DEPARTMENT OF PHYSICS AND ASTROPHYSICS

Report on

BALL MILLING

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Aim

To synthesize the nanoparticles by mechanical milling and do XRD analysis.

Apparatus

Coarse Salt (ZnO), Ball Milling Machine, cylindrical containers, Balls (of two different sizes),weighing balance.

Introduction

Milling is a core fabrication process in powder technology. It is a method used to break down the solid into powder. A ball mill is a type of grinder which consists of a cylinder (which is made up of steel). The cylinder rotates around a horizontal axis. It is partially filled with the grinding medium (in our case it is air) and the material to be grounded. Materials which can be used as media are ceramic balls and stainless steel balls. We have used Zirconia balls in the lab.

Coarse Material (ZnO)

- Zinc Oxide is an inorganic compound, found in the Earth's crust as the mineral zincite. It is widely used as an additive in various materials such as rubbers, plastics, ceramics, etc.
- It is a white powder that is insoluble in water.
- The molar mass of ZnO is 81.408 g/mol.
- It has a hexagonal structure and is stable. *We are using Wurtzite in our lab.*
- It is a relatively soft material. Its elastic constants are smaller than those of other semiconductors, such as GaN.
- It has a wide band gap semiconductor of the II-VI semiconductor group**.**
- It has a large band gap of 3.3 eV at room temperature.

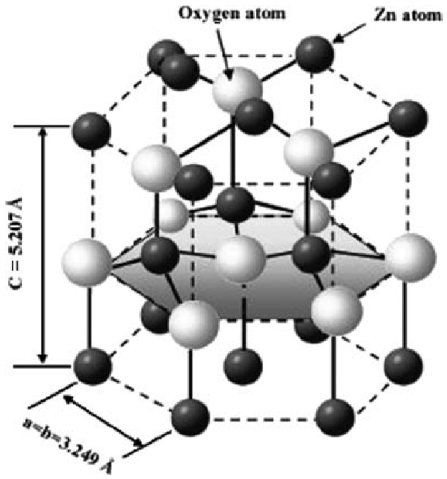


Fig: The Wurtzite Structure of ZnO.

Planetary Ball Milling

Planetary Ball Mills are used when the **highest degree of fineness** is required. They provide the energy input necessary for **mechanical alloying**. A typical planetary ball mill consists of one turn disc (sometimes called turntable) and two or four bowls. The turn disc rotates in one direction while the bowls rotate in the opposite direction.

Principle of working:

Planetary Ball Mills consist of the cylindrical grinding jars which are filled with loose grinding balls. The disc rotates around a common central axis while jars rotate about their own axis. The resulting centrifugal and acting acceleration forces lead to strong grinding effects. Furthermore, there are forces working according to the Coriolis acceleration. The result is an intensive grinding effect between the grinding balls and the sample.

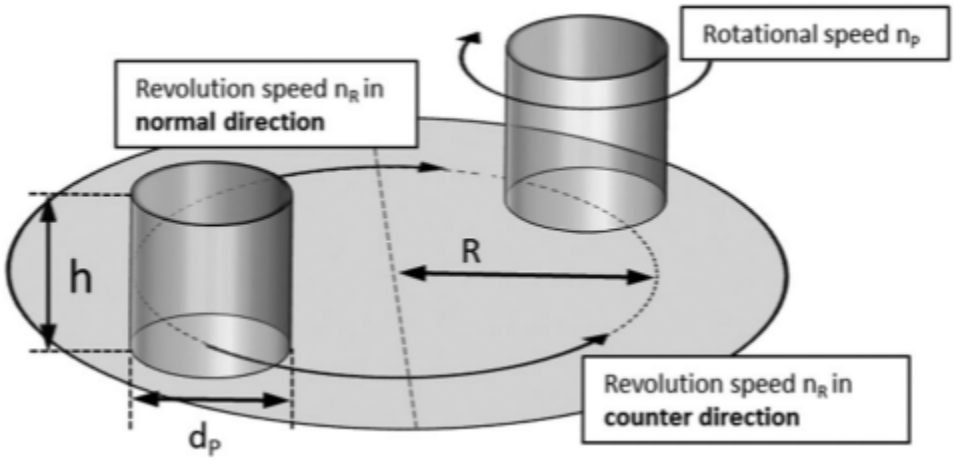


Fig: Scheme of planetary disks with movement in a normal and counter direction; with jar height h; jar diameter dP; revolution radius R.

The selection of the right grinding jar and the correct filling level has a big impact on the grinding result. A jar filling should consist of about 1/3 sample and 1/3 ball charge. The remaining third is the free jar volume that is necessary for the movement of the balls.**We are using steel jars in our lab.**

Variables involved in Ball Milling

The particle size reduction depends on the following basic factors:

1. type of mill,
2. milling container,
3. milling speed,

4. milling time,
5. type, size, and size distribution of the grinding medium,
6. ball-to-powder weight ratio,
7. extent of filling the vial,
8. milling atmosphere,
9. process control agent, and
10. temperature of milling

Advantages

- cost-effectiveness
- reliability
- ease of operation
- reproducible results due to energy and speed control
- Besides particle size reduction, ball mills are also widely used for mixing, blending and dispersing, amorphization of materials and mechanical alloying

Disadvantages

- More possibility of contamination
- formation of nanomaterials with irregular shape
- noise
- long milling and cleaning times

XRD

To study and characterize the crystalline structure of a material, a powerful non-destructive technique of X-ray diffraction is used. XRD peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the atomic positions within the lattice planes. Consequently, the XRD pattern is the fingerprint of periodic atomic arrangements in each material.The XRD analysis is done with an X-ray source of Cu Kα radiation ($\lambda = 1.5406$ Å). The standard database (JCPDS database) for XRD pattern is used for hkl identification for a large variety of crystalline structures.

