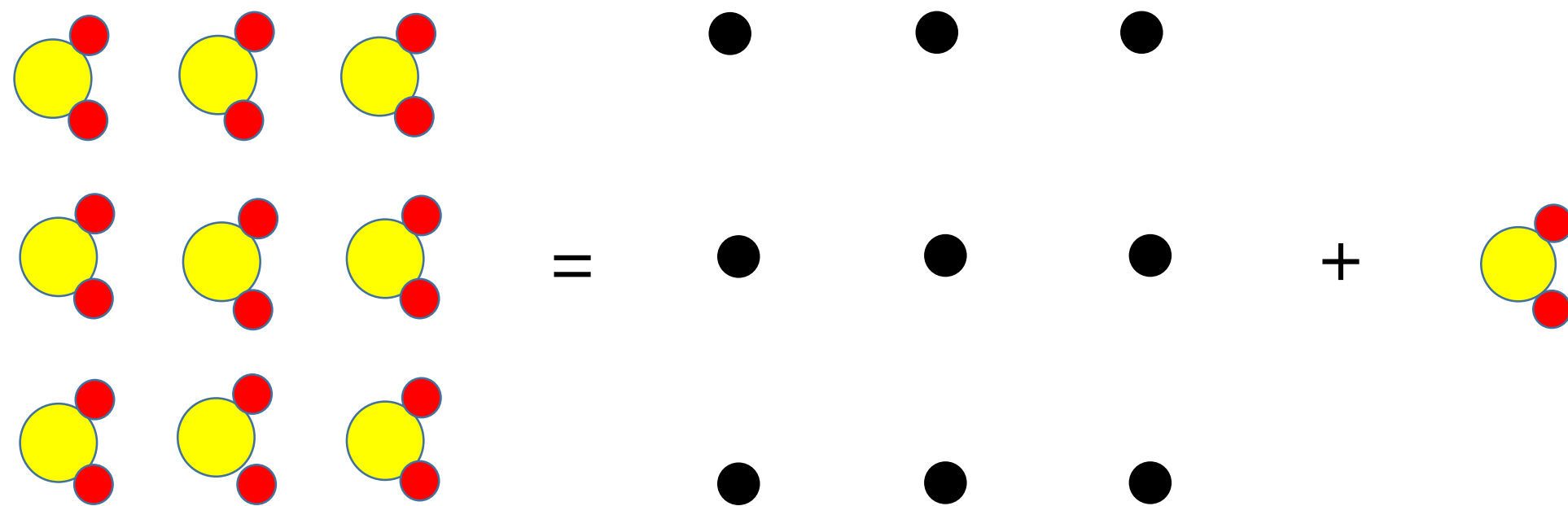


## Crystal vs Amorphous

- Crystal : 원자가 3차원적 주기성, 규칙성, 반복성을 가지고 배열하는 상태 (결정)
- Amorphous : 원자 배열의 규칙성이 결여된 상태 (비정질)

# Basic Theory

Crystal structure can be obtained by attaching atoms, groups of atoms or molecules which are called basis (motif) to the lattice sites of the lattice point.



**Crystal structure = Crystal lattice + Basis (Motif)**

## Single Crystal vs Poly Crystal

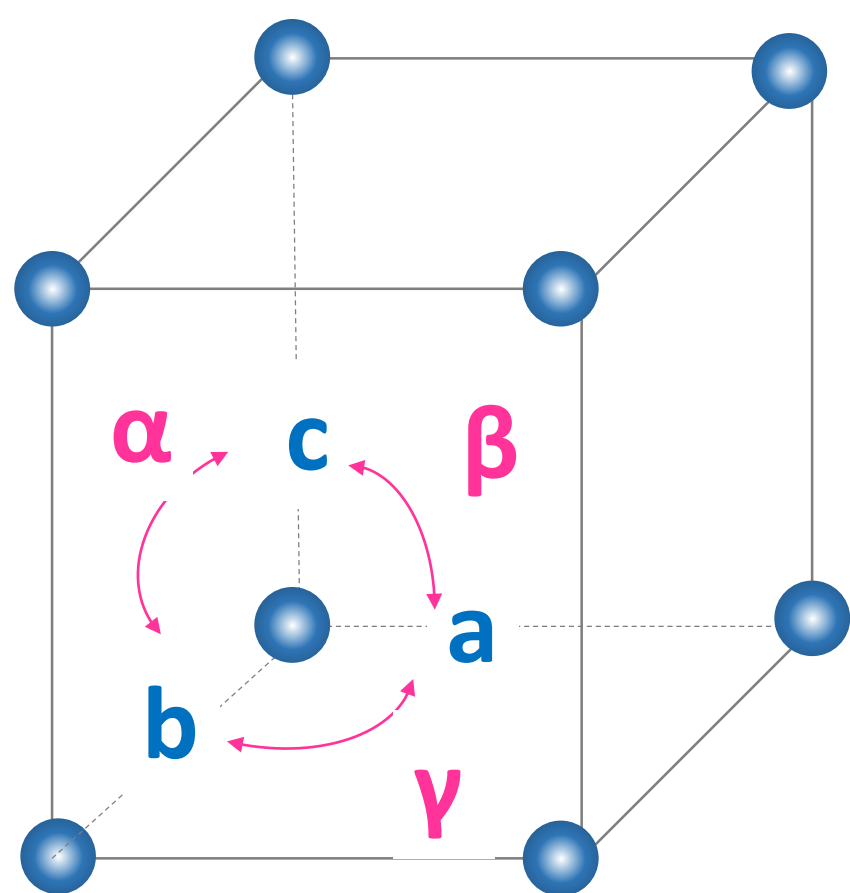
- Single Crystal (단결정):  
하나의 개체 전체에 원자의 규칙성과 반복성이 유지되고 있는 상태
- Poly Crystal (다결정):  
서로 다른 방향을 가진 미세 단결정들이 존재하고 있는 상태

## Random vs Preferred Orientation

- Random: 미세 단결정들이 다양한 방향으로 균일하게 섞여 있는 경우
- Preferred Orientation : 미세 단결정들이 특정한 방향으로 배열되어 있는 경우

# 7 Crystal system & 14 Bravais lattice

## ➤ 7 Crystal System



- Cubic :  $a = b = c$ ,  $\alpha = \beta = \gamma = 90^\circ$
- Hexagonal :  $a = b \neq c$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$
- Tetragonal :  $a = b \neq c$ ,  $\alpha = \beta = \gamma = 90^\circ$
- Orthorhombic :  $a \neq b \neq c$ ,  $\alpha = \beta = \gamma = 90^\circ$
- Monoclinic :  $a \neq b \neq c$ ,  $\alpha = \gamma = 90^\circ \neq \beta$
- Trigonal :  $a \neq b \neq c$ ,  $\alpha = \beta = \gamma < 120^\circ$ ,  $\neq 90^\circ$
- Triclinic :  $a \neq b \neq c$ ,  $\alpha \neq \beta \neq \gamma$

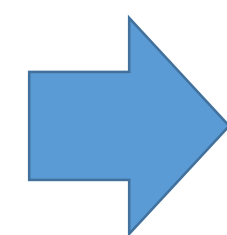
7 Crystal System

+

14 Bravais Lattices

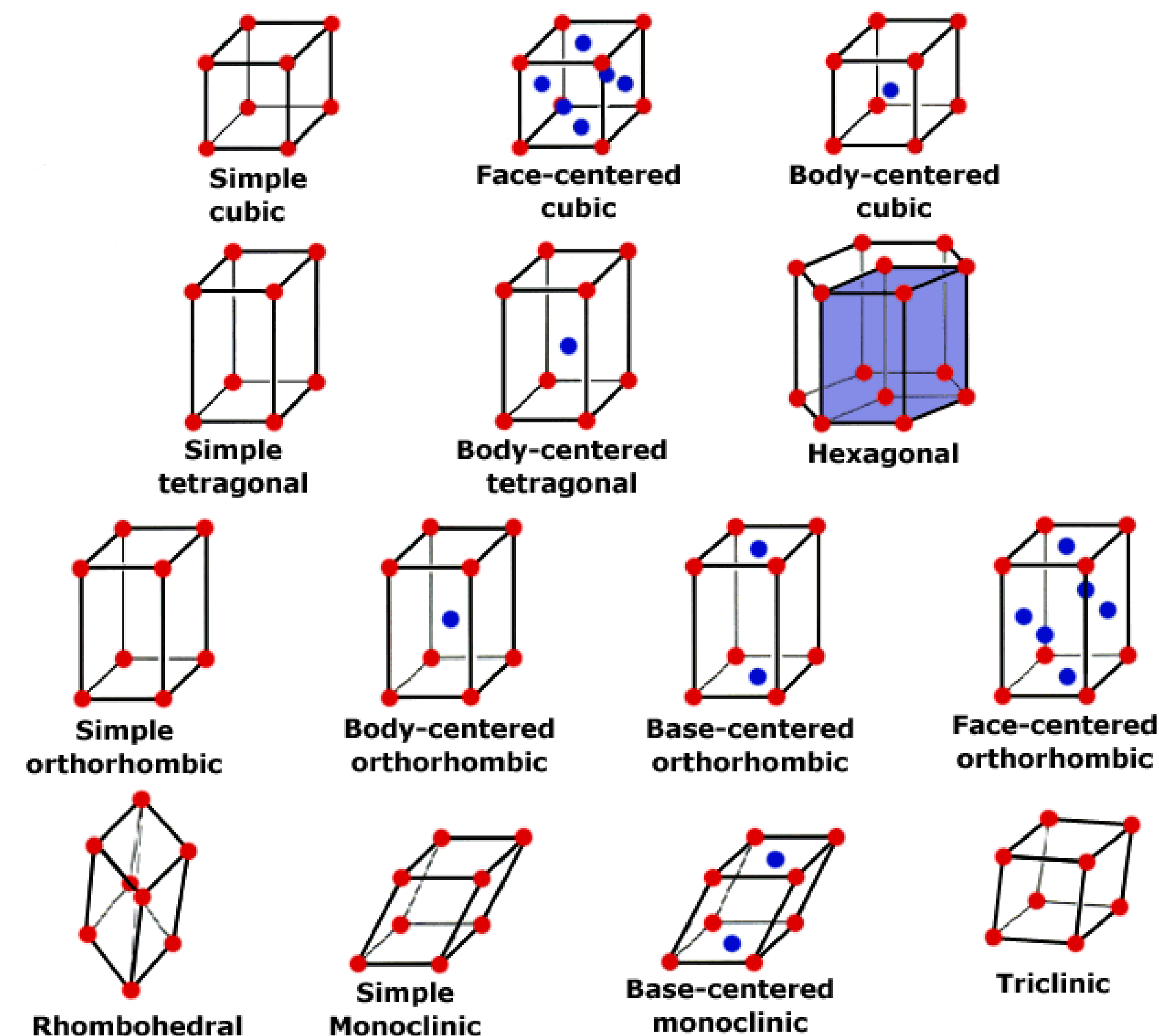
+

32 Crystallographic Point Groups



**230 space groups**

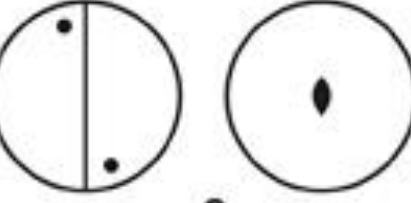
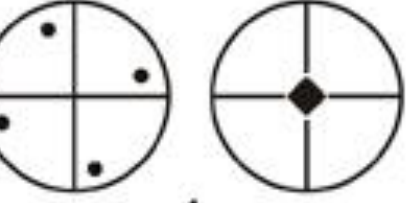
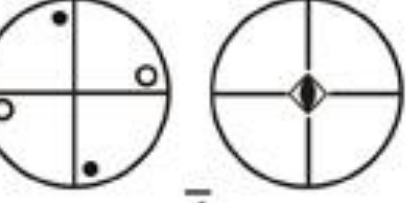
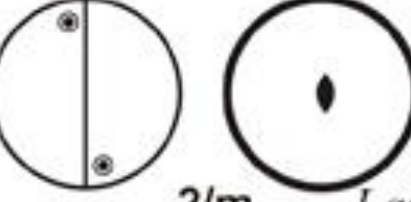
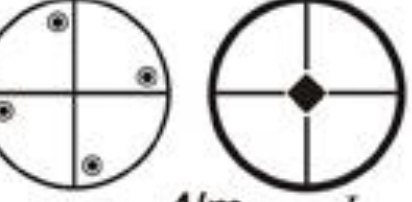
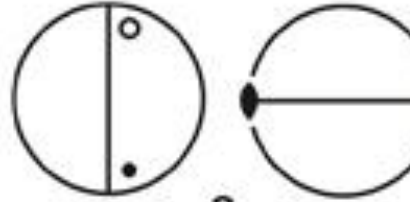
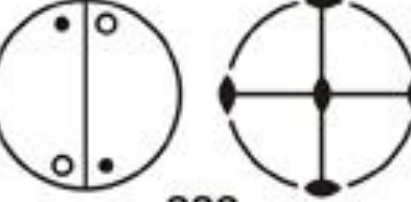
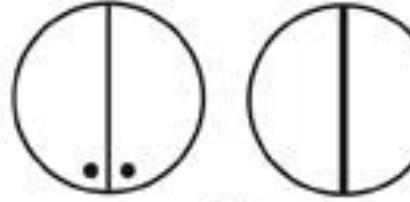
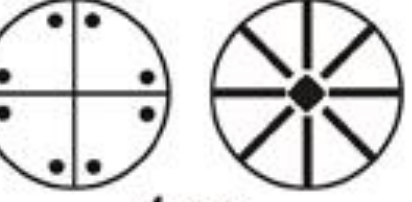
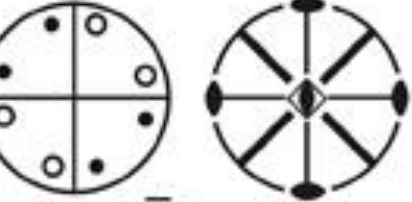
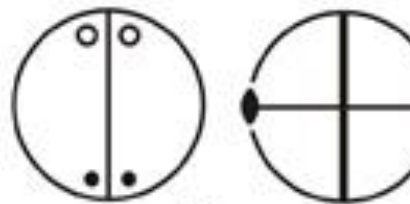
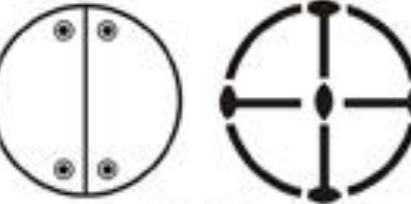
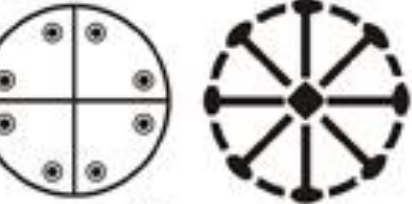
## ➤ 14 Bravais lattices



# 32 point of groups

14 plane lattices + 32 point groups  
→ 230 Space groups

| Crystal Class | Bravais Lattices | Point Groups                                            |
|---------------|------------------|---------------------------------------------------------|
| Triclinic     | P                | 1, $\bar{1}$                                            |
| Monoclinic    | P, C             | 2, m, 2/m                                               |
| Orthorhombic  | P, C, F, I       | 222, mm2, 2/m 2/m 2/m                                   |
| Trigonal      | P, R             | 3, $\bar{3}$ , 32, 3m, $\bar{3}2/m$                     |
| Hexagonal     | P                | 6, $\bar{6}$ , 6/m, 622, 6mm, $\bar{6}m2$ , 6/m 2/m 2/m |
| Tetragonal    | P, I             | 4, $\bar{4}$ , 4/m, 422, 4mm, $\bar{4}2m$ , 4/m 2/m 2/m |
| Isometric     | P, F, I          | 23, 2/m $\bar{3}$ , 432, $\bar{4}3m$ , 4/m $\bar{3}2/m$ |

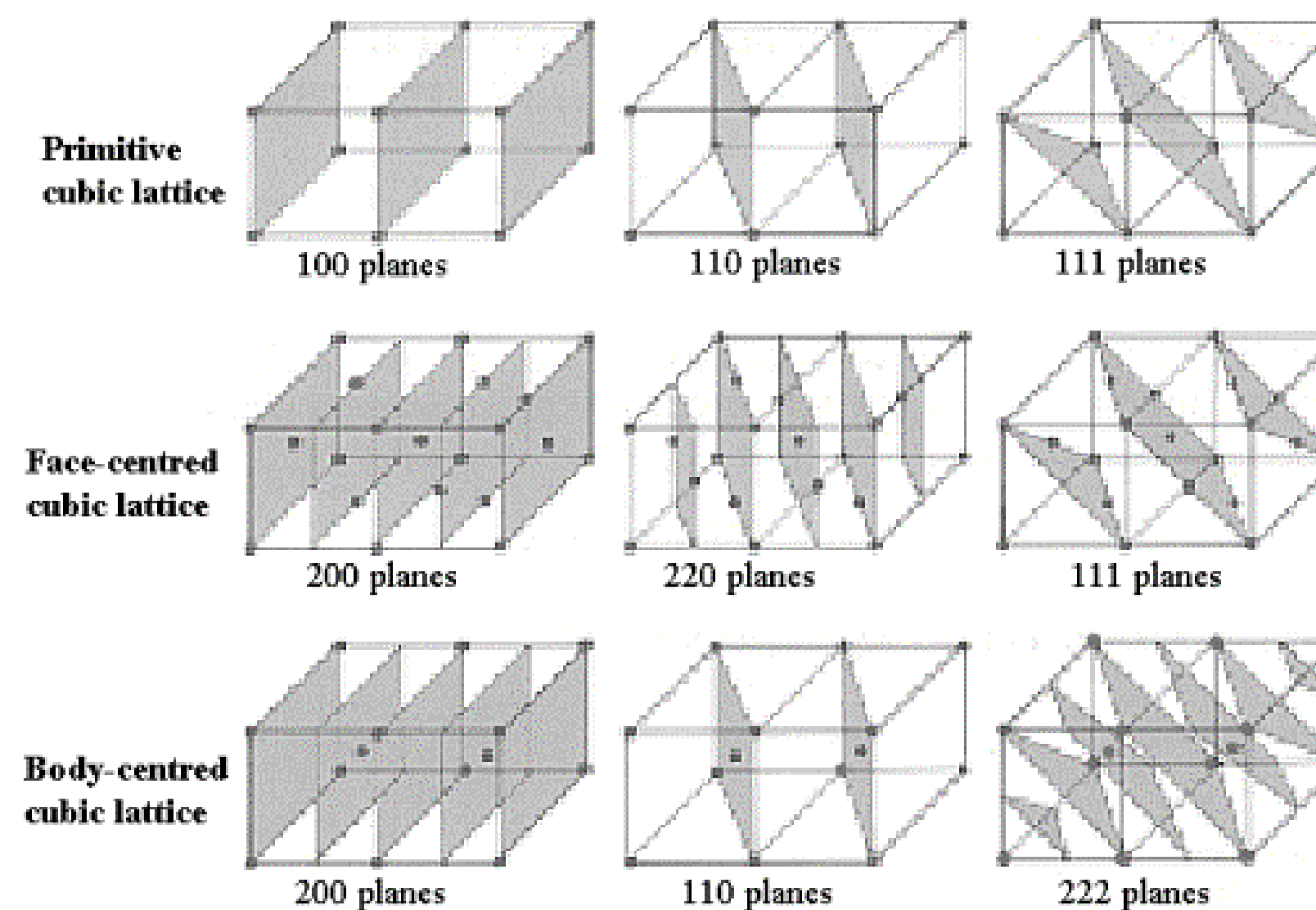
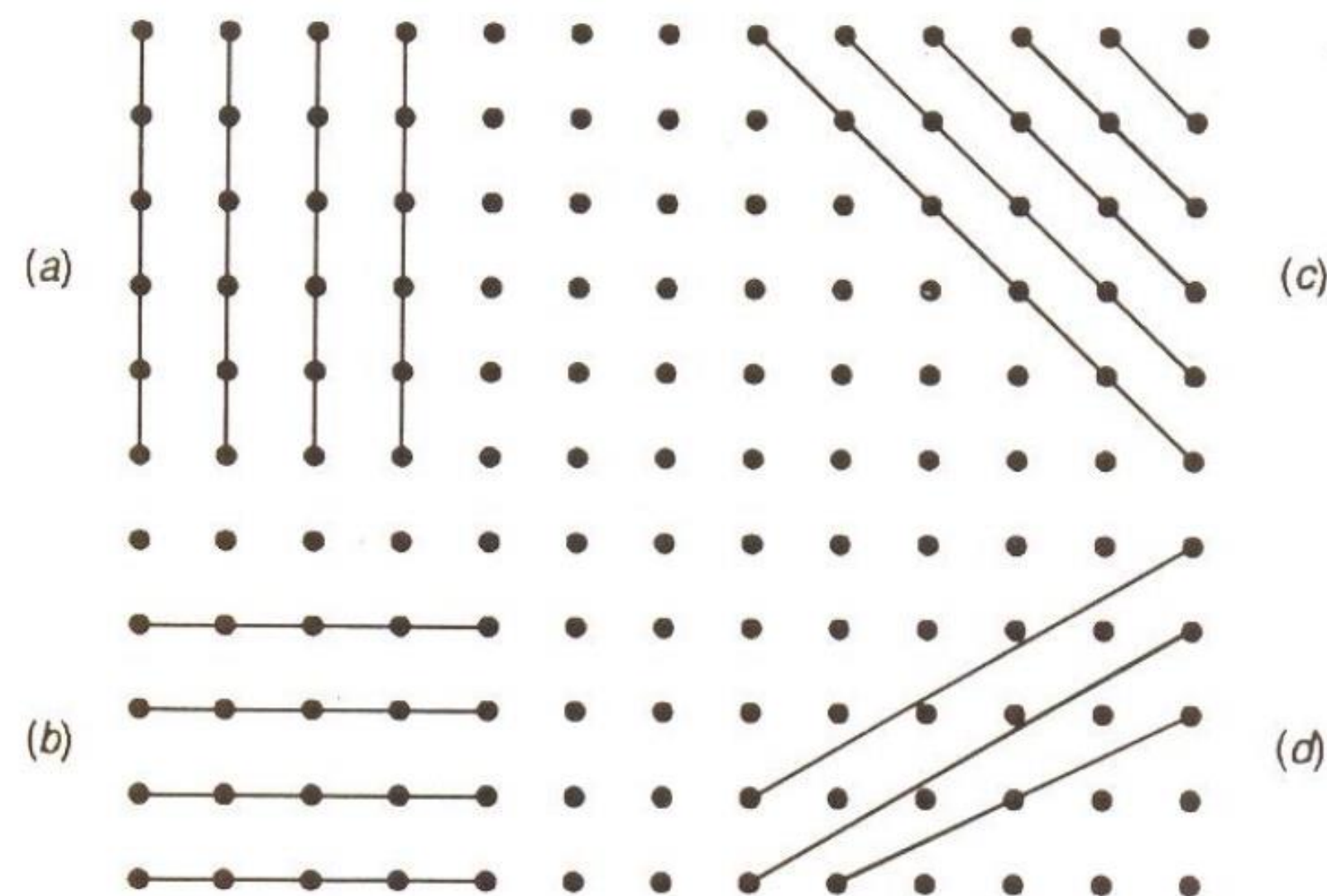
|                                                                                | Triclinic                                                                                                    | Monoclinic (1st setting)                                                                                 | Tetragonal                                                                                                 |
|--------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------|
| $\chi$                                                                         | <br>1                     | <br>2                 | <br>4                   |
| $\bar{\chi}$<br>(even)                                                         | —                                                                                                            | <br>m (=2)            | <br>$\bar{4}$           |
| $\bar{\chi}$<br>(even)<br>plus<br>centre<br>and<br>$\bar{\chi}$<br>(odd)       | <br>$\bar{1}$ <i>Laue</i> | <br>2/m <i>Laue</i>   | <br>4/m <i>Laue</i>     |
|                                                                                | Monoclinic (2nd setting)                                                                                     |                                                                                                          | Orthorhombic                                                                                               |
| $\chi 2$                                                                       | <br>2                    | <br>222              | <br>422                |
| $\chi m$                                                                       | <br>m                   | <br>mm2             | <br>4mm               |
| $\bar{\chi} 2$<br>(even)<br>or<br>$\bar{\chi} m$<br>(even)                     | —                                                                                                            | —                                                                                                        | <br>$\bar{4}2m$       |
| $\chi 2$<br>or<br>$\chi m$<br>plus<br>centre<br>and<br>$\bar{\chi} m$<br>(odd) | <br>2/m <i>Laue</i>     | <br>mmm <i>Laue</i> | <br>4/mmm <i>Laue</i> |

# Lattice Plane

Lattice Plane is a plane which intersects atoms of a unit cell across the whole 3D lattice.

