

Structural analysis by X-ray Diffraction

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Abstract: There are various methods for measuring the intensity of a scattered X-ray beam (hereafter referred to as diffracted X-ray beam) from crystalline materials, and each method has the respective advantage. The most common method is to measure the X-ray diffraction intensity from a powder sample as a function of scattering angle (it is also called diffraction angle) by using a diffractometer. Due to this fact, in this research note, we present the several key points of structural analysis which are required to obtain the structural information of powder samples.

Keywords: Structure, crystal system, X-ray, miller index.

I. INTRODUCTION

X-ray diffraction crystallography for powder samples is well-established and widely used in the field of materials characterization to obtain information on the atomic scale structure of various substances in a variety of states. Of course, there have been numerous advances in this field, since the discovery of X-ray diffraction from crystals in 1912 by Max von Laue and in 1913 by W.L. Bragg and W.H. Bragg. The origin of crystallography is traced to the study for the external appearance of natural minerals and a large amount of data have been systematized by applying geometry and group theory. Then, crystallography becomes a valuable method for the general consideration of how crystals can be built from small units, corresponding to the infinite repetition of identical structural units in space. Many excellent and exhaustive books on the X-ray diffraction and crystallography are available, but the undergraduate students, young researchers and engineers who wish to become acquainted with this subject frequently find them overwhelming. They find it difficult to identify and understand the essential points in the limited time available to them, particularly on how to estimate useful structural information from the X-ray diffraction data. Since X-ray powder diffraction is one of the most common and leading methods in materials research, adequate knowledge of the subject is essential.

II. IDENTIFICATION OF AN UNKNOWN SAMPLE BY X-RAY DIFFRACTION

There are rather few cases, where structural analysis for completely unknown substances are needed, because we usually have some preliminary information, such as possible constituent elements and their volume in a sample. In addition a comparison of the measured diffraction data with those of a large number of standard substances can be made without any difficulty in a short time by the recent developments of computer and database search software. The powder diffraction database compiles for about 50,000 substances, named by JCPDS cards (Joint Committee on Powder Diffraction Standards) with the cooperation of many societies in U.S.A. Canada, United Kingdom, and France [1]. Then, we may identify an unknown substance of interest by searching the diffraction data so as to find one, which exactly matches the pattern of the unknown substance compiled in the database. This procedure was originally proposed by Hanawalt *et al.* [2,3] using the concept that the powder diffraction pattern of a substance is characteristic of that substance, like a fingerprint and the measured powder diffraction pattern is quite likely to be reproduced by the simple sum of those of pure substances if a sample contains two components or more.

A. Crystal system:

In dividing space by three sets of planes, we can of course produce unit cells of various shapes, depending on how we arrange the planes. For example, if the planes in the three sets are all equally spaced and mutually perpendicular, the unit cell is cubic. In this case the vectors **a**, **b**, **c** are all equal and at right angles to one another, or $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$. By thus giving special values to the axial lengths and angles, we can produce unit cells of various shapes and therefore

various kinds of point lattices, since the points of the lattice are located at the cell corners. It turns out that only seven different kinds of cells are necessary to include all the possible point lattices. These correspond to the seven crystal systems into which all crystals can be classified. These systems are listed in Table I [4-6].

Table I: Crystal systems and d-spacing

Systems	Axial lengths and angles	Lattice symbol*	d-spacing and miller index
Cubic	$a=b=c, \alpha=\beta=\gamma=90^\circ$	P, I, F	$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	P, I	$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	P, I, C, F	$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	P	$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$
Rhombohedral (Trigonal)	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	P	$\frac{1}{d^2} = \frac{1}{V^2} \left[S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2(S_{12}hk + S_{23}kl + S_{13}hl) \right]$ $S_{11} = b^2c^2 \sin^2 \alpha, S_{22} = a^2c^2 \sin^2 \beta, S_{33} = a^2b \sin^2 \gamma$ $S_{12} = abc^2 (\cos \alpha \cos \beta - \cos \gamma),$ $S_{13} = a^2bc (\cos \gamma \cos \beta - \cos \alpha),$ $S_{23} = ab^2c (\cos \alpha \cos \gamma - \cos \beta),$ $V = abc \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$
Monoclinic	$a \neq b \neq c, \alpha = \beta = 90^\circ \neq \gamma$	P, C	
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	P	
*Simple - P, Body centered - I, Face-centered - F, Base centered - C			

The determination of an unknown structure proceeds in three major steps:

- (1) The shape and size of the unit cell are deduced from the angular positions of the diffraction lines.
- (2) The number of atoms per unit cell is then computed from the shape and size of the unit cell, the chemical composition of the specimen, and its measured density.
- (3) Finally, the positions of the atoms within the unit cell are deduced from the relative intensities of the diffraction lines.

B. Indexing patterns:

i) cubic crystals:

A cubic crystal gives diffraction lines whose $\sin^2 \theta$ values satisfy the following equation, obtained by combining the Bragg law with the plane-spacing equation for the cubic system (Table I):

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

Where sum $s = (h^2 + k^2 + l^2)$ is always integral and $\frac{\lambda^2}{4a^2}$ is a constant for any one pattern, the problem of indexing the pattern of a cubic substance is one of finding a set of integers s which will yield a constant quotient when divided one by one into the observed $\sin^2 \theta$ values. (Certain integers, such as 7, 15, 23, 28, 31, etc., are impossible because they cannot be formed by the sum of three squared integers.) Once the proper integers s are found, the indices hkl of each line can be written down [5,6]. For a example, we will consider fig.1. and major steps given in Table II.