Procedure

1. Containers and balls were cleaned using acetone solution.
2. Placed acetone containing beaker with balls in the Digital Ultrasonic Cleanser for 30 minutes at room temperature for cleaning the balls.
3. Coarse salt and balls were weighed in such a way that the balls to salt ratio was 10:1. We weighed 5 grams of ZnO and balls roughly 50 grams using a digital weighing machine.
4. Ball bearings of two different sizes(50 gms) and measured ZnO were inserted into the grinding jars.
5. Placed the jars inside the milling case.

6. Set the necessary mill operations on the digital panel of the mill.
7. After completion,let the machine rest for at-least 15 minutes before opening the container.
8. The time period for the milling was taken to be 3 hours, 6 hours and 12 hours.
9. Collected the ZnO powder using the spatula and stored it in a labelled vial.
10. The obtained samples were then analysed by carrying out their X-ray diffractions.
11. Then we calculated the size using the Debye-Scherrer formula and WH Method.

Formula Used

Crystallite size is determined by using **Debye-Scherrer formula**,

$$d = \frac{0.9\,\lambda}{\beta\, cos\,\theta}$$

where d is the crystallite size, λ is the wavelength of the X-radiation used, β is the peak width at half the maximum intensity in rad, and θ is the Bragg angle.

We can write $\beta = \frac{0.9\,\lambda}{d\, cos\,\theta}$

So, $ln\,(B) = ln(\frac{0.9\lambda}{d}) + ln(\frac{1}{cos\theta})$

The graph between ln(B) vs ln($\frac{1}{cos\theta}$) is plotted and from its intercept, we can calculate the value of d.

To calculate lattice parameters a and c, we use :

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

Where hkl are miller indices.

Also, according to the **Williamson Hall equation**, there is a broadening of intensity peak due to micro-strain contribution. Hence Debye Scherrer formula can be modified as -

$$B_{total} = B_d + B_e$$

Where, $B_d = \frac{K\lambda}{dcos\theta}$ is due to bragg's diffraction

& $B_e = 4\varepsilon tan\theta$ due to strain contribution

such that

$$B_{total} = \frac{K\lambda}{d\cos\theta} + 4\varepsilon tan\theta$$

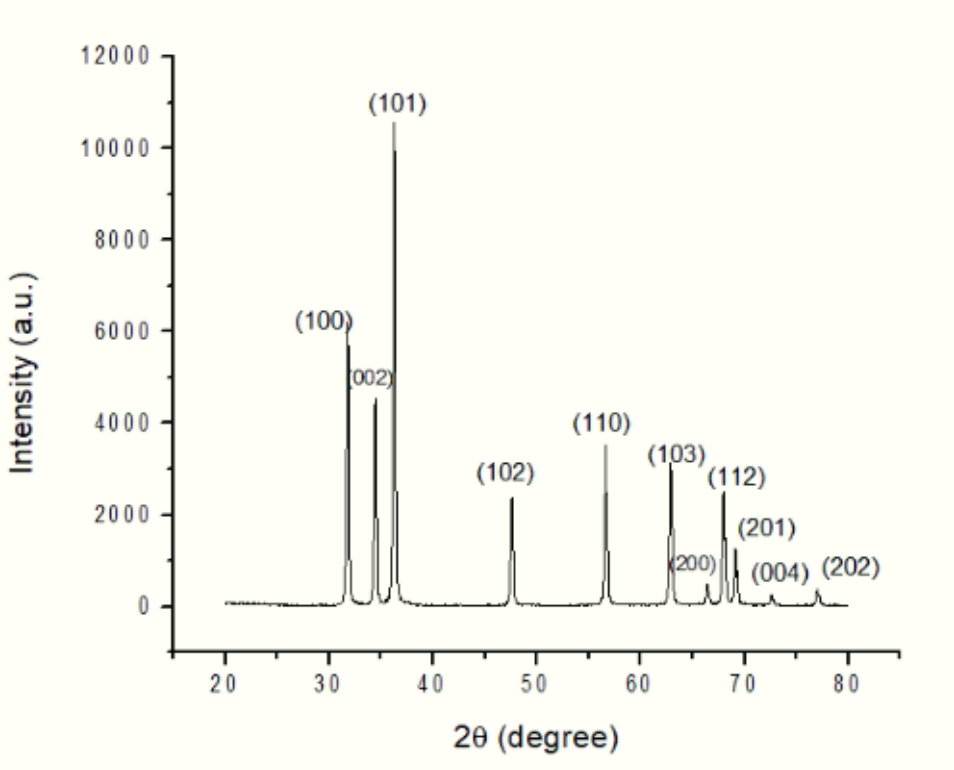
$$B_{total}\cos\theta = 4\varepsilon sin\theta + \frac{K\lambda}{d}$$

Thus, by plotting the graph between $B_{total}\cos\theta$ vs $4sin\theta$ and from its intercept we can calculate the value of d.

Observations and Calculation

Wavelength λ = 1.5406 A
Plate RPM = 200 RPM
Bowl RPM = 284 RPM
No of cycles = 15
Weight of balls = 50 g
Weight of powder to be grounded = 5 g

Case 1: Using precursor



XRD for precursor

(a) Using Debye Scherrer Formula

S.No.	Peak Position 2θ (°)	(hkl)	FWHM β (°)	d(nm)
1	31.80308	(100)	0.24536	33.66637
2	34.46284	(002)	0.24347	34.16280
3	36.29738	(101)	0.25360	32.96608
4	47.60626	(102)	0.27171	31.95641
5	56.65632	(110)	0.30467	29.62253
6	62.92311	(103)	0.32430	28.71864
7	66.44439	(200)	0.33476	28.36798
8	68.02084	(112)	0.34450	27.81922
9	69.15331	(201)	0.36038	26.77322
10	72.63646	(004)	0.30050	32.81072
11	77.04036	(202)	0.34174	29.71232

