Kingdom of Saudi Arabia
Al-Imam Mohammad Ibn Saud Islamic University

Lattice parameters and crystallite size of Cubic and hexagonal structures

A graduation project submitted to the Department of Physics in partial fulfillment of the requirements for the degree of Bachelor of Science in Applied Physics

By:

RASHED IBRAHIM ALMUWALLAD

Supervisor:

Dr Ahmad Alkoud

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Abstract

The fundamental principles of X-ray diffraction (XRD) technique including instrumentation, Bragg's law and Scherrer formula are given in the first part of this report. In the second part, XRD is used to characterize two powders (ZnO and Fe_2O_3). The lattice parameters of both structural hexagonal and cubic are determined by using the inter-planar distance (d), while the crystallite size is determined by Scherrer formula for iron oxide sample.

خلاصة البحث:

تم التطرق في الجزء الاول من هذا البحث إلى المفاهيم ألاساسية لتقنية حيود الاشعة السينية, كيفية حساب معاملات الشبكة لأنواع مختلفة من الصيغ البلورية. في الجزء الثاني تم قياس حيود الأسعة السينية لعينتين ؛حيث تم حساب معاملات الشبكة لصيغتين مختلفتين كما تم استنتاج حجم الحبيبات من خلال علاقة شيرر.

Introduction

X-ray diffraction is one of the most important characterization tools used in materials science. It can be used for the identification of elements, determination of the lattice parameters, crystalline size of (a) , (c) ,…etc.

In this final research project, we have two parts:

The first part is dedicated to the principles of X-ray diffraction including instrumentation and Bragg's law.

In the second part, the structural properties of Zinc and iron oxides are investigated by XRD. We determine the lattice parameters and crystallite size by using Scherrer.

Chapter 1: Theoretical background

1. X-Ray Diffraction

1.1. Definition

X-rays are electromagnetic radiation of wavelength about 1 Å (10-10 m), which is about the same size as an atom [4]. They occur in that portion of the electromagnetic spectrum between gamma-rays and the ultraviolet. The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at the atomic level. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science. X-ray powder diffraction (XRD) is a rapid analytical technique and it the most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology. There are several parameters that can be determined by X-ray diffraction such as lattice parameters, crystallites size and residual strain (macrostrain).

1.2. Fundamental Principles

X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law:

$$n\lambda = 2dsin(\theta)$$ [1]

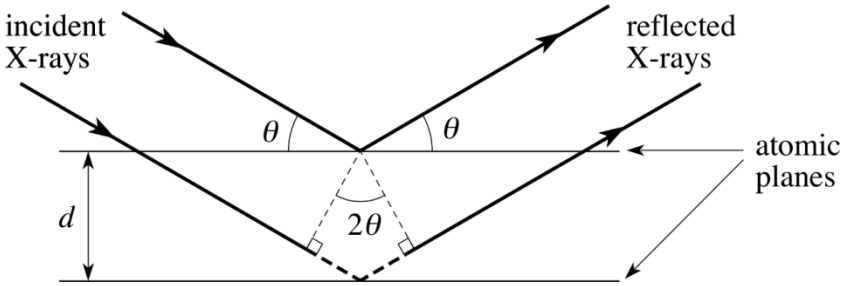

Figure 1. X-ray diffraction principle,

These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θangles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacing allows identification of the elements because each element has a set of unique d-spacing. Typically, this is achieved by comparison of d-spacing with standard reference patterns.

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays.

Powder diffraction data can be collected using either transmission or reflection geometry, as shown below.

