

Zno nanoparticles: Synthesis and crystal structure study

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المستخلص

تم استخدام نترات الزنك ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) و هيدروكسيد الصوديوم (NaOH) لتحضير اوكسيد الزنك النانوي باستخدام تفاعل ذي خطوة واحدة عند درجة حرارة 80°C . أشار نمط حيود الأشعة السينية الى كون المادة المحضرة متعددة التبلور ذات تركيب بلوري سداسي. نفذت تصفية ريتفيلد باستخدام برنامج fullprof للحصول على معلومات شبكية أكثر دقة وقد كانت $a = 3.250353 \pm 0.00009 \text{ \AA}$, $c = 5.207006 \pm 0.00020 \text{ \AA}$ والنسبة $c/a = 1.601981$. تم حساب الحجم الحبيبي باستخدام معادلة ديبيي – شيرر وقد كان بحدود 30 nm. كما درس تأثير الإنفعال الداخلي على عرض قمم حيود الأشعة السينية باستخدام معادلة وليامسون – هول وقد وجد ان حجم الحبيبات بحدود 31.5 nm والإنفعال الداخلي الناشئ هو 6×10^{-4} . درست طبيعة السطح للعينة المحضرة بالمجهر الألكتروني الماسح ووجد تطابقاً جيداً بحجم الحبيبات مع ما تم الحصول عليه بمعادلت ديبيي – شيرر ووليامسون – هول.

الكلمات المفتاحية: الزنك النانوي , تصفية ريتفيلد, مخطط وليامسون – هول, حجم الحبيبات

Abstract

($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and (NaOH) are used for synthesis ZnO nanostructures by one step reaction at 80°C . X-ray diffraction (XRD) pattern refers polycrystalline nature with a hexagonal structure. Rietveld refinement (carried out by fullprof software) of XRD patterns provide accurate values for the lattice parameter $a = 3.250353 \pm 0.00009 \text{ \AA}$, $c = 5.207006 \pm 0.00020 \text{ \AA}$ where c/a ratio is 1.601981. The average crystalline size was calculated by Debye-Scherrer method about 30 nm. The effects of strain in X-ray line broadening of ZnO nanoparticles (NPs) were investigated by Williamson-Hall method revealed that the peak broadening is not only due to reduced coherently diffracting domain size but also due to a significant strain distribution. The extracted particle size is about 31.5 nm and internal lattice strain value was found to be 6×10^{-4} . The morphological and topographical studies were carried out by using scanning electron microscopy SEM, the average particle size is matched with that obtained by Debye-Scherrer and Williamson-Hall methods.

Keywords; ZnO nanoparticles, Rietveld refinement, Williamson-Hall plot, grain size

Introduction

Zinc oxide (ZnO) has been regarded as one of the most promising materials for 1D nanostructure due to its potential applications in electronics, optics, and photonics nanostructure. That is revealed according to its distinguished characteristics such as direct and wide band gap (approximately 3.37 eV), large excitonic binding energy (up to 60 meV). It crystallizes in two forms, hexagonal wurtzite and cubic zinc blende. A hexagonal close-packed lattice takes place with space group of ($P 6_3 m c$) and the ratio of $c / a = 1.602$. Tetrahedral symmetry plays a vital role for the polarity of