Average crystallite size d = 30.59784 nm

Lattice Parameters

For plane (100) $\theta = 15.901^{\circ}$

Bragg's Law: $2D \sin\theta = \lambda$ $\lambda = 0.15405$ nm

$$D = \frac{0.077025}{\sin 15.901}$$

Planar spacing D = 2.81 Å

And, using $\frac{1}{D^2} = \frac{4}{3}\frac{(h^2+k^2+hk)}{a^2} + \frac{l^2}{c^2}$

We get, a = 3.24 Å

Similarly, for plane (002) θ = 17.231

Using Bragg's law $2D \sin\theta = \lambda$ $\lambda = 0.15405$ nm

$$D = \frac{0.077025}{\sin 17.231}$$

D = 2.60 Å

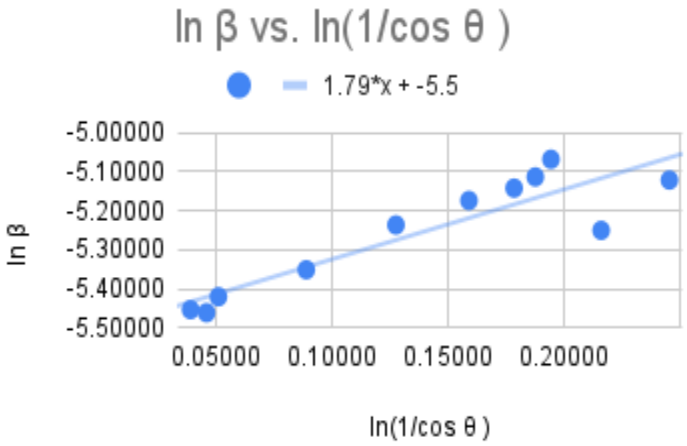
And, using $\frac{1}{D^2} = \frac{4}{3}\frac{(h^2+k^2+hk)}{a^2} + \frac{l^2}{c^2}$

We get, c = 5.2 Å

Therefore, $\frac{c}{a} = 1.605$

(b) Using $ln(\beta) = ln(\frac{0.9\lambda}{d}) + ln(\frac{1}{cos\theta})$

S.No.	ln(1/cos θ)	ln β
1	0.03902	-5.45326
2	0.04592	-5.46099
3	0.05103	-5.42022
4	0.08890	-5.35125
5	0.12756	-5.23675
6	0.15901	-5.17431
7	0.17847	-5.14257
8	0.18761	-5.11389
9	0.19435	-5.06882
10	0.21599	-5.25053
11	0.24540	-5.12193



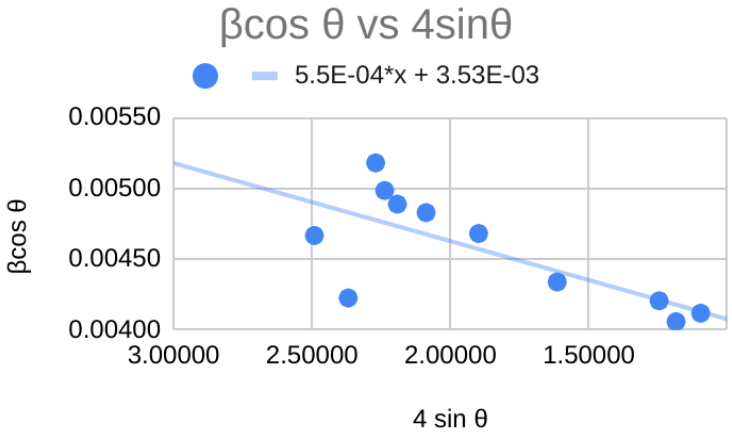
y-intercept = -5.50298 = $ln(\frac{0.9\lambda}{d})$

Average crystallite size d = 34.02910 nm

(c) Using Williamson-Hall Method

$$B_{total}cos\theta = 4\varepsilon sin\theta + \frac{K\lambda}{d}$$

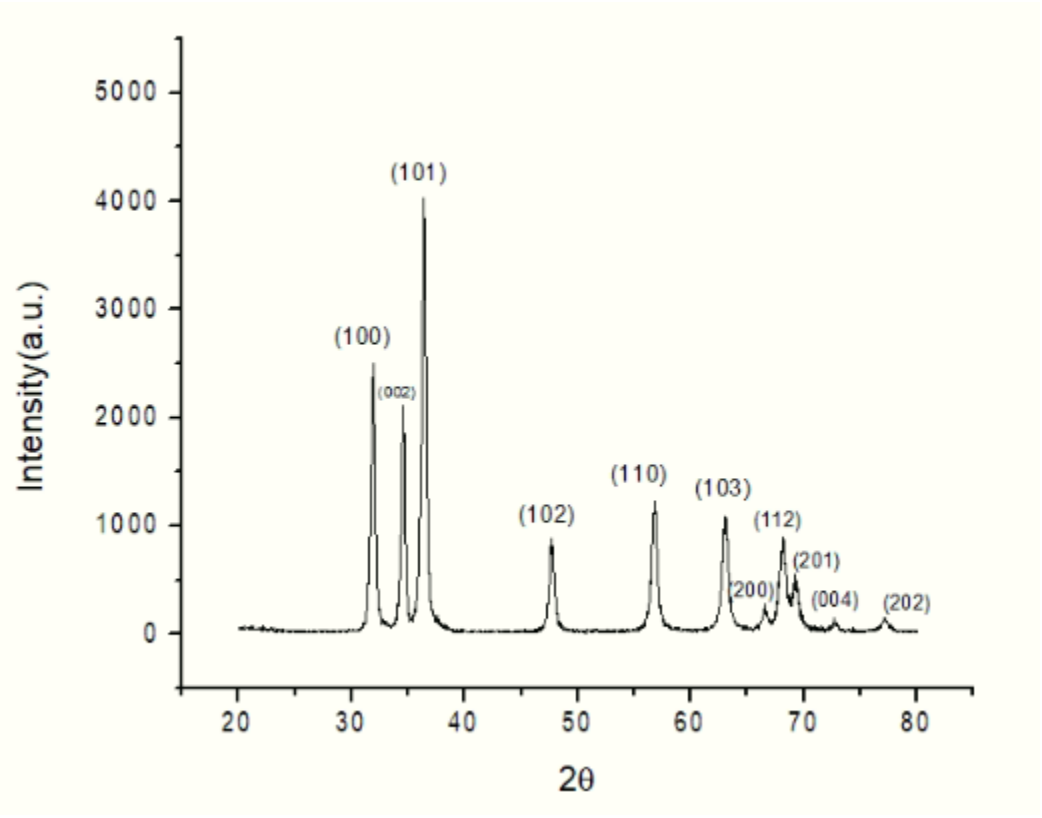
S.No.	4 sin θ	βcos θ
1	1.09594	0.00412
2	1.18493	0.00406
3	1.24594	0.00421
4	1.61438	0.00434
5	1.89808	0.00468
6	2.08771	0.00483
7	2.19155	0.00489
8	2.23737	0.00498
9	2.27003	0.00518
10	2.36908	0.00423
11	2.49116	0.00467



