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Influence of transition metal (Cu, Al) ions doping on structural and optical properties of ZnO nanopowders

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Abstract
Al doped ZnO, Cu doped ZnO Nanoparticles were successfully synthesized by Sol-Gel Method and Zinc Chloride(ZnCl2),Potassium Hydroxide(KOH), Aluminum Nitrate(Al(NO3)2, Copper Nitrate (Cu(NO3)2) and Ethanol(C_2H_6O) were used as a precursors. The structural and optical properties of Nanoparticles were analyzed by means of XRD (X-Ray Diffraction), SEM (Scanning Electron Microscopy) and FTIR (Fourier Transform Infra-Red spectroscopy). The results of Cu doped ZnO and Al-doped ZnO nanoparticles were also compared to investigate the structural and optical properties. XRD analysis reveals that both the samples crystallizes in hexagonal wurtzite structure and exhibit no impurity phase. The crystalline size of 28.43 nm and 6.87 nm are obtained in Cu doped ZnO and Al doped ZnO Nanoparticles. Therefore, the decrease in the crystalline size can be seen with the change in doping element. The optical properties also depend on the type of doping due to the Al-N bond intensity, The Al doped ZnO powder is stronger than Cu doped ZnO.

Keywords: Sol-Gel, ZnO Nanoparticles, Cu doped ZnO, Al doped ZnO, XRD, SEM, FTIR

1. Introduction
In last few decades, Metal oxide nanoparticles were experimentally studied due to their various applications in the field of spintronics, photoelectronic, sensor, lasing devices and light emitting diodes etc. The properties of these nanomaterials can be easily altered due to quantum confinement and enhanced surface to volume ratio [1-3]. Among the nanoscale metal oxides, the semiconductor ZnO is considered as the host material in the research community due to its interesting, electrical, optical and magnetic properties. ZnO has wide band gap 3.37 eV, large bond strength and large exciton binding energy (60 meV) at room temperature [4-5]. As a wide band gap material, ZnO is used in solid state blue to ultraviolet (UV) opto- electronics, including laser developments. In addition, due to its non-centrosymmetric crystallographic phase, ZnO shows the piezoelectric property, which is highly useful for the fabrication of devices, such as electromagnetic coupled sensors and actuators. ZnO also have much simpler crystal growth technology resulting in a potentially low cost, chemically stable, high transparency and environment friendly ZnO based devices. Recently, micro- and nanostructured components of ZnO such as nanowires, nanorods, tetra pods, nanobelts, nanoflowers, nanoparticles, etc., have been obtained by using various physical and chemical techniques. ZnO has received worldwide attention due to wide range of applications such as transparent conductive contacts, solar cells, laser diodes, ultraviolet lasers, thin film transistors, optoelectronic and piezoelectric applications and surface acoustic wave devices [6-13]. Various methods like sputtering, chemical vapor deposition, Molecular beam epitaxy, spray pyrolysis, pulsed laser deposition and solgel process were used for the synthesis of ZnO [14-18].

Doping in ZnO helps in tuning chemical, physical and electrical properties by the incorporation of the dopant in lattices of ZnO. Several dopants such as Fe, Cr, Al, Cu, Co, Mn, Mg, S, P, etc. can lead to an increase in the surface area of the ZnO based powders. Some transition metal elements have close ionic radius parameter to that of Zn2+, which means these elements can easily penetrate into ZnO crystal lattice or substitute Zn2+ position in crystal. The control of properties for metal-doped ZnO and band gap engineering of nanomaterials is of utmost importance for tunable light emitting diodes (LEDs) and other optoelectronic devices [19-21].

