

Laboratory Module 1

INDEXING DIFFRACTION PATTERNS FROM CUBIC MATERIALS

LEARNING OBJECTIVES

Upon completion of this module you will be able to index an X-ray diffraction pattern, identify the Bravais lattice, and calculate the lattice parameters for materials having cubic structures.

BACKGROUND

We need to know about crystal structures because structure, to a large extent, determines properties. X-ray diffraction (XRD) is one of a number of experimental tools that are used to identify the structures of crystalline solids.

The XRD patterns, the product of an XRD experiment, are somewhat like fingerprints in that they are unique to the material that is being examined. The information in an XRD pattern is a direct result of two things:

- (1) The size and shape of the unit cells, which determine the relative positions of the diffraction peaks;
- (2) Atomic positions within the unit cell, which determine the relative intensities of the diffraction peaks (remember the structure factor?).

Taking these things into account, we can calculate the size and shape of a unit cell from the positions of the XRD peaks and we can determine the positions of the atoms in the unit cell from the intensities of the diffraction peaks.

Full identification of crystal structures is a multi-step process that consists of:

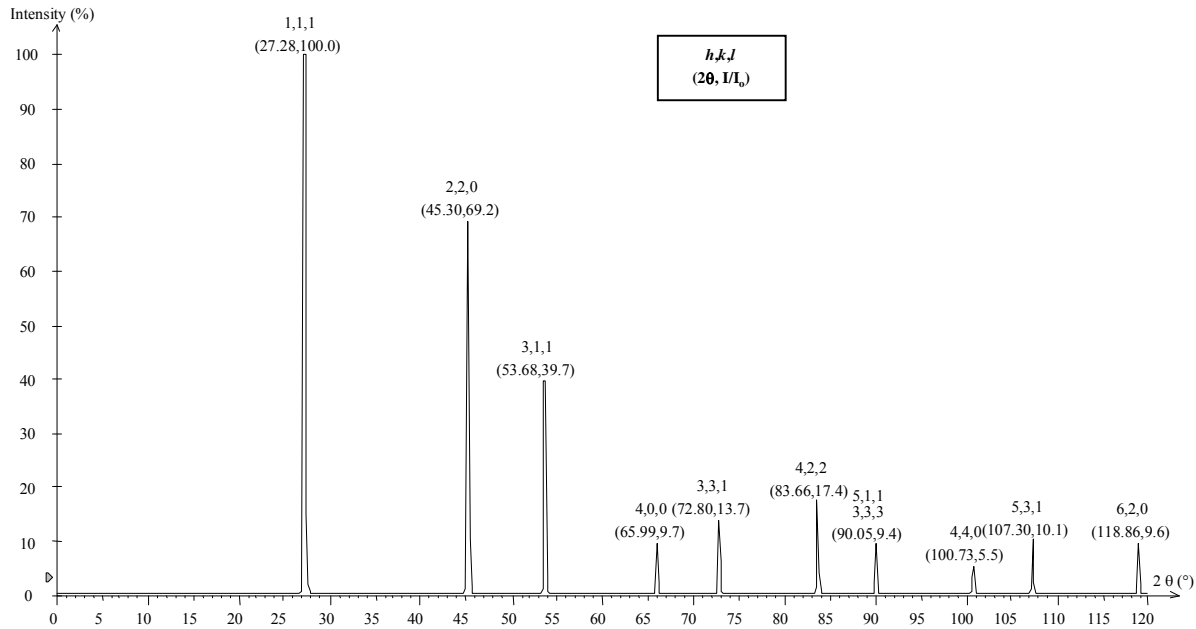
- (1) Calculation of the size and shape of the unit cell from the XRD peak positions;
- (2) Computation of the number of atoms/unit cell from the size and shape of the cell, chemical composition, and measured density;
- (3) Determination of atom positions from the relative intensities of the XRD peaks

We will only concern ourselves with step (1), calculation of the size and shape of the unit cell from XRD peak positions. We loosely refer to this as “indexing.”

