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**DETERMINATION OF VARIOUS CRYSTALLITE
PARAMETERS FOR ZnO NANOPARTICLES WITH
VARIOUS COMPRESSION TEMPERATURES**

by

ZIA UDDIN

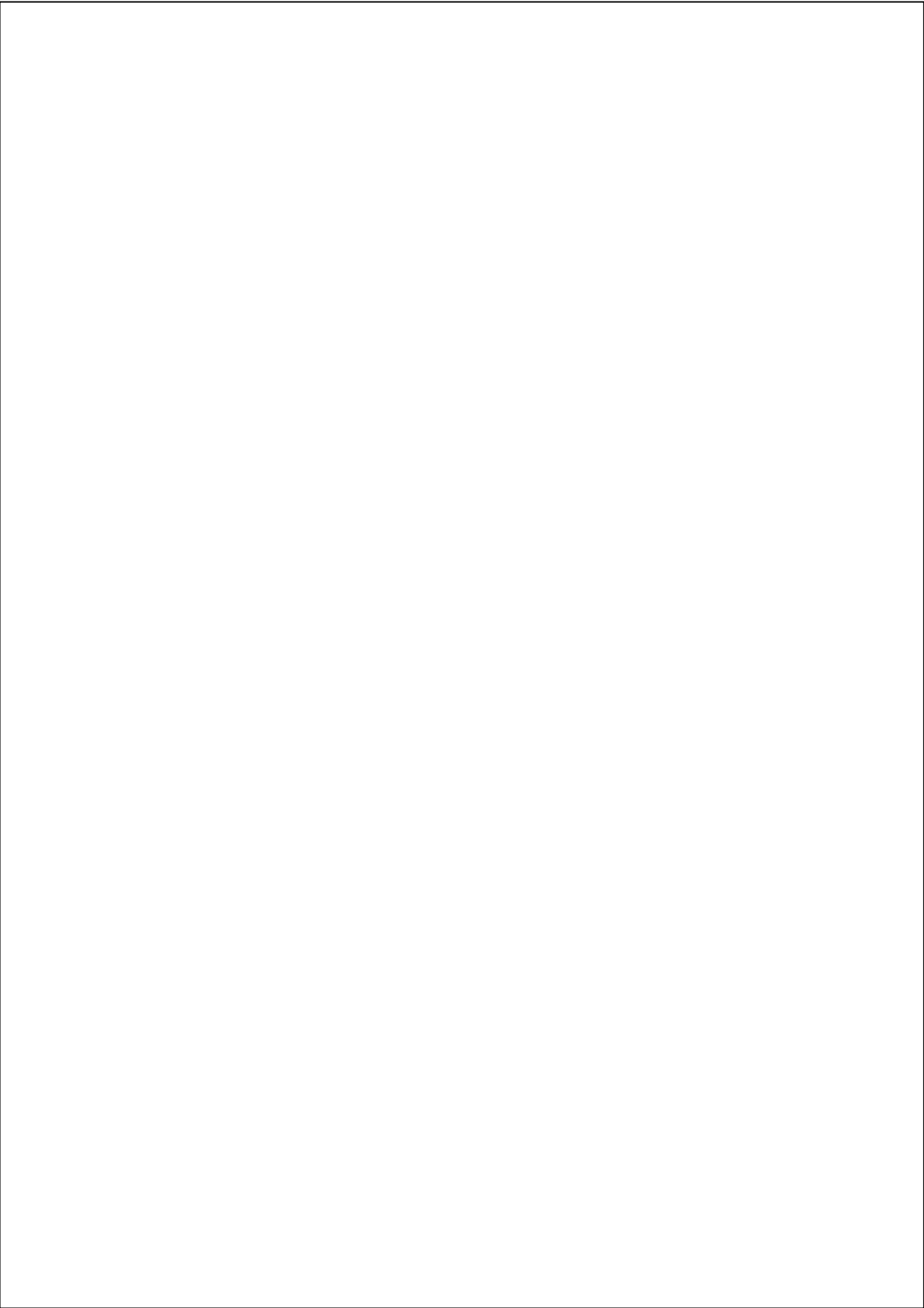
MOHAMMAD JABER UDDIN

¹⁴
**BACHELOR OF SCIENCE IN ELECTRICAL AND ELECTRONIC
ENGINEERING**



Department of Electrical and Electronic Engineering
INTERNATIONAL ISLAMIC UNIVERSITY CHITTAGONG

MAY 2021



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MOHAMMAD JABER UDDIN

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A thesis
submitted as partial fulfilment of the requirement for the degree of
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ELECTRONIC ENGINEERING**

Department of Electrical and Electronic Engineering
INTERNATIONAL ISLAMIC UNIVERSITY CHITTAGONG

MAY 2021

CERTIFICATE OF APPROVAL

The thesis entitled as “**Determination of various crystallite parameters for ZnO nanoparticles with various compression temperatures**” submitted by **Zia Uddin**, bearing Matric ID. **ET163014** and **Mohammad Jaber Uddin**, bearing Matric ID. **ET163021** of session **Spring 2020**, to the Department of Electrical and Electronic Engineering, International Islamic University Chittagong, has been accepted as satisfactory in partial fulfilment of the requirements for the degree of Bachelor of Science in Engineering and approved for the examination held on **28 May, 2021**.

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DECLARATION

It is hereby declared that this work has been done by us and no portion of the work contained in this thesis/project has been submitted elsewhere for the award of any degree or diploma.

Zia Uddin

Mohammad Jaber Uddin

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⁵
In the name of Allah, the Most Gracious and the Most Merciful
Alhamdulillah, all praises and gratitude to the Allah for the strengths and His blessing
in completing this thesis. his thesis has been kept on track and been seen through to
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Authors

ABSTRACT

In this work, ZnO films were made utilizing the standard blade coating procedure at different compression temperatures (50 to 90 °C temperature at 120 MPa compression). The films were characterized using X-ray Diffraction (XRD) techniques. For advanced material characterization, the XRD method is a very powerful state-of-the-art technology. It allows accurate information on crystalline phase structure, crystal orientations (shape and size), and other structural or crystallite parameters such as lattice parameters, stresses, strains, crystallite size, and crystal defects. The XRD data has been analysed using different methods, such as the Modified Scherrer method, Wagner-Agua method (W-A), Halder-Wagner method (H-W), Size-Strain Plot (SSP) method, and the Williamson-Hall (W-H) method. The results were compared to observe the effects of compression temperatures on various crystallite parameters. From the analysis, it is evident that ZnO nanoparticles are crystallite in nature with a hexagonal wurtzite phase. The crystallite size calculated from the SSP and W-A Method matches very well with the crystallite size observed in the Scherrer method and slightly different from the W-H method. The crystallite size is relatively high for the films prepared at 70 °C temperature at 120 MPa pressure for all methods. Moreover, the modified W-H methods were used to determine different elastic parameters. In terms of strain computation, it is significantly lower than the value of other methods. This increase in estimated strain value of the SSP, H-W and W-A methods is actually because of the contribution of low and mid angle XRD data as well as the attribution of lattice dislocations. Among all the methods, the SSP and W-A methods are more accurate and more favoured since the points fit the linear line much better than in any other techniques. However, changes in various crystallite properties caused by various annealing temperature at 120 MPa pressure are also utilized to explain the performance of the Dye-sensitized solar cells. The photovoltaic performance of the sample at 70 °C temperature compression was shown to be better where the crystallite size was relatively large.

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LIST OF ABBREVIATIONS

XPPA	X-ray Peak Profile Analysis
NP	Nanoparticle
ZnO	Zinc Oxide
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
EPR	Electron Spin Resonance
FTIR	Fourier Transform Infrared Spectroscopy
XRD	X-ray Diffraction
PEN	Polyethylene naphthalate
DSCs	Plastic dye-sensitized solar cells
T	°C temperature
MPa	Mega pascal
UDM	Uniform Deformation Model
USDM	Uniform Stress Deformation Model
UEDM	Uniform Deformation Energy Density Model
SSP	Size-Strain Plot
H-W	Halder-wagner
W-A	Wagner-agua
LED	Light Emitting Devices
DLS	Dynamic Light Scattering

CHAPTER 1

INTRODUCTION

1.1 Introduction

Materials science and engineering have been the term used to describe the general branch of engineering dealing with materials since the 1960s. In that this field is a true combination of fundamental scientific studies and practical engineering, this designation is accurate. Many modern areas, such as metallurgy, ceramic engineering, polymer chemistry, condensed matter physics, and physical chemistry, have contributed to it [1].

The development of essentially new materials is needed for progress in all areas of technology, including metallurgy, machine construction, instrument design, electrical engineering, and electronics [2].

Because of the high surface-to-volume ratio, nanoscale materials also have different properties than their bulk counterparts, resulting in an exponential increase in reactivity at the molecular level. Electronic, optical, and chemical properties are among them, although the mechanical characteristics of nanoparticles (NPs) can also vary greatly [3]. Because of their academic interest and the potential technical applications in different fields, they can be the subject of intense research. A variety of methods, including mechanical, chemical, and other pathways, can be used to create such nanostructures [4].

Nanoparticles are particles with a one-dimensional scale of less than 100 nanometres. As nanoparticles are used to create traditional materials, their properties change. While a bulk material's physical properties should remain constant regardless of its size, size-dependent properties are often observed at the nanoscale. As a result, as a material's size reaches the nanoscale and the percentage of atoms on its surface begins to become important [5], its properties typically change.

There has recently been a lot of interest in the preparation, characterization, and application of semiconductor nanoparticles, which are essential in a lot of new technologies. Because of their large surface area or quantum size effect, when semiconductor materials are reduced to the nanoscale, their physical and chemical properties change dramatically, resulting in unique properties. The semiconductor's conductivity as well as its optical properties (absorption coefficient and refractive index) can be modified. Semiconductor nanomaterials and devices are still in the research

stage, but they have the potential to be used in a wide range of fields, including solar cells, nanoscale electronic devices, light-emitting diodes, laser technology, waveguide, chemical and biosensors, packaging films, super absorbents, armour, automobile parts, and catalysts.

Many types of diodes, including light-emitting diodes, silicon controlled rectifiers, and digital and analog integrated circuits, would benefit significantly from further advancements in nanotechnology. Semiconductor nanomaterials such as Si, Si-Ge, GaAs, AlGaAs, InP, InGaAs, GaN, AlGaIn, SiC, ZnS, ZnSe, AlInGaP, CdSe, CdS, and HgCdTe, among others, have a wide range of applications in computers, palm pilots, laptops, cell phones, pagers, CD players, TV remotes, mobile terminals, satellite dishes, fiber networks, traffic signals, car taillights, and air bags.

Semiconductor nanocrystals (NCs) are made from a wide range of materials. Based on the periodic table groups into which these elements are formed, they are referred to as II-VI, III-V, or IV-VI semiconductor nanocrystals. For eg, silicon and germanium relate to group IV, while GaN, GaP, GaAs, InP, and InAs relate to group III-V, and ZnO, ZnS, CdS, CdSe, and CdTe relate to group II-VI [6]. Because of the potential application in optoelectronic devices in both the visible and UV regions, such as light emitting diodes (LEDs) and laser diodes, wide band gap semiconductors, such as GaN, ZnO, InN, and AlN, have gained more interest among semiconductor materials. Zinc oxide (ZnO) is a wide band gap semiconductor that has been extensively studied due to its fundamental and technological importance. Its high exciton binding energy (60 meV) may lead to lasing action based on exciton recombination even above room temperature. It has a high band gap energy (3.37 eV), a large exciton binding energy, and excellent chemical stability; all of these properties indicate that it has a wide range of practical applications, including gas sensors, ceramics, field-emission instruments, and luminescent materials [7–9,10]. At room temperature and higher temperatures, ZnO's large exciton binding energy allows for extreme near-band-edge excitonic emission [11]. Because of its ferromagnetic activity at room temperature when doped with transition metals, ZnO has recently gained interest for spintronic applications [12].

ZnO has many fundamental advantages over its chief competitor, GaN: (1) its free exciton has a binding energy of 60 meV, which is much higher than GaN's (21–25 meV); (2) it has a native substrate; (3) wet chemical processing is possible; and (4) it is more resistant to radiation damage (although both are much better than Si or GaAs) [13]. It also has a high electron mobility in its undoped state, as well as excellent thermal

conductivity and transparency. The material's thermal stability allows for high temperature activity, and its high band gap ensures a wide breakdown field. As a result, ZnO is an excellent material for electronic devices that need a great deal of power and operate at high temperatures.

ZnO nanoparticles are usually white powders that are almost insoluble in water.

Plastics, ceramics, glass, asphalt, rubber (e.g. automotive tires), lubricants, paints, ointments, adhesives, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, fire retardants, and other materials and products all use the powder as an ingredient. While ZnO is found naturally in the Earth's crust as the mineral zincite, the majority of ZnO used commercially is synthesized. ZnO is nontoxic and skin-friendly, making it an ideal additive for textiles and surfaces that come into contact with people. The increased surface area of nanoscale ZnO over bulk ZnO has the potential to improve material function efficiency.

Chemical vapor process, spray pyrolysis, laser synthesis techniques, chemical precipitation, sol gel, and vapor condensation method are all methods that can be used to make oxide nanoparticles like ZnO NP. The vapor condensation approach has been considered the most attractive of these techniques due to its robust and efficient control of nanoparticle shape and size without the need for expensive and complex equipment. It's also crucial and characterizes the particles to make sure they're nanoscale. The word "characterization" is used in material science to describe the broad and general processes used to investigate a material's properties and structure. For a scientific understanding of the content, this basic process is needed. Mechanical testing, thermal analysis, and density measurement are all examples of characterization methods used to investigate material properties and microscopic structures. Newer and more modern methods are increasingly being developed to complement the centuries-old characterization techniques. Characterization helps in identifying the composition and structure of materials, as well as determining whether or not the process was effective. Some methods are qualitative some are quantitative.

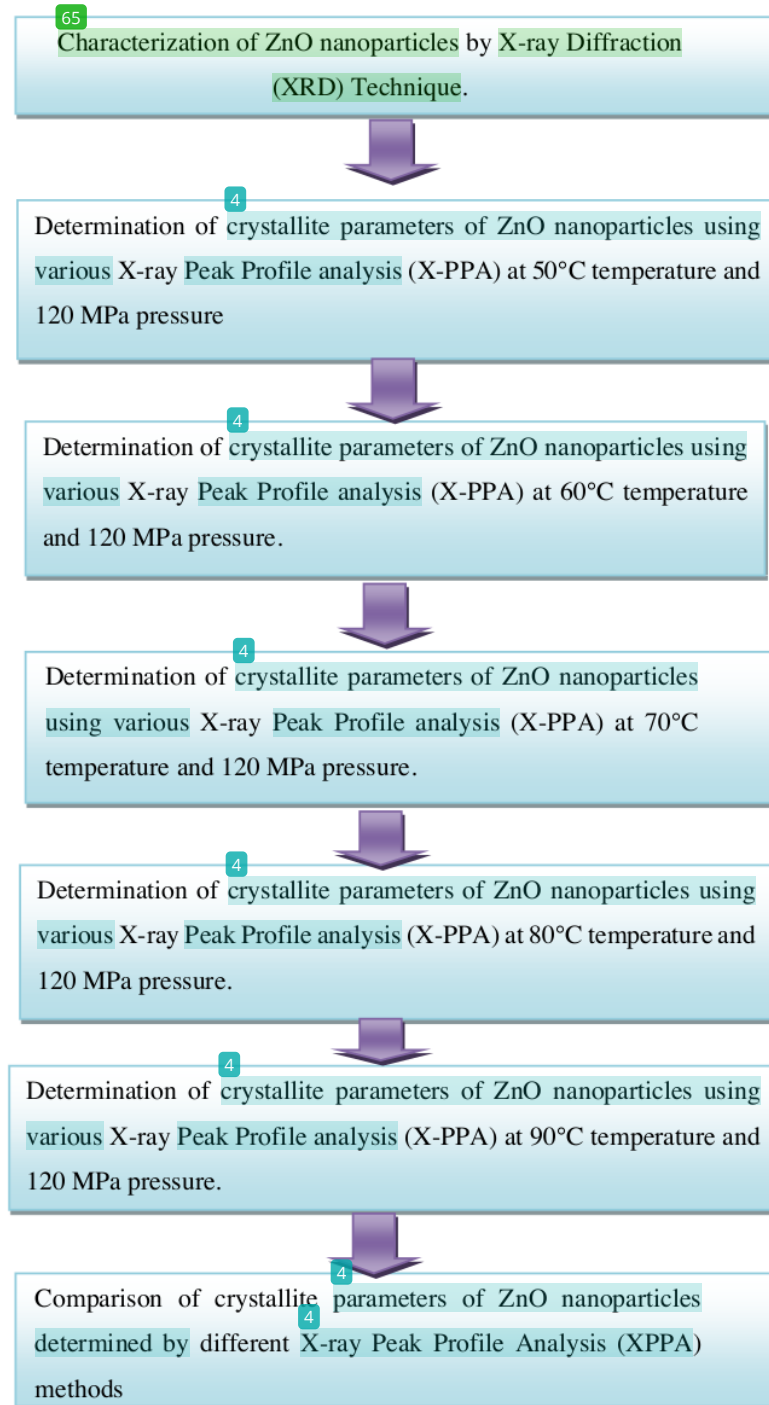
There are a variety of material characterization techniques available, such as Scanning electron microscope (SEM) analysis, energy dispersive X-ray analysis (EDX), transmission electron microscope (TEM) analysis, scanning tunnelling microscopy (STM), atomic force microscopy (AFM), Raman spectroscopy, ultraviolet-visible spectrometry (UV-vis), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), dynamic light scattering (DLS), X-ray diffraction

(XRD), and zeta potential analysis offer more advantages to observe submicron-sized materials. One of the most widely used methods for characterizing NPs is X-ray diffraction (XRD). XRD is used to determine the crystalline structure, phase nature, lattice parameters, and crystalline grain size. XRD methods, which are widely used in powder form after drying their corresponding colloidal solutions, have the advantage of producing statistically representative, volume-averaged values [14].

1.2 Objectives

- Characterization of ZnO nanoparticles by X-ray Diffraction (XRD) Technique.
- Detail study of different X-ray Peak Profile Analysis (XPPA) methods i.e. modified Scherrer Formula, Williamson-Hall Method (UDM, USDM and UDEDM), Size-Strain Plot (SSP) Method, Halder-Wagner Method and Wagner-Agua Method at different annealing temperature i.e. 50°C temperature, 60°C temperature, 70°C temperature, 80°C temperature and 90°C temperature and 120 MPa pressure.
- Determination of crystallite parameters of ZnO nanoparticles using different X-ray Peak Profile Analysis (XPPA) methods i.e. modified Scherrer Formula, Williamson-Hall Method (UDM, USDM and UDEDM), Size-Strain Plot (SSP) Method, Halder-Wagner Method and Wagner-Agua Method at different annealing temperature i.e. 50°C temperature, 60°C temperature, 70°C temperature, 80°C temperature and 90°C temperature and 120 MPa pressure.
- Observation the effect of various compression temperatures on different crystallite parameters such as crystal size, lattice strain, stress, energy density etc.
- Comparison of Geometrical parameters of ZnO nanoparticles determined by different X-ray Peak Profile Analysis (XPPA) methods.

1.3 Outline of this work



1.4 Thesis Layout

- The thesis is organized by six different chapters.
- Chapter one provides a general introduction and objectives of this study.
- Chapter two discusses about literature review, introduction of ZnO, the underlying theories and fundamental properties of ZnO. It also explains different application of ZnO. A summary of different material characterization techniques is also presented in this chapter.
- Chapter three gives a brief description of the X-ray Diffraction (XRD) techniques.
- Chapter four provides the exploration of experimental work and methodology conducted to estimate the value of different parameters.
- Chapter five presents analysis of the results obtained and compared different crystallite parameters of ZnO films at different annealing temperature.
- Chapter six provides the summary according to the finding of this study. In addition, some limitations and suggestion for future researchers also discuss there

LITERATURE REVIEW

2.1 Introduction

The wide band-gap of semiconductor nanomaterials has attracted considerable attention. Because of its physical-chemical properties, such as mechanical, electrical, optical, magnetic, and chemical sensing properties, zinc oxide is a versatile material among these different semiconductors oxide nanomaterials. It has a 3.5 eV wide band gap. UV light emitters, spin functional devices, gas sensors, transparent electronics, and surface acoustic wave devices are some of the applications. It is also used in the biomedical field.

Nanoparticles are significant research materials for biotechnology and pharmacology applications. They connect the fields of bulk materials and molecular structures. While the physical properties of bulk materials remain constant regardless of size, the physical and chemical properties of nanoparticles are determined by their size. As a material's size approaches nanoscale proportions and the percentage of atoms at the surface of a material becomes important, its properties change [15].

Because of its semiconducting properties, ZnO plays an important role in electronics, making it a promising candidate for optoelectronic device fabrication. ZnO thin films have a structure that exhibits high conductivity, high carrier mobility, chemical stability, and visible transparency. It's both non-toxic and environmentally friendly, and it's made out of inexpensive materials. They include high exciton binding energy, the ability to develop high-quality single crystal substrate at a low cost, and crystal growth that is simple. ZnO materials based dye sensitized solar cells have been developed and have achieved high efficiency in solar cell technology due to the properties such as high transparency and conductivity. Because of their chemical and thermal stability, ZnO-based solar cells are expected to be a viable substitute for Si-based solar cells. This oxide has recently gained a lot of interest in the scientific community as a "future substance."

For the synthesis of ZnO nanomaterials, various synthesis techniques are used, including bottom-up approaches such as sol-gel, chemical precipitation, and top-down ball milling. Precipitation produces a high-quality, high-purity nano powder. The characterization of ZnO nanoparticles was carried out in this analysis, and the particle size was calculated using the XRD technique.

2.2 Nanoparticles

Nanoparticles are particles with a single dimension of less than 100 nanometers. As nanoparticles are used to make traditional materials, their properties change. This is usually due to the fact that nanoparticles have a higher surface area per weight than larger particles, making them more reactive to other molecules. Nanoparticles are used in a variety of fields, or are being investigated for use in a variety of fields.

Nanoparticles are of considerable interest to scientists because they act as a contact between bulk materials and atomic or molecular structures. The physical properties of a bulk material should remain constant regardless of its size, but size-dependent properties are often observed at the nanoscale. As a result, as the size of a material reaches the Nano scale and the percentage of atoms on its surface begins to become important, the properties of the material change. The percentage of atoms at the surface of bulk materials greater than one micrometer (or micron) is negligible as compared to the total number of atoms in the material. Since nanoparticles are small enough to confine their electrons and create quantum effects, they frequently have unexpected optical properties. Quantum confinement in semiconductor particles, surface Plasmon resonance in certain metal particles, and superparamagnetism in magnetic materials are all size-dependent property changes [16].

2.2.1 Characteristics of nanoparticles

- A bulk material should have constant physical properties regardless of size, but size-dependent properties are frequently observed at the Nanoscale. As a result, as a material's size reaches the Nano scale and the percentage of atoms on its surface becomes important, its properties change.
- The percentage of atoms at the surface of bulk materials greater than one micrometer (or micron) is negligible as compared to the total number of atoms in the substance. The broad surface area of the material, which dominates the contributions of the small bulk of the material, is thus primarily responsible for the interesting and often unexpected properties of nanoparticles.
- Nanoparticles of usually yellow gold and gray silicon are red in color; gold nanoparticles melt at much lower temperatures (nearly 300° C for 2.5 nm size) than gold slabs (1064° C); and solar radiation absorption in photovoltaic cells is much higher in materials composed of nanoparticles than in thin films of continuous sheets of material; and the smaller the particles, the greater the so-called absorption coefficient.

- Nanoparticle suspensions are possible so the particle surface's contact with the solvent is high enough to overcome density differences, which would otherwise cause a material to sink or coat in a liquid.
- Because nanoparticles are small enough to confine their electrons and create quantum effects, they frequently have unexpected optical properties. In solution, gold nanoparticles, for example, appear deep red to black.
- Nanoparticles have a large surface area to volume ratio, which provides a powerful driving force for diffusion, especially at high temperatures.
- Furthermore, nanoparticles have been discovered to add additional properties to a variety of everyday materials. The presence of titanium dioxide nanoparticles, for example, causes a self-cleaning effect, and since the particles are so small, they cannot be seen. As compared to its bulk substitute, zinc oxide particles have been found to have better UV blocking properties. This is one of the reasons why it is commonly used in the formulation of sunscreen lotions, because it is totally photosensitive.

2.2.2 Benefits of nanoparticles

The Benefits of using nanoparticles include the following:

- Because of the ability to produce different intensities of colors in solutions by adjusting the thickness of the nanoshell, the aspect ratio, and the percentage of gold, nanoparticles are widely used in bioimaging applications. For example, a 20-nm gold solution produces a wine red color, whereas a 20-nm platinum solution produces a yellowish-gray color [17].
- They monitor and maintain drug release during transportation and at the site of localization, affecting drug organ delivery and subsequent clearance in order to improve drug therapeutic effectiveness while reducing side effects.
- Gold nanoparticles, for example, have the benefit of melting at lower temperatures (300 °C for 2.5 nm size) than their bulkier equivalents (gold slabs melt at 1064 °C) [18].
- Targeting ligands may be attached to the surface of particles, or magnetic guidance can be used to achieve site-specific targeting.
- Oral, nasal, parenteral, intraocular, and other routes of administration are possible with the system.
- It may come as a surprise, but the rubber industry uses more than half of the Zinc Oxide produced. In the vulcanization of rubber, ZnO is combined with stearic acid to create tires, shoe soles, and even hockey pucks.

- Antibacterial and deodorizing properties are also found in zinc oxide. As a result, it's used in medicinal products like baby powder and creams to treat things like diaper rash, other skin irritations, and even dandruff. It is also used in sunblocks and can be seen on the nose and lips of lifeguards at the beach due to its reflective properties.

2.2.3 Constraints of nanoparticles

In spite of these Benefits, nanoparticles do have Constraints.

- Because of the small size and wide surface area, nanoparticles may clump together, causing physical handling difficult in both liquid and dry types.
- Besides that, due to the small particle size and large surface area, drug loading and burst release are easily reached.
- Until nanoparticles can be made commercially accessible, these functional issues must be resolved. The current analysis examines the most recent advances in nanoparticulate drug delivery systems, as well as surface modification problems, drug loading methods, release control, and nanoparticle applications.
- When their size is in the micrometre range, they appear on the skin as an opaque white film, causing customers to be hesitant to use sunscreens that contain them. These oxides, on the other hand, are transparent and do not show up on the skin when used as nanoparticles (NPs), but they maintain or even improve their UV-sunscreening properties [19].

2.3 Zinc oxide

Zinc oxide, also known as zincite, is an inorganic compound that only occurs in nature in crystalline form. It's a widely known semiconductor in our modern practice. Owing to the presence of manganese impurity, it is typically orange or red in color [20]. It usually takes the form of a white crystalline powder that is nearly water insoluble. Synthetically produced ZnO contributes for the majority of commercial ZnO. The semiconductor group II-VI includes ZnO, which is a large bandgap semiconductor. Because of oxygen vacancies, the semiconductor is doped n-type. High electron mobility, excellent transparency, large bandgap for semiconductivity, high room-temperature luminescence, and so on are all advantages of this material. These characteristics are used in electrodes for liquid crystal displays, energy-saving and heat-protecting windows, electronic applications of ZnO such as thin-film transistors and light emitting diodes, and ceramics plastic. The wurtzite structure of zinc oxide (ZnO) is stable, with lattice spacing of $a = 0.325$ nanometers and $c = 0.521$ nanometers. It's used in transparent electronics, ultraviolet (UV) light emitters, piezoelectric

devices, and chemical sensors because of its special properties and applications. The synthesis, characterization, and device applications of ZnO nanomaterials have received considerable attention due to their remarkable physical properties, which have sparked interest in device miniaturization.

2.3.1 Structure of the crystal

Hexagonal wurtzite and cubic zincblende are the two major types of zinc oxide crystallization. At ambient temperatures, the wurtzite structure is the most stable and therefore the most common. By growing ZnO on substrates with a cubic lattice structure, the zincblende shape can be stabilized. The zinc and oxide centres are tetrahedral in both cases, which is the most common geometry for Zn (II). At moderately high pressures of about 10 GPa, ZnO converts to the rocksalt motif. There is no inversion symmetry in hexagonal and zincblende polymorphs (reflection of a crystal relative to any given point does not transform it into itself). Piezoelectricity of hexagonal and zincblende ZnO, as well as pyroelectricity of hexagonal ZnO, are caused by this and other lattice symmetry properties.

The lattice constants are $a = 3.25$ and $c = 5.2$, with a ratio of $c/a = 1.60$, which is similar to the optimal value of $c/a = 1.633$ for hexagonal cells. The bonding in ZnO is mostly ionic ($\text{Zn}^{2+}-\text{O}^{2-}$), as it is in most group II–VI materials, with radii of 0.074 nm for Zn^{2+} and 0.140 nm for O^{2-} . This property explains why wurtzite rather than zinc blende structure forms preferentially, as well as ZnO's high piezoelectricity. Zinc and oxygen planes are electrically charged due to the polar Zn-O bonds. In most relative materials, certain planes rebuild at the atomic level to preserve electrical neutrality, but not in ZnO, whose surfaces are atomically smooth, stable, and show no reconstruction. This ZnO anomaly is not perfectly known. In addition to the origin of charges on ZnO planes, experiments using wurtzite structures explained the origin of surface flatness and the absence of reconstruction at ZnO wurtzite surfaces [20].

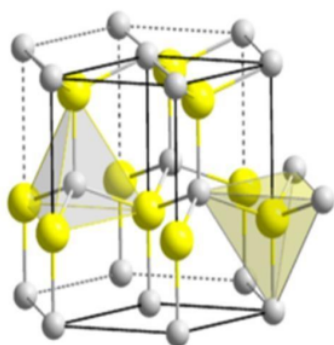


Fig. 2.1 Wurtzite structure of zinc oxide [21]

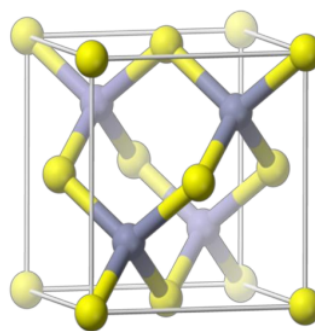


Fig. 2.2 Zinc cube blende [21]

2.3.2 Physical characteristics

Some physical characteristics of ZnO are ¹³³summarized in Table 2.1 [22].

Table 2.1 Physical parameters of ZnO

Physical parameters	¹⁰⁰ Values
Stable phase at 300 K	Wurtzite
Lattice parameters in nm at 300 K	
a	0.32495
c	0.52069
c/a	1.602 (ideal hexagonal structure shows 1.63)
u	0.345
Energy band gap (eV)	3.37, direct
Density (g/cm ³)	5.606
Refractive index	2.008–2.029
⁴⁹ Melting point (°C)	¹⁹⁷⁵
Thermal conductivity (W/K.cm)	^{0.6–1.2}
⁴⁰ Exciton binding energy (meV)	60
Electron effective mass (m _o)	0.24
Electron Hall mobility at 300 K for low n-type conductivity (cm ² /Vs)	200

⁴⁹ Linear expansion coefficient (/°C)	a: 6.5×10^{-6} and c: 3.0×10^{-6}
Static dielectric constant	8.656
⁹⁰ Hole effective mass (m_0)	0.59
Hole Hall mobility at 300 K for low p-type conductivity (cm^2/Vs)	5–50
⁵ Intrinsic carrier concentration	$<106 \text{ cm}^{-3}$ (max n-type doping) $>1020 \text{ cm}^{-3}$ electrons; max p-type doping $<1017 \text{ cm}^{-3}$ holes)

The free electron mass is denoted by the symbol m_0 .⁹³ Energy band gap, excitons binding energy, electron effective mass, hole effective mass, hole hall mobility, and lattice parameter are some of the physical parameters that are simple and easy to understand. It should also be remembered that some of these data are still subject to uncertainty. Since there are few records of p-type ZnO, the hole mobility and effective mass are still up for discussion.⁴⁰ Similarly, the values for thermal conductivity indicate a wide range of values, which may be due to defects such as dislocations.

⁴¹ 2.3.3 Mechanical Properties

ZnO is a relatively soft material, with a hardness of just 4.5. Its elastic constants are lower than those of other III-V semiconductors such as GaN. ZnO has a high heat ability and conductivity, low thermal expansion coefficients, and high melting points, to mention a few characteristics.⁷ Because of its higher exciton binding energy (60 meV),⁷ ZnO has been proposed as a more promising UV emitting phosphor than GaN. The maximum piezoelectric tensor is found in ZnO among the tetrahedrally bonded semiconductors. This makes it a crucial material for a wide range of piezoelectric applications that involve a high degree of electromechanical coupling.⁶⁷ As the loading of synthesized ZnO nanoparticles is increased, the deformation is reduced. The mechanical properties such as Hardness, tensile strength, 100 percent and 300 percent modulus, tear strength, and elongation at break are all enhanced without compromising other properties⁵⁷ [23]. A Cure Characteristics and Mechanical Properties of ZnO nano-

particles as Activator in Unfilled Natural Rubber, Rudeerat Suntakol.

2.3.4 Piezoelectric effect and polar surfaces

The piezoelectricity of ZnO has been extensively investigated for applications such as force sensing, acoustic wave resonator, and acousto-optic modulator, among others. The origin of piezoelectricity is due to its crystal structure, which has tetrahedrally bound oxygen and zinc atoms. In such a structure which is non-centrosymmetric, the centre of positive charge and negative charge can be displaced due to external pressure induced lattice distortion. This displacement results in local dipole moments; thus, a macroscopic dipole moment appears over the entire crystal. In fact, among the tetrahedrally bonded semiconductors, ZnO has the highest tensor which provides a large electro-mechanical coupling [24]. The spontaneous polarization and polar face dominated nanostructures are another consequence of the non-centrosymmetric ZnO crystal structure. The crystal structure of ZnO can be visualized as a tetrahedral bond between oxygen and zinc atoms. These tetrahedrons are stacked in a specific direction. The location of positive charge is displaced from that of negative charge in that set particular direction due to the effect of random polarization. A charged ZnO surface is the end product of this random polarization. The charged surface produces a specific nano-ring and nano-coil structure in order to minimize energy.

2.3.5 Electrical properties

Fundamental research into the electrical properties of ZnO nanostructures is critical for future nanoelectronics applications. At room temperature, ZnO has a wide band gap of 3.3 eV. Higher breakdown voltages, the ability to withstand massive electric fields, and high-temperature and high-power operations are all benefits of a large band gap. In the absence of doping, ZnO has an n-type character. The most common source of n-type character is non-stoichiometry. ZnO nano-wires are said to exhibit n-type semiconductor behaviour due to defects such as oxygen vacancies and zinc interstitial. The complexity of p-type doping is the biggest barrier to ZnO being used in a wide range of applications in electronics and photonics. ZnO nanostructures with effective p-type doping will have a lot more applications in nano scale electronics and optoelectronics in the future. P-n junction diodes and light emitting diodes (LED) can be made from P-type and n-type ZnO nano wires [25].

2.3.6 Optical properties

In the visible and near ultraviolet ranges of the spectrum, ZnO is a wide band gap semiconductor with high optical transparency and Luminescence. As a result, it's often used in light-emitting diodes and solar cells. The exciton binding energy of ZnO nanoparticles is approximately 60 meV. This means that the excitonic transition in ZnO nanoparticles will occur at room temperature as well. Furthermore, zinc oxide is both environmentally friendly and simple to synthesize [26]. Zinc oxide is transparent to visible light but absorbs intensely ultraviolet light below 3655 Å. White pigments absorb more light than other white pigments. Standard zinc oxide appears white in the visible wavelength range. The band gap energy (between the valence and conducting bands) is 3.2 eV, which is equivalent to 3655 Å photons of energy. Zinc oxide is photoconductive when exposed to ultra violet radiation. Doped zinc oxide is a candidate for new generations of devices because of its optical and semiconductor properties. Solar cells need a clear conductive coating, and the best materials are indium tin oxide and zinc oxide (doped).

ZnO nanostructures' intrinsic optical properties are being investigated intensively that can be used in photonic devices. ZnO nano-structures' photo-luminescence (PL) spectra have been extensively studied [27]. The photo-luminescence spectra of ZnO nano-rods have revealed excitonic emissions. Quantum size confinement has been shown to increase the exciton binding energy significantly. There is a strong emission peak at 380 nm due to a band-to-band transition, as well as a green-yellow emission band due to oxygen vacancy. ZnO nano-wire is a promising material for UV emission, according to PL spectra, but its UV lasing property is of greater importance and interest. ZnO nano-wire/nano-rod is a natural candidate for optical wave-guide due to its near-cylindrical geometry and high refractive index (2.0). The excitonic recombination lowers the lasing threshold, and quantum confinement yields a significant density of states at the band edges and improves radiative efficiency, which are both advantages of ZnO nano-wire lasers. The use of dielectric nano-wires to direct optical waves has also made significant progress. ZnO nano-wires have recently been identified as a sub-wavelength optical wave-guide. ZnO nano-wire driven optically pumped light emission and was coupled into SnO₂ nano-ribbon. These results suggest that ZnO nanostructures may be important aspects in integrated optoelectronic circuits.

