Introduction to X-Ray Diffraction (XRD)

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XRD Fundamental Concepts

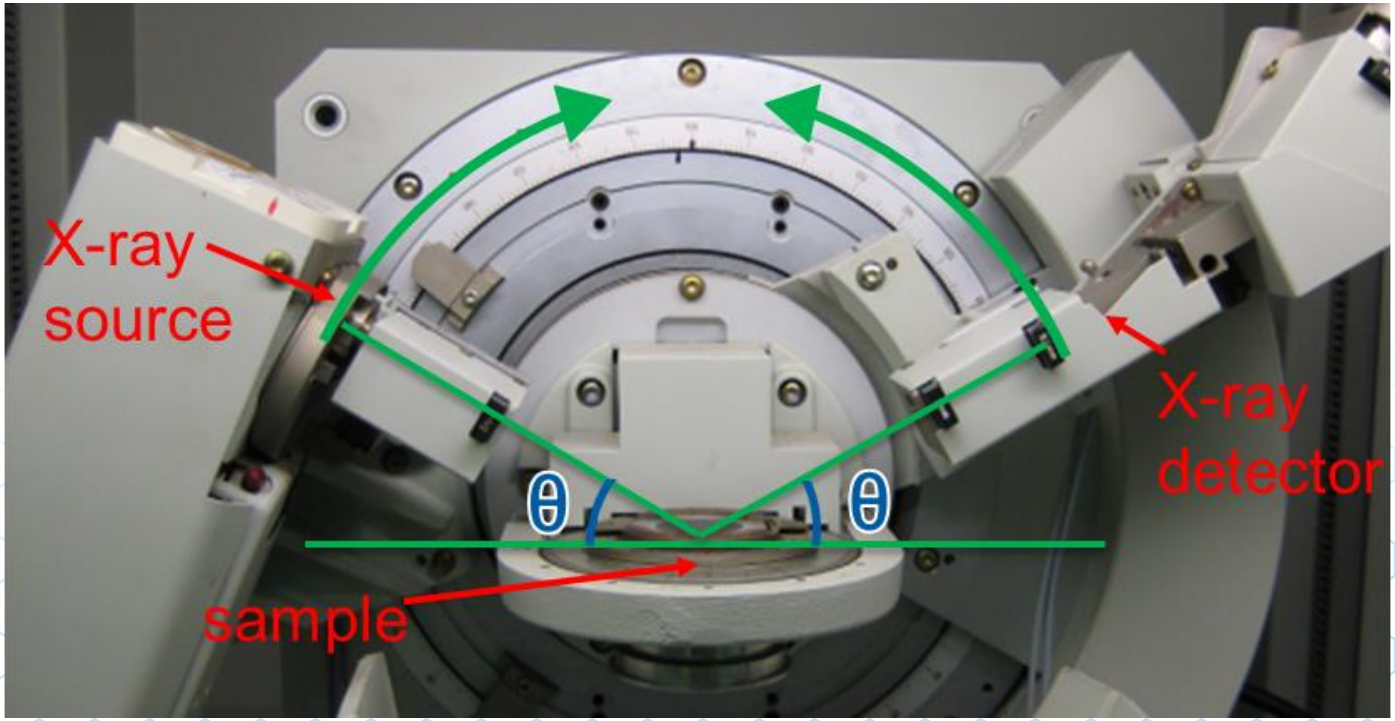
XRD Benefits

- **One of the few techniques that can detect material phase**
  - Critical in quality management of materials manufacturing as phases determine properties.
  - Complementary to chemistry testing of elements present in a sample.

- **Non-destructive**
  - Bulk samples are crushed to powder but powder can be used for other testing after XRD.

