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Comparative Study of Pure Zno and Copper Doped Zno Nanoparticles Synthesised via Co-precipitation Method

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Abstract

The ZnO nanoparticles has unique properties like wide band gap energy, large excitation energy, acts as a functional material near UV emission, optical transparency [1]. It has versatile applications in optoelectronic devices, which creates the immense interest in its synthesis. Pure ZnO & Copper doped ZnO nanoparticles were prepared by Controlled Precipitation method. The structural characterization of the samples was investigated by X-ray diffraction and Scanning electron microscopy. The crystalline size of Pure ZnO nanoparticle is 22nm & Copper doped Nanoparticle is 11 nm is revealed by XRD. SEM micrographs reveals that both images are cluster shaped. The FT-IR showed that various functional groups have been formed. UV visible spectroscopy determines the band gap energy of ZnO nanoparticles

Keywords: Copper Doped ZnO, FTIR, Pure ZnO, SEM, UV, XRD

1. Introduction

Nanotechnology is the branch of engineering which deals with the design and manufacture of extremely small electronic circuits and mechanical devices built at the molecular level of matter. It enables the ability to build a molecular system with atom by atom reproducing multiple variety of nanomachines. Recently, Nanocrystalline powder with uniform size and shape has shown interesting properties. Particularly nanocrystalline metal oxides has numerous important properties like catalytic, electrical and optical properties. Nanocrystalline powders differ from metal oxides in macro, micro and bulk material structres. Hence ZnO is one of the metal oxides which attracts due to its band gap energy of 3.37eV and large excitation binding energy of 60meV at room temperature. ZnO, is applied for UV lasers and optoelectronic devices [1]. Furthermore, ZnO with its good electrical and optical properties can be used in many applications such as photoconductors, integrated sensors and transparent conducting oxides electrodes. Nanocrystalline ZnO powders have been for use in piezoelectric sensors, gas sensors and solar cell applications. Up to now, many soft chemical synthesis are applied in fabricating nanocrystalline ZnO powders, like hydrothermal, spray pyrolysis and precipitation or sol-gel methods. It is a white hexagonal structured crystal or white powder called Zinc white. It is Soluble in acids and alkalis. ZnO occurs in nature as Zincates. Crystalline ZnO has the piezoelectric effect and is thermo chromic, it changes from white to yellow on heating. Zinc oxide is a II-IV semiconductor. It is a hexagonal crystal structure. The most common applications are in laser diodes due to its excitation and bi-excitation energies of 60meV &15meV.

2. Experimental

2.1 Pure ZnO Nanoparticle Synthesis

Pure zinc oxide nanoparticles samples have been synthesised by co-precipitation method. Analytical grade of purity zinc acetate dehydrate 3M $Zn(CH_3COO)_2H_2O$,

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Potassium hydroxide KOH. We dissolved 6.585 g of $Zn(CH_3COO)_2H_2O$ in 100 ml H_2O under heating and continuous stirring of 15 minutes (solution 1). An amount of 3.366 g KOH was dissolved in 10 ml H_2O under heating and continuous stirring (solution 2). The solution 1 was added drop wise to the solution 2. After adjusting the pH value to 12, the final mixture solution was stirred under heating for 10 minutes. Then the solution turns into jelly milky white precipitate. To remove the impurities the precipitate was washed several times with ethanol. The precipitate was dried in hot air oven at 80 °C.