Al^{3+} has been the most used do pant element due to its small ionic radius and low material cost. The substitution of Zn^{2+} ions with Al^{3+} in ZnO lattice improves the electrical conductivity through the increase of charge carriers where it is reported that the electron concentration increases from 10^{16} to $10^{21}/cm^{-3}$. Al doped ZnO nanopowders are both conductive and transparent in the visible region and thus can be utilized in transparent conductive pastes. The Cu Concentration in ZnO nanoparticles is more successful in producing Ferromagnetism. It can also exhibit RTFM. Cu additive has significant effects on their crucial optical properties they are widely used for practical solar energy harvesting applications such as sun-light photo catalyst and photovoltaic devices [22-23].

In this paper, we have reported the influence of transition metal (Al, Cu) dopant on structural and optical properties of ZnO nanoparticles synthesized using sol-gel process. The sol-gel method is preferred due to its low cost, simplicity and the high crystalline quality. The properties of nanoparticles are analyzed by performing various characterizations X Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier transform Infra-Red (FTIR) spectroscopy.

2. Experimental Procedure

2.1 Chemicals

Zinc chloride (ZnCl2), Sodium Hydroxide (NaOH), Aluminum Nitrate Al(NO3)2, Copper Nitrate (Cu(NO3)2) and Ethanol(C_2H_6O) were purchased and used without any purification.

2.2 Preparation of Al doped ZnO, Cu doped ZnO Nanoparticles

The following procedure is carried out for the synthesis of Al doped ZnO, Cu doped ZnO nanoparticles at room temperature by the wet chemical method. For preparing Al doped ZnO nanoparticles, the two solutions one containing an aqueous ethanol solution of ZnCl2 0.2 M and the other containing aqueous ethanol solution of Al(No3)2 0.2M are kept under constant stirring using magnetic stirrer for one hour. After complete dissolution of Zinc chloride, 0.2M Al(No3)2 aqueous solution was added under high speed constant stirring drop by drop (slowly for 45 min) touching the walls of the vessel.Then, this solution was sub-sequently stirred with a magnetic stirrer at room temperature. The aqueous solution of NaOH 0.2 M was prepared and added to the mixed solution. The reaction was allowed to proceed for 2 hours after the addition of NaOH. The beaker was sealed at this condition for 2 h. The solution was allowed to settle overnight and further, the supernatant solution was detached carefully. The remaining solution was centrifuged for 10 min and the precipitate was removed. Thus precipitated solution cleaned three times with deionized water and ethanol to remove the by-products which were bound with the nanoparticles and then dried in a vacuum oven at a maximum temperature of 70°C for several hours until solvent evaporated. The end product was finally grinded to obtain Nanocrystalline Al doped ZnO particles.

In a similar manner, Cu doped ZnO nanoparticles were synthesized using aqueous solution of Copper nitrate Cu(NO3)2 in place of Aluminum Nitrate Al(NO3)2 in the above process. Further, the samples Al doped ZnO and Cu doped ZnO nanoparticles were characterized.