INDEXING A DIFFRACTION PATTERN

When you index a diffraction pattern, you assign the correct Miller indices to each peak (reflection) in the diffraction pattern. An XRD pattern is properly indexed when ALL of the

peaks in the diffraction pattern are labeled and no peaks expected for the particular structure are missing.



This is an example of a properly indexed diffraction pattern. All peaks are accounted for. One now needs only to assign the correct Bravais lattice and to calculate lattice parameters.

How to we correctly index a pattern? The correct procedures follow.

PROCEDURE FOR INDEXING AN XRD PATTERN

The procedures are standard. They work for any crystal structure regardless of whether the material is a metal, a ceramic, a semiconductor, a zeolite, etc... There are two methods of analysis. You will do both. I will refer to the first as the “mathematical method.” I will refer to the second as the “analytical method.” The details are covered below.

Mathematical Method

Interplanar spacings in cubic crystals can be written in terms of lattice parameters using the plane spacing equation:

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

You should recall Bragg’s law ($\lambda = 2d \sin \theta$), which can be re-written either as:

$$\lambda^2 = 4d^2 \sin^2 \theta \text{ OR } \sin^2 \theta = \frac{\lambda^2}{4d^2}$$

Combining this relationship with the plane spacing equation gives us a new relationship:

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

which can be rearranged to:

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

The term in parentheses $\left(\frac{\lambda^2}{4a^2} \right)$ is constant for any one pattern (because the X-ray wavelength λ and the lattice parameters a do not change*). Thus $\sin^2 \theta$ is proportional to $h^2 + k^2 + l^2$. This proportionality shows that planes with higher Miller indices will diffract at higher values of θ .

Since $\left(\frac{\lambda^2}{4a^2} \right)$ is constant for any pattern, we can write the following relationship for any two different planes:

$$\frac{\sin^2 \theta_1}{\sin^2 \theta_2} = \frac{\left(\frac{\lambda^2}{4a^2} \right) (h_1^2 + k_1^2 + l_1^2)}{\left(\frac{\lambda^2}{4a^2} \right) (h_2^2 + k_2^2 + l_2^2)} \text{ or } \frac{\sin^2 \theta_1}{\sin^2 \theta_2} = \frac{(h_1^2 + k_1^2 + l_1^2)}{(h_2^2 + k_2^2 + l_2^2)}.$$

The ratio of $\sin^2 \theta$ values scales with the ratio of $h^2 + k^2 + l^2$ values.

In cubic systems, the first XRD peak in the XRD pattern will be due to diffraction from planes with the lowest Miller indices, which interestingly enough are the close packed planes (*i.e.*: simple cubic, (100), $h^2 + k^2 + l^2 = 1$; body-centered cubic, (110) $h^2 + k^2 + l^2 = 2$; and face-centered cubic, (111) $h^2 + k^2 + l^2 = 3$).

Since h , k , and l are always integers, we can obtain $h^2 + k^2 + l^2$ values by dividing the $\sin^2 \theta$ values for the different XRD peaks with the minimum one in the pattern (*i.e.*, the $\sin^2 \theta$ value from the first XRD peak) and multiplying that ratio by the proper integer (either 1, 2 or 3). This should yield a list of integers that represent the various $h^2 + k^2 + l^2$ values. You can identify the

* NOTE: The lattice parameters are assumed to be constant. Changes may occur if temperature changes.

correct Bravais lattice by recognizing the sequence of allowed reflections for cubic lattices (*i.e.*, the sequence of allowed peaks written in terms of the quadratic form of the Miller indices).

