Scientia Africana, Vol. 14 (No.1), June 2015. Pp 158-164
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DETERMINATION OF NI(II) CRYSTAL STRUCTURE BY POWDER X-RAY DIFFRACTION

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Received: 08-05-15
Accepted:05-06-15

ABSTRACT

X-ray powder diffraction pattern was used to determine the length of the unit cell, "a", the lattice structure type, and the number of atoms per unit cell of Ni(II) crystal. The "a" value was determined to be 23.66 ± 0.005 Å, particle size of 34.87 nm, volume 13.24 Å and Strain value $\varepsilon = 9.8 \times 10^{-3}$*. The cell search on PXRD patterns shows that the nickel (II) complex crystallizes in cubic structure with space group Fd3m and Z = 8. The experimental value of "a" was determined to be 23.66 ± 0.005 Å. It was deduced that the structure being face-centered cubic has the same number of electrons and therefore make one eighth of the actual unit cell. Taking this into consideration, each unit cell contains 4 atoms. The morphology and elemental composition of the Ni(II) was determined using Scanning Electron Microscopy coupled with Energy-Dispersive X-ray analysis. It was concluded that the unit cells and space groups were determined directly from the powder diffraction data.*

Key Words: Powder X-ray Diffraction, unit cell, Crystal Structure

INTRODUCTION

Structure of materials is an important aspect in inorganic materials chemistry, because it determines the nature of the pores, which can be exploited for many important applications. Research has shown that the formation of a particular structure can be controlled by the careful design and choice of ligands, but in practice it is not very easy [1-11]. Each crystal produces unique Powder X-ray diffraction pattern and can be used to determine its structure, phase composition, unit cell lattice parameters; Bravais lattice symmetry, strain, orientation and crystallite size [8, 10]. The unit cell is the basic repeating unit that defines a crystal structure [8]. Powder X-ray diffraction gives a diffraction pattern for the bulk material of a crystalline solid and contains much more information, rather than of a single crystal, which does not necessarily represent the overall material [8, 9]. Powder X-ray diffraction data could result in a breakthrough for solving difficult structural problems, in particular when appropriate software tools are applied [10]. Powder X-ray diffraction data are collected from compressing one dimensional space; they are statistics of numerous crystals. The crystal structure of a compound is determined from the size of the unit cell, intensities of the reflections, position of atoms and the relative number of electron per atom. In structure solution an initial approximate structure is obtained from experimental data without having any prior knowledge of the arrangement of the atoms and molecules [5, 6]. The size and shape of the unit cell is determined from the positions of the lines, which can also be called indexing the pattern. The unit cell is the smallest divisible unit of a given mineral with symmetrical characteristics that are unique to its crystalline structure. A structure's unit– cell is a spatial arrangement of atoms which are tiled in a three- dimensional space to form the crystal. The unit- cell is determined by its unique lattice parameters, the length of the cell edges, and the angles between them [9, 10]. The positions of the atoms inside the unit-cell are described by the set of atomic position measured from a given lattice point [1, 3]. The scanning electron microscopy uses a focused beam of high-energy electrons to generate a variety of signals from the surface of a solid specimen. The signals reveal information about the sample, including external morphology, topography, chemical composition, crystalline structure, and orientation of materials making up the sample [12]. The aim of this research is to determine the crystal lattice structure of Ni(II) crystal powder. Powder diffraction and visualization methods provided convenient and unambiguous ways of comparing the arrangements of molecules in crystals; values of "a" were useful as a final check of the accuracy of the predicted crystals [11].

MATERIALS AND METHODS

The Ni(II) complex was synthesized by slow evaporation of the filtrate of the mixture of nickel(II) sulfate hexahydrate with mixed ligands of 4-amino-1,2,4-triazole and phenylmalonate at 30 °C, and the blue block-like crystals were ground into powder for the powder X-ray diffraction studies.