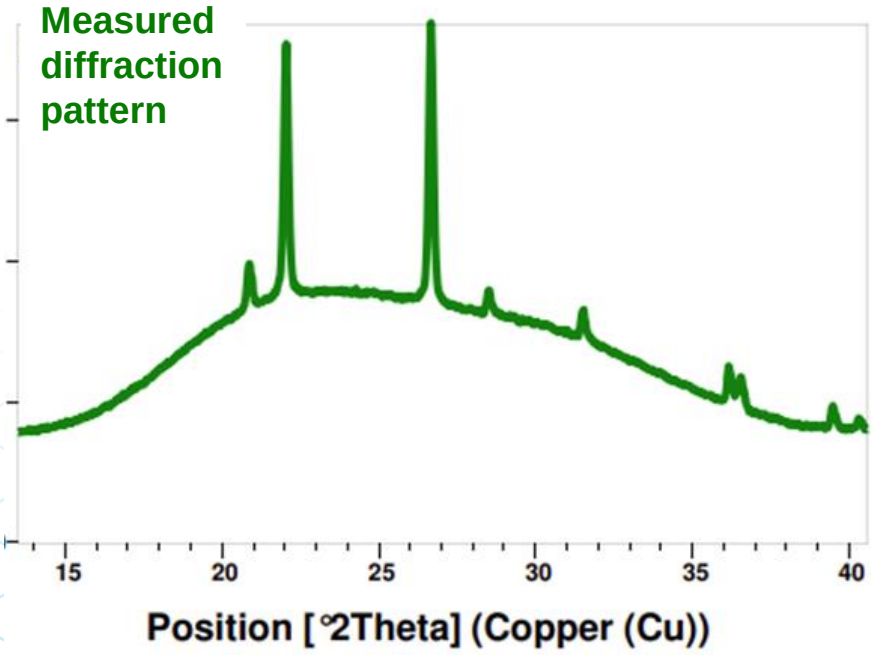
XRD Operation

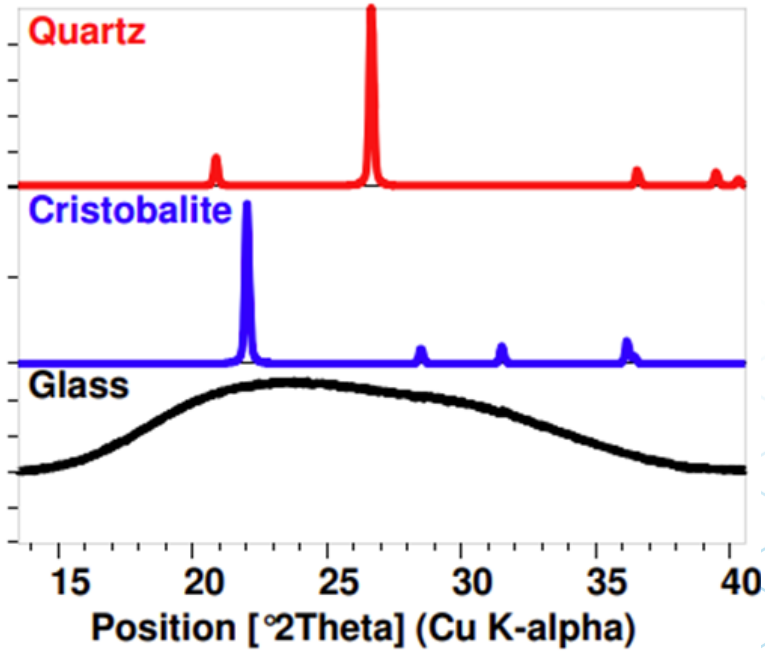
- Traditionally, the source and detector rotate around the sample to measure x-ray intensity at all potential angles.



Crystalline Diffraction Patterns

- At each angle, intensity is recorded.
- The angle and intensity pattern is a unique fingerprint for each phase.
- Multi-phase materials are superimposed on each other.

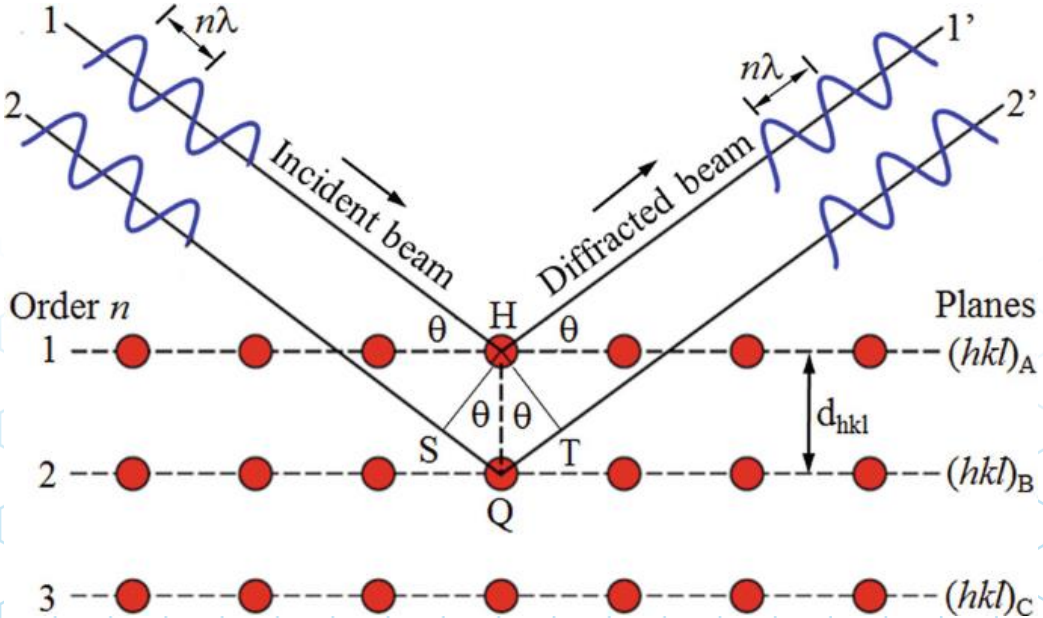




Measuring Planar Spacing

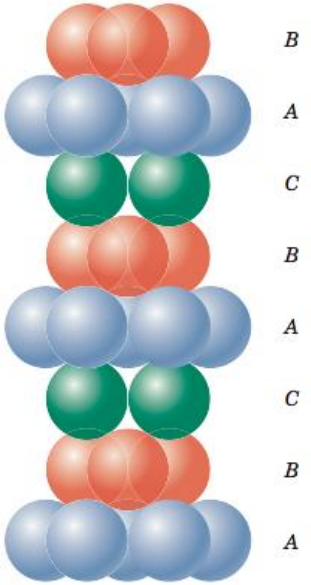
- X-rays diffract off atoms and constructively interfere at angles, θ, related to the planar spacing, d_{hkl}.
  - X-rays of wavelength λ
  - *n* is a positive integer (1, 2, 3, etc.)

