Analytical Methods for Materials

Laboratory Module #1

Crystal Structure Determination for Cubic Crystals

Suggested Reading

1. C. Suryanarayana and M.G. Norton, *X-ray Diffraction A Practical Approach*, (Plenum Press, New York, 1998), pages 97-152.
2. B.D. Cullity and S.R. Stock, *Elements of X-ray Diffraction, 3rd edition*, (Prentice Hall, Upper Saddle River, NJ, 2001), Ch. 10, pages 295-315.

Steps for Crystal Structure Determination

- Calculate size and shape of unit cell from angular positions of diffraction peaks

- Calculate the number of atoms per unit cell from unit cell shape and size, chemical composition, and measured density.

- Deduce the atom positions within the unit cell from the relative intensities of the diffraction peaks.

Indexing

- Assign correct Miller indices to each peak in the diffraction pattern.
- Only correct when <u>all</u> peaks are accounted for.
- Process is easy for simple structures and very tedious for more complex crystals.

Generation and Treatment of Data

- Record diffraction pattern over as wide a range of 2θ as possible.

- Calculate value of $\sin^2\theta$ for each diffraction line. You can also determine the value of d_{hkl} for each line. It can also be used to determine crystal structure.

- We will do this later for unknowns.

Generation and Treatment of Data - cont'd

- Values of $\sin^2\theta$ always contain systematic errors. These errors can interfere with the determination of structures, particularly for non-cubic crystals.

- We can remove these errors from the data by calibrating the diffractometer by mixing a standard (i.e., a substance of known lattice parameter) with the unknown.

CUBIC CRYSTALS

Recall Bragg's Law

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

Rearrange

$$\lambda^2 = 4d^2\sin^2\theta$$

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

The only variable quantity

For cubic crystals

- Obtain interplanar spacing, d_{hkl}, from the plane spacing equation:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad \text{or} \quad \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

For cubic crystals

- Substitute plane-spacing equation into Bragg's law:

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

or

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

VERY IMPORTANT

For any single diffraction pattern

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

THUS

$$\sin^2\theta \propto \underbrace{h^2 + k^2 + l^2}_{\text{Integer}}$$

Integer

Related to indices of diffracting planes as θ increases, planes with higher order Miller indices will diffract

Methods

- Mathematical
- Analytical
- Both methods are based upon manipulations of Bragg's law and the plane-spacing equations.

Mathematical Method of Indexing Cubic crystals

For any two different reflections/planes, θ_1 and θ_2

$$\frac{\sin^2\theta_1}{\sin^2\theta_2} = \frac{h_1^2 + k_1^2 + l_1^2}{h_2^2 + k_2^2 + l_2^2} = \frac{k_1}{k_2}$$