y-intercept = 0.003526 = $\frac{0.9\lambda}{d}$

Average crystallite size d = 39.31709 nm

Case 2: Milling time = 3 hr



XRD Plot of milling ZnO powder for three hours.

(a) Using Debye Scherrer Formula

S.No.	Peak Position 2θ (°)	(hkl)	FWHM β (°)	d(nm)
1	31.90807	(100)	0.48778	16.93907
2	34.57508	(002)	0.41834	19.88848
3	36.40585	(101)	0.52102	16.05082
4	47.71746	(102)	0.55087	15.76887
5	56.77912	(110)	0.63377	14.24857
6	63.04109	(103)	0.68657	13.57375
7	67.67069	(200)	0.32578	29.35701
8	68.14405	(112)	0.63385	15.13084

9	69.25334	(201)	0.72674	13.28445
10	72.73028	(004)	0.45203	21.82501
11	77.15294	(202)	0.58155	17.47372

Average crystallite size d = 17.59460 nm

Lattice Parameters

For plane (100) $\theta = 15.954$

Bragg's Law: $2D \sin\theta = \lambda$ $\lambda = 0.15405$ nm

$$D = \frac{0.077025}{\sin 15.954}$$

Planar spacing $d = 2.80$ Å

And, using $\frac{1}{D^2} = \frac{4}{3}\frac{(h^2+k^2+hk)}{a^2} + \frac{l^2}{c^2}$

We get, $a = 3.23$ Å

Similarly, for plane (002) $\theta = 17.288$

Using Bragg's law $2D\sin\theta = \lambda$ $\lambda = 0.15405$ nm

$$D = \frac{0.077025}{\sin 17.288}$$

$D = 2.59$ Å

And, using $\frac{1}{D^2} = \frac{4}{3}\frac{(h^2+k^2+hk)}{a^2} + \frac{l^2}{c^2}$

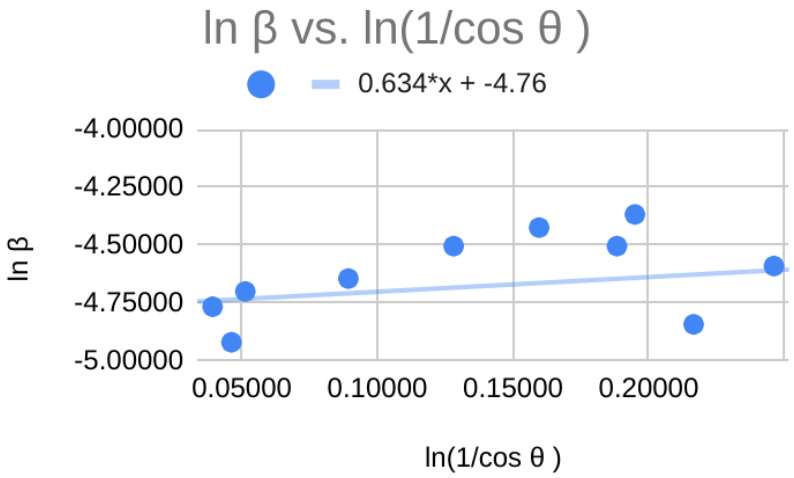
We get, $c = 5.18$ Å

Therefore, $\frac{c}{a} = 1.604$

(b) Using $ln(\beta) = ln(\frac{0.9\lambda}{d}) + ln(\frac{1}{cos\theta})$

S.No.	ln(1/cos θ)	ln β
1	0.03928	-4.76612
2	0.04623	-4.91969
3	0.05134	-4.70019
4	0.08933	-4.64448
5	0.12813	-4.50430
6	0.15964	-4.42427

7	0.18556	-5.16975
8	0.18834	-4.50417
9	0.19495	-4.36741
10	0.21660	-4.84223
11	0.24619	-4.59029



y-intercept = -4.76477 = $ln(\frac{0.9\lambda}{d})$

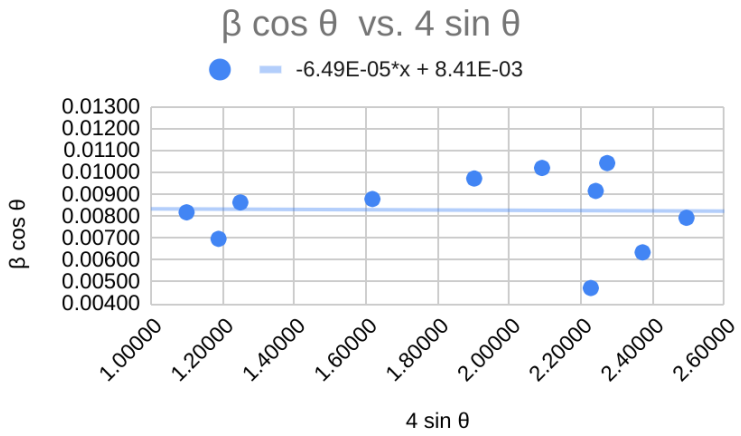
Average crystallite size d = 16.26472 nm

