Module Name: Indexing of a Cubic Crystal X-Ray Diffraction Patterns by Mathematical Method

1. Learning Outcomes

Upon completion of this module the learner will be able to: -

- Remember the X-ray diffraction.
- Understand the phenomenon or indexing of an X-ray diffraction pattern.
- Apply to an unknown crystal structure
- Analyze to identify the Bravais lattice
- Evaluate the lattice parameters for crystalline materials.
- Create animation/visual effects of X-ray diffraction pattern.

2. Introduction

When analyzing the X-ray diffraction pattern of a cubic crystal, it is crucial to correctly index the observed peaks. Indexing is the procedure of determining the orientation and spacing of a crystal lattice based on the observed diffraction peaks. This data can then be used to calculate the parameters of the unit cell and the crystal structure.

The diffraction pattern of cubic crystals typically consists of a series of evenly spaced peaks along each of the three principal axes. The peak spacing can be used to determine the crystal's lattice spacing in each direction. It is possible to determine the orientation of the crystal lattice by analyzing the symmetry of the diffraction pattern and comparing it to known crystal structures.

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Manually using tables of known diffraction angles or by automatically using computer software, the indexing procedure can be performed. Therefore, the indexing of cubic crystal X-ray diffraction patterns is a crucial phase in determining crystal structures and can provide valuable information about the arrangement of atoms within the crystal lattice.

Furthermore, X-ray diffraction (XRD) patterns, obtained from XRD experiments, exhibit a distinct characteristic akin to fingerprints, as they are exclusive to the material under investigation. The data present in an X-ray diffraction (XRD) pattern is a consequence of two distinct factors:

- The relative positions of diffraction peaks are determined by the size and shape of the unit cells.
- The relative intensities of diffraction peaks are determined by the atomic positions within the unit cell.

In this module, the main focus is on the size and shape of the unit cells, for understanding, it is known as indexing of an X-ray pattern.

3. Procedure/Methodology

The process of assigning the appropriate Miller indices to individual peaks, also known as reflections, within a diffraction pattern is commonly referred to as indexing. The proper indexing of an X-ray diffraction (XRD) pattern is achieved when all the peaks present in the diffraction pattern are appropriately labelled, and there are no missing peaks that are expected for the specific structure being analyzed.

One of example of fully indexed pattern is shown below.

