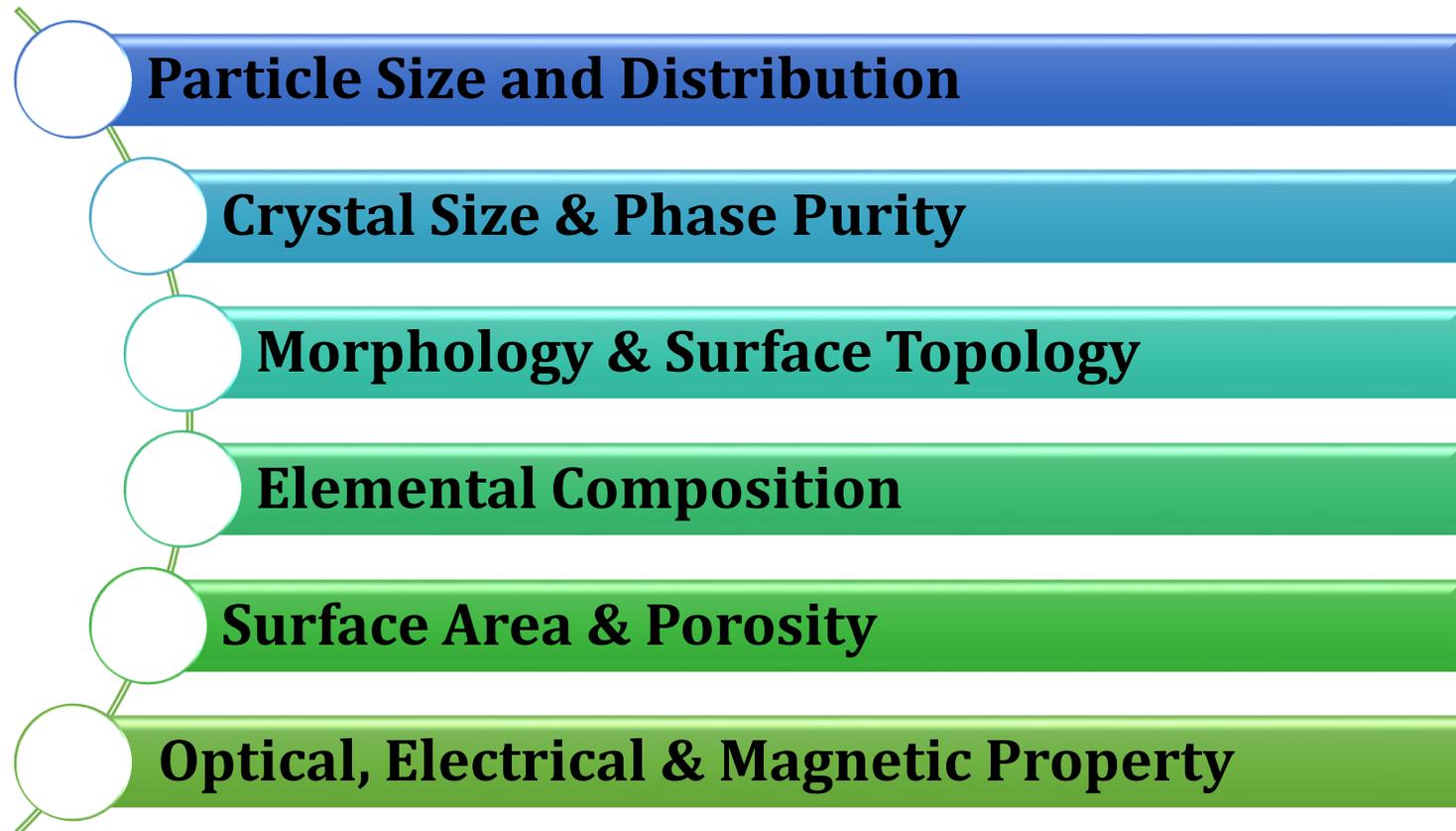


# Characterization Techniques For Nanomaterials

Characterization of nanomaterials involves determining



# X-RAY DIFFRACTION (XRD) FOR NANOMATERIALS

- X-Ray Diffraction (XRD) is a **non-destructive analytical technique** used to study the **crystal structure, phase composition, and crystallite size** of materials.