Primitive	$h^2 + k^2 + l^2 = 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 16 \dots$
Body-centered	$h^2 + k^2 + l^2 = 2, 4, 6, 8, 10, 12, 14, 16 \dots$
Face-centered	$h^2 + k^2 + l^2 = 3, 4, 8, 11, 12, 16, 19, 20, 24, 27, 32 \dots$
Diamond cubic	$h^2 + k^2 + l^2 = 3, 8, 11, 16, 19, 24, 27, 32 \dots$

The lattice parameters can be calculated from:

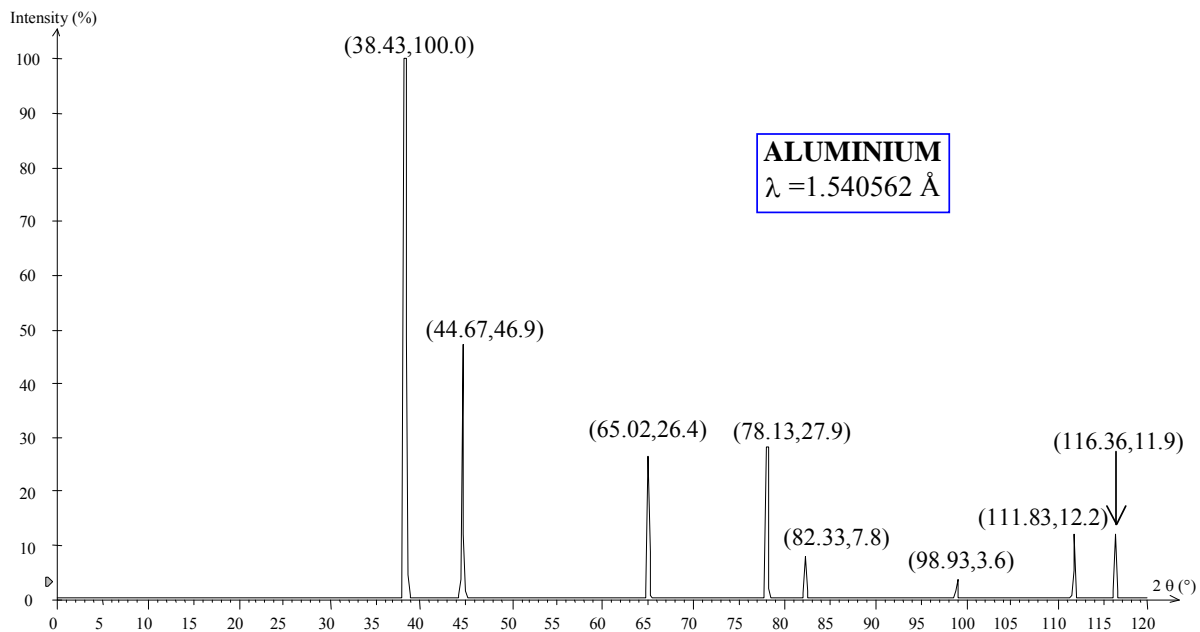
$$\sin^2 \theta = \left(\frac{\lambda^2}{4a^2} \right) (h^2 + k^2 + l^2)$$

which can be re-written as:

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

Worked Example

Consider the following XRD pattern for Aluminum, which was collected using $\text{CuK}\alpha$ radiation.



Index this pattern and determine the lattice parameters.

Steps:

- (1) Identify the peaks.
- (2) Determine $\sin^2 \theta$.
- (3) Calculate the ratio $\sin^2 \theta / \sin^2 \theta_{\min}$ and multiply by the appropriate integers.
- (4) Select the result from (3) that yields $h^2 + k^2 + l^2$ as an integer.
- (5) Compare results with the sequences of $h^2 + k^2 + l^2$ values to identify the Bravais lattice.
- (6) Calculate lattice parameters.

Here we go!

- (1) Identify the peaks and their proper 2θ values. Eight peaks for this pattern. Note: most patterns will contain α_1 and α_2 peaks at higher angles. It is common to neglect α_2 peaks.

Peak No.	2θ	$\sin^2 \theta$	$1 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$2 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$3 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43							
2	44.67							
3	65.02							
4	78.13							
5	82.33							
6	98.93							
7	111.83							
8	116.36							

- (2) Determine $\sin^2 \theta$.