ZnO that arises along the hexagonal axis. Piezoelectricity and spontaneous polarization are the direct consequence of polar symmetry of ZnO along the hexagonal axis. The structure of ZnO, can be described as a number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions, stacked alternately along the c-axis.(1,2), Controlling size and structural details of nanoparticles (NPs) are necessary to study their size-dependent properties and correlated it to the wide areas of nanotechnology applications. Because of large surface-to-volume ratio and spatial confinement of carriers, researches on one-dimensional nanostructures have attracted great interest. (3) X-ray line profile analysis (XLPA) is a powerful tool for characterizing the microstructure of crystalline materials in terms of size and strain (4). It has the advantage to provide average values of physically relevant parameters. However, the appropriate interpretation needs the assistance of other methods, especially the electron microscopy. The concomitant application of XLPA and scanning electron microscopy SEM provides probably the best complex microstructure characterization. The most straightforward microstructure properties obtained by XLPA are the (i) average crystallite size and (ii) size distribution, (iii) average dislocation density and (iv) the character of dislocations, (v) slip activity, (vi) active Burgers vectors and (vii) planar defect densities, or (viii) different types of internal stresses of first and second order, (ix) and long-range-internal stresses prevailing in heterogeneous microstructures. Nano crystalline materials can either be in the form of loose powders or compact bulk materials, ceramics, ionic crystals or metals and they have been produced by different methods. XLPA has the great advantage that it can be applied for all different types of materials irrespective of synthesis or constitution. The microstructure of this type of materials can be divided into two fundamental features: (i) the grain or crystallite size and (ii) the structure of lattice defects. The ideal powder diffraction pattern consists of narrow, symmetrical peaks at the exact Bragg positions. A number of different types of deviations from the ideal peak profile are conceivable: (a) peak shifts, (b) peak broadening, (c) peak asymmetries and (d) anisotropic broadening or peak shape, where the anisotropy is meant in terms of hkl dependence. There is no one-to-one correlation between the different peak profile features and the different microstructural properties. It is the experimentators skills and task to find the appropriate interpretation of X-ray line profiles. (5,6) In this paper, we report on the structural properties of the synthesis of ZnO NPs and present various microstructure parameters using x-ray diffraction and SEM

Materials and experimental methods

Synthesis and processing

ZnO nanoparticles were prepared according to the manner described elsewhere. (7,8) Reagents used in this work are NaOH and $Zn(NO_3)_2 \cdot 6H_2O$ (Sigma Aldrich). One molarity NaOH solution was added to the solution of 0.5M- $Zn(NO_3)_2 \cdot 6H_2O$. The mixture was kept stirred at 80°C for three hours. The centrifuge is used to obtain ZnO from the above mixture, and then washed several times with deionized water. The product was dried at 80°C in an oven for several hours.

Product characterizations

The X-ray diffraction pattern of the prepared sample ZnO NPs was obtained by using (Shimadzu XRD-6000) goniometer with copper target ($\text{Cu K}\alpha$, 1.5406 Å), (40 kV, 30 mA). The ZnO nano powder was mounted in an aluminum sample holder. Step-scan data were collected from range (20-120)° with a step width of 0.02° and a counting time of 5 sec/step. The divergence, scattering and receiving slits were 1.0°, 1.0°, 0.15 (mm) respectively with monochromator. The surface morphology was analyzed by using SEM.

Results and Discussion

X-Ray diffraction studies

Peak indexing

X-ray diffraction pattern of ZnO of the prepared powder is presented in Fig .1. Its exhibited three strong diffraction peaks at of 2θ (31.727°, 34.379°, 36.235°) associated with planes (100) , (002), (101) and other peaks for (102), (110), (103),(200) and (112) planes. So, this pattern refers to the pure ZnO with hexagonal wurtzite type structure as it is compared with (PDF #36-1451) .