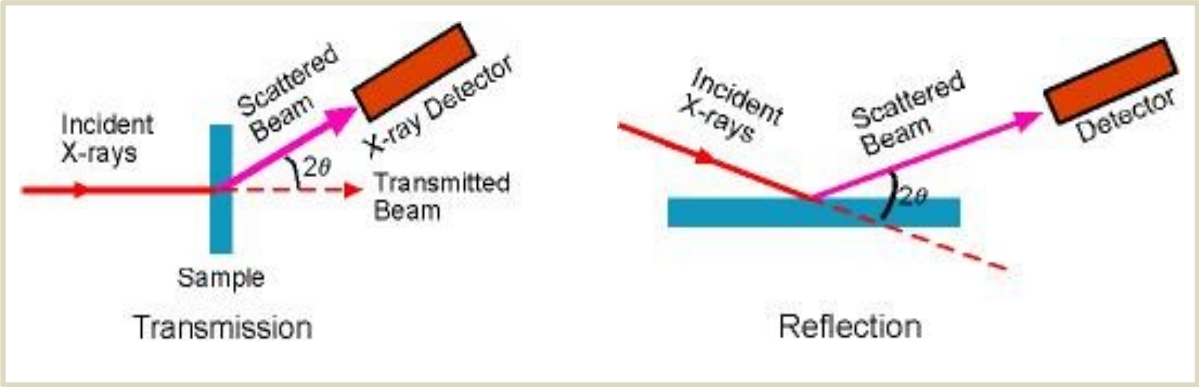

Figure 2. Reflection and transmission scattering rays in materials

1.3. XRD Instrumentation

In general, the experimental diffraction of waves by crystalline solids is composed of three parts: Source, samples and detectors.

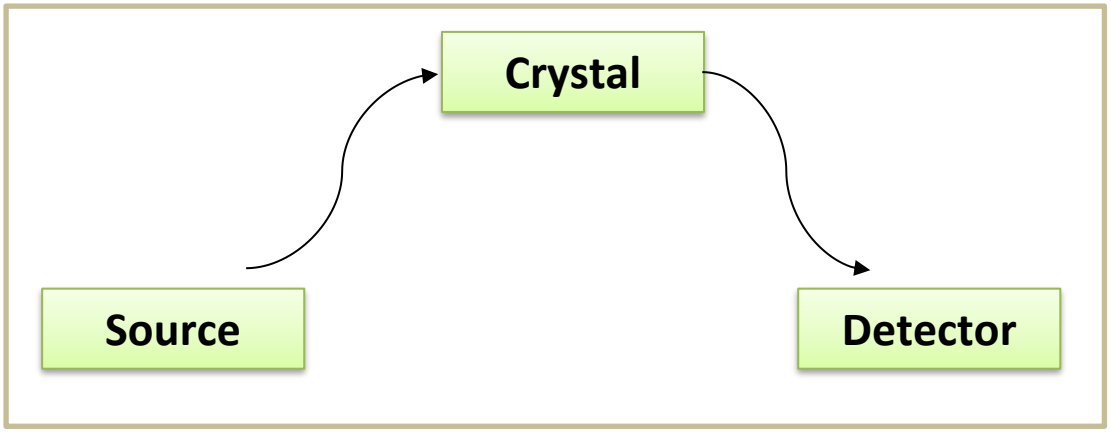

Figure 3. Wave diffraction principles

In the case of X-ray diffraction, the same geometrie will be used and the diffractometer consist of three basic elements: an X-ray tube, a sample holder and an X-ray detector.

