Kingdom of Saudi Arabia
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Indexation of the crystal structure of In_2O_3 and Ni based on XRD measurements

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

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Abstract

The fundamental principles of X-ray diffraction (XRD) technique, how to index cubic structure, Scherer method are given in the first part of this report. In the second part, We used XRD to characterize two powders (Ni and In_2O_3). The crystal structure is determined based on the Miller indices values, while the crystallite size is calculated by Scherrer method.

خلاصة البحث:

حيود الاشعة السينية من أكثر الطرق استخداما لدراسة خصائص وتحديد المواد البلورية شيوعاً، إذ أنه بالإمكان تحديد الصيغة البلورية, حجم الحبيبات, حساب معاملات الشبكة إلى غير ذلك من الخواص. في الجزء الاول من البحث, تم إعطاء المفاهيم الأساسية لتقنية حيود الاشعة السينية, كيفية تحديد معاملات ميلر واستنتاج الصيغة البلورية كما تم التطرق لطريقة Scherrer في حساب حجم الحبيبات. وفي الجزء الثاني تم قياس حيود الأسعة السينية لعينتين ؛حيث تم حساب معاملات ميل لكل القمم مما مكن من تحديد صيغتهما البلورية كما تم حساب حجم الحبيبات باستخدام طريقة شيرر.

Introduction

X-ray diffraction (XRD) is one of the most important characterization tools used in solid state chemistry and materials science. It can be used for the identification of elements, indexation of structure, determination of the lattice parameters, crystalline size,…etc.

In this final research project, we used XRD technique to study the structural of different powders. In the first part, we explain the principle of XRD, instrumentation used for the measurements and the methods used for the indexation of cubic structures and the calculation of crystallite size. The second part is dedicated to the XRD measurements of two samples. We determined the crystal structure of Nickel and Indium oxide based on the XRD data. In addition, Scherer method is used to determine the crystallite size.

Chapter 1: Theoretical background

1. X-Ray Diffraction

1.1. Definition

X-rays are electromagnetic radiation of wavelength about 1Å (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:

$$\boldsymbol{n\lambda = 2d\sin(\theta)} \quad \textbf{(1)}$$

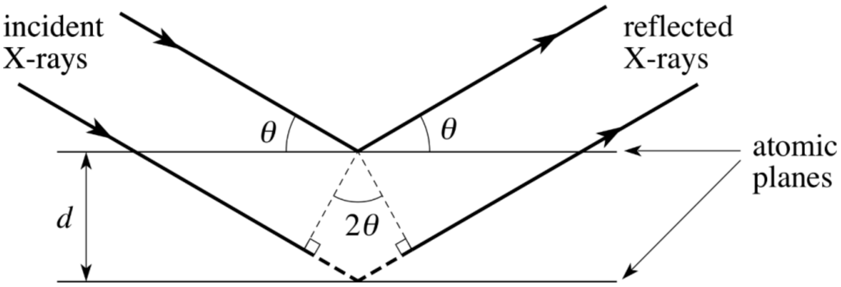


Figure 1. X-ray diffraction principle,

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.