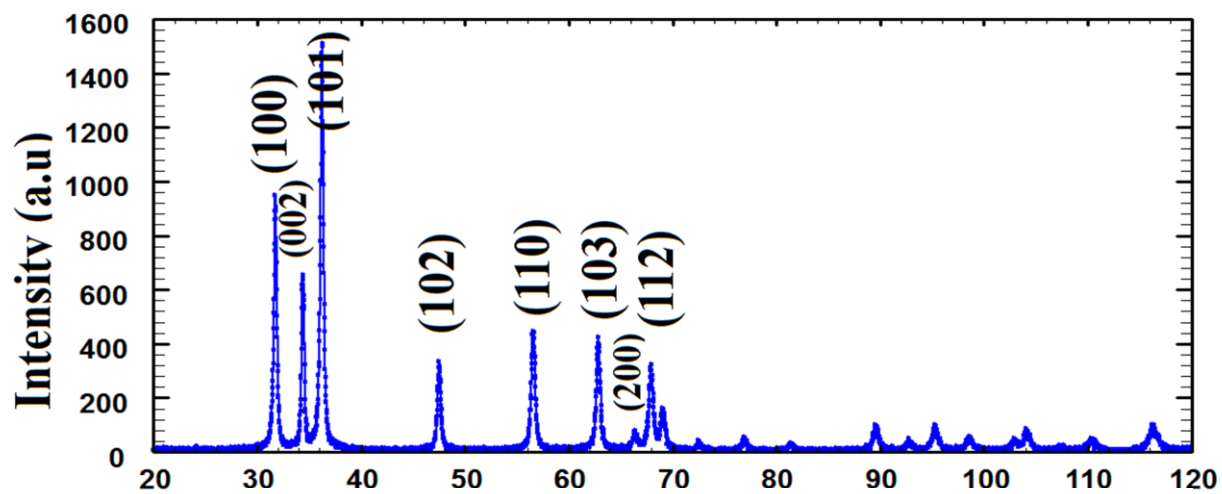


Figure (1): XRD pattern of the ZnO nanopowder

Particle size calculation

From XRD pattern of the ZnO nanopowder, the crystalline size of the samples is calculated using Debye - Scherer equation (9).

$$D = K\lambda / \beta_{hkl} \cos\theta \quad \dots\dots\dots(1)$$

Where D is the average crystallite size , λ is the wavelength of the X-ray radiation ($\text{Cu K}\alpha = 0.15406 \text{ nm}$) , K is the shape coefficient for the reciprocal lattice point about 0.94 for spherical crystallites, θ is the diffraction angle and β_{hkl} is the full width at half maximum height (in radian) . The average crystallite size D is about 30 nm for different planes is presented in table .(1).

Instrumental broadening

When particle size is less than 100 nm, appreciable broadening in x-ray diffraction lines will occur. Diffraction pattern will show broadening because of particle size and strain. The observed line broadening will be used to estimate the average size of the particles. The total broadening of the diffraction peak is due to the sample and the instrument. The sample broadening is described by Williamson - Hall equation (9,10) :

$$\beta_{hkl} * \cos\theta = \left[\frac{K\lambda}{D} \right] + [4\varepsilon * \sin\theta] \quad \dots\dots\dots(2)$$

Where ε is strain and β_{hkl} instrumental broadening. The average particle size D and the strain of the experimentally observed broadening of several peaks will be computed simultaneously using *least squares method*. So instrumental Broadening calculations for several planes is plotted with (2θ) as in fig.2. Williamson and Hall proposed a method for deconvoluting size and strain broadening by looking at the peak width as a function of 2θ . Here, Williamson-Hall plot is plotted with $(\sin\theta)$ on the x-axis and $(\beta\cos\theta)$ on the y-axis (in radians), fig.3. A linear fit is got for the data. From the linear fit, particle size and strain (ε) are extracted from y-intercept and slope respectively (10). The extracted particle size $\langle D \rangle_v$ is 31.5 nm and internal lattice strain value was found to be 6×10^{-4}

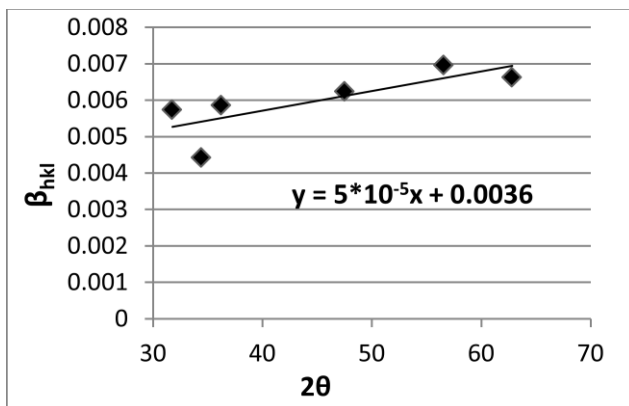


Figure (2): Williamson- Hall Plot is indicating line broadening value due to the equipment