2.3.7 Chemical properties

ZnO has the following chemical properties [28]:

- ZnO is found in the mineral zincite and as zinc white, a white powder. Due to manganese impurity, it is typically orange or red in colour.
- Crystalline zinc oxide is thermochromic, when heated, crystalline zinc oxide changes color from white to yellow, and returns to white when cooled. At high temperatures, a slight loss of oxygen causes this color shift.
- Zinc oxide is amphoteric, meaning it reacts with acids as well as alkalis. It reacts with acid to form zinc sulphate, which is a well-known compound. Zincates are formed when alkali is added.
$$\text{ZnO} + 2 \text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2\text{O} \quad \text{ZnO} + 2 \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2(\text{Zn}(\text{OH})_4)$$
- At around 1975 °C, ZnO decomposes to zinc vapor and oxygen, suggesting its high stability. ZnO is converted to Zn, which is more volatile, when heated with carbon.
$$\text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO}$$
- The following reaction is extremely important in zinc pyrometallurgy-
$$\text{ZnO} + \text{CO} \rightarrow \text{Zn} + \text{CO}_2$$
- Water solubility of commercial zinc oxide is 0.005g/litre, which is measurable but poor.

2.3.8 Applications of ZnO

The inorganic compound zinc oxide (ZnO) has the formula ZnO. It comes as a white powder that is water insoluble. The mineral zincite contains ZnO, which can be found in the Earth's crust. However, the majority of commercially available ZnO is synthetic. Zinc oxide is a common ingredient in medical ointments for treating skin irritations. Zinc oxide has recently found applications in semiconductors, concrete, ceramic and glass compositions, and even cigarette filters [29]. ZnO's property has its own collection of applications. ZnO's large band gap allows it to form clusters of ZnO nano-crystals and ZnO nano-wires. Synthesis of P-N homojunctions has also been documented in some literatures due to the large band gap. Many fine optical devices can be fabricated using ZnO's 60 meV free-exciton binding energy, because such ZnO's large exciton binding energy allows it to persist at room temperature and higher temperatures. Non-linear optical devices can be made with ZnO crystals and thin films because they show second- and third-order non-linear optical behavior. In general, the ability to tune the physical properties of these oxides, such as zinc oxide, becomes the driving force behind

the creation of smart application devices [30]. The electrical, optical, magnetic, and chemical properties of cations with mixed valence states and anions with deficiencies can be fine-tuned by permuting and combining their two basic structural characteristics (vacancies). The numerous applications of ZnO are summarized in Fig. 2.3.

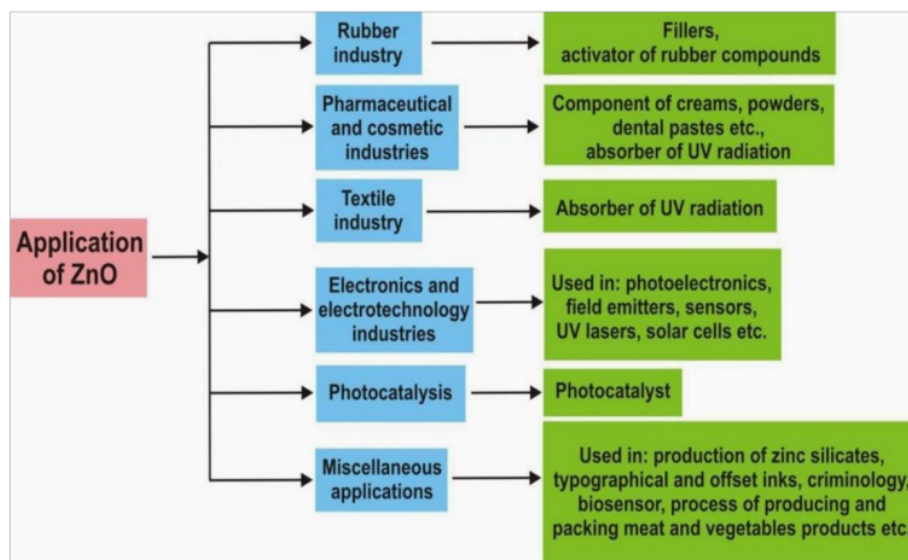


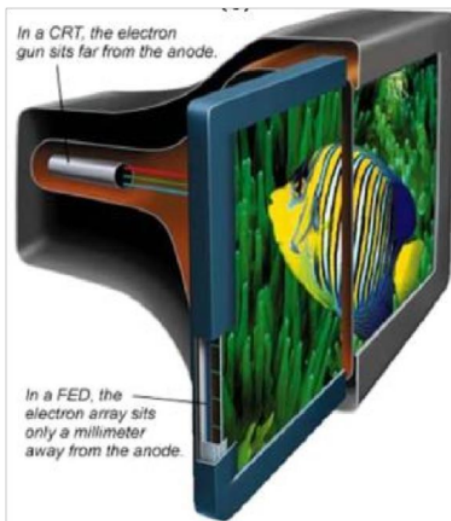
Fig. 2.3 ZnO applications are represented in schematic form [30]



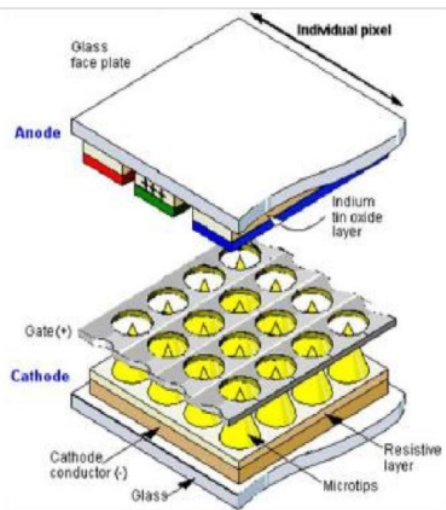
(a)



(b)



(c)



(d)

Fig. 2.4 Pictorials of some applications of ZnO (a) pure green and blue LEDs (b) Cathode Ray Tube (c) TV and (d) Solar cells [30]

2.3.9 ZnO Nanostructures with Morphology Control.

Nanostructured materials are a type of material with dimensions ranging from 1 to 100 nanometers. Because of the increased performance of the materials, this property has the most possible applications. Among all known materials, ZnO offers a wide range of particle structure variations. ZnO can be found in three different dimensions: one-dimensional (1-D), two-dimensional (2-D), and three-dimensional (3-D). Nano-rods, needles, rings, ribbons, tubes, belts, cables, and combs are examples of one-dimensional nano-structures, which make up the largest category of all. Zinc oxide is available in two-dimensional forms such as nano-plates, nano-sheets, and nano-pellets. Many solution-based chemical methods have often included a calcination step as the final step in the synthesis of hierarchical porous ZnO micro-/nano-structures.

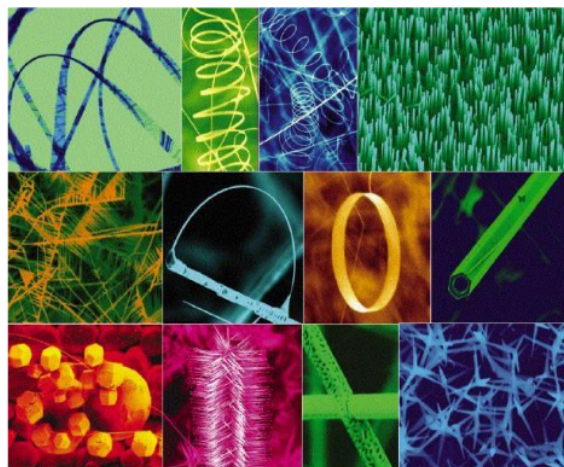


Fig. 2.5 Various nanostructures of ZnO [30].

2.4 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is an effective non-destructive method for determining the properties of crystalline materials. It shows crystal structure, phase, preferred crystal orientation (texture), and other structural parameters including average grain size, crystallinity, strain, and crystal defects. Constructive interference of a monochromatic X-ray beam diffracted at specific angles from each set of lattice planes in a sample produces X-ray diffraction peaks. The distribution of atoms within the lattice is what determines the peak intensities. As a result, the fingerprint of periodic atomic arrangements in a given material is the X-ray diffraction pattern. The phase detection of

a wide range of X-ray diffraction patterns is possible using the ICDD (International Centre for Diffraction Data) data base.

The Schematic diagram of X-ray Diffraction (XRD) technique is shown in Fig. 2.6.

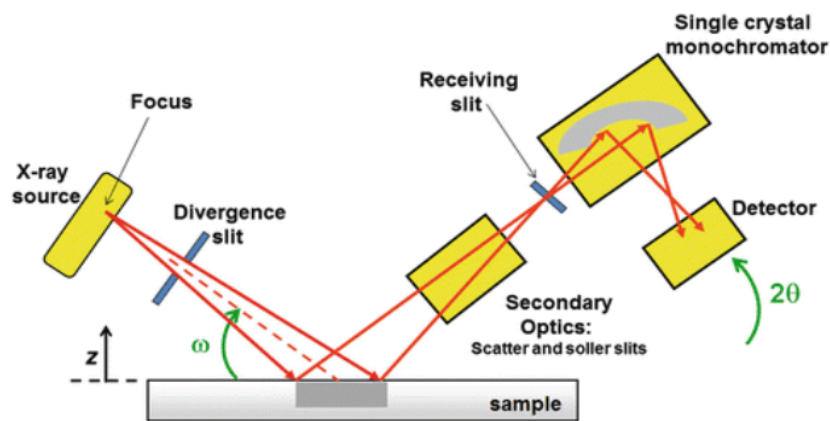


Fig. 2.6 X-ray Diffraction (XRD) technique schematic diagram [31]

This approach is crucial because, similar to how fingerprints can be used to identify a person, diffraction data can be used to identify a substance. The atomic arrangements of the material are determined using XRD patterns. It can also be used to differentiate between crystalline and nanocrystalline materials. The structural analysis is carried out by comparing the X-ray diffraction pattern analysis to an internationally recognized database (JCPDs).

CHAPTER 3

76

X-RAY DIFFRACTION (XRD)

3.1 Introduction

X-ray diffraction (XRD) is a non-destructive technique for analyzing a wide range of materials, including fluids, powders, and crystals. X-ray powder diffraction (XRD) is a rapid analytical technique that can provide information on unit cell dimensions and is mainly used for phase identification of crystalline materials. XRD is an indispensable method for materials characterization and quality control, from research to manufacturing and engineering.

X-ray diffraction techniques are used to identify crystalline phases in a variety of materials, as well as to perform quantitative phase analysis after the identification. In elucidating the three-dimensional atomic structure of crystalline solids, X-ray diffraction techniques are superior. Materials' properties and functions are primarily determined by their crystal structures. As a result, X-ray diffraction techniques have become an indispensable tool in materials research, development, and production [32].

3.2 X-ray (XRD) Diffraction's Historical Background

Wilhelm Conrad Röntgen, a physics professor at the University of Würzburg in Germany, discovered X-ray in 1895, allowing scientists and researchers to investigate the structure of crystals. During the interwar period, due to the importance of radiotherapy in the marketplace, much work had gone into calculating dose, or the strength of x-ray radiation. Physicists were more concerned with the wavelength of x-rays. When x-rays impinged on and were diffracted by a crystal, they generated interference patterns, and historical accounts sometimes assert that the 1912 x-ray diffraction experiment proved beyond a reasonable doubt that x-rays are electromagnetic waves. However, the proof was demonstrated using both models of x-rays: EM radiation and the bunched-up, particle-like theory by Max von Laue, who was awarded the Nobel Prize for the discovery. Crystallographers were beginning to believe in the space-lattice-like structure of crystals at the same time, which von Laue explored with his friend Paul Peter Ewald. In one conversation, Ewald revealed that if the approximate wavelengths were right, the spacing between lattice points might be a reasonable distance for causing X-ray interference [33]. At the same time as the diffraction spots were caused by X-rays impinging on a normal array of scatters, in this case, the repeating arrangement of atoms

within the crystal, ¹⁰⁷ Von Laue's experiment provided evidence for the wave existence of X-rays and the space lattice of crystals. The scatters resulted in a constant series of spherical waves that interfered destructively in most directions, but constructively in others, resulting in bright spots on the photographic plate [34]. ⁸ The Braggs, father and son, were the ones who focused on x-rays as a crystallographic instrument, ultimately concluding that they were electromagnetic waves. Their findings confirmed that x-rays had an atomic-scale wavelength, 1000 times smaller than visible light, allowing them to interact with lattices and yield details about crystal structure that visible light could never provide. This was the first instrument to produce photographs from which solid-state atomic structures could be inferred, and it was widely used in the twentieth century. ⁸ The Braggs were effective in defining very simple structures like rock salt (NaCl) [35]. In addition, studies of the intensities of x-rays reflected by crystals confirmed Niels Bohr's atomic model and a hypothesis of chemical bonding. The Braggs published a highly influential textbook on x-rays and crystal structure, educated a large number of people, and built a large collaborative network. ⁸

However, progressing from simple to more complex structures was difficult due to the difficulty of inferring the structure of matter from x-ray data. In the 1920s, inorganic chemistry molecules were studied, and in the 1930s, Desmond Bernal and coworkers, including Dorothy Crowfoot (later Hodgkin), determined the structure of sterols. ⁸ Other biologically interesting molecules, such as penicillin and vitamin B12, were also determined in the following decades. X-ray research has always necessitated a great deal of effort and imagination [35]. ⁸

Structure determination by X-ray techniques, however, does not yield a clear path from experimental data to structure even today [1964]. In difficult situations, the scientist can only come up with a solution after putting in a lot of mental effort, which includes chemical awareness, creativity, and intuition. Furthermore, experimental data is often subjected to a variety of mathematical treatments, which must be tailored to the situation. Add in the fact that the more complex the structure, the larger the amount of experimental data that must be collected and processed. ⁸ It was possible to do the calculations with a pencil and paper for relatively simple compounds. Electronic computers are almost always needed nowadays, and their introduction has significantly improved the ability to perform structure determinations [35]. However, it is not always possible to simply feed in the experimental data and get the figures that provide the final structure; the scientist's ability to manage the data remains crucial.

⁸ Other life science sub-fields, such as virology, introduced X-ray analysis techniques in the 1930s, when ⁸ crystalline forms of plant viruses were being prepared, making xray analysis possible. Crick and Watson concluded in 1956 that a small virus comprises similar subunits that are ⁸ packed together in a normal pattern. ¹⁰⁹ During the same time period, they worked on the structure of DNA, for which they and Maurice Wilkins were awarded the Nobel Prize in 1962. Rosalind Franklin, who died in 1958, was famously overlooked ⁸ for her contribution to DNA analysis, but historians have since made amends [35].

⁹⁶ 3.3 Bragg's Law

X-ray powder diffraction (XRD) is a flexible, non-destructive, simple, and analytical technique for determining the phase of crystalline materials. The Bragg's law [36] is the fundamental principle underlying the diffraction method of structural analysis.

⁴⁸ The basic principle behind Bragg's Law is that when it is satisfied, X-ray beams dispersed from successive planes in the crystal (as shown) can travel distances varying by exactly one wavelength (for $n=1$); this can be proven reasonably easily from a geometrical consideration of the above diagram. When X-rays scattered from successive planes meet the X-ray detector in this particular direction, i.e. at the angle determined by Bragg's Law, they will interact constructively, registering the passing of an extreme beam called the diffracted beam. Of course, it's the atoms with their electronic clouds that disperse the X-rays, not the planes in the crystal (since planes are abstract mathematical objects). However, Bragg's concept of comparing atoms to planes proved to be a significant simplification of the topic, and as a result, we still refer to individual diffracted beams as being "reflected" from specific "planes," despite the fact that we now know that it is the atoms who perform the scattering. We don't need to know much more about planes at this stage, but if you're curious, click here [37].

⁷⁷ Crystals' atoms interact with X-rays in such a way that interference results. ⁵ The interaction can be compared to the waves being reflected by the atoms in a crystal structure. The reflections, however, arise from the atomic planes since a crystal structure is made up of an ordered arrangement of atoms. Consider a monochromatic X-ray beam ⁴⁶ that enters a crystal with one of its planes angled at an angle of [38] to the incoming beam. Two such X-rays are shown in Figure 3.1, where the spacing between the atomic planes occurs over the width, d .

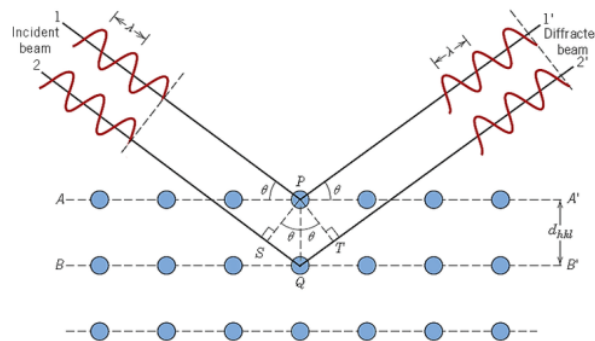


Fig. 3.1 X-rays that are monochromatic and enter a crystal [43]

Ray A reflects at an angle equal to its angle of incidence off the upper atomic plane. Ray B, on the other hand, reflects at the same angle off the lower atomic plane. Ray B, on the other hand, moves a distance of $2a$ further in the crystal than Ray A. Rays A and B will be in phase when they leave the crystal if the distance $2a$ is equal to an integral number of wavelengths (n), and positive interference will occur. If $2a$ is not an integral number of wavelengths, disruptive interference will occur, and the waves will be weaker than when they first reached the crystal. Thus, the condition for constructive interference to occur is

$$n\lambda = 2a$$

However, using trigonometry, we can calculate the distance $2a$ between the atomic planes in terms of the spacing d .

$$a = d \sin \theta$$

$$\text{or, } 2a = 2d \sin \theta$$

$$\text{Thus, } n\lambda = 2d \sin \theta$$

This is known as **Bragg's Law** for X-ray diffraction [43].

It states that if we know the wavelength, λ , of the X-rays entering the crystal and can determine the angle, θ , of the diffracted X-rays exiting the crystal, we can calculate the spacing (d -spacing) between the atomic planes.

3.4 X-ray Powder Diffraction Fundamental Principles (XRD)

In 1912, Max von Laue discovered that crystalline substances function as three-dimensional diffraction gratings for X-ray wavelengths that are close to plane spacing

in a crystal lattice. The technique of X-ray diffraction is now widely used to research crystal structures and atomic spacing.

Compounds may be classified using a database of diffraction patterns since most materials have special diffraction patterns. The purity of a sample, as well as the composition of any impurities present, can be determined using its diffraction pattern. A diffraction pattern can also be used to assess and refine a crystal structure's lattice parameters. The Rietveld refinement method can be used to refine a theoretical structure. The Scherrer formula, which relates particle size to peak width [39], can also be used to calculate the powder particle size. Constructive interference of monochromatic X-rays and a crystalline sample is the basis of X-ray diffraction. A cathode ray tube produces the X-rays, which are then filtered to produce monochromatic radiation, collimated to focus the beam, and guided at the sample. When Bragg's Law ($n\lambda = 2d \sin\theta$) is satisfied, positive interference (and a diffracted ray) results from the interaction of incident rays with the sample. The wavelength of electromagnetic radiation is related to the diffraction angle and lattice spacing in a crystalline sample by this law. The observed, processed, and counted diffracted X-rays are then analyzed. Due to the random orientation of the powdered material, scanning the sample across a range of 2 angles should yield all possible diffraction directions of the lattice. Since each mineral has its own collection of d-spacings, converting the diffraction peaks to d-spacings allows the mineral to be identified. This is usually accomplished by comparing d-spacings to normal reference patterns [40]. The generation of X-rays in an X-ray tube is the basis of all diffraction methods. The diffracted rays are obtained after these X-rays are guided at the sample. The angle between the incident and diffracted rays is a significant factor in all diffraction [40]. Beyond that, the instrumentation for powder and single crystal diffraction varies.

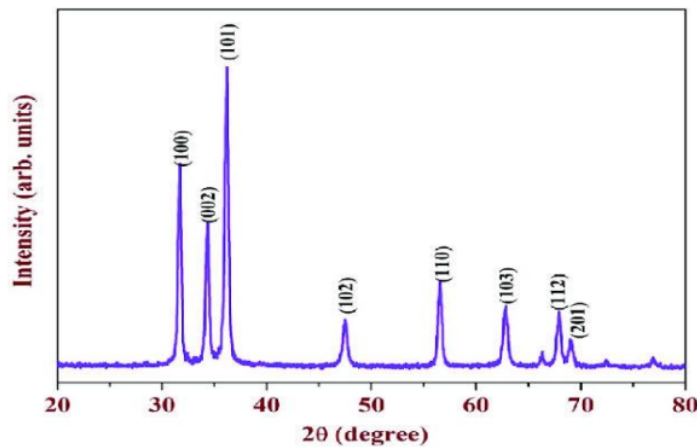


Fig. 3.2 Typical ZnO nano-particles XRD spectrum [44]

3.5 The X-ray Diffraction (XRD) machine's working theory

An X-ray tube, a sample holder, and an X-ray detector are the three basic components of an X-ray diffractometer. In a cathode ray tube, X-rays are generated by heating a filament to create electrons, then applying a voltage to accelerate the electrons toward a target and bombarding the target material with electrons. Characteristic X-ray spectra are formed when electrons have enough energy to dislodge inner shell electrons of the target material [40]. These spectra are made up of several elements, the most common of which is K_α and K_β . K_α consists, in part, of $K_{\alpha 1}$ and $K_{\alpha 2}$. $K_{\alpha 1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha 2}$. The wavelengths used are specific to the target material (Cu, Fe, Mo, Cr). Filtering, either with foils or crystal monochromators, is necessary to obtain monochromatic X-rays for diffraction. Because the wavelengths of $K_{\alpha 1}$ and $K_{\alpha 2}$ are sufficiently close, a weighted average of the two is used. $\text{CuK}\alpha$ radiation = $1.5418 \text{ \AA}$ makes copper the most common target material for single-crystal diffraction. These X-rays are collimated before being aimed at the sample. The strength of the reflected X-rays is recorded as the sample and detectors are rotated. Constructive interference occurs when the geometry of the incident X-rays impinging on the sample follows the Bragg Equation, resulting in a peak in intensity. This X-ray signal is recorded and processed by a detector, which then converts the signal to a count rate, which is then sent to a system like a printer or computer monitor [41].

An X-ray diffractometer's geometry is such that the sample rotates at an angle θ in the direction of the collimated X-ray beam, while the X-ray detector is placed on an arm

that rotates at an angle of 2θ to absorb the diffracted X-rays. A goniometer is an instrument that is used to maintain the angle and rotate the sample.



Fig. 3.3 An X-ray diffraction machine in practice.

3.6 The Benefits of XRD

The Benefits of XRD are summarized below [42]:

- Because air does not absorb X-rays very well, the specimen does not need to be in an evacuated chamber.
- In the vast majority of instances, it provides a comprehensive mineral identification.
- There is very little sample preparation needed.
- XRD equipment is widely available.
- It's a quick and effective method for determining the identity of unknown minerals and materials.
- It only necessitates the preparation of a small sample for analysis.
- The data is reasonably simple to interpret once it has been collected.
- Instruments for XRD estimation are widely available.

3.7 XRD's limitations

XRD technique has the following limitation [42]:

- If the crystal sample is not isometric, measuring unit cells can be difficult.
- Peak overlay will happen, and it gets worse for high-angle reflections.
- Lighter elements do not have a good interaction with them.
- The sample should be homogeneous in order to better distinguish an unknown powder content.
- XRD analysis usually necessitates the use of standard reference data.
- Grinding samples to a powder is a common requirement for sample preparation.
- It is limited in scale. XRD readings often miss small structures that are only present in trace quantities, resulting in distorted findings.

3.8 XRD Technique Application

- To determine how a specific material system is formed.
- Unit cell structure, lattice parameters, and miller indices will be investigated.
- Determine the types of phases in the material.
- Determination of the sample's crystalline and amorphous material.
- To assess average crystallite size, strain, or micro-strain effects in bulk and thin-film materials.
- Researching structural and thermal distortions.

CHAPTER 4

EXPERIMENTAL AND METHODOLOGY

4.1 Introduction

One of the most widely used techniques for creating thin films on broad surfaces is doctor blade (or tape casting). Tape casting is a relatively recent process that was developed in the 1940's as a way of shaping thin sheets of piezoelectric materials and capacitors [43] and is now a widely used precision coating technique. One patent, granted in 1952, concerns the use of aqueous and non-aqueous slurries by a doctor blading system on moving piaster batts [44]. A well-mixed slurry containing a suspension of ceramic particles as well as other additives (such as binders, dispersants, or plasticizers) is mounted on a substrate beyond the doctor blade in the doctor blading method. The slurry spreads on the substrate to form a thin film, which dries to form a gel-layer when a constant relative movement is formed between the blade and the substrate. The doctor blading can cover substrates with a wide range of wet film thicknesses ranging from 20 to several hundred microns and can work at speeds up to several meters per minute.

4.2 Experimental investigation

4.2.1 Film preparation

ZnO films were made in this experiment using the traditional blade coating process. ZnO nanoparticles (100 nm, purchased from Sigma Aldrich, which are off-white to tan in color and have a pH value of 6-9) and ethanol (99.5 percent) or (0.1 gm/ml) were used to make the blade coating paste. The homogenizer was used to distribute the solution for five minutes. An ultrasonic vibrator was used to clean the substrates in acetone and methanol, respectively. The substrates were then dried with nitrogen gas flow and treated for 20 minutes in a UV-ozone chamber. Using polyimide tape as a frame and spacer, the paste was coated (doctor blade coating) onto the ITO (Indium tin oxide) coated PEN (Polyethylene naphthalate) substrates (15 Ω /square). For one hour, all of the samples were air dried at room temperature. After that, the film was compressed (using the Mini TEST Press-10) at different compression pressures varying from 90 to 150 MPa. There was a tendency for ZnO nanoparticles to peel away from the substrate due to compression. ZnO film photoanodes were compressed at 120 MPa with annealing temperatures ranging from 50°C to 90°C to solve the problem.

4.2.2 Film characterization

Our supervisor, Dr. Md. Shamimul Haque Choudhury, conducted XRD during his Master's program in Japan using an XRD method (Rigaku RINT 2100 diffractometer). A Cu target has been added to the scheme. The X-ray tube voltage and current were set to 40 kV and 30 mA, respectively, and a Ni-filtered Cu Ka radiation of $\lambda = 1.5408 \text{ \AA}$ was used.

Modified Scherrer Method, Modified Williamson-Hall (W-H) models, Size-Strain Plot (SSP), Halder-Wagner (H-W) Method, and Wagner-Agua Method were all used to characterize the XRD properties.

4.3 Methodology

4.3.1 Modified Scherrer Method

4.3.1.1 Introduction

The average size of nano crystallites in nano crystalline bulk materials can be determined using X-ray diffraction. In 1981, Paul Scherrer, the first scientist, published his findings in a paper that included the Scherrer equation [45].

This is because "crystallite size" is not the same as "particle size," and X-Ray diffraction is sensitive to the crystallite size inside the particles. From the well-known Scherrer formula the average crystallite size, D , is:

$$D = \frac{K\lambda}{\beta_{hkl} \cos \theta} \quad (4.1)$$

where λ is the X-ray wavelength in nanometer (nm), β_{hkl} is the peak width of the diffraction peak profile at half maximum height resulting from small crystallite size in radians and K is a constant related to crystallite shape, normally taken as 0.9. The value of β_{hkl} in 2θ axis of diffraction profile must be in radians. The θ can be in degrees or radians, since the $\cos \theta$ corresponds to the same number;

$$\cos \frac{\pi}{4} = \cos 45^\circ = \frac{\sqrt{2}}{2} \quad (4.2)$$

For spherical crystals with cubic unit cells, it can be taken as 0.89 or 0.9 for Full Width Half Maximum (FWHM). The paper "Scherrer after sixty years" published in 1978 [46] is a good reference for a good discussion of K .

The integrated width of the pure profile (β) is isolated from that of the observed diffraction profile (B) in a traditional approximation [47], assuming that both profiles are Gaussian or Cauchy.

In the case of Cauchy $B = b + \beta$, where b is the instrument profile width, $B^2 = b^2 + \beta^2$ if Gaussian profile is accepted. If the pure profile broadens due to both crystallite size and lattice strain, another statement must be made about the shapes of the two contributing line profiles. Normally, these are either Gaussian or both Cauchy, in which case $B^2 = B_m^2 + B_n^2$ or $B = B_m + B_n$ are used. B_m is the line width resulting from small crystallite size, and B_n is the line broadening due to the lattice strain. Then we have [48]:

$$\varepsilon = \frac{B_n}{4. \tan \theta} \quad (4.3)$$

$$\text{Strain} = \text{Change in size} / \text{Original size} \quad (4.4)$$

The Cauchy function is commonly thought to be fairly well approximated, while the Gaussian function yielded significantly greater errors. To distinguish between the size and strain contributions:

$$B = \frac{\lambda}{D \cos \theta} + 4. \varepsilon \tan \theta \quad (4.5)$$

Two diffraction peaks must be used to measure two unknown parameters D and ε in the case of crystallite size and lattice pressure.

When there is no mechanical activation such as ball milling or mechanical alloying, or the crystallite size is due to nucleation and growth at high temperatures, we must only be concerned with corrections for instrumental profile width when considering the Scherrer equation with obtained value of

If crystals are smaller than 1000 Å or 100 nm, the Scherrer equation predicts crystallite thickness. The easiest way to get the Scherrer equation is to use the Bragg's Law derivation, $\lambda = 2d \sin \theta$.

Allowing the diffraction angle to broaden from a sharp diffraction peak from an infinite single crystal with perfect 3-dimensional order while keeping the wavelength λ constant. Diffraction from a group of planes separated by d^* occurs at a specific θ^* for a single crystal, resulting in $\lambda = 2d^* \sin \theta^*$.

Diffraction from a large number of tiny crystals deviates $\pm \Delta \theta$ from θ^* for many small nano crystals.

This corresponds to $2\Delta \theta$ on the diffraction pattern's 2θ axis. The value of corresponds to the FWHM or β_{hkl} value, which is roughly half of $2\Delta \theta$. To put it another way, because $\Delta \theta$ can be positive or negative, the absolute value must be used, and it represents the half width of the shape line deviation in 2θ axes (full width at half

maximum height, β_{hkl}). $\lambda = 2\Delta d \cdot \cos\theta \cdot \Delta\theta$, is the derivative in d and θ of Bragg's Law with constant λ .

The thickness $\Delta d = D$ can be taken as;

$$D = \Delta d = \frac{\lambda}{2\cos\theta \cdot \Delta\theta} = \frac{\lambda}{\cos\theta \cdot \beta_{hkl}} \quad (4.6)$$

By applying a shape factor K , which is near the value of unit (0.9), the Scherrer equation can be given as:

$$D = \frac{0.9\lambda}{\beta_{hkl}\cos\theta} \quad (4.7)$$

The derivation method is taken by Alexander in Klug and Alexander "X-ray Diffraction" [49] to explain the Scherrer equation. It is also easily adoptable to define the dependency of any two terms in the Bragg equation in terms of variability. Grainy patterns can be analyzed in terms of a statistical analysis to grain size for crystals longer than 1000 Å (100 nm), but this is rarely done because grain size can be determined more easily in this size range from optical or electron microscopy studies.

4.3.1.2 Modified Scherrer Equation

If a particular nano crystal has N different peaks in the range of $0-180^\circ$ (2θ) or $0-90^\circ$ (θ), it is presumed that all of these N peaks have the same D value for the crystal scale. However, during the first author's extensive research on various nano ceramic crystals that were synthesized or minerally obtained, it was surprising to discover that each peak yields a different value and that the results obtained from each peak are subject to systematic error.

The existence of a systematic error in Scherrer's formula was confirmed after further investigation. In fact since $D = \frac{K\lambda}{\beta_{hkl}\cos\theta}$, if D is going to be a fixed value for different peaks of a substance, considering that K and λ and therefore $K\lambda$ are fixed values, then it is essential that $\beta_{hkl}\cos\theta$ be a fixed multiple during $0 < 2\theta < 180^\circ$ or $0 < \theta < 90^\circ$. Suppose that for a crystallite size of 5nm, obtained at a peak of say $2\theta = 10^\circ$ ($\theta = 5^\circ$) by using $K = 0.89$ and

$\lambda = 0.15405$ nm. Then β_{10° must be,

$$\beta_{10^\circ} = \frac{0.89 \times 0.15405}{5 \cos 5^\circ} = 0.0275(\text{rad}) = 1.576^\circ \quad (4.8)$$

Now, suppose that the N th peak of this nano crystal occurs at $2\theta = 170^\circ$ (or $\theta = 85^\circ$), then;

$$\mathcal{B}_{170^\circ} = \frac{0.89 \times 0.15405}{5 \cos 85^\circ} = 0.3146(\text{rad}) = 18.03^\circ \quad (4.9)$$

This means that the ratio of $18.03^\circ/1.576=11.44$ must be applied for $\mathcal{B}_{170^\circ}/\mathcal{B}_{10^\circ}$. In other words, if the first peak has a β_{10° of about 2 mm on a computer display, or a paper plot 21 cm wide on A4 paper, the last peak must have a β_{170° of more than 22.88 mm and a peak base of more than 45.76 mm (4.576 cm).

This has never been confirmed and thus cannot be accurate. The modified Scherrer formula is based on the idea that we can reduce errors and obtain the average value of D by using the least squares method to mathematically reduce the source of errors over all peaks (or any number of peaks).

The basic Scherrer formula can be written as:

$$\mathcal{B} = \frac{K \lambda}{D \cos \theta} = \frac{K \lambda}{D} \cdot \frac{1}{\cos \theta} \quad (4.10)$$

Now by making logarithm on both sides;

$$\ln \mathcal{B}_{hkl} = \ln \frac{K \lambda}{D \cos \theta} = \ln \frac{K \lambda}{D} + \ln \frac{1}{\cos \theta} \quad (4.11)$$

If we plot the $\ln \beta$ results against $\ln(1/\cos \theta)$, we should get a straight line with a slope of around one and an intercept of around $\ln K/D$. Since $\tan 45^\circ = 1$ in theory, this straight line must have a 45-degree slope (Fig. 4.1). The least squares method, however, gives the best slope and most reliable $\ln K/L$ since errors are correlated with experimental results. The exponential of the intercept is obtained after obtaining the intercept:

$$e^{\ln \frac{K \lambda}{D}} = \frac{K \lambda}{D} \quad (4.12)$$

Having $K = 0.9$ and λ (such as $\lambda = 0.15405$ nm), a single value of D in nanometer can be calculated [49].

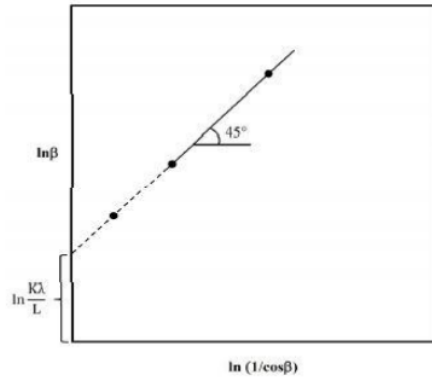


Fig. 4.1: Modified scherrer equation plot [49].

4.3.2 Williamson-Hall method (1953)

4.3.2.1 Introduction

The Williamson-Hall system, which was developed in 1953, has been used for the past five decades. The plots caused by strain were highlighted by W-H plots. The peak width derived from crystallite size differs from $1/\cos\theta$, while the strain differs from $\tan\theta$. This difference in behavior as a function of 2θ allows us to distinguish between the effects of strain and size on peak expansion. When the width of peaks as a function of 2θ was studied by Williamson-Hall, deconvoluted sizes and strain-induced expansion were used to simplify integral breadth approaches [50], [51].

However, the peak expansion was used in the size-strain method and the Williamson-Hall method to calculate the size of crystallite and strain in ceramics. For each XRD reflection peak consistent with the compound step in chosen ranges in XRD, physical parameters such as strain values were calculated using the W-H plot and SSP (size-strain plot) approaches. There are three modified W-H models [52]. They are:

- Uniform deformation model (UDM)
- Uniform Stress Deformation Model (USDM)
- Uniform Deformation Energy Density Model (UEDM)

4.3.2.2 Uniform deformation model (UDM)

The line broadening due to the finite size of the coherent scattering area and the internal tension in the prepared film are also taken into account in the Williamson-Hall approach. The diffraction line broadening, according to Williamson and Hall, is caused by crystallite size and strain contribution. However, by considering the peak width as a function of 2θ [53], the XPPA by W-H methods is a simpler approach that specifically distinguishes between size-induced and strain-induced peak broadening. The formula was used to quantify the strain-induced broadening in powders due to crystal imperfection and distortion,

$$\varepsilon = \beta_{hkl}/(4\tan\theta) \quad (4.13)$$

From eqs. (4.7) and (4.11), the peak width from crystallite size varies as $1/\cos\theta$ and strain varies as $\tan\theta$, according to the findings. The sum of the contributions of crystallite size and strain in the material now represents the complete peak broadening, which can be written as [54],

$$\mathcal{B}_{hkl} = \mathcal{B}_D + \mathcal{B}_\varepsilon \quad (4.14)$$

where $\mathcal{B}D$ denotes crystallite size contribution, $\mathcal{B}\epsilon$ denotes strain-induced broadening, and $\mathcal{B}hkl$ denotes the width of the half-maximum amplitude of instrumental corrected broadening. Eq. (4.6) is used to measure the instrumental corrected broadening of each diffraction peak. The observed line breadth is the sum of Eqs. (4.7) and (4.11) and given as [55] if the particle size and strain contributions to line broadening are independent of each other and both have a Cauchy-like profile,

$$\mathcal{B}_{hkl} = \frac{K\lambda}{D \cos\theta} + 4\epsilon \tan\theta \quad (4.15)$$

By rearranging Eq. (4.15), we get

$$\mathcal{B}_{hkl} \cos\theta_{hkl} = \frac{K\lambda}{D} + 4\epsilon \sin\theta_{hkl} \quad (4.16)$$

The uniform deformation model (UDM) is described by Eq. (4.16), which is Williamson–Hall equation. Equation (4.16) is known as the uniform deformation model since it assumes uniform strain in all crystallographic directions (UDM). The crystal in this model is assumed to be isotropic in nature, and the properties of the material are assumed to be independent of the measurement direction. The crystalline size D was calculated from the y-intercept, and the micro-strain ϵ was estimated from the slope of the linear fit, based on the values of $\mathcal{B}_{hkl} \cos\theta_{hkl}$ on the y-axis as a function of $4 \sin\theta_{hkl}$ on the x-axis (Fig. 4.2). Figure 4.2 depicts the UDM for ZnO nanoparticles. This strain may be caused by the lattice shrinkage that was observed during the lattice parameter measurement.