(c) Using Williamson-Hall Method

$$B_{total}cos\theta = 4\varepsilon sin\theta + \frac{K\lambda}{d}$$

S.No.	4 sin θ	βcos θ
1	1.09946	0.00819
2	1.18867	0.00697
3	1.24953	0.00864
4	1.61793	0.00879
5	1.90186	0.00973
6	2.09122	0.01021
7	2.22723	0.00472
8	2.24094	0.00916
9	2.27291	0.01044

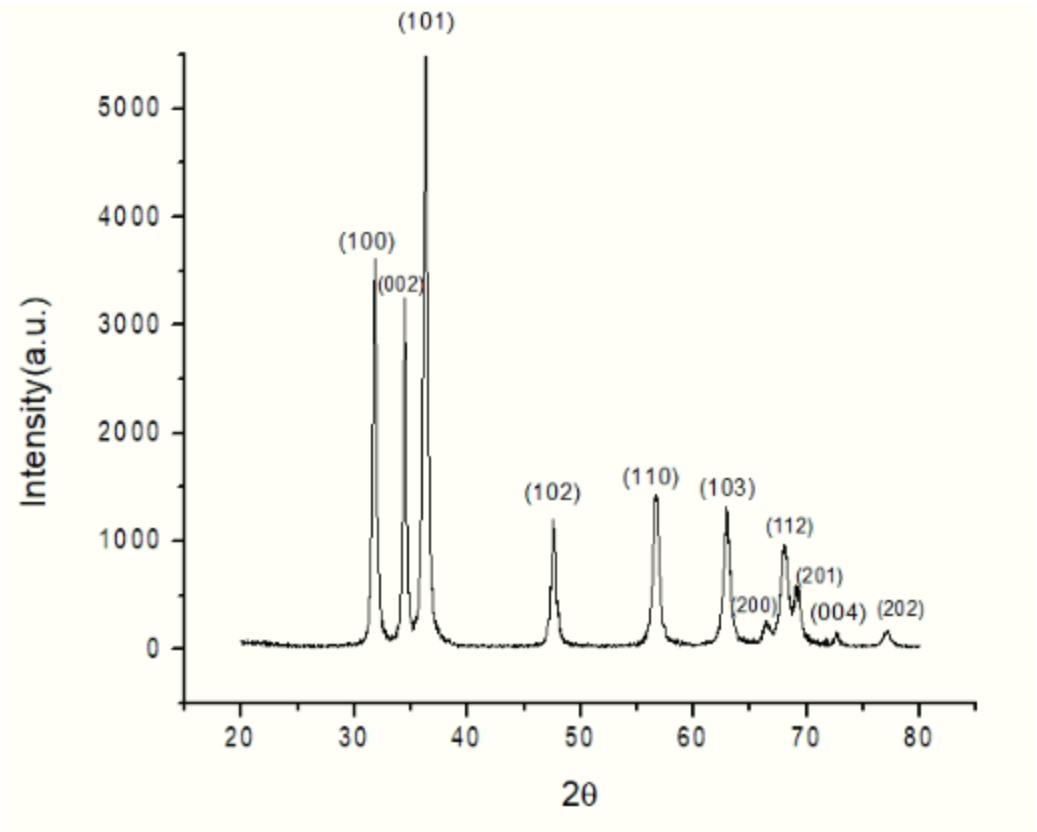
10	2.37172	0.00635
11	2.49423	0.00794



y-intercept = 0.00841 = $\frac{0.9\lambda}{d}$

Average crystallite size d = 16.48991 nm

Case 3: Milling time = 6 hr



XRD Plot of milling ZnO powder for 6 hours.

(a) Using Debye Scherrer Formula

S.No.	Peak Position 2θ (°)	(hkl)	FWHM β (°)	d(nm)
1	31.78447	(100)	0.45065	18.32908
2	34.44805	(002)	0.37536	22.15815
3	36.28076	(101)	0.50547	16.53867
4	47.59877	(102)	0.56150	15.46327
5	56.65939	(110)	0.67306	13.40925
6	62.92833	(103)	0.71431	13.03876
7	66.53514	(200)	0.98417	9.65422
8	68.01054	(112)	0.77361	12.38756
9	69.13800	(201)	0.79130	12.19214
10	72.61513	(004)	0.38018	25.93054

11	77.07721	(202)	0.57628	17.62423

Average crystallite size d = 16.06599 nm

Lattice Parameters

For plane (100) $2\theta = 31.78447$

Bragg's Law: $2D \sin\theta = \lambda$ $\lambda = 0.15405$ nm

$$D = \frac{0.077025}{\sin 15.89}$$

Planar spacing $D = 2.81$ Å

And, using $\frac{1}{D^2} = \frac{4}{3}\frac{(h^2+k^2+hk)}{a^2} + \frac{l^2}{c^2}$

We get, $a = 3.24$ Å

Similarly, for plane (002) $2\theta = 34.44805$

Using Bragg's law $2D \sin\theta = \lambda$ $\lambda = 0.15405$ nm

$$D = \frac{0.077025}{\sin 17.224}$$

$D = 2.60$ Å

And, using $\frac{1}{D^2} = \frac{4}{3}\frac{(h^2+k^2+hk)}{a^2} + \frac{l^2}{c^2}$