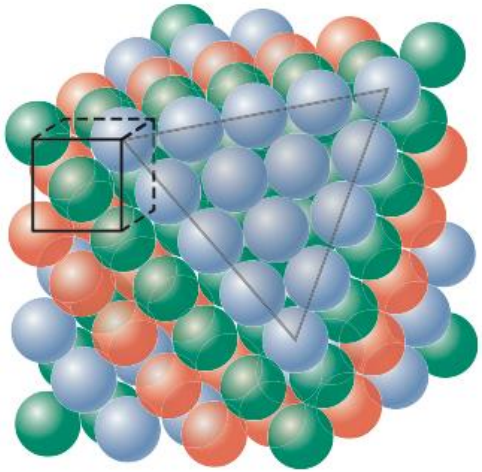
$$n\lambda = 2d_{hkl}\sin(\theta)$$

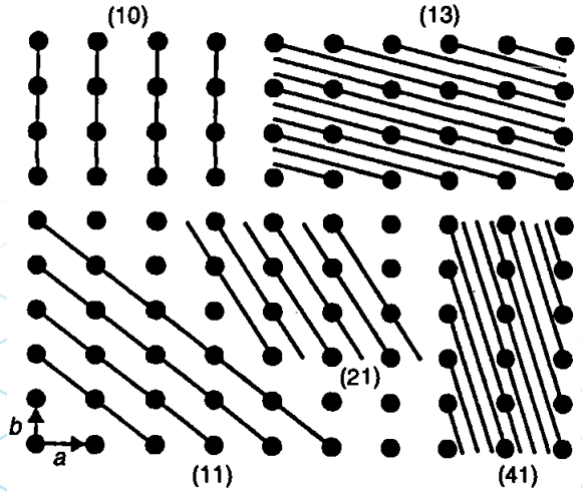


Stacking of Atoms in Crystal Structures

- Atoms stack in known ways for crystalline materials (metals, ceramics, some polymers).
- The stacking sequence and atomic size can be identified with sets of planes.



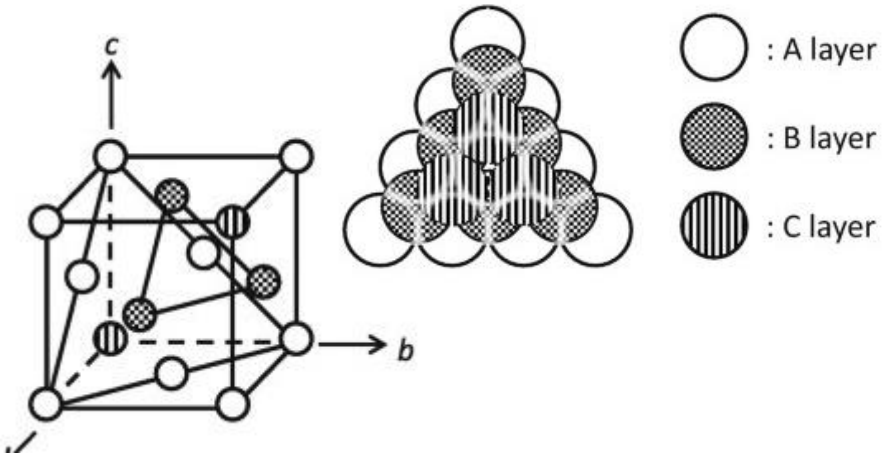


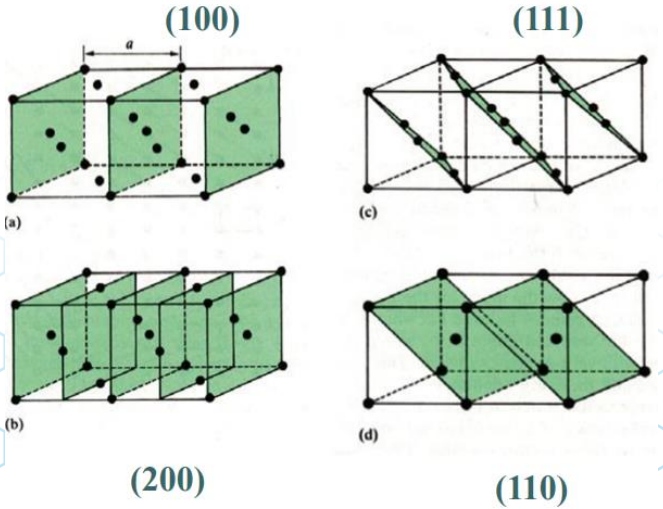


Microstructure and Phase ID

Microstructure Basics

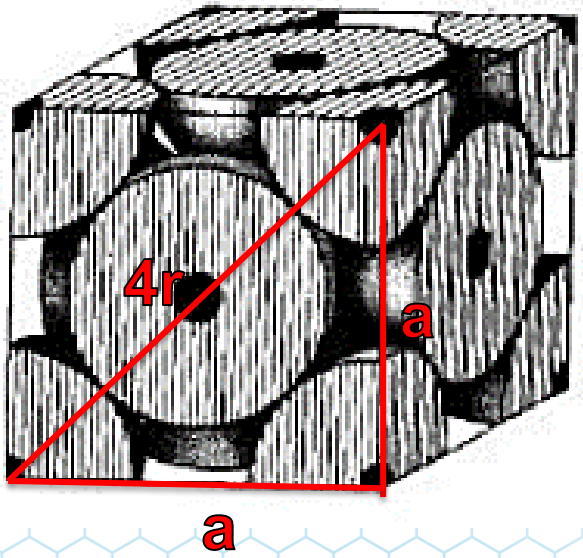
- Crystalline materials (metals and ceramics, some plastics) can be separated into 7 different crystal structures.
  - Cubic is shown on the right
- These crystals provide relationships between the stacks of atoms that make up crystalline materials.
- To describe a particular layer of atoms, we use Miller Indices.
  - Represented by “(hkl)” where h, k, and l are whole numbers





Identifying a Crystal

- In addition to the crystal structure, the placement of atoms adds context to the dimensions and spacing of the stacked atomic planes.
- Our previous example is Face-centered cubic, meaning the atoms reside on the faces and corners of the cubic cell.
- We can then calculate the lattice parameter (side lengths) of the cubic cell based on the radii of the atoms of our material.
  - In this example, all sides are the same length, but in other crystals sides *a*, *b*, and *c* can be different lengths.

