Synthesis and processing technique to reduce the particle size of ZnO pellet by hybrid vibrational annealing and dry quenching set up

Nirlipta Kar Kar

Siksha 'O' Anusandhan(deemed to be) University

Sushanta Kamilla (✉ sushantakamilla@soa.ac.in)

ITER, Siksha 'O' Anusandhan(Deemed to be) University

Article

Keywords: ZnO nanoparticles, Thermo-vibrational annealing, Vibrational dry quenching, XRD, HRTEM

Posted Date: February 1st, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1252822/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Synthesis and processing technique to reduce the particle size of ZnO pellet by hybrid vibrational annealing and dry quenching set up

Nirlipta Kar¹, Sushanta Kumar Kamilla^{1,*}

Department of Physics,

Semiconductor Research Laboratory,

Faculty of Engineering and Technology(ITER),

Siksha 'O' Anusandhan (Deemed to be) University, Bhubaneswar-751030, Odisha, India

* Corresponding author. E-mail: sushantakamilla@soa.ac.in

*ORCHID Id : [0000-0003-1673-6445](https://orcid.org/0000-0003-1673-6445)

ABSTRACT

The reduction in particle size of ZnO pellet in the nanoscale range was achieved using a hybrid thermo-vibrational annealing and dry-quenching set-up, which was designed and fabricated in-house and is simple and low-cost to operate. Initially, ZnO pellets were synthesized through pyrophoric method and then annealed at 800⁰C in this processing device. To confine grain growth during the recrystallization stage of annealing, vibrational energy was applied during annealing and dry-quenching to cool. This step-by-step post-synthesis technique involves the simultaneous application of thermal and mechanical vibrational energy to the ZnO pellet for 4 hours, followed by vibrational-dry quenching. Both annealed pellets, i.e., ZnO annealed without vibration and ZnO annealed with vibration, were studied using XRD, SEM, HRTEM, FTIR, UV-Visible, and Raman spectroscopy to conduct a comparative investigation of various structural, microstructural, and optical properties. Although both ZnO pellets had polycrystalline hexagonal wurtzite structures without any secondary phases, the average crystallite sizes of ZnO pellets with vibration were smaller than those without vibration, which

were 36.566nm and 25.308nm, respectively, according to the XRD data. Analysis using SEM and HRTEM yielded similar confirmatory results. FTIR and Raman examinations revealed the presence of various functional groups and vibrational modes, which were confirmed by experimental results. The greater optical bandgap of 3.36 eV seen in the UV-Visible spectra of the ZnO with vibration sample indicates that it is a promising material for the creation of enhanced electrical, optoelectronic, and sensor devices based on ZnO nanoparticles, among other applications.

Keywords ZnO nanoparticles, Thermo-vibrational annealing, Vibrational dry quenching, XRD, HRTEM

1 Introduction

In recent years, synthesis and structural characterization of nanomaterials with customizable physical and chemical properties (by varying their particle size and shape) have found increased research interest. Since their high surface-to-volume ratio, high porosity and quantum size effects, reduced melting points, more active sites on the surface, and improved physical appearance, chemical and magnetic properties as compared to their bulk counterparts, nanocrystalline materials have revolutionised a wide range of fields, including science, engineering, and technology. The improvement in the properties of nanocrystalline materials makes them a promising material for use in various research avenues, such as nano-sensors, fuel cells, nano-sorbents, catalysis, energy storage and conversion, optoelectronics, etc.[1-2]. Metal oxide semiconductor (MOS) nanomaterials with reduced particle size have recently become an area of interest in the semiconductor field because of their excellent optical and electrical properties, which are used in sensors, transparent electronics, piezoelectric transducers, ceramics, electro-optical devices, etc.[3-4]. It has been noted that among the many MOS materials, ZnO nanoparticles (ZNPs) have received more attention because they are inexpensive, biocompatible, non-toxic, and can be used in a variety of applications, including

gas sensors [5-6], solar cells [7], photocatalysis [8], varistors [9-10], electrochemical cells [11], ultraviolet (UV) photodetectors [12], optoelectronics devices [13] and acoustic devices [14]. Besides this, these materials are used in different cosmetics, medicines, textiles, food packaging, biosensors, antibacterial agents, etc. [15].

One of the most important properties of ZnO is an n-type II-VI compound semiconductor material with a wide and direct bandgap of 3.37eV [16] [16] and its high 60meV exciton binding energy at 300K [17]. For photonic devices that can be operated at room temperature (RT), an exciton binding energy high enough to enable near-band-edge exciton emission even at room temperature or high temperature is an attractive option [18]. In addition, excellent photocatalytic nature of ZnO makes it a suitable candidate for fossil fuels[19]. Research is ongoing to further enhance its usefulness in a variety of scientific domains by manipulating its size in the nanoscale region, which has numerous advantages (1-100nm). It's because ZnO's physical, optical, and magnetic properties in this size range are superior to those in its broader size range, and this is why.

In order to reduce the particle size of ZnO pellet to the nanoscale, many energy-saving methods have been described, which are divided into three phases, such as solid, liquid, and vapour phase, which are carried out via different routes (like physical, chemical and biological) [20]. For example, various widely used methods are co-precipitation method [21], hydrothermal method [22-23], spray pyrolysis [24], microemulsion process [25], sol-gel [26-27], and solution combustion synthesis (SCS) technique [28]. Because it is less expensive, simpler, greener, and uses less energy than other approaches, the combustion process has become increasingly popular for synthesising ZnO powders. In the combustion method, well-crystalline nano-powders with high purity are formed in a shorter time without the use of expensive instruments. Recent studies have shown that the particle size of ZnO powders ranged between 20nm-50nm using the SCS method [29-32]. In addition, doping with transition metals (Co, Ni,

etc.) and lowering the annealing temperature have both been found to reduce particle size [33]. However, the synthesis of ZnO powder, which is not suited for many device applications, such as gas sensors, solar cells, varistors, and spintronics, is a significant shortcoming of such approaches. As a result, pellets or thin films of material are frequently required. Although some researchers have reported the production of ZnO pellets with a particle size in the nanoscale [34-37], the big question arises whether it is possible to reduce the grain and particle size of MOS materials during annealing, which generally increases during the recrystallization stage. To the best of our knowledge, studies on the concept of reduction of grain or particle size of oxide semiconductor pellets during heat treatment are yet to be available.

