



Effect of Ag Doping on Properties of Al-Doped ZnO Nanoparticles Varies as $\text{Zn}_{1-x-y}\text{Ag}_x\text{Al}_y\text{O}$

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Abstract

In present study, undoped ZnO, $\text{Zn}_{0.8}\text{Ag}_{0.2}\text{O}$, $\text{Zn}_{0.8}\text{Al}_{0.2}\text{O}$ and $\text{Zn}_{0.6}\text{Al}_{0.2}\text{Ag}_{0.2}\text{O}$ samples are synthesized by simple solution method. X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray spectroscopy (EDX) and UV-visible (UV-Vis) spectroscopy are used to perform the characterization of undoped, doped and codoped samples. XRD analysis is exposed that hexagonal wurtzite crystalline structure obtained for undoped, doped and codoped samples without any extra representation of impurity phases. The crystalline size is when evaluated by using Scherrer, It has 44, 49, 41 and 37nm for undoped ZnO, $\text{Zn}_{0.8}\text{Ag}_{0.2}\text{O}$, $\text{Zn}_{0.8}\text{Al}_{0.2}\text{O}$ and $\text{Zn}_{0.6}\text{Al}_{0.2}\text{Ag}_{0.2}\text{O}$ samples. Similarly, the crystalline size and strain are also evaluated by Williamson hall (W-H) and size strain plot (SSP) for the undoped, doped and codoped nanoparticles. The evaluated crystalline size by SSP is three times greater than the result of the scherrer method. The SEM exposes that surface morphology of nanoparticle samples, in this case is the formation of large agglomeration in spherical shape with nanocrystallites of undoped and doped ZnO with apparent and definite boundaries. EDS points out the replacement of Al^{3+} and Ag^+ with Zn^{2+} in ZnO matrix and consequences in the development of single-phase $\text{Zn}_{1-x-y}\text{Ag}_x\text{Al}_y\text{O}$. The blueshift is shown in UV-Vis absorption spectra because the band gap value increases with the increase in doping, except Ag^+ doped ZnO nanoparticles.



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Introduction

Recently, research areas were more concentrated about the nanotechnology¹. The nanotechnology is act as more active for new or improved properties which are exhibited by nanoparticles. The unique physical and chemical properties shown by the

particles then these particles used as in important property of material in the development of novel nanodevices². In term of nanotechnology, Zinc Oxide (ZnO) has one of advanced and unique material in optoelectronics applications because of its direct band gap and large exciton binding

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energy³. The formation of ZnO nanorods, nanowires can be developed by as-prepared powders that useful and attractive in many application in the light emitting devices, transparent conducting oxides, optoelectronic devices, UV photo detectors and ferromagnetic devices⁴. For last few decades, most of researches have been focused on different transition metals such as Fe, Co, Ni, and Mn that is used in ZnO as a dopant which useful to get a advanced and modified properties of ZnO nanoparticles which is useful to make a dramatic change in most of a applications⁵. The n-type doping in ZnO is native defect because it acquires conductivity by Zinc interstitials and oxygen voids⁶. The production of p-type ZnO is also performed by using silver doping which is effective for recent research⁷.

These transition metals doped and codoped in ZnO nanoparticles were synthesized by following different routes for example co-precipitation, solution route, sol-gel, hydrothermal method etc⁸⁻⁹. Sebastian et. al. has revealed that a single phase established by the X-ray diffraction (XRD) for the codoped ZnO nanoparticles and these samples are prepared by co-precipitation method and SEM reveals that there is no surface prediction of any impurities and EDS to verify the hope for stoichiometry¹⁰. Lojkowski et. al. confirmed that different dopant Mn^{2+} , Ni^{2+} , Co^{2+} and Cr^{3+} ions are doped in ZnO nanopowders that is synthesised by using a solvothermal reaction and X-ray diffraction was detected that no phases or compounds other than ZnO and as impurities content increases which responsible to decrease the grain size of doped powders samples from 20nm¹¹.

In this present study, we have prepared the undoped, doped and codoped ZnO nanoparticles by using chemical precipitation method and then these as-prepared nanoparticles have been characterized for the structural, optical and morphological properties.