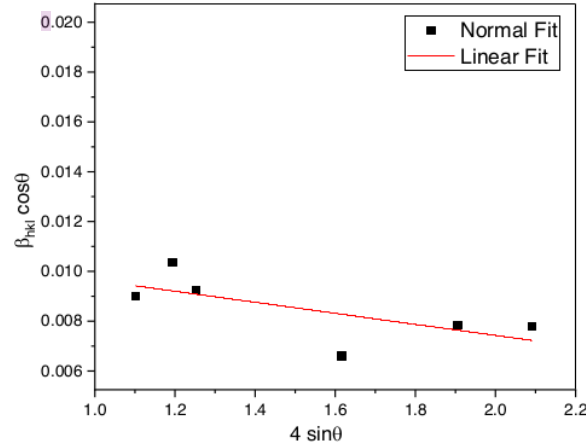


Fig. 4.2: Plot of $\beta_{hkl} \cos\theta_{hkl}$ versus $4 \sin\theta_{hkl}$

4.3.2.3 ⁶ Uniform stress deformation model (USDM)

The homogeneity and isotropy assumptions are often violated. An anisotropic solution was used to introduce a more practical scenario. An an-isotropic strain modifies the Williamson–Hall equation, as a result. The lattice ¹⁰⁸ deformation stress is believed to be constant in all crystallographic directions in the uniform stress deformation model (USDM), and the particles are assumed to have a minimal microstrain. The strain is referred to by Hooke's law in USDM, and there is a linear proportionality between stress and strain as determined by Hooke's law

$$\sigma = \epsilon Y_{hkl} \text{ or } \epsilon = \sigma / Y_{hkl}, \quad (4.17)$$

where σ is the stress of the crystal, ϵ is anisotropic microstrain, this will depend on the crystallographic directions and Y_{hkl} is the modulus of elasticity or Young's modulus. This equation is only a rough approximation, and it is only true for a very small strain; as strain increases, the particles deviate from the linear proportionality. The Williamson–Hall equation is modified in this method by substituting the value of ϵ in Eq (4.16), we get

$$\mathcal{B}_{hkl} \cos \theta_{hkl} = \frac{K\lambda}{D} + 4 \cdot \sigma \cdot \frac{\sin \theta_{hkl}}{Y_{hkl}} \quad (4.18)$$

For a hexagonal crystal, Young's modulus is given by the following relation,

$$Y_{hkl} = \frac{\left[h^2 + \frac{(h+2k)^2}{3} + \left(\frac{a}{c} \right)^2 \right]^2}{s_{11} \left(h^2 + \frac{(h+2k)^2}{3} \right)^2 + s_{33} \left(\frac{a}{c} \right)^4 + (2s_{13} + s_{44}) \left(h^2 + \frac{(h+2k)^2}{3} \right) \left(\frac{a}{c} \right)^2} \quad (4.19)$$

⁵⁸ where 'a' and 'c' are lattice parameters; s_{11} , s_{13} , s_{33} and s_{44} are the elastic compliances of ZnO with values ¹⁰⁵ 7.658×10^{-12} , -2.206×10^{-12} , 6.940×10^{-12} and $23.57 \times 10^{-12} \text{ m}^2 \text{ N}^{-1}$, respectively [56]. Young's modulus, Y_{hkl} , for hexagonal ZnO nanoparticles was calculated as $\sim 127 \text{ GPa}$.

The uniform deformation stress can be calculated from the slope of the linear fit, and the y-intercept gives the crystallite size, when plotting ¹⁶⁰ $\mathcal{B}_{hkl} \cos \theta_{hkl}$ as a function of ¹⁵¹ $4 \sin \theta / Y_{hkl}$ (Fig. 4.3). If the Young's modulus, Y_{hkl} , of hexagonal ZnO nano-particles is determined, the strain ϵ can be measured.

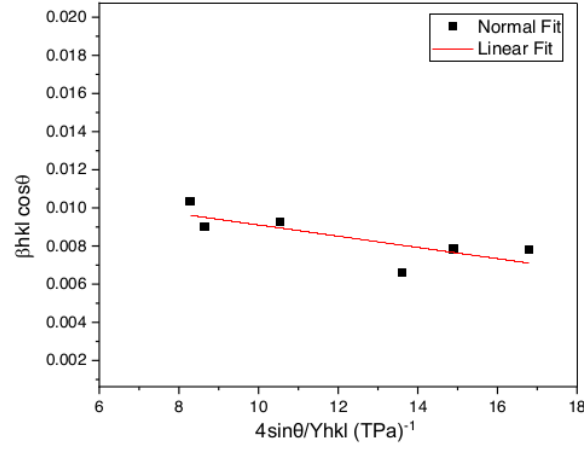


Fig. 4.3: Plot of $\beta_{hkl} \cos \theta_{hkl}$ versus $4 \sin \theta / Y_{hkl}$

4.3.2.4 Uniform deformation energy density model (UDEM)

The USDM model assumes a linear relationship between stress and strain, according to Hook's law, while the UDM model assumes the crystal is isotropic. However, since different defects, dislocations, and agglomerates cause imperfections in almost all crystals, the isotropic nature and linear proportionality between stress and strain cannot be considered in real crystals. As a result, a new model is required to research various crystal microstructures. For this function, the Uniform deformation energy density model (UDEM) is used, which takes into account uniform anisotropic lattice strain in all crystallographic directions, with the density of deformation energy as the cause of that uniform anisotropic lattice strain [57].

Energy density (μ), according to Hooke's law, is proportional to strain.

$$\mu_{ed} = (\epsilon^2 Y_{hkl})/2 \text{ or } \epsilon = \sqrt{\frac{2\mu_{ed}}{Y_{hkl}}} \quad (4.20)$$

Where Y_{hkl} is the anisotropic Young's modulus.

Then, Eq. (4.18) can be rewritten according to the energy and strain relation as

$$\beta_{hkl} \cos \theta_{hkl} = \left(\frac{K\lambda}{D}\right) + (4 \sin \theta_{hkl} \left(\frac{2\mu_{ed}}{Y_{hkl}}\right)^{1/2}) \quad (4.21)$$

Plot of $\beta_{hkl} \cos \theta_{hkl}$ versus $4 \sin \theta_{hkl} (2/Y_{hkl})^{1/2}$ was done (Fig. 4.4) and the anisotropic energy density μ_{ed} was estimated from the slope of the linear fit and the crystallite size D from the y-intercept. Previously, we knew that $\sigma = \epsilon Y_{hkl}$ and $\mu_{ed} = (\epsilon^2 Y_{hkl})/2$, where

the stress σ was calculated as $\mu_{ed} = (\sigma^2/2Y_{hkl})$. The lattice strain can be calculated by knowing the Y_{hkl} value.

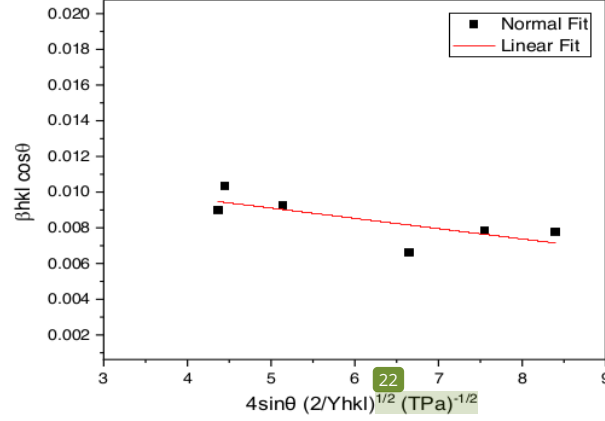


Fig. 4.4: Plot of $\beta_{hkl} \cos \theta_{hkl}$ versus $4 \sin \theta_{hkl} (2/Y_{hkl})^{1/2}$

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4.3.3 Size-strain plot (SSP)

The Williamson-Hall method takes into account peak broadening as a function of diffraction angle (2), which is thought to be a combination of size and strain induced broadening. There are, however, models that deal with the analysis of peak profiles. One such method is the Size-Strain plot (SSP), which assumes that the XRD peak profile is a combination of Lorentzian and Gaussian functions, with the size broadened profile labeled as a Lorentz function and the strain broadened profile labelled as a Gaussian function [58]. As a result, the total SSP broadening can be written as

$$\beta_{hkl} = \beta_L + \beta_G$$

The peak broadening due to Lorentz and Gaussian functions, respectively, is β_L and β_G .

Furthermore, the SSP approach often produces a better result for isotropic broadening since it prioritizes low angle reflections, which have higher accuracy and precision, over higher angle reflections. This is because XRD data is of poorer quality at higher angles, and peaks are usually heavily overlapped at higher diffracting angles.

As a result, the SSP calculation is done using the following equation.

$$(d_{hkl} \beta_{hkl} \cos \theta_{hkl})^2 = \frac{K}{D} (d_{hkl}^2 \beta_{hkl} \cos \theta_{hkl}) + \left(\frac{1}{2}\right)^2 \quad (4.22)$$

where d_{hkl} is the lattice distance between the $\langle h k l \rangle$ planes and for the hexagonal crystal structure,

$$d_{hkl} = \frac{a}{\sqrt{4/3(h^2 + k^2 + hk) + \left(\frac{a}{c}\right)^2}} \quad (4.23)$$

K is a constant that depends on the shape of the particles; for spherical particles it is given as $\frac{3}{4}$ and ϵ is a measure of the apparent strain which is related to the root mean square (RMS) strain ϵ_{RMS} .

$$\langle \epsilon_{RMS} \rangle = \left(\frac{\epsilon}{36\pi} \right) \quad (4.24)$$

In Fig. 4.5, similarly to the W-H methods, the term $(d_{hkl} \beta_{hkl} \cos \theta)^2$ is plotted with respect to $(d_{hkl}^2 \beta_{hkl} \cos \theta)$ for the all orientation peaks of ZnO-NPs with the wurtzite hexagonal phase. In this case, the particle size is determined from the slope of the linearly fitted data and the root of the y-intercept gives the strain.

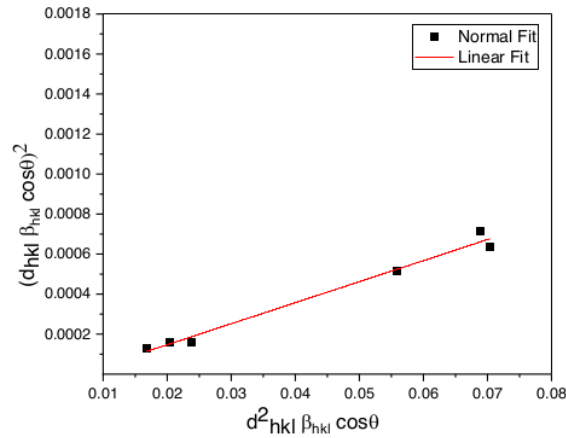


Fig. 4.5: Plot of $(d_{hkl} \beta_{hkl} \cos \theta)^2$ versus $(d_{hkl}^2 \beta_{hkl} \cos \theta)$

4.3.4 Halder-Wagner Method

Size broadening of the XRD peak profile was assumed to be a Lorentzian function in the SSP system, while strain broadening was assumed to be a Gaussian function. However, the XRD peak is neither a Lorentzian nor a Gaussian function, since the XRD peak region matches well with the Gaussian function, but its tail falls off too quickly

without matching, and the tails of the profile, on the other hand, match well with the Lorentz function, but do not match the XRD peak region [59,60]. To get around this problem, the Halder-Wagner approach is used, which is based on the assumption that peak broadening is a symmetric Voigt function [60, 61] because it is a convolution of Lorentzian and Gaussian functions [66]. As a result, the full width at half limit of the physical profile for the Voigt function can be written using the Halder-Wagner Method as

$$\beta_{hkl}^2 = \beta_L \beta_{hkl} + \beta_G^2 \quad (4.25)$$

Where, β_L and β_G are the full width at half maximum of the Lorentzian and Gaussian function. This approach has the advantage of giving more weight to peaks in the low and mid angle ranges, where there is less duplication of diffracting peaks. According to the Halder-Wagner Method, the relationship between crystallite size and lattice strain is now:

$$(\beta_{hkl}^* / d_{hkl}^*)^2 = \frac{1}{D} \cdot (\beta_{hkl}^* / d_{hkl}^*)^2 + \left(\frac{\epsilon}{2}\right)^2 \quad (4.26)$$

Where $\beta_{hkl}^* = \beta_{hkl} \cdot \cos\theta / \lambda$ and $d_{hkl}^* = 2d_{hkl} \cdot \sin\theta / \lambda$.

Plot of equation (4.26), with $(\beta_{hkl}^* / d_{hkl}^*)^2$ term along X-axis and $(\beta_{hkl}^* / d_{hkl}^*)^2$ along Y-axis for each peak of the XRD pattern, is shown in Fig. 4.6. The slope of the plotted straight line provides the average size, whereas the intercept gives the intrinsic strain of the ZnO nanocrystals.

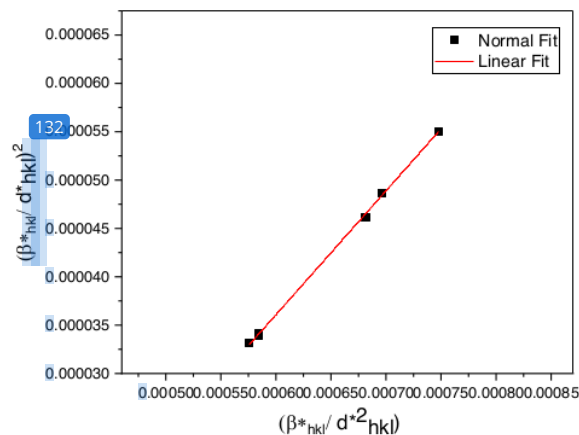


Fig. 4.6: Halder-Wagner plot for ZnO nanoparticles.

4.3.5 Wagner-Agua Method

The method proposed by Wagner and Agua to determine crystallite size and strain has also been considered. Describes the Wagner and Agua equation [62],

$$(\mathcal{B}_{hkl} \cos \theta_{hkl})^2 = (4\varepsilon_{WA} \sin \theta_{hkl})^2 + \left(\frac{K\lambda}{D_{WA}}\right)^2 \quad (4.27)$$

Where D_{WA} and ε_{WA} represent the Wagner-Agua crystallite size and lattice strain, respectively. The W-A plots of Zn-nanoparticles are drawn taking $(\mathcal{B}_{hkl} \cos \theta_{hkl})^2$ and $(4 \sin \theta_{hkl})^2$ in the vertical and horizontal axis, respectively. In the Wagner-Agua (W-A) plots shown in Fig. 4.7, We fit the experimental data with linear fits, from which the slope yields the strain (ε_{WA}), and the intercept on the vertical axis yields a crystallite size calculation (DWA).

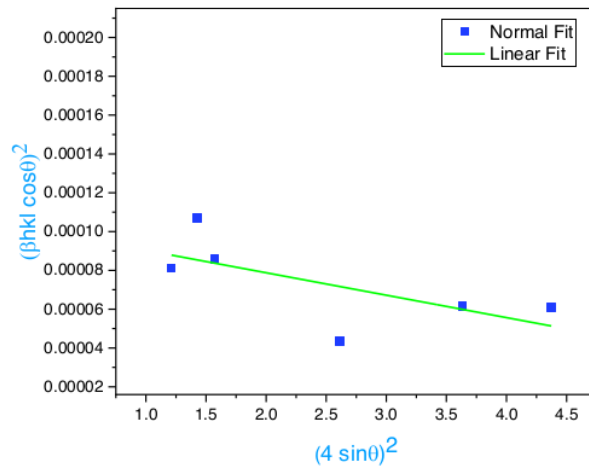


Fig. 4.7: Wagner-Agua plot for ZnO nanoparticles

4.3.6 Determination of lattice parameters

As ZnO crystallizes, the oxygen atoms are arranged in a hexagonal close packed form, with zinc atoms occupying half of the tetrahedral sites. The atoms Zn and O are tetrahedrally coordinated to each other and thus have the same position. All of the octahedral and half of the tetrahedral sites in the zinc structure are empty. Bragg's law [63] states that

$$n\lambda = 2d \sin \theta \quad (4.28)$$

Where n is the order of diffraction (usually $n = 1$), λ is the X-ray wavelength and d is the spacing between planes of given Miller indices h, k and l . The plane spacing d is

related to the lattice constants a , c , and Miller indices in the ZnO hexagonal structure by the following relationship [63],

$$\frac{1}{d^2_{(hkl)}} = \frac{4}{3} ((h^2 + hk + k^2)/a^2) + l^2/c^2 \quad (4.29)$$

With the first-order approximation, $n = 1$;

$$\sin^2\theta = \frac{\lambda^2}{4a^2} \left[\frac{4}{3} (h^2 + k^2 + hk) + \left(\frac{a}{c}\right)^2 l^2 \right] \quad (4.30)$$

The lattice constant a for $\langle 100 \rangle$ plane is calculated by [63],

$$a = \frac{\lambda}{\sqrt{3} \sin\theta_{(100)}} \quad (4.31)$$

For the $\langle 002 \rangle$ plane, the lattice constant c is calculated by [63],

$$c = \frac{\lambda}{\sin\theta_{(002)}} \quad (4.32)$$

The unit cell volume V is obtained from the following equation [64]

$$V = \frac{\sqrt{3}a^2c}{2} \quad (4.33)$$

The dislocation density (δ), which represents the amount of defects in the sample is defined as the length of dislocation lines per unit volume of the crystal and is calculated using the Eq. [65],

$$\delta = \frac{1}{D^2}$$

where D is the crystallite size. And δ is the dislocation density.

The Zn–O bond length L is given by [66],

$$L = \sqrt{\left(\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2\right)} \quad (4.34)$$

where u is the positional parameter in the wurtzite structure and is a measure of the amount by which each atom is displaced with respect to the next along the 'c' axis. 'u' is given by

$$u = \frac{a^2}{3c^2} + 0.25 \quad (4.35)$$

The correlation between the c/a ratio and u is that as the c/a ratio decreases, the u rises, causing the four tetrahedral distances to remain nearly constant due to tetrahedral angle distortion.

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 Introduction

X-ray diffraction analysis was used to classify the ZnO-NPs in this chapter (XRD). The sample product was crystalline with a hexagonal wurtzite phase, according to the XRD results. X-ray peak broadening was used to investigate the crystalline development of ZnO-NPs. The individual contributions of crystallite sizes and lattice strain on the peak broadening of ZnO-NPs were studied using the Halder-Wagner Method, Wagner-Aguia Method, Williamsone-Hall (W-H) analysis, and size-strain plot method. The physical parameters such as strain, stress and energy density values were calculated more precisely for all the reflection peaks of XRD corresponding to the wurtzite hexagonal phase of ZnO lying in the range of 50°C-90°C at 120 MPa from the modified form of the W-H plot assuming a uniform deformation model (UDM), uniform stress deformation model (USDM), uniform deformation energy density model (UDEDM), size-strain plot method (SSP) and by the Halder-Wagner Method and Wagner-Aguia Method.

5.2 XRD analysis of ZnO nanoparticles with 50T at 120 MPa

The XRD patterns of the prepared samples of ZnO nanoparticles formed under 50°C temperatures at 120 MPa pressure were shown in Fig.5.1. Which is determined by placing the value of 2θ along x-axis and β (intensity) along y-axis. All the diffraction peaks could be well indexed as the ZnO wurtzite structure found in the standard reference data. The data has been provided by our supervisor Dr. Md. Shamimul Haque Choudhury.

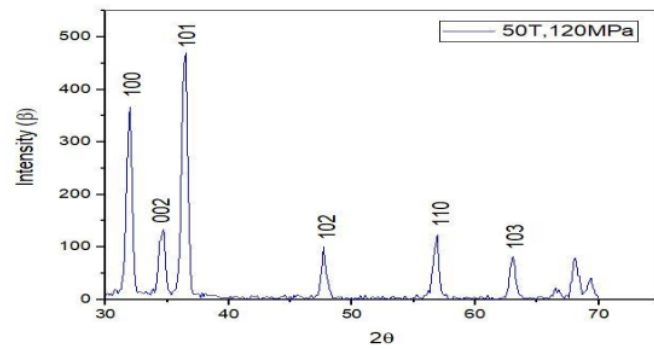


Fig. 5.1 XRD pattern of ZnO nanoparticles with 50T, 120 MPa

Analysis of first peak (100)

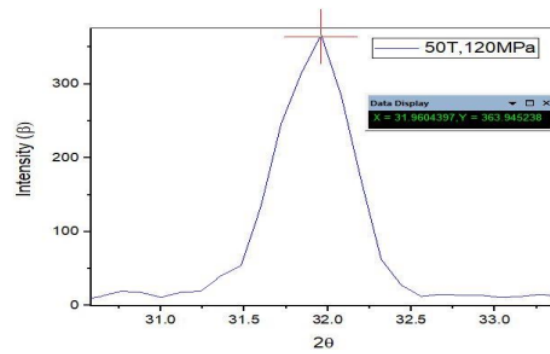


Fig. 5.2 Measurement of 2θ of peak (100)

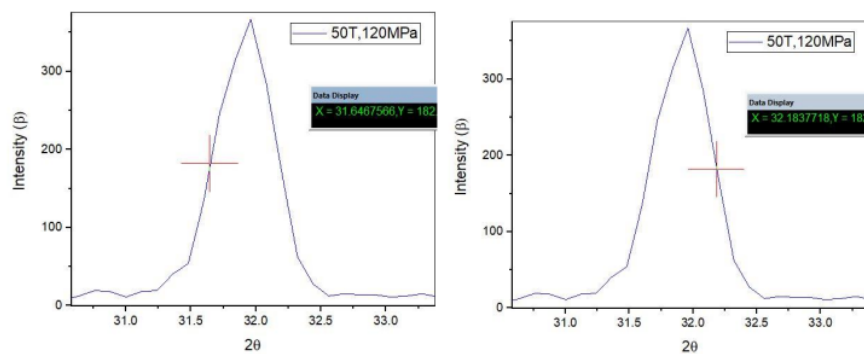


Fig. 5.3 Measurement of β_{hkl} of peak (100)

For (100) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = (32.1837 - 31.6467) = 0.537$$

$$\text{In radian, } \beta_{hkl} = 0.537 \times \pi / 180 = 0.00937244$$

Analysis of second peak (002)

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 31.96044$$

$$\theta = 15.98022$$

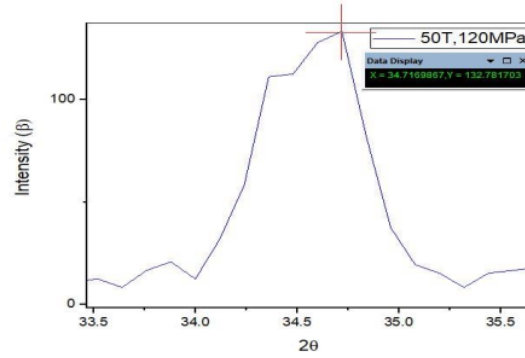


Fig. 5.4 Measurement of 2θ of peak (002)

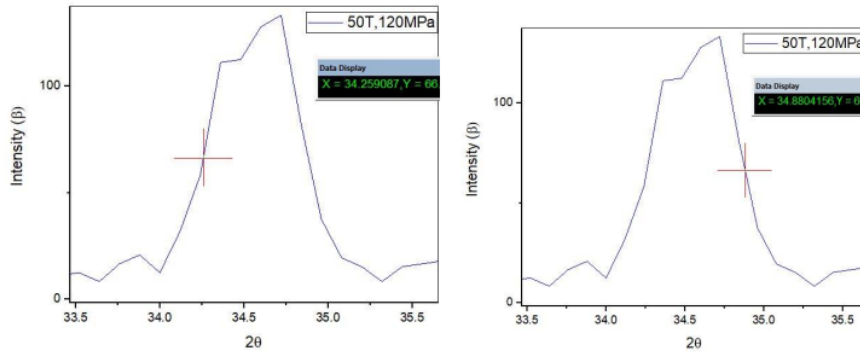


Fig. 5.5 Measurement of β_{hkl} of peak (002)

For (002) peak, ⁴the line broadening at full width half maximum (FWHM),

$$\beta_{hkl} = (34.8804 - 34.259) = 0.6214$$

$$\text{In radian, } \beta_{hkl} = 0.6214 \times \pi / 180 = 0.010845501$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 34.7159$$

$$\theta = 17.35795$$

Analysis of third peak (101)

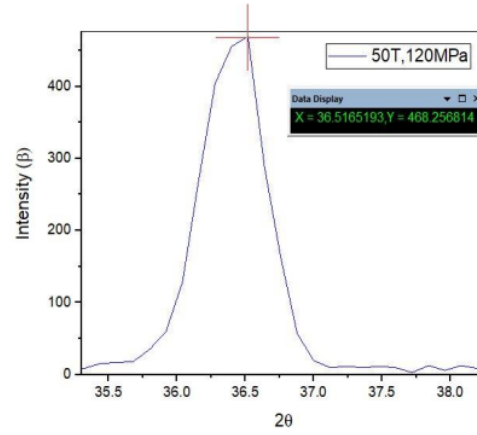


Fig. 5.6 Measurement of 2θ of peak (101)

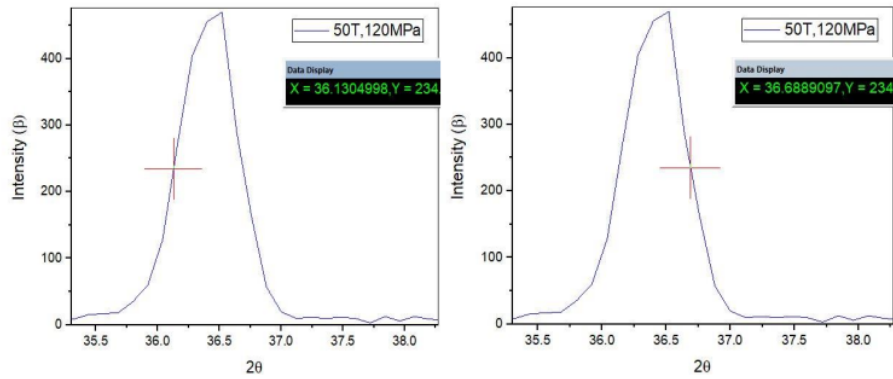


Fig. 5.7 Measurement of β_{hkl} of peak (101)

For (101) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = (36.6889 - 36.1305) = 0.5584$$

In radian, $\beta_{hkl} = 0.5584 \times \pi / 180 = 0.009745941$

Here, $K = 0.9$

$\lambda = 0.154 \text{ nm}$

$2\theta = 36.51652$

$\theta = 18.25826$

Analysis of fourth peak (102)

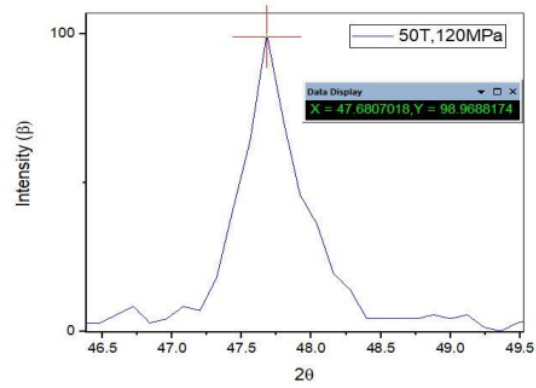


Fig. 5.8 Measurement of 2θ of peak (102)

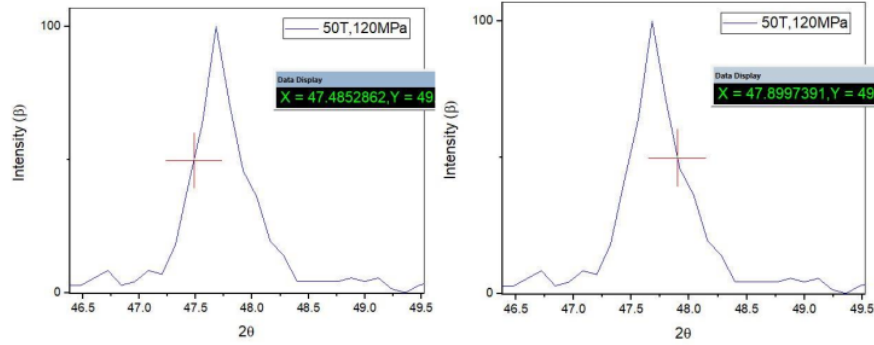


Fig. 5.9 Measurement of β_{hkl} of peak (102)

For (102) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = (47.899 - 47.4852) = 0.4138$$

In radian, $\beta_{hkl} = 0.4138 \times \pi / 180 = 0.007222189$

Here, $K = 0.9$

$\lambda = 0.154 \text{ nm}$

$2\theta = 47.6807$

$\theta = 23.84035$

Analysis of fifth peak (110)

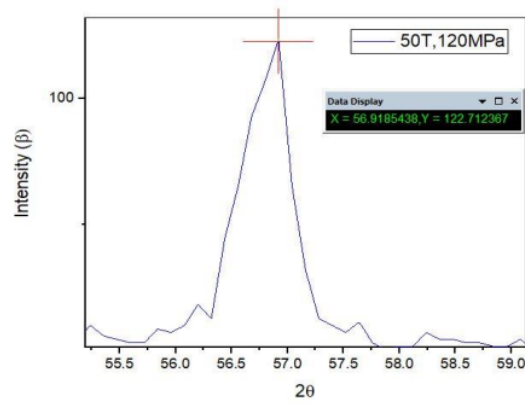


Fig. 5.10 Measurement of 2θ of peak (110)

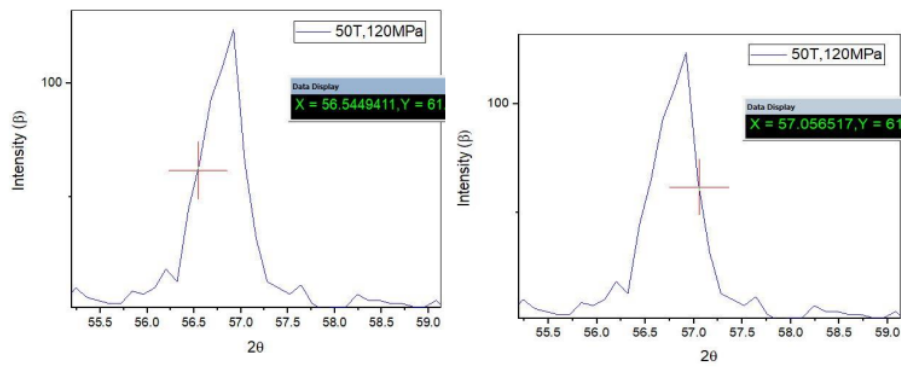


Fig. 5.11 Measurement of β_{hkl} of peak (110)

For (110) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = (57.0565 - 56.54494) = 0.51156$$

In radian, $\beta_{hkl} = 0.51156 \times \pi / 180 = 0.008928427$

Here, $K = 0.9$

$\lambda = 0.154 \text{ nm}$

$2\theta = 56.91854$

$\theta = 28.45927$

Analysis of six peaks (103)

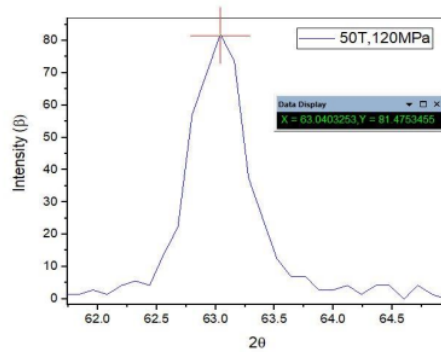


Fig. 5.12 Measurement of 2θ of peak (103)

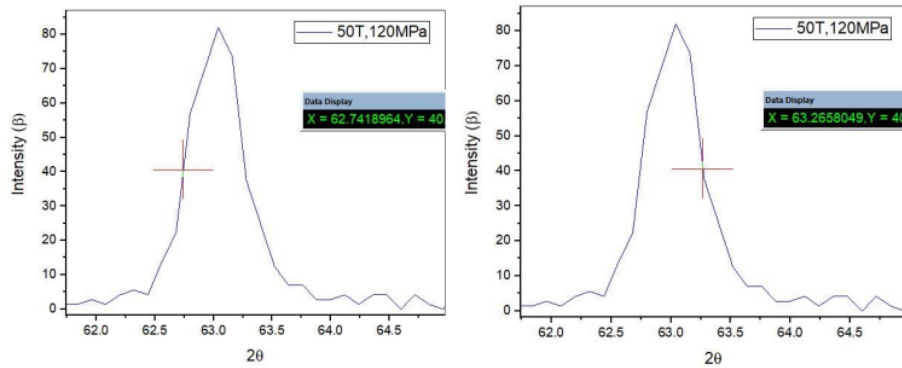


Fig. 5.13 Measurement of β_{hkl} of peak (103)

For (103) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = (63.2658 - 62.74189) = 0.52391$$

$$\text{In radian, } \beta_{hkl} = 0.52391 \times \pi / 180 = 0.009143976$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 63.0403$$

$$\theta = 31.52015$$

5.3 XRD analysis of ZnO nanoparticles with 60T at 120 MPa

The XRD patterns of the prepared samples of ZnO nanoparticles formed under 60°C temperatures at 120 MPa pressure were shown in Fig. 5.14. Which is determined by placing the value of 2θ along x-axis and β (intensity) along y-axis. All the diffraction

peaks could be well indexed as the ZnO wurtzite structure found in the standard reference data. The data has been provided by our supervisor Dr. Md. Shamimul Haque Choudhury.