To address the current gaps in knowledge, we therefore made ZnO pellets by applying mechanical vibrational energy during annealing followed by vibrational dry quenching using hybrid thermo-vibrational annealing and dry-quenching setup. This was done to obtain nano-grains and particles after synthesizing ZnO pellets by the pyrophoric method. The entire assembly was made inexpensively and with less instrumentation. A comparative analysis was carried out between ZnO without vibration (ZWOV) and ZnO with vibration (ZWV) pellets through a systematic study of their structural, microstructural, morphological, and optical properties using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX) spectroscopy, High-Resolution Transmission Electron Microscopy (HRTEM), Fourier Transform Infrared (FTIR) spectroscopy, UV-Visible, and Raman spectroscopy.

2Experimental Procedure

2.1Synthesis of ZnO pellet

The chemicals used in our experiments are zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$], ethylene glycol $[(\text{CH}_2\text{OH})_2]$, glycerol($\text{C}_3\text{H}_8\text{O}_3$), 2-propanol ($\text{CH}_3\text{CHOHCH}_3$), tri-ethyl amine $[\text{N}(\text{CH}_2\text{CH}_3)_3]$, and nitric acid (HNO_3). All the chemicals are brought from Merck

company, maintaining 99.9% purity. Throughout the experiment, distilled water was used as per the requirements. To obtain our desired sample of a particular amount, zinc acetate dihydrate, ethylene glycol, and glycerol were added in a beaker with proper measurements followed by the addition of distilled water as per the requirements. Then the mixture was continuously stirred using a glass rod until the formation of a transparent solution. After that, 2-propanol, and tri-ethylene amine (TEA), were added with stirring slowly for a few minutes, then filtrated to obtain a dust particle-free clear solution. For the auto-combustion process, 20ml of TEA, 10ml of nitric acid, and some distilled water were added to the solution with proper mixing, which was then allowed to heat at $\sim 200^{\circ}\text{C}$, keeping it on a hot plate. After nearly 15-20 minutes, combustion of the solution occurred, and the solution turned into a black color powder. The obtained powders are collected in an alumina crucible and calcinated in a high-temperature muffle furnace at 700°C for 5hrs to remove carbon and other impurities if present. To get more fine powders of ZnO, it was grinded several times in an agate mortar. Then by adding 4-5 drops of polyvinyl alcohol (acts as a binder) and applying 6 tons of pressure using a hydraulic press, the fine powders were pelletized of diameter 15mm and thickness 3mm. For the removal of internal stress and lattice defects, the pellets were annealed at 800°C for 4 hours by using a “hybrid thermo-vibrational annealing and dry-quenching setup”. Detail description of this setup and its principle is discussed below.

2.2 Detail description of the Experimental setup

Scheme 1 represents a perspective view of our designed nano-crytalline material processing device having the facility of thermo-vibrational annealing as well as vibrational dry quenching. Here, vibrational energy is applied to the synthesized ZnO pellets during annealing and dry quenching to reduce its grain size during the recrystallization stage of annealing as well as quenching time.

The whole setup comprises two chambers, one over the other connected with a mechanical vibrator. The first chamber is used for annealing, and the second is for dry-quenching of the pellet, where the platform is associated with a huge vibrator providing vibrational energy during annealing as well as dry-quenching.

The first chamber consists of a horizontal tube furnace, an alumina crucible, sample, thermocouple, inert gas inlet, and outlet port. The maximum temperature range of this tube furnace is limited upto 1000⁰C, which is measured by the thermocouple associated with it. Further, the two ports (i.e., gas inlet and outlet) which are attached to the walls of this chamber are used for providing an inert atmosphere within it. Here, we have used argon gas that is inserted through the inlet port and exits through the outlet port to prevent contamination from other impurities present in the surroundings.

The second chamber consists of primary, secondary, and ternary containers, a lid cover, gas inlet, outlet port, ice cubes, multiple thermo-cool sheets, silica aerogel, and an exhaust fan. The annealed pellet is subjected to dry-cooling in the second chamber to obtain defects-free nanocrystalline material. The primary container is used for placing the annealed sample for dry-quenching purposes. The gap between primary and secondary containers is filled with many small pieceof ice for sudden cooling of the annealed pellet. Further, multiple thermo-cool sheets and silica aerogel, which are good thermal insulators, are used inside the gap between inner and outer metallic containers, as shown in Scheme 1, to prevent the radiations from the surroundings enter the chamber. For the removal of water vapours if present inside the walls of the primary container, an exhaust fan is also connected.

Scheme 1 Schematic diagram of thermo-vibrational annealing attached with vibrational dry quenching setup

2.3 Working

First, annealing of the cold-worked pellet was done at 800°C for 4 hours, keeping it at the middle of the horizontal tube furnace. Here, a small rectangular shape of alumina crucible was used as the sample holder. To avoid heat radiation, both ends of the tube were closed with two thick iron plates. To prevent contamination from the surroundings, an inert gas environment was created in the furnace by a continuous flow of Argon gas through two narrow pipes (gas inlet and outlet), which were inserted through two small holes of the plates, as shown in Scheme 1. Temperature measurement was done by using the thermocouple during the annealing process. After annealing, the sample was suddenly put into the primary container of the second chamber by opening the lid cover for a quick cooling process. To avoid grain regrowth, vibrational energy is also applied during quenching. Some ice pieces were taken inside the

inner metallic container for dry quenching. The exhaust fan was also used to remove any form of moisture that could occur during this process.

2.4 Sample Characterization

The analysis of crystal structure, phase identification, and average crystallite size of both the prepared ZnO pellets ZWOV and ZWV were determined by X-ray diffractometer (model-H12, Rigaku Ultima IV, Japan) using $\text{CuK}\alpha$ radiation ($\lambda=1.54\text{\AA}$) in the 2θ range of 20° - 90° with the scan rate of $0.01^\circ/\text{s}$. Surface morphological including the shape and size of grains were studied through Scanning Electron Microscopy (SEM) by using Hitachi-S3400N with the operating potential of 15kV. High Resolution Transmission Electron Microscopy (HRTEM) of both samples were carried out to accurately study their particle size and structure by using JEOL F200, operating at 200kV. Using image-J software, average grain size and particle size were calculated. The presence of several functional groups was investigated by Fourier Transform Infrared Spectroscopy (FTIR) using Spectrum Two-104789 in the wavenumber range of 400 - 4000cm^{-1} . The absorption spectra were recorded using a UV-Visible Spectrometer with Shimadzu UV-2450 in the wavelength range of 200 - 800nm at room temperature to determine the sample bandgap. Finally, Raman spectra of both the annealed ZnO pellets were observed using a Raman spectrometer with Diode LASER ($\lambda=437\text{nm}$).