Peak No.	2θ	$\sin^2 \theta$	$1 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$2 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$3 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083						
2	44.67	0.1444						
3	65.02	0.2888						
4	78.13	0.3972						
5	82.33	0.4333						
6	98.93	0.5776						
7	111.83	0.6859						
8	116.36	0.7220						

(3) Calculate the ratio $\sin^2 \theta / \sin^2 \theta_{\min}$ and multiply by the appropriate integers.

Peak No.	2θ	$\sin^2 \theta$	$1 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$2 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$3 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000			
2	44.67	0.1444	1.333	2.667	4.000			
3	65.02	0.2888	2.667	5.333	8.000			
4	78.13	0.3972	3.667	7.333	11.000			
5	82.33	0.4333	4.000	8.000	12.000			
6	98.93	0.5776	5.333	10.665	15.998			
7	111.83	0.6859	6.333	12.665	18.998			
8	116.36	0.7220	6.666	13.331	19.997			

(4) Select the result from (3) that most closely yields $h^2 + k^2 + l^2$ as a series of integers.

Peak No.	2θ	$\sin^2 \theta$	$1 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$2 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$3 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000			
2	44.67	0.1444	1.333	2.667	4.000			
3	65.02	0.2888	2.667	5.333	8.000			
4	78.13	0.3972	3.667	7.333	11.000			
5	82.33	0.4333	4.000	8.000	12.000			
6	98.93	0.5776	5.333	10.665	15.998			
7	111.83	0.6859	6.333	12.665	18.998			
8	116.36	0.7220	6.666	13.331	19.997			

(5) Compare results with the sequences of $h^2 + k^2 + l^2$ values to identify the miller indices for the appropriate peaks and the Bravais lattice.

Peak No.	2θ	$\sin^2 \theta$	$1 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$2 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$3 \times \frac{\sin^2 \theta}{\sin^2 \theta_{\min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000	3	111	4.0538
2	44.67	0.1444	1.333	2.667	4.000	4	200	4.0539
3	65.02	0.2888	2.667	5.333	8.000	8	220	4.0538
4	78.13	0.3972	3.667	7.333	11.000	11	311	4.0538
5	82.33	0.4333	4.000	8.000	12.000	12	222	4.0538
6	98.93	0.5776	5.333	10.665	15.998	16	400	4.0541
7	111.83	0.6859	6.333	12.665	18.998	19	331	4.0540
8	116.36	0.7220	6.666	13.331	19.997	20	420	4.0541

Bravais lattice is Face-Centered Cubic

(6) Calculate lattice parameters.

Peak No.	2θ	$\sin^2\theta$	$1 \times \frac{\sin^2\theta}{\sin^2\theta_{\min}}$	$2 \times \frac{\sin^2\theta}{\sin^2\theta_{\min}}$	$3 \times \frac{\sin^2\theta}{\sin^2\theta_{\min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000	3	111	4.0538
2	44.67	0.1444	1.333	2.667	4.000	4	200	4.0539
3	65.02	0.2888	2.667	5.333	8.000	8	220	4.0538
4	78.13	0.3972	3.667	7.333	11.000	11	311	4.0538
5	82.33	0.4333	4.000	8.000	12.000	12	222	4.0538
6	98.93	0.5776	5.333	10.665	15.998	16	400	4.0541
7	111.83	0.6859	6.333	12.665	18.998	19	331	4.0540
8	116.36	0.7220	6.666	13.331	19.997	20	420	4.0541

Average lattice parameter is 4.0539 Å

Analytical Method

This is an alternative approach that will yield the same results as the mathematical method. It will give you a nice comparison.

Recall:

$$\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)(h^2 + k^2 + l^2) \text{ and } \left(\frac{\lambda^2}{4a^2}\right) = \text{constant for all patterns}$$

If we let $K = \left(\frac{\lambda^2}{4a^2}\right)$, we can re-write these equations as:

$$\sin^2\theta = K(h^2 + k^2 + l^2)$$

For any cubic system, the possible values of $h^2 + k^2 + l^2$ correspond to the sequence:

$$h^2 + k^2 + l^2 = 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, \dots$$

If we determine $\sin^2\theta$ for each peak and we divide the values by the integers 2, 3, 4, 5, 6, 8, 9, 10, 11, ..., we can obtain a common quotient, which is the value of K corresponding to $h^2 + k^2 + l^2 = 1$.

