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Archives of Applied Science Research, 2010, 2 (5):378-385

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ISSN 0975-508X

CODEN (USA) AASRC9

# Synthesis and characterization of silver doped ZnO nanoparticles

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## ABSTRACT

Nanocrystals of undoped and silver doped zinc oxide ( $Zn_{1-x}Ag_xO$  (where  $x = 0.00$  to  $0.05$ ) were synthesized by coprecipitation method. Crystalline phases and optical absorption of prepared samples were determined by X-ray diffraction and UV-visible spectrophotometer. The average particles size was determined from X-ray line broadening. X-ray analyses reveals that Ag doped ZnO crystallizes in hexagonal wurtzite structure. The incorporation of  $Ag^+$  in the place of  $Zn^{2+}$  provoked an increase in the size of nanocrystals as compared to undoped or pure ZnO. Optical absorption measurement indicates red shift in the absorption band edge upon Ag doping. The band gap values of as prepared undoped and doped with silver samples are found to decrease with increase in temperature from 300 to 800 °C.

**Keywords:** Nanoparticles, Co-precipitation, Optical absorption, XRD, UV-vis spectrophotometer.

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## INTRODUCTION

Nanocrystalline materials have attracted a wide attention due to their unique properties and immense potential application in nano device fabrication [1-4]. Zinc oxide (ZnO), a direct wide bandgap (3.4 eV at Room temperature) II-VI compound n-type semiconductor, has a stable wurtzite structure with lattice spacing  $a = 0.325$  nm and  $c = 0.521$  nm and composed of a number of alternating planes with tetrahedrally-coordinated  $O^{2-}$  and  $Zn^{2+}$  ions, stacked alternately along the c-axis. It has attracted intensive research effort for its unique properties and versatile applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors and spintronics [5-14]. It has been proposed to be a more promising UV emitting phosphor than GaN because of its larger exciton binding energy (60 meV). All these predominant properties make ZnO a great potential in the field of nanotechnology.

Nano zinc oxide is non-toxic, with wide band gap has also been identified as a promising semiconductor material for exhibiting ferromagnetism (RTFM) at room temperature when doped with most of the transition metal elements [15]. Transition metal doped nanostructure is an effective method to adjust the energy level surface states of ZnO, which can further improve by the changes in doping concentrations of doped materials and hence in its physical and especially optical properties [16].

The coprecipitation method is one of the most appropriate ways of synthesizing a nanopowder. Coprecipitation is the name given by analytical chemists to a phenomenon whereby the fractional precipitation of a specified ion in a solution results in the precipitation not only of the target ion but also of other ions existing side by side in the solution. The additional precipitation of unwanted ions is, of course, an impediment to the analytical process [17]. Some of the most commonly substances used in coprecipitation operations are hydroxides, carbonates, sulphates and oxalates.

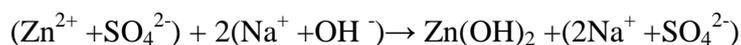
In the present work we used the coprecipitation method to prepare undoped and silver doped nanoparticles with nearly uniform and controlled size. The high quality of  $Zn_{1-x}Ag_xO$  (where  $x=0.00$  to  $0.05$ ) nanoparticles were successfully synthesized.

## MATERIALS AND METHODS

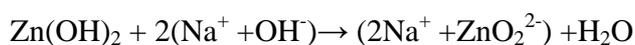
Synthesis of  $Zn_{1-x}Ag_xO$  (where  $x = 0.0$  to  $0.05$ ) nanoparticles were fabricated by the coprecipitation method [18]. All chemicals used are of analytical grade purity. X-Ray Diffraction (XRD) with  $CuK_{\alpha}$  radiation (Mini-desktop, Rigacu) patterns was obtained to examine the phase composition of the powder samples. The optical absorption spectra were recorded on Shimadzu double beam double monochromator spectrophotometer (UV-2550), equipped with integrated sphere assembly ISR-240A in the range of 190 to 900 nm.