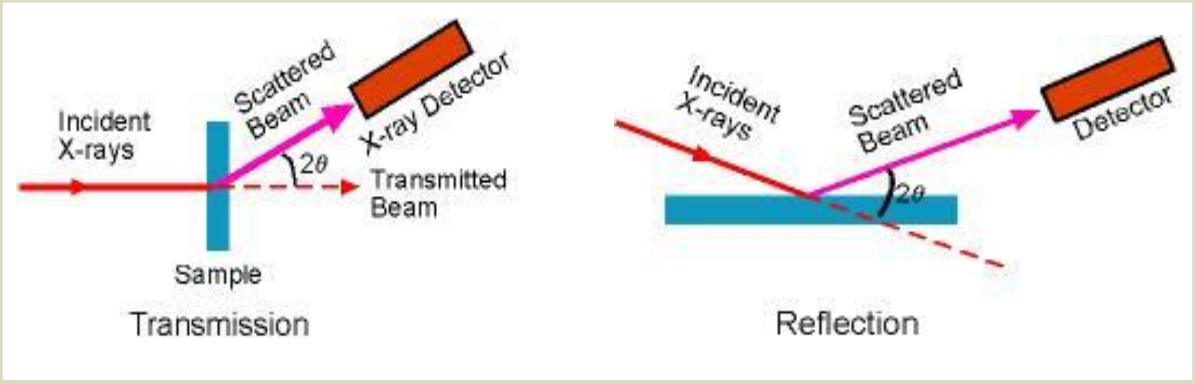


Figure 2. Reflection and transmission scattering rays in materials

1.3. XRD Instrumentation

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

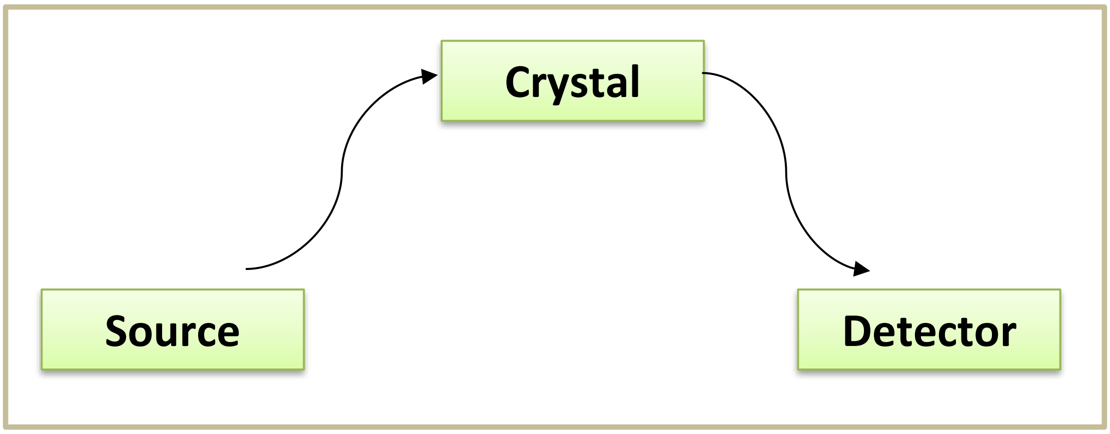


Figure 3. Wave diffraction principles

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.

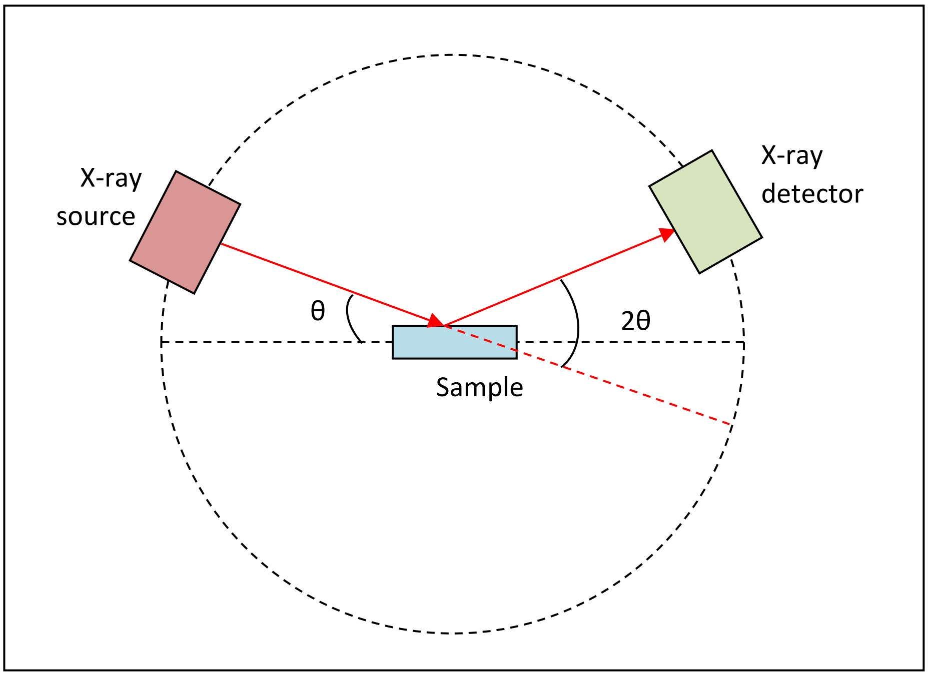


Figure 4. X-ray diffractometer components

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.