Table 1: Example of trial calculation of XRD pattern given in figure 1

2θ	$\sin \theta$	$4\sin^2 \theta / \lambda^2$	Ratio	Ratio*3	$h^2+k^2+l^2$	hkl	$a(nm)$
38.46	0.3292	18.2310	$\frac{18.2310}{18.2310} = 1.00$	3	3	111	0.405653
44.7	0.380081	24.3020	$\frac{24.3020}{18.2310} = 1.33$	3.99	4	200	0.405704
65.1	0.537793	48.6542	$\frac{48.6542}{18.2310} = 2.67$	8.01	8	220	0.405494
78.26	0.630813	66.9411	$\frac{66.9411}{18.2310} = 3.67$	11.01	11	311	0.405368
82.44	0.658678	72.9856	$\frac{72.9856}{18.2310} = 4.00$	12.00	12	222	0.405482
99.08	0.760575	97.3140	$\frac{97.3140}{18.2310} = 5.33$	15.99	16	400	0.405483

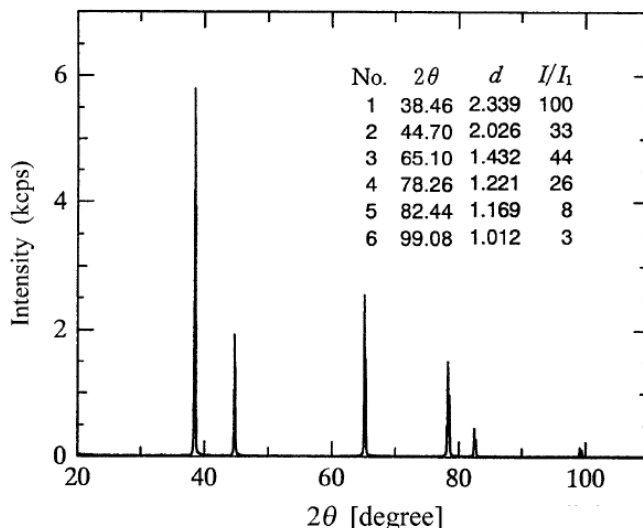


Fig. 1:- X-ray diffraction pattern of a metal sample with cubic structure obtained by Cu-K_α radiation [5].

ii) Indexing patterns of non-cubic crystals:

The problem of indexing powder patterns becomes more difficult as the number of unknown parameters increases. There is only one unknown parameter for cubic crystals, the cell edge *a*, but noncubic crystals have two or more, and special graphical and analytical techniques [5-8] have had to be devised in order to index the patterns of such crystals. Analytical methods of indexing involve arithmetical manipulation of the observed $\sin^2 \theta$ values in an attempt to find certain relationships between them. Since each crystal system is characterized by particular relationships between $\sin^2 \theta$ values, recognition of these relationships identifies the crystal system and leads to a solution of the line indices.

For a simple example, we will consider observed values of *d* for the 10 lines are listed in Table II and proceeds in these major steps:

- Column 1:- Find the peak position. There are peak finding programs (e.g., Xfit, powderX, etc.) that can help you determine if a broad peak is composed of two or more peaks.
- Column 2:- Calculate the d-spacing (using Bragg's law $n\lambda = 2d \sin\theta$)
- Column 3:- Convert to $1/d^2$.
- Column 4:- Find any common multiples and divide by that common divisor. (divided by 0.0948 and then multiply by 2)
- Column 5:- Find other common multiples or similar differences between numbers.
- Column 6:- Find corresponding hkl's
- Column 7:- Estimate the lattice parameters

It looks tetragonal, so we'll get lattice constant $a = b = 4.594 \text{ \AA}$ and $c = 2.959 \text{ \AA}$, (using $\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$) and all the peaks are indexed.

Table II: Example of trial calculation of noncubic crystal

2Theta (deg)	d (Å)	1/d ²		common	hkl
1	2	3	4	5	6
27.4344	3.2484	0.0948	2.0000		110
30.1790	2.9590	0.1142	2.4104	2.4104	001
36.0710	2.4880	0.1615	3.4094	2.4094	101
39.1885	2.2970	0.1895	4.0001		200
41.2390	2.1874	0.2090	4.4110	2.4110	111
44.0389	2.0546	0.2369	4.9996		210
56.6232	1.6242	0.3791	8.0002		220
62.7525	1.4795	0.4569	9.6418	9.6418	002
64.0439	1.4527	0.4738	10.0002		310
68.9969	1.3600	0.5406	11.4098	2.4098	301

III. CONCLUDING REMARK

X-ray diffraction analysis is used not only to identify the phase of unknown substance, as well as the estimation of the lattice parameters, but also to determine the concentration of that phase in the mixture. The peak profile is also employed to estimate the particle size of very small crystals called “crystallites” in a powder sample.

Recommended websites:

- <http://www.matter.org.uk/diffraction/>
- <http://www.ngsir.netfirms.com/englishhtm/Diffraction.htm>
- www.ccp14.ac.uk

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