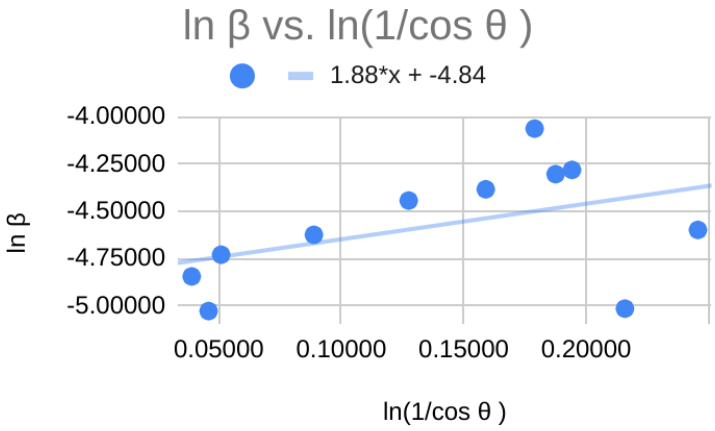
We get, $c = 5.2$ Å

Therefore, $\frac{c}{a} = 1.605$

(b) Using $ln(\beta) = ln(\frac{0.9\lambda}{d}) + ln(\frac{1}{cos\theta})$

S.No.	ln(1/cos θ)	ln β
1	0.03897	-4.84529
2	0.04588	-5.02810
3	0.05098	-4.73049
4	0.08887	-4.62537
5	0.12757	-4.44415
6	0.15903	-4.38467
7	0.17899	-4.06418
8	0.18755	-4.30491

9	0.19426	-4.28231
10	0.21586	-5.01534
11	0.24566	-4.59939



y-intercept = -4.83692 = $ln(\frac{0.9\lambda}{d})$

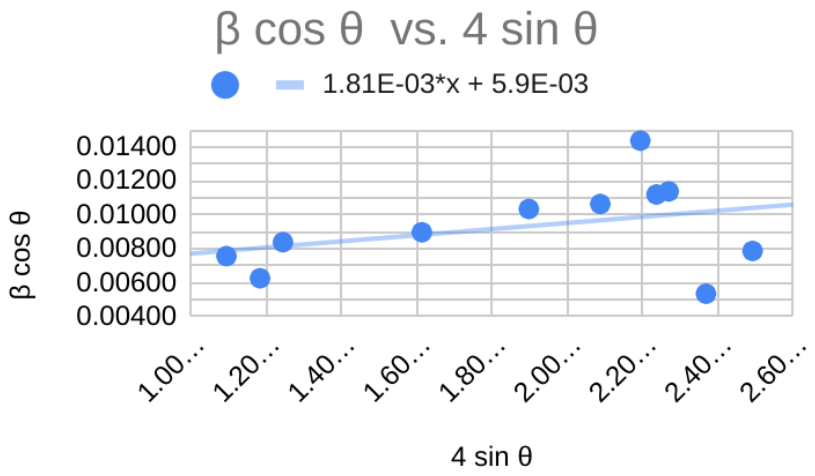
Average crystallite size d = 17.48162 nm

(c) Using Williamson-Hall Method

$$B_{total}cos\theta = 4\varepsilon sin\theta + \frac{K\lambda}{d}$$

S.No.	4 sin θ	βcos θ
1	1.09532	0.00756
2	1.18443	0.00626
3	1.24538	0.00838
4	1.61414	0.00897
5	1.89818	0.01034
6	2.08786	0.01063
7	2.19420	0.01436
8	2.23708	0.01119
9	2.26959	0.01137
10	2.36848	0.00535

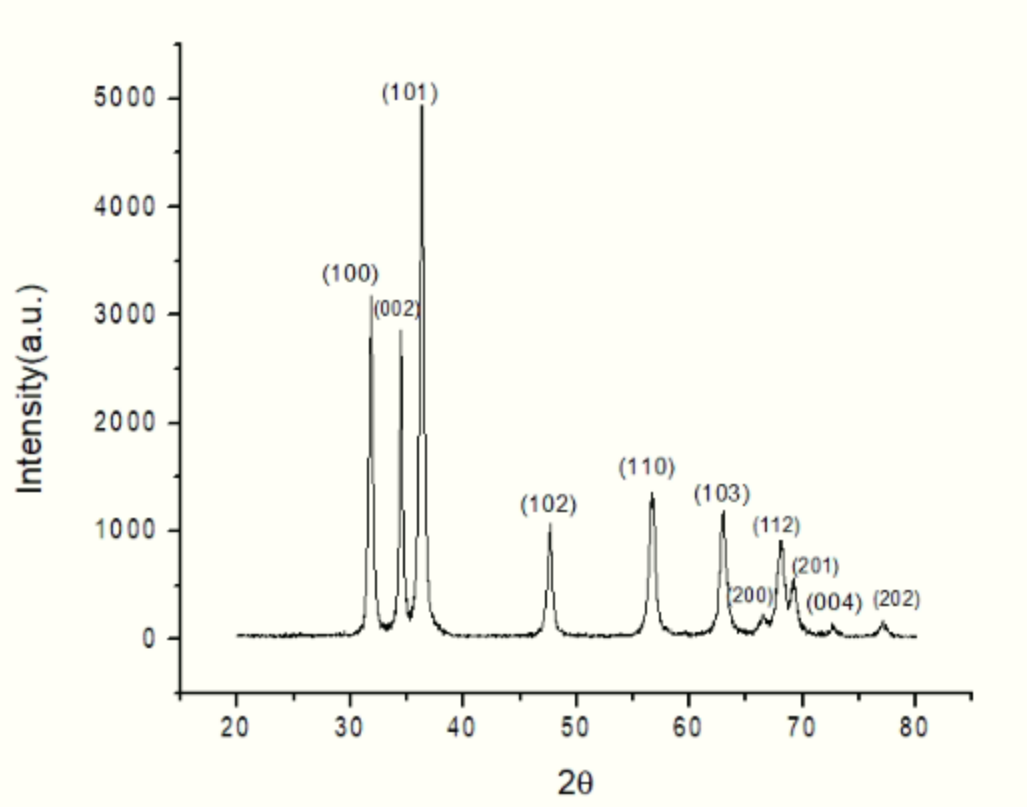
11	2.49217	0.00787



y-intercept = 0.005902 = $\frac{0.9\lambda}{d}$

d = 23.49155 nm

Case 3: Milling time = 12 hr



XRD Plot of milling ZnO powder for 12 hours.