There are many ways of constructing lattice planes through a lattice.

The perpendicular separation between each plane is called the d-spacing.



# Lattice Plane

Cubic

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Orthorhombic

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

Hexagonal

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

Monoclinic

$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$$

- Indexing – the process of determining unit cell shape and size
- Involves assigning the correct (hkl) indices to each reflection
- Straightforward for **cubic** symmetry:

$$\lambda = 2d \sin \theta \quad \xrightarrow{\quad} \quad \frac{1}{d^2} = \frac{4 \sin^2 \theta}{\lambda^2}$$

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)}{a^2} \quad \xrightarrow{\quad} \quad \frac{\sin^2 \theta}{(h^2 + k^2 + l^2)} = \frac{\lambda^2}{4a^2} \quad \rightarrow \quad \frac{4 \sin^2 \theta}{\lambda^2} = \frac{(h^2 + k^2 + l^2)}{a^2}$$

- Quotient  **$l^2 / 4a^2$  : constant** for any pattern (l and a are fixed)
- Sum  $(h^2 + k^2 + l^2)$  : integer
- $(h^2 + k^2 + l^2) / \sin^2 \theta \rightarrow$  Constant
- $(h^2 + k^2 + l^2) \rightarrow$  Miller indices (h k l)

- For each **Bravais lattice** type, the following general rules apply:

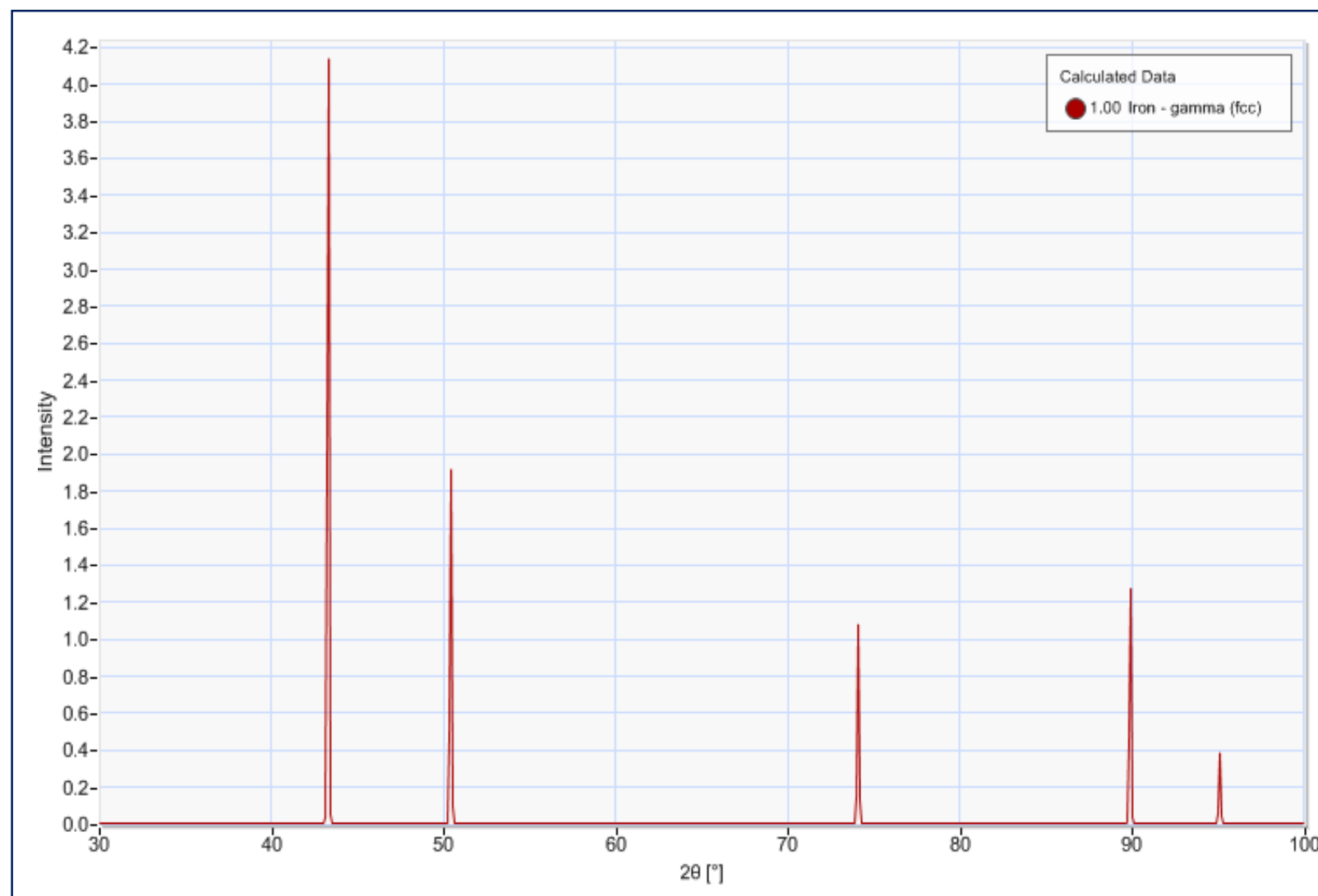
- **Primitive:** All values of h, k, l are allowed
- **Body centred:** Values of  $h + k + l = 2n$  only are allowed (where n is integral)
- **Face centred:** Values of h, k, l all odd or all even are allowed (0 counts as even)

# Example: Indexing XRD Pattern

21

## ❖ Sequence to index a powder diffraction pattern

- 1) Convert  $d$  or  $q$  values to  $\sin^2 q$  values if necessary
- 2) Divide  $\sin^2 q$  values by allowed  $(h^2 + k^2 + l^2)$  for primitive, body centred or face centred unit cells
- 3) Inspect  $\sin^2 q / (h^2 + k^2 + l^2)$  values  $\rightarrow$  are they constant?
- 4) If "No" repeat steps 2 - 3; if yes continue to step 5
- 5) Assign Miller indices  $(hkl)$  for each reflection
- 6) Determine the cubic cell constant,  $a$



At a given wavelength,

### Knowns

- 1) One of the Fe allotropes
- 2) Reflections positions

### Unknowns

- 1) Lattice Type
- 2) Cell Parameter

| Peak      | 1st  | 2nd  | 3rd  | 4th  | 5th  |
|-----------|------|------|------|------|------|
| $2\theta$ | 43.9 | 50.9 | 74.8 | 90.3 | 95.5 |

## Example: Indexing XRD Pattern

- Is the material **primitive cubic**? Conditions: **all values of h, k, l allowed**

| Line | $2\theta$ | $\sin^2\theta$ | $hkl$ | $h^2+k^2+l^2$ | $\sin^2\theta / (h^2+k^2+l^2)$ |
|------|-----------|----------------|-------|---------------|--------------------------------|
| 1    | 43.9      | 0.140          | 100   | 1             | 0.140                          |
| 2    | 50.9      | 0.185          | 110   | 2             | 0.093                          |
| 3    | 74.8      | 0.369          | 111   | 3             | 0.123                          |
| 4    | 90.3      | 0.503          | 200   | 4             | 0.123                          |
| 5    | 95.5      | 0.548          | 210   | 5             | 0.110                          |

- Values of  $\sin^2\theta / (h^2 + k^2 + l^2)$  are **not constant**  $\rightarrow$  **not primitive cubic**

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

- Then, is the material **Body-centered cubic**? Conditions:  **$h + k + l = 2n$**

| Line | $2\theta$ | $\sin^2\theta$ | $hkl$ | $h^2+k^2+l^2$ | $\sin^2\theta / (h^2+k^2+l^2)$ |
|------|-----------|----------------|-------|---------------|--------------------------------|
| 1    | 43.9      | 0.140          | 110   | 2             | 0.0700                         |
| 2    | 50.9      | 0.185          | 200   | 4             | 0.0463                         |
| 3    | 74.8      | 0.369          | 211   | 6             | 0.0615                         |
| 4    | 90.3      | 0.503          | 220   | 8             | 0.0629                         |
| 5    | 95.5      | 0.548          | 310   | 10            | 0.0548                         |

- Values of  $\sin^2\theta / (h^2 + k^2 + l^2)$  **not constant**  $\rightarrow$  **not Body-centred cubic**

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

## Example: Indexing XRD Pattern

- Then, is the material **Face-centered cubic**? Conditions:  $h, k, l$  all odd or even

| Line | $2\theta$ | $\sin^2 \theta$ | $hkl$ | $h^2 + k^2 + l^2$ | $\sin^2 \theta / (h^2 + k^2 + l^2)$ |
|------|-----------|-----------------|-------|-------------------|-------------------------------------|
| 1    | 43.9      | 0.140           | 111   | 3                 | 0.0467                              |
| 2    | 50.9      | 0.185           | 200   | 4                 | 0.0463                              |
| 3    | 74.8      | 0.369           | 220   | 8                 | 0.0461                              |
| 4    | 90.3      | 0.503           | 311   | 11                | 0.0457                              |
| 5    | 95.5      | 0.548           | 222   | 12                | 0.0457                              |

- Values of  $\sin^2 \theta / (h^2 + k^2 + l^2)$  are constant  $\rightarrow$  Face-centered cubic

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

# Structure Factor & Systematic Absences

$$F_{hkl} = \sum_1^N f_n e^{2\pi i(hu_n + kv_n + lw_n)} \quad I \propto |F|^2$$

- $h, k, l$ : indices of the diffraction plane under consideration
- $u, v, w$ : coordinates of the atoms in the lattice
- $N$ : number of atoms
- $f_n$ : scattering factor of a particular type of atom

| Bravais Lattice | Reflections possibly present                 | Reflections necessarily absent |
|-----------------|----------------------------------------------|--------------------------------|
| Simple          | All                                          | None                           |
| Body Centered   | (h+k+l): Even                                | (h+k+l): Odd                   |
| Face Centered   | h, k, and l unmixed i.e. all odd or all even | h, k, and l: mixed             |

## Permitted Reflections

|              |                                                                     |
|--------------|---------------------------------------------------------------------|
| Simple Cubic | (100), (110), (111), (200), (210), (211), (220), (300), (221) ..... |
| BCC          | (110), (200), (211), (220), (310), (222)....                        |
| FCC          | (111), (200), (220), (311).....                                     |

# Structure Factor & Systematic Absences

❖ Sequence to derive the systematic absence conditions for a Bravais lattice?

- 1) Write down the structure factor expression
- 2) Identify Bravais lattice type: primitive (P), body-(B), face-(F), or side-(A, B, C) centered
- 3) Write down fractional coordinates (u,v,w) of unique atoms in unit cell
- 4) Insert coordinates into structure factor expression – need one term per atom
- 5) Factorise the expression in  $f$
- 6) Does the exponential term resolve to +1 or -1 for particular combinations of  $(hkl)$ ?
- 7) Does  $F_{hkl}^2$  have zero value?
  - If YES – reflections corresponding to conditions on  $(hkl)$  are systematically absent
  - If NO – reflections have measurable intensity, i.e. not systematically absent

❖ The following relations are useful:

- Where  $n$  is integral and even:  $e^{i\pi n} = 1$
- Where  $n$  is integral and odd:  $e^{i\pi n} = -1$

# Systematic absences: Primitive Cell

- A primitive cell contains one atom located at the origin (0, 0, 0)

- The structure factor is:

$$F_{hkl} = \sum_1^N f_n e^{i2\pi(hu_n + kv_n + lw_n)}$$

- For  $(u, v, w) = (0, 0, 0)$ :  $F_{hkl} = fe^{i2\pi(h_n \times 0 + k_n \times 0 + l_n \times 0)}$

- Thus:

$$F_{hkl} = fe^{i2\pi(0)}$$

- Hence:

$$F_{hkl} = f$$

- Giving:

$$|F_{hkl}|^2 = f^2$$

- The structure factor is thus the same for all reflections

→ No systematic absences

# Systematic absences: Primitive Cell

- A body centered cell contains two atoms located at  $(0, 0, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
- The structure factor is:
- For  $(u, v, w) = (0, 0, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ :  $F_{hkl} = fe^{i2\pi(h_n \times 0 + k_n \times 0 + l_n \times 0)} + fe^{i2\pi(h_n \times \frac{1}{2} + k_n \times \frac{1}{2} + l_n \times \frac{1}{2})}$
- Thus:  $F_{hkl} = fe^{i2\pi(0)} + fe^{i2\pi(\frac{h}{2} + \frac{k}{2} + \frac{l}{2})}$
- Hence:  $F_{hkl} = f(1 + e^{i\pi(h+k+l)})$
- If  $h + k + l = \text{even}$ , we obtain:  $F_{hkl} = f(1+1) = 2f$
- Thus:  $|F_{hkl}|^2 = 4f^2$
- Now:  $F_{hkl} = f(1 + e^{i\pi(h+k+l)})$
- If  $h + k + l = \text{odd}$ , we obtain:  $F_{hkl} = f(1-1) = 0$
- Thus:  $|F_{hkl}|^2 = 0$
- Thus reflections with  **$h + k + l = \text{even}$  are observed**, e.g.  $(1\ 1\ 0)$
- Whereas reflections with  **$h + k + l = \text{odd}$  are systematically absent**, e.g.  $(1\ 0\ 0)$

## Systematic absences: Faced Cubic Cell

- A face centered cell contains four atoms located at  $(0, 0, 0)$ ,  $(0, \frac{1}{2}, \frac{1}{2})$ ,  $(\frac{1}{2}, 0, \frac{1}{2})$  and  $(\frac{1}{2}, \frac{1}{2}, 0)$

- The structure factor is: 
$$F_{hkl} = \sum_1^N f_n e^{i2\pi(hu_n + kv_n + lw_n)}$$

- For  $(u, v, w) = (0, 0, 0)$ ,  $(0, \frac{1}{2}, \frac{1}{2})$ ,  $(\frac{1}{2}, 0, \frac{1}{2})$  and  $(\frac{1}{2}, \frac{1}{2}, 0)$  :

$$F_{hkl} = fe^{i2\pi(h_n \times 0 + k_n \times 0 + l_n \times 0)} + fe^{i2\pi(h_n \times 0 + k_n \times \frac{1}{2} + l_n \times \frac{1}{2})} + fe^{i2\pi(h_n \times \frac{1}{2} + k_n \times 0 + l_n \times \frac{1}{2})} + fe^{i2\pi(h_n \times \frac{1}{2} + k_n \times \frac{1}{2} + l_n \times 0)}$$

- Thus: 
$$F_{hkl} = f \left( 1 + e^{i\pi(k+l)} + e^{i\pi(h+l)} + e^{i\pi(h+k)} \right)$$

- Hence: 
$$F_{hkl} = fe^{i2\pi(0)} + fe^{i2\pi\left(\frac{k}{2} + \frac{l}{2}\right)} + fe^{i2\pi\left(\frac{h}{2} + \frac{l}{2}\right)} + fe^{i2\pi\left(\frac{h}{2} + \frac{k}{2}\right)}$$

## Systematic absences: Faced Cubic Cell

- Now:  $F_{hkl} = f(1 + e^{i\pi(k+l)} + e^{i\pi(h+l)} + e^{i\pi(h+k)})$
- If h, k and l are unmixed ( $k + l$ ), ( $h + l$ ), ( $h + k$ ) = even, giving:  $F_{hkl} = f(1+1+1+1)$
- Thus:  $F_{hkl} = 4f$
- Hence:  $|F_{hkl}|^2 = 16f$
- If h, k and l are mixed the sum of the exponentials is zero:  $F_{hkl} = f(1+1-1-1)$
- Thus:  $F_{hkl} = 0$
- Hence:  $|F_{hkl}|^2 = 0$
- Thus reflections with ***h, k and l unmixed are observed***, e.g. (1 1 1), (2 0 0)
- Whereas reflections with ***h, k and l mixed are systematically absent***, e.g. (1 0 0), (1 1 0)

# Systematic absences: Summary

- Systematic absences found for the Bravais lattice types:

| Bravais lattice | Reflections possibly present                                      | Systematic absences                                         |
|-----------------|-------------------------------------------------------------------|-------------------------------------------------------------|
| Primitive       | All                                                               | None                                                        |
| Side centered   | k and l unmixed (A)<br>h and l unmixed (B)<br>h and k unmixed (C) | k and l mixed (A)<br>h and l mixed (B)<br>h and k mixed (C) |
| Body centered   | (h+k+l) even                                                      | (h+k+l) odd                                                 |
| Face centered   | h, k, l unmixed                                                   | h, k, l mixed                                               |

- These rules apply to all lattice symmetries because the structure factor is independent of unit cell shape and size.

# Hardware

# XRDs & XRF in UCRF

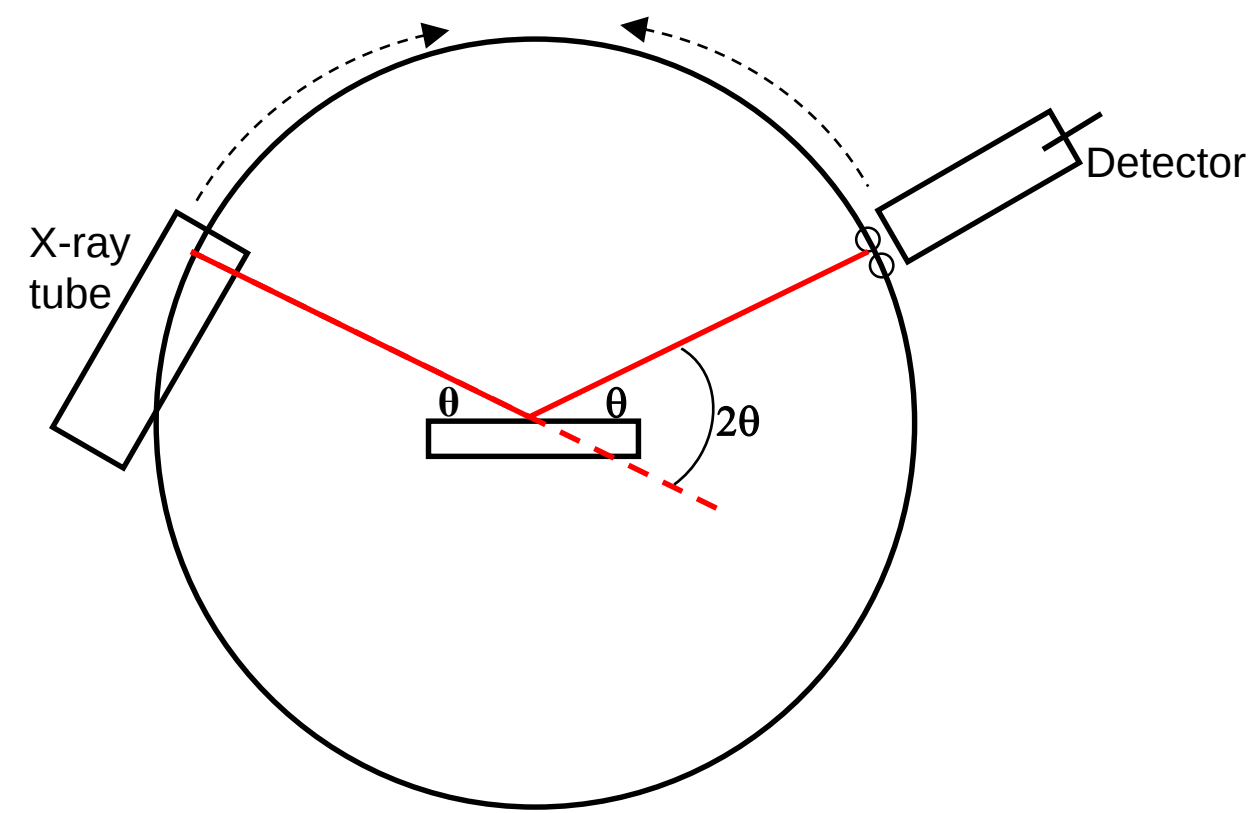
| High Power XRD [X1] | High Resolution XRD [X2] | Normal XRD [X3] | XRF [X4] | High Resolution Powder XRD [X5] |
|---------------------|--------------------------|-----------------|----------|---------------------------------|
|---------------------|--------------------------|-----------------|----------|---------------------------------|



|                                       |                                                      |                                                      |                                    |                                        |
|---------------------------------------|------------------------------------------------------|------------------------------------------------------|------------------------------------|----------------------------------------|
| Bldg.102 B101-2                       | Bldg.102 B101-2                                      | Bldg.102 B101-2                                      | Bldg.102 B101-2                    | Bldg.102 B101-2                        |
| 의뢰/자율사용 가능                            | 의뢰 가능                                                | 의뢰/자율사용 가능                                           | 의뢰 가능                              | 의뢰 가능                                  |
| DMAX-2500PC                           | D8 DISCOVER                                          | D8 ADVANCE                                           | T8 Tiger                           | Smart Lab                              |
| 40 kV 200 mA (Cu Ka)                  | 40 kV 40 mA (Cu Ka)                                  | 40 kV 40 mA (Cu Ka)                                  | 40 kV 40 mA (Rh)                   | 40 kV 200 mA (Cu Ka)                   |
| R (FWHM) : 0.12 ° (LaB <sub>6</sub> ) | R (FWHM) : 0.036 ° (Al <sub>2</sub> O <sub>3</sub> ) | R (FWHM) : 0.058 ° (Al <sub>2</sub> O <sub>3</sub> ) | R: 3 eV (vs. EDS 150 eV)           | R (FWHM) : 0.036 ° (LaB <sub>6</sub> ) |
| 2θ : 0.8° ~ 110°                      | 2θ : 5° ~ 110°                                       | 2θ : 10° ~ 110°                                      | <sup>4</sup> Be to <sup>92</sup> U | 2θ : 10° ~ 110°                        |
| Operation mode: Vertical              | Operation mode: Horizontal                           | Operation mode: Vertical                             | Operation mode: Reverse            | Operation mode: Vertical               |
| Goniometer : θ-2θ Coupled             | Goniometer : θ-2θ Coupled                            | Goniometer : θ-θ Coupled                             | -                                  | Goniometer : θ-2θ Coupled              |
| 분말 상 분석                               | 박막 결정 구조 분석                                          | 분말 상 분석                                              | 원소별 정량분석 (반정량)                     | 분말 결정 구조 분석                            |
| 분말 0.5mg, 박막 (1μm 이상)                 | Bulk & 극박막 (1μm 이하)                                  | 분말 0.3g, Bulk, 액상                                    | 분말 10g, 액상                         | 분말 0.5mg, 박막 (1μm 이상), 액상              |