The sample was ground and lightly packed into a 10.00 mm borosilicate sample holder. The powder pattern indexing, phase identification and space group were done with software program using the reference database supplied with the instrument. The structure of the Ni(II) complex was determined by Powder X-ray diffraction data collected on X'Pert PRO diffractometer (PANalytical) using Cu Kα radiation (λ_1 = 1.54056 Å) with X'celerator detector. The diffraction data were recorded at room temperature with a step size of 0.001° in scan step time [s]:16.5100 ° at 25 °C in the 2θ range of 5°- 60°. In this work, in order to successfully index the powder diffraction pattern, the pattern was pretreated by calculating and subtracting the back ground then smoothing before stripping $K\alpha_2$ radiation. The powder diffraction pattern was indexed using peak positions read from the powder diffraction profiles by X-CELL method [Neumann, 2003] then the indexing result was refined with the Pawley program. The positions of the atoms within the unit cell were deduced from the relative intensities of the diffraction lines. The particle size D was estimated from the Scherrer's equation [13]:

$$D = \frac{\mathrm{K}\lambda}{\beta\ \mathrm{COS}\theta}$$

Where D is the particle size, k = 0.89 is a correction factor to account for particle shapes, β is the full width at half maximum (FWHM) of the most intense diffraction peak (2θ), λ = 1.5406 Å, the wavelength of Cu target, and θ is the Bragg angle. Strain value ε, was evaluated by using the following relation [14].

$$\varepsilon = \frac{\beta \mathrm{Cos}\theta}{4}$$

Scientia Africana, Vol. 14 (No.1), June 2015. Pp 158-164
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Using a method similar to that given in the literature [15], a spreadsheet was used to find ‘a’. The 2θ was divided by 2 to get θ. Next, $\sin^2\theta$ was calculated and divided by a common factor to get integer values which correspond with *hkl*. The Miller indices were extrapolated to determine the apparent crystal lattice. The following equations are used to calculate the volume V of the unit cell [12]:

Cubic: $V = a^3$

The particle size, morphology and elemental composition of the Ni(II) were determined using Scanning Electron Microscopy coupled with Energy-Dispersive X-ray analysis. SEM and EDAX methods were used to further provide structural information to build the trial structures.

RESULTS AND DISCUSSION

Figure 1 shows the schematic representation of the nickel(II) complex Powder x-ray diffractogram. Preliminary indexing of the pattern gave a cubic crystal system with the space group *Fd3m* and lattice parameters $\alpha = 90.0°$, $a = 23.66$ Å (2.37 nm). For cubic crystal structures, all of the constants (a,b,c) are equal and are referred to as *a*.

