

## Role of Method of Prepartion for Co-Doping in Structural and Optical Properties of Ag –Doped ZnO Nanoparticles

N. SHARMA<sup>1</sup>, S. KUMAR<sup>1</sup>

<sup>1</sup>Department of Physics, Arni University, Kangra (Himachal Pradesh)

Corresponding Author: nehasdr6600@gmail.com

### Abstract

The present work has been prepared on the basis of undoped, doped and co-doped ZnO as  $Zn_{1-x-y}Ag_xCo_yO$  NPs which are synthesized by two different methods; sol- gel method and chemical precipitation method. The prepared doped and co-doped ZnO NPs are described on the basis of properties by using different characterization techniques XRD, SEM/ EDX and UV-Vis for both methods individually. X-ray diffraction analysis proves that double wurtzite phase exist for the co-doped sample when these samples are synthesized by sol-gel method; whereas a single hexagonal crystalline wurtzite phase appears, without indicating any extra doping phase detection; It is shown by all samples when synthesized by chemical precipitation method. From XRD, both crystallite size and lattice strain are evaluated by scherrer, williamson hall method and size strain plot for all samples. SEM micrographs clearly depict it that with increasing doping concentration, the formation of agglomeration size increases. UV-Vis techniques are analysed to find out the optical band gap used as in optoelectronic properties for that sample synthesized by solution route method. The band gap decreases with increase in the dopant concentration which is affected by crystalline size. All results were evaluated by the chemical precipitation method having obtained good output as compare to the results obtained by sol- gel method. This optical band gap was used in optoelectronic application.

**Keywords:** Sol-Gel Method, Chemical precipitation Method, XRD, UV- Vis.

### Introduction

Recently, more of researches are focused on the attractive application of nanomaterials and preparation of nanostructures by different types of metal oxides available in the latest world of technology. <sup>1</sup> At nanoscale level, ZnO is important and attractive metal oxides because it has a hexagonal or wurtzite structure of n-type II–VI semiconductor among other nanostructures. The doped ZnO nanomaterial was prepared by addition of some impurity of the transition metals such as Mn, Co, Fe, and Ni within the main compound ZnO.<sup>2-3</sup> Therefore, ZnO nanomaterial was prepared by following one method among various methods, including simple solution route, sol-gel, hydrothermal, vapour phase transport (VPT), spray pyrolysis and others.<sup>4-6</sup>

Bhattacharyya et. al (2008) prepared Co doped ZnO Nps, there is no any extra cobalt impurity phase formed that is not affected the size of ZnO nanocrystals and it is reflected a ferromagnetism property. <sup>7</sup> Tao Liu et al. (2008) reported that the about 5 nm in size shown by Co-doped ZnO nanoparticles. <sup>8</sup> According to their results of ZnO, a good replacement of zinc ions with cobalt ions from its substitutional zinc sites. Similarly, Silver ions can act as an acceptor in Ag doped ZnO Nps due to substitution of zinc ion. Yan et al. concluded in its study that interstitial sites were less effective than substitutional sites. <sup>9</sup> In this paper, two different types of methods were used to synthesize the undoped, doped, (Ag, Co) co-doped ZnO-NPs by Sol-Gel method and by chemical precipitation method at 500°C.

Then analytical characterization techniques like XRD, UV-Vis, SEM and FTIR were performed to find out details about the size and structure, optical properties. XRD procedure is used to report on the mean crystalline size of the compounds obtained from powder. For estimation on the strain evaluate by three different types of Scherrer method, Williamson-hall (W-H) analysis and size-strain method (SSP) were used by undoped, doped and (Ag, Co) co-doped ZnO-NPs heated at 500<sup>0</sup>c due to lattice deformation.