1.4. Structure factor

Structure factor of a lattice with basis

$$S_G = \sum_j f_j \, exp[-i\vec{G}.\vec{r}_j](1)$$

$$\vec{r}_j = x_j\vec{a}_1 + y_j\vec{a}_2 + z_j\vec{a}_3$$

$$\vec{r}_j.\vec{G} = 2\pi(hx_j + ky_j + lz_j)$$

$$S_G = \sum_j f_j \, exp[-i2\pi((hx_j + ky_j + lz_j)]$$

- x_j , y_j and z_j are the position of the atoms
- h,k and l are the miller indices.
- f_j is the atomic factor

Structure factor of the BCC lattice

The unit primitive cell contains two atoms located at (0,0,0) and (1/2,/12,1/2)

The structure factor is :

$$S_G = f[exp[-i2\pi((h0 + k0 + l0)] + exp[-i2\pi((h/2 + k/2 + l/2)]$$

$$S_G = f[1 + exp(-i\pi((h + k + l)](2)$$

Using the Euler's formula (for our case θ=π) :

$$cos\,\theta = \frac{e^{i\theta} + e^{-i\theta}}{2}$$

Finally, we obtain :

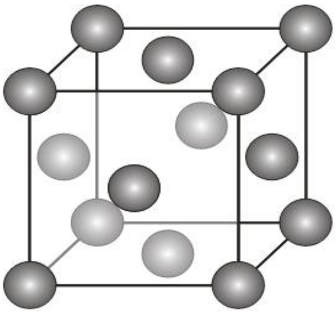
$$S_G = \begin{cases} 0(h + k + l \rightarrow odd) \\ 2f(h + k + l \rightarrow even) \end{cases}$$

Structure factor of the FCC lattice

The unit primitive cell contains four atoms located at (0,0,0) ,(1/2,/12,0), (0,1/2,1/2) and (1/2,0,1/2)

The structure factor is :

$$S_G = f[exp[-i2\pi((h0 + k0 + l0)] +$$
$$exp[-i2\pi((0 + k/2 + l/2) +$$
$$exp[-i2\pi((h/2 + 0 + l/2)] +$$
$$exp[-i2\pi((h/2 + k/2 + 0)]$$



After the use of the Euler's formula (for our case θ=π), we obtain:

$$S_G = \begin{cases} 0 \quad hkl\ are\ partly\ even\ and\ partly\ odd \\ 4f \quad All\ are\ even\ or\ all\ are\ odd \end{cases}$$

1.5. Scherer formula

Scherer's method is used to calculate the crystallite size of the powders by using the following formula:

$$D = \frac{k\lambda}{\beta \cos{(\theta)}} \tag{3}$$

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 **B** is the full-width at half-maximum (FWHM) of the peak (radians).

Chapter 2: Experimental results

2.1. Experimental

2.1.1 Samples

Commercially powders of Ni and In_2O_3 were characterized by XRD.

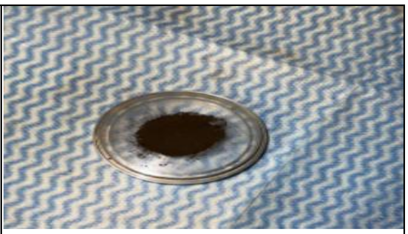
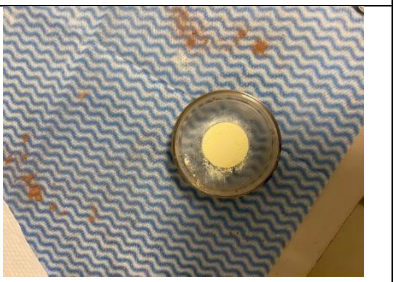
Ni	
In_2O_3	

Figure 5. Powders used in this work (a) Ni, (b) In_2O_3

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.6. Bruker D8 Discover diffractometer

2.2. Results

X-ray diffraction measurements are performed for two samples and based on the data, the crystal structures are indexed by calculating the Miller indcies. Furthermore, Scherrer formula is used to calculate the crystallite size.

2.2.1. Indexation of cubic structure

From Bargg's law

$$\boldsymbol{n\lambda = 2d\sin(\theta)}\ \textbf{(3)}$$

For cubic structure:

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

$$(8)\ \sin\theta = \frac{\lambda}{2d}$$

$$\mathrm{Sin}^2\theta = \frac{\lambda^2}{4d^2} \quad (9)$$

$$\mathrm{Sin}^2\theta = \frac{\lambda^2}{4}\left(\frac{h^2+k^2+l^2}{a^2}\right) \ (5)$$

$$h^2 + k^2 + l^2 = \frac{4a^2\sin^2\theta}{\lambda^2} \quad (6)$$

The Miller indices are deduced by using the equation (6)

2.2.1.1. Indexation of Ni powder

Fig.7 Shows X-ray diffraction patterns of Ni powder.