3 Results and Discussion

3.1 X-ray diffraction (XRD) analysis

3.1.1 Scherrer method

Fig.1 represents XRD patterns of annealed ZWOV and ZWV pellets with 2θ ranges from 20° to 90° . The multiple diffraction peaks obtained by (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (202), (104) and (203) planes illustrate hexagonal wurtzite phase and polycrystalline nature of both the samples. Both the samples are free from impurity as no

other peaks are found other than ZnO peaks. The ‘ 2θ ’ values of ZWOV and ZWV pellets are in good compliance with their corresponding JCPDS files #89-1397 and #79-0205, respectively, which are given in Table 1. From the XRD patterns, it is observed that with the application of mechanical vibrational energy during annealing as well as dry quenching to the sample, peak intensity decreases with broadened width, i.e., the increase of FWHM (Full width at half maximum), indicating a significant impact of the vibrational annealing and dry quenching over the crystallization of ZWV sample. This result is confirmed from the Debye Scherrer formula which is given in Eq.1.

By taking some intense peaks like (100), (002), (101), (102), (110), (103), and (112), the average crystallite size of both the samples is calculated using Debye Scherrer’s equation [38], which is given by,

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

Where D = average crystallite size, k is the Scherrer constant (≈ 0.9), λ is the wavelength of $\text{CuK}\alpha$ radiation ($1.54\text{\AA}$), β is the FWHM of peak and θ is the Bragg’s angle.

From Eq. 1, ‘ D ’ of ZWOV and ZWV pellets were calculated as 36.566nm and 25.308nm, respectively.

(a)

(b)

Fig.1 XRD patterns of annealed pellets **a** ZWOV and ZWV samples, **b** Zoomed in version of (101) peak

A slight decrease of lattice parameters ‘ a ’ and ‘ c ’ is observed in ZWV samples as compared to ZWOV. The lattice parameters and interplanar spacing, ‘ d ’ is calculated by using the following Eqs. 2-5 [39-40],

$$a = \frac{\lambda}{\sqrt{3}\sin\theta_{100}} \quad (2)$$

$$c = \frac{\lambda}{\sin\theta_{002}} \quad (3)$$

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

$$d = \frac{\lambda}{2\sin\theta} \quad (\text{Bragg's equation}) \quad (5)$$

The calculated ‘ a ’, ‘ c ’ and ‘ d ’ (d_{Bragg} and $d_{theoretical}$) values nearly match their corresponding JCPDS files, as shown in Table2. The slight decrease of lattice constants and ‘ d ’ values of ZWV samples are may be due to the “surface energy effect” of the nanoparticles resulting from the thermo-vibrational annealing and vibrational dry quenching. Smaller nanoparticles of ZWV samples leads to a high surface-to-volume ratio. As a result, large numbers of atoms present on the surface provide a downward force to the particle due to high surface energy, which results in a slight decrease in interplanar spacing and lattice constants. Slight shifting of peaks towards higher angles is may be due to the decrease of microstructural lattice parameters and crystallite size occurring for the pressure on the surface of smaller particles.

Table1 Estimation of average crystallite size from different intense peaks of ZWOV and ZWV pellets

		ZWOV				ZWV		
hkl	2 θ (deg.)	2 θ - JCPDS#89- 1397 (deg.)	β (deg.)	D (nm)	2 θ (deg.)	2 θ - JCPDS#79- 0205(deg.)	β (deg.)	D (nm)
100	31.714	31.737	0.211	39.60	31.95	31.85	0.335	24.75
002	34.375	34.379	0.213	39.60	34.618	34.552	0.33	25.2
101	36.198	36.215	0.225	49.50	36.443	36.36	0.35	23.89
102	47.466	47.484	0.278	31.5	47.734	47.698	0.344	25.34
110	56.527	56.536	0.28	28.28	56.77	56.75	0.354	25.67
103	62.796	62.777	0.267	26.654	63.083	63.093	0.349	26.65
112	67.91	67.868	0.267	36.47	68.163	68.168	0.375	25.66

Table2 List of calculated values of lattice parameters(‘ a ’ and ‘ c ’) and interplanar spacing in ZWOV and ZWV

Sample	$c(\text{\AA}^0)$	$a(\text{\AA}^0)$	$d_{\text{Bragg}}(\text{\AA}^0)$	$d_{\text{theoretical}}(\text{\AA}^0)$
ZWOV	5.2116	3.2540	2.4786	2.4837
ZWV	5.1761	3.2306	2.4624	2.4618

Unit cell volume(V) was calculated for hexagonal wurtzite structure using,

$$V = \frac{\sqrt{3}}{2} a^2 c \quad (6)$$

It was observed that the value of ‘ V ’ also decreases with the application of mechanical vibration to the sample. For ZnO without vibration (ZWOV) and ZnO with vibration (ZWV), ‘ V ’ was found to be 47.791 Å^3 and 46.784 Å^3 , respectively.

The bond length(L) of Zn-O was calculated by using the following equation[39],

$$L = \sqrt{\left[\frac{a^2}{3} + (0.5 - u)^2 \times c^2\right]} \quad (7)$$

Where, u is the position parameter which is given by,

$$u = \left(\frac{a^2}{3c^2}\right) + 0.25 \quad (8)$$

Table 3 represents a comparative calculated value of c/a ratio, unit cell volume(V), bond length(L) of ZWOV, and ZWV pellets. The reason for the slight decrease of unit cell volume and bond length in ZWV sample is due to the reduction of lattice parameters. As there is no change in the c/a ratio (~ 1.6) as per the hexagonal structure, we can say that there is no impact of vibrational energy on the crystal structure of ZnO lattice.