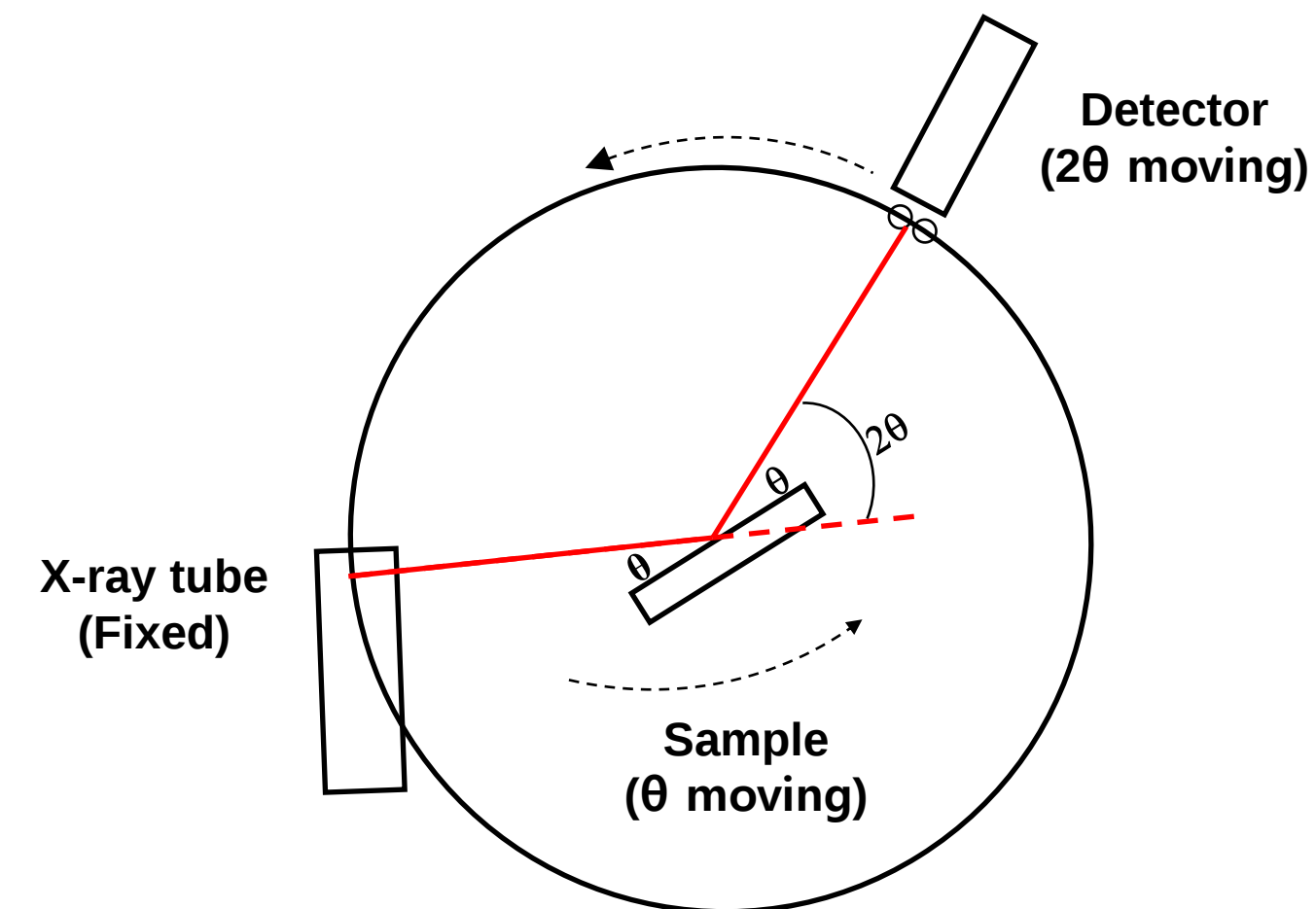
# Goniometer Type

## $\theta - \theta$ Geometry



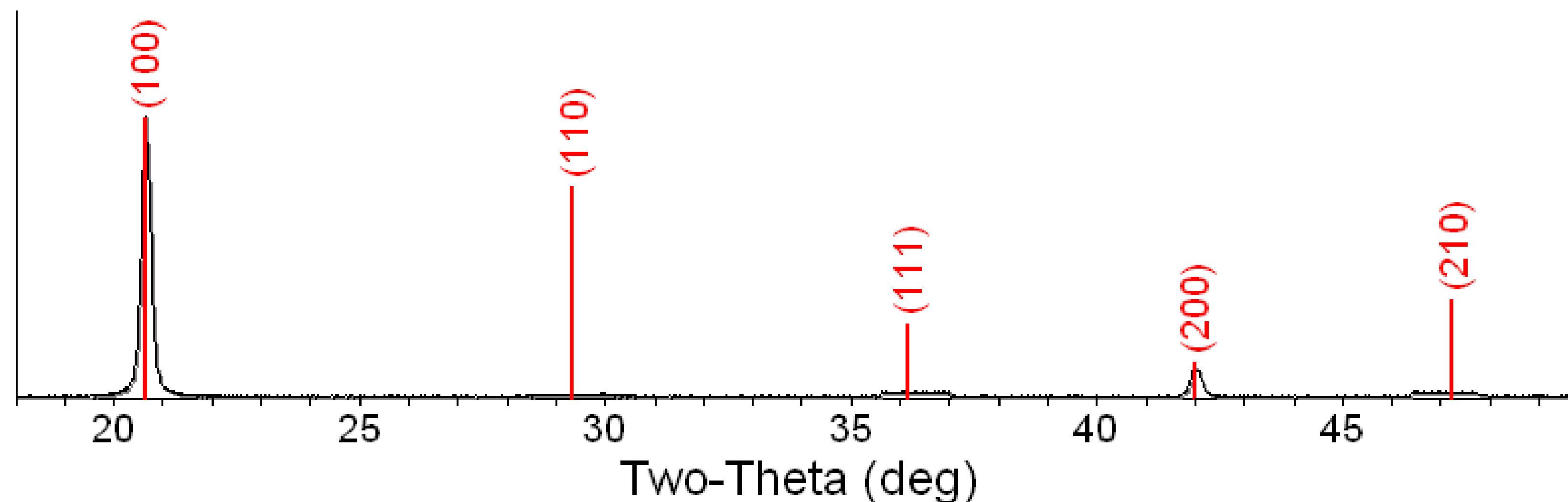
- 장점 : Sampling 제한 없음.
- 단점 : 저각 측정 제한. (From 10 degree)
- 장비 : NXRD

## $\theta - 2\theta$ Geometry



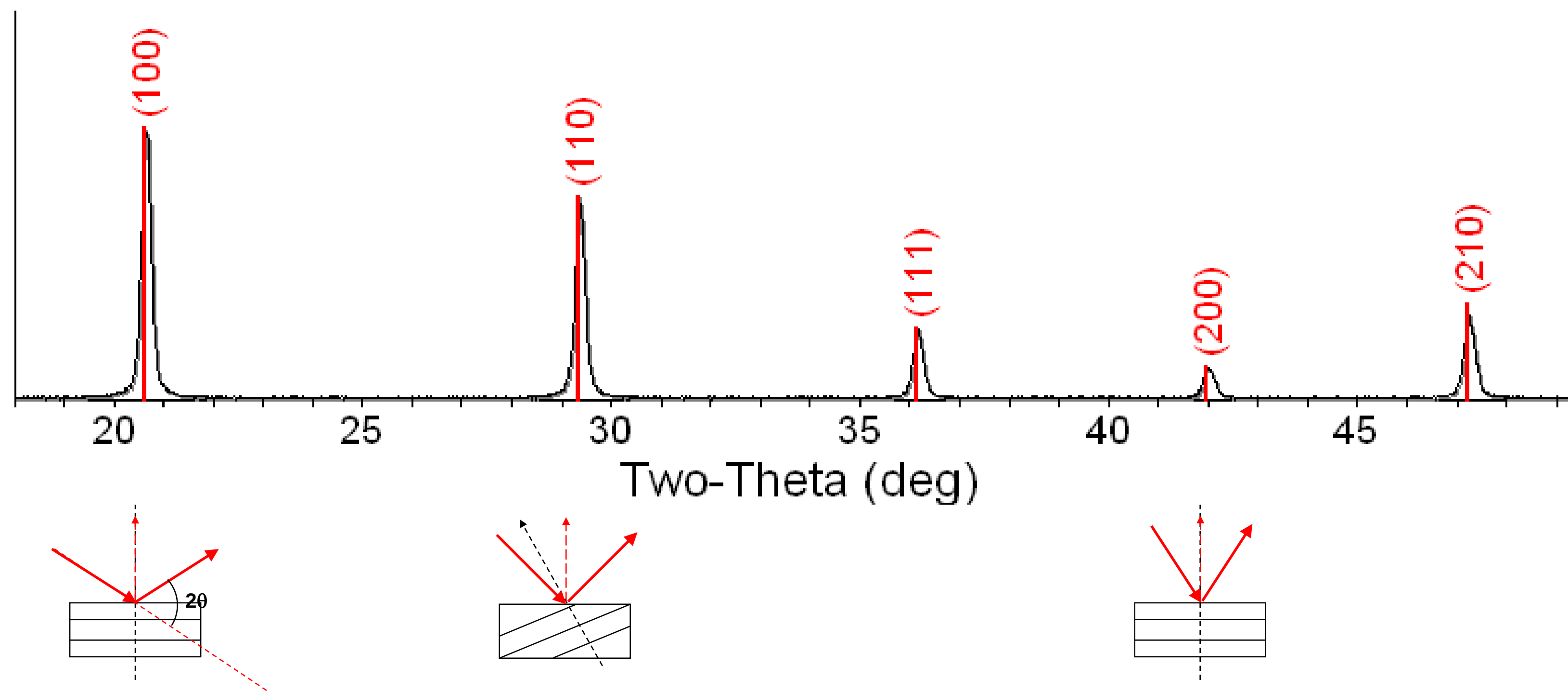
- 장점 : 저각 측정 가능. (From 0.8 degree)
- 단점 : Sampling 제한 있음. (Liquid 측정불가)
- 장비 : HPXRD

# Single Crystal XRD Patterns in $\theta/2\theta$ or $\theta/\theta$ mode

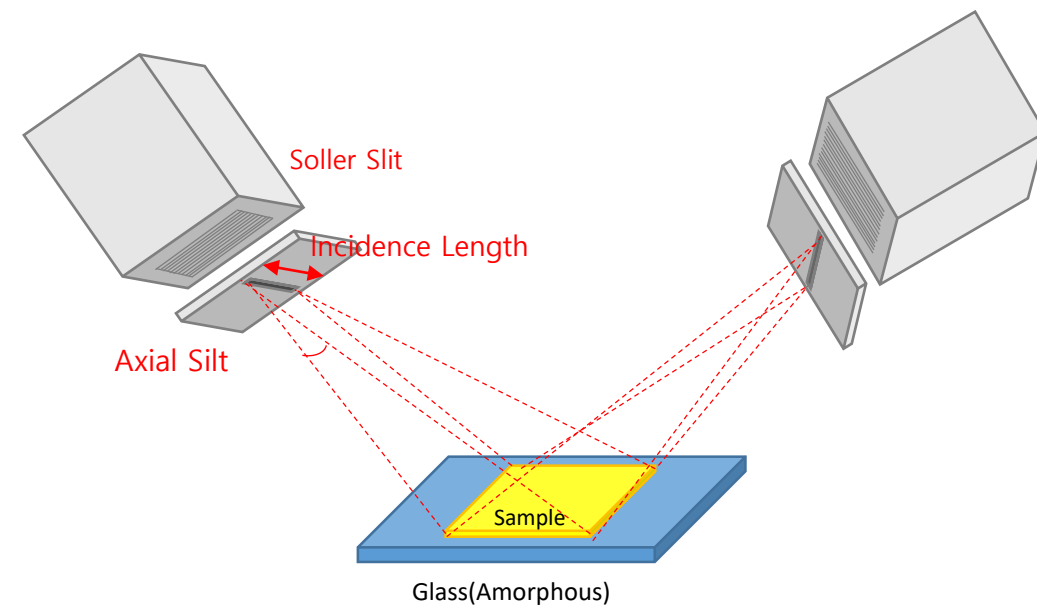


→ Produce only one family of peaks in the diffraction pattern.

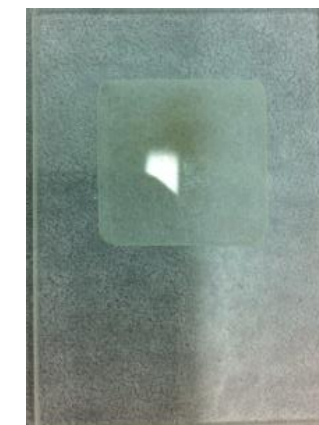
# Poly Crystal XRD Patterns in $\theta/2\theta$ or $\theta/\theta$ mode



- 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).
- Basic assumptions of powder diffraction are that for every set of planes there is an equal number of crystallites that will diffract and that there is a **statistically relevant number of crystallites**, not just one or two.



|                              |                     |            |
|------------------------------|---------------------|------------|
| Divergence Slit (DS)         | 1/6, 1/2, 1, 2, 4 ° | 발산각 제한     |
| Divergence Height Slit (DHS) | 10/ 5/ 2/ 1.2 mm    | Beam 높이 제한 |
| Receiving Slit (RS)          | 0.15, 0.3, 0.6 mm   | Beam 폭 제한  |
| Scattering Slit (SS)         | 1/6, 1/2, 1, 2, 4 ° | 산란각 제한     |
| Soller Slit (SS)             | 2.5 °               | 수직 발산 제한   |



Powder (GLS)  
R: 20 mm  
D: 1 mm



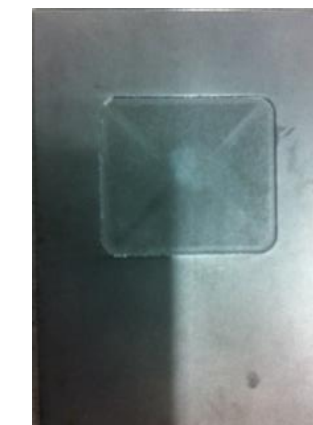
Powder (GLS)  
R: 5 mm  
D: 0.2 mm



Bulk (Al)  
R: 20 mm  
D: 2 mm



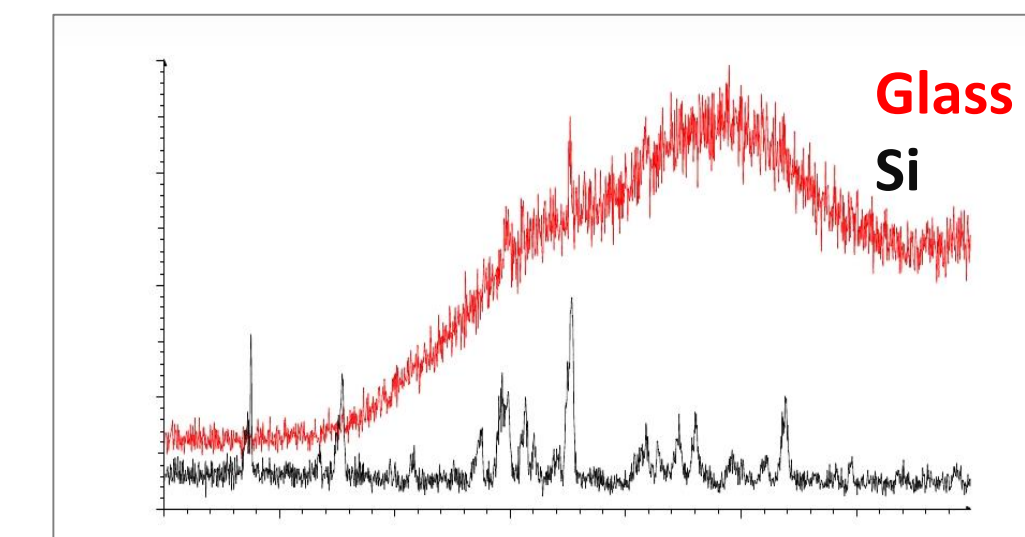
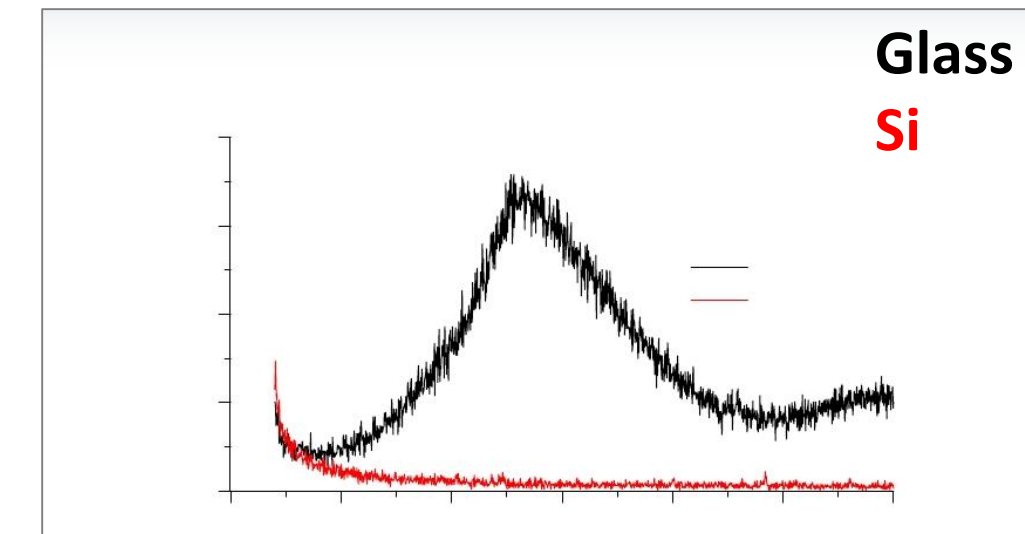
Powder (GLS)  
R: 18 mm  
D: 1 mm



Powder (Si)  
R: 20 mm  
D: 0.2 mm

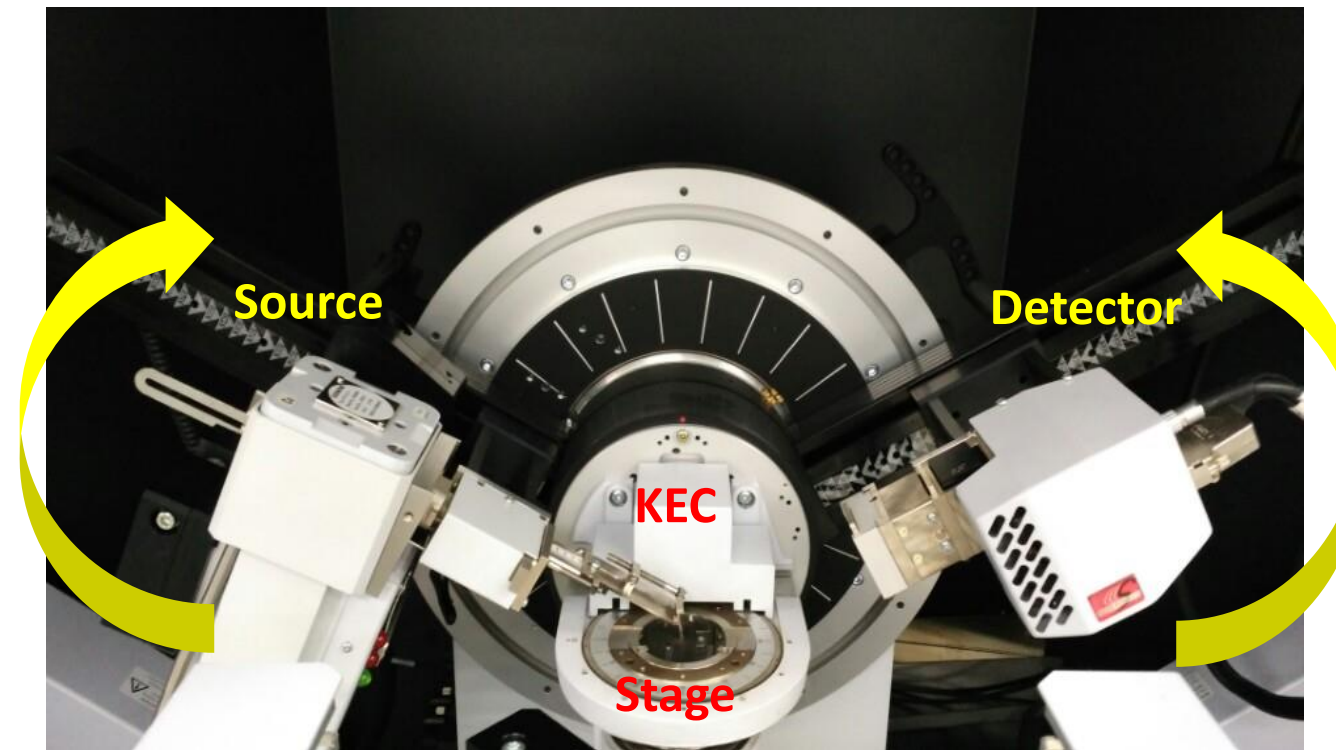


Bulk (Al)  
R: 18 mm  
D: 2 mm



## ❖ Spec

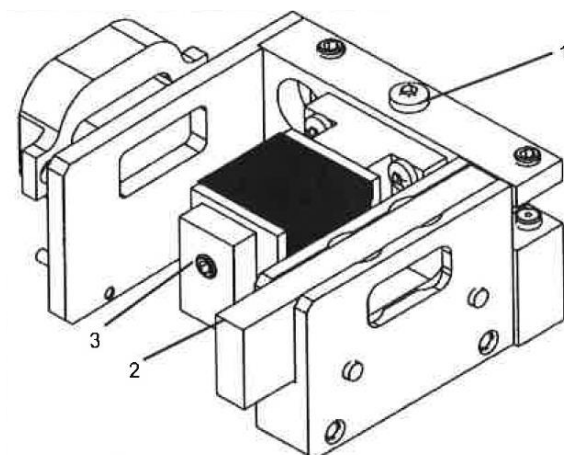
- 1) Target : Cu ( $K_{a1}$  : 1.54056Å &  $K_{a2}$  : 1.54442Å)
- 2) Power : 18kW (40KV, 200mA)
- 3) Dual goniometer : Standard & Auto Sample Changer
- 4) Variable Slit system
- 5)  $2\theta$  range : 0.8 ° ~ 130 °
- 6) Attachment : in-situ Variable Temperature
  - Temperature : 20 °C ~ 1500 °C



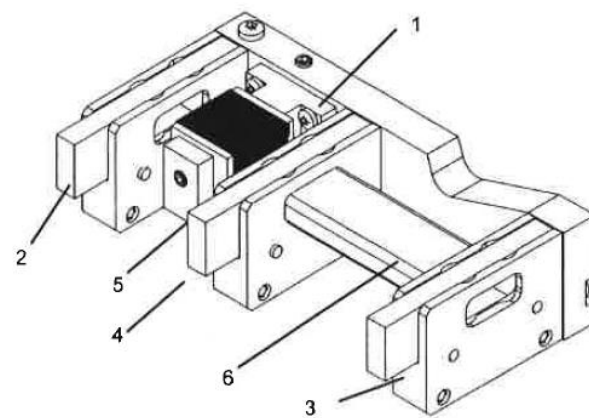
## ❖ Spec

- 1) Target : Cu ( $K_{a1}$  : 1.54056 Å &  $K_{a2}$  : 1.54442 Å)
- 2) Power : 4kW (40 KV, 40 mA)
- 3) Goniometer: Auto Sample Changer & Manual Operation
- 4) Slit system Not variable
- 5)  $2\theta$  range: 10 ° ~ 130 °

## ❖ Aperture Slit system



## ❖ Detector Slit system



## ❖ Instrument parameters for NXRD

| Slits                                      | Value               |
|--------------------------------------------|---------------------|
| Divergence Silt                            | 0.6 mm (= 0.3°)     |
| Axial Soller Silt                          | 2.5 °               |
| Anti-Scatter Silt                          | 0.6 mm (= 0.3°)     |
| Secondary monochromatoer anti-scatter Slit | 1 mm                |
| Receiving Slit                             | 0.1 mm              |
| Linear Detector                            | 3 ° Detector Opeing |