## Materials and Methods

### Procedure

Zinc acetate, silver nitrate and cobalt nitrate powders had been taken as appropriate amount to form undoped and Zn<sub>1-x</sub>Co<sub>x</sub>Ag<sub>0.2</sub>O (x =0, 0.2M) nanoparticles. All the powders with 99.9% purity were used for the synthesis of nanoparticles. All of three different acetate, nitrates were dissolved separately in deionized water and ethanol ratios which is 80:20. When all three individually mixed properly, then a solution was formed. The solution was allowed to stand for 60 min under stirring. The whole experiment had been performed at room temperature. After that, there was drop wise addition of ammonia into the solution. Sodium hydroxide has been added into above prepared solution for the precipitation.

For sol- gel method, put this solution into the hot plate for 4 hour to make a gel type crystal and then heat treatment was performed on these crystal by put into oven at 500<sup>0</sup>C for 1 hour. In case of chemical precipitation method, above ppt solution was put into a constant etching water bath for mixing all content properly into the solution at 60<sup>0</sup>C. After that, distilled water has been used to filter the solution properly to remove any contaminations. Now, the solution was allowed to dry in oven at 500<sup>0</sup>C for 4 hour.

### Characteristics

Finally, the dried samples were properly grinded to form fine powder for both cases. “D8 focus” XRD measurement apparatus was used with scanning rate of 0.01 sec to determine the phase determination and crystallite size of nanoparticles. The optical properties of the samples were studied by using UV-Visible Spectrophotometer (model Hitachi U-3900H). To identify morphology we use scanning electron microscopy (JSM- 6610LV, JEOL) for the gold coated palettes.

## Result and Discussions:

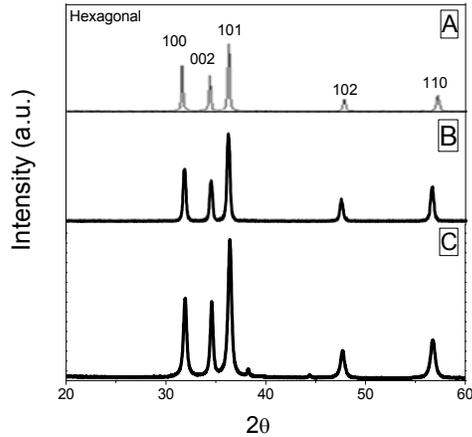
### XRD ANALYSIS

In this study, our aims were based on the results attained by comparing two different methods (i.e. Sol-Gel Method, Chemical precipitation method) used to synthesize for same samples.

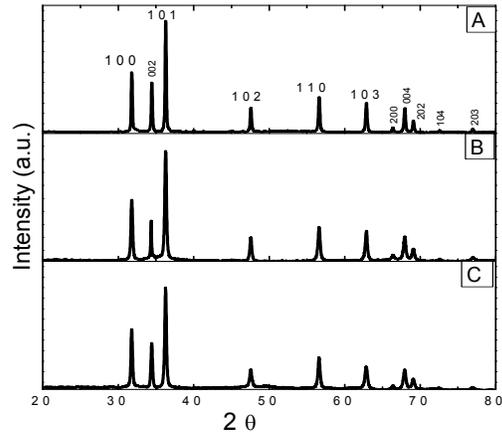
XRD result was clearly shown in fig1, for undoped, Ag doped and codoped ZnO nanoparticles were synthesized by chemical precipitation method. For undoped and doped samples are shown diffraction peaks corresponds to the hexagonal wurtzite crystalline single phase but a double phase hexagonal wurtzite structure exist for the co-doped ZnO nanoparticles. The higher intensity peaks are shifted towards higher angle for undoped and co-doped ZnO nanoparticles as shown in fig1 may be due to replacement of host material with co-dopant elements. It may also cause the compressive strain development in the present in

the crystal. For hexagonal phase, the lattice parameters such as the lattice constants (a, b, and c) and the crystalline size are decreased for undoped and codoped ZnO nanoparticles cases. For Ag-doped cases the higher intensity peak is shifted towards the lower angles that why the lattice parameter and crystalline sizes are increased, which confirm by literature.<sup>10</sup>