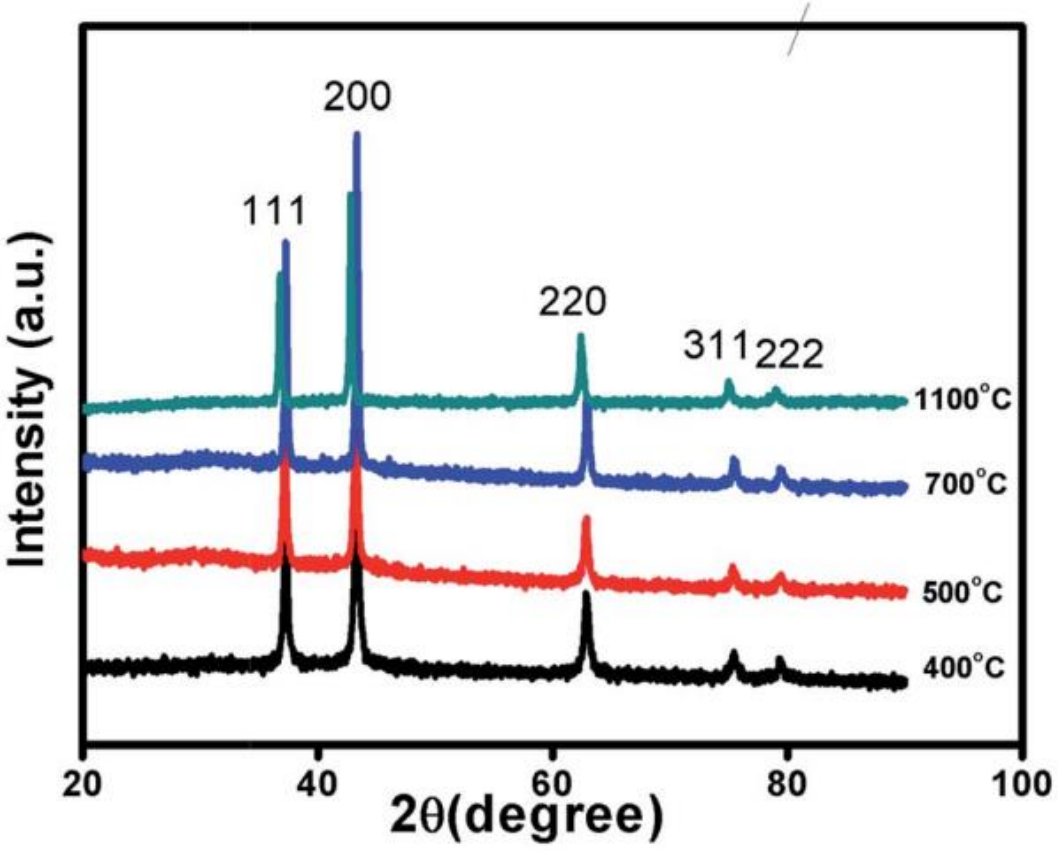


Fig. 1 Characterization of sample. X-ray diffraction pattern of non-stoichiometric $Ni_{1-\delta}O$ samples sintered at different temperature as indicated.

Citation: RSC Adv., 2018, 8, 5882–5890; https://doi.org/10.1039/C8RA00157J

Standard Data Sheet:

Now, to index let's take a standard data sheet [JCPDS Card No.: 00-001-1258] with following details.

Chemical Formula: Ni; Compound Name: Nickel; Lattice parameter a = 3.54 Å

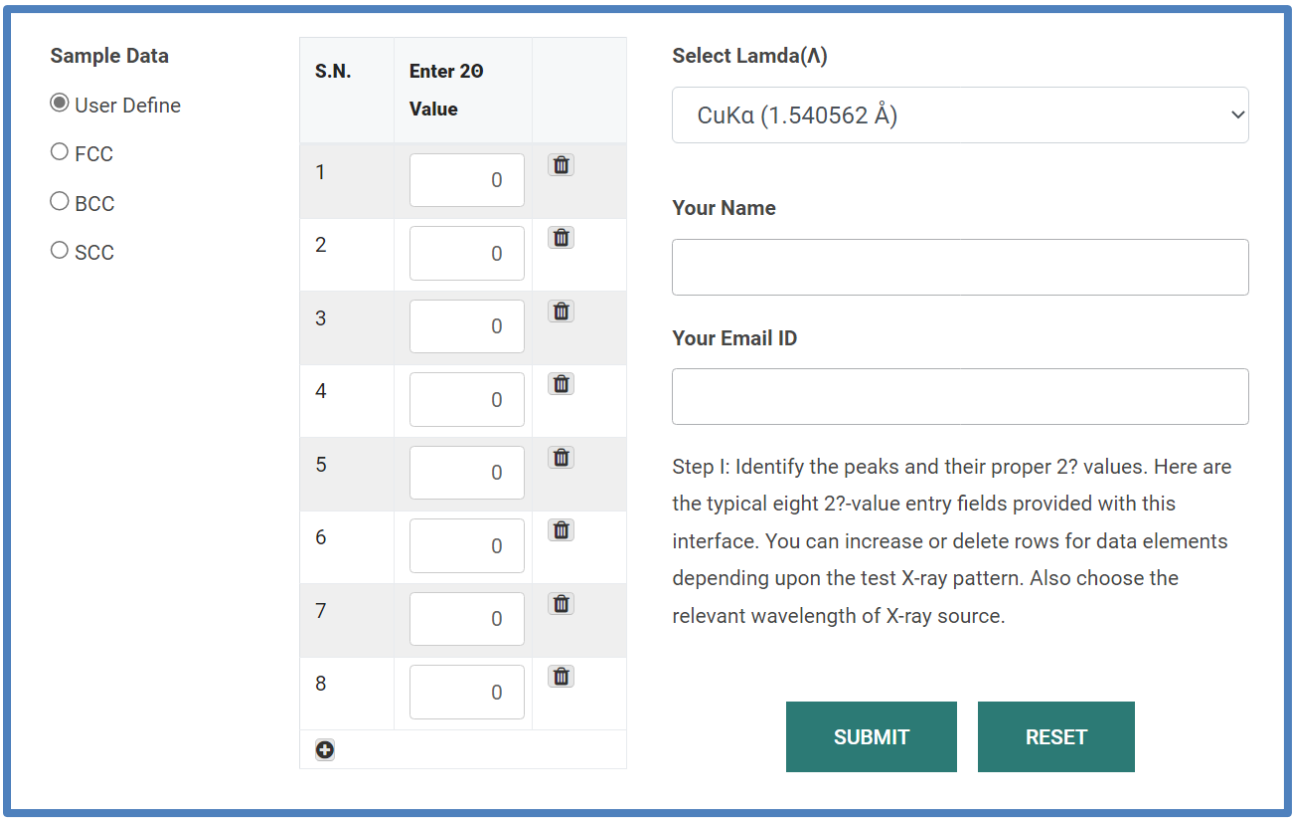
Space Group: Fm-3m (225); Crystal Structure = FCC