### Coprecipitation method

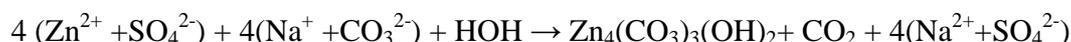
The starting materials,  $ZnSO_4 \cdot 7H_2O$ ,  $Na_2CO_3$ ,  $NaOH$ ,  $AgNO_3$  were used without further purification. In a typical synthesis of undoped ZnO, 0.1 M  $ZnSO_4 \cdot 7H_2O$  was dissolved in distilled water. Separately, a buffer solution (pH = 4.6) was prepared by dissolving appropriate amounts of sodium hydroxide and sodium carbonate in distilled water. The pH of buffer solution was selected so as to cause precipitation of basic zinc carbonate. Buffer solution was then added drop wise to the vigorously stirred zinc sulphate solution to produce a white, gelatinous zinc basic carbonate precipitate. The reactions for obtaining basic zinc carbonate are written as:  
Sodium hydroxide precipitates; the white, gelatinous zinc hydroxide:



The precipitate is soluble in sodium hydroxide reagent, resulting zincates, which behave like a weak acid:



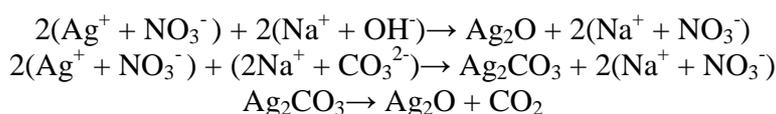
Sodium carbonate precipitates with zinc salts the white basic carbonate with variable composition:



After addition of buffer solution the mixture was stirred for two hours at room temperature. The precipitates were filtered and washed with distilled water. The precipitates were dried in oven at 110°C for two hours and calcinated at 300 °C, 400 °C, 500 °C, 800 °C and 1000 °C in muffle furnace. The basic zinc carbonate precipitate was decomposed in zinc oxide; a nano white powder. Decomposition reaction of basic zinc carbonate (hydrozincite) in zinc oxide is written as:



For the synthesis of ZnO doped with transition metal (silver) a solid mixture of 1 -5% AgNO<sub>3</sub> in ZnSO<sub>4</sub>.7H<sub>2</sub>O was dissolved separately in 50 ml distilled water and then mixed with buffer solution of sodium carbonate and sodium hydroxide, followed by the same procedure as for undoped ZnO. Sodium hydroxide precipitates the silver oxide. Sodium carbonate precipitates the silver carbonate, which decomposes in silver oxide. The reactions are written as:



## RESULTS AND DISCUSSION

**X-ray diffraction studies:** All the samples analyzed; pure and silver doped ZnO nano powders; presented are hexagonal wurtzite structure. Figures 1-(a)&(b) show the XRD diffraction patterns of Zn<sub>1-x</sub>Ag<sub>x</sub>O (x =0.0 to 0.05) powder samples at 800 and 1000°C temperatures. Undoped and Ag doped ZnO samples were calcined at 800 and 1000 °C in muffle furnace to ascertain the formation of different nanocrystalline phases. The diffraction patterns of samples can be indexed to the hexagonal wurtzite structure of ZnO. XRD diffraction pattern indicated only characteristic peaks for crystalline ZnO without those indicating the presence of Ag at 800 °C; while at 1000 °C; clear Ag peaks are observed for x = 0.01 to 0.05. It is clearly observed from the XRD patterns that with the increase in temperature of calcinations at 300 to 1000 °C, the diffraction peaks become shaper and stronger; which suggest that the crystal quality of the nanoparticles are improved and the particles size are increased. The mean crystalline size was calculated from the full-width at half-maximum (FWHM) of XRD lines by using the Debye-Scherrer formula:

$$D_{h,k,l} = 0.9\lambda / (\beta_{h,k,l}\cos\theta)$$

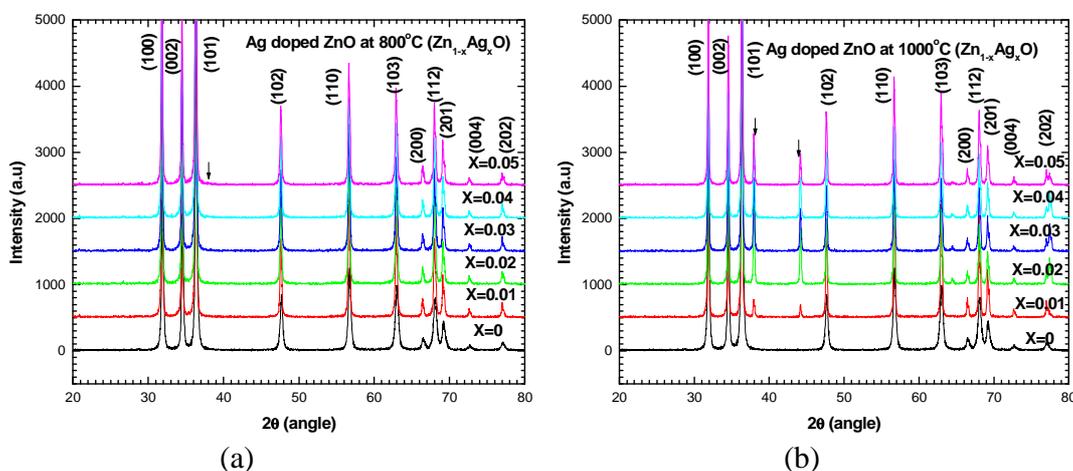
where D is the average crystalline diameter, λ is the wave-length in angstrom, β is the line width at half – maximum and θ is the Bragg angle. We used the most intense peak (101) in the XRD patterns to calculate the average crystalline size. It can be seen that the average size of nanoparticles increased as the heating temperature is increased and decreased as the doping percentage of silver metal is increased. It also indicates that the size of crystallites can be

adjusted by controlling the annealing temperature. The calculated values of particles size are presented in Table- 1 for undoped and Ag doped (1-5%) ZnO at 800 °C and 1000 °C. The size of undoped and Ag doped ZnO nanoparticles at 800°C are in the range of 27.8 to 39.8 nm and at 1000°C are in the range of 30 to 44 nm respectively. The particles size at 500 °C are about 12 nm for undoped ZnO; while 26 nm for Ag doped ZnO at 5% doping respectively.

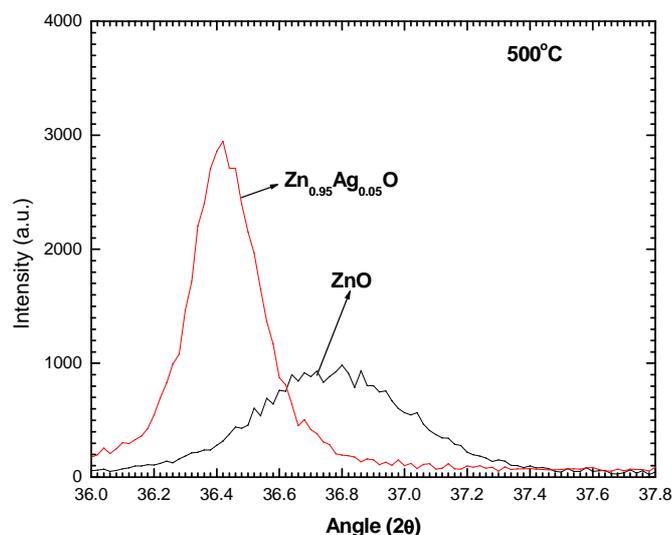
Fig.2 shows the most intense peaks of undoped ZnO and silver doped ZnO, keeping the doping concentration at 5% and the sintered temperature at 500 °C. When ZnO doped with Ag<sup>+</sup> the peak is moved towards lower angle in relation to pure ZnO. This occurs because of the difference between the ionic radii of the elements (Zn<sup>2+</sup> = 0.088 nm, Ag<sup>+</sup> = 0.122 nm) [19].