**1(a). Preparation of NPs with synthesis by Sol-Gel Method**



**Fig 1:** The XRD pattern of (a) Undoped ZnO -NPs, (b) Zn<sub>0.8</sub>Ag<sub>0.2</sub>O, (c) Zn<sub>0.6</sub>Co<sub>0.2</sub>Ag<sub>0.2</sub>O; synthesized by Sol- Gel method



**Fig 2:** The XRD pattern of (a) Undoped ZnO, (b) Zn<sub>0.8</sub>Ag<sub>0.2</sub>O, (c) Zn<sub>0.6</sub>Co<sub>0.2</sub>Ag<sub>0.2</sub>O; synthesized by chemical precipitation method

The ionic radius value for doped elements Ag<sup>+</sup> is 115 pm, Co<sup>2+</sup> is 70 pm and for Zn<sup>2+</sup> is 74 pm. Due to this reason, lattice parameters and crystalline sizes are increases for these samples when are synthesized by solution route method. In ZnO lattice, a higher ionic radii substitution take place at doped (Ag-) and co-doped (Ag-Co) process, that why the lattice parameters values go on increasing way due to expansion strain. The value of crystalline size also increases as there is increase in doping in the synthesis process. All the lattice parameter, crystalline size have been evaluated as mentioned in table 1, 2; these values are calculated by using the following below formulas

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \tag{1}$$

$$V = \frac{\sqrt{3}a^2c}{2} = 0.866a^2c \tag{2}$$

$$L = \sqrt{\frac{a^2}{3} + \left( \frac{1}{2} - u \right)^2 c^2} \tag{3}$$

$$\beta_s = \beta_s + \beta_D \tag{4}$$

$$\beta_{hkl} \cos \theta = \left( \frac{k\lambda}{D} \right) + (4\varepsilon \sin \theta) \tag{5}$$

To evaluate the crystallite size of nanoparticles, Scherrer equation [9]

$D = \left( \frac{K\lambda}{\beta_D \cos \theta} \right)$ , Where D (nm) is the crystalline size, k is a constant (equal to 0.94) and  $\lambda$  is the wavelength of the radiation (1.542 Å),  $\beta_D$  is width of peak at the half maximum intensity, and  $\theta$  is the position of peak.

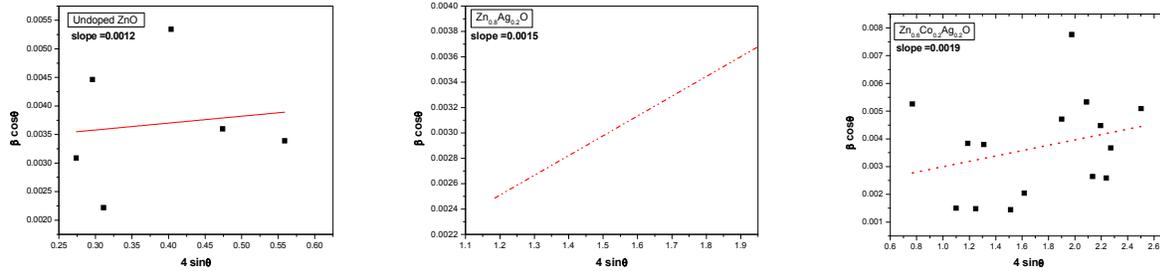


Fig 3: W-H Analysis of (a) Undoped ZnO -NPs, (b) Zn<sub>0.8</sub>Ag<sub>0.2</sub>O, (c) Zn<sub>0.6</sub>Co<sub>0.2</sub>Ag<sub>0.2</sub>O; synthesized by Sol-Gel method