X-ray Radiation: CuKα λ= 1.5405 Å

Peak	2θ	h k l
01	44.3687	1 1 1
02	51.5943	2 0 0
03	76.0818	2 2 0
04	92.0904	3 1 1
05	98.0816	2 2 2
06	122.1653	4 0 0
07	143.9653	3 3 1
08	154.3425	4 2 0

Step I: Identify the peaks and their proper 2θ values. Here, typical eight 2θ values entries field provided with this interface. You can increase or delete row for data entering depending upon the test X-ray pattern. Also choose the relevant wavelength of X-ray source. Users can also choose sample data.

Output of interface



Note: User name and email ID were captured to generate certificate.

Step II: Determine the $\sin^2(\theta)$. Here, the θ should be in radian and then determine $\sin^2(\theta)$.

Output of interface

Peak No.	2Θ	$SIN^2(\Theta)$
1	44.3687	0.1426
2	51.5943	0.1894
3	76.0818	0.3797
4	92.0904	0.5182
5	98.0816	0.5703
6	122.1653	0.7662
7	143.9653	0.9043
8	154.3425	0.9507

Step III: Now determine the $1 \times \frac{\sin^2\theta}{\sin^2\theta_m}$. Here, the θ_m is the lowest angle of peak of the X-ray pattern.

Background: Using the plane spacing equation, interplanar spacings in cubic crystals can be expressed in terms of lattice parameters.

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

Now, on the basis of Bragg's law (λ=2dsinθ) following relation can be written as:

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

Rearranging equations (1) and (2)

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

$$\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)(h^2+k^2+l^2) \quad (3)$$

Since for a given pattern or pattern under consideration, wavelength (λ) and lattice constant (a) are remains the same (do not changes for a given pattern), therefore, in equation (3) the term $\left(\frac{\lambda^2}{4a^2}\right)$ at right hand side is constant for any one of the patterns. Hence,

$$\sin^2\theta \propto (h^2+k^2+l^2) \quad (4)$$

This demonstrates that planes that have higher Miller indices will diffract at greater θ values. Since $\left(\frac{\lambda^2}{4a^2}\right)$ is constant for any pattern, We are able to express the relationship between any two different planes using the following formula:

$$\frac{\sin^2\theta_1^2}{\sin^2\theta_2^2} = \frac{\left(\frac{\lambda^2}{4a^2}\right)(h_1^2+k_1^2+l_1^2)}{\left(\frac{\lambda^2}{4a^2}\right)(h_2^2+k_2^2+l_2^2)} \quad (5)$$

$$\frac{\sin^2\theta_1^2}{\sin^2\theta_2^2} = \frac{(h_1^2+k_1^2+l_1^2)}{(h_2^2+k_2^2+l_2^2)} \quad (6)$$

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

It is important to keep in mind that, for cubic systems, the initial peak in the XRD pattern will be caused by diffraction from planes that have the lowest Miller indices, which interestingly enough are the close packed planes. This indicates following relationships with respect to different unit cells of cubic systems.

(i) Simple Cubic (SC): (1 0 0), $h^2+k^2+l^2=1$

(ii) Body-Centered Cubic (BCC): (1 1 0), $h^2+k^2+l^2=2$

(iii) Face-Centered Cubic (FCC): (1 1 1), $h^2+k^2+l^2=3$

Further, since h, k, and l always are integers, we can obtain $h^2+k^2+l^2$ values by dividing the $\sin^2\theta$ values for the different XRD peaks with minimum of $\sin^2\theta$ and multiplying that ratio by the proper integer (1 or 2 or 3). The result of this should be a list of integers that represent all $h^2+k^2+l^2$ of the different values. Finally, the correct Bravais lattice must be identified by recognizing the sequence of reflections that are permitted for cubic lattices. These are as follows.