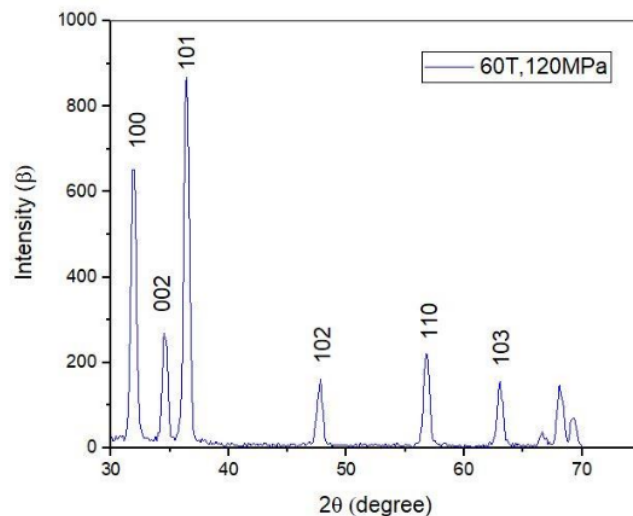


Fig. 5.14 XRD pattern of ZnO nanoparticles with 60T, 120 MPa

Analysis of first peak (100)

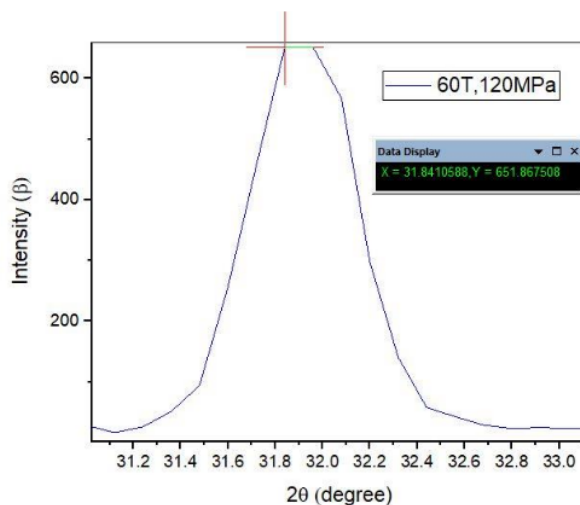


Fig. 5.15 Measurement of 2θ of peak (100)

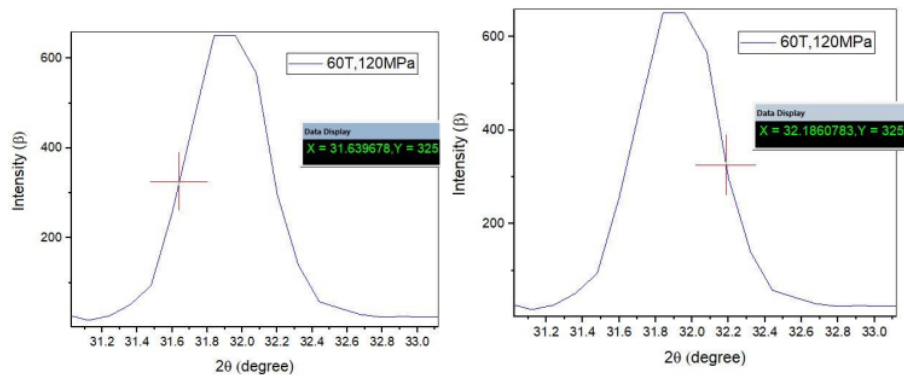


Fig. 5.16 Measurement of β_{hkl} of peak (100)

For (100) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = (32.18607 - 31.63967) = 0.5464$$

$$\text{In radian, } \beta_{hkl} = 0.5464 \times \pi / 180 = 0.009536501$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 31.84105$$

$$\theta = 15.920525$$

Analysis of second peak (002)

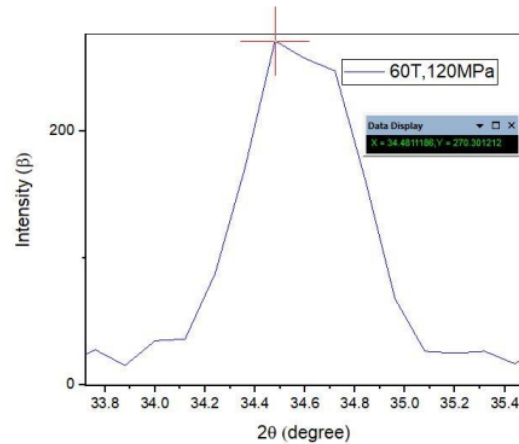


Fig. 5.17 Measurement of 2θ of peak (002)

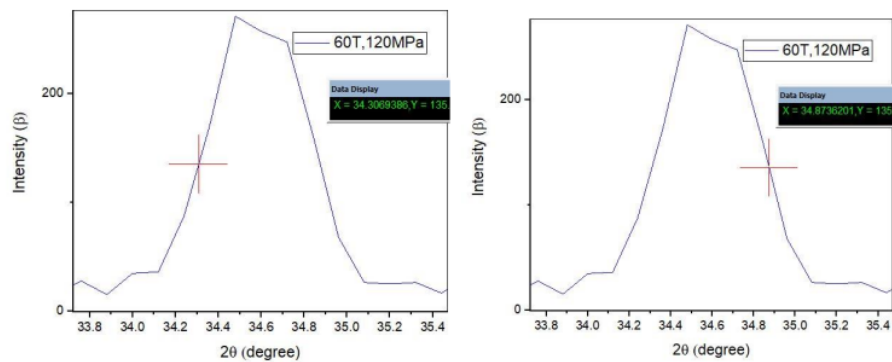


Fig. 5.18 Measurement of β_{hkl} of peak (002)

For (002) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = (34.87362 - 34.30693) = 0.56669$$

$$\text{In radian, } \beta_{hkl} = 0.56669 \times \pi / 180 = 0.009890629$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 34.48111$$

$$\theta = 17.240555$$

Analysis of third peak (101)

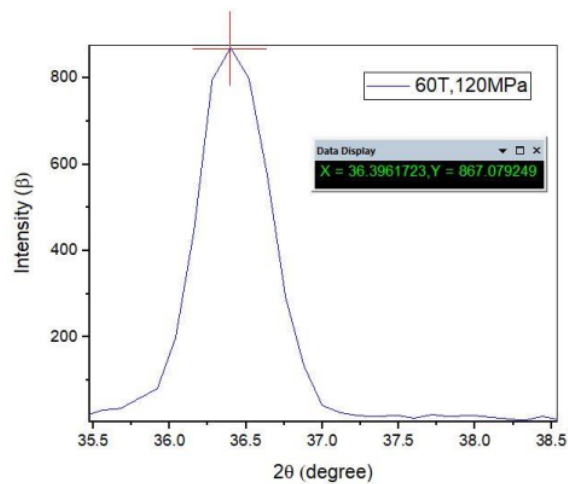


Fig. 5.19 Measurement of 2θ of peak (101)

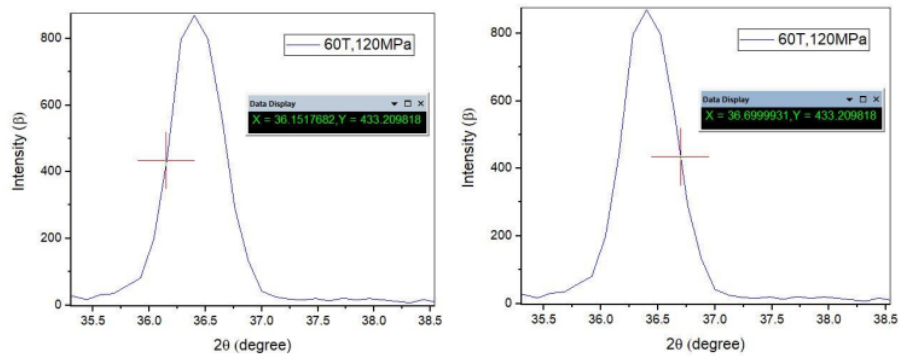


Fig. 5.20 Measurement of β_{hkl} of peak (101)

For (101) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = (36.69999 - 36.151768) = 0.5482$$

$$\text{In radian, } \beta_{hkl} = 0.5482 \times \pi / 180 = 0.009568301$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 36.39617$$

$$\theta = 18.198085$$

Analysis of fourth peak (102)

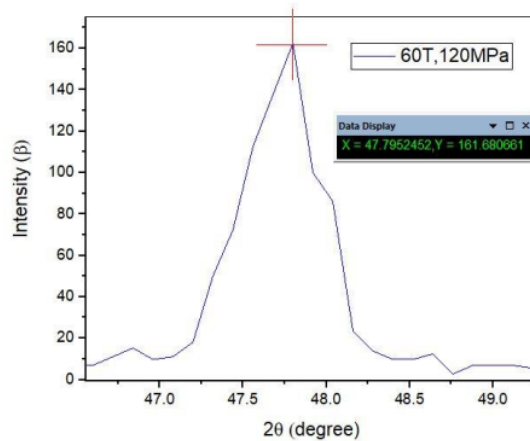


Fig. 5.20 Measurement of 2θ of peak (102)

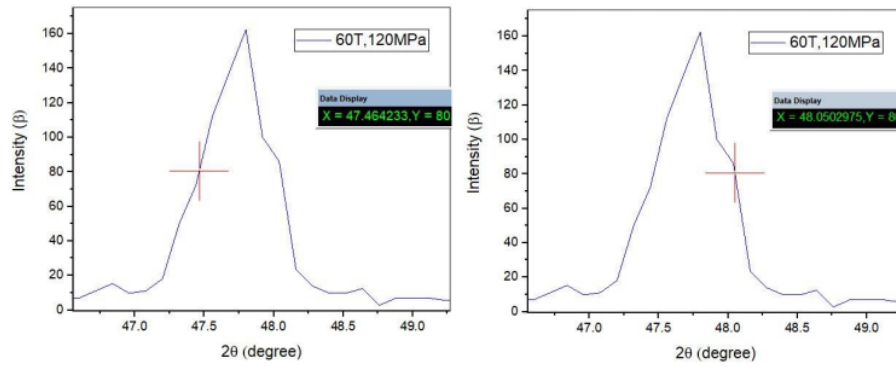


Fig. 5.21 Measurement of β_{hkl} of peak (102)

For (102) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = (48.05029 - 47.46423) = 0.58606$$

$$\text{In radian, } \beta_{hkl} = 0.58606 \times \pi / 180 = 0.010228701$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 47.795245$$

$$\theta = 23.8976225$$

Analysis of fifth peak (110)

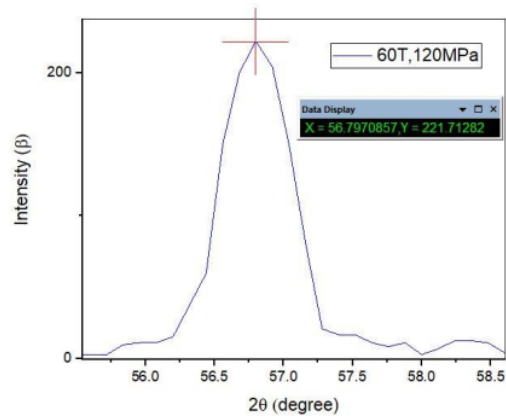


Fig. 5.22 Measurement of 2θ of peak (110)

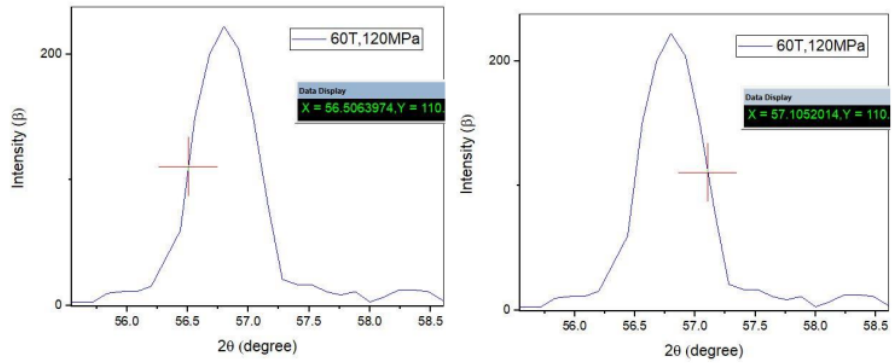


Fig. 5.23 Measurement of β_{hkl} of peak (110)

For (110) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = (57.1052 - 56.50639) = 0.59881$$

$$\text{In radian, } \beta_{hkl} = 0.59881 \times \pi / 180 = 0.010451231$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 56.797085$$

$$\theta = 28.3985425$$

Analysis of sixth peak (103)

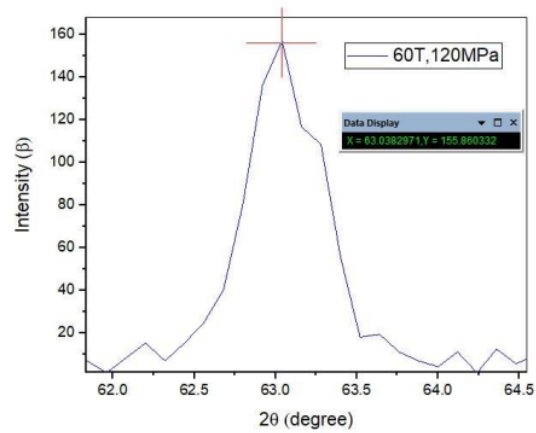


Fig. 5.24 Measurement of 2θ of peak (103)

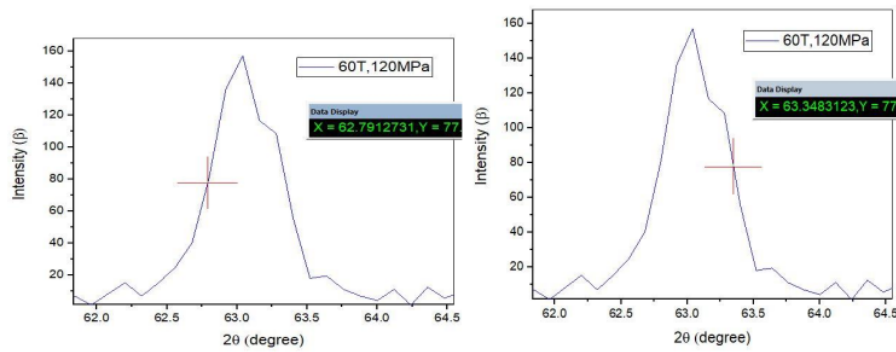


Fig. 5.25 Measurement of β_{hkl} of peak (103)

For (103) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = (63.348312 - 62.79127) = 0.55704$$

$$\text{In radian, } \beta_{hkl} = 0.55704 \times \pi / 180 = 0.00972224$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 63.038297$$

$$\theta = 31.5191485$$

5.4 XRD analysis of ZnO nanoparticles with 70T at 120 MPa

The XRD patterns of the prepared samples of ZnO nanoparticles formed under 60°C temperatures at 120 MPa pressure were shown in **Fig.5.26**. Which is determined by placing the value of 2θ along x-axis and β (intensity) along y-axis. All the diffraction peaks could be well indexed as the ZnO wurtzite structure found in the standard reference data. The data has been provided by our supervisor Dr. Md. Shamimul Haque Choudhury.

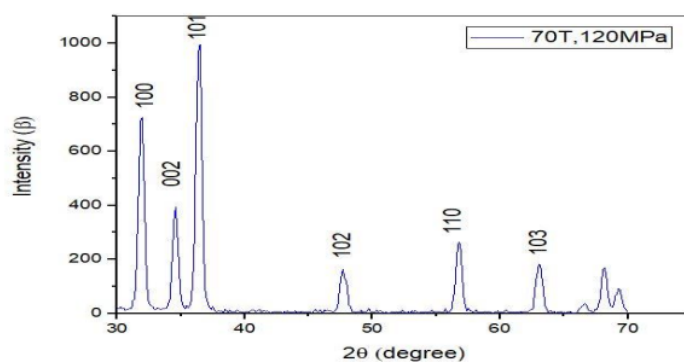


Fig. 5.26 XRD pattern of ZnO nanoparticles with 70T,120 MPa

Analysis of first peak (100)

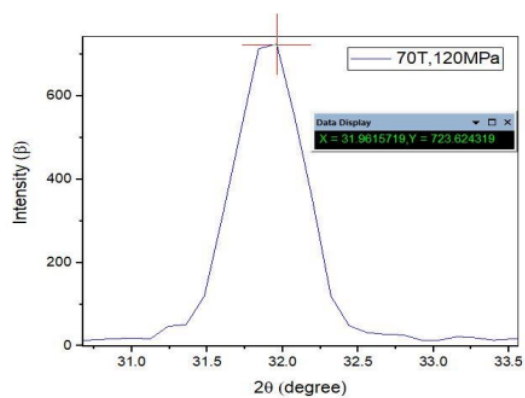


Fig. 5.27 Measurement of 2θ of peak (100)

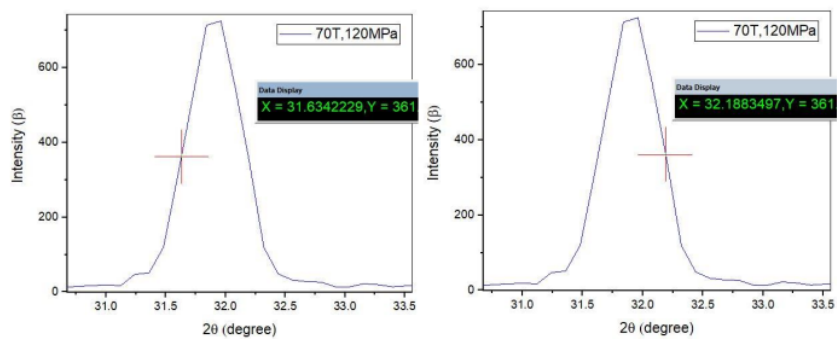


Fig. 5.28 Measurement of β_{hkl} of peak (100)

For (100) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = 32.188349 - 31.634222 = 0.554127$$

$$\text{In radian, } \beta_{hkl} = 0.554127 \times \pi / 180 = 0.009671363$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 31.96157$$

$$\theta = 15.980785$$

Analysis of second peak (002)

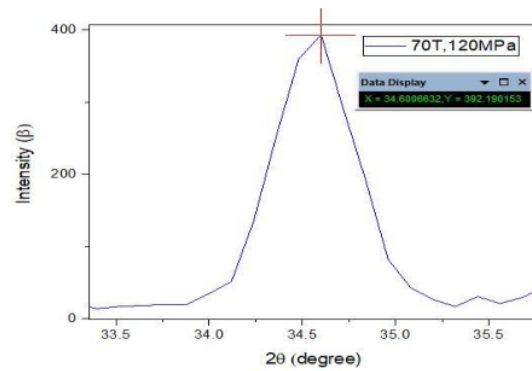


Fig. 5.29 Measurement of 2θ of peak (002)

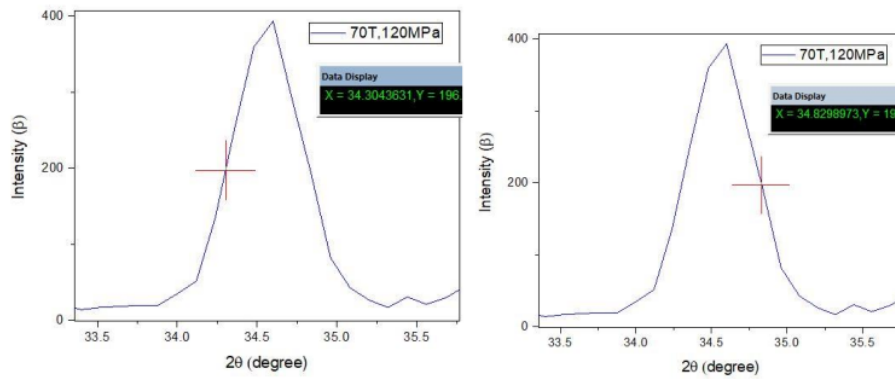


Fig. 5.30 Measurement of β_{hkl} of peak (002)

For (002) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = 34.829897 - 34.304363 = 0.525534$$

$$\text{In radian, } \beta_{hkl} = 0.525534 \times \pi / 180 = 0.00917232$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 34.6006$$

$$\theta = 17.3003$$

Analysis of third peak (101)

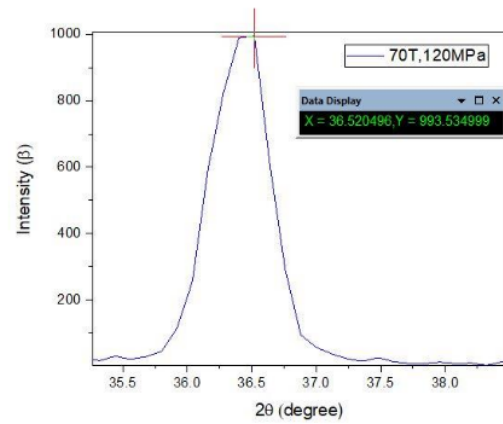


Fig. 5.31 Measurement of 2θ of peak (101)

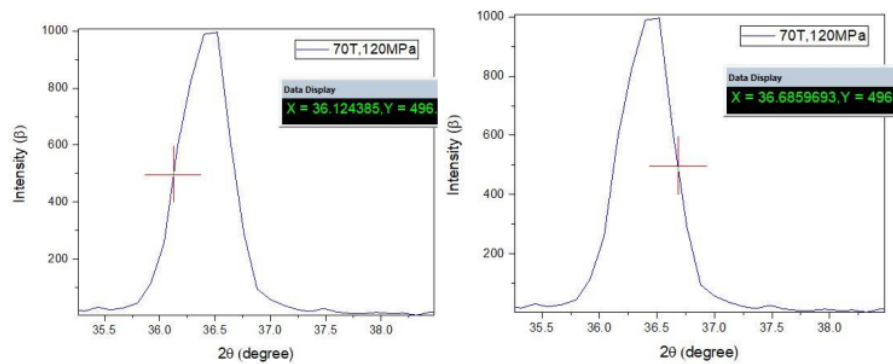


Fig. 5.32 Measurement of β_{hkl} of peak (101)

For (101) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = 36.68596 - 36.12438 = 0.56158$$

$$\text{In radian, } \beta_{hkl} = 0.56158 \times \pi / 180 = 0.009801443$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 36.52049$$

$$\theta = 18.260245$$

Analysis of fourth peak (102)

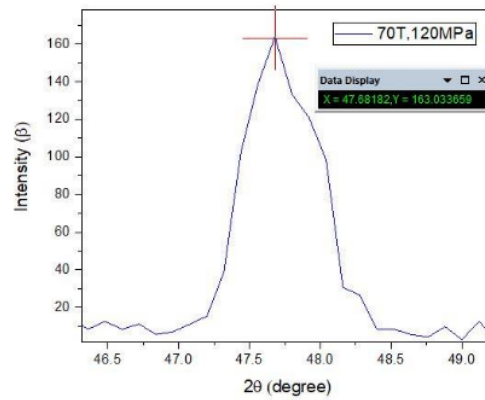


Fig. 5.33 Measurement of 2θ of peak (102)

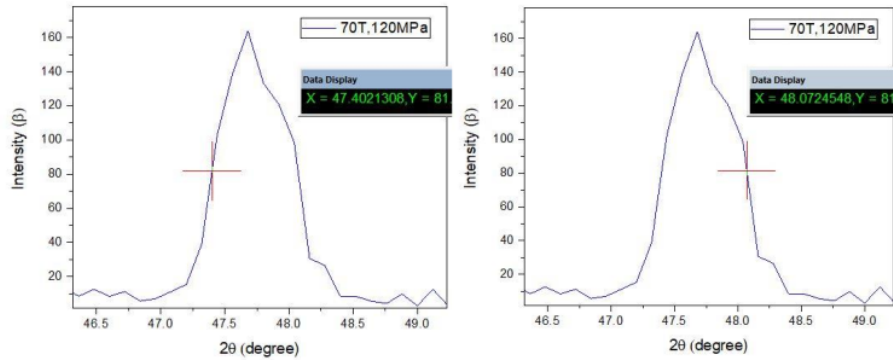


Fig. 5.34 Measurement of β_{hkl} of peak (102)

For (102) peak, the ⁴line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = 48.07245 - 47.40213 = 0.67032$$

$$\text{In radian, } \beta_{hkl} = 0.67032 \times \pi / 180 = 0.011699318$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 47.68182$$

$$\theta = 23.84091$$

Analysis of fifth peak (110)

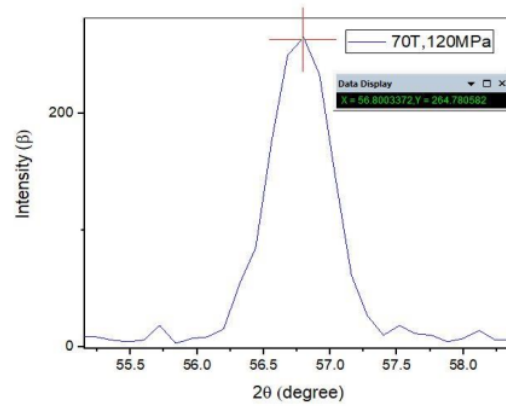


Fig. 5.35 Measurement of 2θ of peak (110)

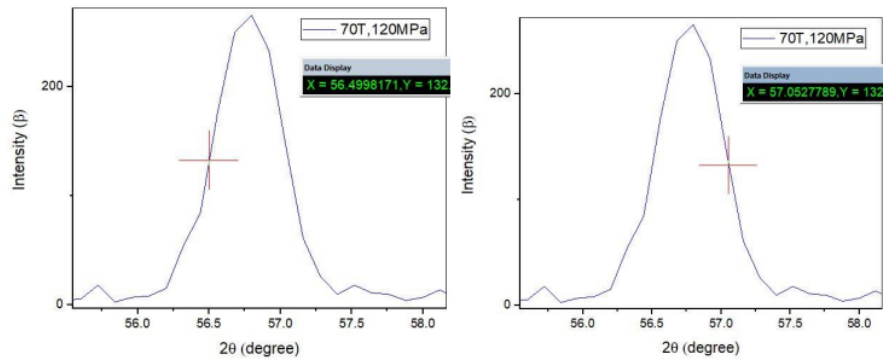


Fig. 5.36 Measurement of β_{hkl} of peak (110)

For (110) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = 57.052778 - 56.4998 = 0.552978$$

$$\text{In radian, } \beta_{hkl} = 0.552978 \times \pi / 180 = 0.009651309$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 56.800337$$

$$\theta = 28.4001685$$

Analysis of six peaks (103)

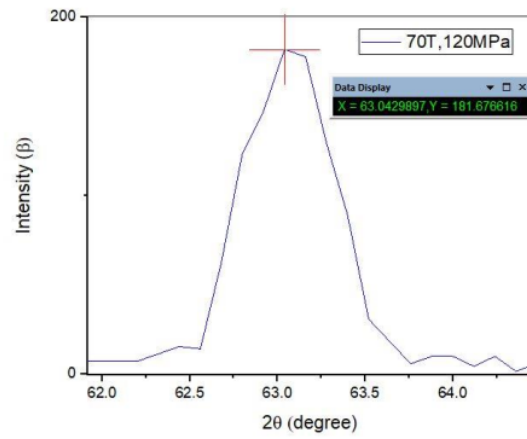


Fig. 5.37 Measurement of 2θ of peak (103)

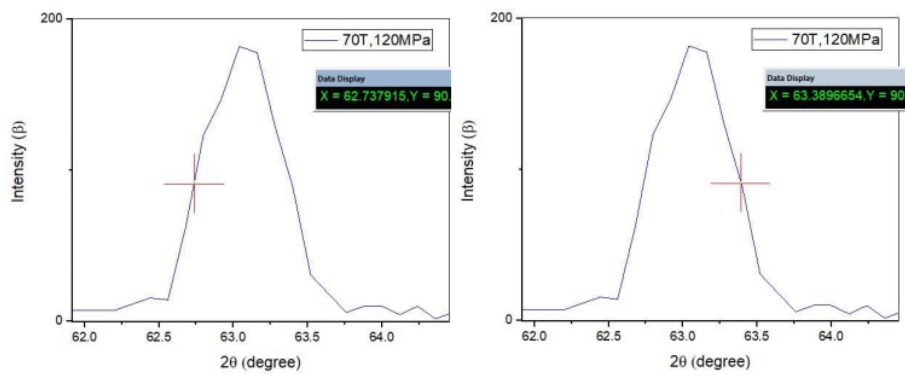


Fig. 5.38 Measurement of β_{hkl} of peak (103)

For (103) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = 63.38966 - 62.7379 = 0.65176$$

$$\text{In radian, } \beta_{hkl} = 0.65176 \times \pi / 180 = 0.011375385$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 63.042999$$

$$\theta = 31.5214995$$

5.5 XRD analysis of ZnO nanoparticles with 80T at 120 MPa

The XRD patterns of the prepared samples of ZnO nanoparticles formed under 80°C temperatures at 120 MPa pressure were shown in **Fig.5.39**. Which is determined by placing the value of 2θ along x-axis and β (intensity) along y-axis. All the diffraction peaks could be well indexed as the ZnO wurtzite structure found in the standard reference data. The data has been provided by our supervisor Dr. Md. Shamimul Haque Choudhury.

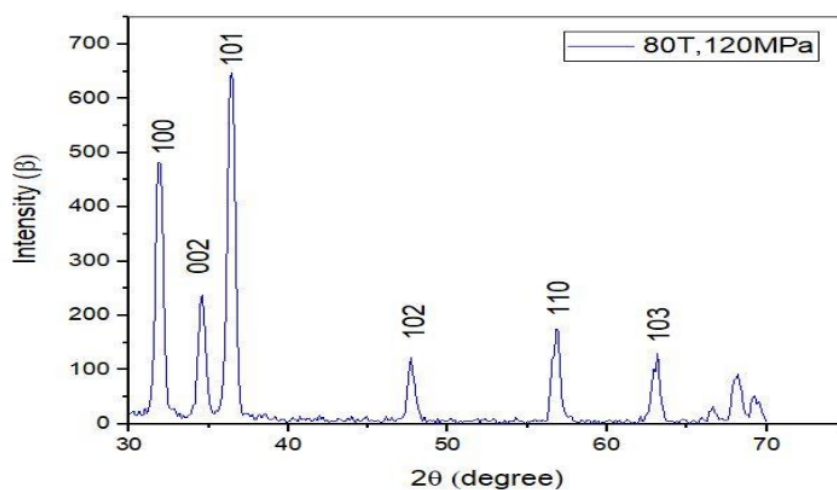


Fig. 5.39 XRD pattern of ZnO nanoparticles with 80T, 120 MPa

Analysis of first peak (100)

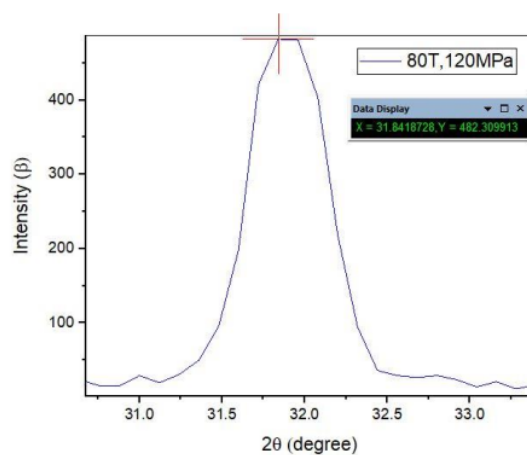


Fig. 5.40 Measurement of 2θ of peak (100)

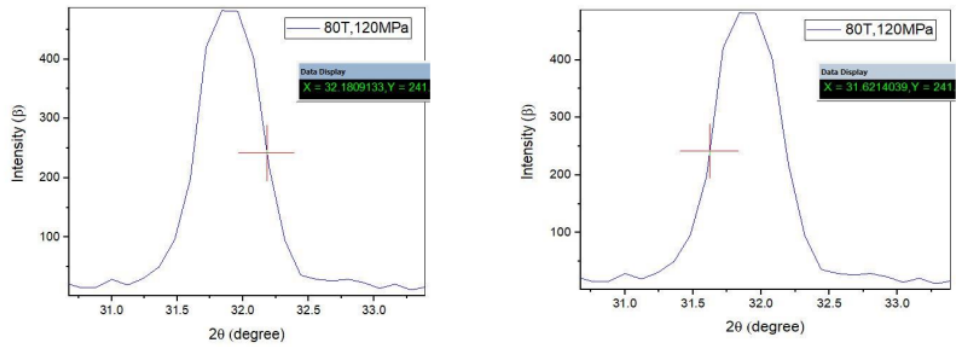


Fig. 5.41 Measurement of β_{hkl} of peak (100)

For (100) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = (32.1809 - 31.6214) = 0.559$$

In radian, $\beta_{hkl} = 0.559 \times \pi/180 = 0.0097$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 31.842$$

$$\theta = 15.921$$

Analysis of second peak (002)

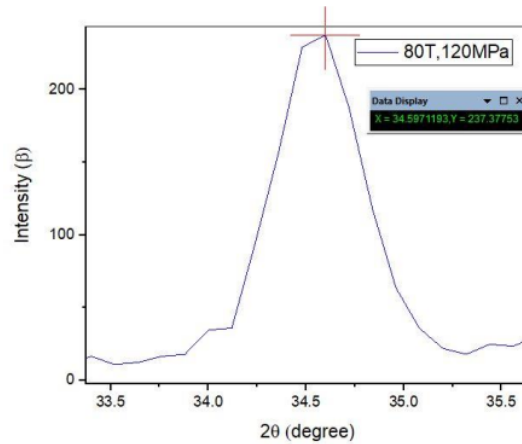


Fig. 5.42 Measurement of 2θ of peak (002)

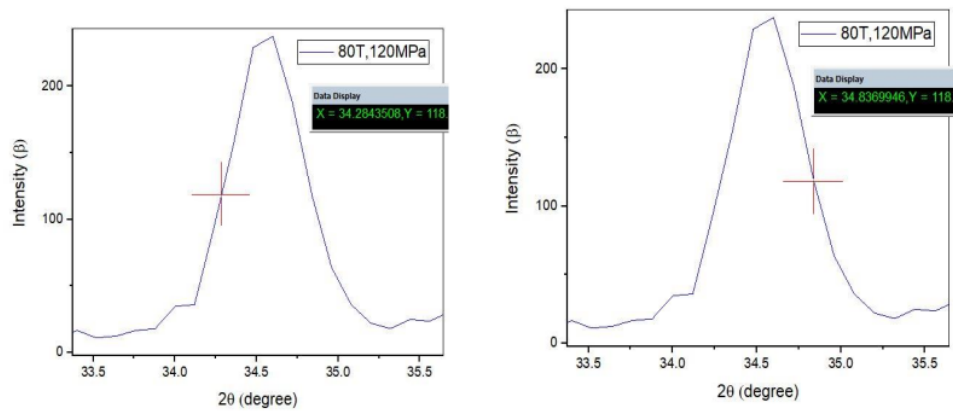


Fig. 5.43 Measurement of β_{hkl} of peak (002)

For (002) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = (34.8369 - 34.2843) = 0.552$$

In radian, $\beta_{hkl} = 0.552 \times \pi/180 = 0.0096$

Here, $K = 0.9$

$\lambda = 0.154 \text{ nm}$

$2\theta = 34.597$

$\theta = 17.298$

Analysis of third peak (101)

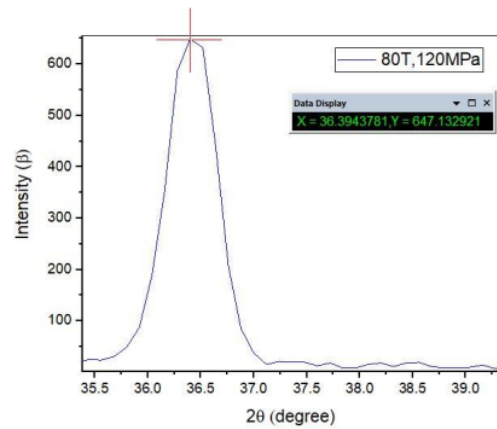


Fig. 5.44 Measurement of 2θ of peak (101)

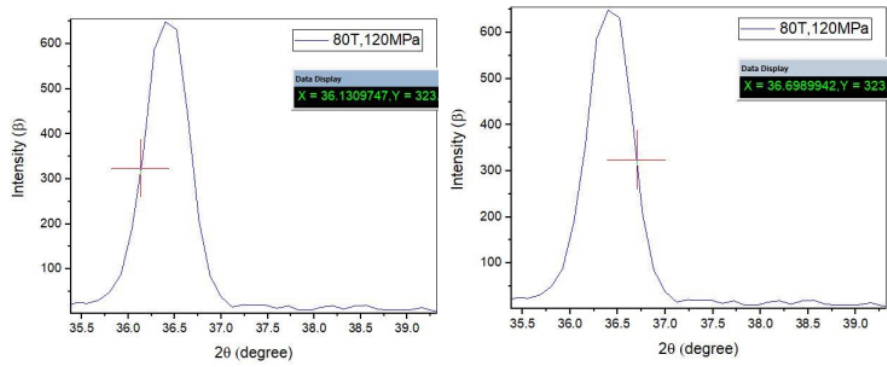


Fig. 5.45 Measurement of β_{hkl} of peak (101)

For (101) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = (36.6989 - 36.1309) = 0.568$$

In radian, $\beta_{hkl} = 0.568 \times \pi/180 = 0.0099$

Here, $K=0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 36.394$$

$$\theta = 18.197$$

Analysis of fourth peak (102)

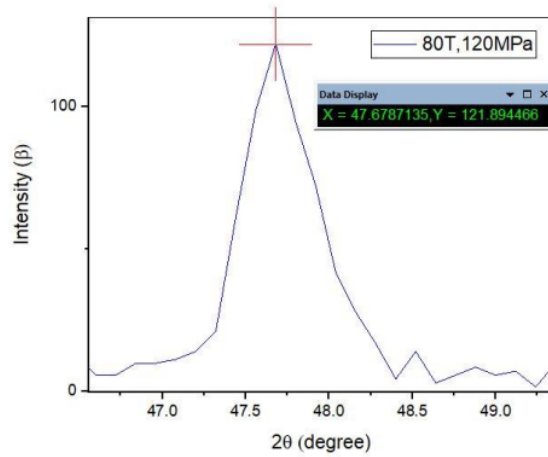


Fig. 5.46 Measurement of 2θ of peak (102)

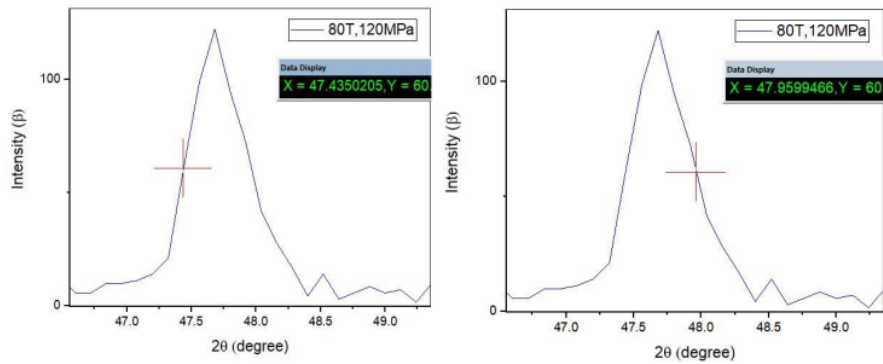


Fig. 5.47 Measurement of β_{hkl} of peak (102)

For (102) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = (47.9599 - 47.4350) = 0.524$$

In radian, $\beta_{hkl} = 0.524 \times \pi/180 = 0.0091$

Here, $K = 0.9$

$\lambda = 0.154 \text{ nm}$

$2\theta = 47.6787$

$\theta = 23.839$

Analysis of fifth peak (110)