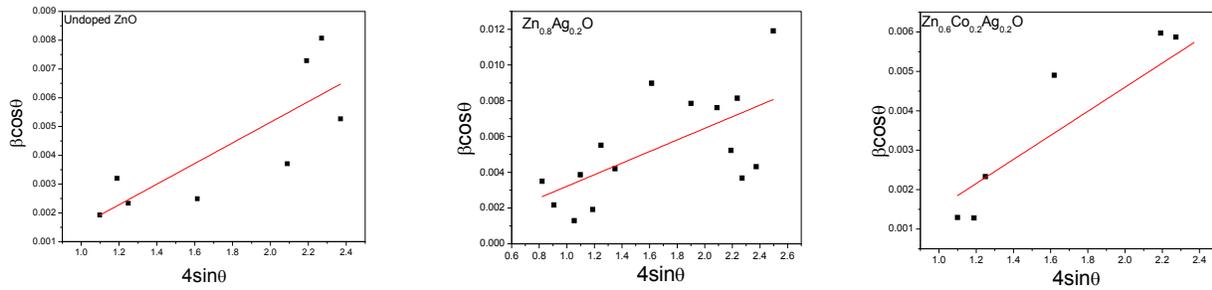


Fig 4: SSP of (a) Undoped ZnO -NPs, (b) Zn<sub>0.8</sub>Ag<sub>0.2</sub>O, (c) Zn<sub>0.6</sub>Co<sub>0.2</sub>Ag<sub>0.2</sub>O; synthesized by Sol-Gel method

Table 1: Lattice parameter for undoped, single doped and codoped ZnO nanoparticles; synthesized by Sol-Gel method

Sr. No.	(mol%) Concentration	Lattice Parameter (nm)			Structure	V(nm <sup>3</sup> )	L(nm)
		a= b	c	c/a			
1	undoped	3.241	5.245	1.612	Hexagonal	47.51	1.896
2	Zn <sub>0.8</sub> Ag <sub>0.2</sub> O	3.249	5.248	1.599	Hexagonal	47.58	1.972
3	Zn <sub>0.6</sub> Co <sub>0.2</sub> Ag <sub>0.2</sub> O	3.236	5.201	1.607	Hexagonal	47.44	1.971

Table 2: Calculated crystalline Size (D) for undoped and codoped ZnO nanoparticles by Scherrer, Size Strain Plot and WH plot

Compound	Sol-Gel Method						
	Scherrer D(nm)	WH D(nm)	Size strain plot(nm)				
			D(nm)	$\epsilon$	$Y \times 10^9$	$\sigma \times 10^9$	$u \times 10^9$
undoped ZnO	72.12	85.52	96.04	0.001	144	0.144	0.072
Zn <sub>0.8</sub> Ag <sub>0.2</sub> O	96.79	116.30	141.79	0.003	127	28.42	3.404
Zn <sub>0.6</sub> Co <sub>0.2</sub> Ag <sub>0.2</sub> O	88.76	71.53	108.72	0.005	118	17.44	8.72

In W-H method, the graph is plotted between the terms  $4\sin\theta$  with respect to  $\beta \cos \theta$  by using equation (5) as mentioned in fig 3. This method is used mostly to find out the strain and the particle size; whereas slope of the linearly fitted data which explain value of strain and the particle size calculated by

the root of the y-intercept from W-H plot and written in table2. In case of size-strain plot, the graph between  $(d_{hkl}\beta_{hkl} \cos\theta)^2$  with respect to  $(d_{hkl}^2\beta_{hkl} \cos\theta)$  has been plotted. From fig 2 and 3, the slope of the linearly fitted data is used to explain the particle size and value of strain is calculated by the root of the y-intercept for both methods. The crystalline sizes were evaluated by all these method for both the cases as mentioned in table3 and 4.

$$(d_{hkl}\beta_{hkl} \cos\theta)^2 = \frac{K}{D} (d_{hkl}^2\beta_{hkl} \cos\theta) + (\varepsilon/2)^2 \quad (6)$$