(i) Primitive or Simple Cubic (SC):

$$h^2+k^2+l^2 = 1,2,3,4,5,6,8,9\ ,10,11,12,13,14,16\ldots. \quad (7)$$

(ii) Body-Centered Cubic (BCC):

$$h^2+k^2+l^2 = 2,4,6,8,10,12,14,16\ldots. \quad (8)$$

(iii) Face-Centered Cubic (SC):

$$\mathrm{h}^2+\mathrm{k}^2+\mathrm{l}^2 = 3,,4,8,11,12,16,19,20,24,27,32\ldots.. \quad (9)$$

Output of interface

Peak No.	2Θ	$SIN^2(\Theta)$	1 X ($SIN^2(\Theta) / SIN^2(\Theta_{min})$)
1	44.3687	0.1426	1.0000
2	51.5943	0.1894	1.3284
3	76.0818	0.3797	2.6634
4	92.0904	0.5182	3.6349
5	98.0816	0.5703	4.0000
6	122.1653	0.7662	5.3740
7	143.9653	0.9043	6.3429
8	154.3425	0.9507	6.6682

CALCULATE MORE VALUE

CALCULATE FINAL VALUE

Final Result :

It can be seen that $1 \times \frac{\sin^2 \theta}{\sin^2 \theta_m}$ does not yield integer values (or nearer to integer) for most of the peaks. Therefore, CALCULATE MORE VALUE should be used. If $1 \times \frac{\sin^2 \theta}{\sin^2 \theta_m}$ provided integer values for most of the peaks then CALCULATE FINAL VALUE will be used to finish the calculations.

Step IV: Look at the values of the $1 \times \frac{\sin^2 \theta}{\sin^2 \theta_m}$. If these values are integer or approaching towards integer then click on the "CALCULATE FINAL VALUE". Otherwise, click on the "CALCULATE MORE VALUE". This process will continue till most of the values in the column are integers or approaching towards integers.

Output of interface

Peak No.	2Θ	$SIN^2(\Theta)$	1 X ($SIN^2(\Theta) / SIN^2(\Theta_{min})$)	2 X ($SIN^2(\Theta) / SIN^2(\Theta_{min})$)
1	44.3687	0.1426	1.0000	2.0000
2	51.5943	0.1894	1.3284	2.6567
3	76.0818	0.3797	2.6634	5.3269
4	92.0904	0.5182	3.6349	7.2698
5	98.0816	0.5703	4.0000	8.0000
6	122.1653	0.7662	5.3740	10.7480
7	143.9653	0.9043	6.3429	12.6859
8	154.3425	0.9507	6.6682	13.3364

CALCULATE MORE VALUE

CALCULATE FINAL VALUE

Final Result :

Output of interface

Peak No.	2Θ	$SIN^2(\Theta)$	1 X ($SIN^2(\Theta) / SIN^2(\Theta_{min})$)	2 X ($SIN^2(\Theta) / SIN^2(\Theta_{min})$)	3 X ($SIN^2(\Theta) / SIN^2(\Theta_{min})$)
1	44.3687	0.1426	1.0000	2.0000	3.0000
2	51.5943	0.1894	1.3284	2.6567	3.9851
3	76.0818	0.3797	2.6634	5.3269	7.9903
4	92.0904	0.5182	3.6349	7.2698	10.9047
5	98.0816	0.5703	4.0000	8.0000	12.0000
6	122.1653	0.7662	5.3740	10.7480	16.1219
7	143.9653	0.9043	6.3429	12.6859	19.0288
8	154.3425	0.9507	6.6682	13.3364	20.0045

CALCULATE MORE VALUE

CALCULATE FINAL VALUE

Final Result :

Average lattice parameter is :

Look at the values of the $3 \times \frac{\sin^2 \theta}{\sin^2 \theta_m}$, most of the peaks attains an integer value or approaching towards an integer. In such a case, the process has to be end and click on the CALCULATE FINAL VALUE.

Step V: Now assigning $h^2+k^2+l^2$ values in terms of an integer as identified in previous steps.

Output of interface

Peak No.	2Θ	$SIN^2(\Theta)$	1 X ($SIN^2(\Theta)$ / $SIN^2(\Theta_{min})$)	2 X ($SIN^2(\Theta)$ / $SIN^2(\Theta_{min})$)	3 X ($SIN^2(\Theta)$ / $SIN^2(\Theta_{min})$)	$h^2 + k^2 + l^2$
1	44.3687	0.1426	1.0000	2.0000	3.0000	3
2	51.5943	0.1894	1.3284	2.6567	3.9851	4
3	76.0818	0.3797	2.6634	5.3269	7.9903	8
4	92.0904	0.5182	3.6349	7.2698	10.9047	11
5	98.0816	0.5703	4.0000	8.0000	12.0000	12
6	122.1653	0.7662	5.3740	10.7480	16.1219	16
7	143.9653	0.9043	6.3429	12.6859	19.0288	19
8	154.3425	0.9507	6.6682	13.3364	20.0045	20

Step VI: Corresponding h, k, l values are now assigned against $h^2+k^2+l^2$ values.