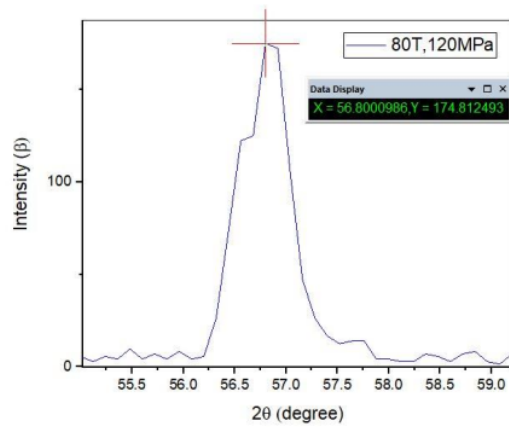


Fig. 5.48 Measurement of 2θ of peak (110)

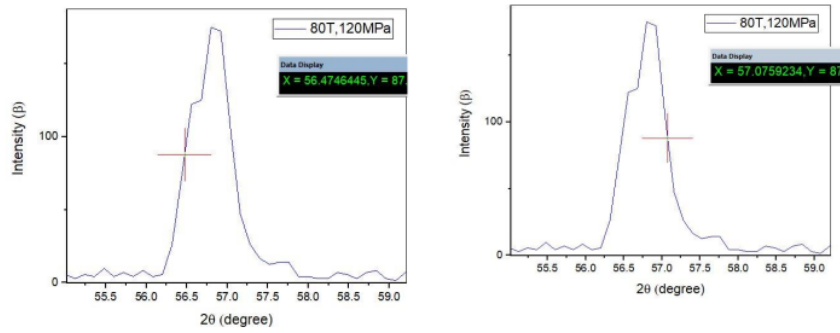


Fig. 5.49 Measurement of β_{hkl} of peak (110)

For (110) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = (57.0759 - 56.4746) = 0.601$$

$$\text{In radian, } \beta_{hkl} = 0.601 \times \pi/180 = 0.0104$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 56.800$$

$$\theta = 28.400$$

Analysis of six peaks (103)

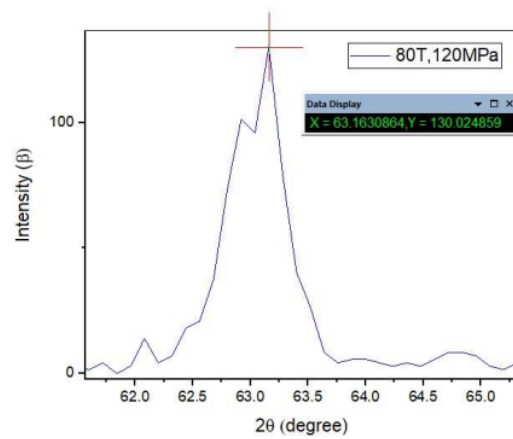


Fig. 5.50 Measurement of 2θ of peak (103)

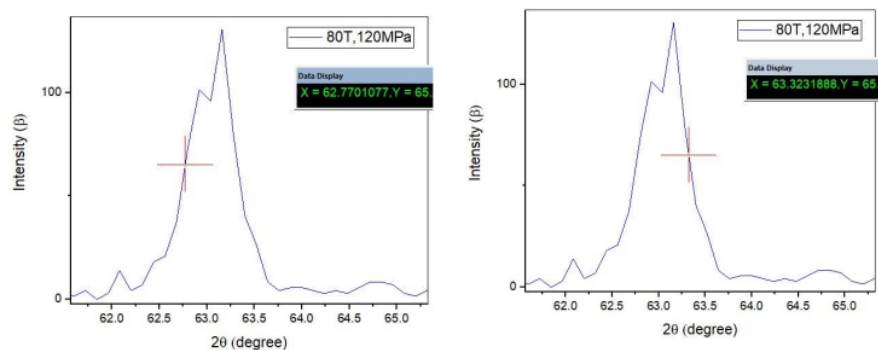


Fig. 5.51 Measurement of β_{hkl} of peak (103)

For (103) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = (63.3231 - 62.7701) = 0.553$$

$$\text{In radian, } \beta_{hkl} = 0.553 \times \pi/180 = 0.0096$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 63.163$$

$$\theta = 31.581$$

5.6 XRD analysis of ZnO nanoparticles at 90T, 120 MPa:

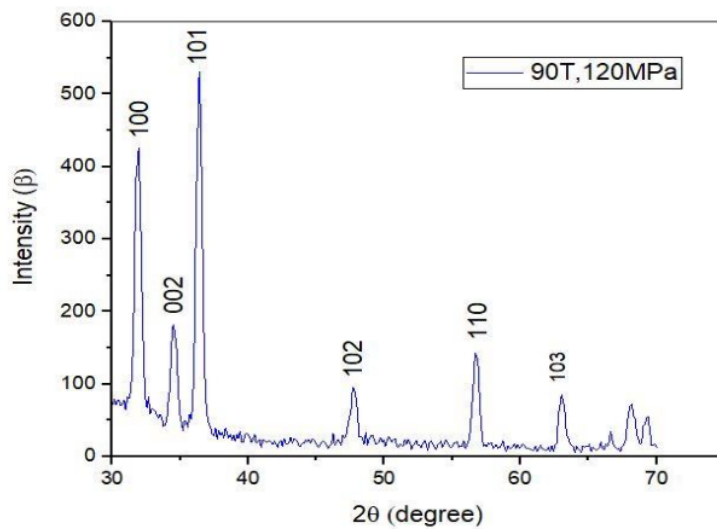


Fig. 5.52 XRD pattern of ZnO nanoparticles with 90T, 120 MPa

Analysis of first peak (100)

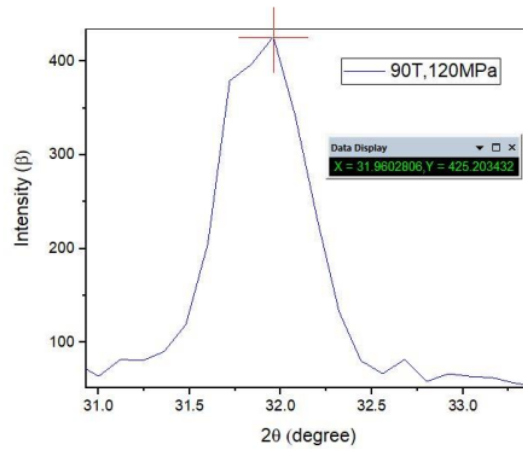


Fig. 5.53 Measurement of 2θ of peak (100)

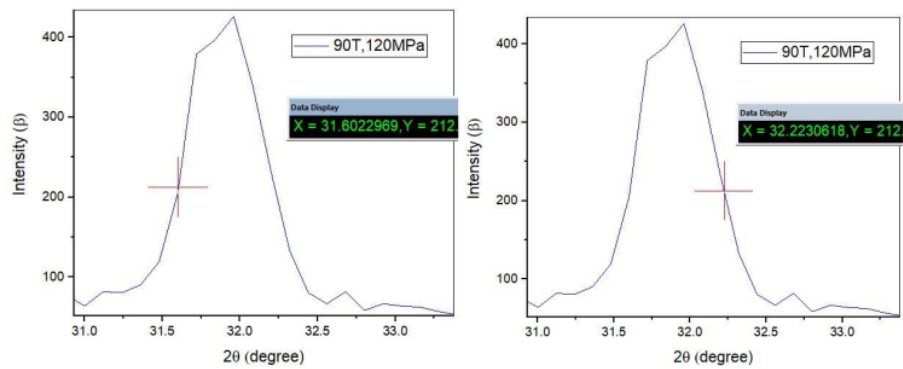


Fig. 5.54 Measurement of β_{hkl} of peak (100)

For (100) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = 32.22306 - 31.602296 = 0.620764$$

$$\text{In radian, } \beta_{hkl} = 0.620764 \times \pi / 180 = 0.010834401$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 31.96028$$

$$\theta = 15.98014$$

Analysis of second peak (002)

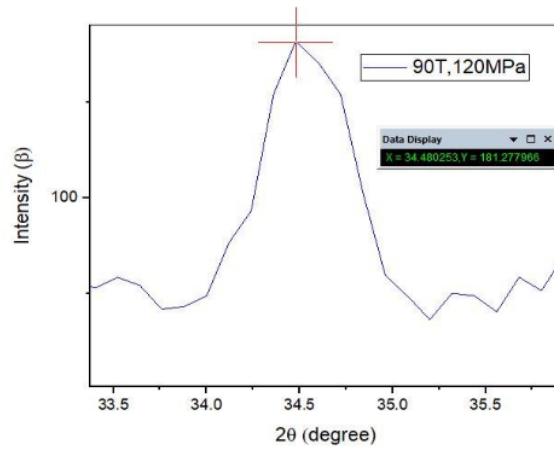


Fig. 5.55 Measurement of 2θ of peak (002)

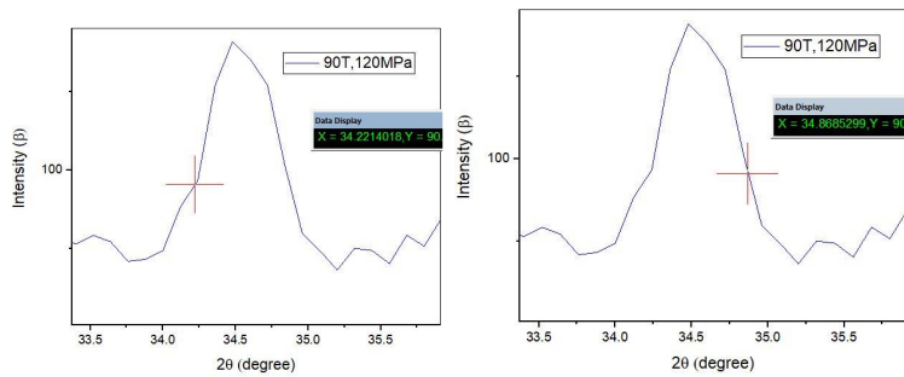


Fig. 5.56 Measurement of β_{hkl} of peak (002)

4
For (002) peak, the line broadening at full width half
maximum (FWHM);

$$\beta_{hkl} = 34.8685 - 34.2214 = 0.6471$$

$$\text{In radian, } \beta_{hkl} = 0.6471 \times \pi / 180 = 0.011294052$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 34.48025$$

$$\theta = 17.240125$$

Analysis of third peak (101)

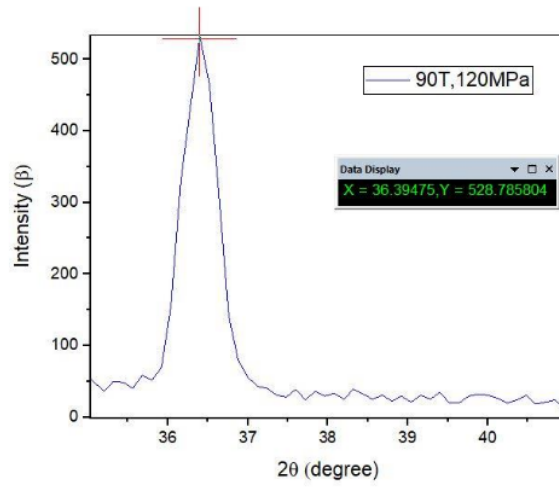


Fig. 5.57 Measurement of 2θ of peak (101)

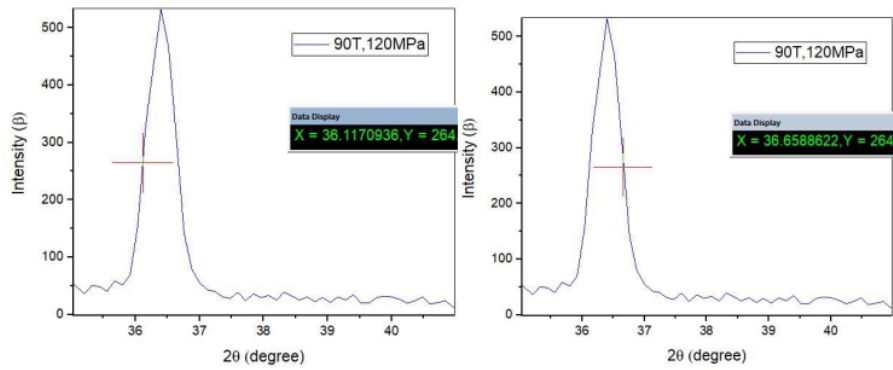


Fig. 5.58 Measurement of β_{hkl} of peak (101)

For (101) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = 36.65886 - 36.11709 = 0.54177$$

$$\text{In radian, } \beta_{hkl} = 0.54177 \times \pi / 180 = 0.009455692$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 36.3947$$

$$\theta = 18.19735$$

Analysis of fourth peak (102)

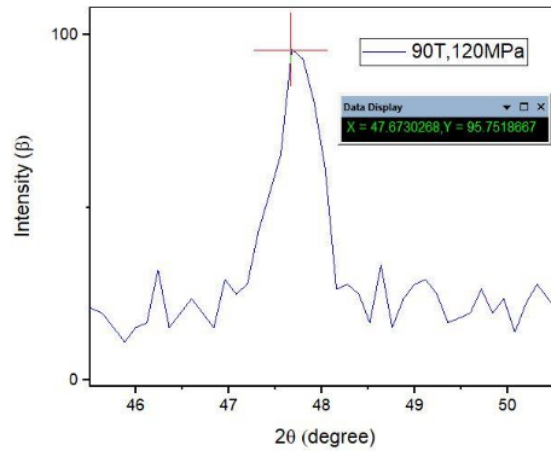


Fig. 5.59 Measurement of 2θ of peak (102)

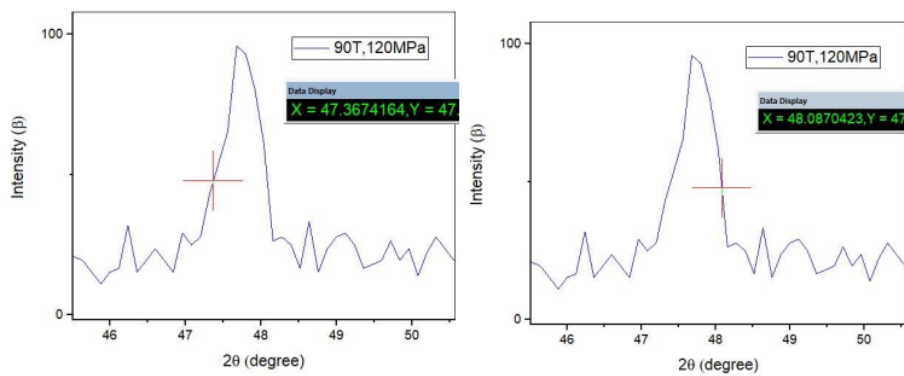


Fig. 5.60 Measurement of β_{hkl} of peak (102)

For (102) peak, the ⁴line broadening at full width half Maximum (FWHM);

$$\beta_{hkl} = 48.08704 - 47.3674 = 0.71964$$

In radian,

$$\beta_{hkl} = 0.71964 \times \pi / 180 = 0.012560117$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 47.673026$$

$$\theta = 23.836513$$

Analysis of fifth peak (110)

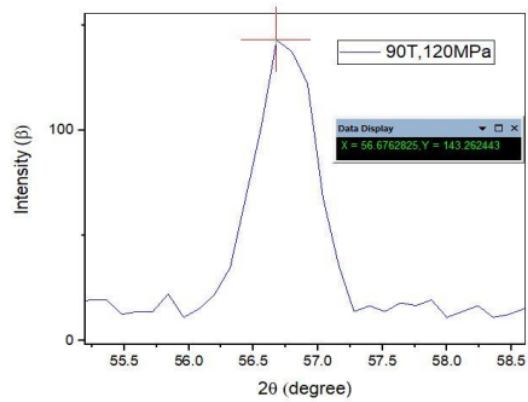


Fig. 5.61 Measurement of 2θ of peak (110)

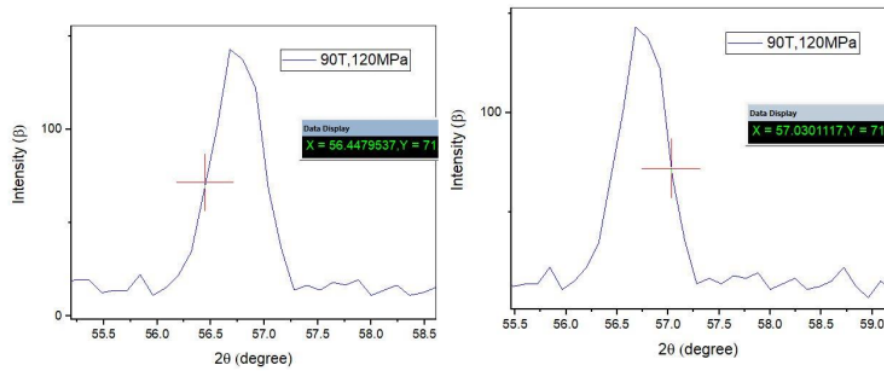


Fig. 5.62 Measurement of β_{hkl} of peak (110)

For (110) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = 57.0301 - 56.4479 = 0.5822$$

In radian,

$$\beta_{hkl} = 0.5822 \times \pi / 180 = 0.010161331$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 56.67628$$

$$\theta = 28.33814$$

Analysis of sixth peak (103)

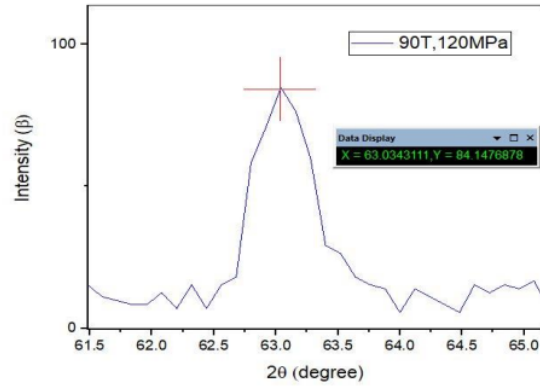


Fig. 5.63 Measurement of 2θ of peak (103)

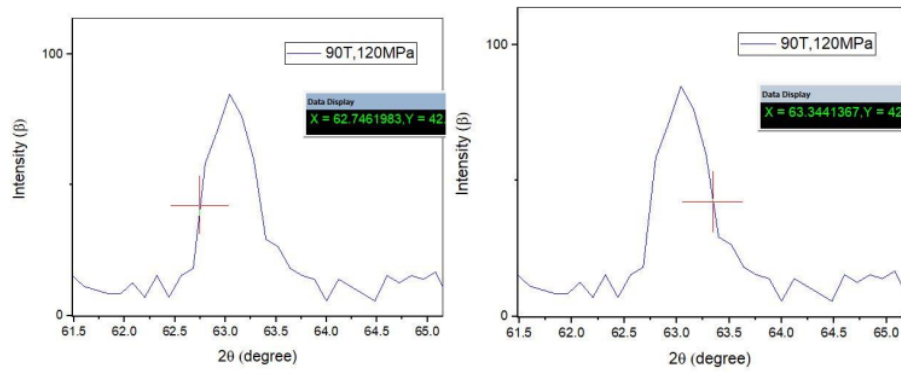


Fig. 5.64 Measurement of β_{hkl} of peak (103)

For (103) peak, the line broadening at full width half maximum (FWHM);

$$\beta_{hkl} = 63.3441 - 62.74619 = 0.59791$$

$$\text{In radian, } \beta_{hkl} = 0.59791 \times \pi / 180 = 0.010435523$$

Here, $K = 0.9$

$$\lambda = 0.154 \text{ nm}$$

$$2\theta = 63.0343$$

$$\theta = 31.51715$$

5.7 Crystallite size determined by Modified Scherrer Method

From chapter 4, we know that the Modified Scherrer equation can be written as,

$$\ln \mathcal{B}_{hkl} = \ln \frac{K \lambda}{D \cos \theta} = \ln \frac{K \lambda}{D} + \ln \frac{1}{\cos \theta} \quad (5.1)$$

Where, D = crystallite size, $K = 0.9$ (constant value for Scherrer's formula) $\lambda = 0.154 \text{ nm}$ (constant value of X-ray Wavelength), $\mathcal{B}_{hkl}$ = the line broadening at Half peak of the Maximum intensity (in radians), θ = the Bragg angle (in degree)

If we plot the results of $\ln \mathcal{B}_{hkl}$ against $\ln(1/\cos \theta)$, then a straight line with a slope of around one and an intercept of about $\ln K/D$ must be obtained. Theoretically this straight line must be with a slope of 45° since $\tan 45^\circ = 1$. But, since errors are associated with experimental data, the least squares method gives the best slope and most accurate $\ln K/D$. After getting the intercept, then the exponential of the intercept is obtained:

$$e^{\ln \frac{K \lambda}{D}} = \frac{K \lambda}{D} \quad (5.2)$$

Having $K = 0.9$ and λ (such as $\lambda = 0.15405 \text{ nm}$), a single value of D in nanometer can be calculated. The value of $\ln \frac{1}{\cos \theta}$ and $\ln \mathcal{B}_{hkl}$ of ZnO nanoparticles for first six peaks at 50°C , 60°C , 70°C , 80°C and 90°C temperature with 120 MPa pressure are shown in Table 5.1, Table 5.2, Table 5.3 Table 5.4 and Table 5.5 below.

Table 5.1 Values for Modified Scherrer Method with 50°C temperature at 120 MPa pressure.

Peak	$\mathcal{B}_{hkl}$	$\mathcal{B}_{hkl}(\text{rad.})$	2θ	θ	$\cos \theta$	$\ln \frac{1}{\cos \theta}$	$\ln \mathcal{B}_{hkl}$
100	0.537	0.0093724 4	31.96044	15.98022	0.9613567 96	0.0394096 63	-4.66998
002	0.6214	0.0108455 01	34.7159	17.35795	0.9544595 41	0.0466100 24	-4.524
101	0.5584	0.0097459 41	36.51652	18.25826	0.9496539 69	0.0516576 04	-4.6309
102	0.4138	0.0072221 89	47.6807	23.84035	0.9146752 48	0.0891861 97	-4.9306
110	0.51156	0.0089284 27	56.91854	28.45927	0.8791560 9	0.1287928 2	-4.71852
103	0.52391	0.0091439	63.0403	31.52015	0.8524563	0.1596332	-4.69466

Table 5.2 Values for Modified Scherrer Method with 60°C temperature at 120 MPa pressure.

Peak	$\mathcal{B}_{hkl}$	$\mathcal{B}_{hkl}$ (rad.)	2θ	θ	$\cos\theta$	$\ln\frac{1}{\cos\theta}$	$\ln \mathcal{B}_{hkl}$
100	0.5464	0.00953	31.8410	15.92053	0.9616431	0.039111	-4.65262863
002	0.5666 9	0.00989 0629	34.4811 1	17.24056	0.9550688 15	0.045971 884	- 4.616167536
101	0.5482 22	0.00956 8301	36.3961 7	18.19809	0.9499824 9	0.051311 726	- 4.649299623
102	0.5860 6	0.01022 8701	47.7952 45	23.89762	0.9142707 66	0.089628 509	- 4.582557687
110	0.5988 1	0.01045 1231	56.7970 85	28.39854	0.8796606 72	0.128219 046	- 4.561035508
103	0.5570 42	0.00972 224	63.0382 97	31.51915	0.8524654 95	0.159622 546	- 4.633339234

Table 5.3 Values for Modified Scherrer Method with 70°C temperature at 120 MPa pressure.

Peak	$\mathcal{B}_{hkl}$	$\mathcal{B}_{hkl}$ (rad.)	2θ	θ	$\cos\theta$	$\ln\frac{1}{\cos\theta}$	$\ln \mathcal{B}_{hkl}$
100	0.5541	0.00967 1363	31.9615	15.98079	0.96135408	0.039412	-4.63858602
002	0.5255	0.00917 232	34.6006	17.3003	0.95475924 2	0.046296 073	-4.69156502
101	0.5615 8	0.00980 1443	36.5204 9	18.26025	0.94964311 5	0.051669 033	-4.62522565
102	0.6703 2	0.01169 9318	47.6818 2	23.84091	0.91467129 8	0.089190 515	-4.44822472
110	0.5529 78	0.00965 1309	56.8003 37	28.40017	0.87964717 4	0.128234 391	-4.64066172
103	0.6517 6	0.01137 5385	63.0429 99	31.5215	0.85244404 4	0.159647 71	-4.47630346

Table 5.4 Values for Modified Scherrer Method with 80°C temperature at 120 MPa pressure.

Peak	$\mathcal{B}_{hkl}$	$\mathcal{B}_{hkl} (rad.)$	2θ	θ	$Cos\theta$	$\ln \frac{1}{cos\theta}$	$\ln \mathcal{B}_{hkl}$
100	0.559	0.0097	31.842	15.921	0.9616	0.0391567 15	-4.635629
002	0.552	0.0096	34.597	17.298	0.9547	0.0463581 24	-4.645992
101	0.568	0.0099	36.394	18.197	0.9499	0.0513985 63	-4.615220
102	0.524	0.0091	47.6787	23.839	0.9146	0.0892684 68	-4.699480
110	0.601	0.0104	56.800	28.400	0.8796	0.1282880 2	-4.565949
103	0.553	0.0096	63.163	31.581	0.8519	0.1602861 3	-4.645992

Table 5.5 Values for Modified Scherrer Method with 90°C temperature at 120 MPa pressure.

Peak	$\mathcal{B}_{hkl}$	$\mathcal{B}_{hkl} (rad.)$	2θ	θ	$Cos\theta$	$\ln \frac{1}{cos\theta}$	$\ln \mathcal{B}_{hkl}$
100	0.6207 64	0.0108344 01	31.9602 8	15.9801 4	0.9613571 8	0.0394092 64	-4.525028
002	0.6471	0.0112940 52	34.4802 5	17.2401 3	0.9550710 4	0.0459695 54	-4.483479
101	0.5417 7	0.0094556 92	36.3947	18.1973 5	0.9499864 96	0.0513075 09	-4.661138
102	0.7196 4	0.0125601 17	47.6730 26	23.8365 1	0.9147023 14	0.0891566 07	-4.377228
110	0.5822	0.0101613 31	56.6762 8	28.3381 4	0.8801615 73	0.1276497 83	-4.589165
103	0.5979 1	0.0104355 23	63.0343	31.5171 5	0.8524837 3	0.1596011 55	-4.562539

¹⁵ If we plot the results of $\ln \beta$ against $\ln (1/\cos \theta)$. The straight line with a slope of around one and the intercept of about $\ln \frac{K \lambda}{D}$ must be obtained by equation (5.4). After getting the

intercept, then the exponential of the intercept is obtained. The crystallite size determines by the equation (5.5).

$$\ln B_{hkl} = \ln \frac{K \lambda}{D} + \ln \frac{1}{\cos \theta} \quad (5.3)$$

$$\ln \frac{K \lambda}{D} = \text{intercept} \quad (5.4)$$

$$\frac{K \lambda}{D} = e^{\text{intercept}} \quad (5.5)$$

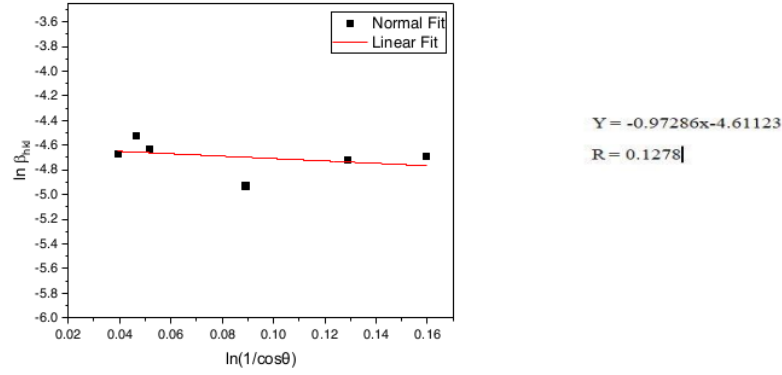


Fig. 5.65: Linear plots of modified scherrer equation and obtained intercepts for ZnO nanoparticles with 50°C temperature at 120 MPa pressure.

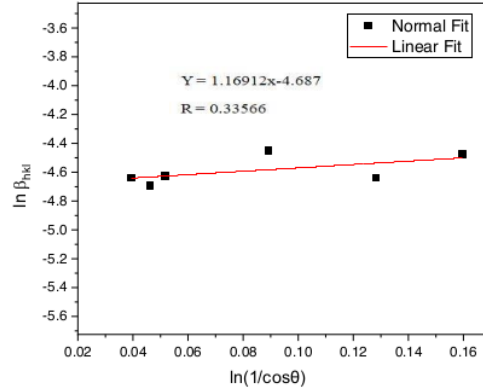


Fig. 5.66: Linear plots of modified scherrer equation and obtained intercepts for ZnO nanoparticles with 60°C temperature at 120 MPa pressure.

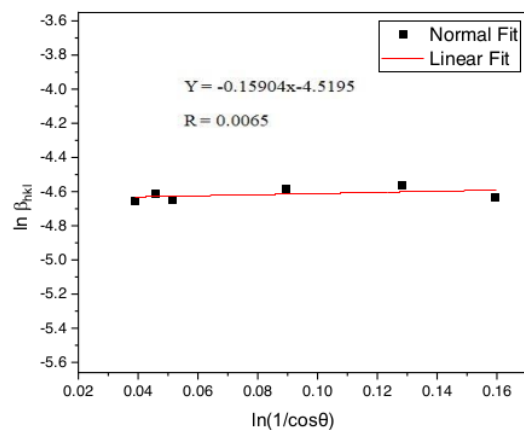


Fig. 5.67: Linear plots of modified scherrer equation and obtained intercepts for ZnO nanoparticles with 70°C temperature at 120 MPa pressure

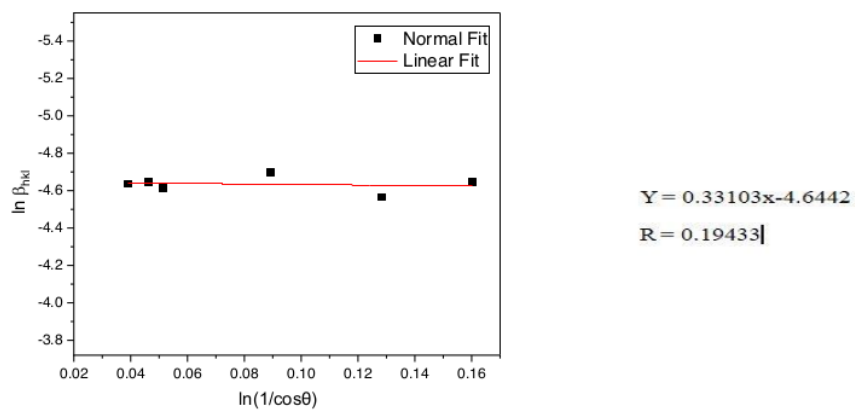


Fig. 5.68: Linear plots of modified scherrer equation and obtained intercepts for ZnO nanoparticles with 80°C temperature at 120 MPa pressure.

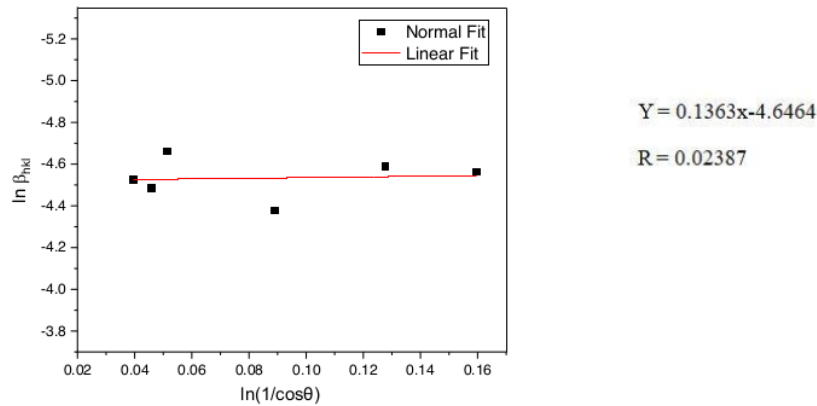


Fig. 5.69: Linear plots of modified scherrer equation and obtained intercepts for ZnO nanoparticles with 90°C temperature at 120 MPa pressure

The values of crystallite size (D) obtained from modified scherrer method with different annealing temperature at constant pressure is:

Temperature	Pressure	Crystallite size (D)
50°C	120 MPa	13.94 nm
60°C	120 MPa	14.4 nm
70°C	120 MPa	15.04 nm
80°C	120 MPa	14.44 nm
90°C	120 MPa	12.72 nm

5.8 Lattice parameters of ZnO nanoparticles with different annealing temperature at 120 MPa pressure.

Three lattice parameters are a, b, and c. When the lattice parameters a and c are held within the ratio of $c/a = 1.63$, a complete wurtzite structure has a hexagonal unit cell. $a = b$ for a hexagonal unit cell. As a result, we can only use the formula below to calculate the values of a and c.

The lattice constant a for the plane <100> is determined as follows:

$$a = \frac{\lambda}{\sqrt{3} \sin \theta_{(100)}} \quad (5.6)$$

For the <002> plane, the lattice constant c is calculated by,

$$c = \frac{\lambda}{\sin \theta_{(002)}} \quad (5.7)$$

Table 5.6 Lattice parameters of ZnO nanoparticles with 50T, 120 MPa

B_{hkl}	Lattice Parameters ($\text{\AA}$)	c/a ratio	Structure
(100)	$a = 3.229$	$c/a = 1.60$	Hexagonal
(002)	$c = 5.1619$		

Table 5.7 Lattice parameters of ZnO nanoparticles at 60T, 120 MPa

B_{hkl}	Lattice Parameters ($\text{\AA}$)	c/a ratio	Structure
(100)	$a = 3.24136$	$c/a = 1.603$	Hexagonal
(002)	$c = 5.19595$		

Table 5.8 Lattice parameters of ZnO nanoparticles at 70T, 120 MPa

B_{hkl}	Lattice Parameters ($\text{\AA}$)	c/a ratio	Structure
(100)	$a = 3.229$	$c/a = 1.6037$	Hexagonal
(002)	$c = 5.1785$		

Table 5.9 Lattice parameters of ZnO nanoparticles with 80T, 120 MPa

B_{hkl}	Lattice Parameters ($\text{\AA}$)	c/a ratio	Structure
(100)	$a = 3.24$	$c/a = 1.60$	Hexagonal
(002)	$c = 5.17$		

Table 5.10 Lattice parameters of ZnO nanoparticles at 90T, 120 MPa

B_{hkl}	Lattice Parameters ($\text{\AA}$)	c/a ratio	Structure
(100)	$a = 3.229$	$c/a = 1.609$	Hexagonal
(002)	$c = 5.19608$		

From the ¹⁶Table 5.6, Table 5.7, Table 5.8, Table 5.9, and ¹⁴⁸Table 5.10 we can say that ¹⁷the structure of ZnO nanoparticles is hexagonal due to the lattice parameters a and c stay within the ratio of c/a = 1.63.

5.9 Dislocation density of ZnO nanoparticles with different annealing temperature at 120 MPa pressure.

²⁶The dislocation density (δ), which represents the amount of defects in the sample is defined as the length of dislocation lines per unit volume of the crystal and is calculated using the Eq.

$$\delta = \frac{1}{D^2}$$

where D is the crystallite size. And δ is the dislocation density.

The variation of dislocation density evaluated from the modified scherrer method for ZnO nanoparticles with different annealing temperature at 120 MPa pressure obtained by the above formula as:

Temperature	Pressure	Crystallite size (D)	Dislocation density (δ)
50°C	120 MPa	13.94 nm	$5.146 \times 10^{-03} \text{ (nm)}^{-2}$
60°C	120 MPa	14.4 nm	$4.82 \times 10^{-03} \text{ (nm)}^{-2}$
70°C	120 MPa	15.04 nm	$4.42 \times 10^{-03} \text{ (nm)}^{-2}$
80°C	120 MPa	14.44 nm	$4.8 \times 10^{-03} \text{ (nm)}^{-2}$
90°C	120 MPa	12.72 nm	$6.18 \times 10^{-03} \text{ (nm)}^{-2}$

5.10 Williamson-Hall Method

¹³The Scherrer formula only takes into account the effect of crystallite size on XRD peak broadening, but it ignores the microstructures of the lattice, i.e. the intrinsic strain that develops in nanocrystals as a result of point defects, grain boundaries, triple junctions, and stacking faults [67, 68]. Many techniques, such as the Williamsons Hall method and the Warren-Averbach method, take into account the effect of strain-induced XRD peak broadening and can be used to calculate the intrinsic strain and particle size. Among these, the Williamson–Hall (W H) approach is the simplest and most straightforward [69, 70]. According to this theory, the size and microstrain of

nanocrystals cause physical line broadening of the X-ray diffraction peak, and the complete broadening can be written as,

$$\beta_{total} = \beta_{size} + \beta_{strain}$$

The average particle size and microstrain were determined in this study using updated W–H equations including UDM, USDM, and UEDM, which were discussed in the previous parts.

5.10.1 Uniform deformation model (UDM)

From chapter 4, we know that the UDM equation can be written as

$$\beta_{hkl} = \frac{K\lambda}{D \cdot \cos\theta} + 4 \cdot \epsilon \cdot \tan\theta \quad (5.8)$$

By rearranging Eq. (5.8), we get

$$\beta_{hkl} \cos\theta_{hkl} = \frac{K\lambda}{D} + 4 \cdot \epsilon \cdot \sin\theta_{hkl} \quad (5.9)$$

Equation (5.9) is an equation of a straight line and is known as the uniform deformation model (UDM) equation, which considers the isotropic nature of the crystals.