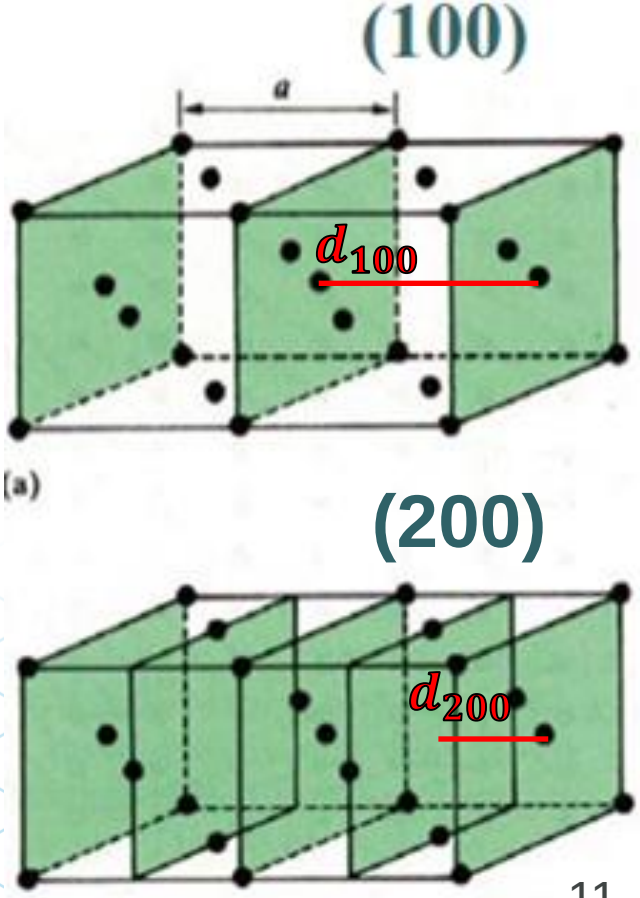


Determining Spacing Between Atomic Planes

- Knowing the size of the crystal cell, the size of the atoms, we can calculate the distance between each stack of atoms for a given (hkl) plane.

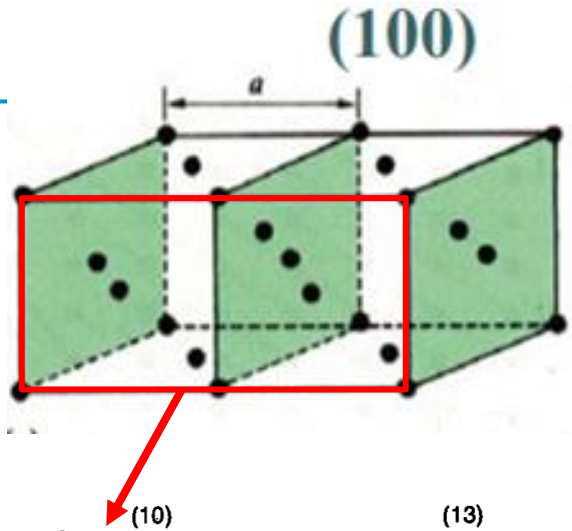
$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

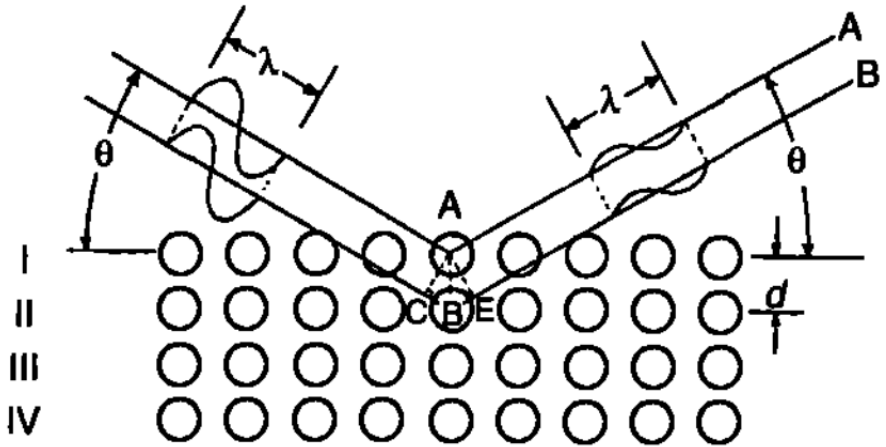
- For any crystal material, a unique set of d_{hkl} spacings can be made as a "fingerprint" of the material in question.



How can we measure those planes?

- Simplify the 3D setup of the atomic stacking to a 2D projection:
- X-rays will diffract off layers of atoms.
- Successive layers of atoms will cause constructive and destructive interference depending on the angle of the incoming X-rays.