K is related to the lattice parameter as follows:

$$K = \left(\frac{\lambda^2}{4a^2}\right) \text{ OR } a = \frac{\lambda}{2\sqrt{K}}$$

If we divide the $\sin^2 \theta$ values for each reflection by K , we get the $h^2 + k^2 + l^2$ values. The sequence of $h^2 + k^2 + l^2$ values can be used to label each XRD peak and to identify the Bravais lattice.

Let's do an example for the Aluminum pattern presented above.

Steps:

- (1) Identify the peaks.
- (2) Determine $\sin^2 \theta$.
- (3) Calculate the ratio $\sin^2 \theta / (\text{integers})$
- (4) Identify the lowest common quotient from (3) and identify the integers to which it corresponds. Let the lowest common quotient be K .
- (5) Divide $\sin^2 \theta$ by K for each peak. This will give you a list of integers corresponding to $h^2 + k^2 + l^2$.
- (6) Select the appropriate pattern of $h^2 + k^2 + l^2$ values and identify the Bravais lattice.
- (7) Calculate lattice parameters.

Here we go again!

(1) Identify the peaks.

Peak No.	2θ	$\sin^2 \theta$	$\frac{\sin^2 \theta}{2}$	$\frac{\sin^2 \theta}{3}$	$\frac{\sin^2 \theta}{4}$	$\frac{\sin^2 \theta}{5}$	$\frac{\sin^2 \theta}{6}$	$\frac{\sin^2 \theta}{8}$
1	38.43							
2	44.67							
3	65.02							
4	78.13							
5	82.33							
6	98.93							
7	111.83							
8	116.36							

(2) Determine $\sin^2 \theta$.

Peak No.	2θ	$\sin^2 \theta$	$\frac{\sin^2 \theta}{2}$	$\frac{\sin^2 \theta}{3}$	$\frac{\sin^2 \theta}{4}$	$\frac{\sin^2 \theta}{5}$	$\frac{\sin^2 \theta}{6}$	$\frac{\sin^2 \theta}{8}$
1	38.43	0.1083						
2	44.67	0.1444						
3	65.02	0.2888						
4	78.13	0.3972						
5	82.33	0.4333						
6	98.93	0.5776						
7	111.83	0.6859						
8	116.36	0.7220						

(3) Calculate the ratio $\sin^2 \theta / (\text{integers})$

Peak No.	2θ	$\sin^2 \theta$	$\frac{\sin^2 \theta}{2}$	$\frac{\sin^2 \theta}{3}$	$\frac{\sin^2 \theta}{4}$	$\frac{\sin^2 \theta}{5}$	$\frac{\sin^2 \theta}{6}$	$\frac{\sin^2 \theta}{8}$
1	38.43	0.1083	0.0542	0.0361	0.0271	0.0217	0.0181	0.0135
2	44.67	0.1444	0.0722	0.0481	0.0361	0.0289	0.0241	0.0181
3	65.02	0.2888	0.1444	0.0963	0.0722	0.0578	0.0481	0.0361
4	78.13	0.3972	0.1986	0.1324	0.0993	0.0794	0.0662	0.0496
5	82.33	0.4333	0.2166	0.1444	0.1083	0.0867	0.0722	0.0542
6	98.93	0.5776	0.2888	0.1925	0.1444	0.1155	0.0963	0.0722
7	111.83	0.6859	0.3430	0.2286	0.1715	0.1372	0.1143	0.0857
8	116.36	0.7220	0.3610	0.2407	0.1805	0.1444	0.1203	0.0903

(4) Identify the lowest common quotient from (3) and identify the integers to which it corresponds. Let the lowest common quotient be K .

