Design and Structural Examination of ZnO Nanoparticles

J. Vinoth Kumar, M. Arunpandian, E. R. Nagarajan

Abstract*: The ZnO nanoparticles were synthesized by simple hydrothermal method and it is confirmed by XRD and SEM characterization techniques. The detailed structural analysis was done using Rietveld refinement technique. By maximum entropy method the bonding feature of ZnO were analyzed. The bonding feature of ZnO was analyzed through 3D and 2D charge density maps. The shape and surface morphology are examined using SEM images, which indicate partially hexagonal structure with average particle size is about 100 nm.

***Keywords*: Rietveld method, Electron density distribution, Nanomaterials, Hydrothermal.**

I. INTRODUCTION

Zinc oxide (ZnO) is most useful for a different way of applications and in material science research group it is an attractive semiconducting compound. Because the properties of ZnO like wide range of direct band gap (3.3 eV), high thermal conductivity and favorable applications in photonics, photo catalytic, sensors, energy conversion and other fields [1]. Otherwise, it also contains low cost, highly abundance, cheap fabrication process and Eco friendly into the environment. Further application of ZnO is UV absorption, sensing and UV light emitting devices. But their properties of ZnO strongly depend on the impurities and defects [2,3].

In any property of the materials basically depends on its electronic bonding behavior. In this aspect, the present study deals with calculate the bond length and electron density at the middle of the bond in ZnO nanoparticles.

II. EXPRIMENTAL

A. Sample preparation

In separately 0.1M solution of $Zn(CH_3COO)_3$ and 0.1M solution of NaOH were synthesized. These solutions was transferred into Teflon lined stainless steel autoclave with 1:1 ratio and in under autogeneous pressure the samples were maintained at 150°C for 12 hrs. Then it was allowed to cool room temperature. Finally the resulting product was separated with purely to use water and ethanol. Then it was dried using oven at 75° C for 24 hrs.

B. Sample characterization

The prepared ZnO samples were analyzed by powder X-ray diffraction using Bruker (D8 advance ECO) diffractometer with CuKα (λ=1.54056 Å) radiation in the range of 10° to 120° in the step size of 0.02°.The microstructure and surface morphology of the as synthesized samples was measured using scanning electron microscopy (SEM) with the Model: ZEISS-EVO 18.

III. RESULTS AND DISCUSSIONS

A. PXRD analysis

The prepared ZnO were characterized by PXRD technique. The phase pure hexagonal system was identified and compared to the standard patterns also shown in Fig. 1. The average crystallite size of observed PXRD pattern is found to be ~ 39 nm, which is calculated by Scherrer equation [4].

B. Rietveld and MEM techniques

The observed raw X-ray diffraction data set were refined using the software JANA 2006 [5], considering the hexagonal system of ZnO with 2 molecules/unit cells in the space group P63mc. The Rietveld refinement [6] is the main tool to refining the crystal structures, its refines and extracts the scale factors, lattice parameters, peak shift and background profile parameters from the observed PXRD patterns.

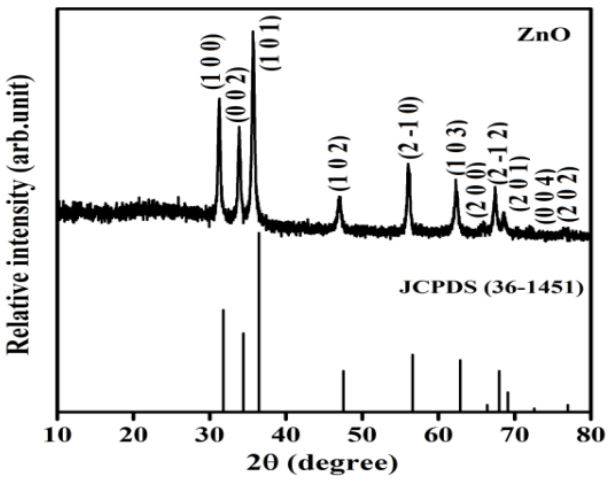

Fig. 1.PXRD patterns of ZnO.

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It is used to fit the observed and calculated XRD profiles. In Zn lattice site (1/3, 2/3, 0) and the O lattice site (1/3, 2/3. 0.375) are the initial parameters for Rietveld refinement techniques. The refined profiles of prepared samples are shown in Fig. 2.