Plotting of this equation (5.9), with the term $(4\sin\theta)$ along X-axis and $(\beta_{hkl} \cdot \cos\theta)$ along Y-axis corresponding to each diffraction peak for ZnO nanoparticles, this plotted straight line is a good fitted line, corresponding to all the values. The slope of this straight line provides the value of the intrinsic strain, whereas the intercept gives the average particle size of the ZnO nanocrystals.

The value of $(4\sin\theta)$ and $(\beta_{hkl} \cdot \cos\theta)$ of ZnO nanoparticles for first six peaks at 27°C, 60°C, 70°C, 80°C and 90°C temperature with 120 MPa pressure are shown in Table 5.11, Table 5.12, Table 5.13, Table 5.14 and Table 5.15 below.

Table 5.11 Values for UDM plot at 50T, 120 MPa.

Peak	$\beta_{hkl}(\text{rad.})$	θ	$\cos\theta$	$4\sin\theta$	$\beta_{hkl} \cos\theta$
100	0.00937244	15.98022	0.961356796	1.101221947	0.009010259
002	0.010845501	17.35795	0.954459541	1.193361537	0.010351592
101	0.009745941	18.25826	0.949653969	1.253202863	0.009255272
102	0.007222189	23.84035	0.914675248	1.616758191	0.006605958
110	0.008928427	28.45927	0.87915609	1.906135651	0.007849481
103	0.009143976	31.52015	0.852456357	2.091193569	0.00779484

Table 5.12: Values for UDM plot at 60T, 120 MPa.

Peak	$\beta_{hkl}(\text{rad.})$	θ	$\cos\theta$	$4\sin\theta$	$\beta_{hkl} \cos\theta$
100	0.009536501	15.92053	0.961643108	1.097214898	0.009170711
002	0.009890629	17.24056	0.955068815	1.185536558	0.009446232
101	0.009568301	18.19809	0.94998249	1.249212669	0.009089719
102	0.010228701	23.89762	0.914270766	1.620414597	0.009351802
110	0.010451231	28.39854	0.879660672	1.902407329	0.009193536
103	0.00972224	31.51915	0.852465495	2.091133966	0.008287874

Table 5.13: Values for UDM plot at 70T, 120 MPa.

Peak	$\beta_{hkl}(\text{rad.})$	θ	$\cos\theta$	$4\sin\theta$	$\beta_{hkl} \cos\theta$
100	0.009671363	31.96157	0.961354081	1.101259867	0.009297605
002	0.00917232	34.6006	0.954759242	1.189519493	0.008757357
101	0.009801443	36.52049	0.949643115	1.253334465	0.009307873
102	0.011699318	47.68182	0.914671298	1.61679395	0.010701031
110	0.009651309	56.800337	0.879647174	1.902507184	0.008489747
103	0.011375385	63.042999	0.852444044	2.09127388	0.009696879

Table 5.14: Values for UDM plot at 80T, 120 MPa.

Peak	$\beta_{hkl}(\text{rad.})$	θ	$\text{Cos}\theta$	$4\sin\theta$	$\beta_{hkl}\cos\theta$
100	0.00976514	15.92094	0.961641145	1.097242424	0.00939056
002	0.00964541	17.2985	0.954768584	1.189399514	0.009209135
101	0.009915064	18.19719	0.949987396	1.24915298	0.009419186
102	0.009160906	23.83935	0.914682302	1.616694334	0.008379318
110	0.010494689	28.4	0.879648573	1.902496836	0.009231638
103	0.00965309	31.58154	0.851895712	2.094845851	0.008223426

Table 5.15: Values for UDM plot at 90T, 120 MPa.

Peak	$\beta_{hkl}(\text{rad.})$	θ	$\text{Cos}\theta$	$4\sin\theta$	$\beta_{hkl}\cos\theta$
100	0.010834401	15.98014	0.96135718	1.101216578	0.010415729
002	0.011294052	17.24013	0.95507104	1.185507887	0.010786622
101	0.009455692	18.19735	0.949986496	1.249163923	0.00898278
102	0.012560117	23.83651	0.914702314	1.61651317	0.011488768
110	0.010161331	28.33814	0.880161573	1.89869684	0.008943613
103	0.010435523	31.51715	0.85248373	2.091015028	0.008896113

In Fig. 5.66, Fig. 5.67, Fig. 5.68, Fig. 5.69 and Fig. 5.70 the plots are drawn by placing the value of $4\sin\theta$ along the x-axis and $\beta_{hkl}\cos\theta$ along y-axis of ZnO nanoparticles. From the figure, y-intercept and slope analysed to determine the crystallite size (D) and lattice strain (ϵ) which is summarized in equation (5.10) and (5.11).

$$D = \frac{k\lambda}{y\text{-intercept}} \quad (5.10)$$

$$\epsilon = \text{slope} \quad (5.11)$$

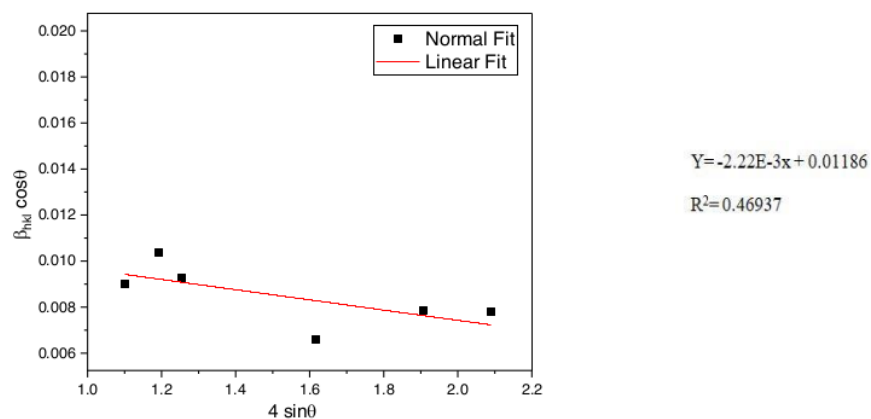


Fig. 5.70 Plot of $\beta_{hkl} \cos \theta$ versus $4 \sin \theta$ for ZnO nanoparticles with 50T at 120 MPa.

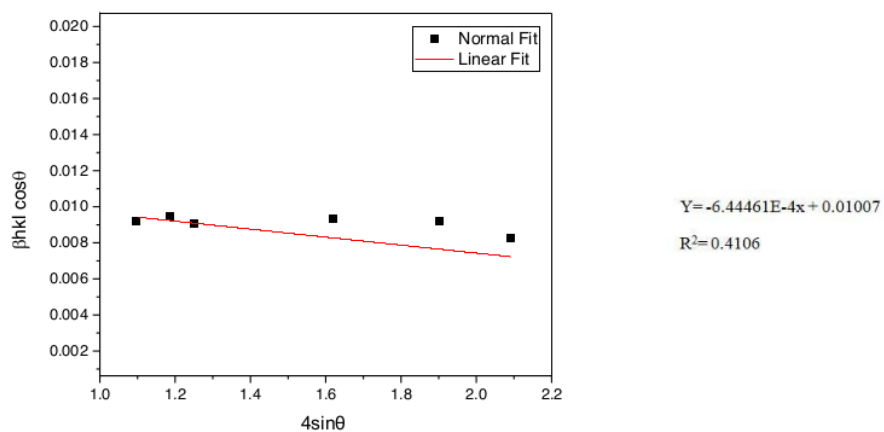
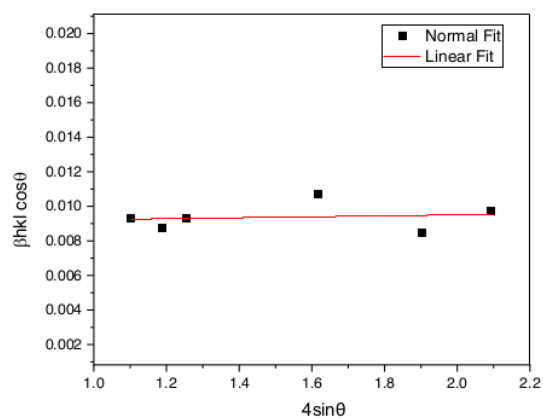


Fig. 5.71 Plot of $\beta_{hkl} \cos \theta$ versus $4 \sin \theta$ for ZnO nanoparticles with 60T at 120 MPa.

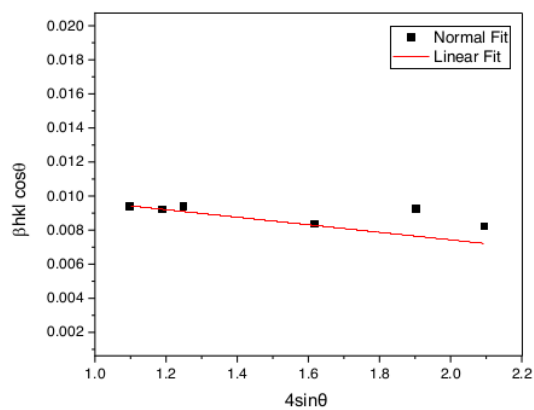


$$Y = 2.72287E-4x + 0.00896$$

$$R^2 = 0.02044$$

4

Fig. 5.72 Plot of $\beta_{hkl} \cos \theta$ versus $4 \sin \theta$ for ZnO nanoparticles with 70T at 120 MPa.



$$Y = -1.25E-3x + 0.01182$$

$$R^2 = 0.20593$$

4

Fig. 5.73 Plot of $\beta_{hkl} \cos \theta$ versus $4 \sin \theta$ for ZnO nanoparticles with 80T at 120 MPa.

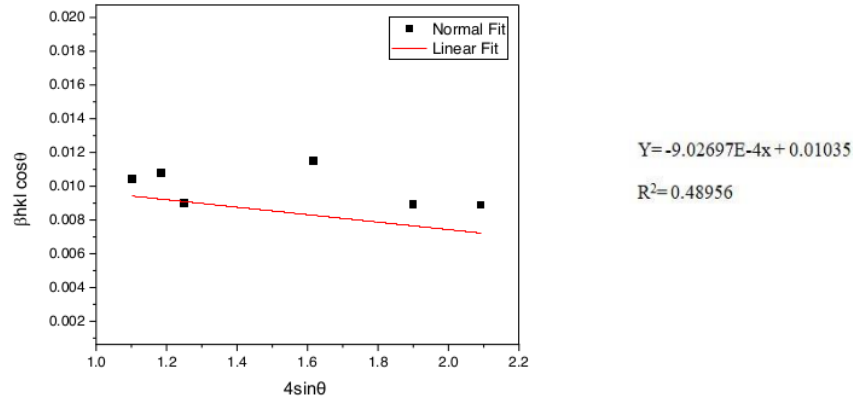


Fig. 5.74 Plot of $\beta_{hkl} \cos \theta$ versus $4 \sin \theta$ for ZnO nanoparticles with 90T at 120 MPa.

The values of crystallite size (D), lattice strain (ϵ) obtained from UDM model with different annealing temperature at constant pressure are

Temperature	Pressure	Crystallite size (D)	Lattice Strain (ϵ)
50°C	120 MPa	11.68 nm	-2.22×10^{-3}
60°C	120 MPa	13.76 nm	-6.44×10^{-4}
70°C	120 MPa	15.46 nm	2.722×10^{-4}
80°C	120 MPa	13.4 nm	-9.027×10^{-4}
90°C	120 MPa	11.72 nm	1.46×10^{-3}

5.10.2 Uniform Stress Deformation Model (USDM)

From chapter 4, we know that According to Hooke's law, stress and strain have a linear relationship, where stress is expressed as $\sigma = \epsilon \cdot Y_{hkl}$, Y_{hkl} being the modulus of elasticity or Young's modulus. So, strain can be expressed as

$$\epsilon = \sigma / Y_{hkl}$$

Because of the size confinement, the intrinsic strain in the crystals causes a small amount of internal tension. USDM took into account stress-induced XRD peak broadening and the anisotropic aspect of Young's modulus [71]. We get by putting the value of ϵ in equation (5.9) and rearrangement,

$$\mathcal{B}_{hkl} \cdot \cos \theta_{hkl} = \frac{K\lambda}{D} + 4 \cdot \sigma \cdot \frac{\sin \theta_{hkl}}{Y_{hkl}} \quad (5.12)$$

This is the ¹uniform stress deformation model, which considers uniform stress in all crystallographic directions and is based on the modified W–H equation. For cubic crystal, ¹Young's modulus Y_{hkl} can be expressed as [72],

$$Y_{hkl} = \frac{s_{11} \left[h^2 + \frac{(h+2k)^2}{3} + \left(\frac{al}{c} \right)^2 \right]^2}{s_{11} \left(h^2 + \frac{(h+2k)^2}{3} \right)^2 + s_{33} \left(\frac{al}{c} \right)^4 + (2s_{13} + s_{44}) \left(h^2 + \frac{(h+2k)^2}{3} \right) \left(\frac{al}{c} \right)^2} \quad (5.13)$$

Plot of equation (5.12), with the term $(4\sin\theta/Y_{hkl})$ along X-axis and $(\beta_{hkl} \cos\theta)$ along Y-axis corresponding to each peak in the XRD pattern for ZnO nanoparticles, ¹the slope of this plotted straight line provides the value of stress, whereas the intercept gives the average particle size of the ZnO nanocrystals.

The value of $(4\sin\theta/Y_{hkl})$ and $(\beta_{hkl} \cos\theta)$ of ZnO nanoparticles for first six peaks at ²⁷50°C, 60°C, 70°C, 80°C and 90°C temperature with 120 MPa pressure are shown in ¹⁶Table 5.16, Table 5.17, Table 5.18 Table 5.19 and Table 5.20 below.

Table 5.16 Values for USDM plot at 50T, 120 MPa

Peak	$\beta_{hkl}(\text{rad.})$	θ	$\cos\theta$	$4\sin\theta$	$\beta_{hkl}\cos\theta$	$Y_{hkl}\text{GPa}$ (10^9)	$4\sin\theta/Y_{hkl}$ (10^{-12})
100	0.0095365	15.92 053	0.9616431	1.097214 8	0.009170 7	127.259	8.622
002	0.0098906	17.24 056	0.9550688	1.185536 5	0.009446 2	144.092	8.227
101	0.0095683	18.19 809	0.9499824	1.249212 6	0.009089 7	118.862	10.511
102	0.0102287	23.89 762	0.9142707	1.620414 5	0.009351 8	118.385	13.68
110	0.0104512	28.39 854	0.8796606	1.902407 3	0.009193 5	127.259	14.95
103	0.0097222	31.51 915	0.8524654	2.091133 9	0.008287 8	124.011	16.856

Table 5.17 Values for USDM plot at 60T, 120 MPa

Peak	$\beta_{hkl}(\text{rad.})$	θ	$\text{Cos}\theta$	$4\sin\theta$	$\beta_{hkl}\cos\theta$	$Y_{hkl}\text{GPa}$ (10^9)	$4\sin\theta/Y_{hkl}$ (10^{-12})
100	0.010834 401	15.98014	0.9613 5718	1.101216 578	0.0104 15729	127.259	8.622
002	0.011294 052	17.24013	0.9550 7104	1.185507 887	0.0107 86622	144.09	8.254
101	0.009455 692	18.19735	0.9499 86496	1.249163 923	0.0089 8278	118.89	10.506
102	0.012560 117	23.83651	0.9147 02314	1.616513 17	0.0114 88768	118.35	13.659
110	0.010161 331	28.33814	0.8801 61573	1.898696 84	0.0089 43613	127.259	14.949
103	0.010435 523	31.51715	0.8524 8373	2.091015 028	0.0088 96113	123.943	16.901

Table 5.18 Values for USDM plot at 70T, 120 MPa

Peak	$\beta_{hkl}(\text{rad.})$	θ	$\text{Cos}\theta$	$4\sin\theta$	$\beta_{hkl}\cos\theta$	$Y_{hkl}\text{GPa}$ a (10^9)	$4\sin\theta/Y_{hkl}$ (10^{-12})
100	0.009671 3	15.98078 5	0.961354 0	1.101259 8	0.009297 6	127.259	8.653
002	0.009172 3	17.3003	0.954759 2	1.189519 4	0.008757 3	144.09	8.2552
101	0.009801 4	18.26024 5	0.949643 1	1.253334 4	0.009307 8	118.86	10.544
102	0.011699 3	23.84091	0.914671 2	1.616793 9	0.010701 0	118.38	13.657
110	0.009651 3	28.40016 8	0.879647 1	1.902507 1	0.008489 7	127.25	14.949
103	0.011375 3	31.52149 9	0.852444 0	2.091273 8	0.009696 8	124.00	16.864

Table 5.19 Values for USDM plot at 80T, 120 MPa

Peak	$\beta_{hkl}(\text{rad.})$	θ	$\text{Cos}\theta$	$4\sin\theta$	$\beta_{hkl}\cos\theta$	$Y_{hkl}\text{GPa}$ (10^9)	$4\sin\theta/Y_{hkl}$ (10^{-12})
100	0.0097	15.921	.9616	1.09724	0.009390	127.259	8.622
002	0.0096	17.298	.9547	1.189399	0.009209	144.09	8.254
101	0.0099	18.197	.9499	1.2491529	0.009419	118.829	10.51
102	0.0091	23.839	.9146	1.616694	0.008379	118.425	13.6
110	0.0104	28.400	.8796	1.902496	0.00923	127.259	14.9
103	0.0096	31.581	.8519	2.0948458	0.0082234	124.09	16.8

Table 5.20 Values for USDM plot at 90T, 120 MPa

Peak	$\beta_{hkl}(\text{rad.})$	θ	$\text{Cos}\theta$	$4\sin\theta$	$\beta_{hkl}\cos\theta$	$Y_{hkl}\text{GPa}$ (10^9)	$4\sin\theta/Y_{hkl}$ (10^{-12})
100	0.009372 44	15.98022	0.9613567 96	1.1012219 47	0.0090102 59	127.25	8.65
002	0.010845 501	17.35795	0.9544595 41	1.1933615 37	0.0103515 92	144.09	8.28
101	0.009745 941	18.25826	0.9496539 69	1.2532028 63	0.0092552 72	118.84	10.54
102	0.007222 189	23.84035	0.9146752 48	1.6167581 91	0.0066059 58	118.409	13.6
110	0.008928 427	28.45927	0.8791560 9	1.9061356 51	0.0078494 81	127.25	14.9
103	0.009143 976	31.52015	0.8524563 57	2.0911935 69	0.0077948 4	124.06	16.8

The value of $4 \cdot \frac{\sin\theta_{hkl}}{Y_{hkl}}$, $\beta_{hkl} \cdot \cos\theta_{hkl}$ and Y_{hkl} of ZnO nanoparticles for first six peaks is shown in Table 5.16, Table 5.17, Table 5.18, Table 5.19 and Table 5.20. In Fig. 5.71, Fig. 5.72, Fig. 5.73, Fig. 5.74 and Fig 5.75 the plots are drawn by placing the value of $4 \cdot \frac{\sin\theta_{hkl}}{Y_{hkl}}$, and $\beta_{hkl} \cdot \cos\theta_{hkl}$ along the x-axis and y-axis respectively. From the corresponding plot y-intercept and slope have been considered for the purpose of obtaining crystallite size (D), strain (ϵ) and stress (σ) which is summarized in the following equation.

$$D = \frac{k\lambda}{y\text{-intercept}} \quad (5.14)$$

$$\sigma = \text{slope} \quad (5.15)$$

$$\varepsilon = \frac{\sigma}{Y_{hkl}} \quad (5.16)$$

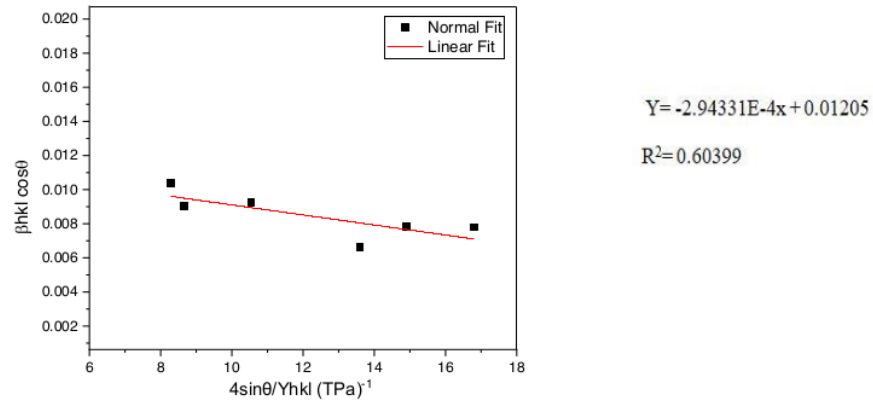


Fig. 5.75 Plot of $\beta_{hkl} \cos \theta$ versus $4 \cdot \frac{\sin \theta_{hkl}}{Y_{hkl}}$ for ZnO nanoparticles with 50T at 120 MPa

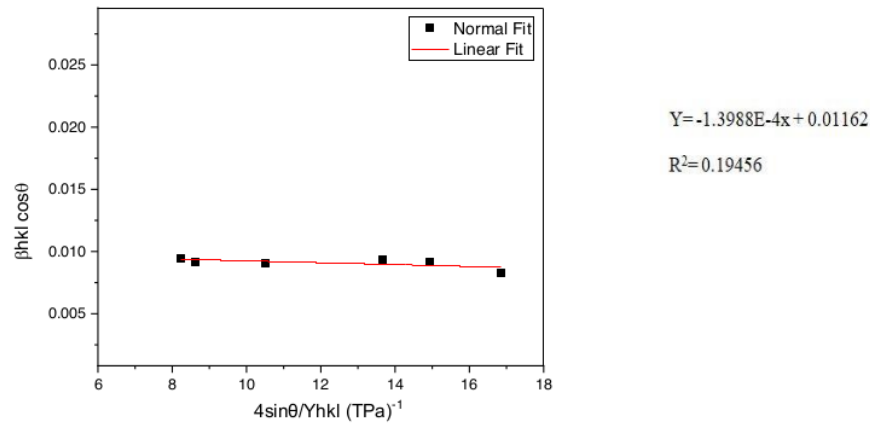
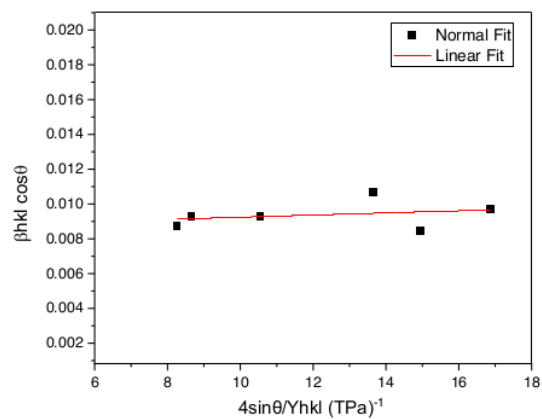


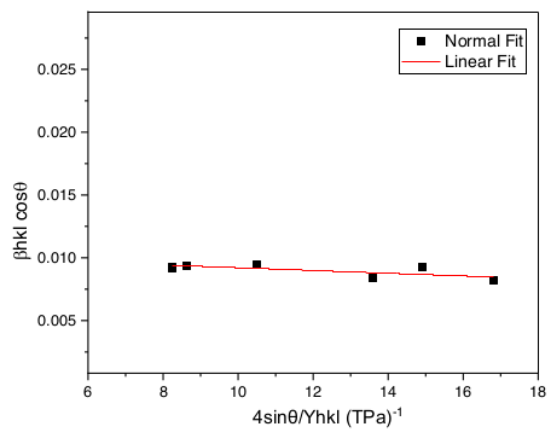
Fig. 5.76 Plot of $\beta_{hkl} \cos \theta$ versus $4 \cdot \frac{\sin \theta_{hkl}}{Y_{hkl}}$ for ZnO nanoparticles with 60T at 120 MPa



$$Y = -1.0974E-4x + 0.0103$$

$$R^2 = 0.52595$$

4
Fig. 5.77 Plot of $\beta_{hkl} \cos \theta$ versus $4 \cdot \frac{\sin \theta_{hkl}}{Y_{hkl}}$ for ZnO nanoparticles with 70T at 120 MPa



$$Y = -7.58336E-5x + 0.01001$$

$$R^2 = 0.42219$$

4
Fig. 5.78 Plot of $\beta_{hkl} \cos \theta$ versus $4 \cdot \frac{\sin \theta_{hkl}}{Y_{hkl}}$ for ZnO nanoparticles with 80T at 120 MPa

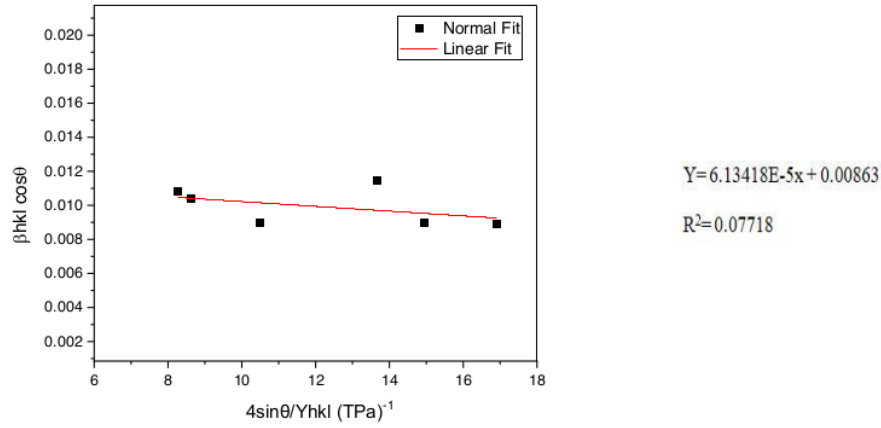


Fig. 5.79 Plot of $\beta_{hkl} \cos \theta$ versus $4 \cdot \frac{\sin \theta_{hkl}}{Y_{hkl}}$ for ZnO nanoparticles with 90T at 120 MPa

The values of crystallite size (D), lattice strain (ϵ) and stress (σ) obtained from USDM model with different annealing temperature at constant pressure are

Temperature	Pressure	Crystallite size (D)	stress (σ)	Lattice Strain (ϵ)
50°C	120 MPa	11.5 nm	-2.943×10^{-04} Pa	$-2.32E-15$
60°C	120 MPa	13.86 nm	-7.58×10^{-04} Pa	$-5.99E-15$
70°C	120 MPa	16.11 nm	6.13×10^{-04} Pa	$4.84E-15$
80°C	120 MPa	13.45 nm	-1.097×10^{-04} Pa	$-8.66E-16$
90°C	120 MPa	11.92 nm	-1.39×10^{-04} Pa	$-1.10E-15$

5.10.3 Uniform Deformation Energy Density Model (UEDM)

From chapter 4, we know that the UEDM equation can be written as

$$\beta_{hkl} \cos \theta_{hkl} = \left(\frac{K\lambda}{D} \right) + \left(4 \sin \theta_{hkl} \left(\frac{2\mu_{ed}}{Y_{hkl}} \right)^{1/2} \right) \quad (5.17)$$

Equation (5.17) is a straight line equation and is known as the uniform deformation energy density model (UEDM) equation [73]. From this model, energy density value of the crystals can be calculated as per equation (5.17). Plot of this equation (5.17), with the term $4 \sin \theta_{hkl} \left(\frac{2}{Y_{hkl}} \right)^{1/2}$ along X-axis and $\beta_{hkl} \cos \theta_{hkl}$ along Y-axis corresponding

to each diffraction peak for ZnO nanoparticles, the intercept of the plotted straight line provides the average size, whereas the slope gives the energy density value.

Table 5.21 Values for UDEDM plot at 50T, 120 MPa

Peak	$\beta_{hkl}(\text{rad.})$	θ	$\cos\theta$	$4\sin\theta$	$\beta_{hkl}\cos\theta$	$Y_{hkl}\text{GPa}$ (10^9)	$4\sin\theta$ ($2/Y_{hkl}$) ^{1/2} (10^{-6})
100	0.009536	15.92 053	0.9616 43	1.097214	0.009170	127.259	4.3497
002	0.009890	17.24 056	0.9550 68	1.185536	0.009446	144.092	4.4168
101	0.009568	18.19 809	0.9499 82	1.249212	0.009089	118.862	5.1242
102	0.010228	23.89 762	0.9142 70	1.620414	0.009351	118.385	6.6602
110	0.010451	28.39 854	0.8796 60	1.902407	0.009193	127.259	7.5417
103	0.009722	31.51 915	0.8524 65	2.091133	0.008287	124.011	8.3978

Table 5.22 Values for UDEDM plot at 60T, 120 MPa

Peak	$\beta_{hkl}(\text{rad.})$	θ	$\cos\theta$	$4\sin\theta$	$\beta_{hkl}\cos\theta$	$Y_{hkl}\text{GPa}$ (10^9)	$4\sin\theta$ ($2/Y_{hkl}$) ^{1/2} (10^{-6})
100	0.009372	15.9 8022	0.9613 56	1.101221	0.00901 0	127.25	4.365
002	0.010845	17.3 5795	0.9544 59	1.193361	0.01035 1	144.09	4.4459
101	0.009745	18.2 5826	0.9496 53	1.253202	0.00925 5	118.84	5.1405
102	0.007222	23.8 4035	0.9146 75	1.616758	0.00660 5	118.409	6.645
110	0.008928	28.4 5927	0.8791 56	1.906135	0.00784 9	127.25	7.55
103	0.009143	31.5 2015	0.8524 56	2.091193	0.00779 4	124.06	8.398

Table 5.23 Values for UDEDM plot at 70T, 120 MPa

Peak	$\beta_{hkl}(\text{rad.})$	θ	$\text{Cos}\theta$	$4\sin\theta$	$\beta_{hkl}\cos\theta$	$Y_{hkl}\text{GPa}$ (10^9)	$4\sin\theta (2/Y_{hkl})^{1/2}$ (10^{-6})
100	0.0108344	15.98014	0.9613571	1.1012165	0.0104157	127.259	4.3498
002	0.0112940	17.24013	0.9550710	1.1855078	0.0107866	144.09	4.4310
101	0.0094556	18.19735	0.9499864	1.2491639	0.0089827	118.89	5.1233
102	0.0125601	23.83651	0.9147023	1.6165131	0.0114887	118.35	6.6458
110	0.0101613	28.33814	0.8801615	1.8986968	0.0089436	127.259	7.5421
103	0.0104355	31.51715	0.8524837	2.0910150	0.0088961	123.943	8.4149

Table 5.24 Values for UDEDM plot at 80T, 120 MPa

Peak	$\beta_{hkl}(\text{rad.})$	θ	$\text{Cos}\theta$	$4\sin\theta$	$\beta_{hkl}\cos\theta$	$Y_{hkl}\text{GPa}$ (10^9)	$4\sin\theta (2/Y_{hkl})^{1/2}$ (10^{-6})
100	0.009671	15.98078	0.961354	1.101259	0.009297	127.26	4.3657
002	0.009172	17.3003	0.954759	1.189519	0.008757	144.09	4.4316
101	0.009801	18.26024	0.949643	1.253334	0.009307	118.86	5.1410
102	0.011699	23.84091	0.914671	1.616793	0.010701	118.38	6.645
110	0.009651	28.40016	0.879647	1.902507	0.008489	127.25	7.542
103	0.011375	31.52149	0.852444	2.091273	0.009696	124.003	8.3986

Table 5.25 Values for UDEDM plot at 90T, 120 MPa

Peak	$\beta_{hkl}(\text{rad.})$	θ	$\text{Cos}\theta$	$4\sin\theta$	$\beta_{hkl}\cos\theta$	$Y_{hkl}\text{GPa}$ (10^9)	$4\sin\theta (2/Y_{hkl})^{1/2}$ (10^{-6})
100	0.0097651	15.920 94	0.9616411	1.0972424	0.00939 05	127.259	4.349
002	0.0096454	17.298 5	0.9547685	1.1893995	0.00920 91	144.09	4.431
101	0.0099150	18.197 19	0.9499873	1.2491529	0.00941 91	118.829	5.124
102	0.0091609	23.839 35	0.9146823	1.6166943	0.00837 93	118.425	6.643
110	0.0104946	28.4	0.8796485	1.9024968	0.00923 16	127.259	7.542
103	0.0096530	31.581 54	0.8518957	2.0948458	0.00822 34	124.09	8.409

The value of $\beta_{hkl}\cos\theta$ and $4\sin\theta_{hkl} \left(\frac{2}{Y_{hkl}}\right)^{1/2}$ ZnO nanoparticles for first six peaks is shown in [Table 5.21](#), [Table 5.22](#), [Table 5.23](#) [Table 5.24](#) and [Table 5.25](#). In [Fig. 5.76](#), [Fig. 5.77](#), [Fig. 5.78](#) [Fig. 5.79](#) and [Fig. 5.80](#), the plots are drawn by placing the value of $4\sin\theta_{hkl} \left(\frac{2}{Y_{hkl}}\right)^{1/2}$ and $\beta_{hkl}\cos\theta$ along the x-axis and yaxis respectively. From the corresponding plot [y-intercept and slope have been](#) considered for [the purpose of](#) obtaining [crystallite size \(D\)](#), [strain \(\$\epsilon\$ \)](#), [stress \(\$\sigma\$ \)](#) and [energy density \(u\)](#) which is summarized in the following equation:

$$D = \frac{k\lambda}{y\text{-intercept}} \quad (5.18)$$

$$\mu_{ed} = (\text{slope})^2 \quad (5.19)$$

$$\sigma = \sqrt{2u_{ed}Y_{hkl}} \quad (5.20)$$

$$\epsilon = \frac{\sigma}{Y_{hkl}} \quad (5.21)$$

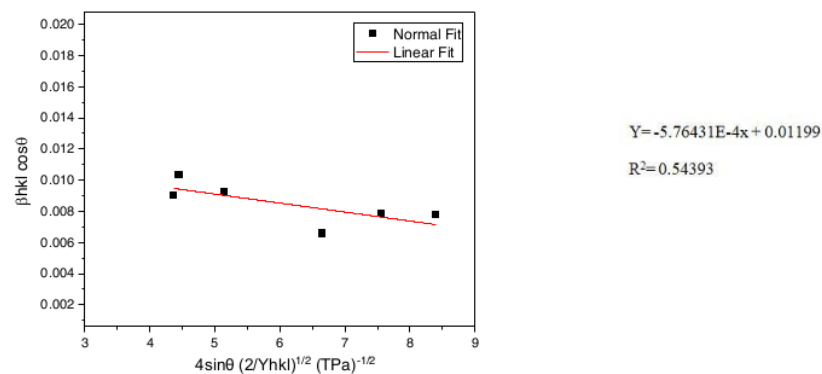


Fig. 5.80 Plot of $4\sin\theta (2/Yhkl)^{1/2}$ versus $\beta hkl\cos\theta$ for ZnO nanoparticles at 50T, 120 MPa.

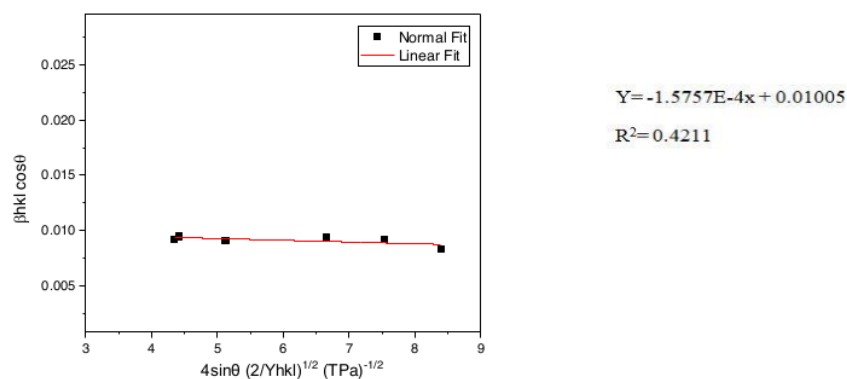


Fig. 5.81 Plot of $4\sin\theta (2/Yhkl)^{1/2}$ versus $\beta hkl\cos\theta$ for ZnO nanoparticles at 60T, 120 MPa.

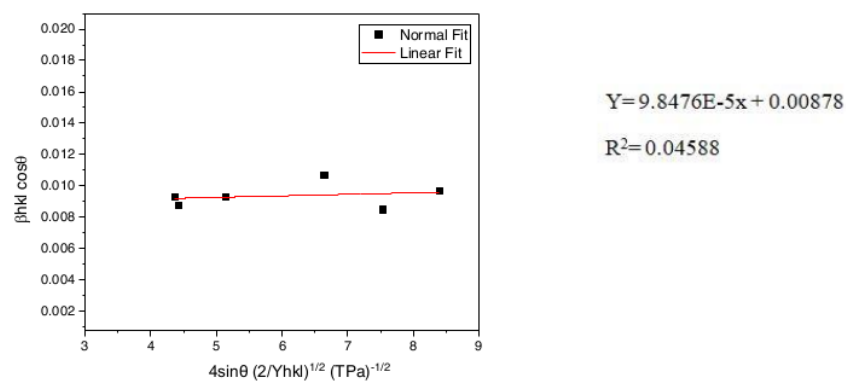


Fig. 5.82 Plot of $4\sin\theta (2/Yhkl)^{1/2}$ versus $\beta hkl\cos\theta$ for ZnO nanoparticles at 70T, 120 MPa.

