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Structural and Optical Properties of Nickel and Silver co-doped ZnO Nanoparticles

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Abstract—*ZnO nanoparticles of nickel and silver co-doped using chemical precipitation route are synthesized. The crystallite size, morphology and optical properties of as prepared nanoparticles are determined by XRD and UV- visible spectra and SEM. XRD analysis shows that the prepared samples are single phase and have hexagonal wurtzite structure. The crystallite size of nanoparticles is determined using Scherrer method. From the optical studies, the band gap is found to be decreased with co-doping of nickel and silver. SEM images reveal that the size lies in nanoparticle range. The FTIR result shows the stretching vibration of the Zn-O bond in Ni doped ZnO nanoparticles. There is a highest intensity peak of ZnO at the wavelength of 550 nm in the PL behavior. The different behaviour of different dopant can be explained on the basis of their different chemical nature and different ionic radii as compared to the host cation.*

Keywords*: XRD, crystallite size, optical band gap, nanoparticles.*

1. INTRODUCTION

Researchers have been looking at the use of nanomaterials due to their better physical and chemical properties compared to bulk materials in recent years. A large number of investigations have focused on transitional metals doped II-VI compound semiconductor ZnO because of its direct band gap of 3.37 eV at room temperature with a large excitation binding energy of 60 meV [1]. ZnO is a key element in many industrial manufacturing processes including paints, cosmetics, plastic, batteries, textile, electrical equipments, rubber, pharmaceuticals, soap etc. with improvement in growth technology of ZnO nanostructures, single crystal and nanoparticles, ZnO devices will become increasing functional in the near future [2]. Metal oxide nanoparticles were extensively investigated due to their applications in the field of spintronics [3], photoelectronics [4], sensor [5], lasing devices [6] and light emitting diodes [7], etc. The properties of these nanomaterials incredibly altered due to quantum confinement and enhanced surface to volume ratio [8]. ZnO is a multifunctional material. The various applications of ZnO nanoparticles depend upon the control of both physical and chemical solvent. The technique of obtaining ZnO using properties such as size, size dispersity, shapeand dispensability [9] .ZnO nanoparticles can be synthesized by various approaches including sol-gel processing, chemical precipitation, mechanical milling, hydrothermal method, spray pyrolysis and mechanochemical synthesis [10]. Various codoped ZnO have also been reported with the expectation that codoping can lead to remarkable changes in the properties of the materials [11-13]. Presence of two different transition ions simultaneously in a host material produces different properties than property due to single transition metal ions. The present study focuses on the preparation of ZnO nanoparticles by chemical precipitation method.

2. MATERIALS AND METHODS

Nickel and silver codoped ZnO nanoparticles were prepared by mixing Zinc acetate dehydrate (Sigma Aldrich,purity 99%) , AR grade nickel nitrate and silver nitrate in mixture of deionized water and ethanol with further purification. Then ammonia solution and sodium hydroxide solution were added. The solution was kept in a water bath at 60^{o}C. Then dried the precipitates at 500^{o} C in oven. .The prepared samples are characterized for phase identification by .For XRD measurements, D8 Focus with scanning rate 0.01 sec was used in range 20^{o}-80^{o} using CuKα radiations at 45 kV and 35 mA. To study surface morphological features, Scanning electron microscope (Joel JSM-6610) operating at a voltage of 10 kV was used. FTIR spectra are recorded at room temperature in the 500-4000 cm^{-1} range using Shimadzu FTIR-8700.To find band gap UV-Visible spectrophotometer (Beckman DU 640) was used.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

The XRD pattern of nickel and silver codoped samples is shown in Figure 1. All the peaks are well matched with the standard pattern of JCPDS (Card No. 36-1451). On comparing with standard ZnO peaks, we find FWHM of the reflection peaks is decreased which shows changes in the crystal strains.

This shift is due to replacement of some Zinc cations with nickel and silver. The results shows that the addition of Ni and Ag atoms as dopants did not affect the lattice patterns of ZnO nanocrystals..The crystallite sizes of the synthesized samples are calculated using Scherer's formula

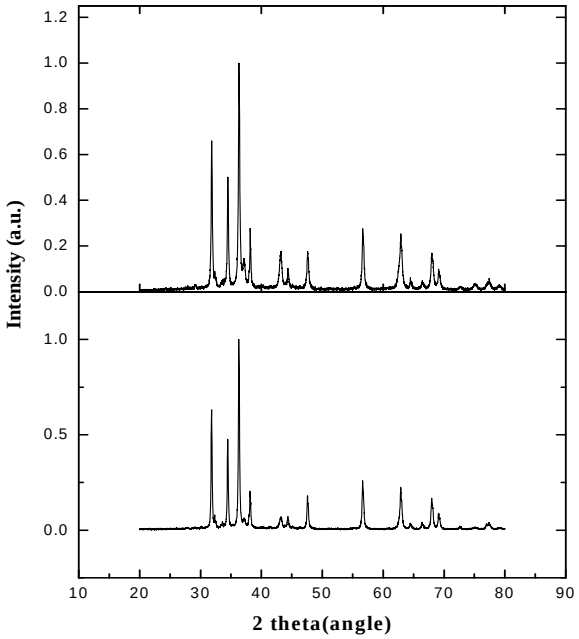


Figure 1: XRD patterns of $Zn_{1-x}Ni_xAg_xO$ samples (a) x = 0.05 at.%, (b) x = 1 at.%

$D = 0.94\lambda / \beta \cos\theta$, where β is full width at half maximum (FWHM), θ is diffraction angle and λ is wavelength of X-rays.Due to difference in atomic radius crystallite size increases. Structural parameters were calculated by using the formula:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{c^2}$$