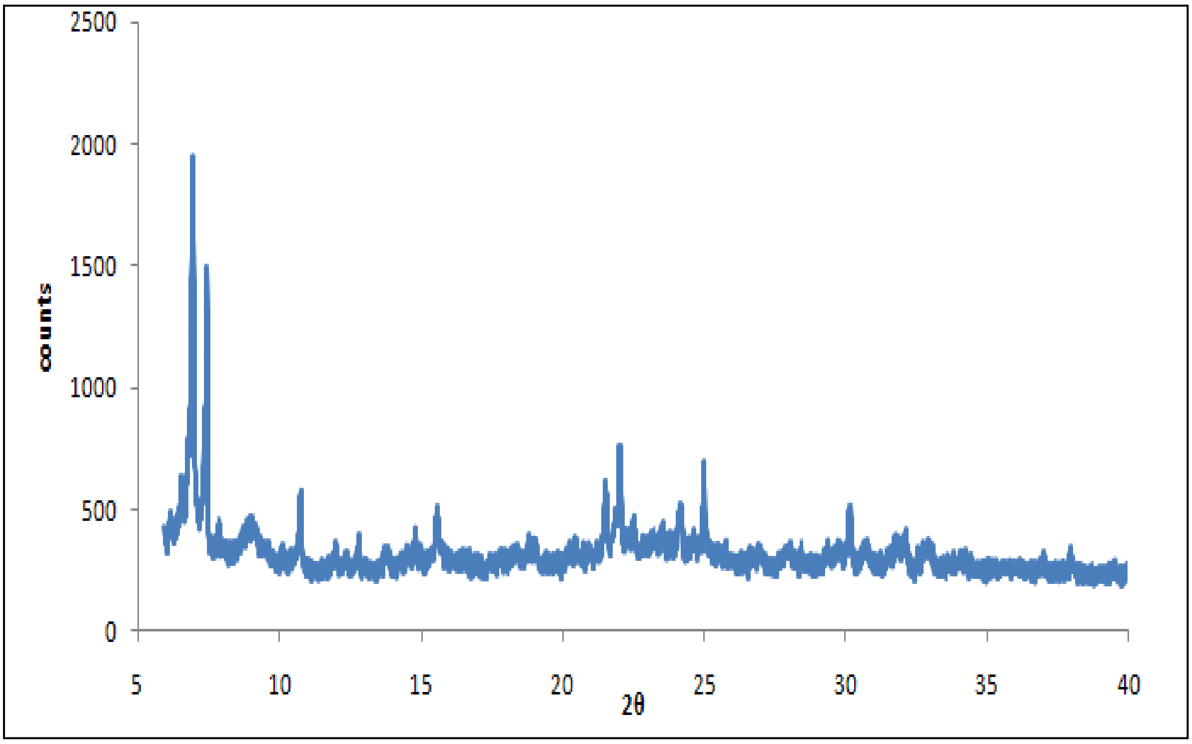
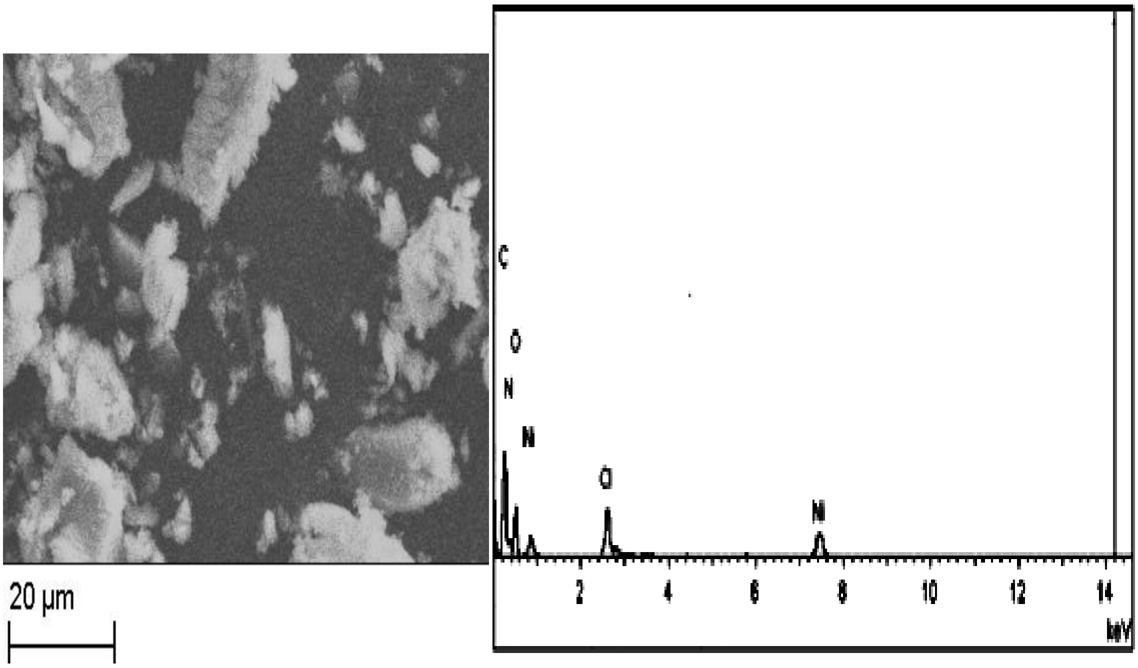


Figure 1. PXRD patterns of compound

Figure 2a-b shows the SEM photograph and EDAX spectrum of the synthesized Ni(II) complex depicting a cube shape in agreement with the powder XRD results. The smaller grain sizes found from powder X-ray diffraction and scanning electron microscopy suggest that this complex is polycrystalline with nanosized crystals.



Figures 2a-b: SEM microphotograph and EDAX spectrum of Ni(II) complex

The X-ray crystal data is given in Table 1. On the basis of the numerical analysis, shown on Table 1, the value of "a" was found to be 23.66 ± 0.005 Å and their respective miller indices as given by the reference cards. Peak positions are determined by the crystal symmetry and dimensions, as well as the X-ray wavelength utilized [1].