Experimental and Methods

$Zn_{1-x-y}M_xAg_yO$ samples have been carried out by chemical precipitation method. The samples have been coded as; undoped ZnO--A, $Zn_{0.8}Ag_{0.2}O$ --B, $Zn_{0.8}Al_{0.2}O$ --C and $Zn_{0.6}Al_{0.2}Ag_{0.2}O$ --D samples. The undoped and co-doped nanoparticles samples have been found due to its different composition of solutions in the host ZnO material. All Chemicals

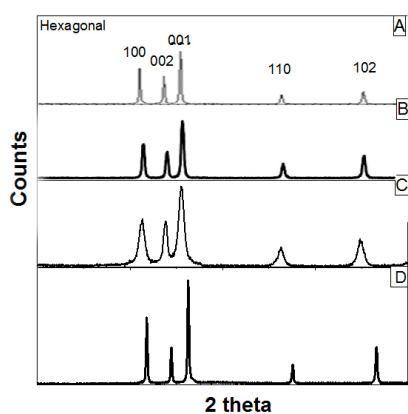


Fig. 1: The XRD pattern of (a) Undoped ZnO -NPs, (b) $Zn_{0.8}Al_{0.2}O$, (c) $Zn_{0.8}Ag_{0.2}O$, (d) $Zn_{0.6}Al_{0.2}Ag_{0.2}O$

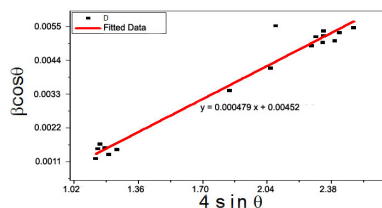
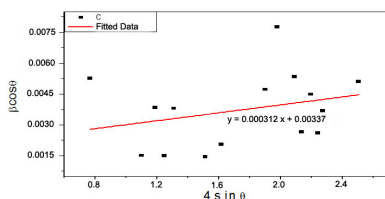
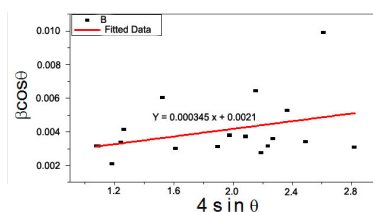
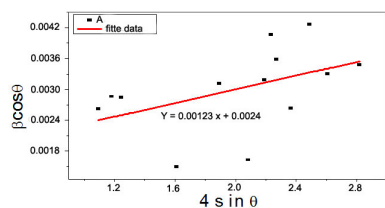


Fig. 2: WH Spectra of (a) Undoped ZnO -NPs, (b) $Zn_{0.8}Al_{0.2}O$, (c) $Zn_{0.8}Ag_{0.2}O$, (d) $Zn_{0.6}Al_{0.2}Ag_{0.2}O$

were accurate purified (99%) which were used for synthesis ZnO nanoparticles. For cleaning and mixing the sample, distilled twice/ deionized water was used instead of simple water. The accurate amount of Zinc acetate, aluminium nitrate and silver, each three different samples mix within 20ml of ethanol and 80 ml of deionized water separately, dissolve above these samples differently in distilled water ratio. With magnetic stirrer all above solutions mixed with host compound ZnO. After that mix all compounds properly in solution, then ammonia solution was prepared by adding 0.44 ratio of ammonia in deionized water. Drop wise ammonia solution added into the above solution because adjusts its pH value in the solution. Due to complete

precipitation was occurred in solutions for this added NaOH solution (4.4 gm of NaOH pallet dissolve in 20ml of ethanol and 80 ml of deionized water). After that put this solution at 60°C for 60 minutes in a water bath, hold the solution at room temperature until ready for filtered precipitates with help of double distilled water and ethanol. Then ready for last stage i.e. set the oven at 500°C, within 80 minutes dried the sample.

Material Characterization:

In XRD studies, the structural properties were performed with PANalytical X'Pert PRO to identify having in $20^\circ \leq 2\theta \leq 90^\circ$ by using with Cu-K α and difference in each step having a size of 0.013°/

Table 1: The structure parameter of un-doped, $\text{Zn}_{0.8}\text{Ag}_{0.2}\text{O}$, $\text{Zn}_{0.8}\text{Al}_{0.2}\text{O}$ and $\text{Zn}_{0.6}\text{Al}_{0.2}\text{Ag}_{0.2}\text{O}$ doped ZnO NPs

Sample label	Lattice parameter			Scherrer	W-H Method			Size strain plot(nm)			
	a = b	c	V		D(nm)	ϵ		D(nm)	ϵ	u	σ
Undoped ZnO	3.248	5.202	47.41	44	58	1.23		121	1.73	51.4	123
$\text{Zn}_{0.8}\text{Ag}_{0.2}\text{O}$	3.249	5.213	47.54	49	67	3.45		130	2.23	63.9	133
$\text{Zn}_{0.8}\text{Al}_{0.2}\text{O}$	3.247	5.194	47.46	41	43	3.12		91	3.58	69.5	154
$\text{Zn}_{0.6}\text{Al}_{0.2}\text{Ag}_{0.2}\text{O}$	3.242	5.181	47.46	37	32	4.79		68	4.93	74.8	194