2.2 Copper Doped ZnO Nanoparticle Synthesis

Copper doped ZnO Synthesis has been synthesized by co precipitation method [5]. Analytical grade of purity zinc sulfate $ZnSO_4.7H_2O$, sodium carbonate Na_2CO_3 and copper sulfate $CuSO_4.H_2O$ were used as starting materials. In a typical experiment we dissolved 18 g of Na_2CO_3 in 170 ml H_2O under heating and continuous stirring (solution 1). An amount of 20 g $ZnSO_4.7H_2O$ was dissolved in 140 ml H_2O under heating and continuous stirring (solution 2). The copper sulfate was added to the solution 2 such to obtain mixture of ZnO doped with 0.24 % Cu. This mixed solution of $ZnSO_4.7H_2O$ and $CuSO_4.H_2O$ [3] was added drop wise to the solution 1. After adjusting the pH value to 11, the final mixture solution was stirred under heating for 10 minutes. The precipitate was separated by filtration, washed several times with distilled water till obtaining the pH value of 7 and dried in air. For preparation of the final samples, the corresponding precursors are heated for 3 h at 500 °C in air.

2.3 Sample Characterization

X-ray Diffraction (XRD) analysis. The XRD patterns have been used to calculate the particle size using Scherrer's formula. FTIR spectrum was used to calculate the various functional groups in nanoparticles and also determined by the transmission and absorptions range. UV-visible spectroscopy was used to determine the band gap energy of the samples. The SEM is used for performing analyses of selected point locations on the sample. These analyses are useful in calculating crystalline structure, chemical compositions and crystal orientations.

3. Results and Discussion

3.1 XRD Analysis

The sample of high purity and crystallinity are prepared. Pure ZnO nanoparticles confirms the study by its clear

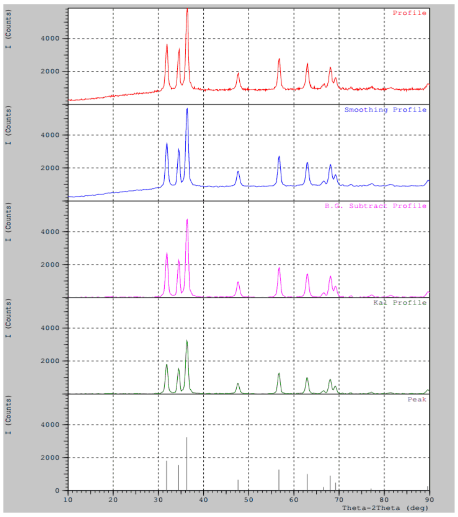

Figure 1. XRD Analysis of Pure ZnO**.**

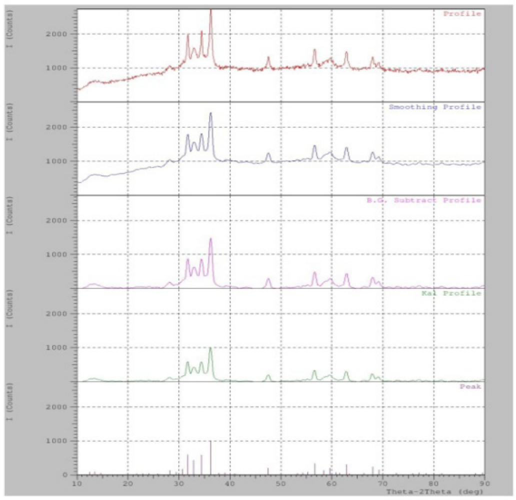

Figure 2. XRD Analysis of Cu doped ZnO.

peaks at 2ϴ = 36.1974nm, 31.7038nm, 34.3602nm in Figure 1.

Cu doped Zno nanoparticles obtained from co precipitation method at temperature 500 °C, is shown in the Figure 2. The diffraction peaks exists at 2ϴ = 36.2292, 31.7710 and 34.4431. The intensity of the diffraction peaks indicates that the samples are hexagonal in structure [4]. Using Debye Scherer's equation (0.9l/βcosϴ) the average particle size obtained for pure ZnO nanoparticle is 22 nm and for Cu doped ZnO nanoparticle is 11 nm. Here Pure ZnO has larger particle size than Cu doped ZnO.