For nanomaterials, XRD is particularly important because:

- ✓ Peak broadening occurs at nanoscale
- ✓ Crystal size strongly affects physical and chemical properties
- ✓ It confirms whether nanoparticles are crystalline or amorphous

# Principle of XRD (Bragg's Law)

- When monochromatic X-rays fall on a crystalline material, they are scattered by atoms arranged in periodic planes. Constructive interference occurs when Bragg's condition is satisfied:

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

- Where:

$n$  = order of diffraction

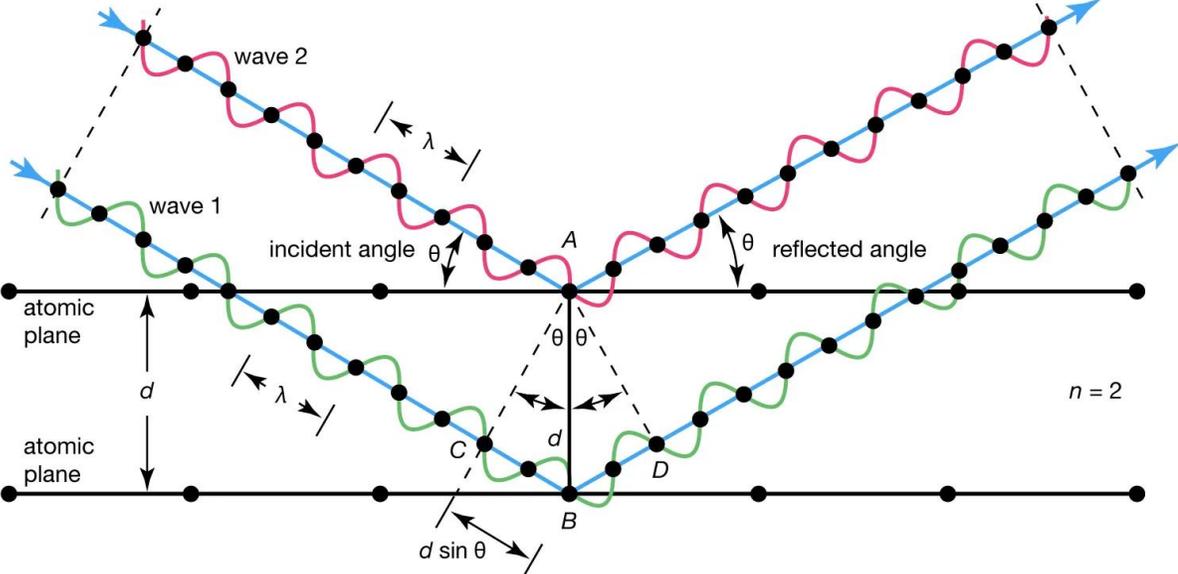
$\lambda$  = wavelength of X-ray

$d$  = interplanar spacing

$\theta$  = diffraction angle

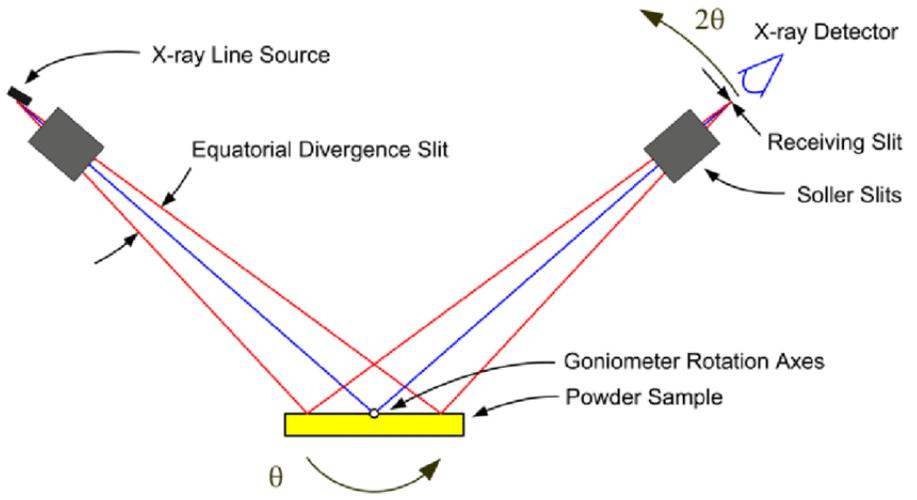
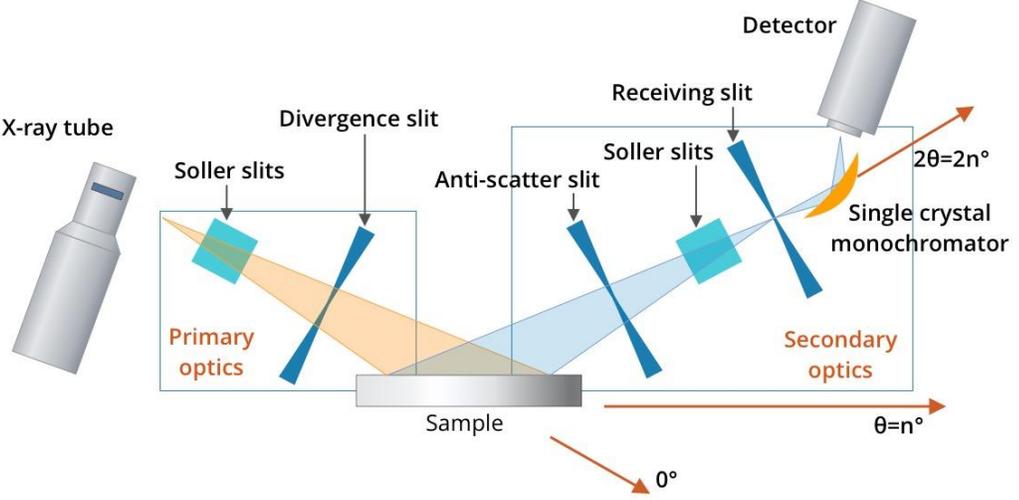
- This condition produces diffraction peaks at specific  $2\theta$  values.