### 1(b). Preparation of NPs with synthesis by Chemical precipitation Method

Similarly, these samples have been synthesized by Chemical precipitation method as shown in fig 2. It clearly shows that a single phase wurtzite hexagonal structure. After matching with JCPDS 00-036-1451 file of standard card. This means that no extra peak exists which is not based on Co and Ag co-doping. The ionic radius value for doped elements  $\text{Ag}^+$  is 115 pm,  $\text{Co}^{2+}$  is 70 pm and for  $\text{Zn}^{2+}$  is 74 pm. Due to this reason, lattice parameters and crystalline sizes are increased for these samples but in case of doped sample, lattice parameters and crystalline size values go in an increasing way due to expansion strain that is mentioned in table 3, 4. The value of crystalline size is also increased as increase in doping in the synthesis process.

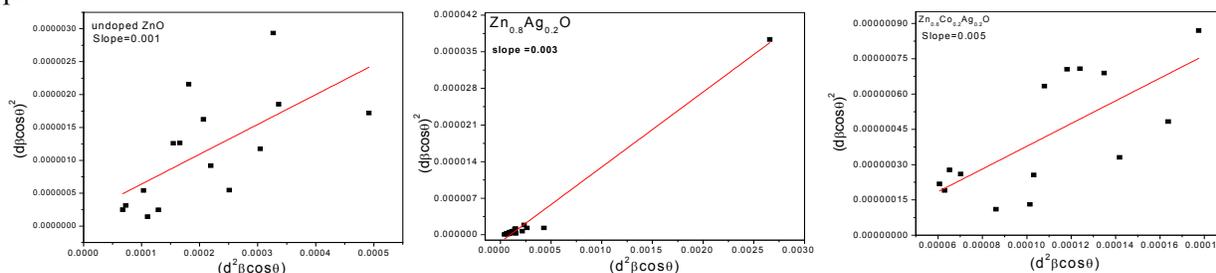


Fig 5: WH Analysis of (a) Undoped ZnO -NPs, (b)  $\text{Zn}_{0.8}\text{Ag}_{0.2}\text{O}$ , (c)  $\text{Zn}_{0.6}\text{Co}_{0.2}\text{Ag}_{0.2}\text{O}$ ; synthesized by Chemical precipitation Method

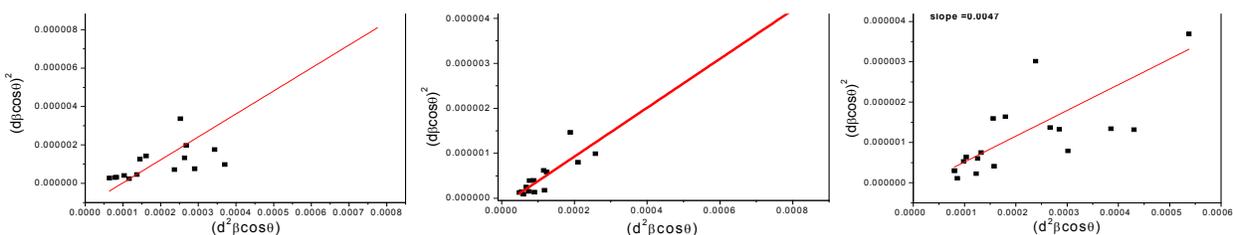


Fig 6: SSP Analysis of (a) Undoped ZnO -NPs, (b)  $\text{Zn}_{0.8}\text{Ag}_{0.2}\text{O}$ , (c)  $\text{Zn}_{0.6}\text{Co}_{0.2}\text{Ag}_{0.2}\text{O}$ ; synthesized by Chemical precipitation method

**Table 3:** Lattice parameter for undoped, single doped and codoped ZnO nanoparticles; synthesized by Chemical precipitation method