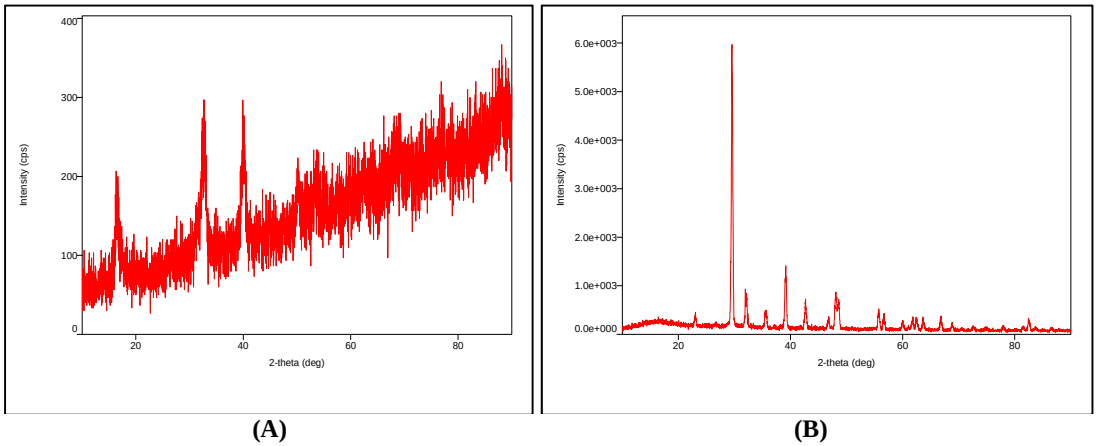
2.3 Characterization

The properties of synthesized Nanoparticles are determined using different characterization techniques. In the present work, structural and optical properties are analyzed. The structural Characterization is performed using X Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The optical characterization is performed using UV–Vis, Fourier Transform Infrared spectroscopy (FTIR). The Confirmation of pure ZnO phase is verified by XRD analysis. The shape and morphology of particles are studied by SEM pictures obtained. Several absorption peaks are observed through FTIR spectrum.

3. Results and Discussion

3.1. X Ray Diffraction (XRD)

XRD was employed to investigate the structural properties and crystallite size, and to rule out the presence of any unwanted impurity phases Fig 1(a) and 1(b) represents the XRD pattern of Cu doped And Al doped ZnO Nanoparticles.



(A) **(B)**

Fig 1(a): XRD Pattern of Cu doped ZnO (b) XRD Pattern Of Al doped ZnO

From this XRD pattern analysis, the peak intensity, position and width, full-width at half Maximum (FWHM) data can be determined. A definite line broadening of the XRD peaks indicates that the prepared material consist of particles in nano scale range. No characteristic peak of impurities was observed which indicates that the doping of the Al, Cu ions does not change the wurtzite structure of ZnO. The Average crystalline size is estimated using Scherrer's formula $D=0.89\lambda/_{\beta}\cos\theta$ where λ, β and θ are the x-ray wavelength (0.154 nm), full width at half maxima (FWHM) of the

diffraction peak and the Bragg's diffraction angle respectively Crystallite size of each samples was calculated using most intense peak and is found to be 28.43 nm and 6.87 nm for Cu doped ZnO and Al doped ZnO Nanoparticles respectively. The decrease in the crystallite size is suggested to be caused by Al dopant due its small ionic radius, which means that Al^{3+} can easily penetrate into ZnO crystal lattice or substitute Zn2+ position in crystal.

3.2 Scanning Electron Microscopy (SEM)

The morphology and Shape of ZnO particles were studied by scanning electron microscopy (SEM). Fig. 2(a) and 2(b) represents the SEM pictures of Al doped ZnO and Cu doped ZnO nano particles at different magnifications 1µm, 100nm and 200nm. These pictures confirm the formation of ZnO nanoparticles. The surface morphology of the material with the granular structure with the round morphology with some aggregation is obtained by using SEM for both the samples.