Both the numerator and denominator are integers that scale with $h\ k\ l$

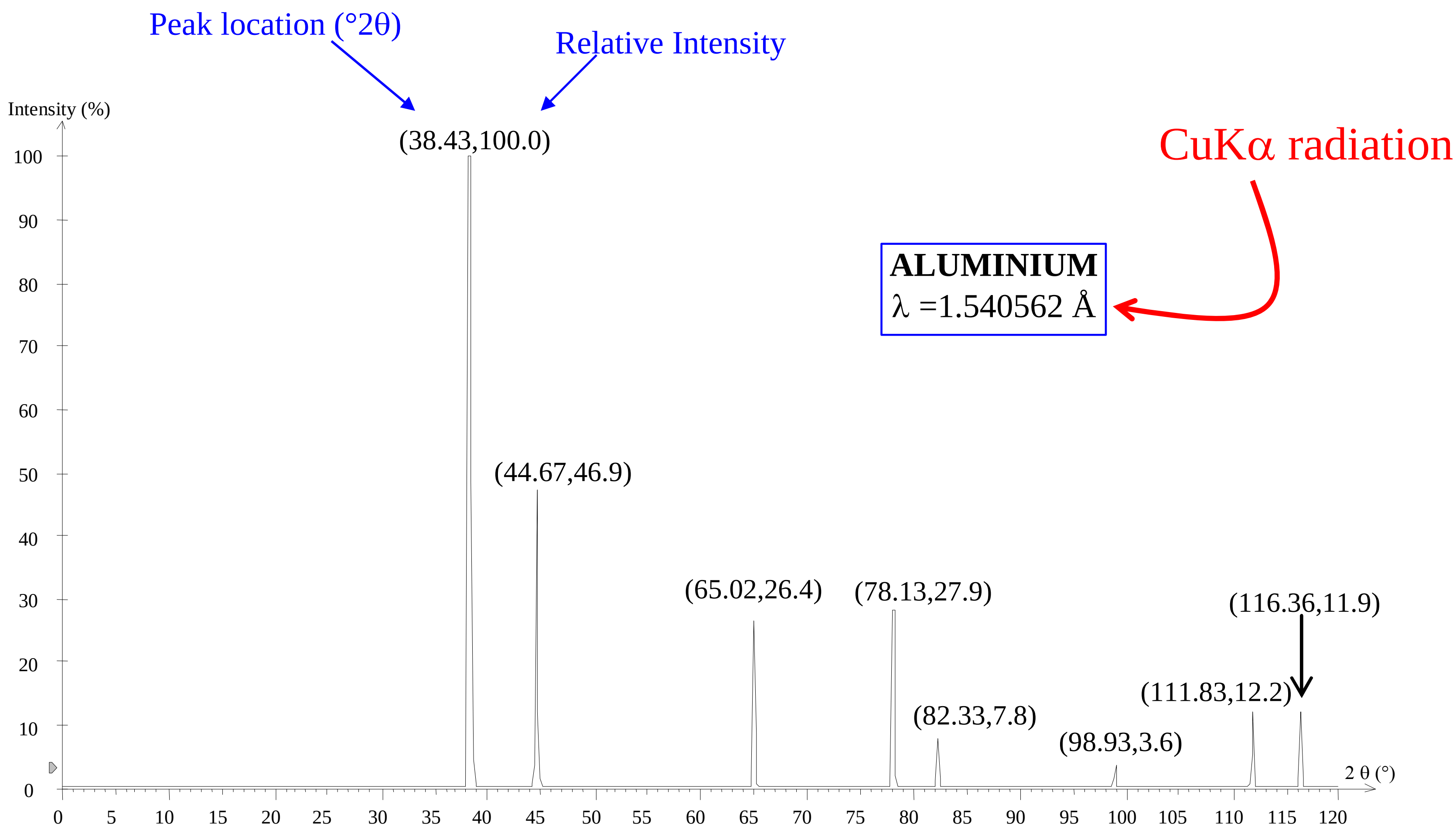
1. Obtain $h^2 + k^2 + l^2$ for a given reflection by dividing the $\sin^2\theta$ values for each reflection with that for the first (*i.e.*, minimum) one

2. Multiply by the appropriate number to obtain an integer (usually 1, 2 or 3)

3. Subsequent integers represent the quadratic form of the Miller indices

Identify Bravais Lattices

- Note the sequence of $h^2 + k^2 + l^2$ values
  - Primitive Cubic
    1,2,3,4,5,6,8,9,10,11,12,13,14,16…
  - Body-centered Cubic
    2,4,6,8,10,12,14,16…
  - Face-centered Cubic
    3,4,8,11,12,16,19,20,24,27,32…
  - Diamond cubic
    3,8,11,16,19,24,27,32...



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

Step 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 in this analysis.

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							

Step 2

- Determine $\sin^2\theta$ for each peak.
  - When using Excel, remember you must convert your angles to radians.

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						

Step 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			

Step 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			

In this case the best number is 3

Step 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	
2	44.67	0.1444	1.333	2.667	4.000	4	200	
3	65.02	0.2888	2.667	5.333	8.000	8	220	
4	78.13	0.3972	3.667	7.333	11.000	11	311	
5	82.33	0.4333	4.000	8.000	12.000	12	222	
6	98.93	0.5776	5.333	10.665	15.998	16	400	
7	111.83	0.6859	6.333	12.665	18.998	19	331	
8	116.36	0.7220	6.666	13.331	19.997	20	420	

Bravais lattice is Face-Centered Cubic

Step 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

We have completed our task because we have:

- Correctly labeled all peaks,
- Correctly determined the Bravais lattice
- Determined the lattice parameter.