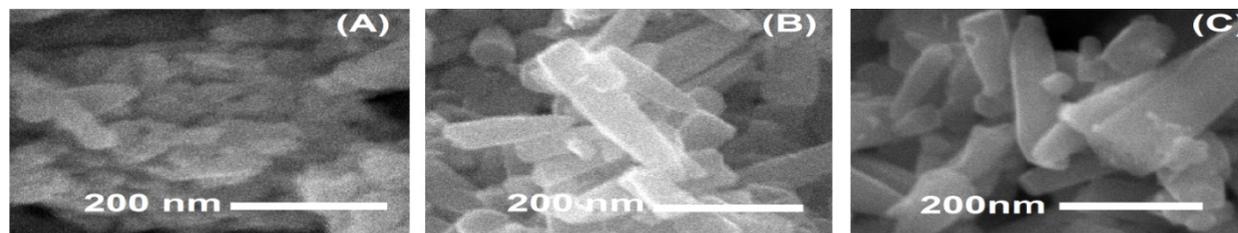
Sr. No.	(mol%) Concentration	Lattice Parameter (nm)			structure	V(nm <sup>3</sup> )	L(nm)
		a= b	c	c/a			
1	undoped	3.241	5.185	1.599	Hexagonal	47.819	1.896
2	$\text{Zn}_{0.8}\text{Ag}_{0.2}\text{O}$	3.253	5.203	1.607	Hexagonal	47.175	1.972
3	$\text{Zn}_{0.6}\text{Co}_{0.2}\text{Ag}_{0.2}\text{O}$	3.256	5.221	1.627	Hexagonal	47.174	1.971

**Table 4:** Calculated crystalline Size (D) for undoped and codoped ZnO nps by scherrer, size strain plot and WH plot.

Compound	Chemical Precipitation Method						
	Scherrer D(nm)	WH D(nm)	Size strain plot(nm)				
			D(nm)	$\epsilon$	$\gamma \times 10^9$	$\sigma \times 10^9$	$u \times 10^9$
undoped ZnO	34.22	45.25	63.04	0.001	144	0.144	0.072
Zn <sub>0.8</sub> Ag <sub>0.2</sub> O	56.70	66.09	74.69	0.0023	127	28.42	3.404
Zn <sub>0.6</sub> Co <sub>0.2</sub> Ag <sub>0.2</sub> O	61.46	71.33	82.12	0.0047	118	17.44	8.72

**Scanning electron microscopy (SEM) / Energy dispersive X-ray spectra (EDX) analysis:**

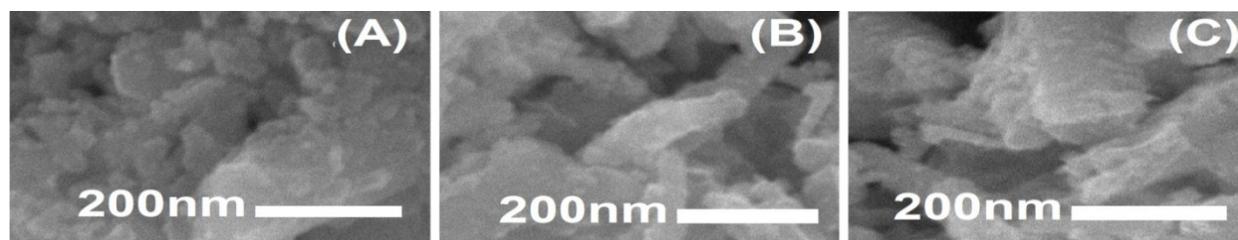
Scanning electron microscopy is examines that the morphological studies perform undoped, doped and co-doped ZnO. These samples are formed a large number of pencil type agglomerate as represented in Fig. 6, when these samples were synthesized chemical precipitation method. These micrographs displayed for the construction of all undoped, doped and co-doped ZnO NPs. It was clear that with increasing doping concentration, the formation of agglomeration size increases as shown in Fig. 7. Singh et.al. (2016) has been also reported on the doped ZnO nanoparticles.<sup>11</sup> These micrographs are exactly holding the XRD results when the crystalline size is high. As a result size of these micrographs increase.