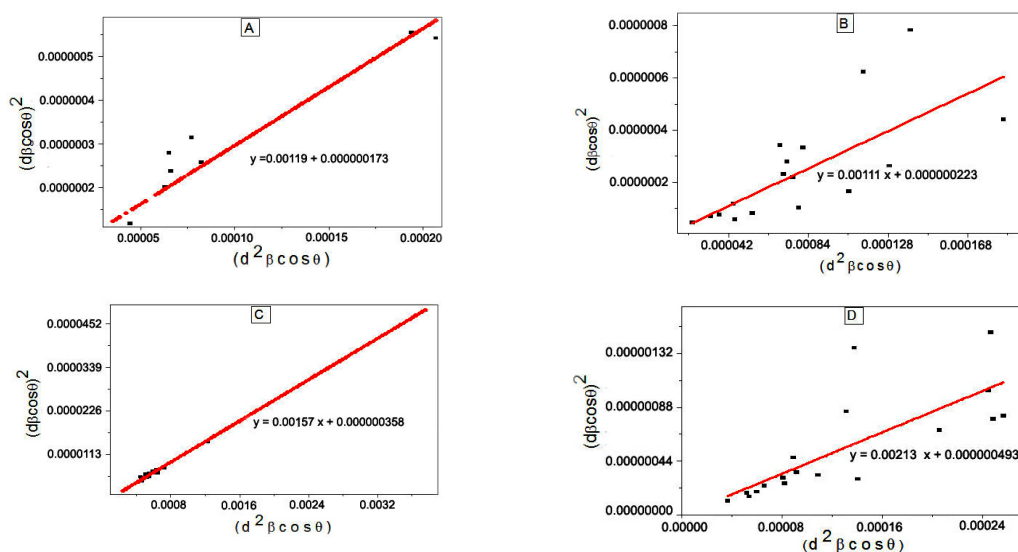


Fig. 3: SSP Spectra of (a) Undoped ZnO -NPs, (b) $\text{Zn}_{0.8}\text{Al}_{0.2}\text{O}$, (c) $\text{Zn}_{0.8}\text{Ag}_{0.2}\text{O}$, (d) $\text{Zn}_{0.6}\text{Al}_{0.2}\text{Ag}_{0.2}\text{O}$

min at room temperature. Then after analyse the structural parameters that evaluating from two

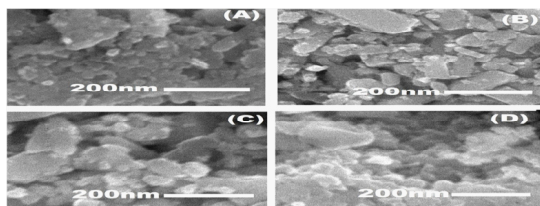


Fig. 4: SEM images of (a) Undoped ZnO -NPs, (b) $\text{Zn}_{0.8}\text{Al}_{0.2}\text{O}$, (c) $\text{Zn}_{0.8}\text{Ag}_{0.2}\text{O}$, (d) $\text{Zn}_{0.6}\text{Al}_{0.2}\text{Ag}_{0.2}\text{O}$

different (Scherrer method, W-H plot and SSP) methods which helpful for getting the different terms like crystallite size and lattice strain for all doped ZnO nps. To identify morphology we use approving out with scanning electron microscopy (JSM-6610LV, JEOL) for the gold coated palettes. The energy-dispersive X-Ray spectra (EDX) study was performed with SEM (Scanning electron microscopy) instrument. The ultraviolet-visible spectrometer (Hitachi UV-3300) was used to identify the optical characterization in the range 200–800 nm.