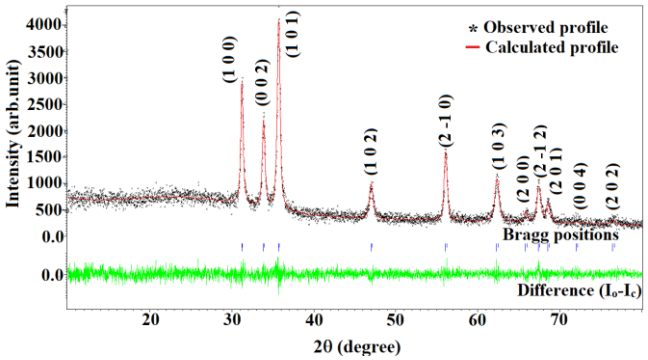


Fig. 2. Reitvield refinement for ZnO nanoparticles.

The refined structural parameters of ZnO are shown in Table 1.

Table 1: Refined structural parameters of ZnO

Parameters	ZnO
a=b(Å)	3.2424(33)
c (Å)	5.197(54)
Volume (Å)	47.31(9)
Density (g/cm^3)	5.70(1)
$F_{(000)}$	76
R_{obs}(%)	1.54
R_p(%)	9.8
GOF	3.01

R_{obs}- observed profile reliability factor
R_P - profile reliability factor
$F_{(000)}$- Number of electrons per unit cell
GOF – Goodness of Fit

C. Charge density analysis

The accurate charge density was evaluated by Maximum Entropy Method (MEM) and it has a important tool for this evaluation. Which is statistical approach proposed by Collins [7]. In Reitveld refinement technique the structure factor are extracted and it is used for the MEM procedure to obtain the electron density distribution in the unit cell.

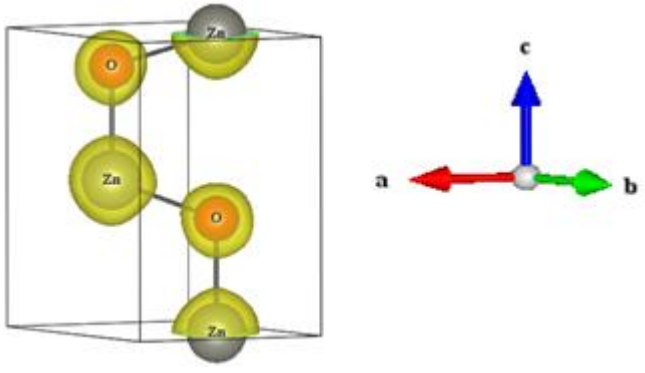
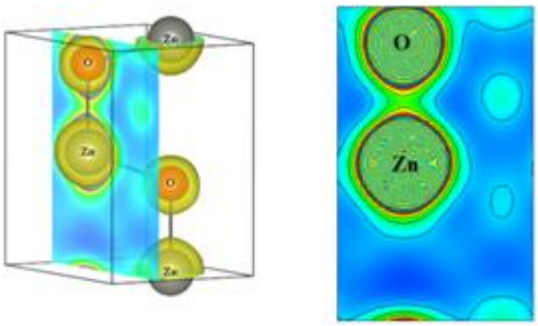


Fig. 3. (a) 3-D unit cell of ZnO using iso-surface level 0.8 e/Å^3.

The electron density gives the accurate picture of distribution of electrons and then it is used for bonding feature and other structural properties. Refined structure factors are used to evaluate the electron density distributions of ZnO using MEM [8]. The Maximum Entropy Method was done by using software DYSNOMIA [9] and their result is visualized by the visualization software VESTA (Visualization for Electronic and Structural Analysis) [10].

a)



b)

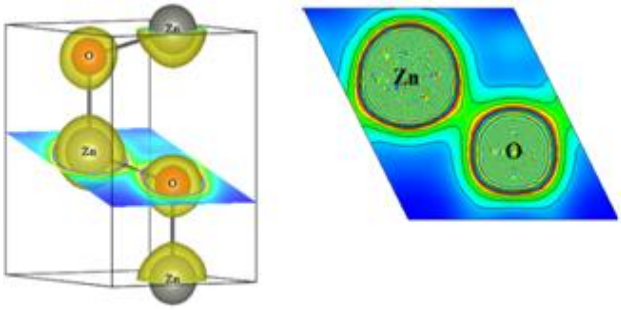


Fig. 4.a) 2D unit cell of (100) plane and (b) 2D unit cell of (014) plane.