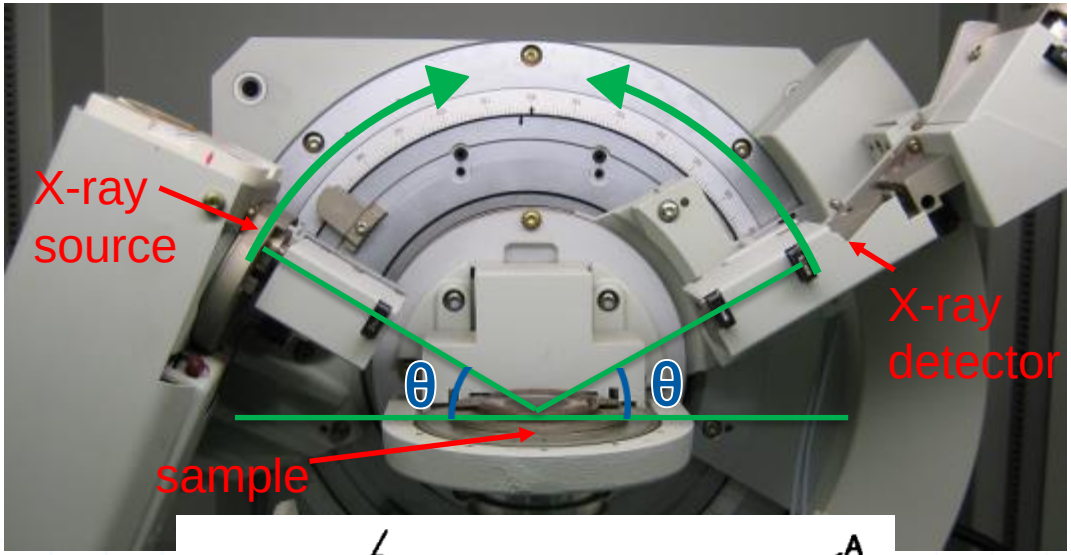


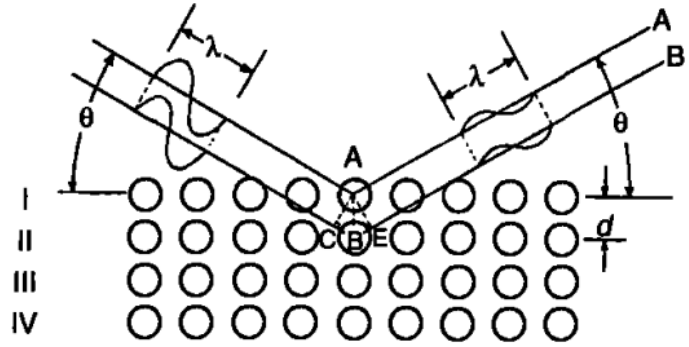


Measuring a sample in XRD

- That unique set of d_{hkl} spacings correlate to a unique set of angles where the x-rays constructively interfere.

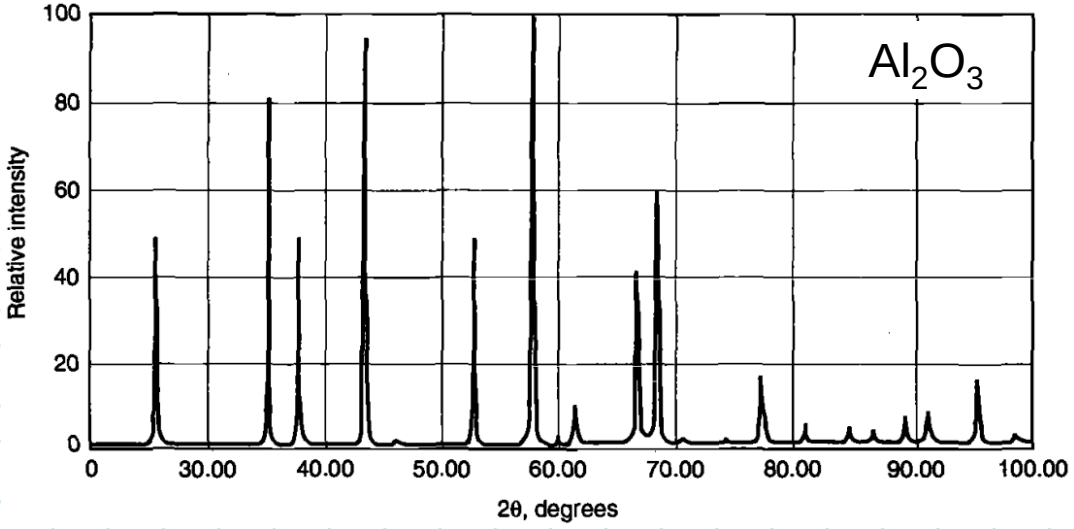
- Traditionally, the x-ray source and detector will rotate around a stationary sample to 2θ ranging from 0° to 180°





Diffraction Pattern

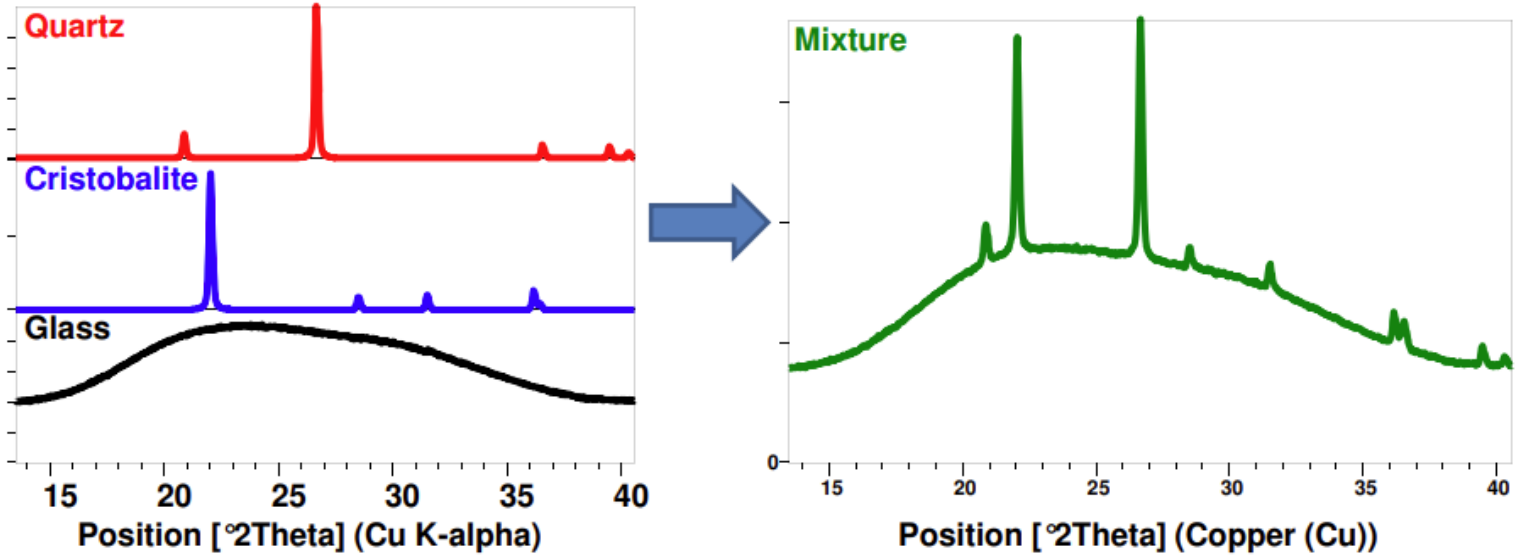
- The amount of constructive interference in the x-rays varies, which results in varied peaks heights (intensities) at specific angles of 2θ
- Most crystal structures have been studies and therefore have “cards” with the angles and intensities for matching a diffraction pattern to a specific material.