**Table 1. Variation of Size with temperature of undoped and Ag doped ZnO nanoparticles**

% of doping of Ag	Average size of particles for sample annealed at temperature 800°C	Average size of particles for sample annealed at temperature 1000°C
0 %	27.8	30.0
1 %	39.8	44.0
2 %	38.0	41.8
3 %	38.0	39.8
4 %	36.2	38.0
5 %	36.0	38.0



**Fig. 1 XRD patterns of pure ZnO and Zn<sub>1-x</sub>Ag<sub>x</sub>O nanoparticles (a) at 800°C and (b) at 1000°C**  
*The arrows indicate the formation of Silver oxides.*



**Fig. 2 Displacement of the most intense peak of the XRD pattern provoked by the insertion of Ag ions in the crystalline lattice of ZnO**

**Optical studies:** The optical absorption spectra of  $Zn_{1-x}Ag_xO$  ( $x=0.00, 0.05$ ) samples by UV-vis spectrophotometer in the range of 200 to 800 nm were presented. From figures 3 – (a) & (b), it can be seen that the excitonic absorption peak of as prepared undoped and silver doped samples appears around 260 nm which is fairly blue shifted from the absorption edge (i.e much below the band gap wavelength of 365 nm,  $E_g = 3.4$  eV) of bulk ZnO. The excitonic absorption peak of as prepared undoped and silver doped samples become broad as the temperature increases. The sharp excitonic peak in the absorption spectra at 300 °C is indeed indicative of the small size distribution of nanocrystal in the samples and broadening of peaks at higher temperatures clearly indicates the increase in size of nanocrystals with the increase of temperatures. It can be observed clearly from figures 3 - (a) & (b) that the absorbance increases from temperature 300 °C to 500 °C but it decreases at the temperature of 800 °C. The energy band gap is determined by using the relationship:

$$\alpha = A (h\nu - E_g)^n$$

where  $h\nu$ = Photon energy,  $\alpha$ = Absorption coefficient ( $\alpha = 4\pi k/\lambda$ ;  $k$  is the absorption index or absorbance,  $\lambda$  is wavelength in nm),  $E_g$  =Energy band gap,  $A$ =constant ,  $n=1/2$  for allowed direct band gap. Exponent  $n$  depends on the type of transition and it may have values  $1/2, 2, 3/2$  and  $3$  corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively [20]. The value of band gap is determined by extrapolating the straight line portion of  $(\alpha h\nu)^2 = 0$  axis; as shown in figure 4(b) at temperature 400 °C. The band gap decreases from 3.05 eV to 3.00 eV with silver (5 %) doping at temperature 400 °C. The Absorption edge values of as prepared undoped and silver doped samples are found to increase with increase in temperature from 300 to 800 °C but the band gap values of as prepared undoped and silver doped samples are found to decrease with increase in temperature from 300 to 800 °C as presented in tables 2 & 3. It is visible from figure 4(a) that in Ag doped ZnO sample the band edge is shifted to lower energy side.

## CONCLUSION

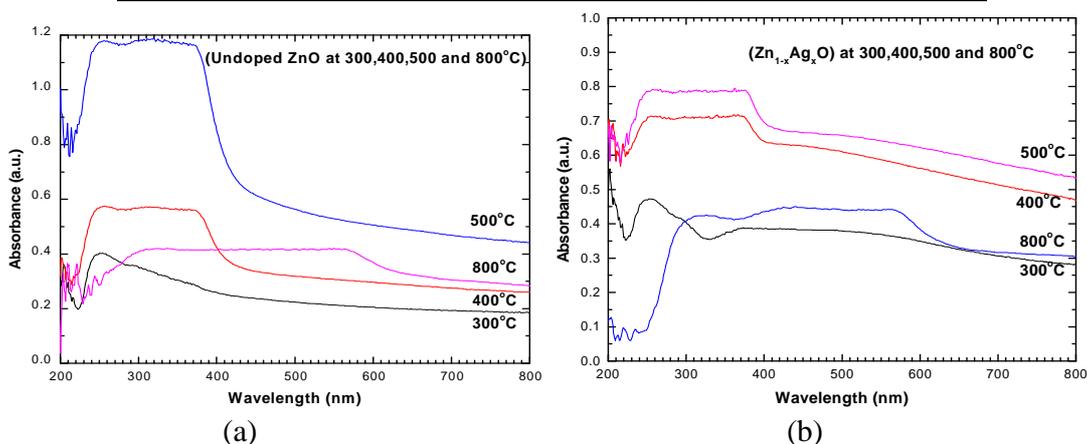
Nanocrystals of undoped and silver doped ZnO were successfully synthesized by using a chemical coprecipitation method. The crystalline structure, optical properties and band gap were determined by XRD and UV-visible spectra. XRD analysis shows the samples prepared in hexagonal phase. The particle size can be adjusted by controlling the reaction temperature. The average size of nanoparticle increased as the heating temperature is increased and decreased as the doping percentage of metals is increased. The strongest absorption peak appears at around 260 nm, which is blue shifted from the absorption edge of bulk ZnO (365 nm). The band gap values of prepared undoped and silver doped samples are found to decrease with increase in temperature from 300 to 800 °C. Optical absorption measurements indicate red shift in the absorption band edge upon Ag doping.