Table 1: Observed 2θ and calculated M, *hkl* values and lattice constant *"a"* for Ni (II) complexs

2θ	counts	FWHM (2θ)	D-spacing (Å)	Rel.Int (%)	θ	$\mathrm{Sin}^2\,\theta$	$\frac{\mathrm{Sin2}\,\theta}{\mathrm{Sin2}\,\theta\mathrm{min}}$	$\frac{\mathrm{S\,in2}\,\theta}{\mathrm{Sin2}\,\theta\mathrm{min}}\mathrm{x\,3}$	M	hkl	a
6.2280	238.39	0.1260	14.19180	12.46	3.114	0.0030	1	3	3	111	24.58
6.5655	388.29	0.0945	13.46290	20.30	3.288	0.0033	1.1	3.3	3	111	23.30
7.0284	1912.70	0.0394	12.57723	100.00	3.5142	0.0038	1.27	3.8	4	200	25.15
7.5168	1280.04	0.0394	11.76112	66.92	3.7584	0.0043	1.43	4.3	4	200	23.52
9.2037	276.12	0.1889	9.60892	14.44	4.60185	0.0064	2.13	6.4	6	211	28.81
10.8201	320.88	0.1102	8.17687	16.78	5.41005	0.0089	2.97	8.9	9	310	24.53
12.0513	218.43	0.0630	7.34408	11.42	6.02565	0.0110	3.67	11.0	11	222	24.36
13.8833	165.86	0.1889	6.37882	8.67	6.94165	0.0146	4.87	14.6	15	410	24.71
14.8933	207.39	0.0945	5.94846	10.84	7.44665	0.0168	5.6	16.8	17	331	24.53
15.6715	392.39	0.0945	5.65478	20.51	7.83575	0.0186	6.2	18.6	19	421	24.65
16.5988	118.47	0.0945	5.34089	6.19	8.2994	0.0208	6.9	20.8	21	332	24.48
18.9011	176.65	0.0945	4.69521	9.24	9.45055	0.0270	8.99	26.96	27	420	24.40

Table 2: Analysis of the diffraction pattern of Nickel (II) complex.

2θ	counts	FWHM (2θ)	D-spacing (Å)	Rel.Int (%)	θ	Sin^2 θ	$\frac{4sin^2\theta}{\lambda^2}$	M	M^2	a
6.2280	238.39	0.1260	14.19180	12.46	3.114	0.0030	0.0051	3	9	24.58
6.5655	388.29	0.0945	13.46290	20.30	3.288	0.0033	0.0056	3	9	23.30
7.0284	1912.70	0.0394	12.57723	100.00	3.5142	0.0038	0.0064	4	16	25.15
7.5168	1280.04	0.0394	11.76112	66.92	3.7584	0.0043	0.0072	4	16	23.52
9.2037	276.12	0.1889	9.60892	14.44	4.60185	0.0064	0.0108	6	36	28.81
10.8201	320.88	0.1102	8.17687	16.78	5.41005	0.0089	0.0150	9	81	24.53
12.0513	218.43	0.0630	7.34408	11.42	6.02565	0.0110	0.0185	11	121	24.36
13.8833	165.86	0.1889	6.37882	8.67	6.94165	0.0146	0.0246	15	225	24.71
14.8933	207.39	0.0945	5.94846	10.84	7.44665	0.0168	0.0283	17	289	24.53
15.6715	392.39	0.0945	5.65478	20.51	7.83575	0.0186	0.0314	19	361	24.65
16.5988	118.47	0.0945	5.34089	6.19	8.2994	0.0208	0.0351	21	441	24.48
18.9011	176.65	0.0945	4.69521	9.24	9.45055	0.0270	0.0455	27	729	24.40
19.1103	147.98	0.1260	4.64429	7.74	9.55515	0.0278	0.0469	28	784	24.56
20.3372	151.49	0.0945	4.36679	7.92	10.1686	0.0312	0.0526	31	961	24.31
21.6722	491.39	0.0472	4.10073	25.69	10.8361	0.0353	0.0595	35	1225	24.26
22.1649	725.17	0.0315	4.01067	37.91	11.0825	0.0369	0.0622	37	1369	24.40
24.1904	772.01	0.0384	3.67620	40.36	12.0952	0.0439	0.0740	44	1936	24.39
24.2969	1073.37	0.0315	3.66336	56.12	12.1485	0.0443	0.0747	44	1936	24.30
25.0885	328.66	0.0945	3.54954	17.18	12.5443	0.0472	0.0796	47	2209	24.33
28.5122	135.13	0.0472	3.13063	7.06	14.2561	0.0606	0.1021	61	3721	24.45
29.4788	319.26	0.0480	3.03014	16.69	14.7394	0.0647	0.1091	65	4225	24.43
30.2476	1590.29	0.0384	2.95240	83.14	15.1238	0.0681	0.1148	68	4624	24.35
30.3317	972.32	0.0768	2.95172	50.83	15.1659	0.0684	0.1153	68	4624	24.34
32.1976	232.23	0.2304	2.77791	12.14	16.0988	0.0769	0.1296	77	5929	24.38
34.1099	108.73	0.2304	2.62642	5.68	17.0550	0.0860	0.1450	86	7396	24.36
35.9713	39.49	0.9216	2.49466	2.06	17.9857	0.0953	0.1606	95	9025	24.31
37.9593	216.31	0.0576	2.36846	11.31	18.9797	0.1058	0.1783	106	11236	24.38
40.1658	20.21	0.9216	2.24329	1.06	20.0829	0.1179	0.1987	118	13924	24.37