**Fig 7:** SEM micrographs of (a) Undoped ZnO -NPs, (b) Zn<sub>0.8</sub>Ag<sub>0.2</sub>O, (c) Zn<sub>0.6</sub>Co<sub>0.2</sub>Ag<sub>0.2</sub>O; synthesized Sol-Gel method

**Table 5:** Atomic percentage of (a) Undoped ZnO -NPs, (b) Zn<sub>0.8</sub>Ag<sub>0.2</sub>O, (c) Zn<sub>0.6</sub>Co<sub>0.2</sub>Ag<sub>0.2</sub>O

Compound	weight percentage Based on sol- gel method				weight percentage Based on chemical precipitation method			
	Zn	Ag	Co	O	Zn	Ag	Co	O
	undoped ZnO	75.5	----	-----	24.5	88.9	-----	-----
Zn <sub>0.8</sub> Ag <sub>0.2</sub> O	67.4	0.15	-----	35.5	76.2	0.18	-----	23.62
Zn <sub>0.6</sub> Co <sub>0.2</sub> Ag <sub>0.2</sub> O	61.5	0.2	0.19	38.1	69.2	0.2	0.19	39.9



**Fig 8:** SEM micrographs of (a) Undoped ZnO -NPs, (b) Zn<sub>0.8</sub>Ag<sub>0.2</sub>O, (c) Zn<sub>0.6</sub>Co<sub>0.2</sub>Ag<sub>0.2</sub>O; synthesized chemical precipitation method

An energy dispersive X-ray (EDS) spectroscopy defines many details about the chemical composition of the samples as shown in Fig 4.

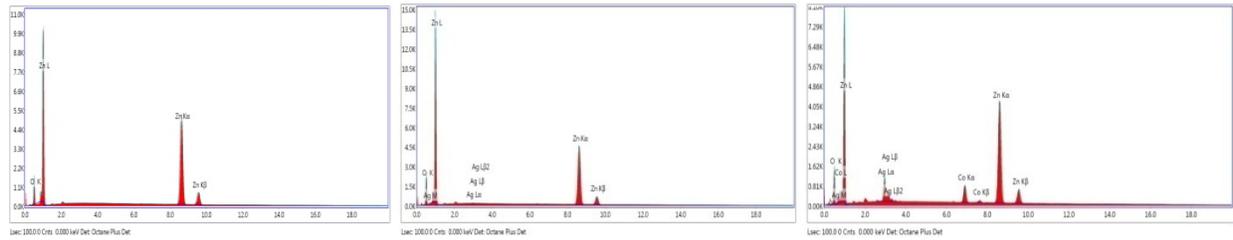


Fig 9: EDS Spectra of (a) Undoped ZnO -NPs, (b) Zn<sub>0.8</sub>Ag<sub>0.2</sub>O, (c) Zn<sub>0.6</sub>Co<sub>0.2</sub>Ag<sub>0.2</sub>O nanoparticles

The EDX spectra of doped and co-doped ZnO sample, which verify the production of undoped, doped and co-doped ZnO nanoparticles is also mentioned in literature.<sup>12</sup> The XRD result of data confirms by EDX that it explained the evidence of O, Zn, Ag and Co of elements for co-doped ZnO nanoparticles case.

### Optical Studies

The UV-Vis spectrophotometer is presented to analyse the optical absorption spectra for undoped, Zn<sub>0.8</sub>Ag<sub>0.2</sub>O doped and Zn<sub>0.6</sub>Co<sub>0.2</sub>Ag<sub>0.2</sub>O codoped ZnO nanoparticles by having range 200-800 nm at room temperature. The energy band gap is determined by using the relationship<sup>13</sup>