**Table 2. Variations of Absorption edge with temperature of undoped and Ag doped ZnO nanoparticles**

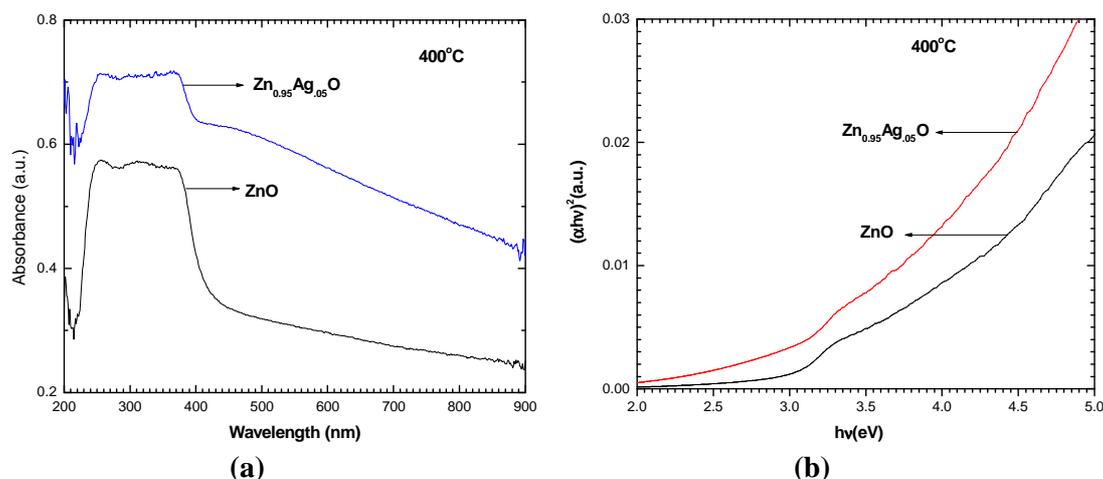
Temperature °C	Absorption edge (nm)	
	Undoped ZnO	5% Ag doped ZnO
300	370	375
400	406	413
500	413	420
800	427	430

**Table 3. Variations of band gap with temperature of undoped and Ag doped ZnO nanoparticles**

Temperature °C	Band Gap eV	
	Undoped ZnO	5% Ag doped ZnO
300	3.35	3.30
400	3.05	3.00
500	3.00	2.95
800	2.90	2.88



**Fig.3 Optical absorption spectra of (a) undoped ZnO nanoparticles and (b) silver doped ZnO nanoparticles at 300, 400, 500 and 800°C**



**Fig. 4 (a) Optical absorption spectra of undoped and silver (5%) doped ZnO nanoparticles at 400°C (b)  $(\alpha h\nu)^2$  vs. photon energy ( $h\nu$ ) for undoped and silver doped ZnO samples at 400°C**

### Acknowledgements

Authors are thankful to Dr. Sanjeev Aggrawal and Nidhi Sekhawat, Kurukshetra University, Kurukshetra for technical support for getting UV-VIS spectra. We are also thankful to the Director, NIT, Kurukshetra for XRD facilities in physics department.

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