3.2 UV-VIS Spectroscopy

The band gap energy was determined based on the numerical derivative of the optical absorption coefficient. The

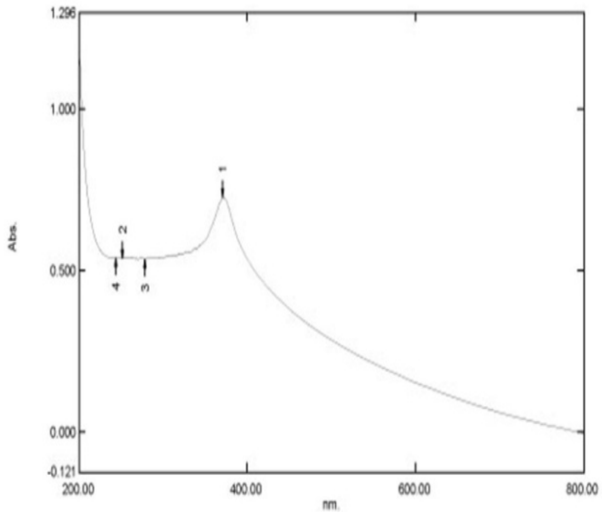

Figure 3. UV-vis of pure ZnO.

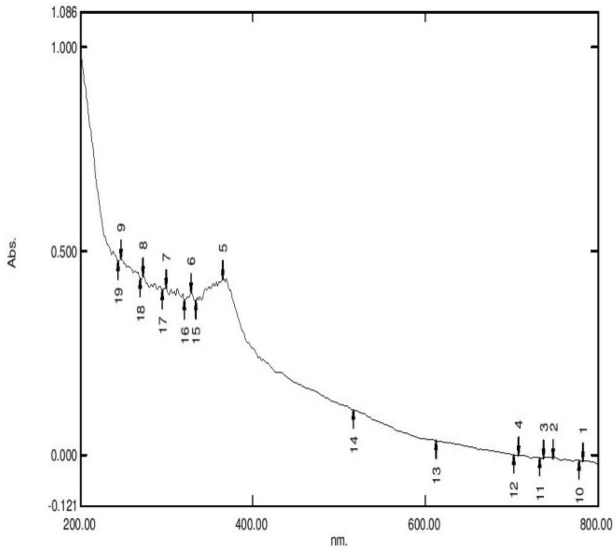

Figure 4. UV-vis of Cu doped ZnO.

fundamental absorption method refers to band to band transitions by using energy relation E = hν. Where h is the Planks constant, ν = c/λ where c is the speed of light in vacuum and l is the constant value of (1.6×10^{-19}).

Figure 3 show that synthesized pure ZnO nanoparticles excitation peaks with the same absorbance intensity at wavelength of 244 to 371. For pure ZnO of wide band Gap energy is 3.37eV. Figure 4 shows the UV-visible absorption spectrum of doped ZnO sample excitation peaks with the same absorbance intensity at wavelength of 783 to 709 [7]. For doped ZnO of wide band Gap energy is 15.86 eV.

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectrum is used to calculate various functional groups present in Pure ZnO and Cu doped Zno nanoparticles and also determined by absorption range.

Figure 5 show that synthesized pure ZnO nanoparticles present in the various functional groups.

Figure 6 shows that synthesized Cu doped ZnO nanoparticles present in the various functional groups [10].

The spectrum reveals that the absorption and intensity of pure and Cu doped ZnO nanoparticles are more are less equal [10].

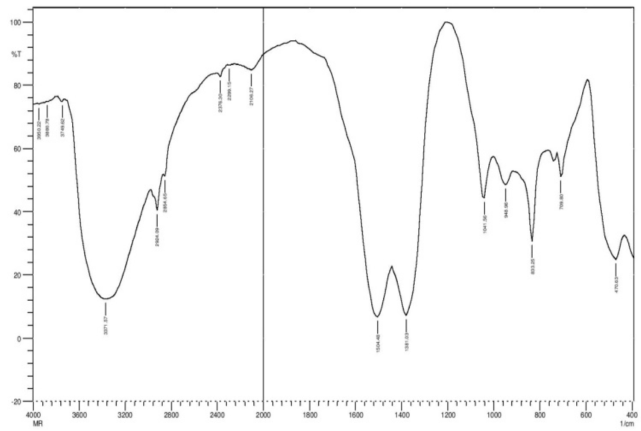

Figure 5. FTIR of Pure ZnO.