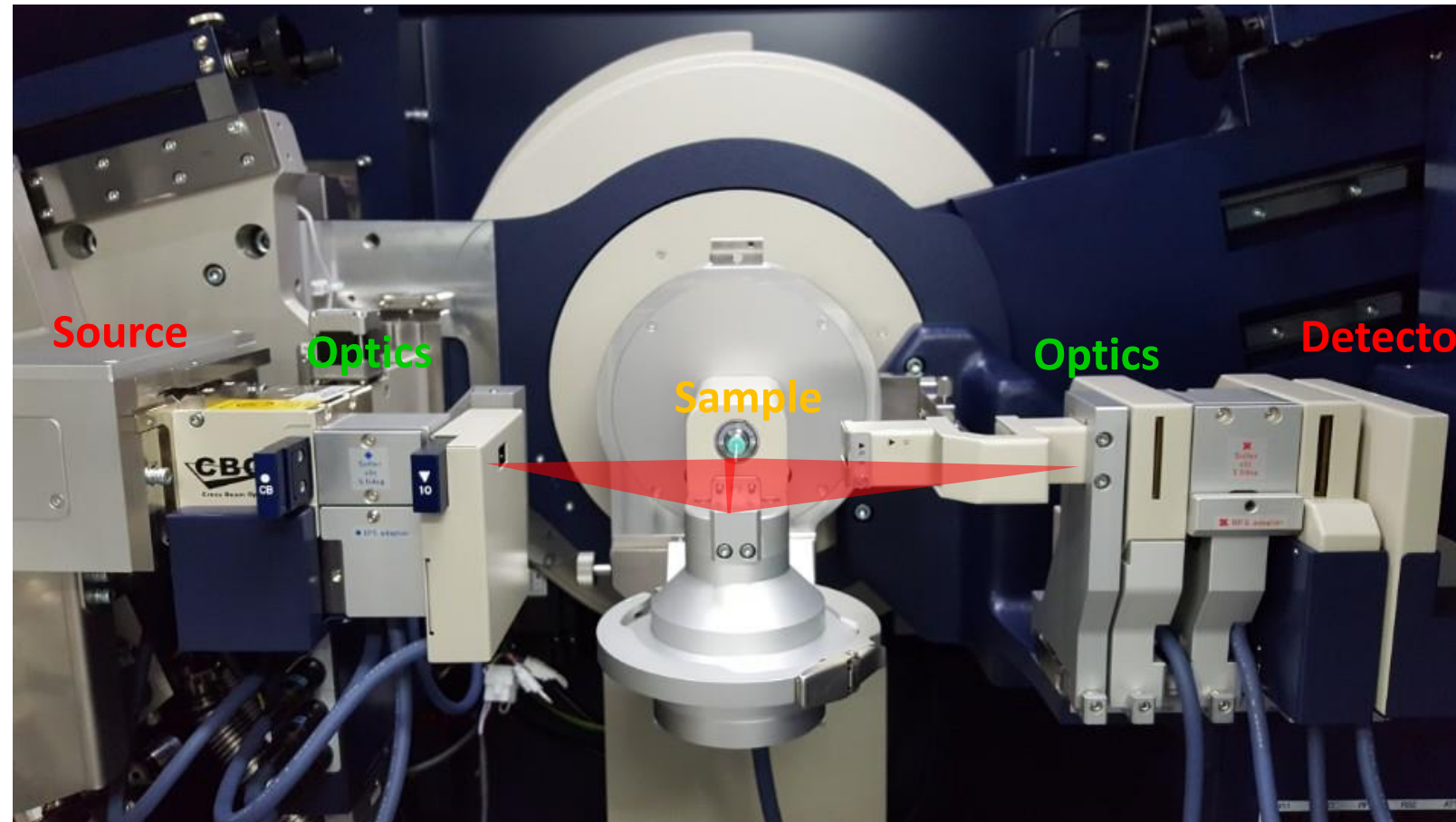
## ❖ NXRD Sample Holder



Powder (PET)  
R: 25 mm  
D: 2 mm

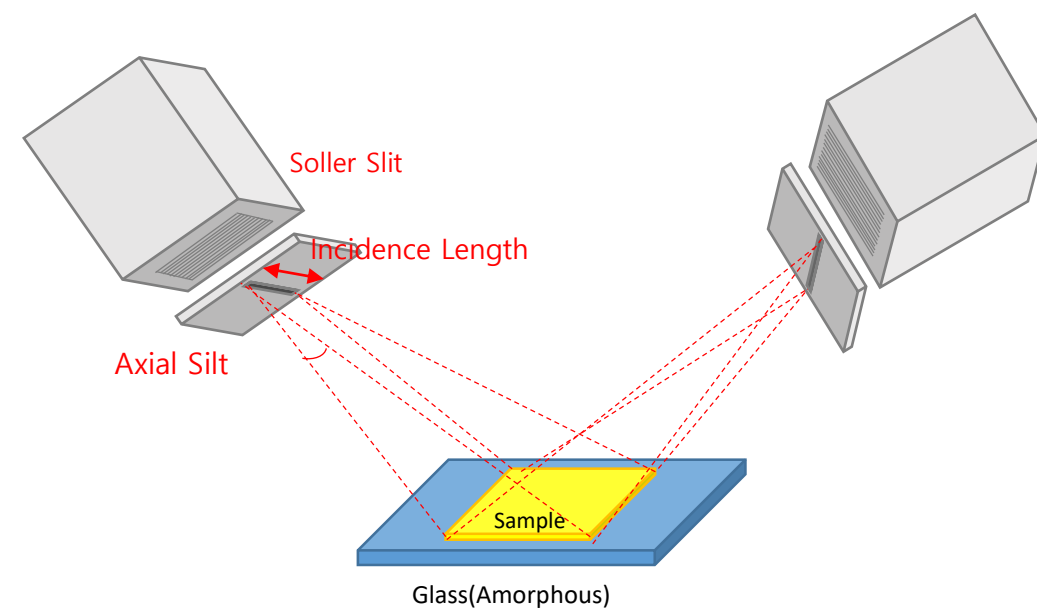


Bulk (PET)  
R: 40 mm  
D: 7 mm

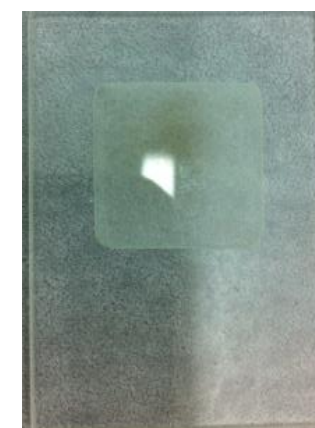


## ❖ Spec

- 1) Target : Cu ( $K_{\alpha 1}$  : 1.54056 Å Only)
- 2) Power : 9kW (45 KV, 200 mA)
- 3) Goniometer : Standard or Auto Sample Changer
- 4) Variable slit system
- 5)  $2\theta$  range :  $10^\circ \sim 130^\circ$
- 6) Attachment : Capillary



|                              |                     |            |
|------------------------------|---------------------|------------|
| Divergence Slit (DS)         | 1/6, 1/2, 1, 2, 4 ° | 발산각 제한     |
| Divergence Height Slit (DHS) | 10/ 5/ 2/ 1.2 mm    | Beam 높이 제한 |
| Receiving Slit (RS)          | 0.15, 0.3, 0.6 mm   | Beam 폭 제한  |
| Scattering Slit (SS)         | 1/6, 1/2, 1, 2, 4 ° | 산란각 제한     |
| Soller Slit (SS)             | 1, 2.5, 5 °         | 수직 발산 제한   |



**Powder (GLS)**  
R: 20 mm  
D: 1 mm



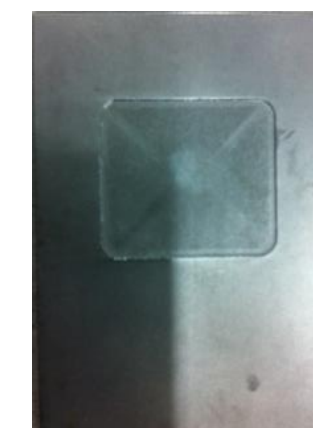
**Powder (GLS)**  
R: 9 mm  
D: 0.2 mm



**Bulk (Al)**  
R: 20 mm  
D: 2 mm



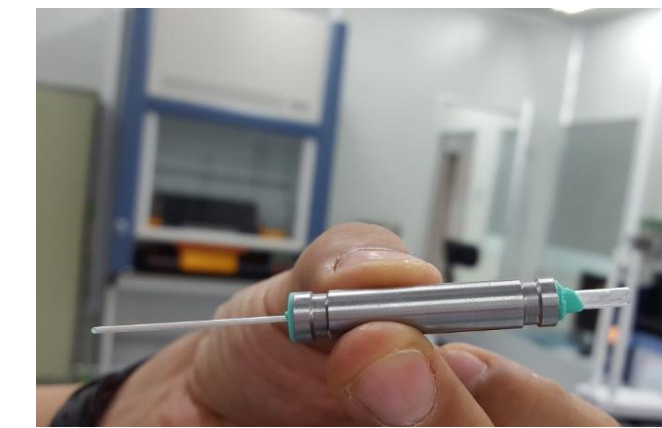
**Powder (GLS)**  
R: 18 mm  
D: 1 mm



**Powder (Si)**  
R: 20 mm  
D: 0.2 mm

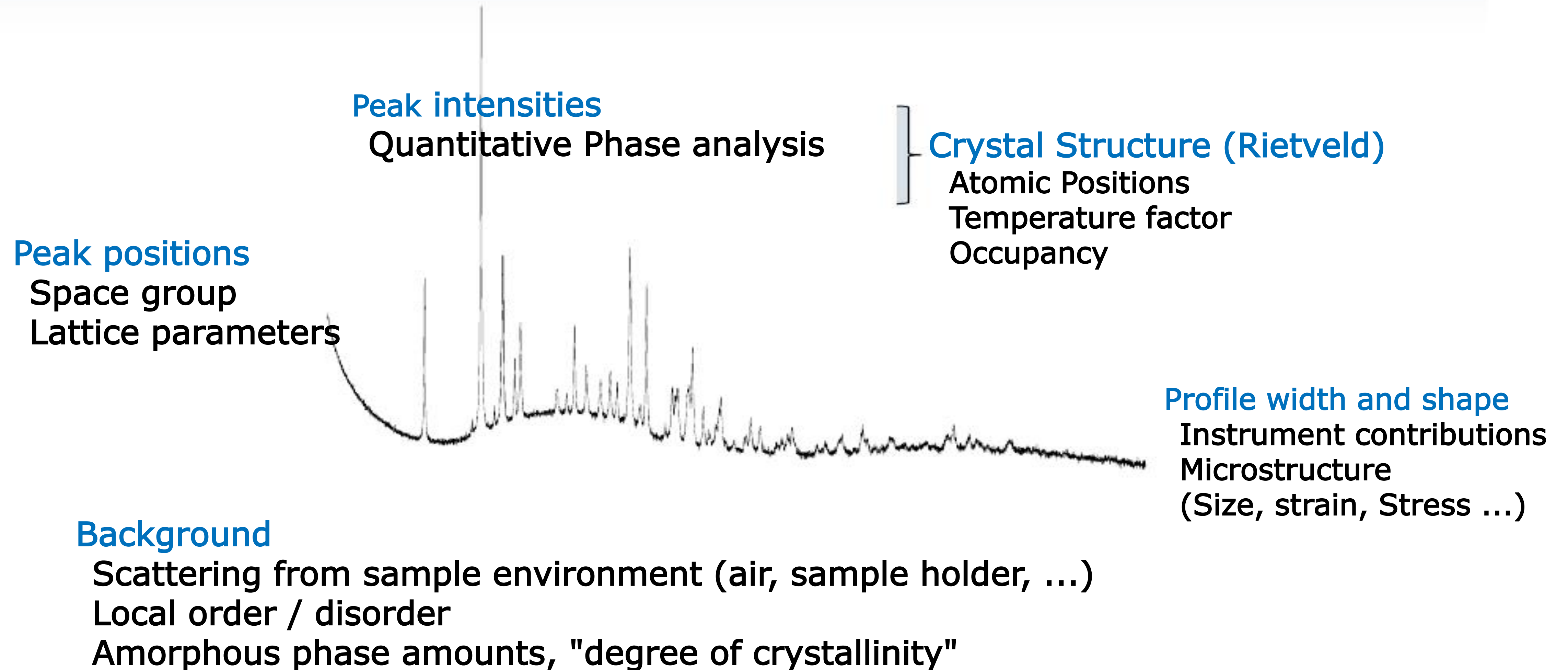


**Bulk (Al)**  
R: 18 mm  
D: 2 mm



**Capillary (GLS)**  
R: 0.9 mm  
L: 5cm

# Application

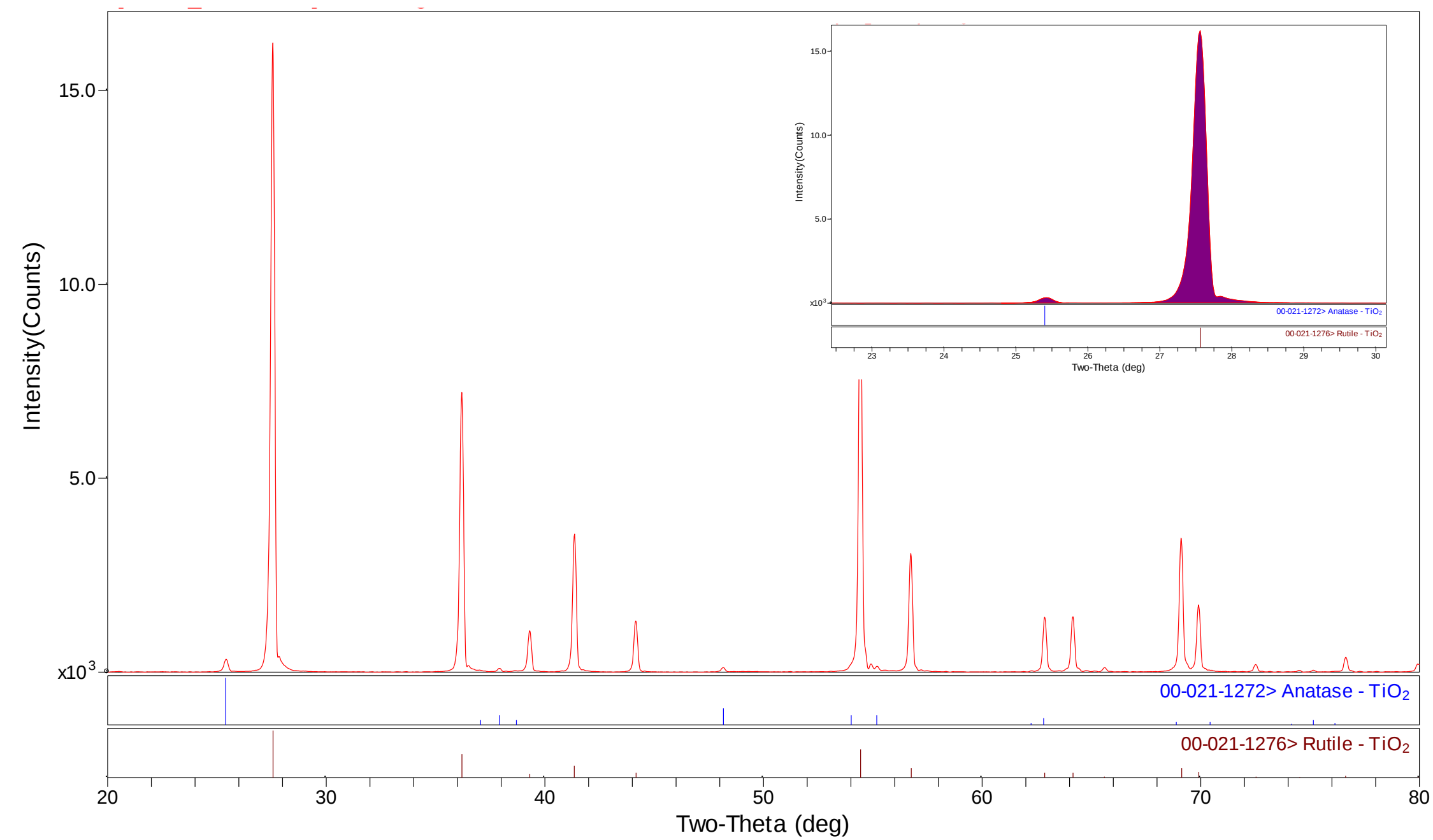


# Applications

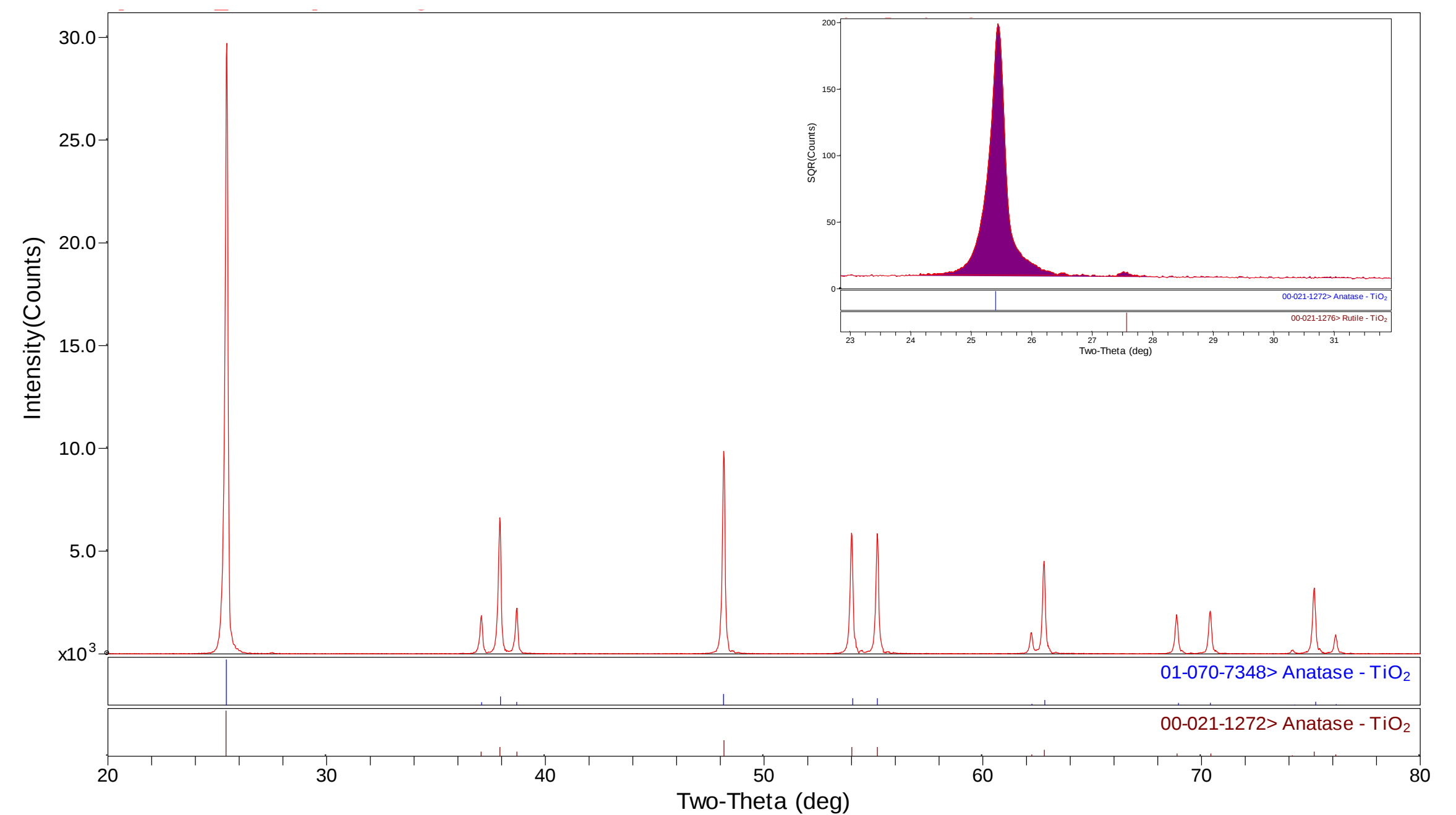
- **Phase ID (Qualitative Phase Analysis)**
  - A powder diffraction pattern can be compared to a database of diffractograms for known materials in order to identify the contents sample.
  - Or one can simply determine the presence or absence of a particular phase.
- **Phase Fraction Analysis**
  - A mixture of two or more crystalline phases can be easily and accurately analyzed in terms of its phase fractions.
- **Lattice Parameter Refinements**
  - Precise lattice parameters can be determined.
- **Rietveld Refinement (Structural Refinement)**
  - The crystal structure of a new or unknown material can be determined when a similar material with a known structure exists.
  - This can be relatively straightforward depending on how similar the new structure is to the known one.
- **Line Shape Analysis**
  - Crystallite size, for example you can determine the approximate size of nanoparticles using the Scherrer equation.
  - Crystalline microstrain, arising from sources such as atomic disorder, non-stoichiometry, (lattice vacancies), dislocations, etc.
- **Structure Solution**
  - The crystal structure of a new or unknown material can be solved *ab initio* even if no information about the material other than its stoichiometry is known
- **Non-conventional diffraction (PDF, Resonant diffraction, and etc)**