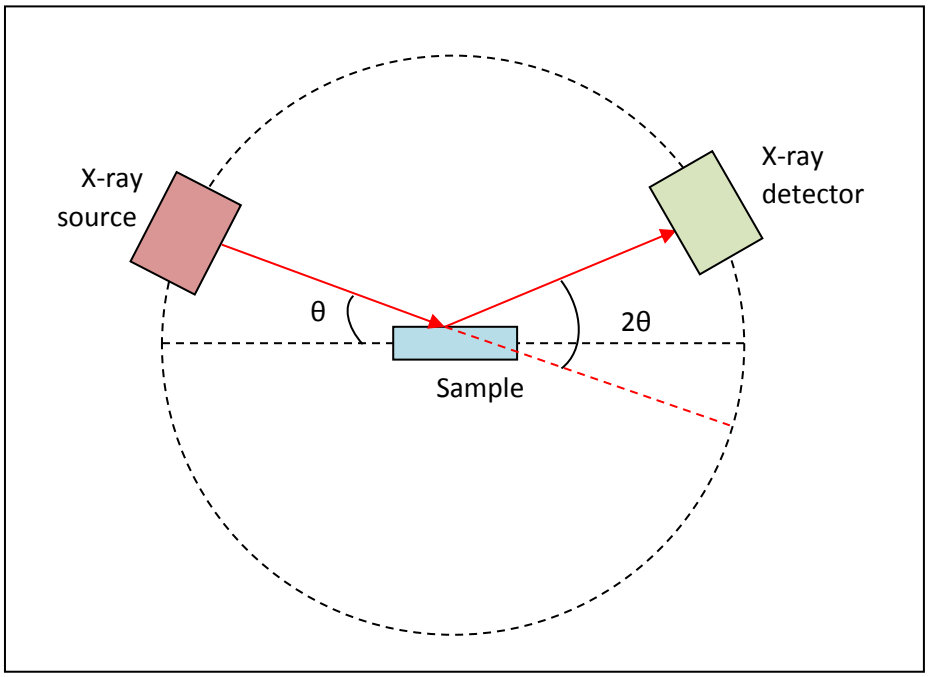

Figure 4. X-ray diffractometer components

1.3.1. Source:

X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. Copper is the most common target material for single-crystal diffraction (And the one we will use in Part 2), with CuKα radiation = 1.5406Å. These X-rays are collimated and directed onto the sample.

1.3.2. Detector:

An x-ray detector generates a pulse of current when it absorbs an x-ray, the ideal detector should produce an output pulse for every incident x-ray. The fraction of photons that produce pulses is the "quantum efficiency" of the detector.

Chapter 2: Experimental and Results

2.1. Experimental

2.1.1 Samples

Two commercially powders of ZnO and Fe_2O_3 are characterized by XRD.

2.1.2. X-ray diffractometer

X-ray powder diffraction (XRD) measurements were performed using Bruker D8 Discover diffractometer (θ-2θ) equipped with Cu-Kα radiation (λ=1.5406 Å) located at the physics department.

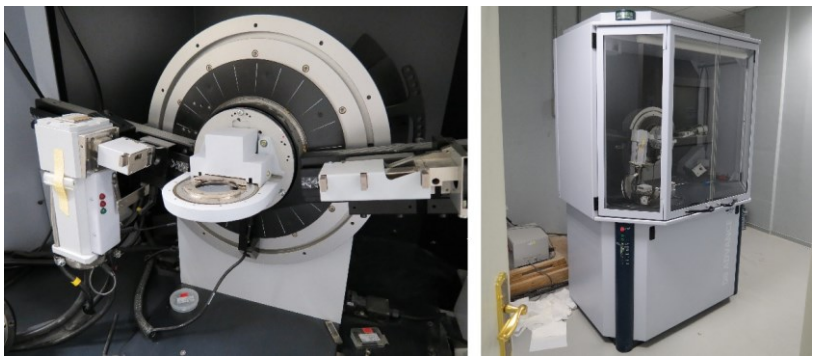

Figure.5. Bruker D8 Discover diffractometer

2.2. Results

2.2.1. Lattice parameters

- ✓ **ZnO powder**
  - ZnO is a Hexagonal structure with the following properties :