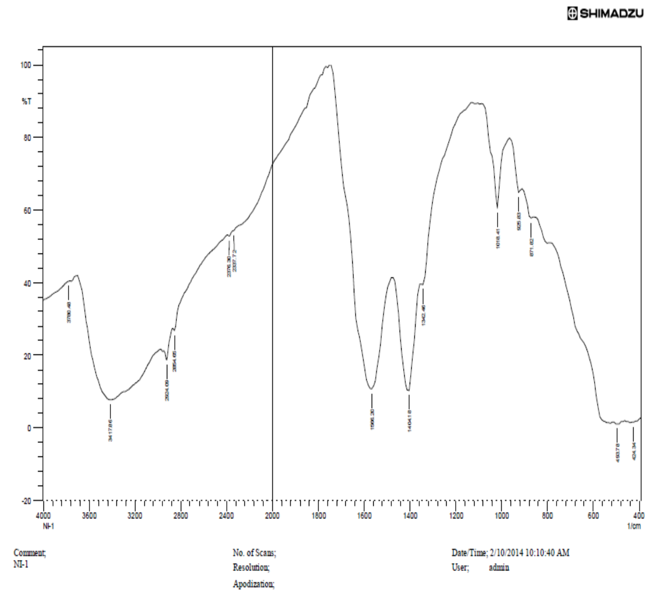

Figure 6. FTIR of Cu doped ZnO.

Table 1. Functional groups present in Pure ZnO

Function Group	Absorption (cm^{-1})	Intensity
Alcohol (O–H stretching)	3417.86	Strong and broad
Alkane (C–H stretching)	2924.09	Medium
Alkane (C–H stretching)	2854.65	Medium
Aromatic (C–H stretching)	1566.20	Medium
Alkane (CH=CH2 stretching)	925.83	Strong

Table 2. Functional groups present in Cu doped ZnO

Function Group	Absorption (cm^{-1})	Intensity
Amine	3371.57	Medium
Carboxylic acid	2924.09	Strong
Aromatic ring	1504.48	Medium
Amine	1381.03	Medium
Alkyl halide	709.80	Strong

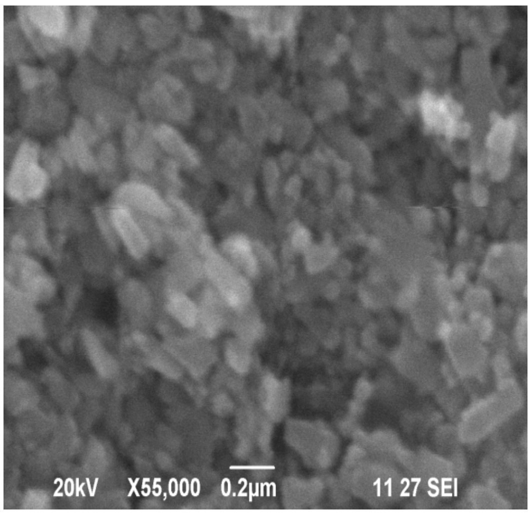

Figure 7. SEM image of Pure ZnO.

3.4 SEM Analysis

The SEM images reveals the structure of the samples.

Figure 7 and 8 shows that the SEM image of pure ZnO nanoparticles. The surface morphology of the synthesized sample is viewed through the high resolution scanning electron microscope.