# Phase Analysis

## Sample A



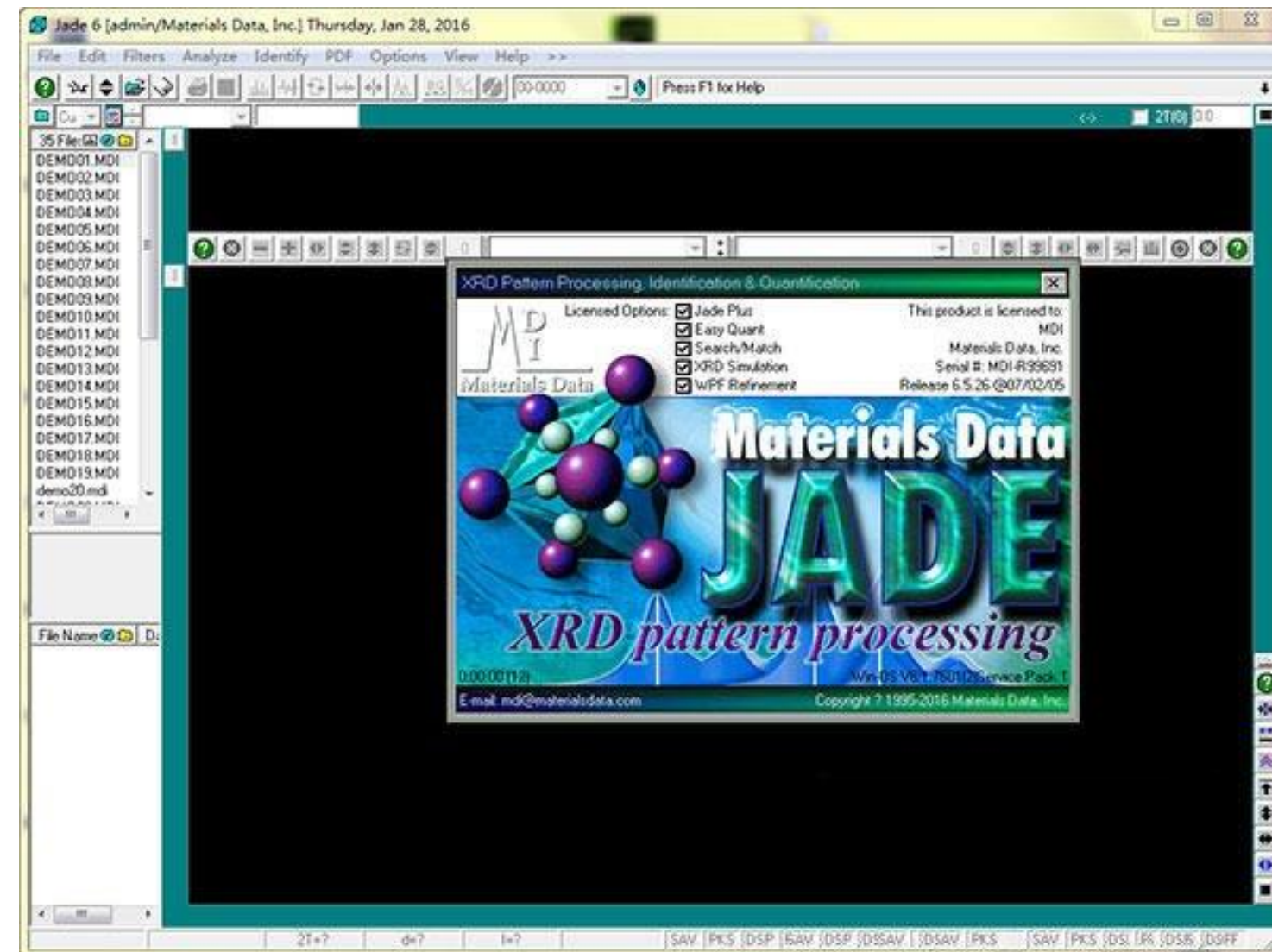
## Sample B



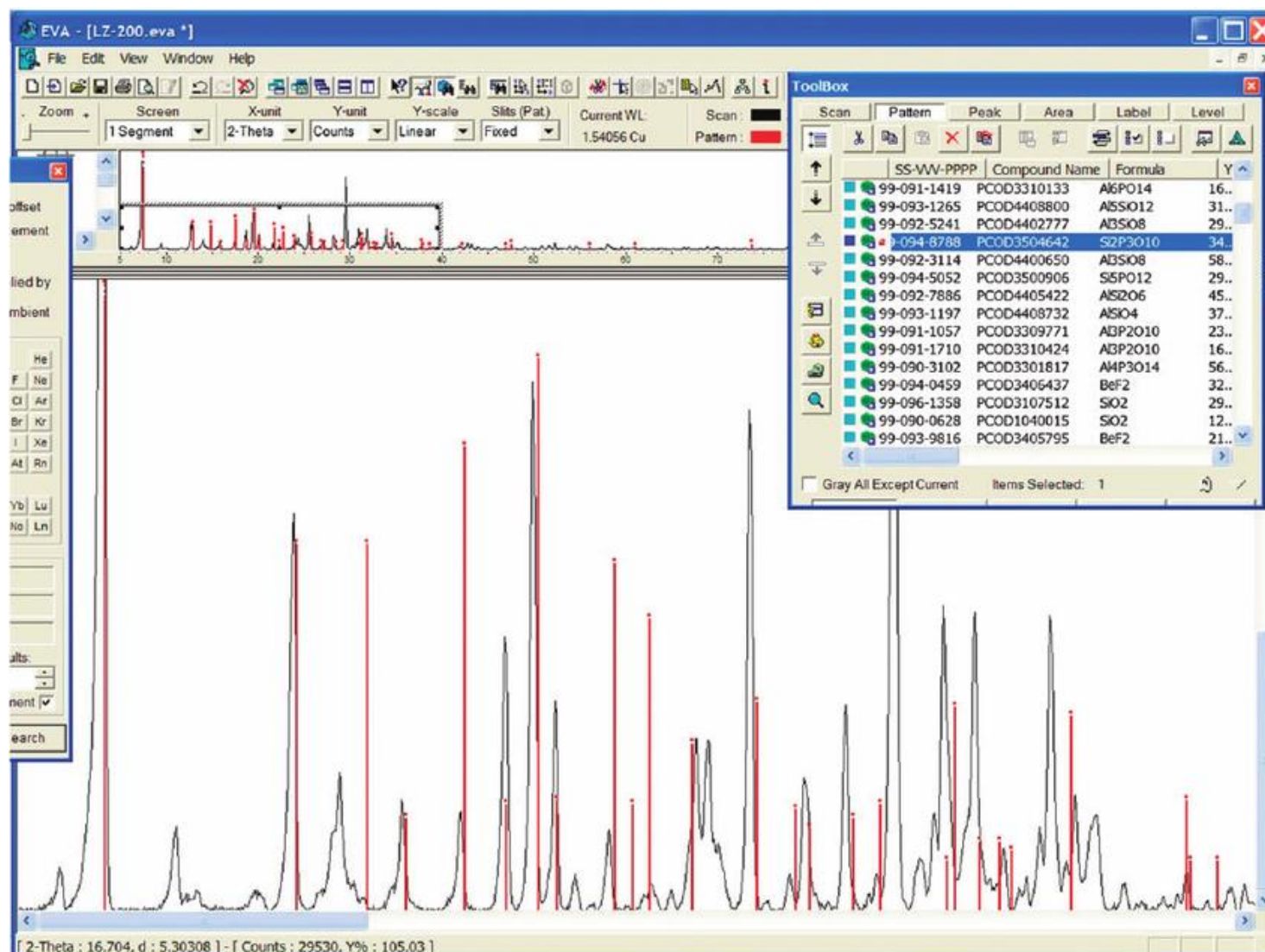
# Software for Powder XRD

43

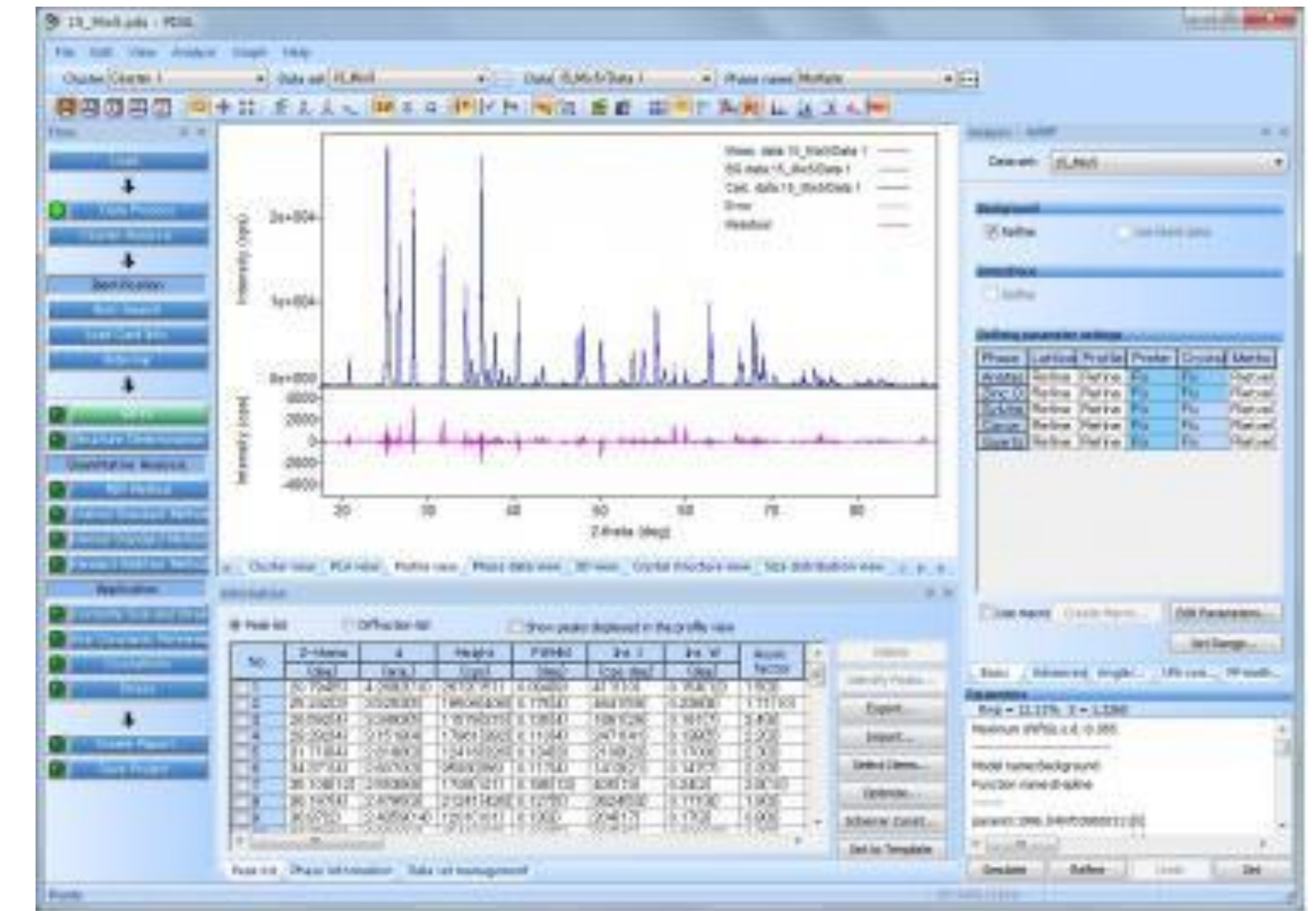
## ❖ JADE (MDI, USA)



## ❖ EVA (Bruker, German)



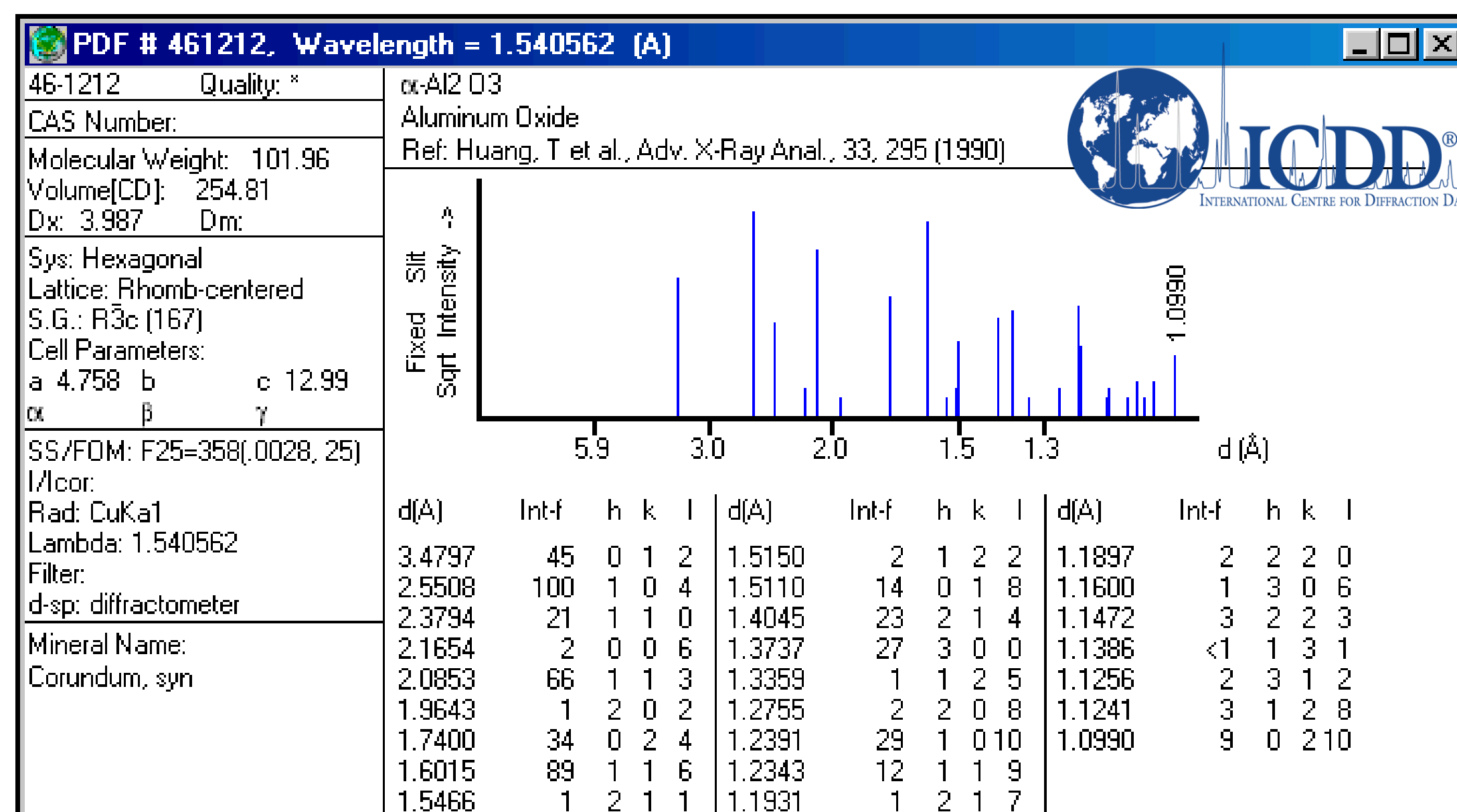
## ❖ PDXL (Rigaku, Japan)



# Database

44

## ❖ ICDD (International Centre for Diffraction Data)



## ❖ COD (Crystallography Open Database)

**Crystallography Open Database**

**COD Home**  
Home  
What's new?

**Accessing COD Data**  
Browse  
Search  
Search by structural formula

**Add Your Data**  
Deposit your data  
Manage depositions  
Manage/release prepublications

**Documentation**  
COD Wiki  
Obtaining COD  
Querying COD  
Citing COD  
COD Mirrors  
Advices to donators  
Useful links

Open-access collection of crystal structures of organic, inorganic, metal-organic compounds and minerals, excluding biopolymers.  
Including data and software from CrystalEye, developed by Nick Day at the department of Chemistry, the University of Cambridge under supervision of Peter Murray-Rust.

All data on this site have been placed in the public domain by the contributors.

Currently there are **384529** entries in the COD.  
Latest deposited structure: 2310785 on **2017-09-27** at **15:05:36 UTC**

[CIFs Donators](#)

# Quantitative Analysis

“ 측정된 물질의 최대 Peak 의 적분강도(I<sub>i</sub>)와 동일한 조건으로 NIST-1976 (Corundum - Al<sub>2</sub>O<sub>3</sub>)를 측정된 X선 적분 강도(I<sub>c</sub>)로 나누어 얻은 수치를 RIR(Reference Intensity Ratio) Value 라고 합니다.”

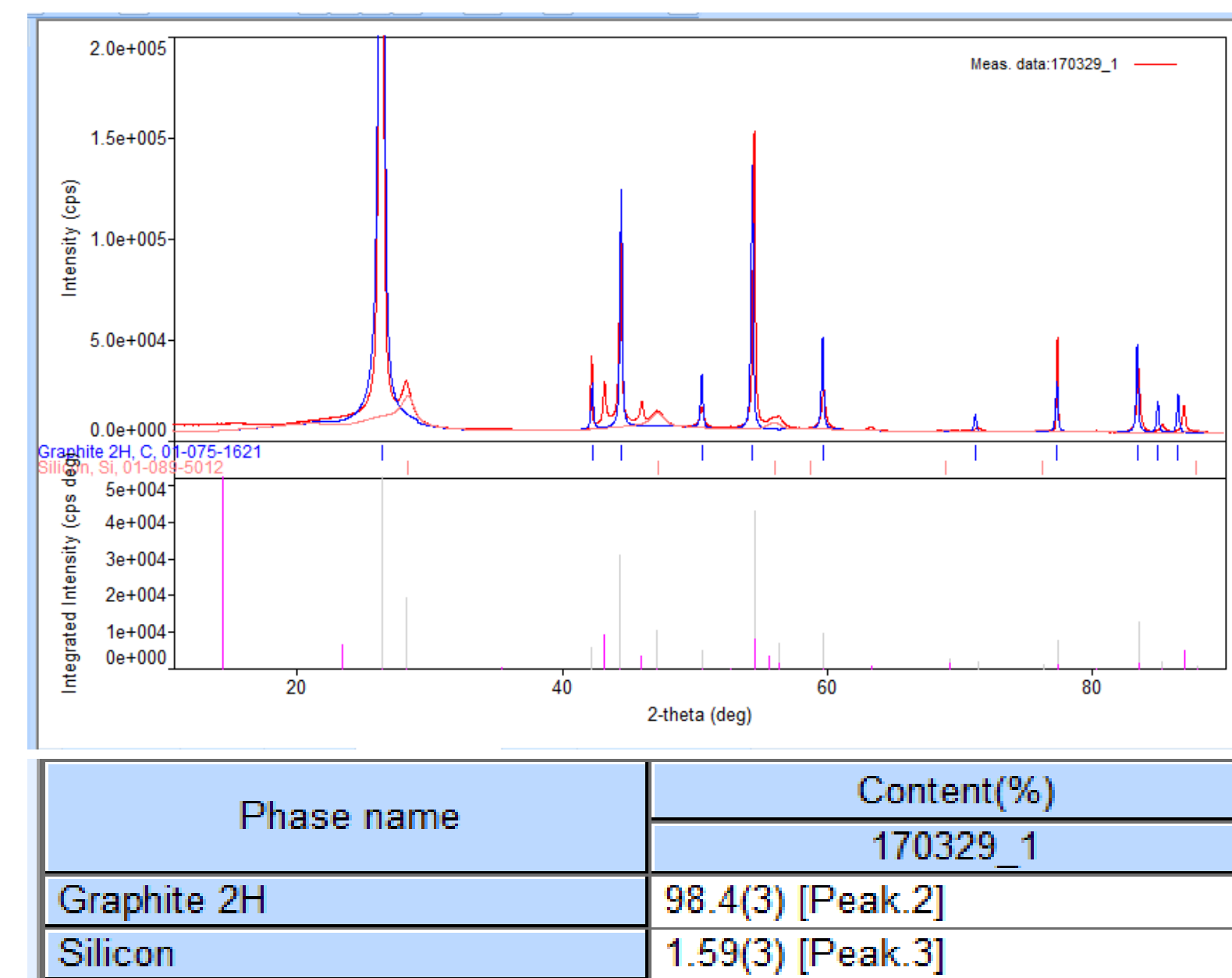
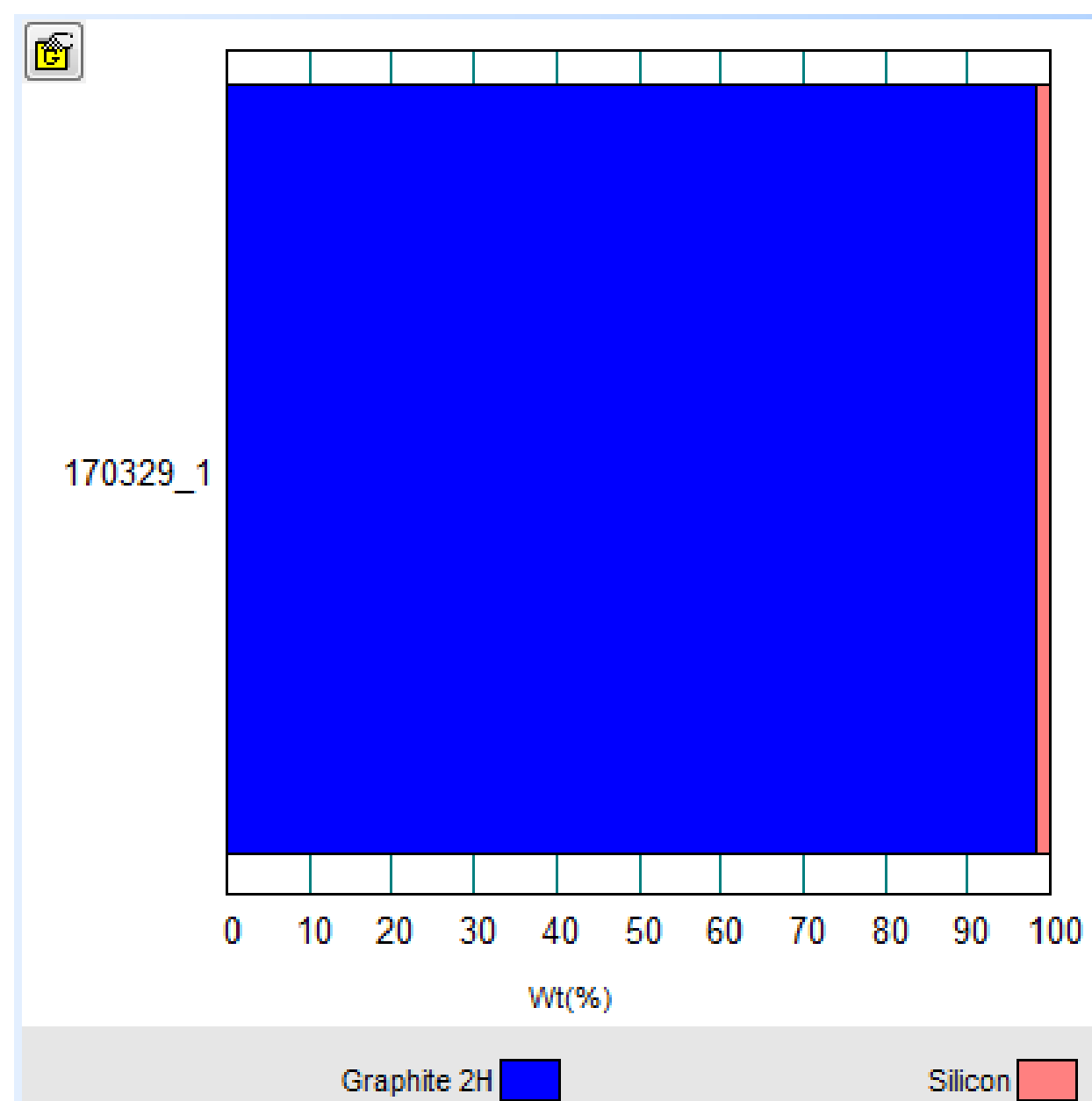
$$\frac{W_i}{W_c} = \frac{1}{R_i} \frac{I_i^{max}}{I_c^{max}}$$

$W_i$  : 측정할 물질의 무게

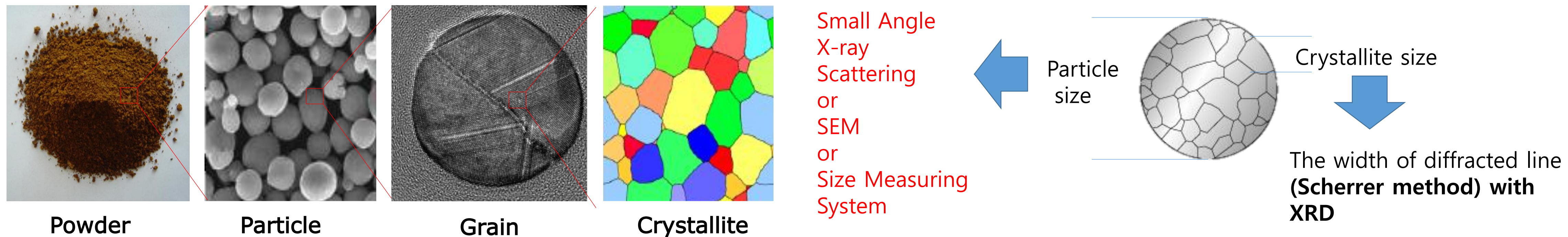
$W_c$  : Corundum(SRM)의 무게

$I_i^{max}$  : 측정물질에 대한 최대 peak의 적분강도

$I_c^{max}$  : Corundum(SRM) 최대 peak의 적분강도



# What is size ?



## ❖ Particle size

- It is a notion introduced for comparing dimensions of solid particles (flecks), liquid particles (droplets), or gaseous particles (bubbles). Size and strain analysis

## ❖ Grain size

- It refers to the diameter of individual grains of sediment, or the lithified particles in clastic rocks.

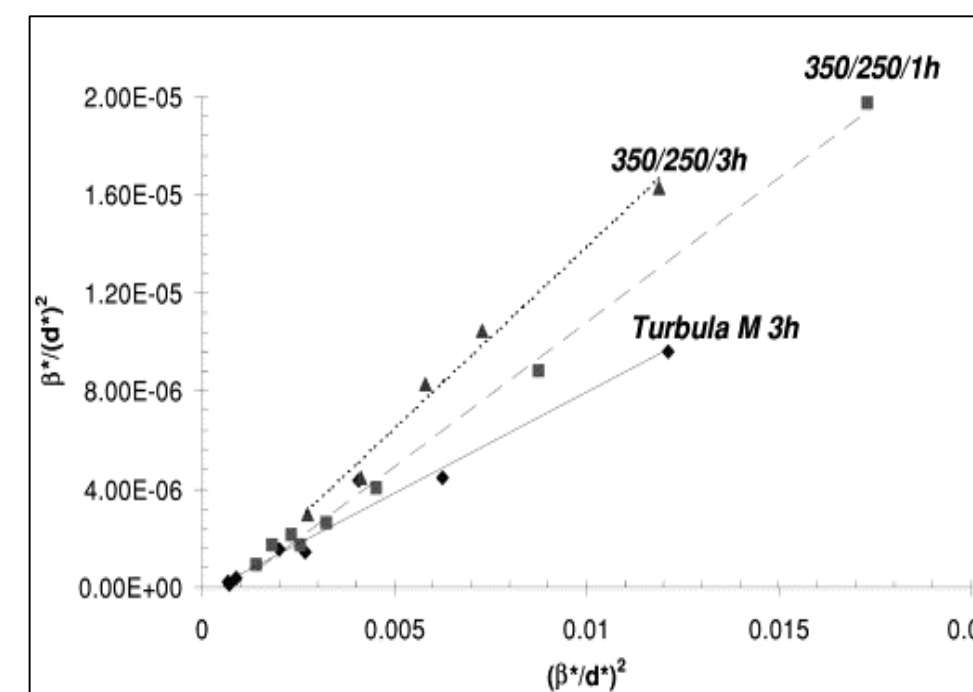
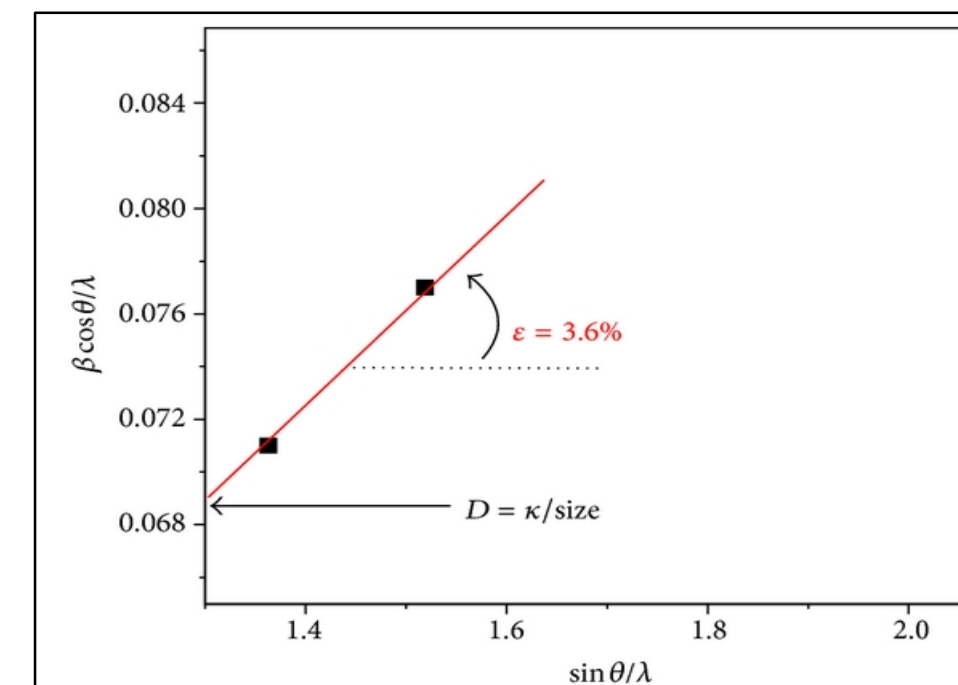
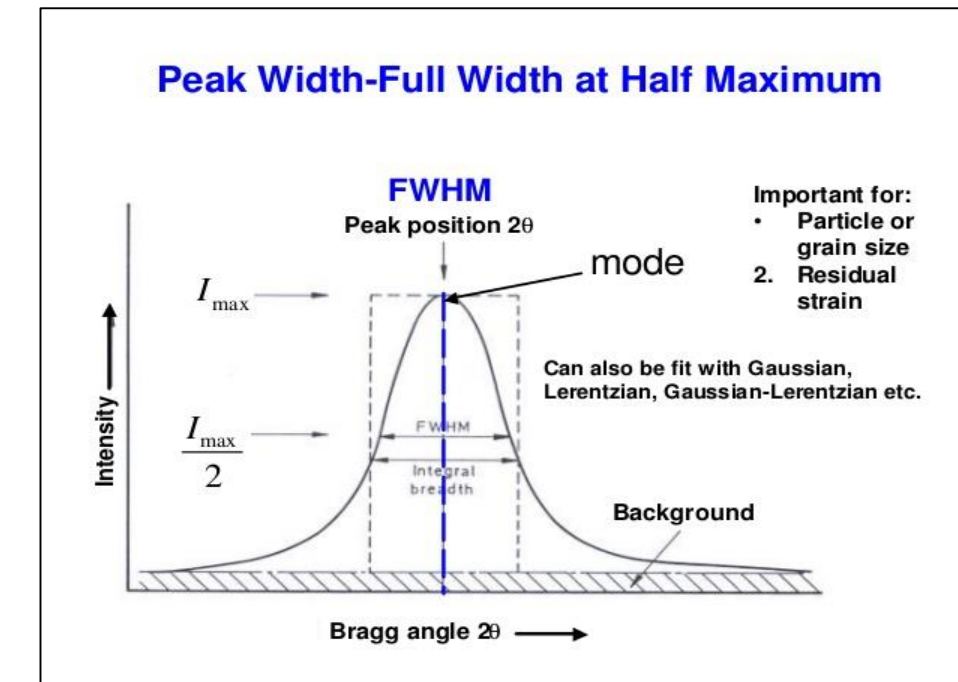
## ❖ Crystallite size

- It refers to the size of a single crystal inside a particle or grain. A single grain can be composed of several crystals.