$$a = b \neq c$$

$$\alpha = \beta = 90° \quad , \quad \gamma = 120°$$

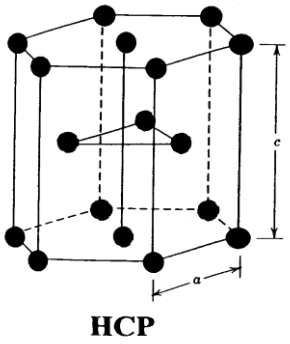

Fig.6. Hexagonal structure

X-ray diffraction patterns are displayed in Fig.7

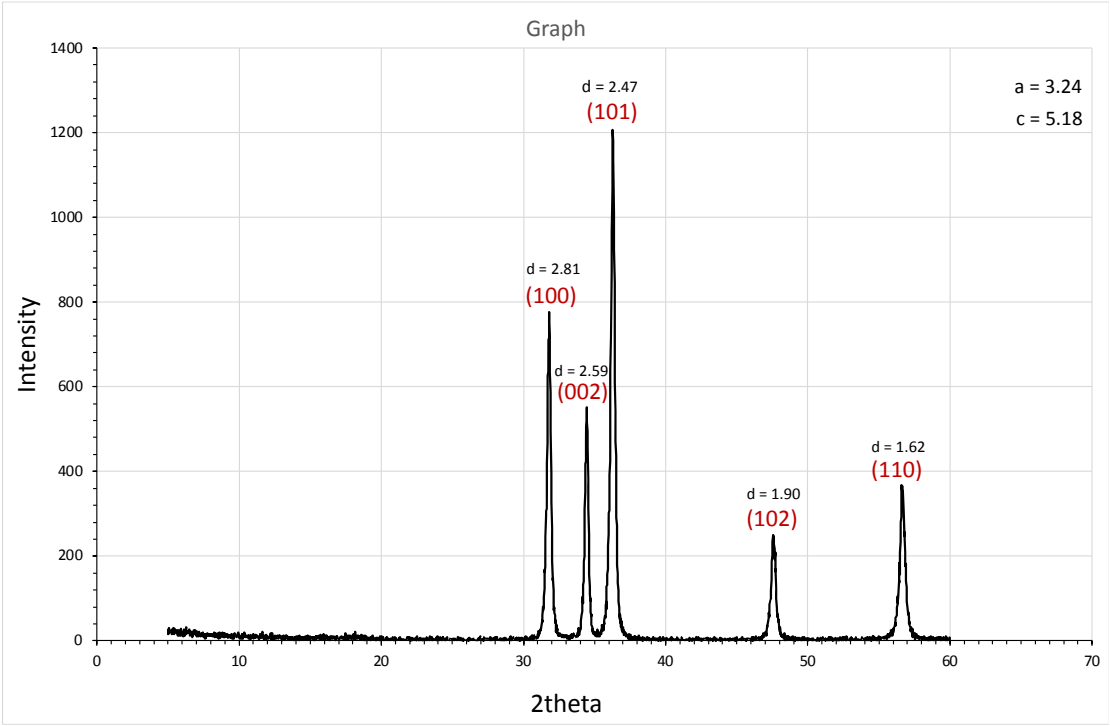

Fig.7. X-ray diffraction patterns of ZnO powder

For the hexagonal structure, the relation between the lattices parameters is given by:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+k^2+l^2}{a^2}\right) + \frac{l^2}{c^2} \qquad (1)$$

From Fig.7, we determine the lattice parameters:

- First step: we will determine the inter-planar distance (d) from Bargg's law (equation 1) for two Miller planes which are: (100) and (002).
- Second step: We will use (equation 1) to determine the lattice parameters a and c.

Using Bragg's Law with θ=15.92° and θ=17.24° and knowing that the wavelength used in the experiments is λ = 1.5418 Å, we find that :

$d_{(100)}$=2.810 Å and $d_{(002)}$=2.59 Å for the plan (100) and (002) respectively.

Using Equation (1) with the value of $d_{(100)}$ and h=1, k=l=0 we get:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2}{a^2}\right)$$

$$\frac{3}{4d^2} = \frac{h^2}{a^2}$$

$$a = \frac{2dh}{\sqrt{3}}$$

a=3.244 Å

Using the same method with the value of $d_{(002)}$ and h=k=0 , l=2 , we get the value of c:

$$\frac{1}{d^2} = \frac{3l^2}{4a^2} + \frac{l^2}{c^2}$$

$$\frac{1}{c^2} = \frac{1}{d^2 l^2} - \frac{3}{4a^2}$$

c=5.202 Å

✓ **Iron oxide powder (Fe3O4)**

Iron oxide is a cubic structure with the following properties :

a = b = c

$\alpha = \beta = \gamma = 90°$

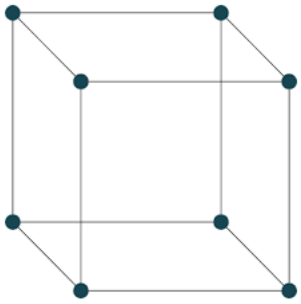

Figure 8 : Cubic Structure :