3-D unit cell is drawn of ZnO as shown in Fig. 3(a). It is clearly seen that there is a spherical in core of Zn and O atoms. The shaded yellow region represented by electron clouds. Two dimensional electron density distributions maps were drawn on (100) and (014) miller plane in contour level 0-2 e/Å3 with interval of 0.25 e/Å3as shown in Fig. 4(a) &(b). In left the corresponding miller planes are shaded.

One dimensional electron density distributions of ZnO were drawn as shown in Fig. 5. It shows that, the system ZnO have contain two bonds, one is positioning at (-x, -y, z+1/2) direction (black) and other one (-y, x-y, z) direction. The bond length, Bond Critical Point (BCP), electron density at the middle of the bond were calculated and tabulated in Table 2.

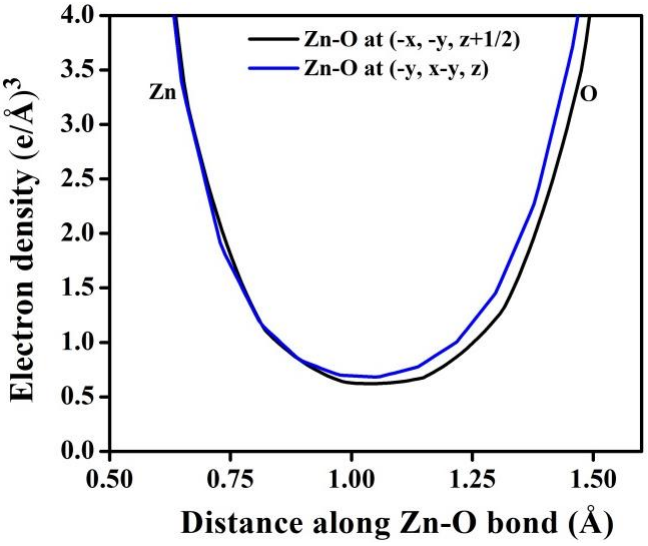


Fig. 5. Mid-bond electron densities of ZnO.

Table 2: Bonding behaviour of ZnO

Position	Bond length(Å)	Bond Critical Point (Å)	Mid bond electron density (e/Å^3)
Zn-O (-x,-y,z+1/2)	1.9699	1.0394	0.6213
Zn-O (-y, x-y, z)	1.9863	1.0480	0.6837

D. Scanning Electron Microscopy Studies

The morphology of the nanostructures was characterized by SEM measurements. Well dispersed and somewhat hexagonal morpholo-gy were observed and the average particle size is ~100 nm shown in Fig. 5.

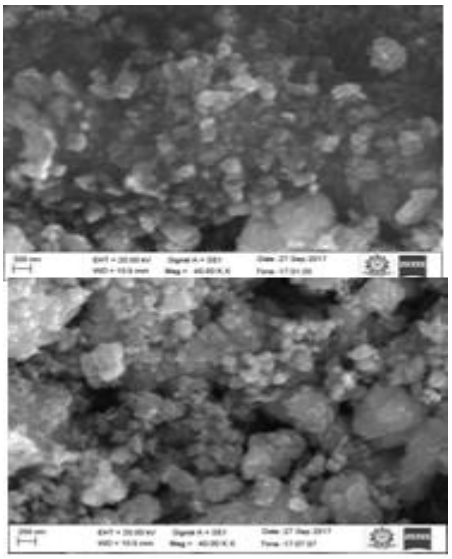


Fig. 6. SEM micrographs of ZnO nanoparticles.

IV. CONCLUSION

Zinc oxide materials were synthesized using solid state sintering process by means of microwave medium. PXRD profiles confirm that the prepared systems with phase pure ZnO. The detailed structural information of prepared system was investigated by Rietveld profile refinement technique. The difference of morphologies between pure and ZnO samples were found in SEM measurements. Charge density distribution analyses have done in maximum entropy method and charge derived properties are consistent with PXRD data.

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