2θ, degrees	Intensity, 0 to 100	d, Å	Miller indices
25.62	67	3.477	012
35.20	89	2.549	104
37.78	35	2.381	110
41.70	1	2.166	006
43.43	100	2.084	113
46.20	1	1.965	202
52.60	45	1.740	024
57.55	100	1.601	116
59.82	4	1.546	211
61.30	12	1.512	122, 018
66.60	40	1.404	214
68.28	53	1.374	300
70.40	2	1.337	125
74.30	2	1.277	208
77.15	22	1.236	1010, 119
80.80	8	1.189	220
84.50	6	1.146	223
86.50	8	1.125	312, 128
89.08	10	1.099	0210
91.00	12	1.081	0012, 134
95.34	18	1.043	226
98.50	1	1.018	042

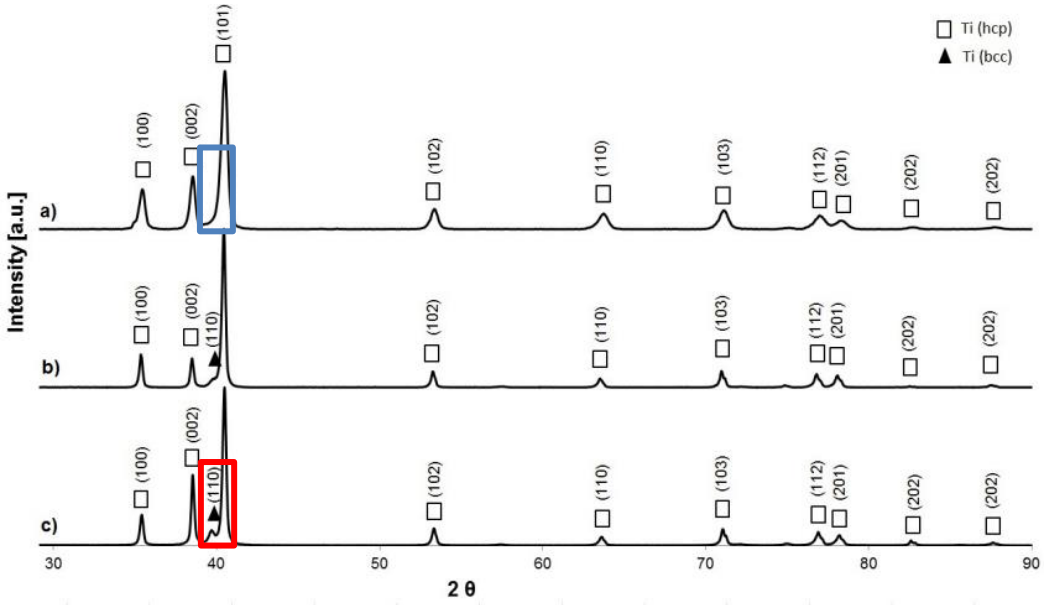
Multi-phase Materials

- Diffraction patterns become a sum of the individual phase diffraction pattern when more that one exists.
- Non-crystalline materials (glass in this case) present as a large, wide bump in the diffraction pattern



A Practical Example – Ti-6Al-4V

- Ti64 is α-Ti (hcp, for strength) and β-Ti (bcc, for ductility)



Process	UTS (MPa)	Elongation (%)
ASTM F136	>860	>10
a SLM	1421 ± 120	3.2 ± 0.5
	1246 ± 134	1.4 ± 0.5
b EBM	976 ± 11	15.0 ± 2.0
	972 ± 14	14.2 ± 1.5
c Wrought	933 ± 7	13.0 ± 1.5
	942 ± 8	12.5 ± 1.2

Figure 9. The XRD (X-ray diffraction) patterns for Ti-6Al-4V alloy obtained in the SLM (**a**), EBM (**b**) and heat-treated and annealed sheet (**c**).