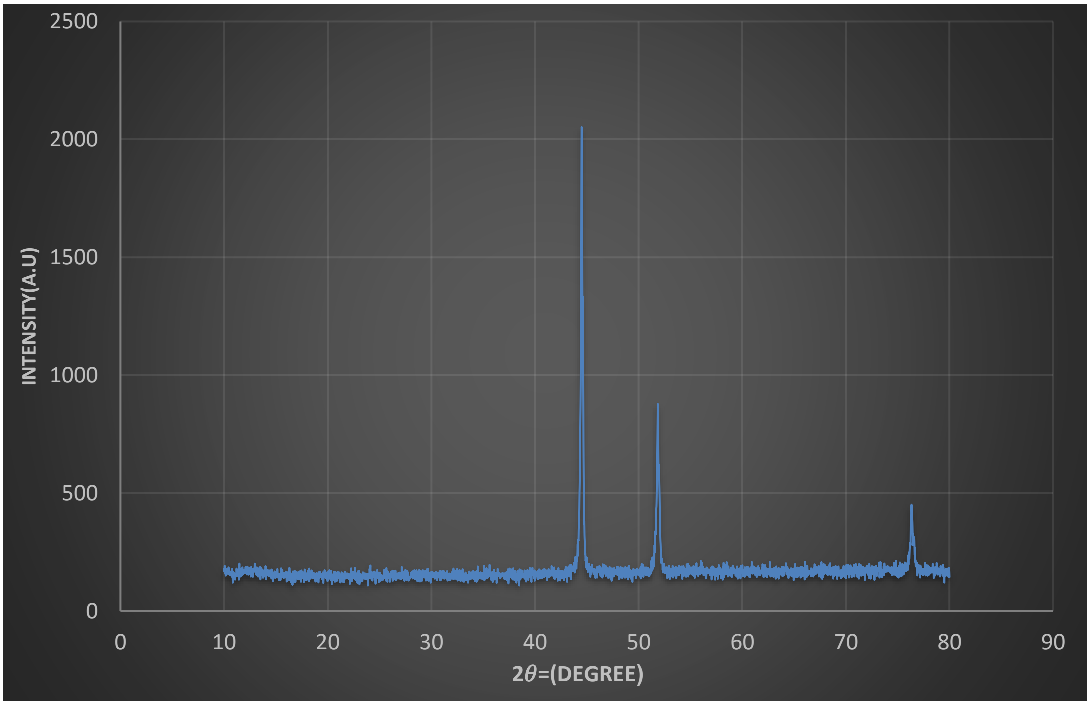


Figure 7. X-ray diffraction patterns of Ni

The Miller indices are calculated by using equation (6): $h^2 + k^2 + l^2 = \frac{4a^2 sin^2\theta}{\lambda^2}$, where a=3.52Å and $\boldsymbol{\lambda} = \mathbf{1.54}$Å. The values are summarized in table below:

Peak	$2\theta°$	$\theta°$	$\sin\theta$	$h^2 + k^2 + l^2$	(hkl)
1	44.52	22.26	0.37	3	(111)
2	51.86	25.93	0.43	4	(200)
3	76.32	38.16	0.61	8	(220)

As can be observed, all (hkl) are even or all are odd.

We can conclude that the crystal **structure of Ni is FCC** according to structure factor rules.

2.2.1.2. Indexation of In_2O_3 powder

Fig.8 Shows X-ray diffraction patterns of In_2O_3 powder.