(a) Using Debye Scherrer Formula

S.No.	Peak Position 2θ (°)	(hkl)	FWHM β (°)	d(nm)
1	31.80700	(100)	0.46371	17.81385
2	34.47250	(002)	0.38821	21.42612
3	36.30627	(101)	0.51338	16.28503
4	47.62394	(102)	0.56368	15.40496
5	56.67291	(110)	0.68907	13.09853
6	62.94126	(103)	0.72161	12.90774
7	66.59833	(200)	1.12354	8.45972
8	68.04763	(112)	0.77082	12.43511
9	69.16172	(201)	0.77171	12.50343
10	72.16869	(004)	0.85100	11.55136
11	77.05431	(202)	0.51751	19.62256

Average crystallite size d = 14.68258 nm

Lattice Parameters

For plane (100) $2\theta = 31.80701^{\circ}$

Bragg's Law: $2D \sin\theta = \lambda$ $\lambda = 0.15405$ nm

$$D = \frac{0.077025}{\sin 15.903}$$

Planar spacing $D = 2.81$ Å

And, using $\frac{1}{D^2} = \frac{4}{3}\frac{(h^2+k^2+hk)}{a^2} + \frac{l^2}{c^2}$

We get, $a = 3.24$ Å

Similarly, for plane (002) $2\theta = 34.4725$

Using Bragg's law $2D \sin\theta = \lambda$ $\lambda = 0.15405$ nm

$$D = \frac{0.077025}{\sin 17.236}$$

$D = 2.60$ Å

And, using $\frac{1}{D^2} = \frac{4}{3}\frac{(h^2+k^2+hk)}{a^2} + \frac{l^2}{c^2}$

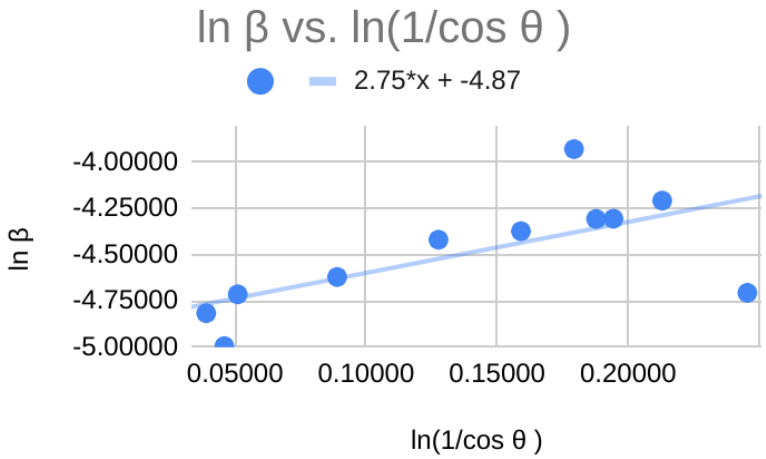
We get, $c = 5.2$ Å

Therefore, $\frac{c}{a} = 1.605$

(b) Using $ln(\beta) = ln(\frac{0.9\lambda}{d}) + ln(\frac{1}{cos\theta})$

S.No.	ln(1/cos θ)	ln β
1	0.03903	-4.81672
2	0.04595	-4.99444
3	0.05105	-4.71497
4	0.08897	-4.62150
5	0.12763	-4.42064
6	0.15910	-4.37450
7	0.17935	-3.93174
8	0.18777	-4.30853
9	0.19440	-4.30737
10	0.21301	-4.20957

11	0.24550	-4.70695



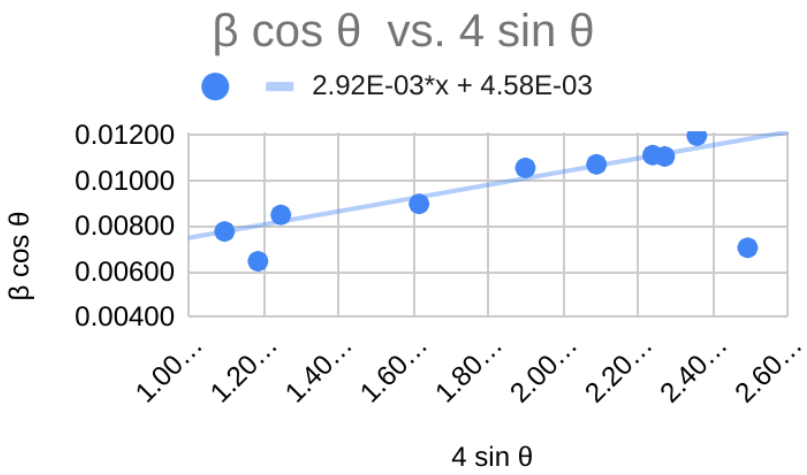
y-intercept = -4.87453 = $ln(\frac{0.9\lambda}{d})$