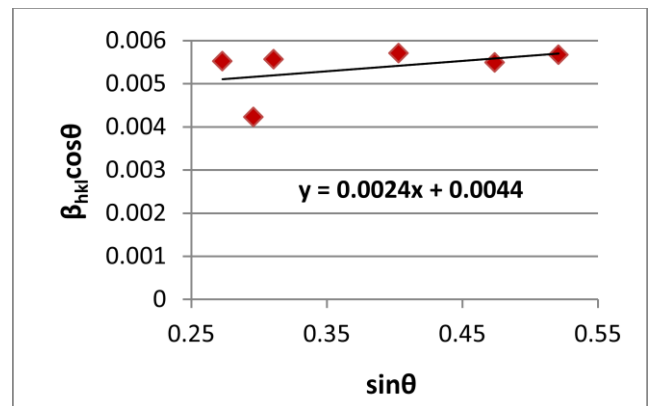


Figure (3): The Williamson-Hall analysis for ZnO nanoparticles. Strain is extracted from the slope of the

Line broadening analysis is most accurate when the broadening due to particle size effects is at least twice the contribution due to instrumental broadening. The size range is calculated over which this technique will be most accurate. A rough upper limit is estimated for reasonable accuracy by looking at the particle size that would lead to broadening equal to the instrumental broadening.

Determination of dislocation density

In materials science, dislocation is a crystallographic defect or irregularity within a crystal structure. The presence of dislocations strongly influences many of the properties of materials. Crystalline solids exhibit a periodic crystal structure. The positions of atoms or molecules occur on repeating fixed distances, determined by the unit cell parameters. However, the arrangement of atom or molecules in most crystalline materials is not perfect. The regular patterns are interrupted by crystallographic defects. The movement of dislocation is impeded by other dislocations present in the sample. Thus, a larger dislocation density implies a higher hardness. It is also known that above a certain grain size limit (~ 20 nm) the strength of materials increases with the decrease of grain size (11,12).

The dislocation density (δ) in the sample was determined using the expression (13):

$$\delta = \frac{15\beta_{hkl}\cos\theta}{4aD} \quad \dots \dots \dots (3)$$

where δ is dislocation density, β_{hkl} is broadening of diffraction line measured at half of its maximum intensity (in radian), θ is Bragg's diffraction angle (in degree), a is lattice constant (in nm) and D is particle size (in nm), the results are in table (1).

Dislocation density increases as the particle size becomes smaller [14]. This is entirely matched with the results that we have obtained.

Determination of texture coefficient

Quantitative information concerning the preferential crystal orientation can be obtained from the texture coefficient, TC, defined as (15):

$$TC(hkl) = \frac{I(hkl)/I_0(hkl)}{N^{-1} \sum_N I(hkl)/I_0(hkl)} \quad \dots \dots \dots (4)$$

Where I is the measured intensity, I_0 is the standard intensity (the intensity of the XRD reference of the randomly oriented grains), Joint Committee on Powder Diffraction Standards, (JCPDS) and N is the number of diffraction peaks. If $TC(hkl) \approx 1$ for all the (hkl) planes are considered, then the NPs are with a randomly oriented crystallite similar to the JCPDS reference, while values higher than 1 indicate the abundance of grains in a given (hkl) direction. Values $0 < TC(hkl) < 1$ indicate the lack of grains oriented in that direction. As $TC(hkl)$ increases, the preferential growth of the crystallites in the direction perpendicular to the hkl plane is greater [16, 17]. We have used six diffraction peaks ((100), (002), (101), (102), (110), (103)), it can be seen that the lowest $TC(hkl)$ was in (002) plane for ZnO NPs, indicating the lack of grains oriented along c -axis of the NPs and the higher rate exhibits (110) and (103) peaks, while other surfaces be a $TC(hkl) \approx 1$. The obtained results are presented in table (1).