Output of interface

$h^2 + k^2 + l^2$	hkl
3	111
4	200
8	220
11	311
12	222
16	400
19	331
20	420

Step VII: Now calculating cubical lattice parameter for corresponding h, k, l values.

Background: The lattice parameter (a) can be calculated by using equation (3). Re-writing it again

$$sin^2\,\theta = \left(\frac{\lambda^2}{4a^2}\right)(h^2 + k^2 + l^2) \qquad (10)$$

This can be further solved for lattice parameter (a).

$$a = \frac{\lambda}{2\sin\theta}\sqrt{(h^2 + k^2 + l^2)} \qquad (10)$$

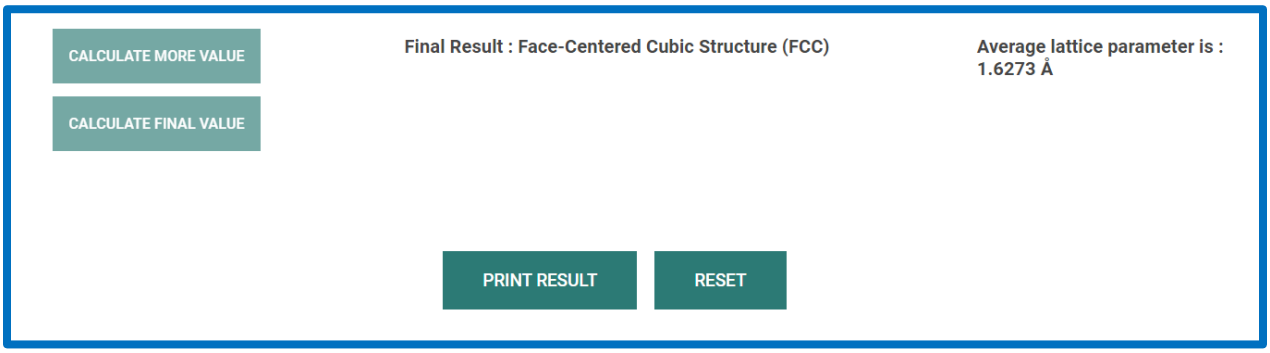
Output of interface

hkl	a(Å)
111	1.6268
200	1.6299
220	1.6278
311	1.6339
222	1.6268
400	1.6207
331	1.6256
420	1.6266

Final Step: Identification of crystal structure by the help of h, k, l values and average lattice parameter of unknown sample.

Here, comparing the $(h^2 + k^2 + l^2)$ values with the equation (7) to (9), it is matches with following

Face-Centered Cubic (FCC): $\mathbf{h^2 + k^2 + l^2 = 3,, 4, 8, 11, 12, 16, 19, 20}$



Print Result:

Indexing X-Ray Diffraction Patterns

Peak No	2Θ	$SIN^2(\Theta)$	1 X ($SIN^2(\Theta)$ / $SIN^2(\Theta_{min})$)	2 X ($SIN^2(\Theta)$ / $SIN^2(\Theta_{min})$)	3 X ($SIN^2(\Theta)$ / $SIN^2(\Theta_{min})$)	$h^2 + k^2 + l^2$	hkl	a(Å)
1	44.3687	0.1426	1	2	3	3	111	1.6268
2	51.5943	0.1894	1.3284	2.6567	3.9851	4	200	1.6299
3	76.0818	0.3797	2.6634	5.3269	7.9903	8	220	1.6278
4	92.0904	0.5182	3.6349	7.2698	10.9047	11	311	1.6339
5	98.0816	0.5703	4	8	12	12	222	1.6268
6	122.1653	0.7662	5.374	10.748	16.1219	16	400	1.6207
7	143.9653	0.9043	6.3429	12.6859	19.0288	19	331	1.6256
8	154.3425	0.9507	6.6682	13.3364	20.0045	20	420	1.6266

Final Result : Face-Centered Cubic Structure (FCC) **Average lattice parameter is : 1.6273 Å**