Average crystallite size d = 18.15149 nm

(c) Using Williamson-Hall Method

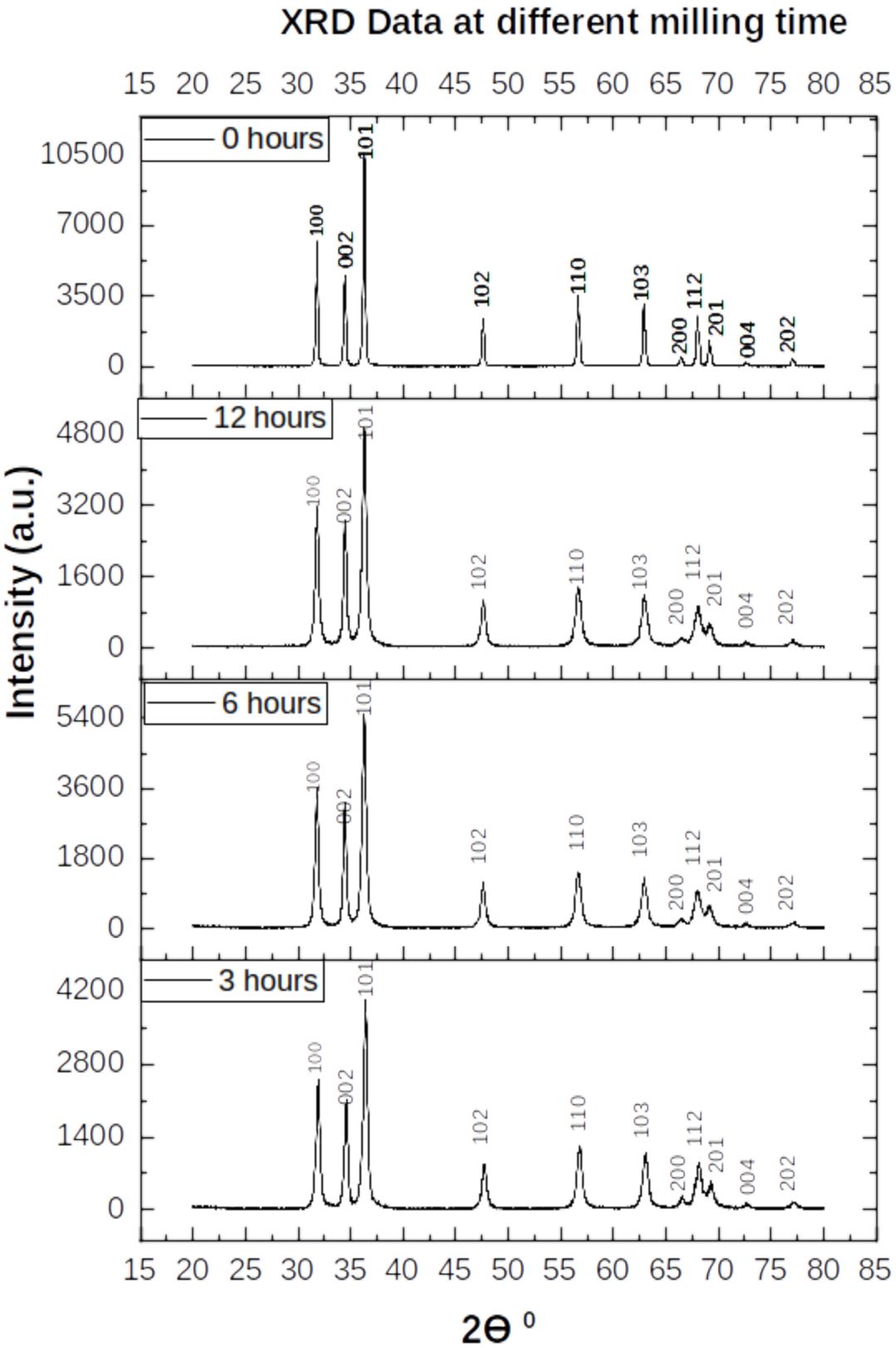
$$B_{total}cos\theta = 4\varepsilon sin\theta + \frac{K\lambda}{d}$$

S.No.	4 sin θ	βcos θ
1	1.09607	0.00778
2	1.18525	0.00647
3	1.24623	0.00851
4	1.61495	0.00900
5	1.89859	0.01059
6	2.08825	0.01074
7	2.19604	0.01639
8	2.23815	0.01115
9	2.27027	0.01109
10	2.35590	0.01200
11	2.49154	0.00707



y-intercept = 0.00458= $\frac{0.9\lambda}{d}$

Average crystallite size d = 30.27152 nm


XRD Data at different milling time
0 hours
12 hours
6 hours
3 hours
100
002
101
102
110
103
112
201
004
202
200
Intensity (a.u.)
2Θ 0

Result

Milling Time	d (nm)- using formula	d (nm) using graph	d (nm) using WH Method	a(A)	c (A)	c/a	Error in c/a Std c/a = 1.598
Precursor	**30.5878**	**34.0291**	**39.3171**	**3.24**	**5.20**	**1.605**	**0.7%**
3 hours	**17.5946**	**16.2647**	**16.4899**	**3.23**	**5.18**	**1.604**	**0.6%**
6 hours	**16.0659**	**17.4816**	**23.4916**	**3.24**	**5.20**	**1.605**	**0.7`%**
12 hours	**14.6826**	**18.1515**	**30.2715**	**3.24**	**5.20**	**1.605**	**0.7%**

Conclusion

- Pure ZnO nanoparticles are synthesised using Ball Milling technique and analysed through XRD.
- We found that the crystallite size of ZnO powder becomes half when it is ball milled for 3 hours and its size increases a little when milling time is increased. This can be due to agglomeration of nanoparticles because of increased contamination with time. The saturation limit is reached and further milling causes the contamination of particles.
- Crystallite size determined using the W-H equation is more than that determined from Scherrer formula as the former involves the effect of line broadening due to strain induced lattice deformation.
- c/a ratio remains constant is similar to the standard value for all ZnO nanoparticles milled at different times. This confirms the wurtzite hexagonal phase in prepared ZnO nanoparticles with no deformation in its structure.

Sources of Error

- Always clean your apparatus immediately after use. It is much easier to clean before the residues become dry and hard. The grinding jars, the grinding medium (i.e., balls) along with the spatula used to collect the sample should be very well cleaned with acetone before and after the milling, to avoid cross contamination.
- Gaseous impurities get into the powder during processing, storing, and handling if proper care is not taken. Finer the powders, contamination will be more because of the large powder surface area. Hence, the sample should be stored in airtight vials to avoid air-borne contamination.
- After the milling is completed, a rest time of about 15 minutes should be given before unclamping the jars to avoid heating outburst.

References:

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(4) C. Suryanarayana, Mechanical Alloying and milling, Progress in Materials Science 46 (2001) 1±184