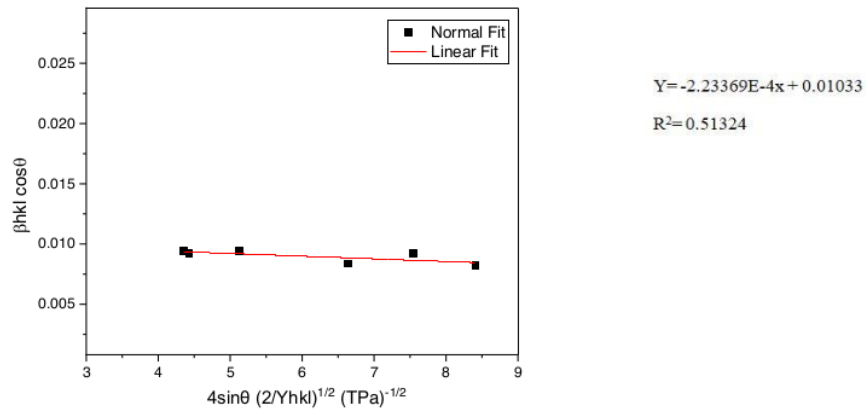


Fig. 5.83 Plot of $4\sin\theta (2/Y_{hkl})^{1/2}$ versus $\beta hkl\cos\theta$ for ZnO nanoparticles at 80T, 120 MPa.

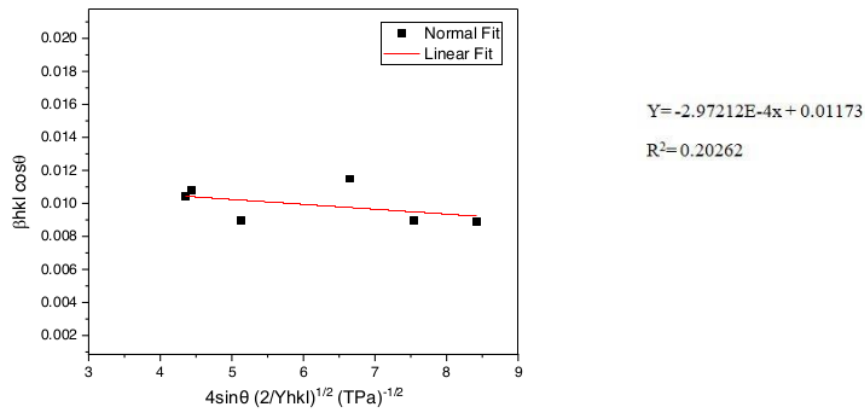


Fig. 5.84 Plot of $4\sin\theta (2/Y_{hkl})^{1/2}$ versus $\beta hkl\cos\theta$ for ZnO nanoparticles at 90T, 120 MPa

32

The values of crystallite size (D), lattice strain (ϵ), stress (σ) and energy density (u) obtained from UDEDM model with different annealing temperature at constant pressure are

Temperature	Pressure	Crystallite size (D)	stress (σ)	Lattice Strain (ϵ)	energy density (u)
50°C	120 MPa	11.6 nm	2.91E+02	2.29E-09	3.32E-07 (Jm ⁻³)
60°C	120 MPa	13.8nm	7.94E+01	6.25E-10	2.48E-08 (Jm ⁻³)
70°C	120 MPa	15.8 nm	4.96E+01	3.91E-10	9.70E-09 (Jm ⁻³)
80°C	120 MPa	13.4 nm	1.13E+02	8.86E-10	4.99E-08 (Jm ⁻³)
90°C	120 MPa	11.8 nm	1.50E+02	1.18E-09	8.83E-08 (Jm ⁻³)

5.11 Size-Strain Plot (SSP) Method

From chapter 4, we know that the Size-Strain Plot (SSP) equation can be written as

$$(d_{hkl} \beta_{hkl} \cos \theta_{hkl})^2 = \frac{K^2}{D^2} (d_{hkl}^2 \beta_{hkl} \cos \theta_{hkl}) + \left(\frac{\epsilon}{2}\right)^2 \quad (5.22)$$

where d_{hkl} is the lattice distance between the $\langle h k l \rangle$ planes and for the hexagonal crystal structure,

$$d_{hkl} = \frac{a}{\sqrt{\frac{4}{3}(h^2 + k^2 + hk) + \left(\frac{a}{c}\right)^2}} \quad (5.23)$$

K is a constant that depends on the shape of the particles. The value of $(d_{hkl}^2 \beta_{hkl} \cos \theta_{hkl})$ and $(d_{hkl} \beta_{hkl} \cos \theta_{hkl})^2$ of ZnO nanoparticles for first six peaks at 50°C, 60°C, 70°C, 80°C and 90°C temperature with 120 MPa pressure are shown in Table 5.26, Table 5.27, Table 5.28 Table 5.29 and Table 5.30 below.

Table 5.26 Values for SSP plot at 50T, 120 MPa

Peak	β_{hkl} (rad.)	Cos θ	$\beta_{hkl} \cos \theta$	d_{hkl} (10 ⁻¹⁰)	d_{hkl}^2 (10 ⁻²⁰)	$d_{hkl}^2 \beta_{hkl} \cos \theta$ (10 ⁻²⁰)	$(d_{hkl} \beta_{hkl} \cos \theta)^2$ (10 ⁻²⁰)
100	0.0093724	0.9613567	0.0090102	2.7963	7.8198	0.0704587	0.0006348
002	0.0108455	0.9544595	0.0103515	2.58095	6.66130	0.0689550	0.0007137
101	0.0097459	0.9496539	0.0092552	2.45877	6.04557	0.0559534	0.0005178
102	0.0072221	0.9146752	0.0066059	1.89660	3.59711	0.0237623	0.0001569
110	0.0089284	0.8791560	0.0078494	1.6145	2.60661	0.0204605	0.0001606
103	0.0091439	0.8524563	0.0077948	1.46544	2.14752	0.0167396	0.0001304

Table 5.27 Values for SSP plot at 60T, 120 MPa.

Peak	β_{hkl} (rad.)	Cos θ	$\beta_{hkl}\cos\theta$	d_{hkl} (10^{-10})	d_{hkl}^2 (10^{-20})	$d_{hkl}^2\beta_{hkl}\cos\theta$ (10^{-20})	$(d_{hkl}\beta_{hkl}\cos\theta)^2$ (10^{-20})
100	0.0095 36501	0.9616 43108	0.009170 711	2.8071	7.879811	0.072263 469	0.000662 707
002	0.0098 90629	0.9550 68815	0.009446 232	2.5979 5	6.749344	0.063755 871	0.000602 253
101	0.0095 68301	0.9499 8249	0.009089 719	2.4697 21	6.099523	0.055442 955	0.000503 961
102	0.0102 28701	0.9142 70766	0.009351 802	1.9066 86	3.63545	0.033998 005	0.000317 943
110	0.0104 51231	0.8796 60672	0.009193 536	1.6206 8	2.626604	0.024147 775	0.000222 003
103	0.0097 2224	0.8524 65495	0.008287 874	1.4739 83	2.172627	0.018006 458	0.000149 235

Table 5.28 Values for SSP plot at 70T, 120 MPa.

Peak	β_{hkl} (rad.)	Cos θ	$\beta_{hkl}\cos\theta$	d_{hkl} (10^{-10})	d_{hkl}^2 (10^{-20})	$d_{hkl}^2\beta_{hkl}\cos\theta$ (10^{-20})	$(d_{hkl}\beta_{hkl}\cos\theta)^2$ (10^{-20})
100	0.0096 71363	0.961354 081	0.009297 605	2.796396	7.81 9831	0.0727 05697	0.0006759 89
002	0.0091 7232	0.954759 242	0.008757 357	2.58925	6.70 4216	0.0587 11209	0.0005141 55
101	0.0098 01443	0.949643 115	0.009307 873	2.460563	6.05 4369	0.0563 53299	0.0005245 29
102	0.0116 99318	0.914671 298	0.010701 031	1.899892	3.60 9589	0.0386 26319	0.0004133 41
110	0.0096 51309	0.879647 174	0.008489 747	1.6145	2.60 661	0.0221 29462	0.0001878 74
103	0.0113 75385	0.852444 044	0.009696 879	1.468858	2.15 7545	0.0209 21453	0.0002028 73

Table 5.29 Values for SSP plot at 80T, 120 MPa.

Peak	β_{hkl} (rad.)	Cos θ	$\beta_{hkl}\cos\theta$	d_{hkl} (10^{-10})	d_{hkl}^2 (10^{-20})	$d_{hkl}^2\beta_{hkl}\cos\theta$ (10^{-20})	$(d_{hkl}\beta_{hkl}\cos\theta)^2$ (10^{-20})
100	0.009765 14	0.96164 1145	0.009390 56	2.805922	7.873 2	0.0739337 57	0.00069427 9
002	0.009645 41	0.95476 8584	0.009209 135	2.585	6.682 225	0.0615375 12	0.00056670 7
101	0.009915 064	0.94998 7396	0.009419 186	2.466124	6.081 769	0.0572853 12	0.00053958 1
102	0.009160 906	0.91468 2302	0.008379 318	1.901182	3.614 494	0.0302869 93	0.00025378 4
110	0.010494 689	0.87964 8573	0.009231 638	1.62	2.624 4	0.0242275 11	0.00022366
103	0.009653 09	0.85189 5712	0.008223 426	1.468482	2.156 44	0.0177333 21	0.00014582 9

Table 5.30 Values for SSP plot at 90T, 120 MPa.

Peak	β_{hkl} (rad.)	Cos θ	$\beta_{hkl}\cos\theta$	d_{hkl} (10^{-10})	d_{hkl}^2 (10^{-20})	$d_{hkl}^2\beta_{hkl}\cos\theta$ (10^{-20})	$(d_{hkl}\beta_{hkl}\cos\theta)^2$ (10^{-20})
100	0.010 8344	0.961357 1	0.010415 7	2.7963 96	7.819831	0.0814492	0.0008483
002	0.011 2940	0.955071 0	0.010786 6	2.5980 4	6.749812	0.0728076	0.0007853
101	0.009 4556	0.949986 4	0.008982 7	2.4624 41	6.063617	0.0544681	0.0004892
102	0.012 5601	0.914702 3	0.011488 7	1.9033 56	3.622765	0.0416211	0.0004781
110	0.010 1613	0.880161 5	0.008943 6	1.6145	2.60661	0.0233125	0.0002084
103	0.010 4355	0.852483 7	0.008896 1	1.4724 64	2.16815	0.0192881	0.0001715

Now, using equation (5.22), a plot is drawn with $(d_{hkl}^2\beta_{hkl}\cos\theta_{hkl})$ term along X-axis and $(d_{hkl}\beta_{hkl}\cos\theta_{hkl})^2$ along Y-axis corresponding to each diffraction peak, which is shown in Fig 5.81, Fig. 5.82, Fig. 5.83, Fig. 5.84 and Fig. 5.85. The slope of the straight line provides the average size obtain by the equation (5.24), whereas the intercept gives the intrinsic strain of the ZnO nanocrystals obtain by equation (5.25)

$$\frac{k\lambda}{D} = \text{slope} \quad (5.24)$$

$$\left(\frac{\epsilon}{2}\right)^2 = y - \text{intercept} \quad (5.25)$$

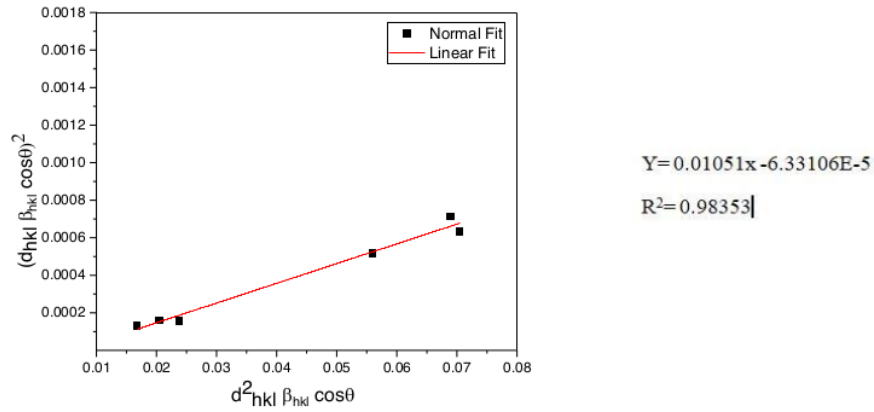


Fig. 5.85 Plot of $(d_{hkl} \beta_{hkl} \cos \theta)^2$ versus $d_{hkl}^2 \beta_{hkl} \cos \theta$ for ZnO nanoparticles at 50T, 120 MPa

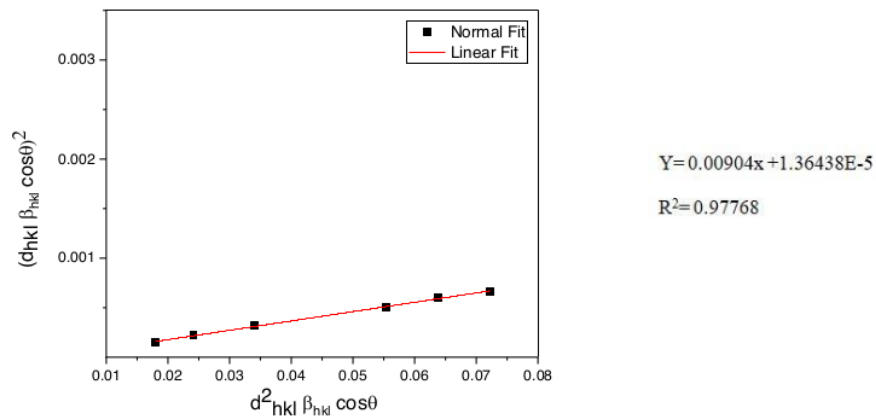


Fig. 5.86 Plot of $(d_{hkl} \beta_{hkl} \cos \theta)^2$ versus $d_{hkl}^2 \beta_{hkl} \cos \theta$ for ZnO nanoparticles at 60T, 120 MPa

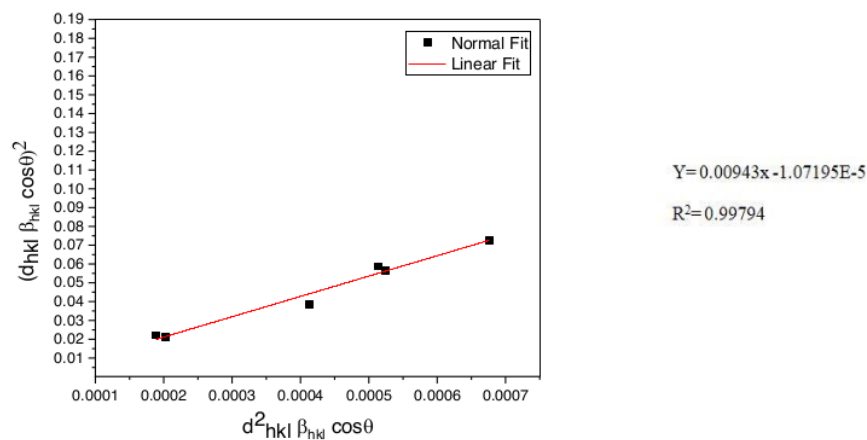


Fig. 5.87 Plot of $(d_{hkl} \beta_{hkl} \cos \theta)^2$ versus $d_{hkl}^2 \beta_{hkl} \cos \theta$ for ZnO nanoparticles at 70T, 120 MPa

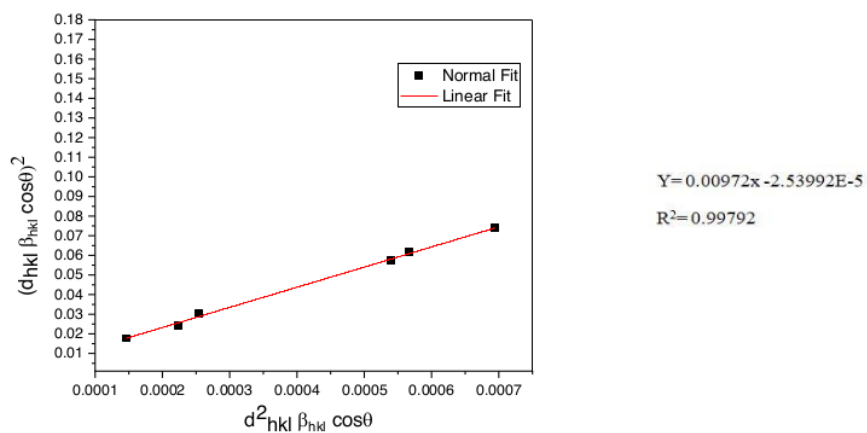


Fig. 5.88 Plot of $(d_{hkl} \beta_{hkl} \cos \theta)^2$ versus $d_{hkl}^2 \beta_{hkl} \cos \theta$ for ZnO nanoparticles at 80T, 120 MPa

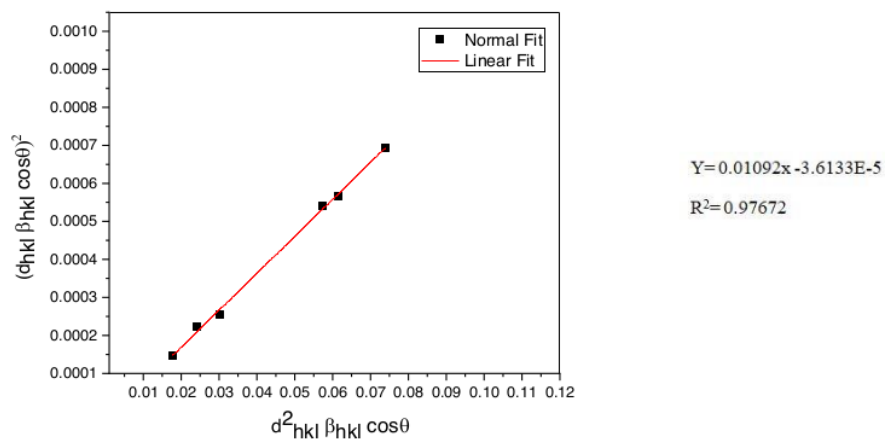


Fig. 5.89 Plot of $(d_{hkl} \beta_{hkl} \cos \theta)^2$ versus $d_{hkl}^2 \beta_{hkl} \cos \theta$ for ZnO nanoparticles at 90T, 120 MPa

32 The values of crystallite size (D), lattice strain (ϵ) obtained from SSP plot with different annealing temperature at constant pressures are

Temperature	Pressure	Crystallite size (D)	Lattice Strain (ϵ)
50°C	120 MPa	13.18744 nm	1.59×10^{-2}
60°C	120 MPa	14.69777 nm	6.55×10^{-3}
70°C	120 MPa	15.33186 nm	7.39×10^{-3}
80°C	120 MPa	14.25926 nm	1.01×10^{-2}
90°C	120 MPa	12.69231 nm	1.20×10^{-2}

5.12 Halder-Wagner Method

From chapter 4, we know that In Halder-Wagner method, the crystallite size and strain profiles are described by the Lorentzian and the Gaussian function, respectively. Consequently, we have

$$\left(\frac{\beta_{hkl}^*}{d_{hkl}^*}\right)^2 = \frac{1}{D} \cdot (\beta_{hkl}^*/d_{hkl}^{*2}) + \left(\frac{\varepsilon}{2}\right)^2 \quad (5.26)$$

In this method used equation (5.26) to determine the crystallite size, and the lattice strain.

Where $\beta_{hkl}^* = \beta_{hkl} \cdot \cos\theta/\lambda$ and $d_{hkl}^* = 2d_{hkl} \cdot \sin\theta/\lambda$. The value of $(\beta_{hkl}^*/d_{hkl}^{*2})$ and $\left(\frac{\beta_{hkl}^*}{d_{hkl}^*}\right)^2$ of ZnO nanoparticles for first six peaks at 50°C, 60°C, 70°C, 80°C and 90°C temperature with 120 MPa pressure are shown in Table 5.31, Table 5.32, Table 5.33 Table 5.34 and Table 5.35 below.

Table 5.31 Values for Halder-Wagner Method at 50T, 120 MPa

Peak	β_{hkl} (rad.)	Cos θ	Sin θ	$\beta_{hkl} \cos \theta$	$\beta_{hkl}^* =$ $\beta_{hkl} \cos \theta / \gamma$	d_{hkl} (10^{-10})	$d_{hkl}^* = 2$ $\cdot d_{hkl} \cdot \sin \theta / \gamma$ (10^{-10})	$(\beta_{hkl}^* /$ $d_{hkl}^{*2})^2$ (10^{20})	$\beta_{hkl}^* /$ d_{hkl}^* (10^2)
100	0.009 37244	0.961 35679 6	0.275 3054 87	0.00901 0259	0.0585 08	2.79639 6	9.9982 23	0.000 03424	0.00 0585 29
002	0.010 84550 1	0.954 45954 1	0.298 3403 84	0.01035 1592	0.0672 18	2.58095	10.000 02	0.000 04518	0.00 0672 178
101	0.009 74594 1	0.949 65396 9	0.313 3007 16	0.00925 5272	0.0600 99	2.45877 5	10.004 36	0.000 03608	0.00 0600 467
102	0.007 22218 9	0.914 67524 8	0.404 1895 48	0.00660 5958	0.0428 96	1.89660 5	9.9556 89	0.000 01.85 6	0.00 0432 785
110	0.008 92842 7	0.879 15609	0.476 5339 13	0.00784 9481	0.0509 71	1.6145	9.9917 4	0.000 02602	0.00 0510 55
103	0.009 14397 6	0.852 45635 7	0.522 7983 92	0.00779 484	0.0506 16	1.46544 4	9.9497 67	0.000 02587	0.00 0511 282

Table 5.32 Values for Halder-Wagner Method at 60T, 120 MPa

Peak	β_{hkl} (rad.)	Cos θ	Sin θ	$\beta_{hkl}\cos$ θ	$\beta_{hkl}^* =$ $\beta_{hkl}\cos$ θ/γ	d_{hkl} (10^{-10})	$d_{hkl}^* = 2$ $*d_{hkl}^* \sin$ $n\theta/\gamma$ (10^{-10})	$(\beta_{hkl}^*/$ $d_{hkl}^*)^2$ (10^{20})	β_{hkl}^* $/d_{hkl}^*$ (10^2 0)
100	0.009 53650 1	0.961 6431 08	0.274 3038 08	0.0091 70711	0.0595 5	2.8071	9.9999 77	0.000 03546 2	0.00 0595 503
002	0.009 89062 9	0.955 0688 15	0.296 3842 23	0.0094 46232	0.0613 39	2.5979 5	9.9998 88	0.000 03625	0.00 0613 405
101	0.009 56830 1	0.949 9824 9	0.312 3032 5	0.0090 89719	0.0590 24	2.4697 21	10.016 91	0.000 0347	0.00 0588 25
102	0.010 22870 1	0.914 2707 66	0.405 1036 09	0.0093 51802	0.0607 26	1.9066 86	10.031 24	0.000 03664	0.00 0603 484
110	0.010 45123 1	0.879 6606 72	0.475 6017 94	0.0091 93536	0.0596 98	1.6206 8	10.010 37	0.000 03556	0.00 0595 747
103	0.009 72224	0.852 4654 95	0.522 7835 14	0.0082 87874	0.0538 17	1.4739 83	10.007 46	0.000 0289	0.00 0537 372

Table 5.33 Values for Halder-Wagner Method at 70T, 120 MPa

Peak	β_{hkl} (rad.)	Cos θ	Sin θ	$\beta_{hkl}\cos$ θ	$\beta_{hkl}^* =$ $\beta_{hkl}\cos$ θ/γ	d_{hkl} (10^{-10})	$d_{hkl}^* = 2$ $*d_{hkl}^* \sin$ $n\theta/\gamma$ (10^{-10})	$(\beta_{hkl}^*/$ $d_{hkl}^*)^2$ (10^{20})	β_{hkl}^* $/d_{hkl}^*$ (10^{20})
100	0.009 67136	0.961 35408	0.27 5314	0.0092 97605	0.0603 74	2.796 396	9.9985 67	0.0000 36	0.000 60391
002	0.009 17232	0.954 75924	0.29 7379	0.0087 57357	0.0568 66	2.589 25	9.9998 81	0.0000 32	0.000 56867
101	0.009 80144	0.949 64311	0.31 3333	0.0093 07873	0.0604 41	2.460 563	10.012 69	0.0000 36	0.000 60287
102	0.011 69931	0.914 67129	0.40 4198	0.0107 01031	0.0694 87	1.899 892	9.9731 6	0.0000 48	0.000 69861
110	0.009 65130	0.879 64717	0.47 5626	0.0084 89747	0.0551 28	1.614 5	9.9727 2	0.0000 30	0.000 55430
103	0.011 37538	0.852 44404	0.52 2818	0.0096 96879	0.0629 67	1.468 858	9.9733 29	0.0000 39	0.000 63304

Table 5.34 Values for Halder-Wagner Method at 80T, 120 MPa

Peak	β_{hkl} (rad.)	Cos θ	Sin θ	$\beta_{hkl} \cos \theta$	$\beta_{hkl}^* = \beta_{hkl} \cos \theta / \gamma$	d_{hkl} (10^{-10})	$d_{hkl}^* = 2 * d_{hkl} * \sin \theta / \gamma$ (10^{-10})	$(\beta_{hkl}^* / d_{hkl}^*)^2$ (10^{20})	$\beta_{hkl}^* / d_{hkl}^*$ (10^{20})
100	0.009 76514	0.961 64114 5	0.27 4310 606	0.0093 9056	0.0609 78	2.805 922	9.9960 29	0.000 03721	0.000 61026 1
002	0.009 64541	0.954 76858 4	0.29 7349 878	0.0092 09135	0.0598	2.585	9.9824 6	0.000 0358	0.000 60009 9
101	0.009 91506 4	0.949 98739 6	0.31 2288 245	0.0094 19186	0.0611 64	2.466 124	10.001 84	0.000 0373	0.000 61141 1
102	0.009 16090 6	0.914 68230 2	0.40 4173 584	0.0083 79318	0.0544 11	1.901 182	9.9793 2	0.000 0297	0.000 54636 9
110	0.010 49468 9	0.879 64857 3	0.47 5624 209	0.0092 31638	0.0599 46	1.62	10.006 64	0.000 0358	0.000 59866 2
103	0.009 65309	0.851 89571 2	0.52 3711 463	0.0082 23426	0.0533 99	1.468 482	9.9878 04	0.000 0285	0.000 53529 4

Table 5.35 Values for Halder-Wagner Method at 90T, 120 MPa

Peak	β_{hkl} (rad.)	Cos θ	Sin θ	$\beta_{hkl} \cos \theta$	$\beta_{hkl}^* = \beta_{hkl} \cos \theta / \gamma$	d_{hkl} (10^{-10})	$d_{hkl}^* = 2 * d_{hkl} * \sin \theta / \gamma$ (10^{-10})	$(\beta_{hkl}^* / d_{hkl}^*)^2$ (10^{20})	$\beta_{hkl}^* / d_{hkl}^*$ (10^{20})
100	0.0108 34401	0.961 35718	0.274 31169	0.010 4157	0.06763 5	2.796 396	9.962132	0.000 04609	0.000 68149
002	0.0112 94052	0.955 07104	0.297 34154 6	0.010 7866 22	0.07004 3	2.598 04	10.03254	0.000 0487	0.000 69589 4
101	0.0094 55692	0.949 98649 6	0.312 28517 8	0.008 9827 8	0.05833	2.462 441	9.986804	0.000 0341	0.000 58484
102	0.0125 60117	0.914 70231 4	0.404 16799 6	0.011 4887 68	0.07460 2	1.903 356	9.990593	0.000 055	0.000 74742 9
110	0.0101 61331	0.880 16157 3	0.475 62420 9	0.008 9436 13	0.05807 5	1.614 5	9.972666	0.000 0339	0.000 58394 2
103	0.0104 35523	0.852 48373	0.523 70343	0.008 8961	0.05776 7	1.472 464	10.01473	0.000 0332	0.000 57597

Plot of equation (5.26), with $(\beta_{hkl}^*/d_{hkl}^*)^2$ term along X-axis and $(\beta_{hkl}^*/d_{hkl}^*)^2$ along Y-axis for each peak of the XRD pattern, is shown in Fig. 5.86, Fig. 5.87, Fig. 5.88, Fig. 5.89 and Fig. 5.90. The slope of the plotted straight line provides the crystallite size by the equation (5.27), whereas the intercept gives the intrinsic strain of the ZnO nanocrystals by the equation (5.28).

$$D = \frac{1}{\text{slope}} \quad (5.27)$$

$$\varepsilon = 2\sqrt{y - \text{intercept}} \quad (5.28)$$

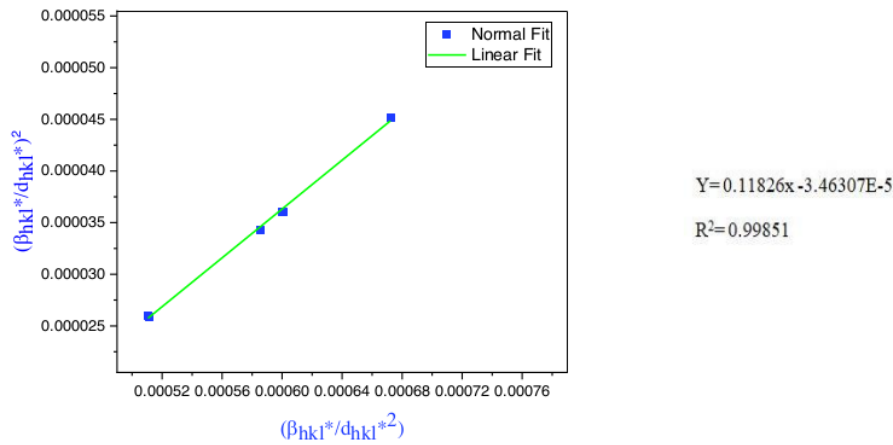


Fig. 5.90 Plot of $\beta_{hkl}^*/d_{hkl}^{*2}$ versus $(\beta_{hkl}^*/d_{hkl}^*)^2$ for ZnO nanoparticles at 50T, 120 MPa.

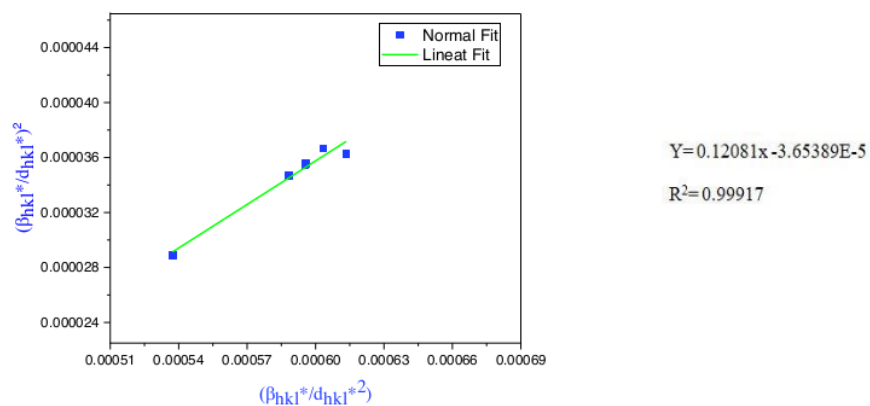


Fig. 5.91 Plot of β_{hkl}^*/d_{hkl}^2 versus $(\beta_{hkl}^*/d_{hkl}^*)^2$ for ZnO nanoparticles at 60T, 120 MPa.

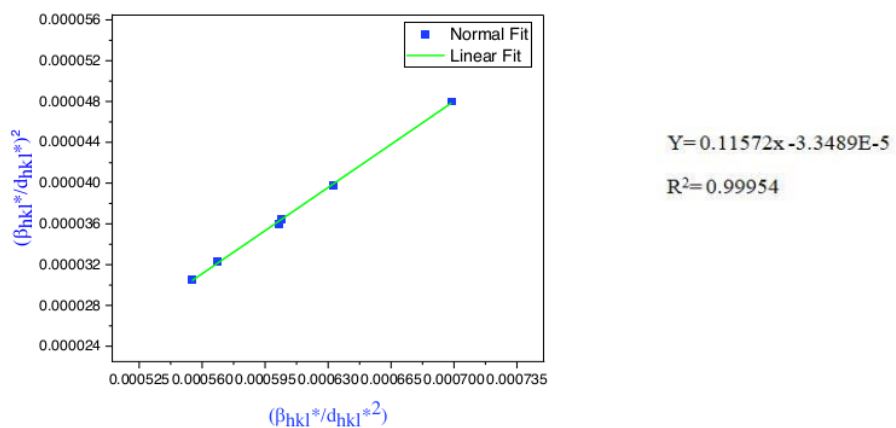


Fig. 5.92 Plot of β_{hkl}^*/d_{hkl}^2 versus $(\beta_{hkl}^*/d_{hkl}^*)^2$ for ZnO nanoparticles at 70T, 120 MPa.

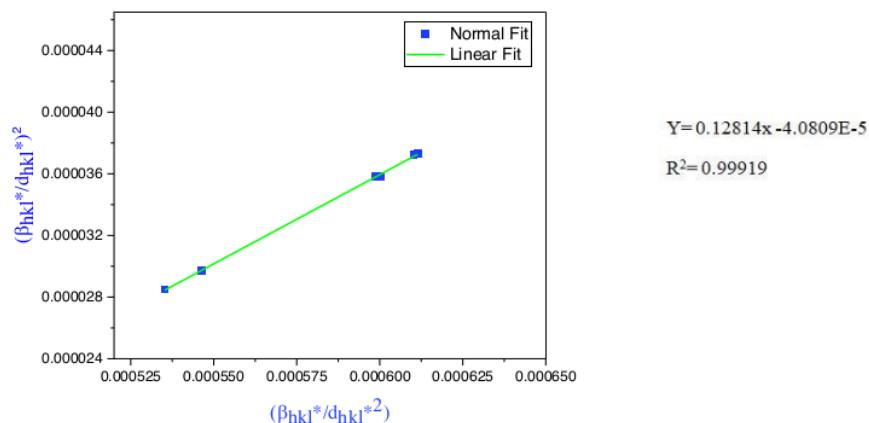


Fig. 5.93 Plot of β_{hkl}^*/d_{hkl}^2 versus $(\beta_{hkl}^*/d_{hkl})^2$ for ZnO nanoparticles at 80T, 120 MPa.

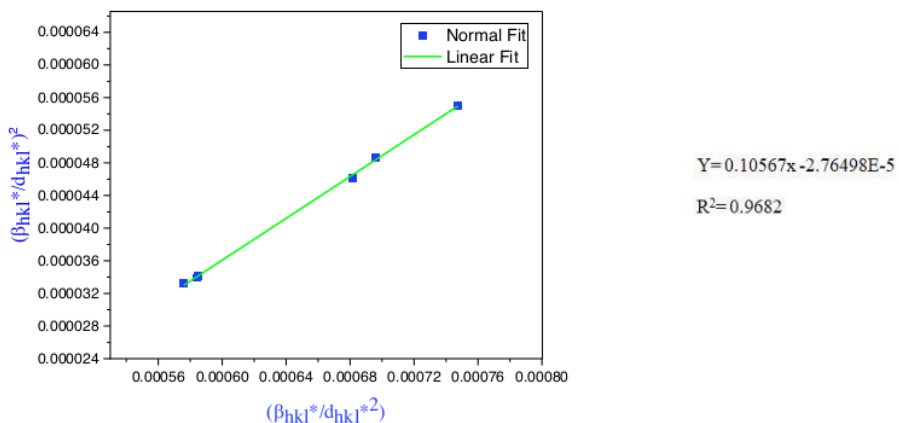


Fig. 5.94 Plot of β_{hkl}^*/d_{hkl}^2 versus $(\beta_{hkl}^*/d_{hkl})^2$ for ZnO nanoparticles at 90T, 120 MPa.

The values of crystallite size (D), lattice strain (ϵ) obtained from Halder-Wagner Method with different annealing temperature at constant pressures are:

Temperature	Pressure	Crystallite size (D)	Lattice Strain (ϵ)
50°C	120 MPa	8.456nm	1.18x10 ⁻²
60°C	120 MPa	9.463nm	1.05x10 ⁻²
70°C	120 MPa	8.28 nm	1.21x10 ⁻²
80°C	120 MPa	8.64 nm	1.16x10 ⁻²
90°C	120 MPa	7.80 nm	1.28x10 ⁻²

5.13 Wagner-Agua Method

From chapter 4, we know that Wagner and Agua also offered an analytical technique applied to determine the values of crystallite size and lattice strain simultaneously by the given relation

$$(\beta_{hkl} \cos \theta_{hkl})^2 = (4\epsilon_{WA} \sin \theta_{hkl})^2 + \left(\frac{K\lambda}{D_{WA}}\right)^2 \quad (5.27)$$

Where D_{WA} and ϵ_{WA} represent the Wagner-Agua crystallite size and lattice strain, respectively. The W-A plots of Zn-nanoparticles are drawn taking $(\beta_{hkl} \cos \theta_{hkl})^2$ and $(4\sin \theta_{hkl})^2$ in the vertical and horizontal axis, respectively. The value of $(\beta_{hkl} \cos \theta_{hkl})^2$ and $(4\sin \theta_{hkl})^2$ of ZnO nanoparticles for first six peaks at 50°C, 60°C, 70°C, 80°C and 90°C temperature with 120 MPa pressure are shown in Table 5.36, Table 5.37, Table 5.38 Table 5.39 and Table 5.40 below.