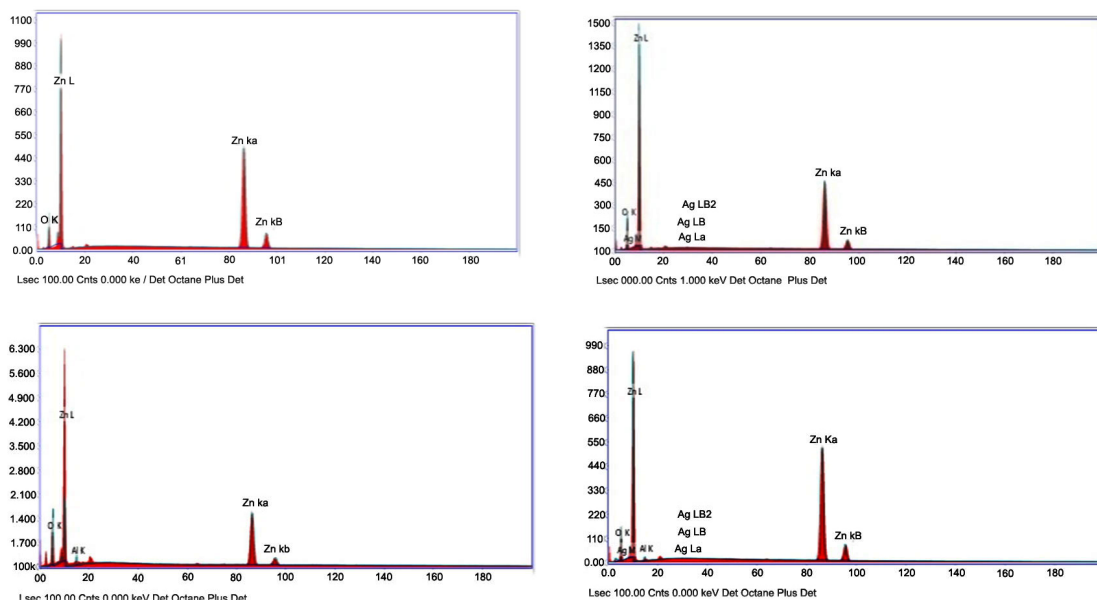


Fig. 5: EDS Spectra of (a) Undoped ZnO -NPs, (b) $\text{Zn}_{0.8}\text{Al}_{0.2}\text{O}$, (c) $\text{Zn}_{0.8}\text{Ag}_{0.2}\text{O}$, (d) $\text{Zn}_{0.6}\text{Al}_{0.2}\text{Ag}_{0.2}\text{O}$ nanoparticles

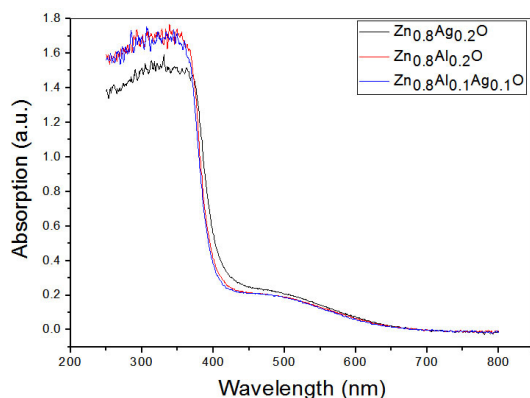


Fig. 6: Plot between optical absorption Vs wavelength for doped and codoped nanoparticles

Experimental Detail

XXRD Diffraction

The structural properties were analyzing the effect of addition of Ag and Al codoped ZnO nanoparticles by using to study the XRD. Fig. 1 is representing the XRD series for codoped ZnO nanoparticles. The single phase is confirmed by preferred orientations (100), (002), (101) i.e. three higher most peaks (all the peaks) of hexagonal wurtzite crystalline structure of ZnO matching with ICDD card. There is no additional peaks are observed corresponding to Ag and Al nanoparticles and it indicates the purity of the samples. The Debye-Scherrer's formula are used to calculate the average nanocrystalline size, where $D = K\lambda / \beta_0 \cos\theta$ (nm) is the crystalline

size, k is a constant (equal to 0.94) and λ is the wavelength (equal to 1.542 Å), β_D is full width at the half maximum intensity, and θ is position of peak.

The intensity of XRD peaks was increased by angles as compared to the undoped ZnO, Al-, and Ag-Al i.e. codoped ZnO samples. This was reason for the occurrence of strain because of insertion of Ag-, Al-, and Ag-Al elements change by Zn ions in the ZnO pattern, which is also clearly similar as shown in literature¹². For Ag- doped ZnO sample was shown an opposite pattern because the Ag^+ was shown the ionic radii (1.15 Å) which is smaller than ionic radii of the Zn^{2+} (0.74 Å) element so tensile strain show existence in ZnO lattice and then lattice parameters increases for Ag doped ZnO nanoparticles. But for Al doped ZnO, the ionic radii of the host element i.e. Zn^{2+} (0.74 Å) which is greater than the ionic radii of doped material i.e. Al^{3+} (0.54 Å) so compressible strain shows existence in ZnO lattice and then for Ag doped ZnO nanoparticles, lattice parameters increases. The crystalline size was evaluated by the scherrer method for undoped, doped and codoped NPs as shown in Table 1.