XRD pattern is displayed in Figure.9 below:

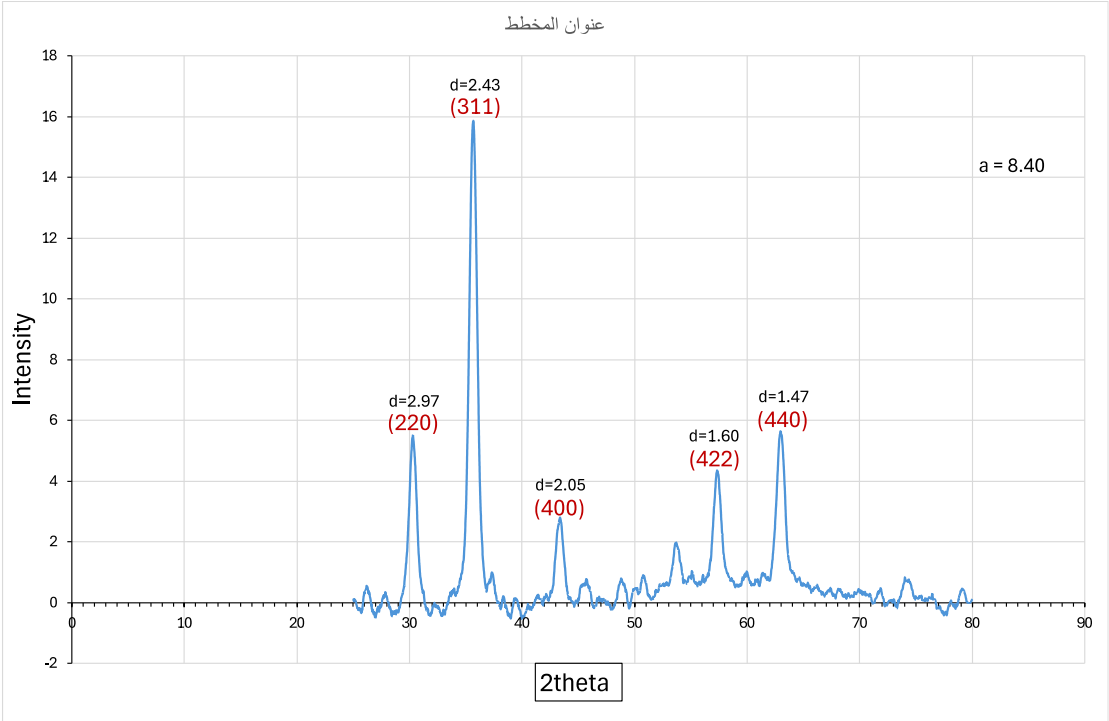

Fig.9. X-ray diffraction patterns of iron oxides

By using Bragg's Law we can find the *interplanar distance* (d):

$2d \sin\theta = n\lambda$ (2)

The normal equation for cubic Structure is:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (3)$$

It well known that for cubic structure a=b=c so we get:

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \quad (4)$$

Where:

d: is the inter-planar distance.

a is the interatomic distance.

h, k, l are Miller indices

From equation (2) and using the peak (220), the value of inter-planar distance is:

d = (1.54)÷ 2sin ($\frac{30}{2}$)

d = 2.97Å

Lattice parameter (a) is determined by using equation (4):

a = (2.97) × $\sqrt{2^2 + 2^2}$

a = 8.40Å

2.2.2. Crystallite size by Scherrer formula

Scherrer's method is used to calculate the average crystallite size by using the following formula:

$$D = \frac{k\lambda}{\beta_{exp}\cos(\theta)} \quad (5)$$

where **k** is the shape factor (~0.8-1.39), **D** is the mean size of the crystallite thickness, **λ** is the wavelength of the X-rays, **θ** is the Bragg angle, and β is the full-width at half-maximum (FWHM) of the peak (radians).