Table 5.36 Values for Wagner-Agua Method plot at 50T, 120 MPa.

Peak	β_{hkl} (rad.)	Cos θ	4sin θ	$\beta_{hkl} \cos \theta$	$(\beta_{hkl} \cos \theta)^2$	$(4\sin \theta)^2$
100	0.0093 7244	0.961356 796	1.1012219 47	0.0090102 59	8.12E-05	1.2126 9
002	0.0108 45501	0.954459 541	1.1933615 37	0.0103515 92	0.000107	1.4241 12
101	0.0097 45941	0.949653 969	1.2532028 63	0.0092552 72	8.57E-05	1.5705 17
102	0.0072 22189	0.914675 248	1.6167581 91	0.0066059 58	4.36E-05	2.6139 07
110	0.0089 28427	0.879156 09	1.9061356 51	0.0078494 81	6.16E-05	3.6333 53
103	0.0091 43976	0.852456 357	2.0911935 69	0.0077948 4	6.08E-05	4.3730 91

Table 5.37 Values for Wagner-Agua Method plot at 60T, 120 MPa.

Peak	βhkl (rad.)	Cos θ	4sin θ	$\beta hkl \cos\theta$	$(\beta hkl \cos\theta)^2$	$(4\sin\theta)^2$
100	0.0093 7244	0.961356 796	1.1012219 47	0.0090102 59	8.41E-05	1.2038 81
002	0.0108 45501	0.954459 541	1.1933615 37	0.0103515 92	8.92E-05	1.4054 97
101	0.0097 45941	0.949653 969	1.2532028 63	0.0092552 72	8.26E-05	1.5605 32
102	0.0072 22189	0.914675 248	1.6167581 91	0.0066059 58	8.75E-05	2.6257 43
110	0.0089 28427	0.879156 09	1.9061356 51	0.0078494 81	8.45E-05	3.6191 54
103	0.0091 43976	0.852456 357	2.0911935 69	0.0077948 4	6.87E-05	4.3728 41

Table 5.38 Values for Wagner-Agua Method plot at 70T, 120 MPa.

Peak	βhkl (rad.)	Cos θ	4sin θ	$\beta hkl \cos\theta$	$(\beta hkl \cos\theta)^2$	$(4\sin\theta)^2$
100	0.009372	0.9613567	1.10122	0.0090102	8.64E-05	1.2127
002	0.010845 501	0.9544595 41	1.19336 1537	0.0103515 92	7.67E-05	1.4149 57
101	0.009745 941	0.9496539 69	1.25320 2863	0.0092552 72	8.66E-05	1.5708 47
102	0.007222 189	0.9146752 48	1.61675 8191	0.0066059 58	0.000115	2.6140 23
110	0.008928 427	0.8791560 9	1.90613 5651	0.0078494 81	7.21E-05	3.6195 34
103	0.009143 976	0.8524563 57	2.09119 3569	0.0077948 4	9.40E-05	4.3734 26

Table 5.39 Values for Wagner-Agua Method plot at 80T, 120 MPa.

Peak	βhkl (rad)	Cos θ	4sin θ	$\beta hkl \cos\theta$	$(\beta hkl \cos\theta)^2$	$(4\sin\theta)^2$
100	0.009372 44	0.9613567 96	1.101221 947	0.0090102 59	8.82E-05	1.2039 41
002	0.010845 501	0.9544595 41	1.193361 537	0.0103515 92	8.48E-05	1.4146 71
101	0.009745 941	0.9496539 69	1.253202 863	0.0092552 72	8.87E-05	1.5603 83
102	0.007222 189	0.9146752 48	1.616758 191	0.0066059 58	7.02E-05	2.6137 01
110	0.008928 427	0.8791560 9	1.906135 651	0.0078494 81	8.52E-05	3.6194 94
103	0.009143 976	0.8524563 57	2.091193 569	0.0077948 4	6.76E-05	4.3883 79

Table 5.40 Values for Wagner-Agua Method plot at 90T, 120 MPa.

Peak	$\beta_{hkl}(\text{rad})$	$\cos\theta$	$4\sin\theta$	$\beta_{hkl} \cos\theta$	$(\beta_{hkl} \cos\theta)^2$	$(4\sin\theta)^2$
100	0.009372 44	0.961356 796	1.101221 947	0.0090102 59	0.000108	1.2126 78
002	0.010845 501	0.954459 541	1.193361 537	0.0103515 92	0.000116	1.4054 29
101	0.009745 941	0.949653 969	1.253202 863	0.0092552 72	8.07E-05	1.5604 11
102	0.007222 189	0.914675 248	1.616758 191	0.0066059 58	0.000132	2.6131 15
110	0.008928 427	0.879156 09	1.906135 651	0.0078494 81	8.00E-05	3.6050 5
103	0.009143 976	0.852456 357	2.091193 569	0.0077948 4	7.91E-05	4.3723 44

The W-A plots of Zn-nanoparticles are drawn taking $(\beta_{hkl} \cos\theta)^2$ and $(4\sin\theta)^2$ in the vertical and horizontal axis, respectively. In the Wagner-Agua (W-A) plots shown in Fig. 5.91, Fig. 5.92, Fig. 5.93, Fig. 5.94 and Fig. 5.95, we make linear fits of the experimental data and from which the slope will yield the strain (ϵ_{WA}) obtained by the equation (5.29) and the intercept on vertical axis results in a measurement of the crystallite size (D_{WA}) obtained by the equation (5.28).

$$D_{WA} = \frac{1}{\sqrt{y\text{-intercept}}} \cdot k\lambda \quad (5.28)$$

$$\epsilon_{WA} = \sqrt{\text{slope}} \quad (5.29)$$

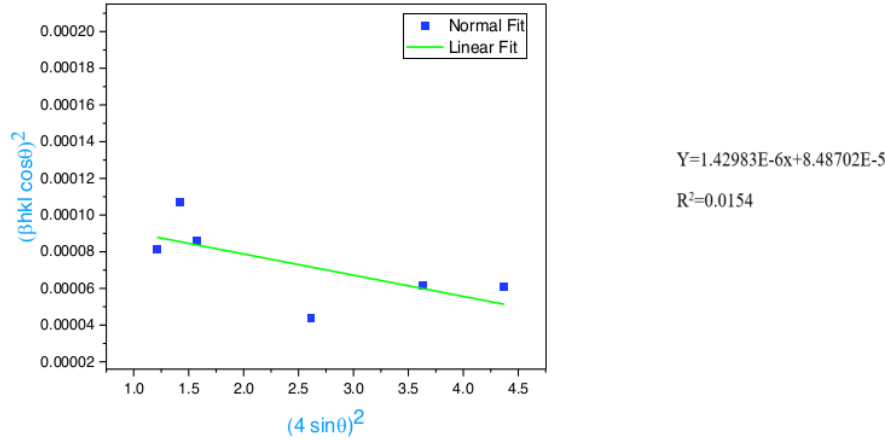


Fig. 5.95 Plot of $(4\sin\theta)^2$ versus $(\beta_{hkl} \cos\theta)^2$ for ZnO nanoparticles at 50T, 120 MPa.

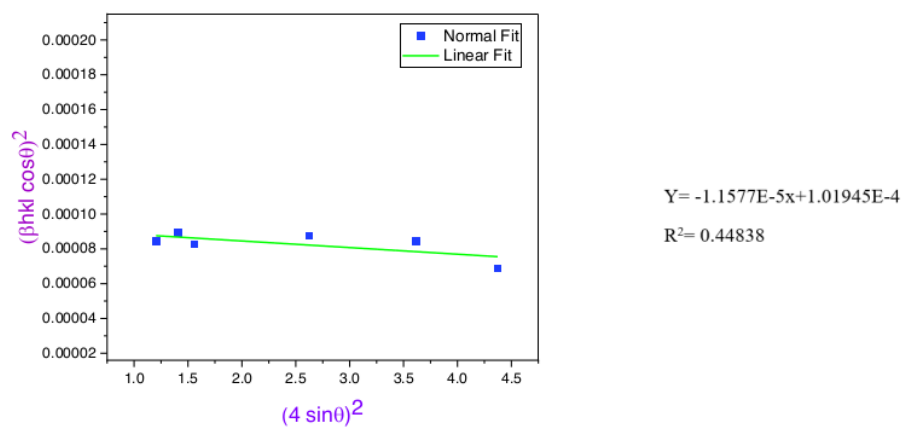


Fig. 5.96 Plot of $(4\sin\theta)^2$ versus $(\beta_{hkl} \cos\theta)^2$ for ZnO nanoparticles at 60T, 120 MPa.

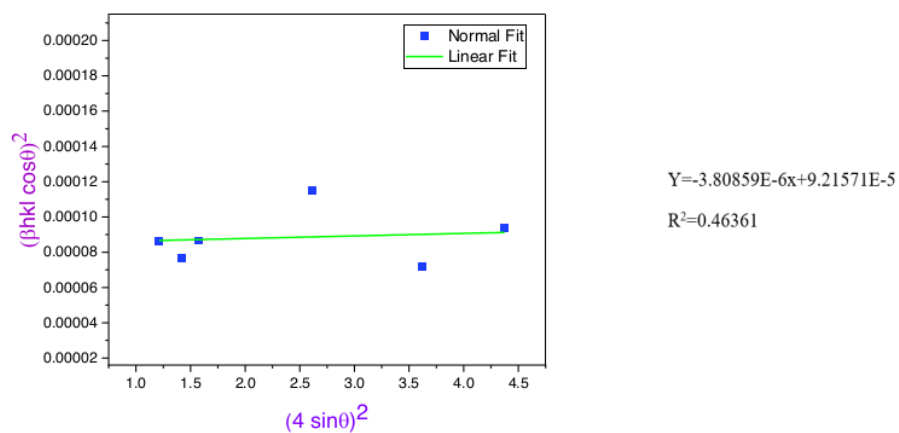


Fig. 5.97 Plot of $(4\sin\theta)^2$ versus $(\beta_{hkl} \cos\theta)^2$ for ZnO nanoparticles at 70T, 120 MPa

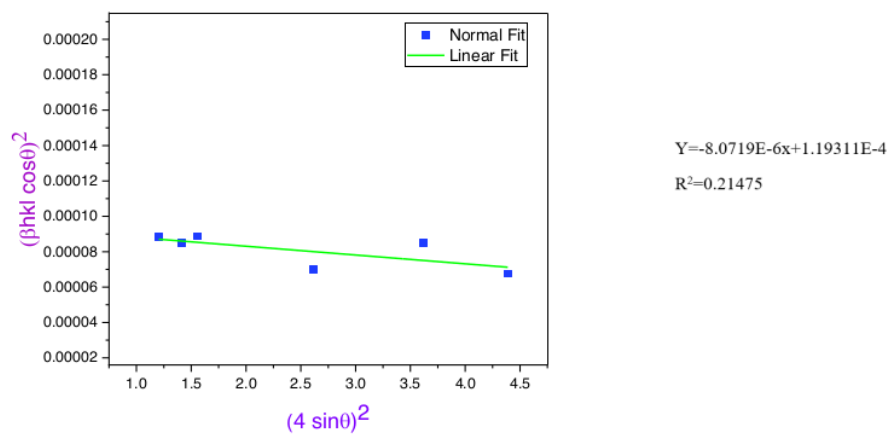


Fig. 5.98 Plot of $(4 \sin \theta)^2$ versus $(\beta_{hkl} \cos \theta)^2$ for ZnO nanoparticles at 80T, 120 MPa

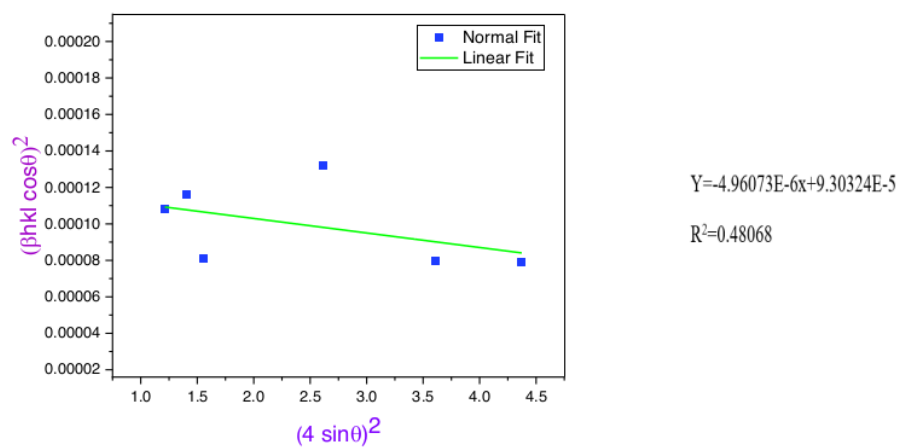


Fig. 5.99 Plot of $(4 \sin \theta)^2$ versus $(\beta_{hkl} \cos \theta)^2$ for ZnO nanoparticles at 90T, 120 MPa

The values of crystallite size (D_{WA}), lattice strain (ϵ_{WA}) obtained from Wagner-Agua Method with different annealing temperature at constant pressure is:

Temperature	Pressure	Crystallite size (D_{WA})	Lattice Strain (ϵ_{WA})
50°C	120 MPa	13.2 nm	3.402×10^{-3}
60°C	120 MPa	14.43 nm	1.95×10^{-3}
70°C	120 MPa	15.04 nm	1.19×10^{-3}
80°C	120 MPa	14.37 nm	2.22×10^{-3}
90°C	120 MPa	12.68 nm	2.84×10^{-3}

5.14 Result Summary and Comparison

Table 5.41 and Table 5.42 provide all the calculated values of average size and the intrinsic strain, including other elastic parameter.

Table 5.41 Average crystallite size of ZnO nanoparticles using different Models.

Temp- eratur e (°C)	Pressu re MPa	Modifie d Scherrer Method	Williamson and Hall Method			Size-Strain Plot (SSP) Method	Halder- Wagner Method	Wagner Agua Method
			UDM	USDM	UDEM			
		D nm	D nm	D nm	D nm	D nm	D nm	D nm
50	120	13.94	11.68	11.5	11.6	13.18	8.45	13.2
60	120	14.4	13.76	13.86	13.8	14.69	9.46	14.43
70	120	15.04	15.46	16.11	15.8	15.33	8.28	15.04
80	120	14.44	13.4	13.45	13.4	14.25	8.64	14.37
90	120	12.72	11.72	11.92	11.8	12.69	7.80	12.68

Table 5.42 Geometrical parameters of ZnO nanoparticles using different Models.

Temperature (°C)	Pres- sure MPa	Williamson and Hall Method						Size- Strain Plot (SSP) Method	Halder - Wagn er Metho d	Wagn er- Agua Meth od
		UDM	USDM		UDEDM					
		ϵ_x 10-3	ϵ_x 10-3	σ Pa	ϵ_x 10-3	σ Pa	μ Jm ⁻³	ϵ_x 10-3	ϵ_x 10-3	ϵ_x 10-3
50	120	-2.22	- 2.32 E-12	-2.943 x 10 ⁻⁰⁴	2.29E- 06	2.91 E02	3.32 E-07	15.9	11.8	3.40
60	120	-6.44 x 10 ⁻¹	- 5.99 E-12	-7.58 x 10 ⁻⁰⁴	6.25E- 07	7.94 E01	2.48 E-08	6.55	10.5	1.95
70	120	2.722 x10 ⁻¹	4.84 E-12	6.13 x 10 ⁻⁰⁴	3.91E- 07	4.96 E01	9.70 E-09	7.39	12.1	1.19
80	120	-9.027 x 10 ⁻¹	- 8.66 E-13	-1.097 x 10 ⁻⁰⁴	8.86E- 07	1.13 E02	4.99 E-08	10.1	11.6	2.22
90	120	-1.25	- 1.10 E-12	-1.39 x 10 ⁻⁰⁴	1.18E- 06	1.50 E02	8.83 E-08	12.0	12.8	2.84

From Modified Scherrer Method, Modified W-H, SSP, and W-A method ²² it is observed that crystalline size (D) is increased from 50°C to 70°C temperature and reduced from 70°C to 90°C temperature and higher at 70°C temperature at 120 MPa pressure.

Variation of crystallite size (D) from Modified Scherrer Method, UDM, USDM, UDEDM, SSP, H-W and W-A method with different annealing temperature at 120 MPa constant pressure are shown in ⁶⁰ fig. 5.96, fig. 5.97, fig. 5.98, fig. 5.99, fig. 5.100, fig. 5.101 and fig. 5.102.

¹ It is also clear from this table average size calculated from ⁴⁴ Modified Scherrer Method, UDM, USDM, UDEDM, SSP, and W-A method are slight difference, but the value of (D) estimated from H-W method are lower than the value obtained from the other method and which are comparable shown in ³⁷ fig. 5.103, fig. 5.104, fig. 5.105, fig. 5.106 and fig. 5.107. In USDM the obtained value of stress (σ) is negative because of low annealing temperature.

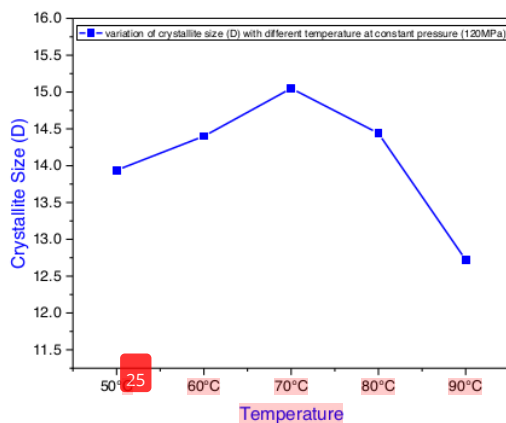


Fig. 5.100 Variation of crystallite size (D) from Modified Scherrer Method with different annealing temperature at 120 MPa constant pressure.

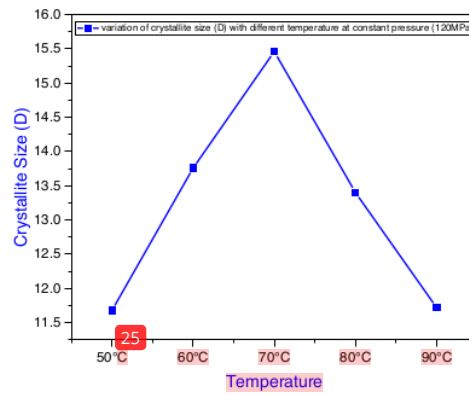


Fig. 5.101 Variation of crystallite size (D) from UDM Method with different annealing temperature at 120 MPa constant pressure.

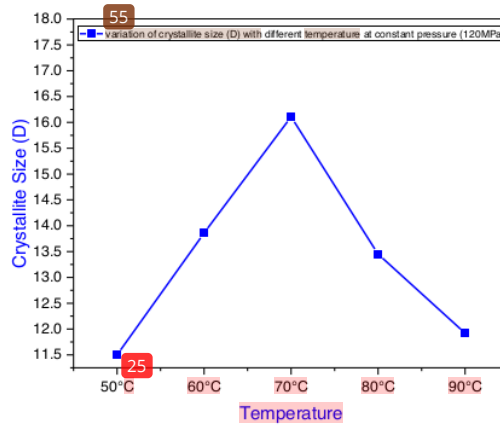


Fig. 5.102 Variation of crystallite size (D) from USDM Method with different annealing temperature at 120 MPa constant pressure.

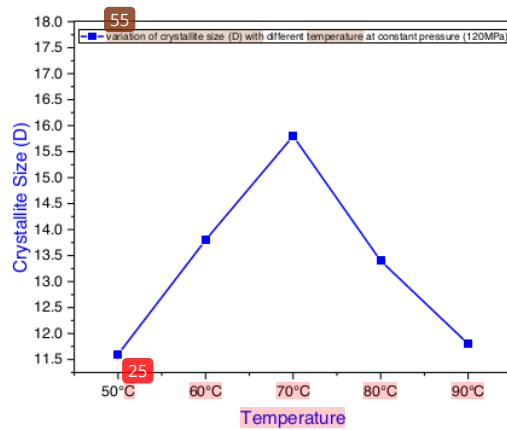


Fig. 5.103 Variation of crystallite size (D) from UDEDM Method with different annealing temperature at 120 MPa constant pressure.

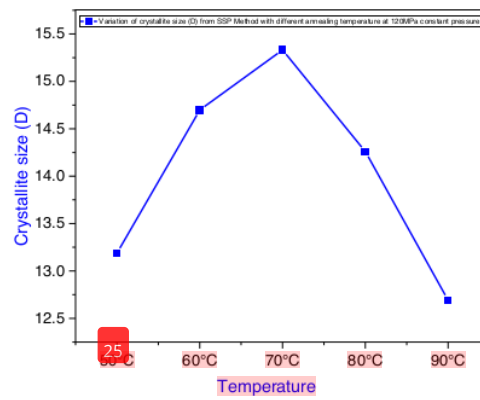


Fig. 5.104 Variation of crystallite size (D) from SSP Method with different annealing temperature at 120 MPa constant pressure.

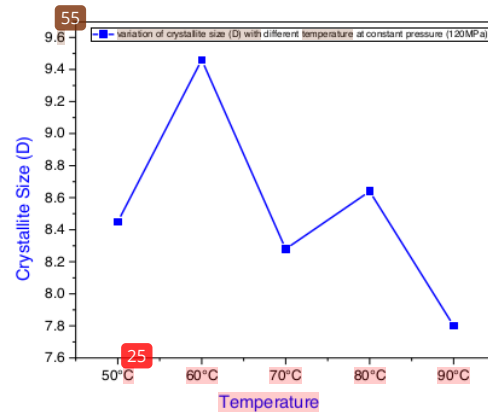


Fig. 5.105 Variation of crystallite size (D) from Halder-Wagner Method with different annealing temperature at 120 MPa constant pressure.

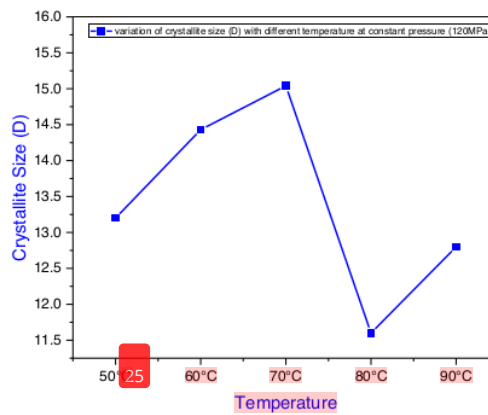


Fig. 5.106 Variation of crystallite size (D) from Wagner-Agua Method with different annealing temperature at 120 MPa constant pressure.

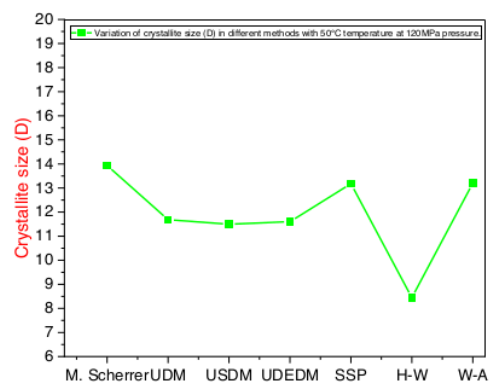


Fig. 5.107 Variation of crystallite size (D) of ZnO nanoparticles in different methods with 50°C temperature at 120 MPa pressure.

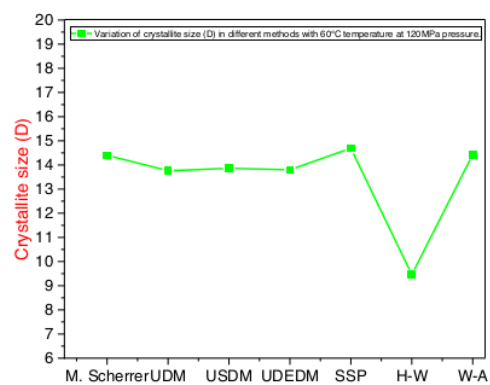


Fig. 5.108 Variation of crystallite size (D) of ZnO nanoparticles in different methods with 60°C temperature at 120 MPa pressure.

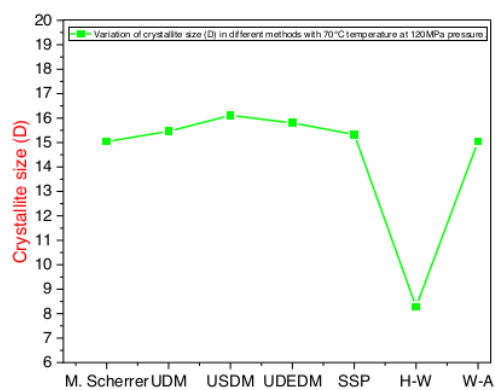


Fig. 5.109 Variation of crystallite size (D) of ZnO nanoparticles in different methods with 70°C temperature at 120 MPa pressure.

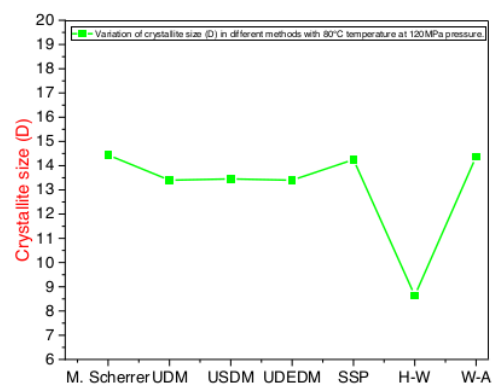


Fig. 5.110 Variation of crystallite size (D) of ZnO nanoparticles in different methods with 80°C temperature at 120 MPa pressure.

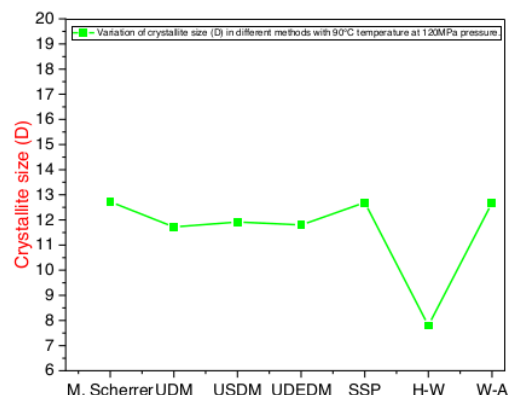


Fig. 5.111 Variation of crystallite size (D) of ZnO nanoparticles in different methods with 90°C temperature at 120 MPa pressure.

The values of lattice strain (ϵ) calculated by W-H modified method are significantly lower than the value of SSP, Halder-Wagner and Wagner-Agua Method shown in **fig. 5.108, fig. 5.109, fig. 5.110, fig. 5.111 and fig. 5.112**. This increase in estimated strain value is actually because of the contribution of low and mid angle XRD data. Further, calculated higher value of strain as obtained in Halder-Wagner method, may be attributed to the lattice dislocations [74], which play a significant role in broadening of the reflection peaks at lower angles.

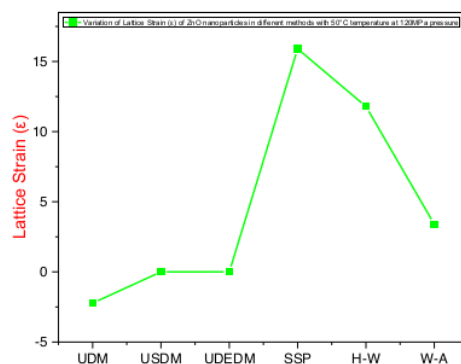


Fig. 5.112 Variation of Lattice Strain (ϵ) of ZnO nanoparticles in different methods with 50°C temperature at 120 MPa pressure.

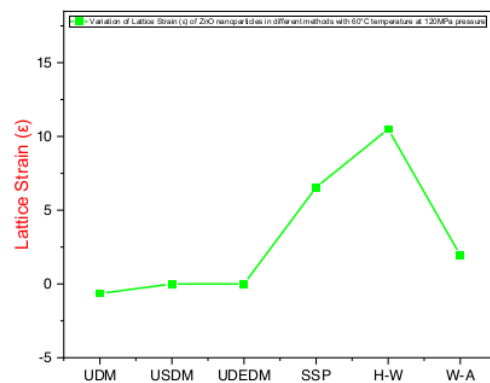


Fig. 5.113 Variation of Lattice Strain (ϵ) of ZnO nanoparticles in different methods with 60°C temperature at 120 MPa pressure.

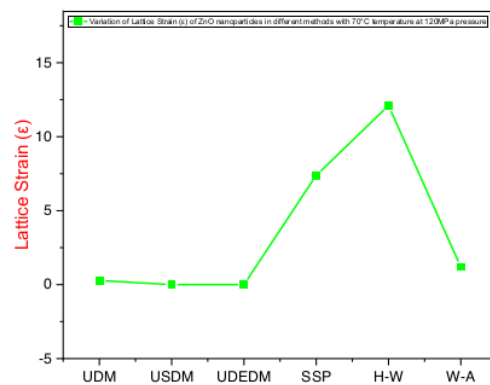


Fig. 5.114 Variation of Lattice Strain (ϵ) of ZnO nanoparticles in different methods with 70°C temperature at 120 MPa pressure.

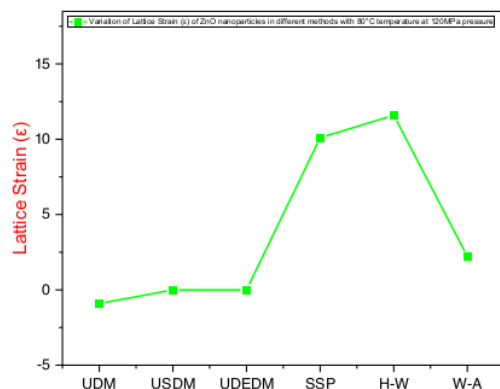


Fig. 5.115 Variation of Lattice Strain (ϵ) of ZnO nanoparticles in different methods with 80°C temperature at 120 MPa pressure.

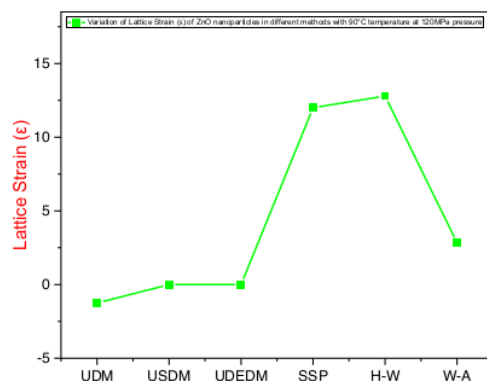


Fig. 5.116 Variation of Lattice Strain (ϵ) of ZnO nanoparticles in different methods with 90°C temperature at 120 MPa pressure.

However, among all other methods, the SSP and W-A method is more accurate and favoured since points fit the linear line much better than any other technique. As a consequence of the annealing temperature at 120 MPa pressure, the crystallite size variation is negligible. Variations in other parameters, on the other hand, are very significant.

Furthermore, changes in various crystallite parameters as a result of annealing temperature at 120 MPa pressure can be used to explain other applications, such as Dye-sensitized solar cells performance.

5.14.1 Effects of compression temperatures on photovoltaic performance and thickness

Before compression, the thickness of the synthesized ZnO nanoparticles was in the 9-10 micrometre range. The thickness was lowered after compression. After 100 MPa compression, the thickness was nearly saturated. At 120 MPa, a uniform compact layer was obtained for compression. Figure 5.117 shows the thickness and open circuit voltage of a ZnO-based DSSC prepared by 120 MPa compression at various temperatures (from 50 °C temperature to 90 °C). By applying heat during compression, the thickness of the film is reduced somewhat, and the open circuit voltage improves as a result. After 70 °C, the thickness and open circuit voltage were nearly saturated, as illustrated in Fig. 5.117.

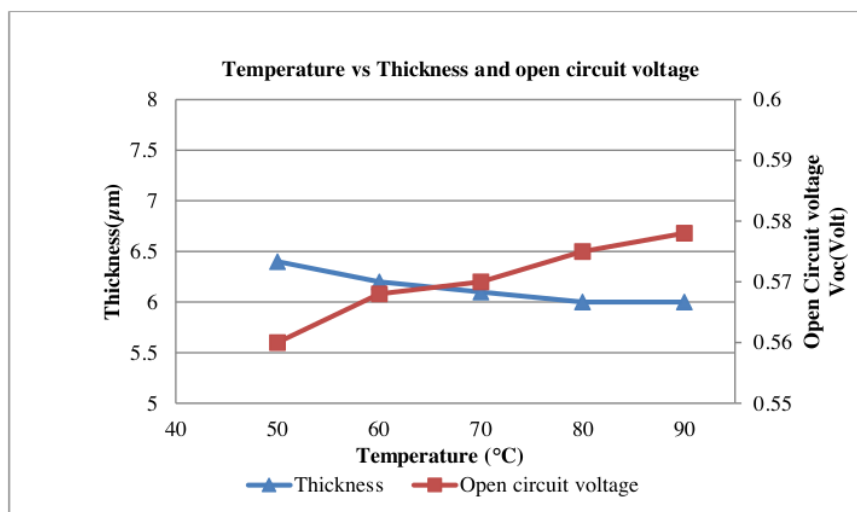


Figure 5.117 The thickness and open circuit voltage of a ZnO-based DSSC prepared by 120 MPa compression at different temperatures.

The effect of heat during compression on the short circuit current density and efficiency of ZnO-based DSSC is shown in Fig. 5.118. The short circuit current density and efficiency were initially improved by increasing the temperature level to 70 °C. The current density and efficiency began to decline when the compression temperature was increased further. It is clear that adding heat during compression improved the current density, fill factor, open circuit voltage, and efficiency. The surface was found to be more uniform during 120 MPa compression at 70 °C heat, with a substantially smaller amount of peeled out area on the film. As a result, when compared to samples prepared under alternative necking circumstances, the photovoltaic performance of this sample was shown to be better.

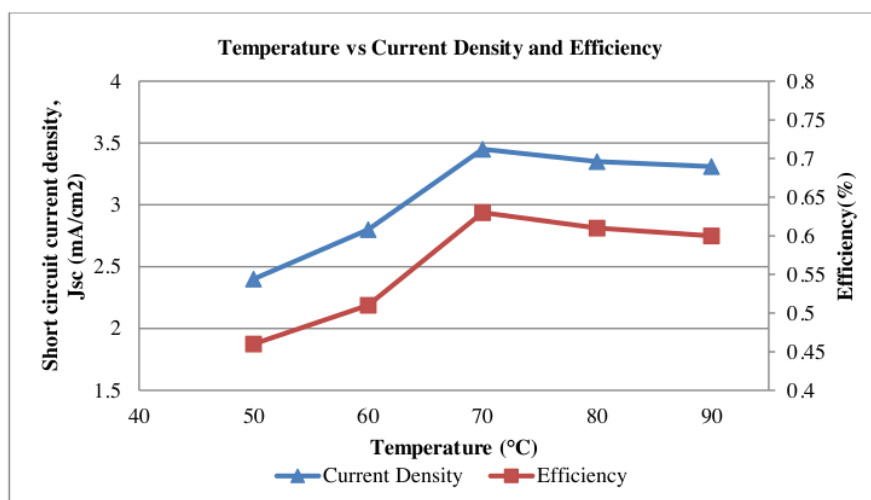


Figure 5.118 ZnO-based DSSC short circuit current density and efficiency prepared by 120 MPa compression at various temperatures.

CHAPTER 6

CONCLUSION

From the results and discussion, we came to the following conclusion:

The ZnO nanoparticles films at different annealing temperatures, compressed at 120 MPa pressure, were prepared by employing the blade coating method, which is further studied through the X-ray Diffraction (XRD) technique for their crystallinity and structural properties. XRD peak broadening analysis has been performed to calculate the various elastic properties of the ZnO nanocrystals, such as intrinsic strain, stress, energy density, using the M. Scherrer plot, different models of Williamson-Hall plot, Size-Strain Plot, Halder-Wagner Method and Wagner-Aggar Method, along with the determination of the average particle size. The structure of ZnO nanoparticles is a hexagonal wurtzite structure with different annealing temperatures at 120 MPa pressure. After comparing all these studies, it has been found that, the average size calculated from the Size-Strain Plot and Wagner-Aggar Method matches very well with the average size observed in the M. Scherrer plot, and different models of the Williamson-Hall plot studies. Different elastic properties have been calculated with the different models of the W-H method, such as the UDM, USDM and UEDM models. So far, strain calculation is concerned, SSP provides the best result, whereas the H-W method gives a very high value of strain, because, it considers the contribution of low and mid angle XRD data, along with the attribution of the lattice dislocations.

Finally, the distribution of the average particle size, calculated from different models using the XRD peak broadening, shows that the average size lies in the range of 11.93 nm, 13.48 nm, 14.43 nm, 13.13 nm and 11.61 nm for 50 °C, 60 °C, 70 °C, 80 °C and 90 °C temperatures at 120 MPa pressure. And the surface was found to be more uniform during 120 MPa compression at 70 °C heat, with a substantially smaller amount of peeled out area on the film. As a result, when compared to samples prepared under alternative necking circumstances, the photovoltaic performance of this sample was shown to be better.

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