3.1.2 Uniform Deformation Model(UDM)

The Uniform deformation model(UDM) is one of the mathematical expressions of Williamson-Hall(W-H) methods for the determination of both crystallite size(D) and lattice strain(ε) of the sample. In this model, it is assumed that total line broadening of the XRD peaks(β_T) is due to the combined contribution of broadening due to crystallite size(β_D) and due to microstrain(β_ε), which can be written as,

$$\beta_T = \beta_D + \beta_\varepsilon \quad (9)$$

From Eq. (1), it can be written as,

$$\beta_D = \frac{k\lambda}{D \cos \theta} \quad (10)$$

$$\text{Similarly, } \beta_\varepsilon = 4\varepsilon \tan \theta \quad (11)$$

Now putting the values of Eq. (10) and (11) in Eq. (9), we have $\beta_T = \frac{k\lambda}{D\cos\theta} + 4\epsilon\tan\theta$

$$\Rightarrow \beta_T \cos\theta = \frac{k\lambda}{D} + 4\epsilon \sin\theta \quad (12)$$

Eq. 12 represents a straight line equation, whereby plotting a graph between $\beta_T \cos\theta$ (in Y-axis) and $4\sin\theta$ (in X-axis), both crystallite size(D) and microstrain(ϵ) can be determined from the Y-intercept and slope of the graph respectively, which is given in Table 3. Fig. 2 represents the W-H plot of both ZWOV and ZWV pellets. A decrease of lattice strain in ZWV pellet was observed, which may be due to the reduction of lattice defects like voids present in the sample due to vibrational annealing.

(a)

(b)

Fig.2 W-H plot of ZnO pellets **a** ZWOV and **b** ZWV annealed at 800°C

Table3 Calculated Structural parameters from XRD patterns of ZWOV and ZWV pellets

Sample	c/a	$V(\text{\AA}^3)$	u	$L(\text{\AA})$	ε
ZWOV	1.6016	47.7907	0.3799	1.9802	0.000986
ZWV	1.6022	46.7844	0.3798	1.9662	0.000878

3.2 Scanning Electron Microscopy (SEM)analysis

Fig.3 represents SEM images and grain size distribution histograms of ZnO pellets annealed at 800°C with and without the presence of mechanical vibrations, respectively. These micrographs show randomly distributed grains, which are more or less spherical. The samples annealed 'with' vibrations have comparatively smaller particles with little porous structure than those

annealed ‘without’ vibrations. The formation of smaller grains of ZWV sample was confirmed from its histogram graphs, as shown in Fig.3. This proves that with applying mechanical vibrational energy to the sample during annealing, the surface-to-volume ratio increases with a reduction in grain size. This little porosity with smaller grains of ZWV sample makes this material more promising to be used for gas sensing applications. Agglomeration of grains at some places in ZWV reveals the existence of more attractive forces between nanoparticles due to the high surface energy of the sample [41]. We go forward for HRTEM analysis to further calculate average particle size.

Fig. 3 SEM micrographs and corresponding grain diameter size distribution histograms of annealed ZWOV and ZWV pellets

3.3 Energy-dispersive X-ray (EDX) spectra analysis

EDX spectra of both the annealed pellets are shown in Fig.4a, b. These spectra reveal the high purity of the annealed pellets as they don't contain any other impurity phases except 'Zn' and 'O' elements due to high annealing temperatures (i.e., at 800°C). The peaks obtained at 1keV, 8.6keV, and 9.6keV represents 'Zn,' and that observed at 0.5keV represents 'O' atom. This is in good agreement with the XRD result, which confirms the successful formation of a single-phase ZnO lattice. The weight and atomic percentages of Zn and O of the two samples are shown in Table 4.

Fig. 4 Energy dispersive spectra of annealed ZnO pellets **a**ZWOV and **b**ZWV

Table 4Elemental constituents' analysis of ZWOV and ZWV pellets

	ZWOV		ZWV	
Elements	Weight%	Atomic%	Weight%	Atomic%
Zn	68.63	65.10	63.49	70.12
O	31.35	34.90	36.51	29.88

3.4 High Resolution Transmission Electron Microscopy (HRTEM) analysis

A deep understanding of the size, shape, and arrangement of particles can be obtained from a High Resolution Transmission Electron Microscopy (HRTEM) image. Fig.5a, b represents

HRTEM images of synthesized ZnO pellets annealed in the presence and absence of mechanical vibrational energy, i.e., ZWOV and ZWV. From these images, it can be observed that our synthesized ZnO pellets are nearly spherical in shape with little porous structure, which is distributed randomly inside the material. But, as compared to the ZWOV sample, the particle size of the ZWV sample is quite small. The calculated average particle size obtained from the histogram of these corresponding images of ZWOV and ZWV samples are 36.185nm and 25.221nm, respectively, which are in good agreement with XRD results.

Fig.5 TEM images and corresponding particle size distribution histograms of ZNPs annealed at 800°C a ZWOV b ZWV

3.5 Fourier Transform Infrared Spectroscopy (FTIR) Studies

Fourier transform infrared (FTIR) spectroscopy of both ZWOV and ZWV samples were carried out to detect several functional groups and chemical bonds associated with the samples. Fig.6 represents the FTIR spectrum of both the prepared samples, recorded in the wavenumber range

of 400-4000 cm^{-1} . Different absorption peaks observed from these spectra are 698.583 cm^{-1} , 885 cm^{-1} , 1033.217 cm^{-1} , 3375 cm^{-1} and 698.701 cm^{-1} , 885 cm^{-1} , 1033.347 cm^{-1} , 3375 cm^{-1} for ZWOV and ZWV samples respectively. The absorption peak found at 698.583 cm^{-1} and 698.701 cm^{-1} corresponds to the C-H out-of-plane bending of alkene groups. The absorption peaks observed at 885 cm^{-1} are ascribed by the presence of some carbonated impurities in the samples[42-43]. The peaks in the range of 1000-1250 cm^{-1} correspond to the vibrational stretching mode of C-N bond, which may result from the reaction of the primary amine group with zinc acetate dihydrate[44-45]. The broad peak obtained at 3375 cm^{-1} is attributed to the vibrational mode of the O-H bond[46]. A slight shifting of peak position is observed in these spectra, which may be due to the effect of particle size as reported in different studies[47-48].