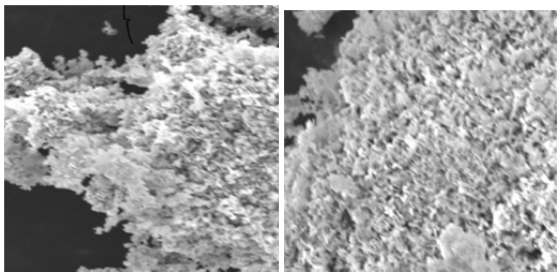
Table 1: crystallite sizes and lattice parameters of

$Zn_{1-x}Ni_xAg_xO$ nanoparticles

Conc.(at%)	D(nm)	a(A^0)	c(A^0)
X = 0.00	28	3.20	5.1
X = 0.02	30	3.21	5.0

3.2 SEM Analysis

$Zn_{1-x}Ni_xAg_xO$ nanoparticles are investigated using scanning electron microscopy (SEM), as shown in figure2.The spectrograph of the sample shows the growth of codoped ZnO nanoparticles. It indicates that the growth isnot exactly in uniform but it is observed like hexagonal nanostructure.The size lies in nanoparticle range.



(a) **(b)**

Figure 2: SEM micrograph of $Zn_{1-x}Ni_xAg_xO$ samples (a) x = 0.05 at.%, (b) x = 1 at.%

3.3 FTIR Analysis

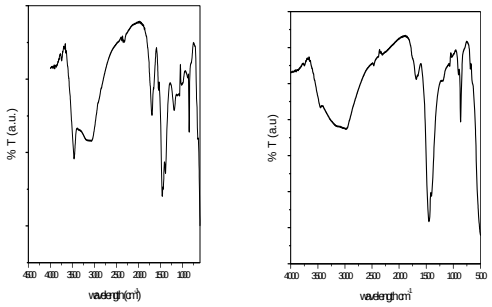


Figure 3: FTIR spectra of $Zn_{1-x}Ni_xAg_xO$ samples (a) x = 0.05 at.%, (b) x = 1 at.%

Figure 3 represents the FTIR spectra of $Zn_{1-x}Ni_xAg_xO$

Powders in the range of 500- 4000 cm^{-1} . Absorption band near to 500 cm^{-1} corresponds to ZnO. The bands near 700 cm^{-1} are assigned to silver. The bands near 800 are due to nitrates. Absorption band near 1500 and 3000 cm^{-1} correspond to the bending vibrations of O-H.Bands between 900-1500 corresponds to oxygen stretching and bands near 1600 are due to H-O-H absorption of mixtures.

3.4 Photoluminiscene Analysis

The photoluminescence originates from the recombination of surface states. The photoluminescence spectra over wavelength range 350-600 is observed. PL spectra of codoped ZnO have highest intensity at the wavelength of 550 nm which is arises due to surface defects which may come during the grinding process of sintered sample.The spectrum exhibits two emission peaks, one is located at around 525 nm, 490 nm.

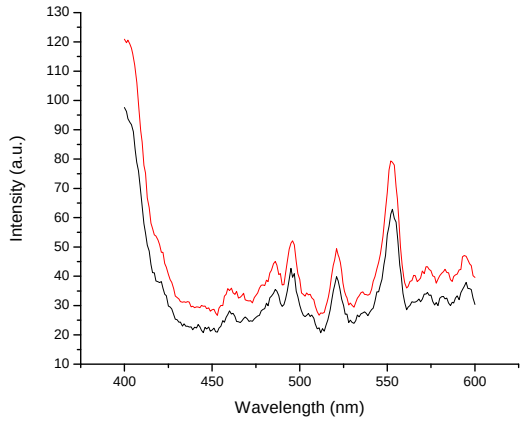


Figure 4: PL Spectra of $Zn_{1-x}Ni_xAg_xO$ samples

(a) x = 0.05 at.%, (b) x = 1 at.%

3.5 Optical Studies

The band gap of samples can be calculated by plotting graph between $[F(R)h\nu]^2$versus energy (hν).

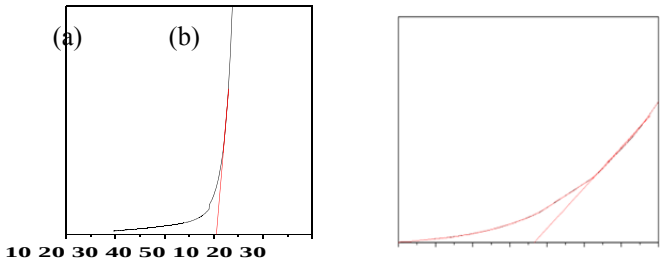


Figure 5: Diffused reflectance spectra of $Zn_{1-x}Ni_xAg_xO$ samples synthesized at 60^0C for 1 hour. (a) x = 0.5 at.%, (b) x = 1 at.%

The band gap values corresponding to these maxima are 3.33 eV, and 3.26 eV, respectively. These values are red-shifed with

respect to the band gap of undoped as well as bulk ZnO (3.37 eV).

4. CONCLUSION

$Zn_{1-x}Ni_xAg_xO$ (x= 0.05,1) nanoparticles were successfully synthesized by chemical precipitation method. From XRD data, it is confirmed that all samples are in the wurtzite hexagonal The crystallite size was found to be increased on doping due to different ionic radii. Band gap is founf to be decreased which can be explained through Kubelka-Munk relation. The FTIR spectroscopy confirms ZnO, C=C, Ag, Ni ,H-O-H bands presents in powder. PL analysis reveals that ZnO have highest intensity at the wavelength of 550 nm.

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