To determine the average crystallite size, the main peak (311) is used:

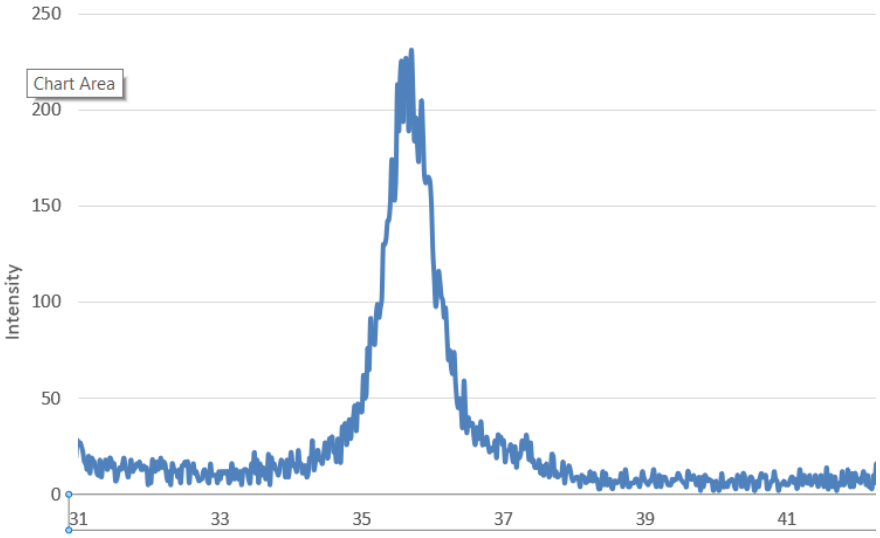

Fig.10. Peak (311) used for Scherrer`s formula

$\beta = 36.68 - 35 = 1.68$ deg

By using : $\frac{\beta\pi}{180}$ ***convert to radian***

$\frac{(1.68)(3.14)}{(180)} = 0.029$, take: $2\theta = 36$, $\theta = 18$

$D = \frac{(0.89)(1.54)}{(0.029)\cos(18)} = 49.6$ **Å** ,

Conclusions

The lattice parameters and crystallite size were determined by XRD diffraction for different crystal structures. The lattice parameters (a,c) of Zinc oxide, which is hexagonal are 3.244 Å and 5.2 Å, respectively. Iron oxide has cubic crystal structure (a=b=c) and the lattice parameter is 8.4 Å. Scherrer method is used to calculate the average crystallite size of iron oxide by using the most intense peak (311). The value is around 49.6Å .

References

- *Elements of X-ray Diffraction, second Edition*, by B.D. Cullity, Addison-Wesley, 1978

- Holder, C. F., & Schaak, R. E. (2019). Tutorial on powder X-ray diffraction for characterizing nanoscale materials. *Acs Nano*, *13*(7), 7359-7365.

- Treacy, M. M., & Higgins, J. B. (2007). *Collection of simulated XRD powder patterns for zeolites fifth (5th) revised edition*. Elsevier.

- Swanson, H. E. (1953). *Standard X-ray diffraction powder patterns* (Vol. 25). US Department of Commerce, National Bureau of Standards.

- Thamaphat, K., Limsuwan, P., & Ngotawornchai, B. (2008). Phase characterization of TiO2 powder by XRD and TEM. *Agriculture and Natural Resources*, *42*(5), 357-361.

- Chauhan, A., & Chauhan, P. (2014). Powder XRD technique and its applications in science and technology. *J Anal Bioanal Tech*, *5*(5), 1-5.

- Poppe, L. J., Paskevich, V. F., Hathaway, J. C., & Blackwood, D. S. (2001). A laboratory manual for X-ray powder diffraction. *US Geological Survey open-file report*, *1*(041), 1-88.

- Srodon, J. (1984). X-ray powder diffraction identification of illitic materials. *CLAYS CLAY MINER. Clays Clay Miner.*, *32*(5), 337.