Table (1): Diffraction angle (2T) , FWHM (β_{hkl}) , grain size (D) , Texture coefficient (TC) and Dislocation density(δ).

(hkl)	2T(°)	β_{hkl} (°)	D(nm)	TC	$\delta \cdot 10^{15}(\text{m}^{-2})$
(100)	31.763	0.322	26	0.99	2.57
(002)	34.419	0.318	27	0.84	2.32
(101)	36.248	0.315	27	0.92	2.28
(102)	47.534	0.299	28	0.98	1.99
(110)	56.585	0.286	32	1.12	1.61
(103)	62.851	0.277	34	1.15	1.41

Rietveld analysis

Rietveld refinements (18) (curried out by fullprof software (19) on the X-ray (XRD) data were done on ZnO NPs, selecting the space group (P 6₃ m c). Figure.(4) depicts the observed, calculated and difference XRD profiles for ZnO NPs after final cycle of refinement. It can be seen that the profiles for observed and calculated one are perfectly matching. The value of goodness of fit or χ^2 [20] comes out to be equal to 1.45 (The goodness of fit of a statistical model describes how well it fits a set of observations. Measures of goodness of fit typically summarize the discrepancy between observed values and the values expected under the model in question), which may be considered to be very good for estimations. The profile fitting procedure adopted was minimizing the χ^2 function. The XRD analyses refer to the hexagonal crystal system. The crystal data and refinement factors of ZnO NPs obtained from XRD data are given in table 2 The obtained lattice parameter of ZnO NPs is shown a good agreement with the literature report ((PDF #36- 1451).