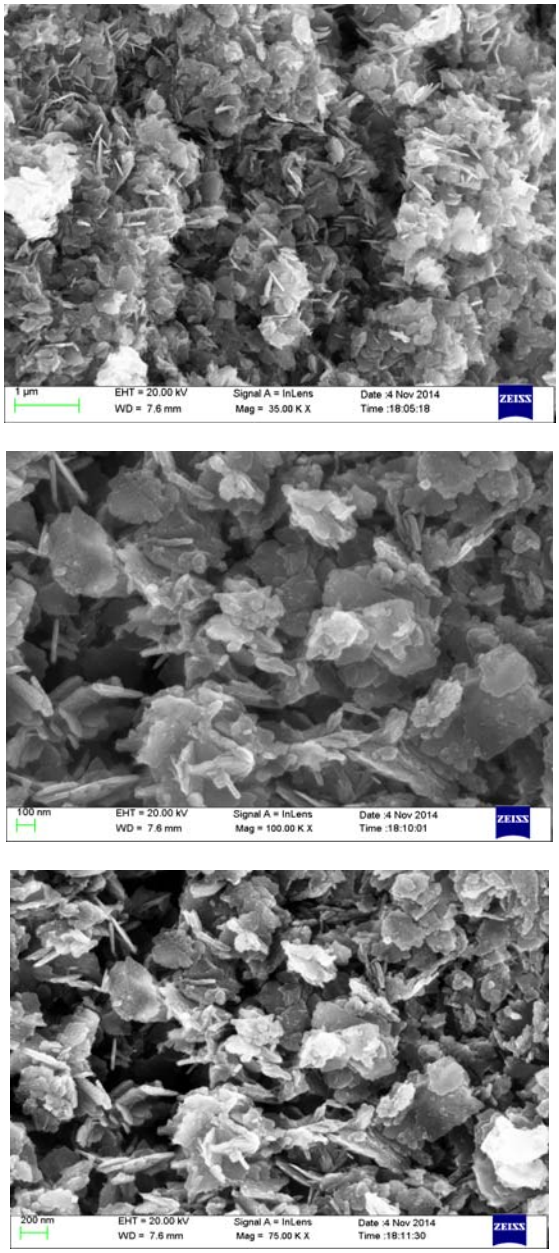


Fig 2(a): SEM images of Al doped ZnO Nanoparticles at 1µm, 100nm, 200nm

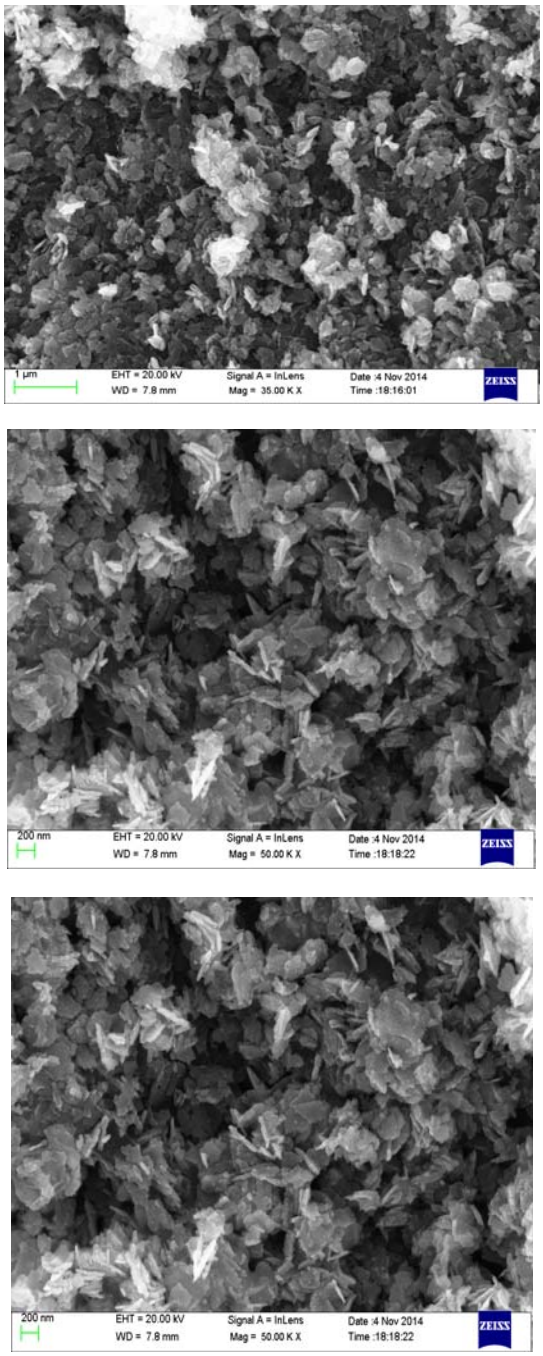
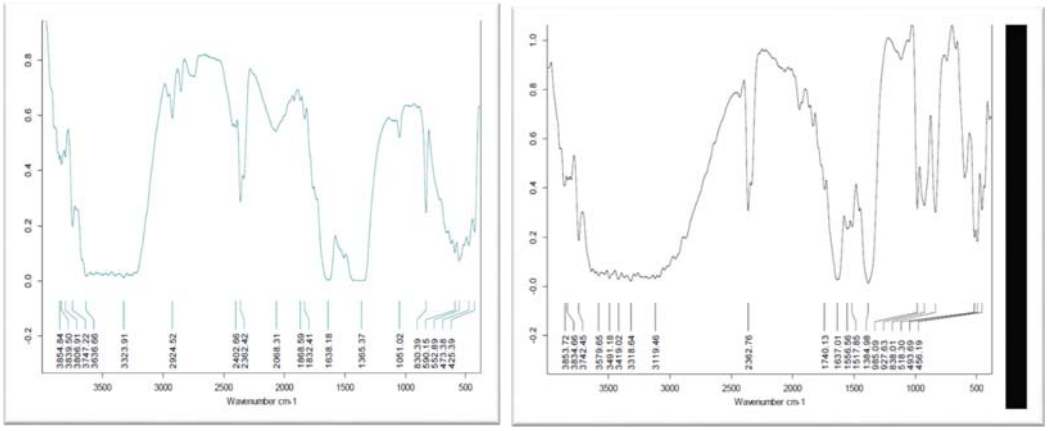