# Size & Strain Analysis

47

- ❖ Scherrer Calculation
  - Analysis of peak width estimate
  - Single line analysis of single peak profile fit
  - Only size or strain analysis
- ❖ Williamsom-Hall method
  - Size and strain analysis
  - analysis of multiple peak profile fits
- ❖ Halder-Wagner method
  - Size and strain analysis
  - Analysis of full pattern fits
- ❖ Rietveld Refinement
  - Analysis of peak width estimate
  - Single line analysis of single peak profile fitting



## ❖ Peak Broadening의 원인 (FWHM의 변화)

- 1) Crystallite size 변화
- 2) 불균일한 Micro Strain
- 3) 격자 결함(stacking fault)

### 1) Crystallite size 변화

$$\text{Scherre Equation : } L = \frac{K \lambda}{B \cos \theta}$$

- L : crystallite size
- B : FWHM
- K : Scherrer constant  $\approx 0.6 \sim 2.5$
- $\lambda$  : Wavelength (ex: Cu =  $1.5406 \text{\AA}$ )

### 2) 불균일한 Micro Strain

$$\text{Strain : } \beta = 4\varepsilon \tan \theta$$

( $0.005\% < \varepsilon < 5\%$ )

- $\varepsilon$  : lattice distortion  
$$\varepsilon = \frac{\Delta d}{d} (\%)$$

→ dislocations, Inclusions, lattice twins

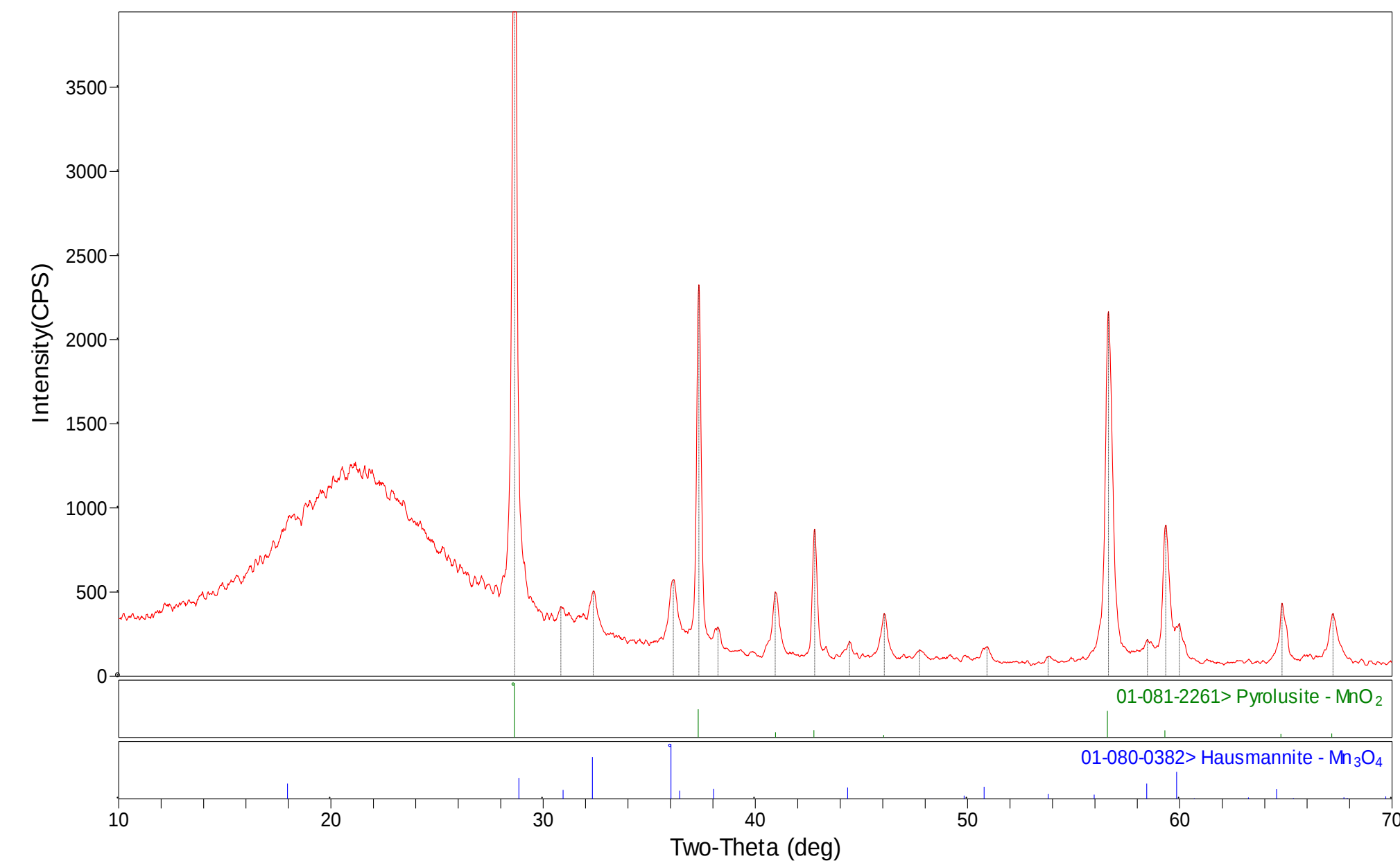
## Crystallite size & strain

- ❖ Lattice strains from displacements of the unit cells about their normal positions.
- ❖ Often produced by dislocations, domain boundaries, surfaces etc.
- ❖ Microstrains are very common in nanocrystalline materials.
- ❖ The peak broadening due to microstrain will vary as :

| William-Hall Method                                                                                            | Halder-Wagner Method                                                                                                 |
|----------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|
| $B_s = \frac{K \lambda}{s \cdot \cos \theta} = \frac{0.9 \cdot \lambda}{s \cdot \cos \theta}$                  | $B_s = \frac{K \lambda}{s \cdot \cos \theta} = \frac{0.9 \cdot \lambda}{s \cdot \cos \theta}$                        |
| $B_\varepsilon = \Delta 2\theta = 4 \cdot \frac{\Delta d}{d} \cdot \tan \theta$                                | $B_\varepsilon^2 = (\Delta 2\theta)^2 = 16 \cdot \left(\frac{\Delta d}{d}\right)^2 \cdot \tan^2 \theta$              |
| $\frac{B \cos \theta}{\lambda} = 4 \cdot \frac{\Delta d}{d} \cdot \frac{\sin \theta}{\lambda} + \frac{0.9}{s}$ | $\frac{B^2}{(\tan \theta)^2} = \frac{K \lambda}{L} \frac{B}{\tan \theta \cdot \sin \theta} + 16 \cdot \varepsilon^2$ |
| $B \cos \theta = \eta \sin \theta + \frac{K \lambda}{L}$                                                       | $\frac{B^2}{(\tan \theta)^2} = \frac{K \lambda}{L} \frac{B}{\tan \theta \sin \theta} + \eta^2$                       |

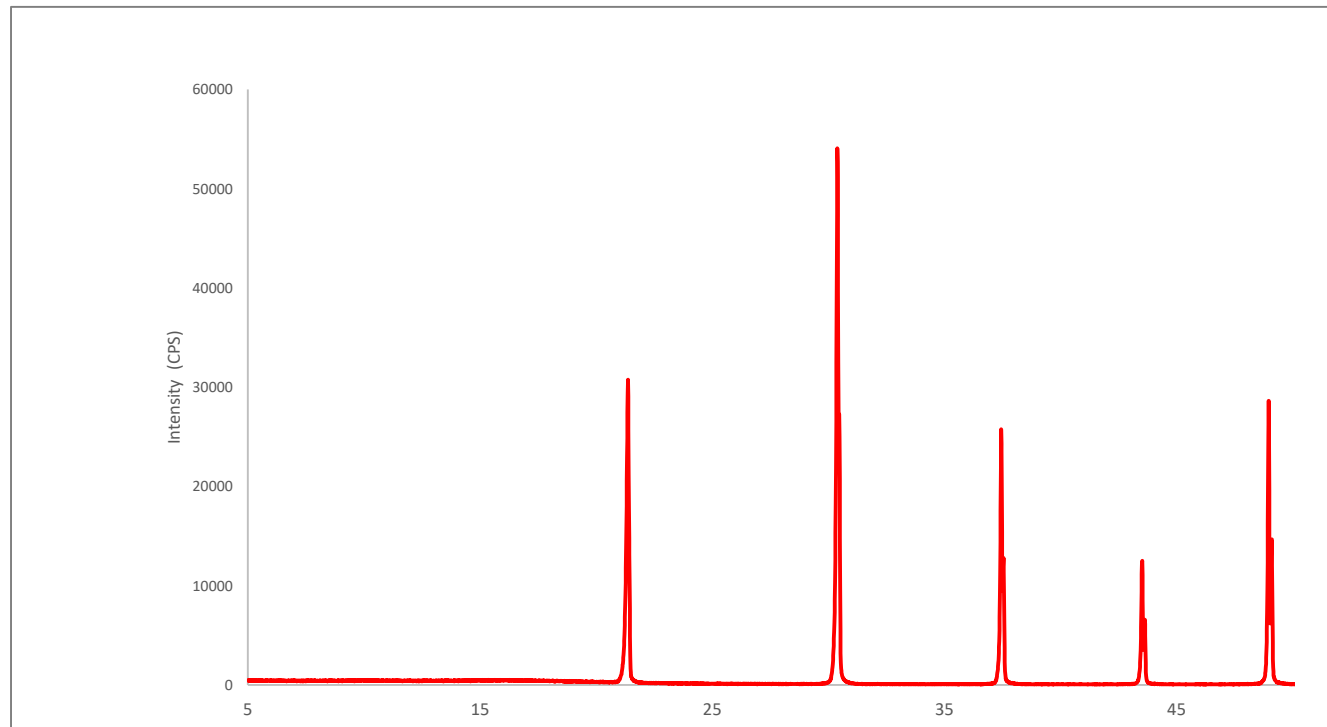
# Crystallinity (결정화도)

- ❖ 결정과 비정질이 공존하는 데이터에서 결정질이 차지하는 비율 (%)
- ❖ 
$$\text{Crystallinity} = \frac{\text{Area}_{\text{crystal}}}{\text{Area}_{\text{amorphous}} + \text{Area}_{\text{crystal}}} \times 100 (\%)$$
- ❖ 원칙적으로 단일 물질이 결정과 비정질로 나타나는 경우에 적용해야 한다.
- ❖ 그러나, 혼합상이더라도 이를 단일물질로 설정하고 결정화도를 계산하기도 한다
- ❖ Search/Match가 필요 없음.
- ❖ 정량 분석이므로 데이터 질이 중요함.
- ❖ BG 설정에 따라 결과값이 달라질 수 있음.
- ❖ 결정화도를 계산하기 위한 각도 범위에 따라 결과값이 달라질 수 있음.

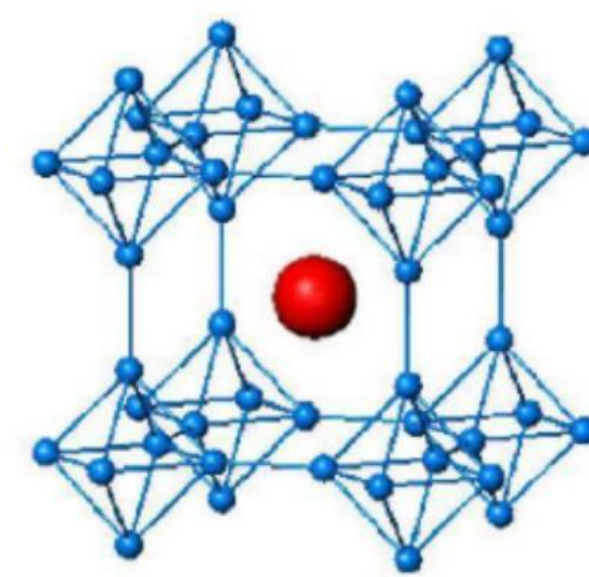
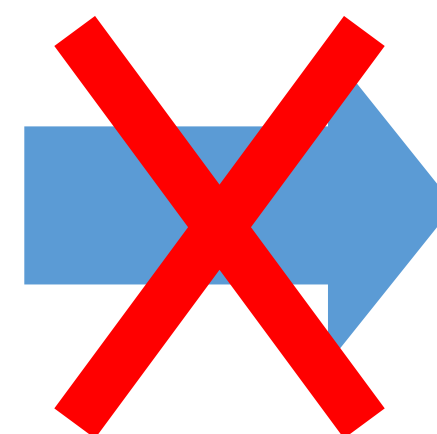


| Profile Fitting Report                                               |        |        |        |       |       |       |
|----------------------------------------------------------------------|--------|--------|--------|-------|-------|-------|
| R = 7.16%, Total Area = 975596 (19740), Crystallinity = 39.21(1.49)% |        |        |        |       |       |       |
| @ 2-Theta                                                            | d(Å)   | Height | Area   | Area% | FWHM  | XS(Å) |
| 20.742                                                               | 4.2790 | 959    | 492389 | 100   | 8.723 | 9     |
| 28.978                                                               | 3.0788 | 145    | 4394   | 0.9   | 0.393 | 241   |

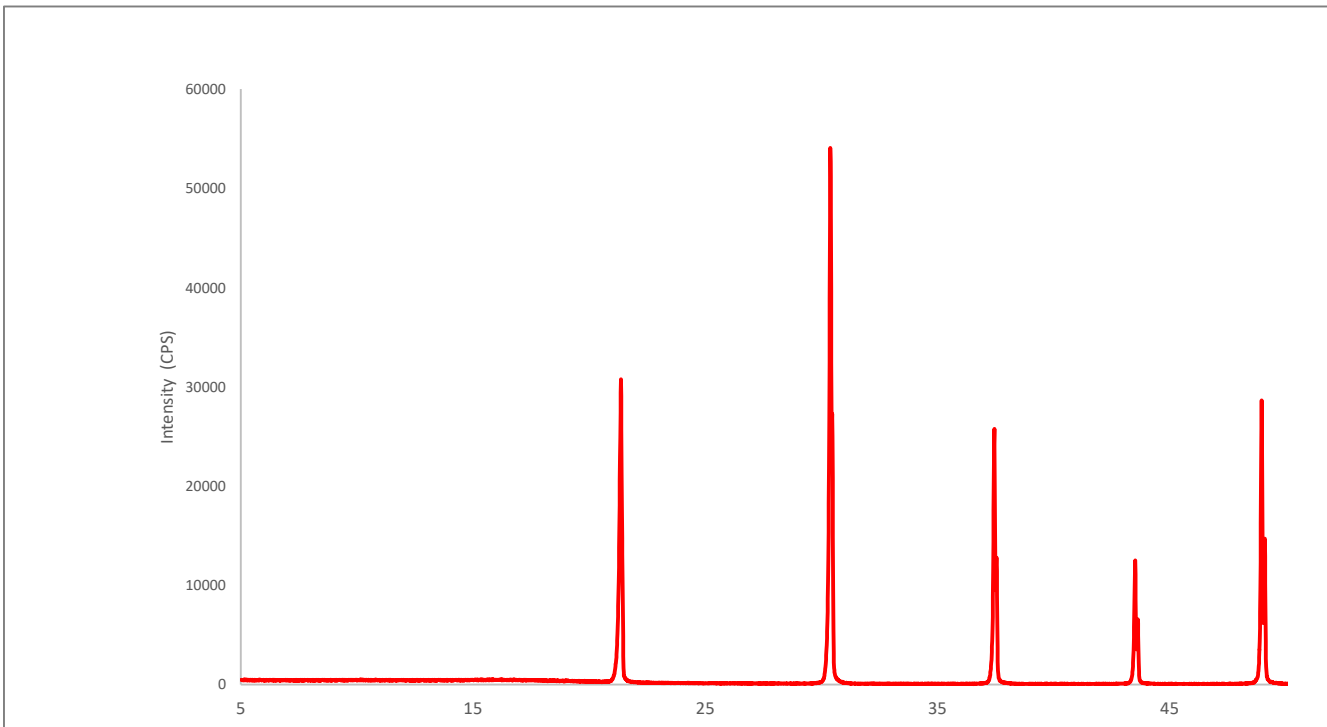
# Rietveld Refinement



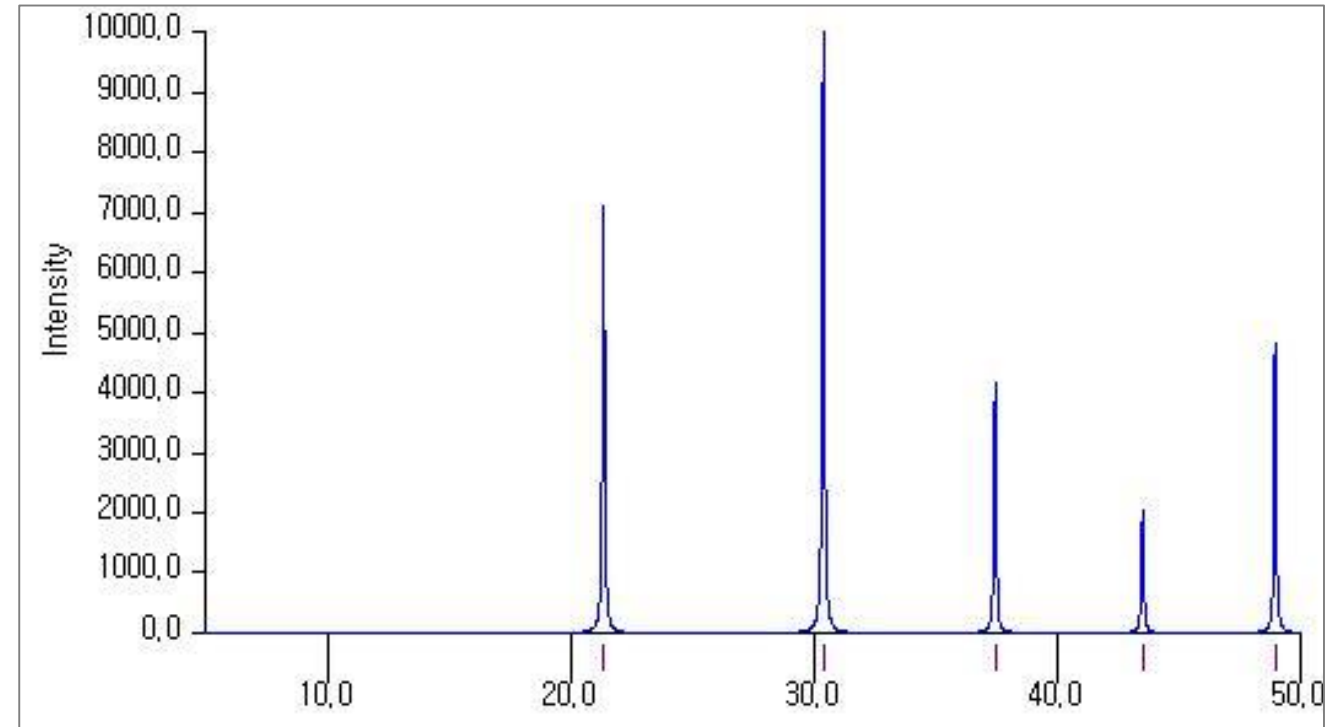
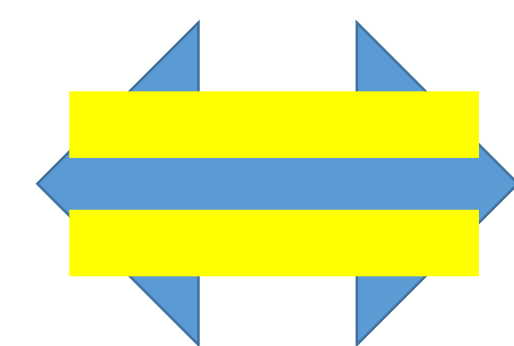
Measured XRD Pattern



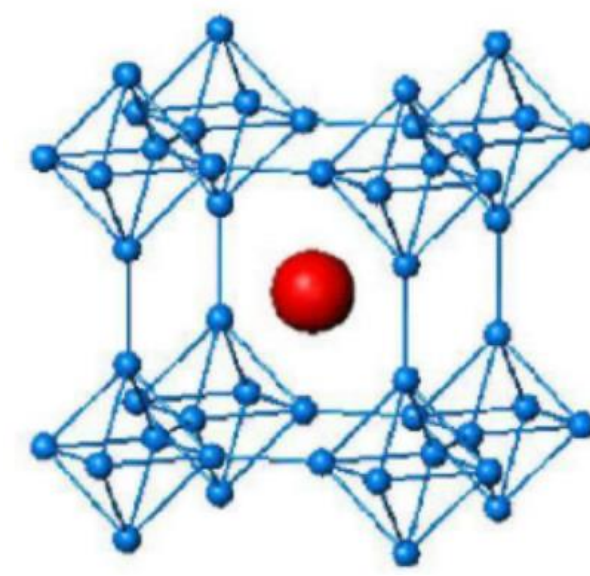
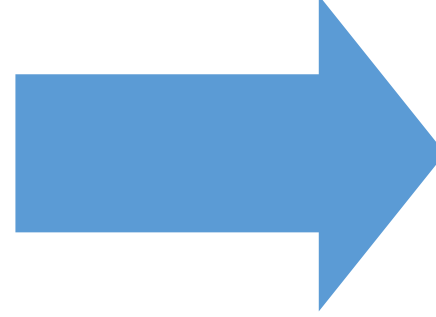
Crystal Structure