$$\alpha = A (h\nu - E_g)^n \quad (6)$$

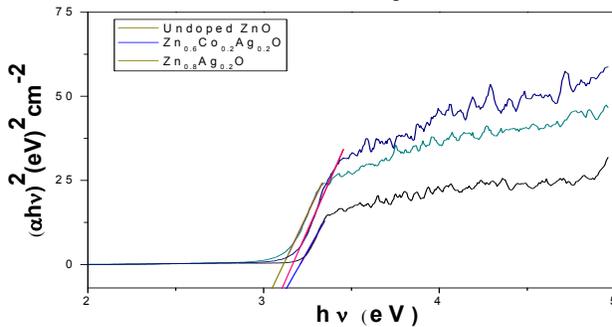


Fig 10(a): Optical absorption spectra, synthesized by sol-gel method

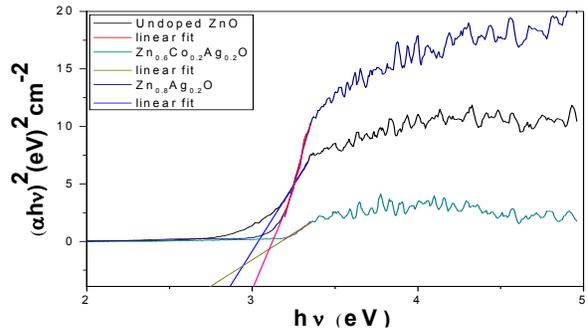


Fig 10(b): Optical absorption spectra, synthesized by chemical precipitation method

Where  $h\nu$ =photonic energy,  $\alpha$ =absorption coefficient ( $\alpha=4\pi K/\lambda$ ;  $k$  is the absorption index or absorbance,  $\lambda$  is the wavelength in nm),  $E_g$ =Energy band gap,  $A$ = constant,  $n=1/2$  for allowed direct band gap.

Table 6: Optical properties of (a) Undoped ZnO -NPs, (b) Zn<sub>0.8</sub>Ag<sub>0.2</sub>O, (c) Zn<sub>0.6</sub>Co<sub>0.2</sub>Ag<sub>0.2</sub>O

Compound	Based on sol- gel method			Based on Chemical precipitation method		
	Wavelength (nm)	Band gap (eV)	Urbach energy (eV)	Wavelength (nm)	Band gap (eV)	Urbach energy (eV)
undoped ZnO	357	3.47	2.531	393	3.156	2.049
Zn <sub>0.8</sub> Ag <sub>0.2</sub> O	366	3.39	1.643	431	2.879	1.833
Zn <sub>0.6</sub> Co <sub>0.2</sub> Ag <sub>0.2</sub> O	379	3.27	0.536	516	2.403	0.783

From fig 9(a), it can be seen that the value of band gap for all that samples which synthesized by Sol-Gel method that effected by the crystalline size i.e. as the crystalline size were decreases so the band gap value increases except for Ag doped sample (its value decreases). Similarly, it was clearly seen that the value of band gap decreases with increases in the dopant concentration when sample were prepared by chemical precipitation method that why these optical properties are use in terms optoelectronic properties in fig 9(b). This optical band gap will used as optoelectronic applications.

## Conclusion

The crystallite size of undoped and codoped ZnO nanopowders were prepared by using chemical precipitation method was analysed by the XRD pattern. The result shows that hexagonal double wurtzite phase exists for the co-doped sample but a single hexagonal crystalline wurtzite phase appears for all samples synthesized by chemical precipitation method. Scherrer, Size strain plot and W-H analysis is determined to calculate the crystalline size. So the crystallite size was increasing all samples for chemical precipitation method. The results is obtained shows that the crystallite size for Ag-doped decreases as compare to the undoped ZnO due to tensile strain but for co-doped ZnO nanoparticles the crystallite size increases due to compressive strain content as compare to the undoped ZnO for sol-gel method. All results of different samples are good pattern when these are synthesized by chemical precipitation method as compare to result of all samples which synthesized by sol-gel method. SEM micrographs are the formation of agglomeration size increases. UV-Vis techniques have been analysed to find out the optical band gap used as in optoelectronic properties for that sample synthesized by chemical precipitation method. The band gap decreases with increases in the dopant concentrate on which affected by crystalline size.

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