Fig 2(b): SEM images of Cu doped ZnO Nanoparticles at 1 µm, 200nm, 100nm

3.3 Fourier Transform Infra-Red Spectroscopy (FTIR)

The formation of the wurtzite ZnO structure in Cu doped ZnO Nanoparticles and Al doped ZnO nanocrystalline powders confirmed by FTIR spectra as shown in Figure 3(a) and 3(b). The FTIR spectra were recorded in the range of 500–35000 cm^{-1} for both the samples. The position and number of absorption bands not only depend on crystal structure and chemical composition but also on crystal morphology. As can be seen, a broad band was observed in the region of 3000–3800 $cm^{-1}$are attributed to symmetric which can be explained as overlapping O–H and C–H stretching modes. There are three well-defined prominent absorption bands, located at 2402.66 cm^{-1}, 16380.16 cm^{-1}, and 1365.61 cm^{-1} are in Cu doped ZnO and absorption bands at 2362.76 cm^{-1}, 1740.13 cm^{-1}, and 1364.98 cm^{-1} in Al doped ZnO Nanopowders are

observed due to the stretching vibration of CO2. The vibration modes around 500 cm^{-1} to 1365.61 cm^{-1} slightly changed with the dopant element, because of variation in the ionic radius of Cu and Al. Due to the bond intensity Al-N. the Al doped ZnO sample is stronger than Cu doped ZnO nanopowder, which proves the sample has the highest crystalline quality, and is also the same as the results of the XRD.



(A) **(B)**

Fig 3(a): FTIR spectrum of Cu doped ZnO (b) FTIR spectrum of Al doped ZnO

4. Conclusion

In summary, in this paper we have successfully synthesized Al doped ZnO and Cu doped ZnO Nanopowders by low cost, Single step Sol-gel process and were characterized using XRD, SEM and FTIR. The results are compared by investigating the structural and optical properties of synthesized particles. XRD measurements revealed that 'Al' and 'Cu' were successfully doped into ZnO nanoparticles In addition, XRD results indicate that crystallite size of ZnO was influenced by 'Al' and 'Cu' doping. SEM images show the formation of agglomerated round shape crystalline nanoparticles of sizes 28.43 nm and 6.87 nm for Cu doped ZnO and Al doped ZnO nanoparticles. The optical properties of nanostructure samples depended on a type of dopant. Due to the Al-N bond intensity, the Al doped ZnO powder is stronger than Cu doped ZnO.

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