Fig. 6FTIR Spectra of both ZWOV and ZWV annealed pellets

3.6 UV-Visible Spectroscopy analysis

UV-Visible absorption spectroscopy is one of the effective techniques used to investigate the optical properties of nanoparticles. Fig. 7a, b represents RT absorption spectra of synthesized

ZnO pellets annealed at 800°C without and with vibrations, respectively, recorded in the 300-800nm wavelength range. A broad absorption band was observed in the range of 351-355nm showing blueshift a blue shift compared to the bulk ZnO (nearly 369nm), which may be due to the effect of smaller-sized particles. As shown in the fig., the exact peak positions of both the ZWOV and ZWV samples were recorded at 353nm and 347nm, respectively. The observed blue shift in the absorption of the ZWV sample may be due to the quantum confinement effect and small particles[46].

(a)

(b)

Fig.7 UV-Visible spectra with Tauc's plot(inset) of **a** ZWOV **b** ZWV samples

The optical bandgap of both the samples was investigated by using the following Tauc's equation [49],

$$(\alpha h\nu)^2 = A (h\nu - E_g) \quad (13)$$

where α is the absorption coefficient, $h\nu$ is the energy of the photon; A is a constant, and E_g is the bandgap to be evaluated. The inset of Fig.7(a)-(b) represents Tauc's plot which determines bandgaps of prepared ZWOV and ZWV samples respectively. The point observed by linear extrapolation of the graph on the X-axis, obtained by plotting $h\nu$ (in the X-axis) versus $(\alpha h\nu)^2$ will give the value of energy bandgap (E_g) of the samples, as shown in the insets of Fig.7a, b. From Tauc's plot, the calculated bandgaps of ZWOV and ZWV samples are 3.33eV and 3.36eV, respectively. Increase in bandgap of ZWV sample implies a decrease of particle size obtained by applying mechanical vibrational energy during annealing.

Due to this higher bandgap, our synthesized ZWV material can be selected as a suitable candidate for high performance electronic and optoelectronic devices.

3.7 Raman Spectroscopy Studies

In order to identify several vibrational modes present in the crystal, lattice defects or any structural disorders, Raman spectroscopy has been used as the most versatile tool. Fig.8 represents room temperature Raman spectra of both the annealed ZnO pellets i.e., ZWOV and ZWV recorded in the range of 200-1200 cm^{-1} . As per the group theory, total phonon normal modes observed at the gamma point of Brillouin zone of a hexagonal wurtzite structured ZnO lattice is $2A_1+2E_1+2B_1+2E_2$. Out of these eight modes, one set of A_1 and E_1 i.e., (A_1 , E_1) are acoustic mode, whereas the remaining set of six modes i.e., (A_1 , E_1 , $2B_1$, $2E_2$) are optical modes. Two polar optical modes A_1 and E_1 are infrared active and are divided into transverse and longitudinal modes denoted as ($A_{1(\text{TO})}$, $A_{1(\text{LO})}$) and ($E_{1(\text{TO})}$, $E_{1(\text{LO})}$). Similarly, the non-polar phonon mode E_2 is categorized into high and low frequency phonon modes i.e., $E_{2\text{H}}$ and $E_{2\text{L}}$ [50-52]. These $E_{2\text{H}}$ and $E_{2\text{L}}$ are associated with oxygen atoms and Zn sublattice respectively [57]. As shown in Fig.8, five major peaks centered at 329.431, 380.248, 435.728, 579.729, 1153,732 cm^{-1} and 327.997, 376.943, 435.159, 576.885, 1150.443 cm^{-1} for ZWOV and ZWV sample respectively are clearly observable. The peaks at 329.431 and 327.997 cm^{-1} are attributed to the multiple phonon scattering of $E_{2\text{H}}$ - $E_{2\text{L}}$ modes of vibration [53]. The peaks observed at 380.248 and 376.943 cm^{-1} are due to $A_{1(\text{LO})}$ mode of vibration [54]. Similarly, high frequency $E_{2\text{H}}$ vibrational mode are assigned to the highly intense peaks at 435.728 and 435.159 cm^{-1} for ZWOV and ZWV samples respectively [55]. As we can see from Fig.8, the peak intensity of the highly intense peak obtained for $E_{2\text{H}}$ mode of ZnO pellet decreases with peak broadening on the application of vibrational energy during annealing as well as dry-quenching, indicating the decrease in particle size. This result matches well with the XRD result, and this band is called as the characteristics band of wurtzite structure. The peaks centered at 579.729 and 576.885 cm^{-1} are assigned to $E_{1(\text{LO})}$ modes, which may be due to oxygen

vacancies, free carriers and zinc interstitial[56]. The broad peaks around 1153.732 and 1150.443 cm^{-1} are due to the optical overtone[57]. A narrow peak centered at 1184.635 cm^{-1} of ZWOV sample may exist due to the second order vibration.

Fig.8 Raman spectrum of ZWOV and ZWV pellets

4Conclusions

A successful synthesis of ZnO pellets were performed through the pyrophoric method followed by annealing at 800 $^{\circ}\text{C}$ for 4 hours using “vibrational annealing and dry quenching” setup. To observe variation in different properties like structure, morphology, microstructure, particle size, composition, optical bandgap and several vibrational modes, a comparative analysis between ZWOV and ZWV samples was studied through several characterizations such as XRD, SEM, EDX, HRTEM, FTIR, UV-Visible and Raman spectroscopy. XRD results reveal a hexagonal wurtzite structure with no impure phases in both the samples. Also, a decrease in average crystallite size of ZnO pellets, annealed in presence of mechanical vibrational energy was observed as compared to that of pellets annealed without vibration, which are found to be

36.566nm and 25.308nm respectively. SEM images signify slight porous arrangement of grains in ZWV with mean grain size calculated from its corresponding histogram, was found to be 68nm, whereas it was nearly 130nm in ZWOV sample. EDX spectra confirm the high purity of both the annealed samples. HRTEM images clarify the decrease in particle size of ZWV samples in comparison to ZWOV samples. FTIR shows the very slight shifting of most of the absorbance peaks towards higher wavenumber sites, which may result due to formation of smaller particle size. The optical bandgaps of both the samples were compared through UV-Visible spectroscopy. From UV-Visible analysis, the increase in bandgap energy (E_g) from 3.33eV to 3.36eV of ZWV samples confirmed the lowering of particle size. From Raman spectroscopy, in addition of the presence of several vibrational modes, a decrease in peak intensity with little broadening was observed in ZWV sample, which corresponds to the XRD results. This work gives a new idea to the scientific community for the synthesizing ZnO pellets of decreased particle size within less instrumentation and low cost, which enhances its ability to be used in different area of nano-fields such as gas sensors, optoelectronics, photocatalysis and several high-energy storage electronic devices.