Another Practical Example – IN718

- IN718 consists of the primary γ phase, and strengthening phases γ’ and γ”

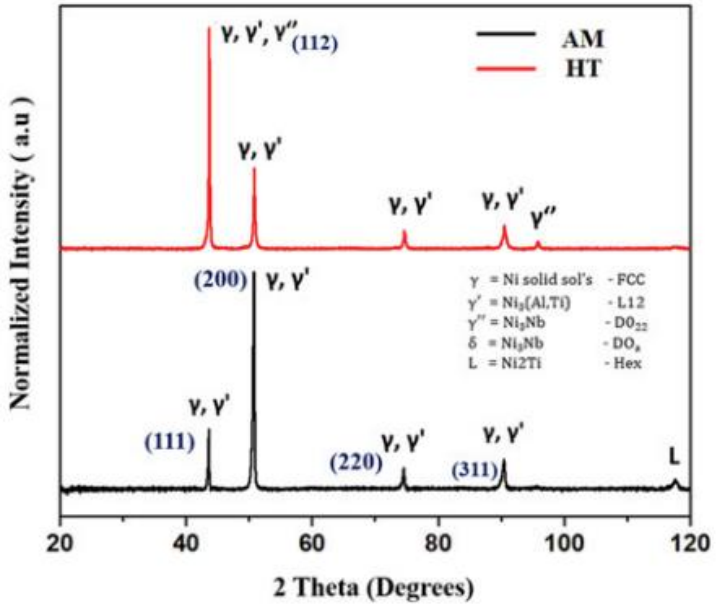


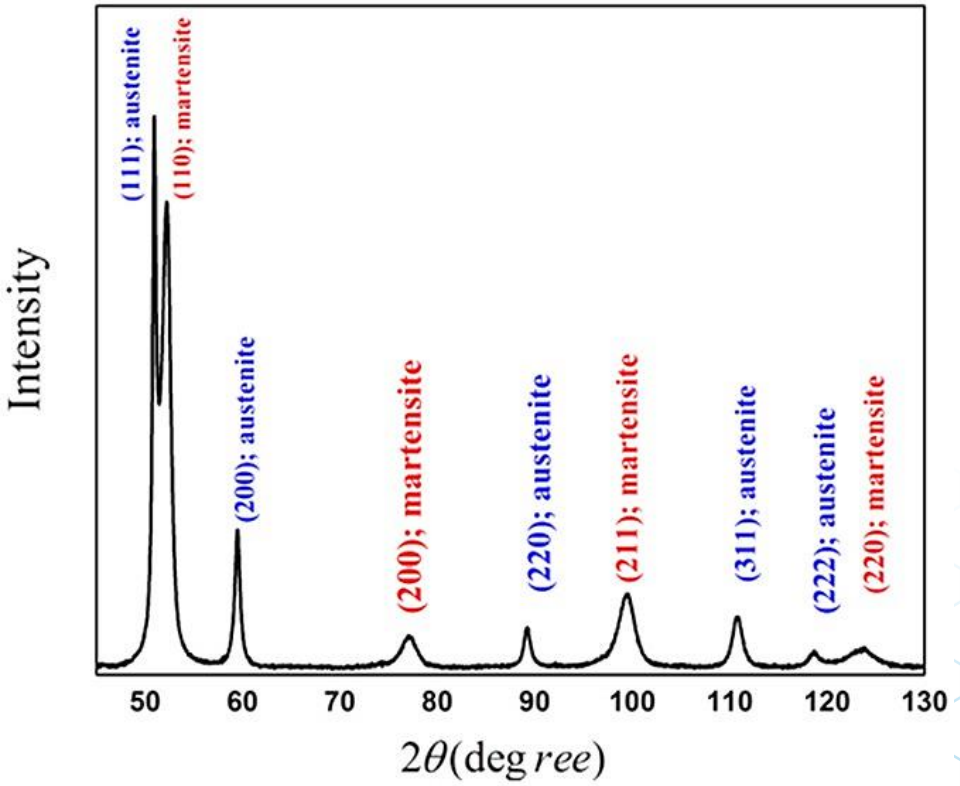
Figure 2. XRD patterns of additively manufactured SLM IN718 and HT SLM IN718.

TABLE II. Variation of yield strength and the onset of critical strain at which the serration begins at a particular temperature.

Temperature (°C)	Yield strength (MPa) AP	Yield strength (MPa) HT	Critical strain (Engineering) %	Critical strain (True) %
RT	817 ± 14	1227 ± 22	–	–
550	785 ± 12	1028 ± 17	10.8	10.2
600	734 ± 09	894 ± 24	12.5	11.7
650	706 ± 11	867 ± 27	18.2	16.7

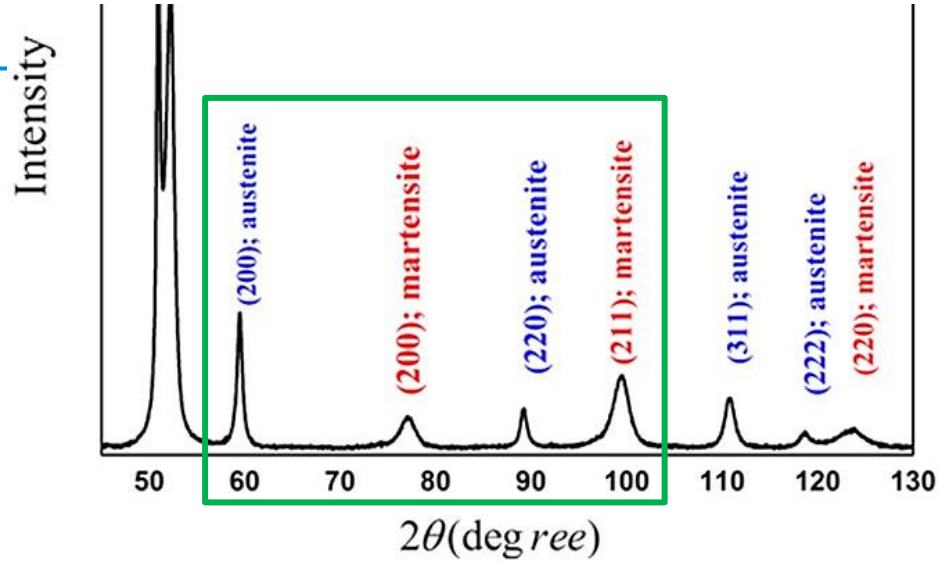
Retained Austenite Testing, an example of phase ID

- Steel are typically comprised of Austenite, Martensite, or both.
  - Austenite provides ductility
  - Martensite provides strength
- In the cases of both, its important to know what the phase composition is to know the balance of strength and ductility.
- Thankfully, Austenite and Martensite are different phases, so their diffraction patterns are different.