Measured XRD Pattern

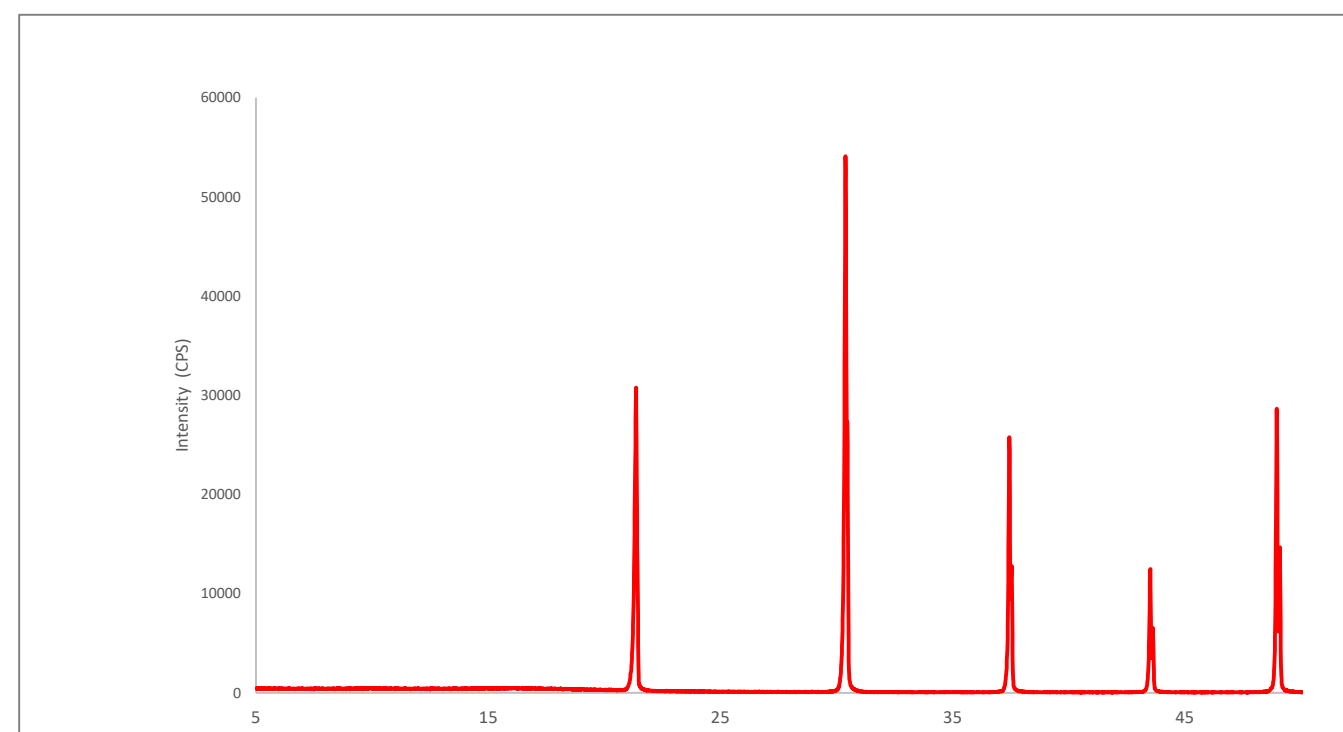


Simulated XRD Pattern

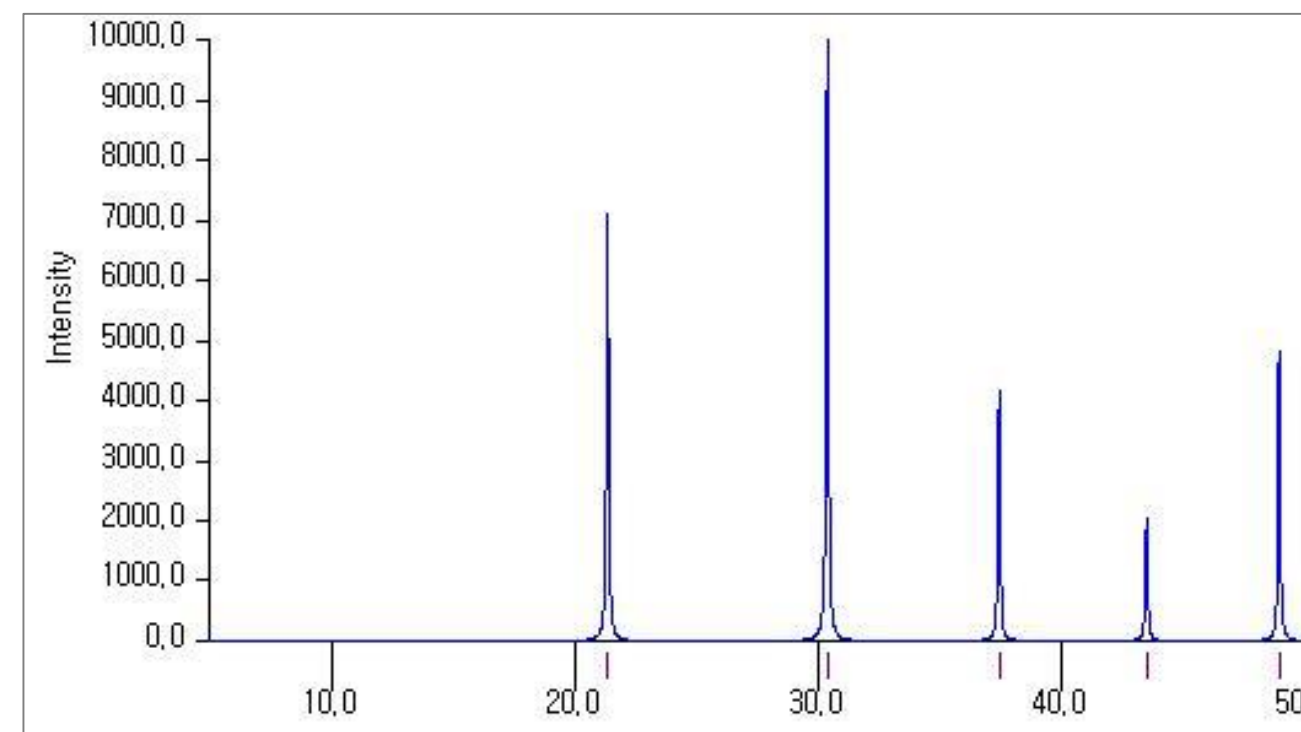


Crystal Structure

# Rietveld Refinement



Measured XRD Pattern



Simulated XRD Pattern

- Minimization of the residual  $Q$  :

$$Q = \sum_i W_i (Y_i - Y_{ci})^2$$

- $Y_i$  : Observed intensity at data point  $i$
- $Y_{ci}$  : Calculated intensity at data point  $i$
- $W_i$  : *Weighting scheme*  $= \frac{1}{\sigma_i^2}$  where  $\sigma_i = Y_i^{1/2}$
- $\sigma_i$  : *Variance of  $Y_i$*

# Rietveld Refinement

## ❖ Rietveld 방법의 조건

- 시편 준비의 중요성 → 정확한 회절 강도 (Step size)
- 실제 구조와 유사한 구조 모델이 필요
- Bragg peak 모양, 두께, 오차 등을 설명할 수 있는 Peak profile 모델이 필요
- 2theta range : 10도 ~ 130도 측정
- Step width : equal or smaller than FWHM/5
- Intensity : 10,000 ~ 20,000 counts in main peak

# Rietveld Refinement

## ❖ Rietveld Refinement 의 장점

- 고온, 저온, 압력을 이용한 실험을 통해 상 변화 연구에 적합
- 정확한 격자 상수 계산 가능
- 혼합물의 정량 분석이 가능

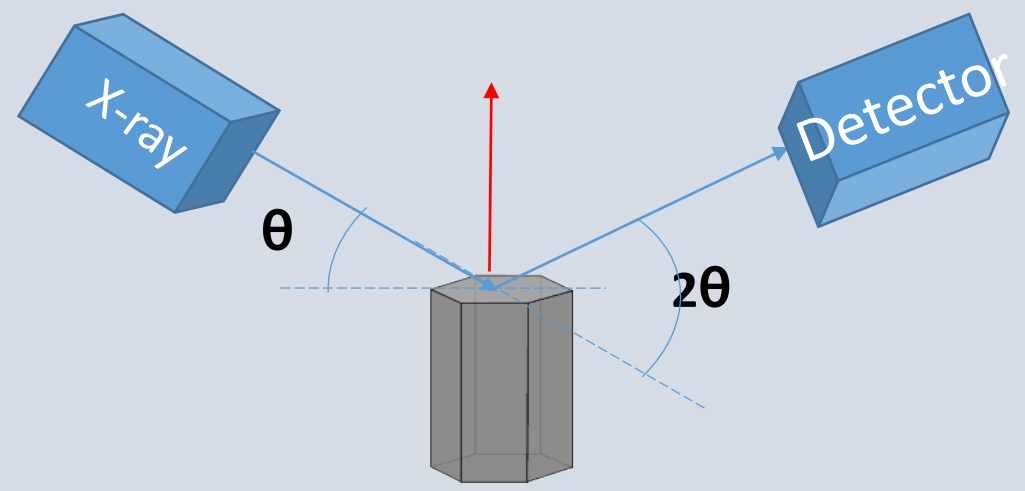
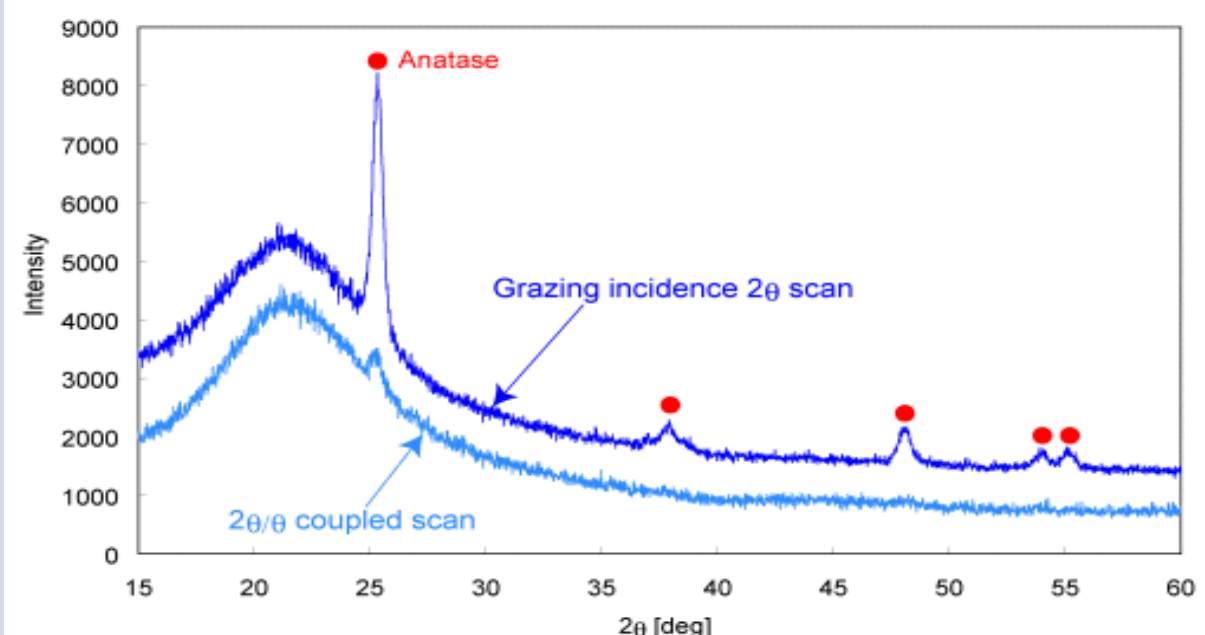
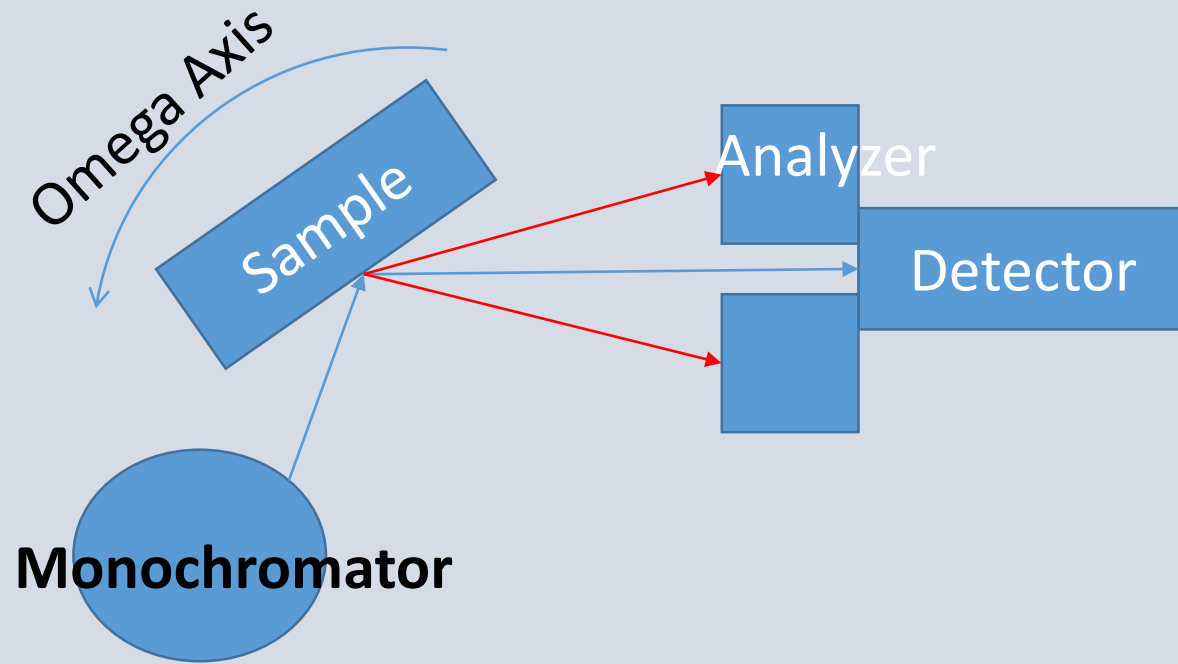
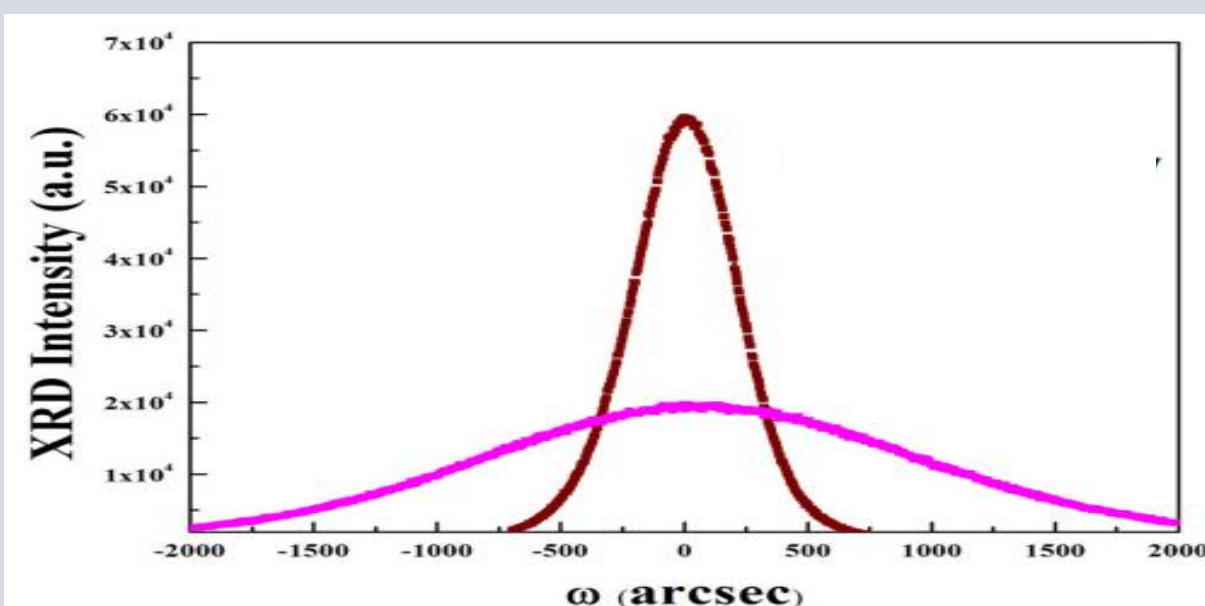
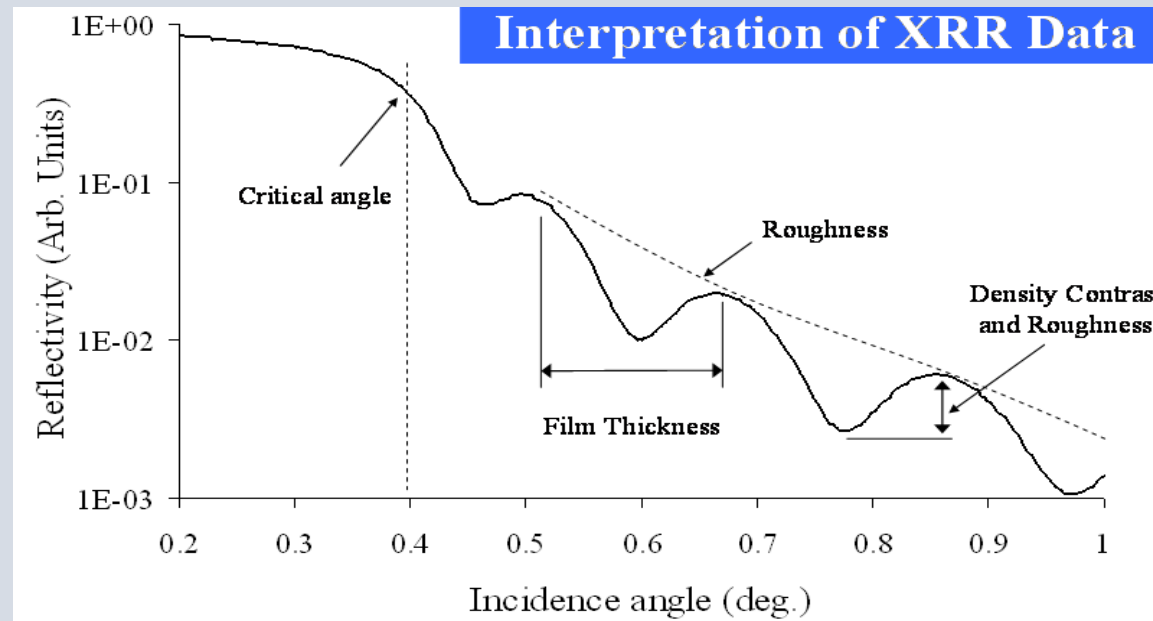
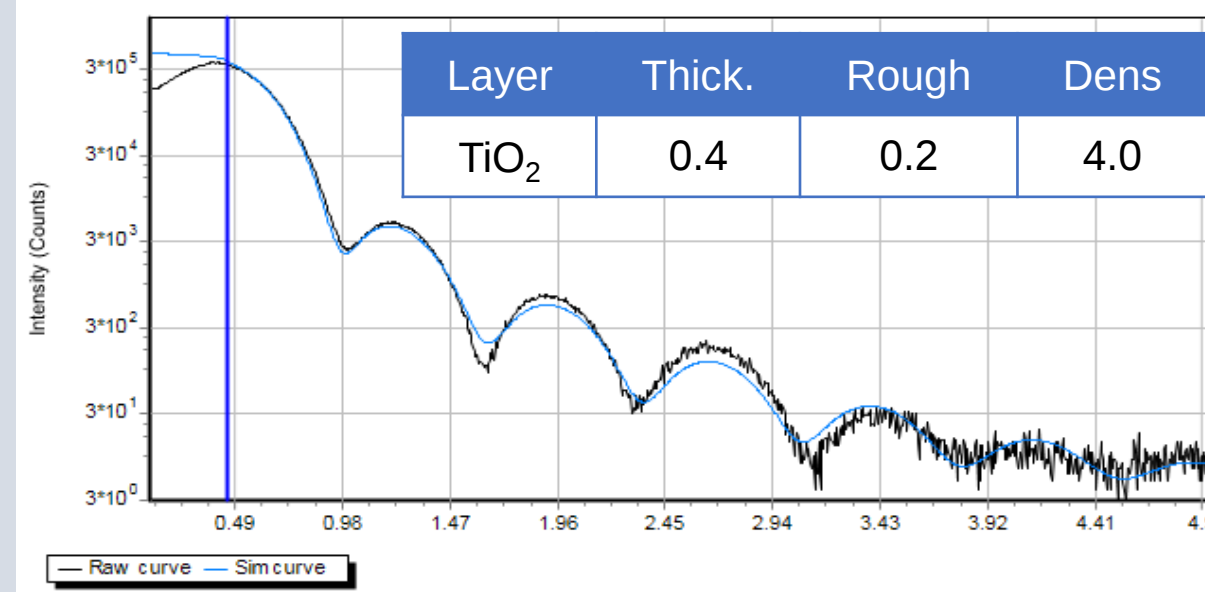
## ❖ Rietveld Refinement 의 단점

- 원자 구조 Parameter, 특히 온도 인자의 정확도가 떨어짐.
- 결정질의 Disorder, preferred orientation을 갖는 경우 정확도가 떨어짐.