Acknowledgements

We are grateful to National Institute of Science Education and Research (NISER), Bhubaneswar for supporting our work and for HRTEM measurements. We are thankful to University of North Odisha for providing facility for UV-Visible spectroscopy and CIF, O.U.A.T., Bhubaneswar for SEM and FTIR measurements. We would also like to thank the Department of Atomic energy, UGC-DAE-CSR, INDORE for Raman spectroscopy measurements.

References

- [1] S.A. Mazari, E. Ali, R. Abro, F.S.A. Khan, I. Ahmed, M. Ahmed, S. Nizamuddin, T.H. Siddiqui, N. Hossain, N.M. Mubarak, and A. Shah, Nanomaterials: applications, waste-

handling, environmental toxicities, and future challenges-A review. Journal of Environmental Chemical Engineering. p.105028(2021).<https://doi.org/10.1016/j.jece.2021.105028>

[2] G. Maduraiveeran, M. Sasidharan, and W. Jin, Earth-abundant transition metal and metal oxide nanomaterials: Synthesis and electrochemical applications. Progress in Materials Science. **106**, p.100574(2019).<https://doi.org/10.1016/j.pmatsci.2019.100574>

[3] T. Zhai, X. Fang, M. Liao, X. Xu, H. Zeng, B. Yoshio, and D. Golberg, A comprehensive review of one-dimensional metal-oxide nanostructure photodetectors. Sensors. **9**(8), pp.6504-6529(2009).<https://doi.org/10.3390/s90806504>

[4] D. Raoufi, Synthesis and microstructural properties of ZnO nanoparticles prepared by precipitation method. Renewable energy. **50**, pp.932-937(2013).<https://doi.org/10.1016/j.renene.2012.08.076>

[5] P. Rai, W.K. Kwak, and Y.T. Yu, Solvothermal synthesis of ZnO nanostructures and their morphology-dependent gas-sensing properties. ACS applied materials & interfaces. **5**(8), pp.3026-3032(2013).<https://doi.org/10.1021/am302811h>

[6] T.J. Hsueh, and C.L. Hsu, Fabrication of gas sensing devices with ZnO nanostructure by the low-temperature oxidation of zinc particles. Sensors and Actuators B: Chemical. **131**(2), pp.572-576(2008).<https://doi.org/10.1016/j.snb.2007.12.045>

[7] W.J. Beek, M.M. Wienk, and R.A. Janssen, Efficient hybrid solar cells from zinc oxide nanoparticles and a conjugated polymer. Advanced Materials. **16**(12), pp.1009-1013(2004).<https://doi.org/10.1002/adma.200306659>

[8] S. Bhatia, and N. Verma, Photocatalytic activity of ZnO nanoparticles with optimization of defects. Materials Research Bulletin. **95**, pp.468-476(2017).<https://doi.org/10.1016/j.materresbull.2017.08.019>

- [9] S.C. Pillai, J.M. Kelly, D.E. McCormack, and R. Ramesh, Self-assembled arrays of ZnO nanoparticles and their application as varistor materials. *Journal of Materials Chemistry*. **14**(10), pp.1572-1578(2004). <https://doi.org/10.1039/B400927D>
- [10] M.H. Wang, Z.Y. Zhao, and T.T. Liu, Synthesis of Pr-doped ZnO nanoparticles by sol-gel method and varistor properties study. *Journal of Alloys and Compounds*. **621**, pp.220-224(2015). <https://doi.org/10.1016/j.jallcom.2014.09.208>
- [11] H. Muthukumar, S.N. Mohammed, N. Chandrasekaran, A.D. Sekar, A. Pugazhendhi, and M. Matheswaran, Effect of iron doped Zinc oxide nanoparticles coating in the anode on current generation in microbial electrochemical cells. *International Journal of Hydrogen Energy*. **44**(4), pp.2407-2416(2019). <https://doi.org/10.1016/j.ijhydene.2018.06.046>
- [12] Y. Jin, J. Wang, B. Sun, J.C. Blakesley, and N.C. Greenham, Solution-processed ultraviolet photodetectors based on colloidal ZnO nanoparticles. *Nano letters*. **8**(6), pp.1649-1653(2008). <https://doi.org/10.1021/nl0803702>
- [13] M. Belhaj, C. Dridi, H. Elhouichet, and J.C. Valmalette, Study of ZnO nanoparticles based hybrid nanocomposites for optoelectronic applications. *Journal of Applied Physics*. **119**(9), p.095501(2016). <https://doi.org/10.1063/1.4942525>
- [14] V. Chivukula, D. Ciplys, M. Shur, and P. Dutta, ZnO nanoparticle surface acoustic wave UV sensor. *Applied Physics Letters*. **96**(23), p.233512(2010). <https://doi.org/10.1063/1.3447932>
- [15] T.C. Bharat, S. Mondal, H.S. Gupta, P.K. Singh, and A.K. Das, Synthesis of doped zinc oxide nanoparticles: a review. *Materials Today: Proceedings*. **11**, pp.767-7759(2019). <https://doi.org/10.1016/j.matpr.2019.03.041>
- [16] S.S. Kumar, P. Venkateswarlu, V.R. Rao, and G.N. Rao, Synthesis, characterization and optical properties of zinc oxide nanoparticles. *International Nano Letters*. **3**(1), pp.1-6(2013).