Analytical Method of Indexing Cubic crystals

Recall

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

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

For all XRD patterns

Let

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

We can write,

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

For any cubic system, the values of $h^2+k^2+l^2$ increase as follows:

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

Table 1.2.6.1. *Assignment of integers $s \le 100$ to triplets h, k, l with $s = h^2 + k^2 + l^2$*

Each triplet represents all 48 triplets resulting from permutations and sign combinations.

s	*h k l*	*s*	*h k l*	*s*	*h k l*	*s*	*h k l*	*s*	*h k l*	*s*	*h k l*
1	1 0 0	25	5 0 0	42	5 4 1	59	7 3 1	74	8 3 1	88	6 6 4
2	1 1 0		4 3 0	43	5 3 3		5 5 3		7 5 0	89	9 2 2
3	1 1 1	26	5 1 0	44	6 2 2	61	6 5 0		7 4 3		8 5 0
4	2 0 0		4 3 1	45	6 3 0		6 4 3	75	7 5 1		8 4 3
5	2 1 0	27	5 1 1		5 4 2	62	7 3 2		5 5 5		7 6 2
6	2 1 1		3 3 3	46	6 3 1		6 5 1	76	6 6 2	90	9 3 0
8	2 2 0	29	5 2 0	48	4 4 4	64	8 0 0	77	8 3 2		8 5 1
9	3 0 0		4 3 2	49	7 0 0	65	8 1 0		6 5 4		7 5 4
	2 2 1	30	5 2 1		6 3 2		7 4 0	78	7 5 2	91	9 3 1
10	3 1 0	32	4 4 0	50	7 1 0		6 5 2	80	8 4 0	93	8 5 2
11	3 1 1	33	5 2 2		5 5 0	66	8 1 1	81	9 0 0	94	9 3 2
12	2 2 2		4 4 1		5 4 3		7 4 1		8 4 1		7 6 3
13	3 2 0	34	5 3 0	51	7 1 1		5 5 4		7 4 4	96	8 4 4
14	3 2 1		4 3 3		5 5 1	67	7 3 3		6 6 3	97	9 4 0
16	4 0 0	35	5 3 1	52	6 4 0	68	8 2 0	82	9 1 0		6 6 5
17	4 1 0	36	6 0 0	53	7 2 0		6 4 4		8 3 3	98	9 4 1
	3 2 2		4 4 2		6 4 1	69	8 2 1	83	9 1 1		8 5 3
18	4 1 1	37	6 1 0	54	7 2 1		7 4 2		7 5 3		7 7 0
	3 3 0	38	6 1 1		6 3 3	70	6 5 3	84	8 4 2	99	9 3 3
19	3 3 1		5 3 2		5 5 2	72	8 2 2	85	9 2 0		7 7 1
20	4 2 0	40	6 2 0	56	6 4 2		6 6 0		7 6 0		7 5 5
21	4 2 1	41	6 2 1	57	7 2 2	73	8 3 0	86	9 2 1	100	10 0 0
22	3 3 2		5 4 0		5 4 4		6 6 1		7 6 1		8 6 0
24	4 2 2		4 4 3	58	7 3 0				6 5 5		