λ^2=2.373

The Figure 3 shows a plot of $\frac{4\sin^2\theta}{\lambda^2}$ against M^2, for a cubic lattice. The slope $\frac{1}{a^2}$ was used to determine value for "*a*". This value was compared with several literatures "*a*" values to deduce the identity of the crystal. Based upon the numerical analysis, as shown in Table 2 and Figure 3, the value of "*a*" *was* found to be 3.485 Å. This value was consistent with the "a" values and their respective Miller indices as given by the reference cards. The *"a" value* may be a quarter of what it actually is. When our calculated "*a*" *was* a quarter, it, along with its Miller indices, matched closely with the information given in the reference cards [16]. The given *"a"* for Ni(II) was 3.499 Å and the experimental value of *"a"* from the slope is 3.485 Å. Therefore it can be stated with reasonable confidence that the powder pattern obtained for Ni(II) complex and the unit cell parameter is in close range with that given in the reference card [16].

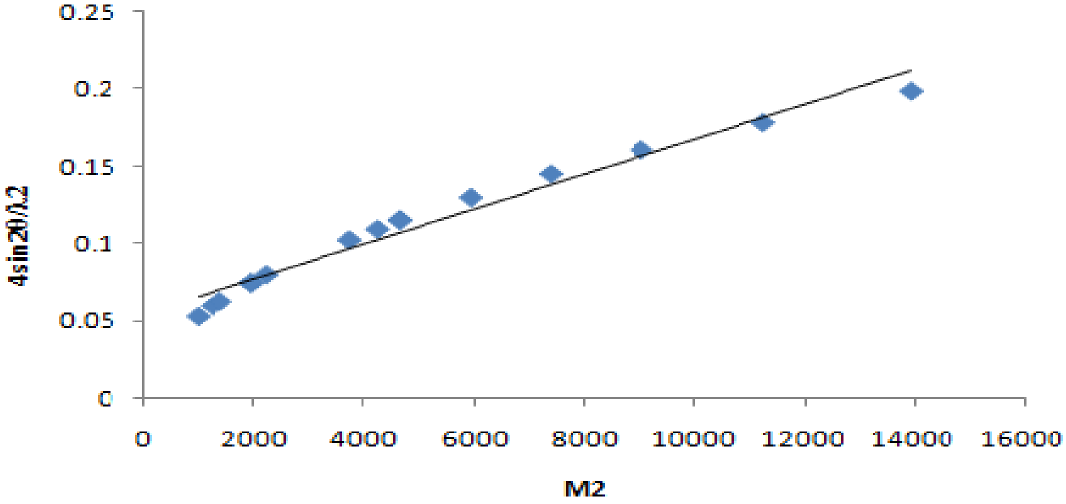


Figure3: Determination of 'a'

The unit cells and space groups were determined directly from the powder diffraction data. Based on the obtained experimental data and literatures, the structure of the Ni(II) complex compound was determined.

The author gratefully acknowledges SHEDA Research Institute Abuja, Nigeria, for providing powder X-ray diffraction, FTIR, SEM and EDX analyses facility.

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