# Why XRD Works Well for Nanomaterials



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Bragg-brentano type diffractometer



# 1. Nanomaterials Are Mostly Crystalline

- Most engineered nanomaterials (metal, metal oxide, semiconductor nanoparticles) possess **ordered atomic arrangements**. XRD is specifically designed to analyze **periodic crystal lattices**.
- When X-rays strike these ordered planes, **constructive interference** occurs according to Bragg's law:

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

- Because nanomaterials retain crystalline order:
  - ✓ They generate diffraction peaks
  - ✓ Their structure can be identified
  - ✓ Their phase can be matched with standard databases
- If a material were completely amorphous, XRD would show only a broad hump. Nanomaterials typically show broadened but distinct peaks, meaning XRD is ideal.

## 2. Nanoscale Crystallites Cause Peak Broadening

- The most important reason XRD works well:
- **As crystallite size decreases → XRD peaks become broader**
- This happens due to the **finite size effect**.
- Physically:
- In bulk crystals → millions of repeating planes → sharp peaks
- In nanocrystals → very few repeating planes → uncertainty in diffraction angle → broadened peaks
- This broadening is mathematically linked to crystallite size using the **Scherrer equation**:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

- Where

$D$  = crystallite size

$\beta$  = peak width (FWHM)

- So:

- ✓ Measure  $\beta$

✓ Calculate  $D$

✓ Obtain size in nanometers

- This direct size–broadening relationship makes XRD extremely suitable for nanoscale materials.

# 3. XRD Measures Crystallite Size (Not Just Presence)

Nanomaterials research is not only about knowing **what material exists**, but also:

- How small the crystals are
- Whether they grow after heat treatment
- Whether synthesis method changes size
- XRD allows:
  - Comparison of peak widths
  - Estimation of crystallite growth or reduction

Example:

- As-synthesized nanoparticle → broad peaks
- Calcined nanoparticle → sharper peaks
- This shows **increase in crystallite size**, easily detected by XRD.

# 4. Phase Identification Is Crucial at Nanoscale

- Nanomaterials often exist in **multiple polymorphs**:

Example:  $\text{TiO}_2$  → anatase, rutile, brookite

- Each phase has different:

- Band gap

- Photocatalytic activity

- Stability

- XRD provides **fingerprint patterns** for each phase.

Thus XRD is vital to:

- ✓ Confirm desired phase

- ✓ Detect secondary impurity phases

- ✓ Study phase transformation at nanoscale

Without XRD, phase purity cannot be reliably verified.

# 5. Sensitive to Lattice Distortion and Strain

- Nanomaterials contain:
  - ✓ Surface defects
  - ✓ Vacancies
  - ✓ Dopant atoms
- These introduce **lattice strain**, which slightly shifts and broadens peaks.
- XRD can detect:
  - Peak shifting → lattice expansion or contraction
  - Additional broadening → microstrain

Hence XRD helps understand:

- ✓ Defect concentration
- ✓ Doping effects
- ✓ Stress inside nanoparticles

This sensitivity makes XRD powerful for nanoscale systems.

## 6. Works with Powdered Nanomaterials

- Most nanomaterials are synthesized as **powders**.
- Powder XRD:
  - ✓ Requires only a small amount
  - ✓ No complex preparation
  - ✓ Random orientation gives complete diffraction information
  - ✓ This convenience makes XRD ideal for routine nanomaterial analysis.

## 7. Non-Destructive Nature

- Nanomaterials are often expensive or hard to synthesize.
- XRD:
  - ✓ Does not destroy sample
  - ✓ Allows further analysis by SEM, TEM, BET, etc.
- This is extremely valuable for multi-technique characterization.

## 8. XRD Provides Average Bulk Information

While TEM examines a **few particles**, XRD analyzes **millions of crystallites simultaneously**.

Thus XRD gives:

- ✓ Statistically reliable average size
- ✓ Overall phase composition

This makes conclusions more representative.