Williamson–Hall (W–H) Methods

The W-H connection is able to get through by following equation¹³:

$$\beta_{hkl} = \beta_s + \beta_D \quad \dots\dots(1)$$

Which means both crystallite size (D) and lattice strain (ϵ) is evaluated by the value of β_{hkl} of a Bragg peak. Due to crystal imperfections and distortion reasons that obtained β_D value arises. Because of small crystallite size, the Bragg peak broadening

happens. Due to Debye-Scherrer formula ($D = K\lambda/\beta \cos\theta$) then substitute in equation (1) we get

$$\beta_{hkl} \cos\theta = (K\lambda/D) + (4\epsilon \sin\theta) \quad \dots\dots(2)$$

From this equation (2), ϵ is inversely proportional to the crystalline size. The graph plotted between the values of $\beta_{hkl} \cos\theta$ and $4\sin\theta$; the crystallite size value has been calculated by the value of y-intercept and strain is obtained from slope in the graph. The outcomes of W-H plot are evaluated for undoped, doped and codoped NPs as shown in Table 1.

Size- Strain Plot Method

In this case of size-strain, parameter can be found that both the crystalline size and the microstrain get together. From equation(3), the graph is plotted between $(D_{hk} \beta_{hkl} \cos\theta)^2$ Vs. $(D_{hk}^2 \beta_{hkl} \cos\theta)$. The crystalline size is calculated by using slope of the linearly fitted data and strain got by y- intercept, as from equation(3). For undoped, doped and codoped NPs, the results are evaluated for SSP method as shown in Table 1.

$$(d_{hkl} \beta_{hkl} \cos\theta)^2 = K/D (d_{hk}^2 \beta_{hkl} \cos\theta) + (\epsilon/2)^2 \quad \dots\dots(3)$$

Scanning Electron Microscope Analysis

The scanning electron microscope (SEM) analysis is used to find out the morphology of undoped, doped and co-doped samples studies. The particles are spherical in shape with large agglomeration. The aggregation is approximately controlled and smaller in size in case of undoped ZnO but large aggregation trends follow Ag doped ZnO, Al doped ZnO, codoped (Ag, Al) samples which are shown in a

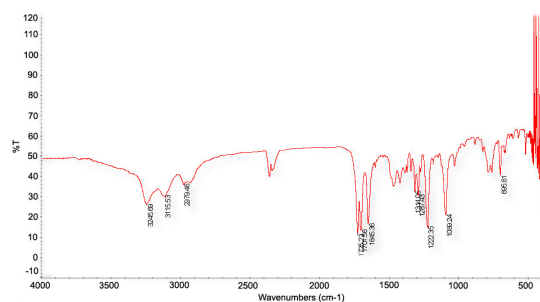


Fig. 7 (b): Spectra for band energy gap ($h\nu$) vs $(\alpha h\nu)^2$ for undoped ZnO nanoparticles

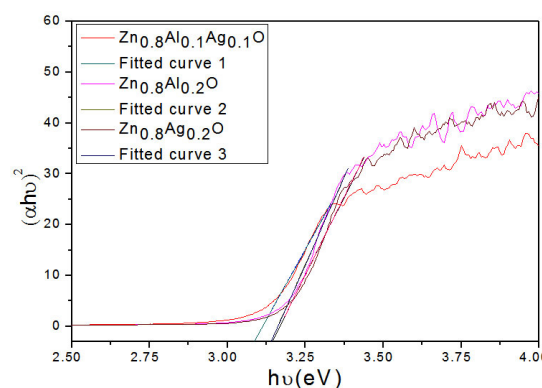


Fig. 7 (a): Spectra for band energy gap ($h\nu$) vs $(\alpha h\nu)^2$ for undoped ZnO nanoparticles

Table 2: Variations of band gap and Urbach energy (eV) with increase in concentration of Co doped ZnO