E. Koch, in *International Tables for Crystallography* (2006). Vol. C., Chapter 1.2, pp. 6-9.

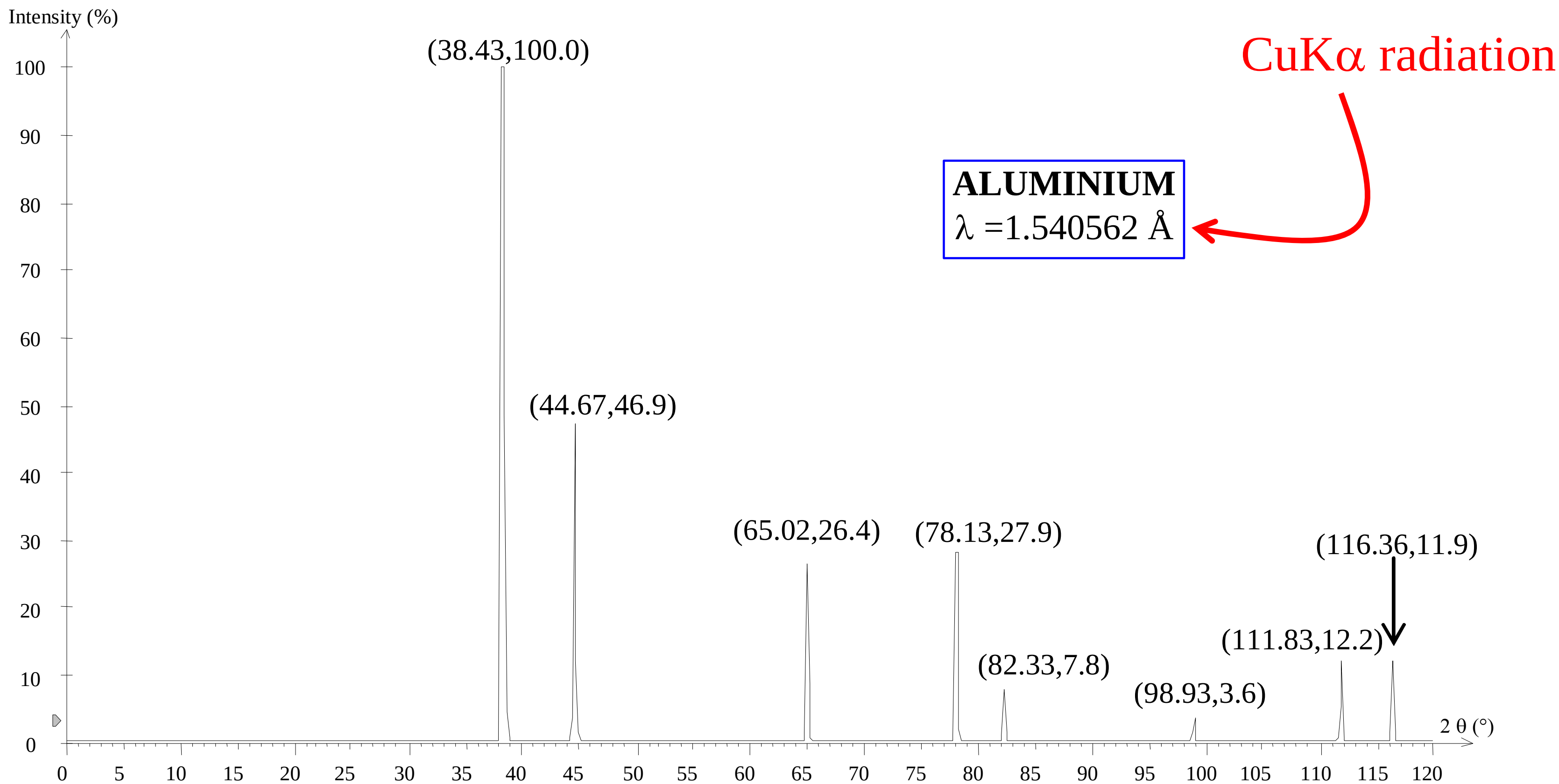
- Determine $\sin^2\theta$ for each peak and divide by the values by the integers 2,3,4,5,6,8,9,10,11…

- From this we will obtain a common quotient, which equals the value of K corresponding to $h^2+k^2+l^2 = 1$

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

- Divide the $\sin^2\theta$ values for each peak by K and we will obtain a list of $h^2+k^2+l^2$ values.

- For cubic crystals, we can use this sequence to identify the Bravais lattice and label each XRD peak.



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

Step 1

- Identify peak locations.

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							

Step 2

- Determine $\sin^2\theta$ for each peak.

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						

Step 3

The integers represent the quadratic forms of the Miller indices.

Calculate the ratio $\sin^2\theta$/(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

Step 4

Identify the lowest common quotient from step 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

$K = 0.0361$

Step 5

Divide $\sin^2\theta$ by K for each peak. This will give you a list of integers corresponding to $h^2+k^2+l^2$ (i.e., the *hkl* values for the diffracting peaks)

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		

Steps 6 and 7

Select the appropriate pattern of $h^2 + k^2 + l^2$ values.
Use them to 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 an fcc Bravais lattice

Calculate lattice parameters as follows.

$$a = \frac{\lambda}{2\sqrt{K}} = \frac{1.540562\ \mathring{A}}{2\sqrt{0.0361}} = \boxed{4.0541\ \mathring{A}}$$

These methods will work for any cubic material

It is a very good idea to use both methods, to double-check your results.

I REQUIRE YOU TO DO BOTH!