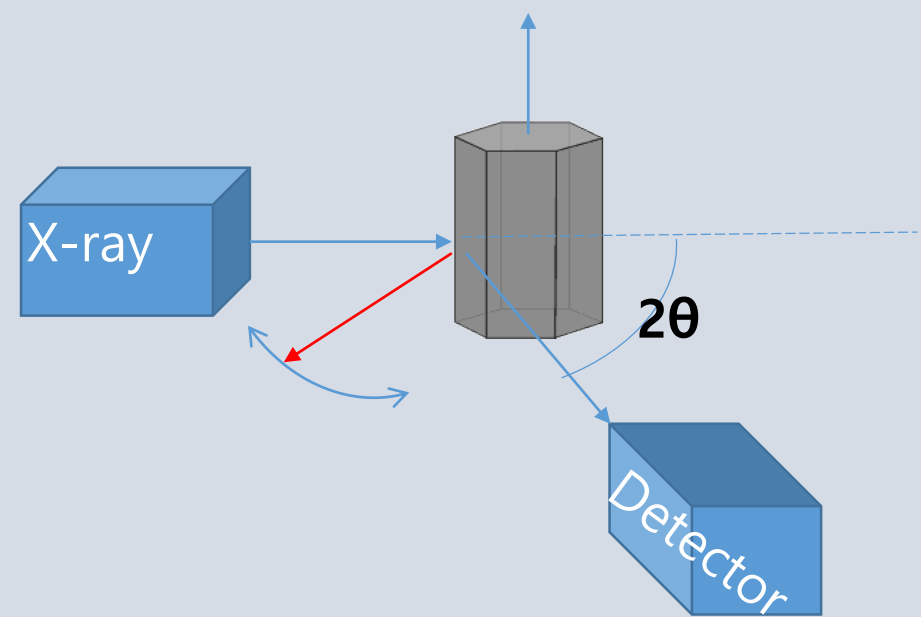
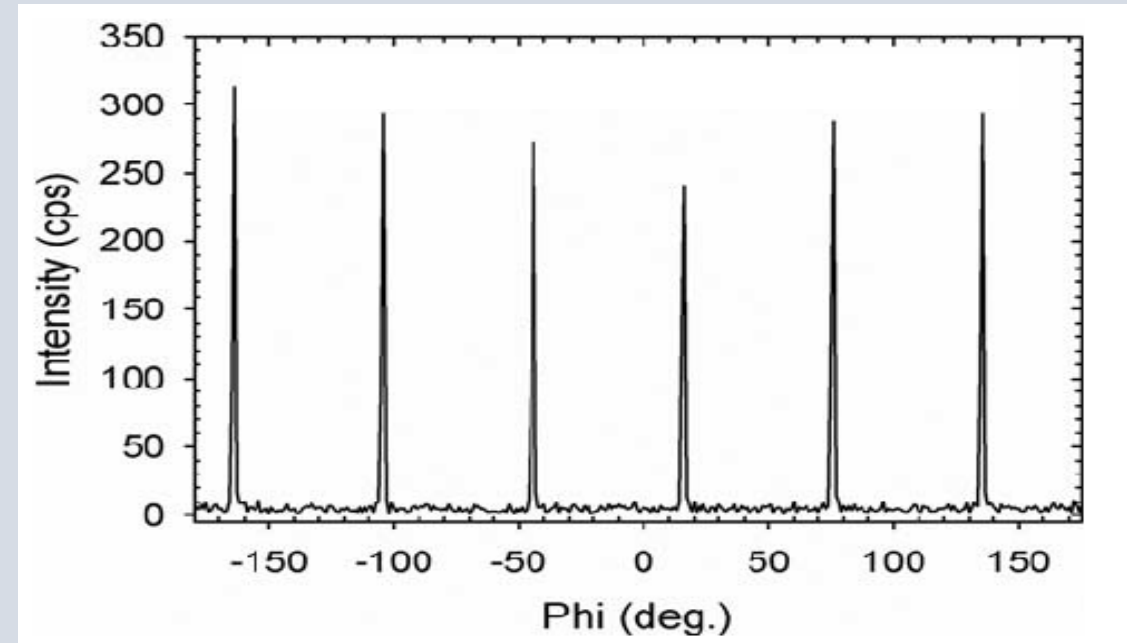
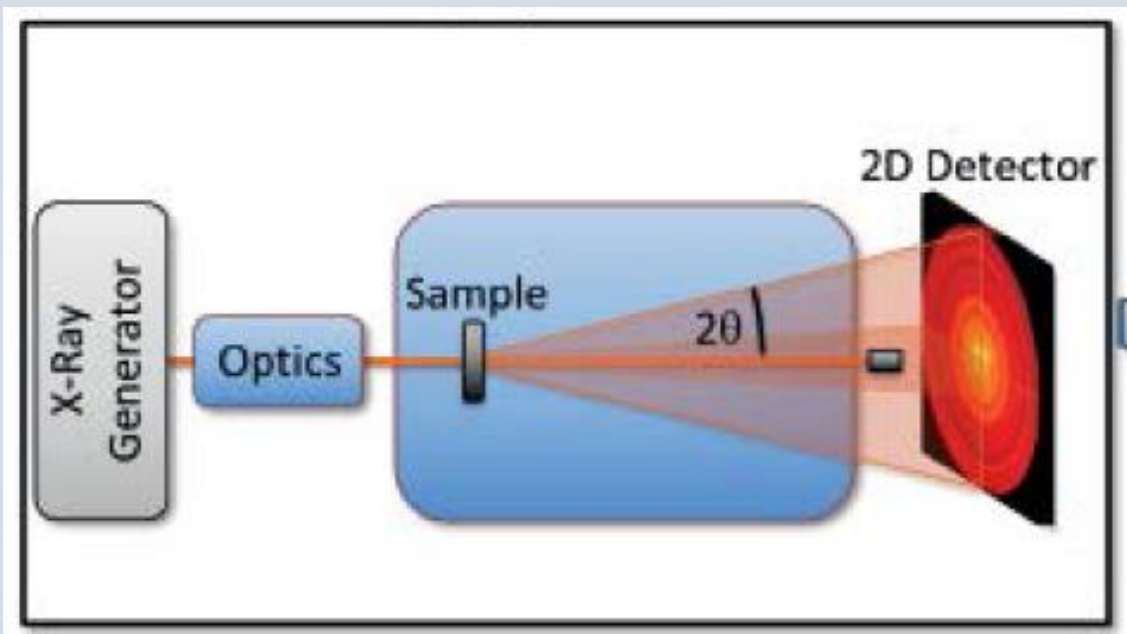
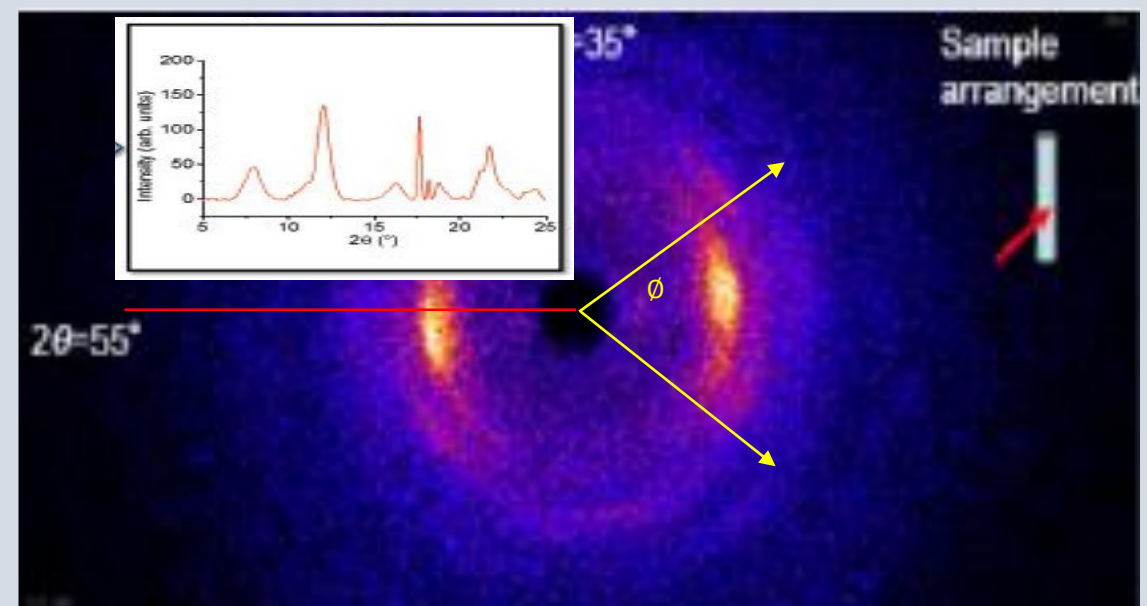
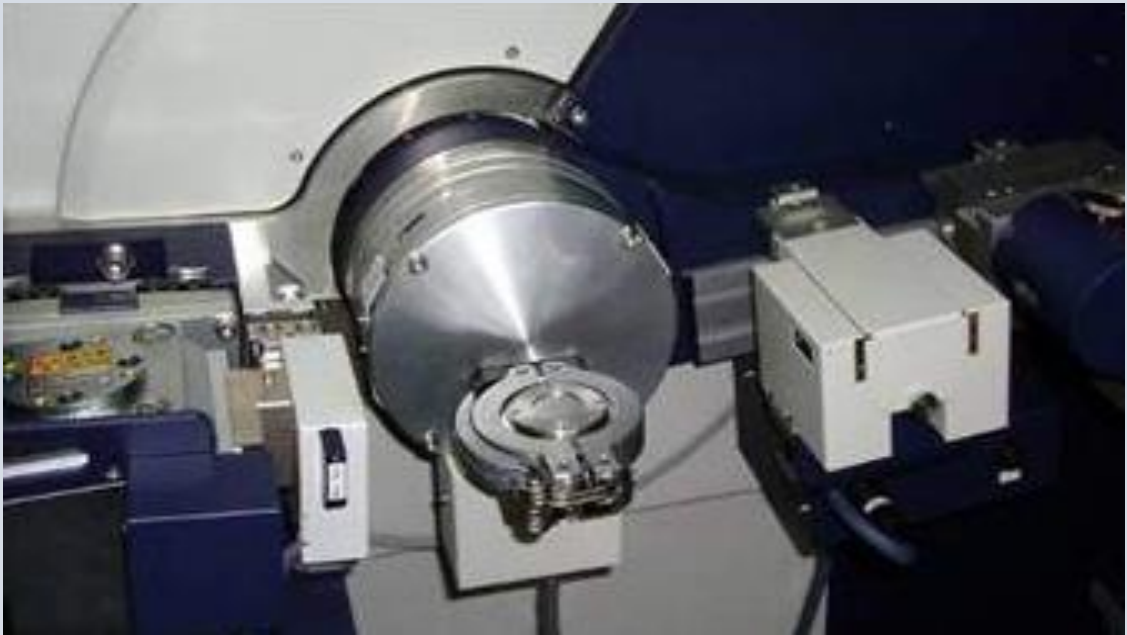
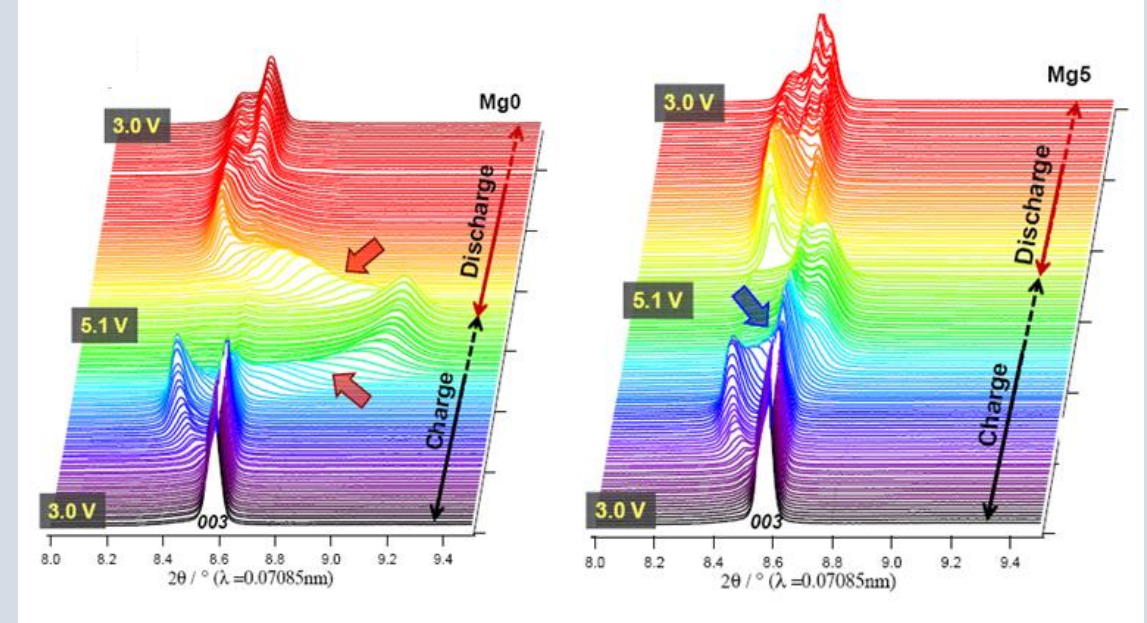
# Available applications I

| Application                                                                                                                                                                                                                                                                              | Explanation                                                                                                                        | Results |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|---------|
| <div>Qualitative Phase Analysis &amp; Quantitative Analysis</div> <div>(RIR method: Reference Intensity Ratio)</div> <div><math display="block">\frac{W_i}{W_c} = \frac{Max(I_i)}{R_i Max(c)}</math></div>                                                                               | <div>PDF Card(International Database)를 이용하여 Search/Match하여 Phase identification</div> <div>RIR method를 이용하여 두 물질의 상대적 비율을 계산</div> |         |
| <div>Crystallite Size (Scherrer equation)</div> <div><math display="block">L = \frac{K \lambda}{B \cos \theta}</math></div> <div>L : Crystallite size<br/>K: Shape Factor 0.94<br/>λ: X-ray wavelength (Cu K<sub>α</sub>: 1.5406Å)<br/>B: FWHM (in radian)<br/>Θ: Diffracted angle</div> | <div>Small angle X-ray Scattering, SEM, Nano measuring system</div> <div></div>                                                    |         |
| <div>Crystallinity</div> <div><math display="block">C = \frac{Area_{crystal}}{Area_{amorphous} + Area_{crystal}} \times 100 (\%)</math></div>                                                                                                                                            | <div>결정과 비정질이 공존하는 데이터에서 비정질 Peak와 결정 peak의 면적비를 계산하여, 결정질이 차지하는 비율 (%)을 계산</div>                                                  |         |

# Available applications II

| Applications                                                                                                                                                                                                           | Purpose                                                                                                                                         | Results                                                                                                                                                                                                                                     |       |        |       |      |                  |     |     |     |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|--------|-------|------|------------------|-----|-----|-----|
| <p>Coupled scan (<math>\theta</math>-<math>2\theta</math> scan) &amp; Glancing(Grazing) Incident Diffraction (Incident angle fixed, <math>2\theta</math> scan)</p> <p>100 nm 이하 박막 시료에서의 회절 Data 수집 및 Intensity 증가</p> |  <p>GID : <math>\theta = 0.1 \sim 2^\circ</math> (Fixed)</p> |                                                                                                                                                          |       |        |       |      |                  |     |     |     |
| <p>Rocking-curve (<math>\omega</math> scan )</p> <p>Peak width(FWHM)을 통한 Crystalline quality 분석</p>                                                                                                                    |  <p>Monochromator</p>                                       |                                                                                                                                                         |       |        |       |      |                  |     |     |     |
| <p>X-Ray Reflectivity (XRR)</p> <p>박막의 층별 분석</p> <p>1) Thickness 2) Density 3) Roughness</p>                                                                                                                           |                                                            |  <table><tr><th>Layer</th><th>Thick.</th><th>Rough</th><th>Dens</th></tr><tr><td>TiO<sub>2</sub></td><td>0.4</td><td>0.2</td><td>4.0</td></tr></table> | Layer | Thick. | Rough | Dens | TiO <sub>2</sub> | 0.4 | 0.2 | 4.0 |
| Layer                                                                                                                                                                                                                  | Thick.                                                                                                                                          | Rough                                                                                                                                                                                                                                       | Dens  |        |       |      |                  |     |     |     |
| TiO <sub>2</sub>                                                                                                                                                                                                       | 0.4                                                                                                                                             | 0.2                                                                                                                                                                                                                                         | 4.0   |        |       |      |                  |     |     |     |

# Not available applications

| Application                                                                                                                                                                                                                           | Purpose                                                                               | Result Image                                                                          |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| <p><b>Epitaxial Film의 quality 확인</b></p> <p>1) In-Plane scan : 시료 단면에 대한 orientation 확인 (<math>2\theta</math>-<math>\omega</math> scan)</p> <p>2) Phi scan : tilt plane에 대한 symmetry 확인</p> $F_0 = \frac{1}{2} [3(\cos^2\theta) - 1]$ |    |    |
| <p><b>2D Image : Fiber의 배향 분석</b></p> <p>- Hermans' orientation function</p>                                                                                                                                                          |   |   |
| <p><b>In situ</b></p> <p>- Variable Temperature XRD</p> <p>- Charging &amp; Discharging: 배터리 Cell 충전 및 방전을 통한 물질의 구조 및 배열 변화 분석</p>                                                                                                   |  |  |

# Sample Preparation

## 시료 별 전처리

### ❖ Powder 시료

- 1) 합성 시료의 경우, 막자 사발에 곱게 갈아준다. 광물 시료의 경우, 고운 체를 이용하여 큰 알갱이를 거른 후 곱게 갈아 줍니다.
- 2) Spatula를 이용하여 분말 시료를 소분하여 Glass Holder 혹은 Low BG Holder 담아 Slide Glass로 표면을 평탄화 해줍니다. 이때, 한꺼번에 분말을 Holder에 담지 않고, 소량씩 담아 Slide Glass로 표면을 평탄화해 줍니다.
- 3) HPXRD 측정 시료의 경우, Holder를 45도 기울여 시료가 유실되는지 확인 후에 측정을 진행합니다.

### ❖ Bulk 시료 (예: 세라믹, 금속 조각)

- 1) Al Holder에 시료의 크기 만큼 고무 찰흙을 잘라서 붙여줍니다. 이 때, 고무찰흙과 시료의 두께가 Holder의 두께보다 약간 크거나 같아야 합니다.
- 2) 고무 찰흙 위에 Bulk 시료를 올려놓고, 두 개의 Slide Glass를 이용하여 시료의 가장자리를 눌러 Holder의 테두리와 동일한 높이를 맞추어 줍니다. 이때, 시료가 중앙으로부터 벗어나거나, 기울어지지 않도록 주의합니다.

## 시료 별 전처리

### ❖ Film 시료

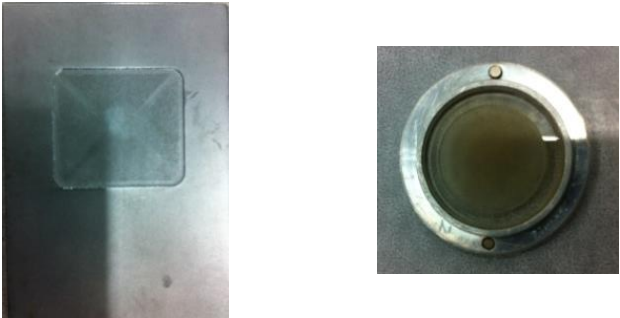
- 1) Film 시료는 대칭성을 고려해서 잘라줍니다. 가급적 자르지 않고 가로, 세로(1x1cm) 이상의 크기의 시료를 추천합니다.
- 2) AI Holder에 고무찰흙을 시료의 크기만큼 잘라서 붙여줍니다. 이 때, 고무찰흙과 시료의 두께가 Holder의 두께보다 약간 크거나 같아야 합니다.
- 3) 자른 Film 형태의 시료를 고무 찰흙 위에 올려놓고, 슬라이드 글라스로 다시 평탄화 해줍니다.

### ❖ 가볍고 부피가 있는 시료 (예: 스펀지)

- 1) 가로, 세로 1cm의 크기로 반듯하게 잘라서, Pellet Die에 기울이지 않고 넣어서 Press를 해줍니다.
- 2) AI Holder에 고무 찰흙을 시료의 크기만큼 잘라서 붙여줍니다. 고무 찰흙을 슬라이드 글라스로 눌러 평탄화 해줍니다.
- 3) Press된 스펀지를 고무 찰흙 위에 올려놓고, 슬라이드 글라스로 평탄화를 해줍니다.

# 시료 별 측정 조건

❖ 분말 시료의 양에 따라 Holder를 정한다. 분말 시료의 양이 충분한 경우, ASC의 18mm Glass Holder를 쓰거나, STD의 Low BG Holder를 사용한다.

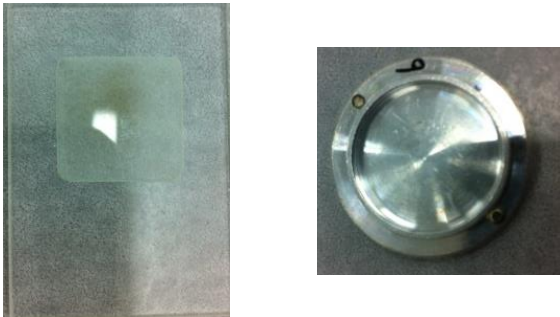
| Sample Holder                                                                     | Divergence Slit | Divergence Height Slit | Scattering Slit | Receiving Slit |
|-----------------------------------------------------------------------------------|-----------------|------------------------|-----------------|----------------|
|  | 1 °             | 10 mm                  | 1 °             | 0.3 mm         |

❖ 분말 시료의 양이 적은 경우, ASC의 5mm Glass Holder를 쓰고, 극소량의 경우 STD의 Low BG Holder를 사용한다.

| Sample Holder                                                                       | Divergence Slit | Divergence Height Slit | Scattering Slit | Receiving Slit |
|-------------------------------------------------------------------------------------|-----------------|------------------------|-----------------|----------------|
|  | 1/2 °           | 5 mm                   | 1/2 °           | 0.3 mm         |

# 시료 별 측정 조건

❖ 박막 시료의 양이 적은 경우, ASC의 Al Holder를 쓰거나, STD의 Glass Holder를 사용한다.

| Sample Holder                                                                     | Divergence Slit | Divergence Height Slit | Scattering Slit | Receiving Slit |
|-----------------------------------------------------------------------------------|-----------------|------------------------|-----------------|----------------|
|  | 1/4 °           | 10 mm                  | 1/4 °           | 0.3 mm         |

❖ Bulk 시료의 경우, ASC의 Bottomless Al Holder를 쓰거나, STD의 Bottomless Al Holder를 사용한다.

| Sample Holder                                                                       | Divergence Slit | Divergence Height Slit | Scattering Slit | Receiving Slit |
|-------------------------------------------------------------------------------------|-----------------|------------------------|-----------------|----------------|
|  | 1 °             | 10 mm                  | 1 °             | 0.3 mm         |

# 주의 사항 (Caution for use)

## Caution for HPXRD

### ❖ Sampling 주의 사항

- HPXRD 시료는 분말, Bulk,  $1\mu\text{m}$  이상의 박막의 경우 측정이 가능합니다. 분말의 시료량은 최소 0.5 mg 이상 부터 가능하나, 이 경우에는 Low BG Holder로만 측정이 가능합니다. (대여불가, 의뢰가능)
- 평균적으로 3 mg의 양이 필요합니다. 분말 시료의 경우 고운 분말 형태여야 하며, 분말 사이에 단단한 입자가 섞여 있을 경우, Mortar로 곱게 갈아 줍니다.
- Bulk 혹은 박막의 경우 가로, 세로, 두께가 1 cm, 1 cm, 2 mm로 준비 합니다. 박막의 경우도 균일하게 시료가 코팅되도록 준비합니다
- Sample displacement error가 발생하지 않도록, sample holder의 표면과 동일한 단차를 유지할 수 있도록 주의합니다.
- HPXRD Geometry는  $\theta$ - $2\theta$  goniometer로 시료가  $\theta$ 의 각도로 기울어지면, detector 각도가  $2\theta$ 로 기울어지는 구조입니다. 따라서 고각으로 기울어지면 시료가 유실될 수 있으므로, 시료를 홀더에 담은 후  $90^\circ$ 로 세워 본 후, 시료 주입기에 로딩을 합니다.
- 시료가 쏟아질 경우, Kaptone Tape (단점: noise 증가)를 부착하거나, 풀 또는 양면테이프 및 에탄올을 이용하여 시료의 유실을 방지합니다.

## Caution for HPXRD

### ❖ 측정 시 주의사항

- X-ray 상태등 및 Control Window를 통하여 장비의 상태를 잘 인지한 후, Door버튼을 누른 후 2초 후에 Door를 열고 닫습니다. 시간 초과 혹은 미달로 인해 X-ray가 강제 Shut down이 발생할 수 있으며, 이럴 경우 신속하게 Door 아래 Control pad에서 reset 버튼을 눌러줍니다.
- HPXRD는 0.8 °부터 측정이 가능하나, Divergence Silt의 각도를 ¼ °로 설정해야 합니다.  
이때 측정된 Intensity가 10만 cps를 넘을 경우, 더 낮은 각도로 설정해야 합니다. (detector 손상 때문)
- HPXRD는 고출력 X선 회절 분석기로 출력이 최대 60 kV, 300 mA로 설정이 가능하나, 관전류 과전류 현상이 발생할 확률이 높아, 40 kV, 200 mA로 사용해야 합니다. 과전류 발생시 Filament Short 발생하므로 주의합니다.
- 시료에 따라서 Optic Setting을 해야 하며, 동일 전처리 및 측정 조건으로 반복 측정을 하는 것이 중요합니다.
- 시료의 특성에 따라서 Divergence Slit, Divergence Height Slit, Scattering Silt, Receiving Slit을 잘 적용하도록 합니다.  
(시료 별 측정조건 자료 참고)
- DHS은 수동으로 변경을 해주어야 합니다. 수동으로 Slit을 변경할 때, 기판 라인과 평행하게 삽입하지 않을 경우 무리하게 넣지 않도록 합니다. (전기적으로 Silt을 제어하는 보드에 물리적 충격이 가해져 고장 발생)

## Caution for NXRD

### ❖ Sampling 주의 사항

- NXRD도 동일하게 분말, Bulk, ,  $1\mu\text{m}$  이상의 박막의 경우 측정이 가능합니다. 하지만, Sample Holder는 size가 크기 때문에 본인의 합성 양에 맞는 Sample Holder 가공을 해오셔야 합니다.
  - 1) 정품 구매 시, Bruker코리아 02-3476-8600으로 전화하셔서 **D8Advance** Sample Holder를 구매하시면 됩니다.
  - 2) 제작 요청 시, Make Lab (기기가공동-107동 103호)로 방문하셔서 Sample Holder 제작 요청하시면 됩니다.
- 평균적으로 3mg의 양이 필요합니다. 분말 시료의 경우 고운 분말 형태여야 하며, 분말 사이에 단단한 입자가 섞여 있을 경우, Mortar로 곱게 갈아 줍니다.
- Bulk or 박막의 경우 가로, 세로, 두께가 1cm, 1cm, 2mm로 준비 합니다. 박막의 경우도 균일하게 시료가 코팅되도록 준비합니다
- Sample Displacement Error가 발생하지 않도록, Sample Holder의 표면과 동일한 단차를 유지할 수 있도록 주의합니다.
- NXRD Geometry는  $\theta$ - $\theta$  Goniometer로 시료의 각도가 고정되어 있고, Source와 Detector가  $\theta$ 의 각도로 움직이면서 측정하는 기기입니다. 따라서, 시료의 유실이 없으며, **액상 시료 분석도 가능합니다.**

## ❖ 측정의 제한

- X-ray 상태등 및 Control Window를 통하여 장비의 상태를 잘 인지한 후, 'Open Door'버튼을 누른 후 2초 후에 Door를 열고 닫 습니다. 시간 초과 혹은 미달로 인해 X-ray가 강제 Shut Down이 발생할 수 있으며, 이럴 경우 Door 아래 " Open Door" 버튼을 다시 누르고 Open합니다.
- NXRD는  $\theta$ - $\theta$  Goniometry로 구성되어 있습니다. X-ray Source와 Detector가 마주보고  $\theta$ 각도로 동일하게 움직이므로 저각 측정이 불가능합니다. 가능한 측정 범위는  $10^\circ$ 부터  $110^\circ$ 까지 입니다.  
**※  $10^\circ$  미만으로 측정하면 Source의 강한 Beam이 Detector를 고장 낼 수 있으므로 반드시 주의하시기 바랍니다.**
- NXRD는 Auto Sampler Changer를 이용하여 측정 가능하며, 또한 Manual Mode로도 측정이 가능합니다. Manual Mode 측정자는 시료 회수가 자동으로 되지 않으니, 측정 완료 시점이 되면 반드시 시료 회수를 하시어(Unload 버튼 클릭), 다음 사용자의 시료와 충돌이 없도록 주의하시기 바랍니다.
- 제작한 Sample Holder 가 측정 중에 Sample Lift에 끼여서 내려오지 않는다면, Sample Holder의 외경을 1mm 이내로 깎아 재사용하기 바랍니다.

# Software & References

## ❖ Software

- 1) GSAS- Rietveld Refinement of Crystal Structures
- 2) FullProf- Rietveld Refinement of Crystal Structures
- 3) Rietan- Rietveld Refinement of Crystal Structures
- 4) PowderCell- Crystal Visualization and Simulated Diffraction Patterns
- 5) JCryst- Stereograms

## ❖ References

- 1) Elements of X-ray Diffraction, 3<sup>rd</sup> Ed., B.D. Cullity and S.R. Stock
- 2) Introduction to X-ray Powder Diffractometry, R. Jenkins and R.L. Snyder
- 3) Basic Solid State Chemistry, 2<sup>nd</sup> Ed., A. West
- 4) X-ray Diffraction Procedures, H. Klug and L. Alexander



THANK YOU