Identifying the key peaks

- We want the following peaks (hkl)
  - γ, Martensite 200 and 211
  - α, Austenite 200 and 220
- Use table 1 in ASTM E975 for the corrective coefficients, R, and measure the intensities off the plot, I:

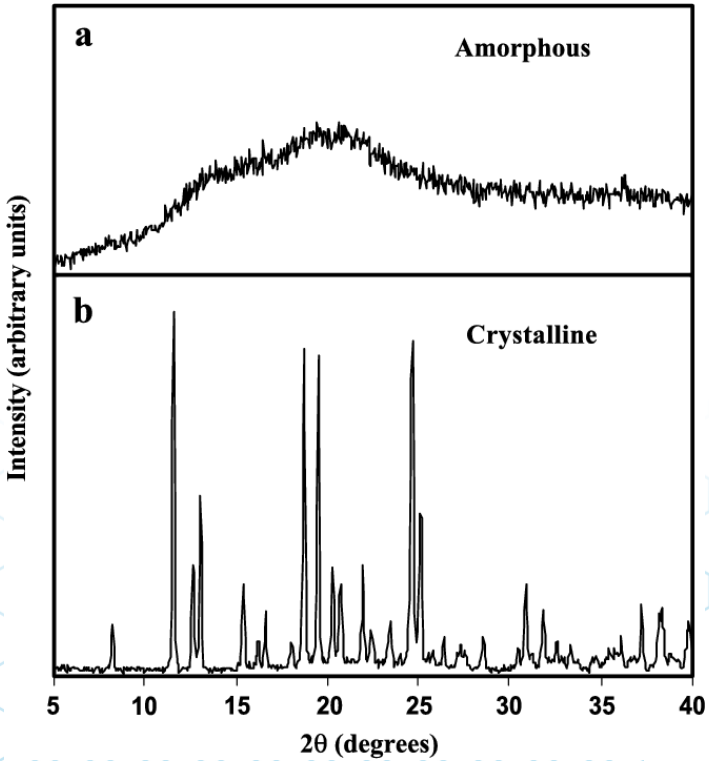


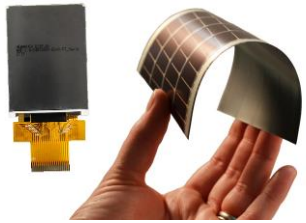
$$\%RA = \frac{0.5 \times \left(\frac{R\alpha_{200}}{R\alpha_{200}} + \frac{R\alpha_{220}}{I\alpha_{220}}\right)}{0.5 \times \left(\frac{R\alpha_{200}}{R\alpha_{200}} + \frac{R\alpha_{220}}{I\alpha_{220}}\right) + 0.5 \times \left(\frac{R\gamma_{200}}{R\gamma_{200}} + \frac{R\gamma_{211}}{I\gamma_{211}}\right)}$$

hkl	R
(α iron,	
110	101.5[C]
200	20.73[C]
211	190.8[C]
(γ iron,	
111	75.24[C]
200	34.78[C]
220	47.88[C]

Other Examples & Applications

- Silica: crystalline vs. amorphous

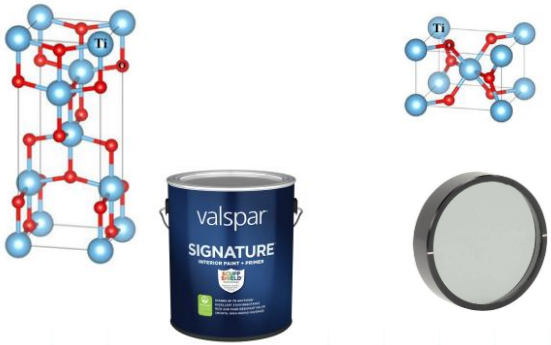


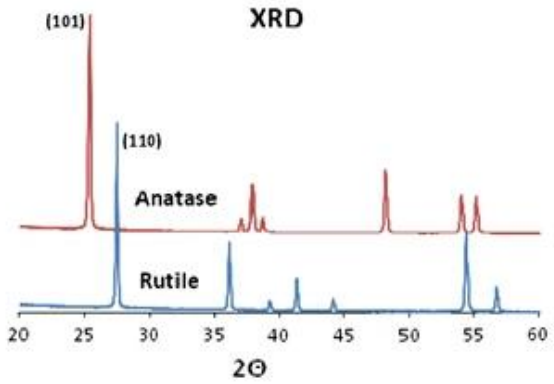


Other Examples & Applications

- Titania:

anatase $TiO_2 \longrightarrow$ rutile TiO_2





Aeroxide P 25	**15% rutile 85% anatase**	35-65 m^2/g	Photocatalyst, heat stabilizer in silicones
Aeroxide P 90	**>95% anatase**	70-110 m^2/g	
Aeroxide T 805	**mixed phase**	35-55 m^2/g	Toner, UV stabilizer in polymers
Aeroxide NKT 90	**≥97% anatase**	50-75 m^2/g	

Summary

Summary of X-Ray Diffraction (XRD)

- XRD provides quantitative and qualitative options for determining material phase, which ultimately defines material performance and properties

- This technique can be used for a variety of ceramics, metals, and amorphous materials

- It is a versatile technique, that when used in combination with analytical chemistry testing and SEM or imaging can provide a wealth of insight into constituent materials.