Compound	Wave-length(nm)	Band gap(eV)	Urbach energy(eV)	weight percentage				Atomic percentage			
				Zn	Ag	Al	O	Zn	Ag	Al	O
undoped ZnO	403	3.07	2.045	87.9	-----	-----	12.1	77.5	----	-----	22.5
Zn _{0.8} Al _{0.2} O	398	3.1	1.656	73	-----	0.16	26.8	71.8	----	0.17	28.03
Zn _{0.8} Ag _{0.2} O	398	3.11	1.863	64.3	0.15	-----	35.5	60.2	0.18	-----	39.62
Zn _{0.6} Al _{0.2} Ag _{0.2} O	396	3.13	0.953	51.9	0.2	0.19	47.7	59.7	0.2	0.2	39.9

reliable and identical shape. It is clearly indicated the crystalline size is relatively same as that of the SEM measurement. The particle size goes on increasing because dopant Ag as shown in Fig. 4(B) but in Fig. 4(C), Al dopant are as some smaller particles size i.e. it both the cases both different dopant disperse equally in the different sites. SEM micrograph is shown as that for undoped ZnO nanoparticles come out in smaller form, rather than the codoped ZAAIO nanoparticles become visible in smaller size which is confirmed by the XRD results. Wu et. al. has also reported on SEM images of undoped Al doped ZnO that effect by Ag nanoparticles as Ag/Zn = 0.05 (b), 0.10 (c) and 0.15 (d) at.%, which indicate almost similar effect of doping particles as shown in studies¹⁴.

The undoped, doped (Ag, Al) and codoped nanoparticles are synthesized by EDX for finding the detail of elemental composition as shown in Fig. 5(a)-(d). The EDX analysis confirms the presence of Ag, Al, O, and Zn in different doped samples, without any extra interpretation of other impurity element. In case of codoped (Zn_{1-x-y}Ag_xAl_yO) samples are hold Ag, Zn, Al, and O elements concluded by EDX spectrum. The EDX spectral peaks of O shown at 0.4keV; Zn come into existence at 0.5, 8.4, and 9 keV; as Ag signal indicated its appearance at 0.4, and 5keV, Al peak come at 0.75keV respectively. The EDX results additional confirm XRD results, which reveal that Ag- and Al-codoped ZnO is effectively as prepared by the chemical precipitation method.

Optical Studies

The UV-Vis spectrophotometer is used to analyse the optical properties of these undoped, doped and codoped ZnO (Zn_{1-x-y}Ag_xAl_yO) nanoparticles, against

as a function of wavelength varies with absorption having range 200-800nm at room temperature. The following relationship is used to determined the energy band gap for absorption

$$\alpha = A (h\nu - E_g)^n \quad \text{.....(4)}$$

Where $h\nu$ = energy, α =absorption coefficient ($\alpha=4\pi K/\lambda$; k is the absorbance, λ is wavelength), E_g = band gap, A = constant, $n=2$ for allowed direct band gap. The plot shows the variation between the direct Vs photon energy for doped ZnO nanoparticles. This variation has been help to analyse, the band gap and Urbach energy value. Suwanboon et. al. also was been found out optical band value for al doped ZnO nps¹⁵. The Urbach energy (eV) was also used to find out the disorder of these ZnO nanoparticles shown in table 1, which express in this relation

$$A = A_0 \exp (h\nu / E_u) \quad \text{.....(5)}$$

From figure 2, the value of band gap increases with increases in the concentration of silver doping. The opposite result is shown for Urbach energy (eV) of Zn_{1-x-y}Ag_xAl_yO nanoparticles for all samples as compile in table 2 i.e. it value decrease with increase the silver content. This reveals that blue shifted occur for ZnO samples which are indicate by representation of increase occur in the band gap value. These band gap values are acquire by doped and codoped samples, which will be effective as in optoelectronic properties.

Conclusions

In this study, the undoped, doped and codoped ZnO nanoparticles were studied to find out their structural, morphological, optical properties that

were synthesised by using a chemical precipitation route. The structure and crystalline size of samples is calculated by X-ray diffraction (XRD). XRD analysis shows that the prepared samples are single phase and have hexagonal wurtzite structure phase in the range of 20-600. The crystallite size is decreased for undoped, Al doped and codoped ZnO nps except for Ag doped ZnO nps as increased with concentration of dopant concentrations, which is determined

using Scherrer, Williamson hall method and size strain plot (SSP) method. The SEM micrographs are showing that agglomeration forms in spherical shape for undoped, doped and codoped ZnO. EDS has shown the formation of doped and codoped (Al^{2+} and Ag^+) in ZnO matrix. The blueshift was indicated for undoped, doped and codoped ZnO in case of UV-Vis absorption spectra.

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