- [17] M. Li, X. Lv, X. Ma, F. Sun, L. Tang, and Z. Wang, Direct synthesis of monodispersed ZnO nanoparticles in an aqueous solution. *Materials Letters*. **61**(3), pp.690-693(2007).<https://doi.org/10.1016/j.matlet.2006.05.043>
- [18] U. Özgür, Y.I. Alivov, C. Liu, A. Teke, M. Reshchikov, S. Doğan, V.C.S.J. Avrutin, S.J. Cho, and A.H. Morkoç, A comprehensive review of ZnO materials and devices. *Journal of applied physics*. **98**(4), p.11(2005).<https://doi.org/10.1063/1.1992666>
- [19] A. Aslinjensipriya, S. Narmadha, S. Deepapriya, D.R. John, I.S. Grace, R.S. Reena, A. Chamundeeswari, M. Jose, and D.S. Jerome, synthesis and characterization of ZnO nanoparticles by novel sol gel technique. *AIP Conference Proceedings*. **2244**(1), 070013(2020).<https://doi.org/10.1063/5.0009181>
- [20] A. Naveed Ul Haq, A. Nadhman, I. Ullah, G. Mustafa, M. Yasin zai, and I. Khan, Synthesis approaches of zinc oxide nanoparticles: the dilemma of ecotoxicity. *Journal of Nanomaterials*. **2017**(2017).<https://doi.org/10.1155/2017/8510342>
- [21] R.E. Adam, G. Pozina, M. Willander, and O. Nur, Synthesis of ZnO nanoparticles by co-precipitation method for solar driven photodegradation of Congo red dye at different pH. *Photonics and Nanostructures-Fundamentals and Applications*. **32**, pp.11-18(2018).<https://doi.org/10.1016/j.photonics.2018.08.005>
- [22] D.B. Bharti, and A.V. Bharati, Synthesis of ZnO nanoparticles using a hydrothermal method and a study its optical activity. *Luminescence*. **32**(3), pp.317-320(2017).<https://doi.org/10.1002/bio.3180>
- [23] N. Kumaresan, K. Ramamurthi, R.R. Babu, K. Sethuraman, and S.M. Babu, Hydrothermally grown ZnO nanoparticles for effective photocatalytic activity. *Applied Surface Science*. **418**, pp.138-146(2017).<https://doi.org/10.1016/j.apsusc.2016.12.231>

- [24] H.R. Ghaffarian, M. Saiedi, M.A. Sayyadnejad, and A.M. Rashidi, A.M., 2011. Synthesis of ZnO nanoparticles by spray pyrolysis method. *Iranian Journal of Chemistry and Chemical Engineering*. 30(57), pp.1-6(2011).
- [25] O.A. Yildirim, and C. Durucan, Synthesis of zinc oxide nanoparticles elaborated by microemulsion method. *Journal of Alloys and Compounds*. **506**(2), pp.944-949(2010). <https://doi.org/10.1016/j.jallcom.2010.07.125>
- [26] Y.T. Chung, M.M. Ba-Abbad, A.W. Mohammad, N.H.H. Hairom, and A. Benamor, Synthesis of minimal-size ZnO nanoparticles through sol–gel method: Taguchi design optimisation. *Materials & Design*. **87**, pp.780-787(2015). <https://doi.org/10.1016/j.matdes.2015.07.040>
- [27] T.V. Kolekar, H.M. Yadav, S.S. Bandgar, and P.Y. Deshmukh, Synthesis by sol–gel method and characterization of ZnO nanoparticles. *Indian streams research journal*. **1**(1), pp.1-4(2011).
- [28] H.V. Vasei, S.M. Masoudpanah, M. Adeli, and M.R. Aboutalebi, Solution combustion synthesis of ZnO powders using CTAB as fuel. *Ceramics International*. **44**(7), pp.7741-7745(2018). <https://doi.org/10.1016/j.jhydene.2021.08.079>
- [29] C.S. Naveen, M.L. Dinesha, and H.J. Jayanna, Effect of fuel to oxidant molar ratio on structural and DC electrical conductivity of ZnO nanoparticles prepared by simple solution combustion method. *Journal of Materials Science & Technology*. **29**(10), pp.898-902(2013). <https://doi.org/10.1016/j.jmst.2013.07.011>
- [30] N. Srinatha, V.D. Kumar, K.G.M. Nair, and B. Angadi, The effect of fuel and fuel-oxidizer combinations on ZnO nanoparticles synthesized by solution combustion technique. *Advanced Powder Technology*. **26**(5), pp.1355-1363(2015). <https://doi.org/10.1016/j.appt.2015.07.010>

- [31] H.V. Vasei, S.M. Masoudpanah, M. Adeli, and M.R. Aboutalebi, Solution combustion synthesis of ZnO powders using CTAB as fuel. *Ceramics International*. **44**(7), pp.7741-7745(2018). <https://doi.org/10.1016/j.ceramint.2018.01.202>
- [32] H.V. Vasei, S.M. Masoudpanah, and M. Habibollahzadeh, Different morphologies of ZnO via solution combustion synthesis: The role of fuel. *Materials Research Bulletin*. **125**, p.110784(2020). <https://doi.org/10.1016/j.materresbull.2020.110784>
- [33] A.A. Azab, E.E. Ateia, and S.A. Esmail, Comparative study on the physical properties of transition metal-doped (Co, Ni, Fe, and Mn) ZnO nanoparticles. *Applied Physics A*. **124**(7), pp.1-10(2018).
- [34] A. Ghosh, N. Kumari, S. Tewari, and A. Bhattacharjee, Structural, electrical and optical studies on ruthenium doped ZnO pellets for device applications. *Materials Science and Engineering: B*. **196**, pp.7-14(2015). <https://doi.org/10.1016/j.mseb.2015.02.012>
- [35] A.K. Singh, Synthesis, characterization, electrical and sensing properties of ZnO nanoparticles. *Advanced Powder Technology*. **21**(6), pp.609-613(2010). <https://doi.org/10.1016/j.appt.2010.02.002>
- [36] R. Herrera-Rivera, A. Maldonado, and M.D.L.L. Olvera, Manufacture of Ag, Cr and Cu-doped ZnO pellets for gas sensor applications. *IEEE*. 1-5(2014). <https://doi.org/10.1109/ICEEE.2014.6978301>
- [37] Y. Zhao, B. Chen, A. Miner, and S. Priya, Low thermal conductivity of Al-doped ZnO with layered and correlated grains. *RSC Advances*. **4**(35), pp.18370-18377(2014). <https://doi.org/10.1039/C4RA01220H>
- [38] N. Abirami, A.M.S. Arulanantham, and K.J. Wilson, Structural and magnetic properties of cobalt doped ZnO thin films deposited by cost effective nebulizer spray pyrolysis technique. *Materials Research Express*. **7**(2), p.026405(2020).