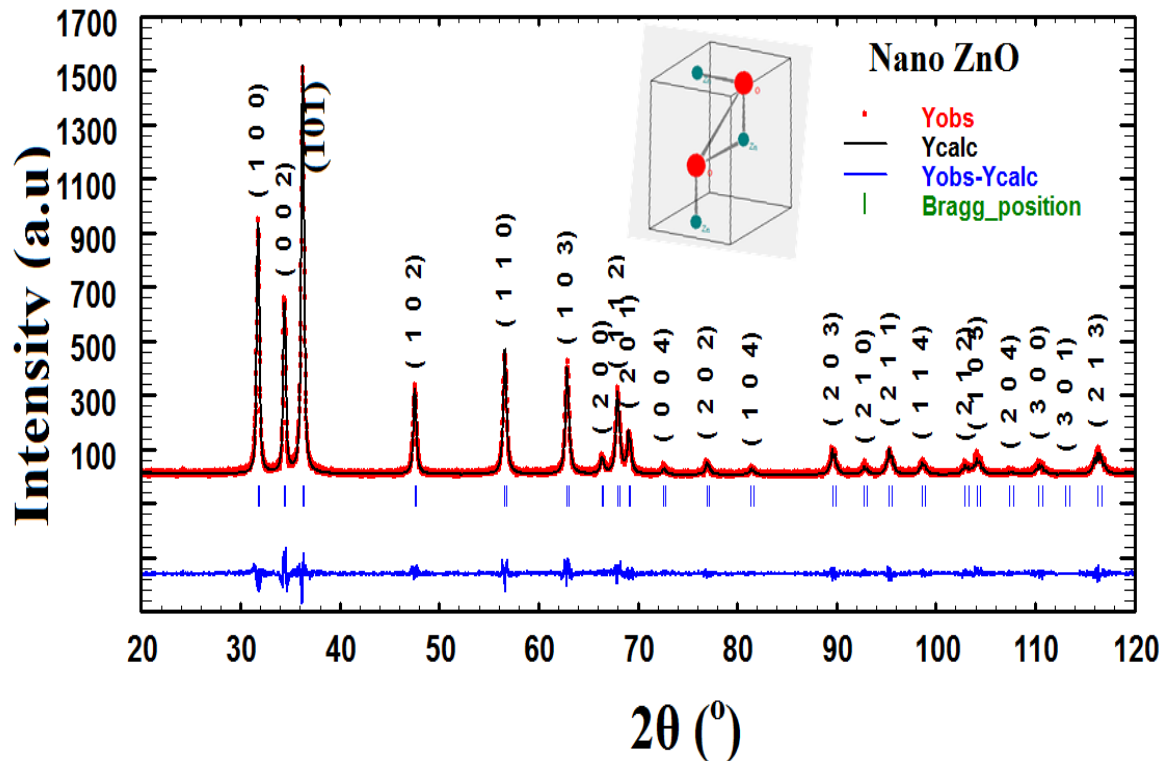


Figure (4): Rietveld refinement of nanocrystalline ZnO

Table (2): Structure parameters, atoms position(x,y,z) and χ^2 from Rietveld

ZnO	Cell parameters(Å)		V(Å ³)	c/a	x	y	z	χ^2
This work	a=3.250353 ±0.00009	c=5.207006 ±0.00020	47.641 ±0.003	1.601981	Zn(1/3)	Zn (2/3)	Zn(0)	1.45
					O(1/3)	O(2/3)	O(0.37651)	
Standard	3.249858	5.206519	47.622830	1.6021	Zn(1/3)	Zn(2/3)	Zn(0)	
					O(1/3)	O(2/3)	(0.3750)	

Characterization in SEM

The size and morphology of the ZnO NPs have been determined by using scanning electron microscopy. Figure 5 shows the typical scanning electron micrograph (SEM) images of ZnO NPs. The SEM image shows random distribution of the ZnO NPs having semi spherical shape and diameter in the range of 25– 40 nm. In fig.5, SEM photo graph shows all particles size good agreement with the size of XRD calculations.

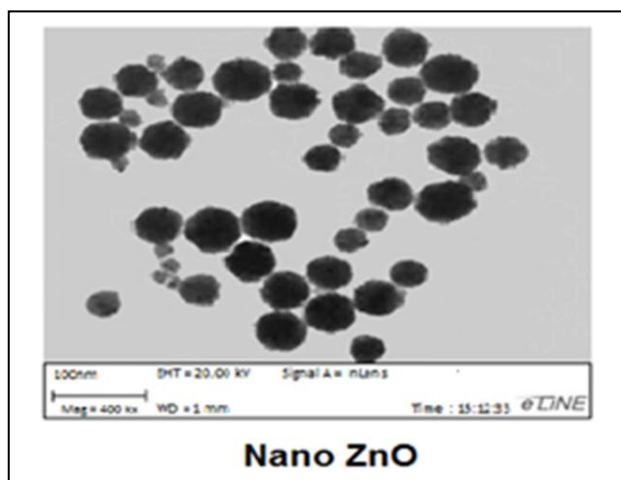


Figure (5): SEM image of ZnO nanopowders.

Conclusion

This work shows that ZnO NPs can be produced in a simple manner. The route of synthesis employed showed to be promising, allowing the obtainment of ZnO NPs of high quality, effortlessness and at relatively low temperatures. The X-ray diffraction results confirmed the synthesis process efficiency, showing only the hexagonal phase pattern, and the nanometric character of the crystallites produced. The SEM image of the sample obtained showed that the powder has, predominantly, a nanometric semi spherical shape morphology.

Rietveld analysis to corrected data has been performed. Correction of asymmetrical to symmetrical diffraction condition is a formalism that lets us combine the use of refinement software FullProf with a surface sensitive to X-ray characterization technique. Results show typical c/a values of 1.601981. Finally, the measurement of particle size (D) is compatible for all measurements.

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