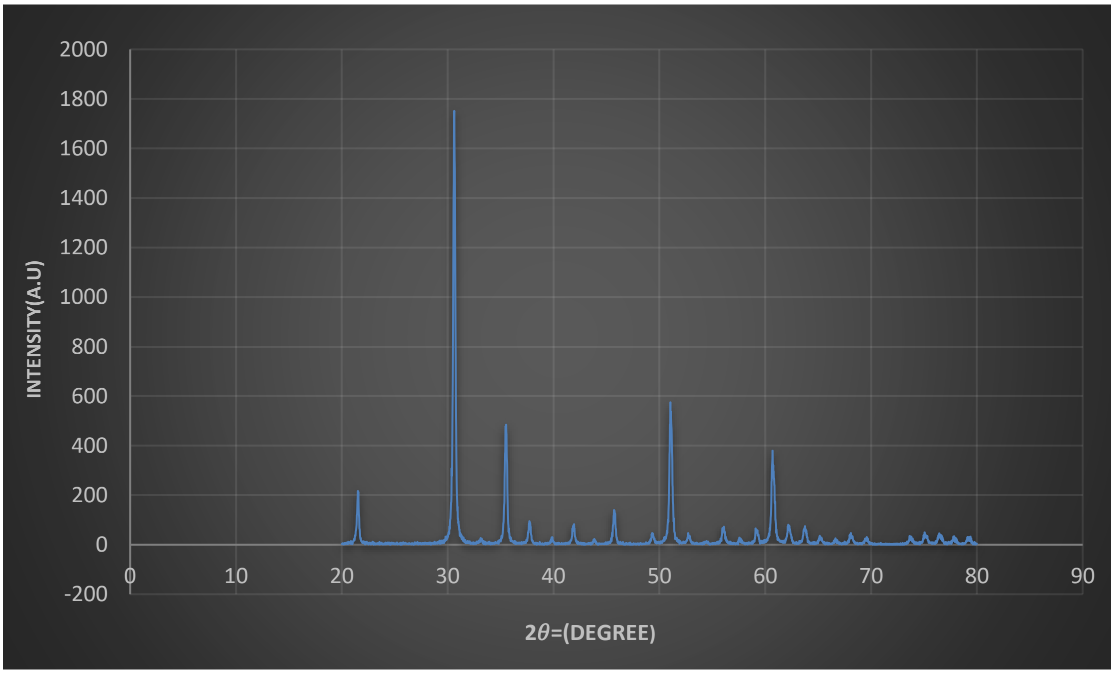


Figure 8. X-ray diffraction patterns of In_2O_3

The same equation is used again to determine the Miller indices for the peaks.

$h^2 + k^2 + l^2 = \frac{4a^2 sin^2\theta}{\lambda^2}$ From equation (6) (a=10Å and $\lambda = 1.54$Å)

The calculated Miller indices are shown in table below:

Peak	$2\theta°$	$\theta°$	$\sin\theta$	$h^2+k^2+l^2$	(hkl)	h+k+l
1	21.54	11	0.19	6	(211)	4
2	30.60	15.50	0.26	12	(222)	6
3	35.56	17.78	0.31	16	(400)	4
4	51.04	26	0.43	32	(440)	8
5	61	30.50	0.51	44	(622)	10

As shown in table, for all peak: h+k+l is even. We conclude that the **structure of In_2O_3 is BCC.**

2.2.2. Average crystallite size by Scherrer formula

The crystallite size is calculated by Scherer formula for In_2O_3 using the most intense peak (222).

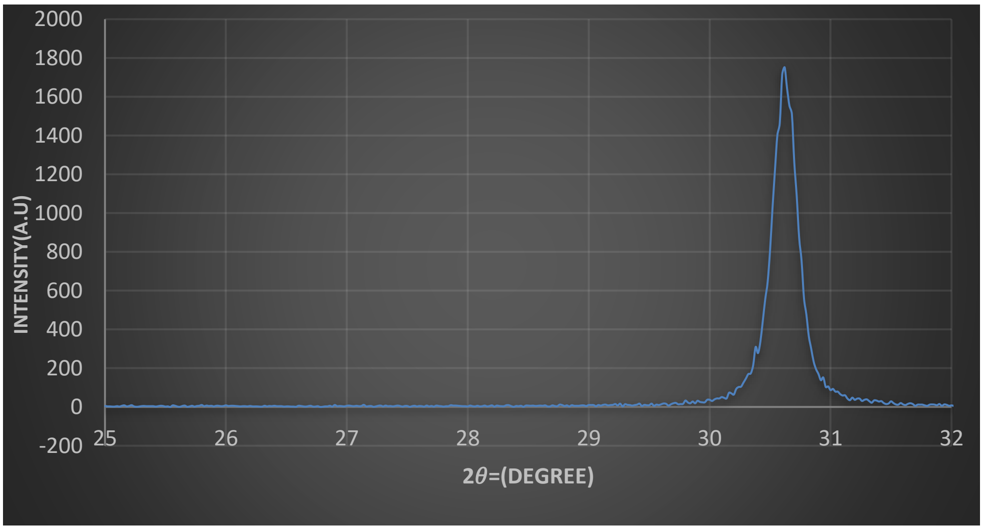


Figure 9. Peak (222) used for Scherrer`s formula

β = 30.86 -30.36 = 0.5deg **By using :** $\frac{\beta\pi}{180}$ ***convert to radian***

= 0.0087 , take: θ=30.6 , 2θ=15.3 $\frac{(0.5)(3.14)}{(180)}$

D = $\frac{(0.89)(1.54)}{(0.0087)\cos(15.3)}$ =163.3 Å , 16.3 **nm**

The crystallite size is : 16.3 nm

Conclusions

Based on the XRD patterns, we calculated the Miller indices for all peaks in Ni and In2O3 powders. From the Miller indices values, we determined the crystal structure for Ni and In_2O_3, which was FCC and BCC, respectively. The average crystallite size was calculated for In_2O_3 by Scherer method. We concluded that XRD can be used to indexes the cubic structure and to calculate the crystallite size of powders.

References

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