- [39] M.A. Ismail, K.K. Taha, A. Modwi, and L. Khezami, ZnO nanoparticles: Surface and X-ray profile analysis. *J. Ovonic Res.* **14**, pp.381-393(2018).
- [40] P.G. Devi, and A.S. Velu, Synthesis, structural and optical properties of pure ZnO and Co doped ZnO nanoparticles prepared by the co-precipitation method. *Journal of Theoretical and Applied Physics.* **10**(3), pp.233-240(2016).
- [41] Prerna, S. Arya, A. Sharma, B. Singh, A. Tomar, S. Singh, and R. Sharma, Morphological and optical characterization of sol-gel synthesized Ni-doped ZnO nanoparticles. *Integrated Ferroelectrics.* **205**(1), pp.1-13(2020). <https://doi.org/10.1080/10584587.2019.1674992>
- [42] G. Nagaraju, G.C. Shivaraju, G. Banuprakash, and D. Rangappa, Photocatalytic activity of ZnO nanoparticles: synthesis via solution combustion method. *Materials Today: Proceedings.* **4**(11), pp.11700-11705(2017). <https://doi.org/10.1016/j.matpr.2017.09.085>
- [43] K. Nejati, Z. Rezvani, and R. Pakizevand, Synthesis of ZnO nanoparticles and investigation of the ionic template effect on their size and shape. *International Nano Letters.* **1**(2), pp.75-81(2011).
- [44] M.M. Ba-Abbad, A.A.H. Kadhum, A.B. Mohamad, M.S. Takriff, and K. Sopian, The effect of process parameters on the size of ZnO nanoparticles synthesized via the sol-gel technique. *Journal of Alloys and Compounds.* **550**, pp.63-70(2013). <https://doi.org/10.1016/j.jallcom.2012.09.076>
- [45] N. Jayarambabu, B.S. Kumari, K.V. Rao, and Y.T. Prabhu, Germination and growth characteristics of mungbean seeds (*Vigna radiata* L.) affected by synthesized zinc oxide nanoparticles. *International Journal of Current Engineering and Technology.* **4**(5), pp.2347-5161(2014).

- [46] S. Zandi, P. Kameli, H. Salamati, H. Ahmadvand, and M. Hakimi, Microstructure and optical properties of ZnO nanoparticles prepared by a simple method. *Physica B: Condensed Matter*. **406**(17), pp.3215-3218(2011). <https://doi.org/10.1016/j.physb.2011.05.026>
- [47] A.K. Zak, M.E. Abrishami, W.A. Majid, R. Yousefi, and S.M. Hosseini, Effects of annealing temperature on some structural and optical properties of ZnO nanoparticles prepared by a modified sol–gel combustion method. *Ceramics International*. **37**(1), pp.393-398(2011). <https://doi.org/10.1016/j.ceramint.2010.08.017>
- [48] R. Wahab, S.G. Ansari, Y.S. Kim, M.A. Dar, and H.S. Shin, Synthesis and characterization of hydrozincite and its conversion into zinc oxide nanoparticles. *Journal of Alloys and Compounds*. **461**(1-2), pp.66-71(2008). <https://doi.org/10.1016/j.jallcom.2007.07.029>
- [49] N. Tripathy, R. Ahmad, H. Kuk, Y.B. Hahn, and G. Khang, Mesoporous ZnO nanoclusters as an ultra-active photocatalyst. *Ceramics International*. **42**(8), pp.9519-9526(2016). <https://doi.org/10.1016/j.ceramint.2016.03.030>
- [50] F. Decremps, J. Pellicer-Porres, A.M. Saitta, J.C. Chervin, and A. Polian, High-pressure Raman spectroscopy study of wurtzite ZnO. *Physical Review B*. **65**(9), p.092101(2002). <https://doi.org/10.1103/PhysRevB.65.092101>
- [51] A. Khan, Raman spectroscopic study of the ZnO nanostructures. *J Pak Mater Soc*. **4**(1), pp.5-9(2010).
- [52] A. Diallo, B.D. Ngom, E. Park, and M. Maaza, Green synthesis of ZnO nanoparticles by *Aspalathus linearis*: structural & optical properties. *Journal of Alloys and Compounds*. **646**, pp.425-430(2015). <https://doi.org/10.1016/j.jallcom.2015.05.242>

- [53] B.S. Reddy, S.V. Reddy, and N.K. Reddy, Physical and magnetic properties of (Co, Ag) doped ZnO nanoparticles. *Journal of Materials Science: Materials in Electronics*. **24**(12), pp.5204-5210(2013).
- [54] S.S. Kanmani, K. Ramachandran, and S. Umapathy, Eosin yellowish dye-sensitized ZnO nanostructure-based solar cells employing solid PEO redox couple electrolyte. *International Journal of Photoenergy*. **2012**(2012). <https://doi.org/10.1155/2012/267824>
- [55] S.J. Chen, Y.C. Liu, C.L. Shao, R. Mu, Y.M. Lu, J.Y. Zhang, D.Z. Shen, and X.W. Fan, Structural and optical properties of uniform ZnO nanosheets. *Advanced Materials*. **17**(5), pp.586-590(2005). <https://doi.org/10.1002/adma.200401263>
- [56] C.M. Ghimbeu, J. Schoonman, M. Lumberras, and M. Siadat, Electrostatic spray deposited zinc oxide films for gas sensor applications. *Applied Surface Science*. **253**(18), pp.7483-7489(2007). <https://doi.org/10.1016/j.apsusc.2007.03.039>
- [57] C.J. Raj, R.K. Joshi, and K.B.R. Varma, Synthesis from zinc oxalate, growth mechanism and optical properties of ZnO nano/micro structures. *Crystal Research and Technology*. **46**(11), pp.1181-1188(2011). <https://doi.org/10.1002/crat.201100201>

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Authorstatement.docx](#)
- [Figurecaptions.docx](#)
- [Noveltystatement.doc](#)
- [ResearchHighlights.docx](#)
- [Tablecaptions.docx](#)
- [ConflictsofInterestStatement2.docx](#)
- [GraphicalAbstract.docx](#)