Peak No.	2θ	$\sin^2 \theta$	$\frac{\sin^2 \theta}{2}$	$\frac{\sin^2 \theta}{3}$	$\frac{\sin^2 \theta}{4}$	$\frac{\sin^2 \theta}{5}$	$\frac{\sin^2 \theta}{6}$	$\frac{\sin^2 \theta}{8}$
1	38.43	0.1083	0.0542	0.0361	0.0271	0.0217	0.0181	0.0135
2	44.67	0.1444	0.0722	0.0481	0.0361	0.0289	0.0241	0.0181
3	65.02	0.2888	0.1444	0.0963	0.0722	0.0578	0.0481	0.0361
4	78.13	0.3972	0.1986	0.1324	0.0993	0.0794	0.0662	0.0496
5	82.33	0.4333	0.2166	0.1444	0.1083	0.0867	0.0722	0.0542
6	98.93	0.5776	0.2888	0.1925	0.1444	0.1155	0.0963	0.0722
7	111.83	0.6859	0.3430	0.2286	0.1715	0.1372	0.1143	0.0857
8	116.36	0.7220	0.3610	0.2407	0.1805	0.1444	0.1203	0.0903

$$K = 0.0361$$

(5) Divide $\sin^2 \theta$ by K for each peak. This will give you a list of integers corresponding to $h^2 + k^2 + l^2$.

Peak No.	2θ	$\sin^2 \theta$	$\frac{\sin^2 \theta}{K}$	$h^2 + k^2 + l^2$	hkl
1	38.43	0.1083	3.000		
2	44.67	0.1444	4.000		
3	65.02	0.2888	8.001		
4	78.13	0.3972	11.001		
5	82.33	0.4333	12.002		
6	98.93	0.5776	16.000		
7	111.83	0.6859	19.001		
8	116.36	0.7220	20.000		

(6) Select the appropriate pattern of $h^2 + k^2 + l^2$ values and identify the Bravais lattice.

Peak No.	2θ	$\sin^2 \theta$	$\frac{\sin^2 \theta}{K}$	$h^2 + k^2 + l^2$	hkl
1	38.43	0.1083	3.000	3	111
2	44.67	0.1444	4.000	4	200
3	65.02	0.2888	8.001	8	220
4	78.13	0.3972	11.001	11	311
5	82.33	0.4333	12.002	12	222
6	98.93	0.5776	16.000	16	400
7	111.83	0.6859	19.001	19	331
8	116.36	0.7220	20.000	20	420

Sequence suggests a Face-Centered Cubic Bravais Lattice

(7) Calculate lattice parameters.

$$a = \frac{\lambda}{2\sqrt{K}} = \frac{1.540562 \text{ \AA}}{2\sqrt{0.0361}} = \underline{4.0541 \text{ \AA}}$$

These methods will work for any cubic material. This means metals, ceramics, ionic crystals, minerals, intermetallics, semiconductors, etc...

LABORATORY INSTRUCTIONS/OBJECTIVES

Each laboratory group will collect an XRD pattern from a material with a cubic microstructure (assigned by the instructor). Students will prepare powders from bulk materials. The bulk materials will have been prepared via arc melting from pure elemental constituents (3N5 purity).

Data is to be collected over the angular range $20^\circ 2\theta - 100^\circ 2\theta$ with a collection step size of 0.02° and collection time of 1s/step. The data is to be indexed using both the mathematical and analytical methods. Lattice parameters are to be estimated based upon the experimental data.

Written lab reports are to be turned in using the Laboratory Template provided on the course website. The written report should briefly describe: (1) the manufacturing method(s) used for the raw material; (2) steps/conditions taken to prepare specimens; (3) conditions used to collect data; methods used to analyze/index the data. Reports should also include discussion of any differences between the collected data and standard results (i.e., ICDD cards).

The objective of this laboratory is to teach you how to properly collect, interpret, and report scientific (i.e., XRD) data.