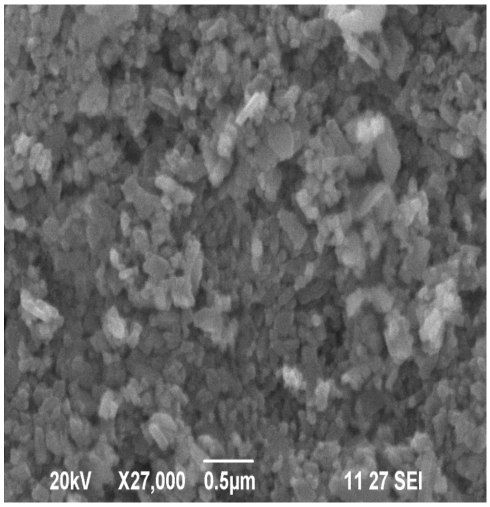

Figure 8. SEM image of Pure ZnO.

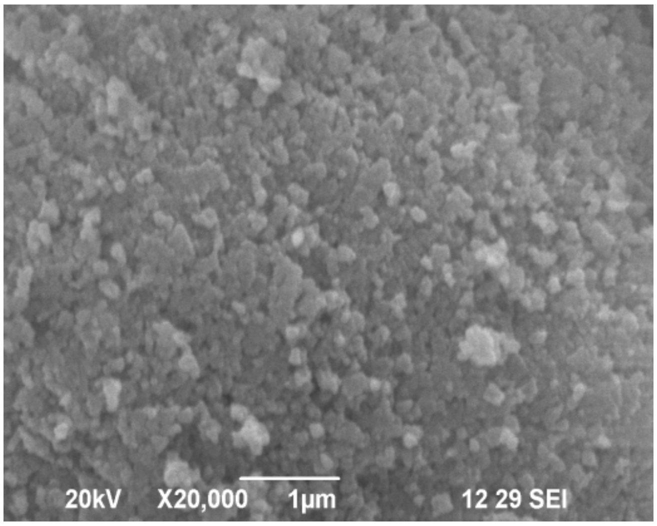

Figure 9. SEM image of Cu doped ZnO.

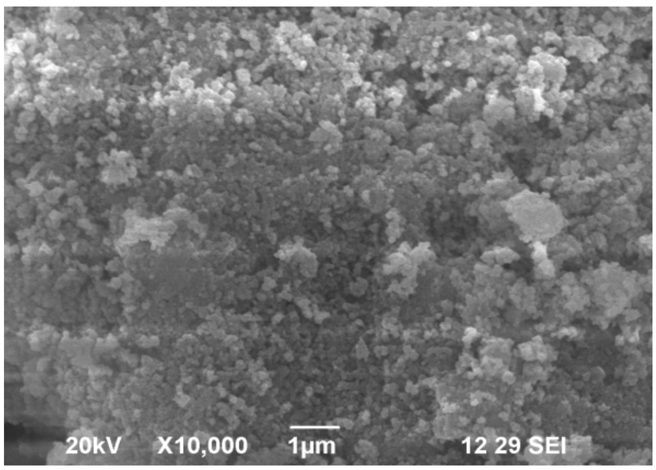

Figure 10. SEM image of Cu doped ZnO.

The Figure 9 and 10 represents the SEM image of Cu doped ZnO nanoparticles shows the cluster like structure. It clearly reveals the formation of Cu doped ZnO nanoparticles.

4. Conclusion

Pure ZnO and copper dopped ZnO nanoparticles were synthesized by co precipitation method. X-ray diffraction analysis confirmed the grain size of the Pure and Cu doped ZnO nanoparticles. The average particle size obtained for pure ZnO nanoparticle is 22 nm and the size was found to decrease in Cu doped ZnO nanoparticle as 11 nm. FTIR showed that various functional groups are present in pure and Cu doped ZnO nanoparticles. The optical transmittance of the UV – VIS measurements indicates that the Pure ZnO and Cu doped ZnO nanoparticles have band gap energy of 4.9 eV and 15.86eV. The band gap energy of doped ZnO was shifted slightly towards longer wavelength region. The SEM results reveal the presence of Pure and Cu doped ZnO nanoparticles are cluster like structure.

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