

Effect of Carbon Spheres on the Structural and Optical Properties of Zinc Aluminate Doped with Copper Prepared by sol-gel Method in Presence of Glycine as Chelating Agent

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Abstract: Sol-gel is used for preparation of zinc aluminate nanomaterials doped with copper in presence of glycine as a chelating agent with different molar ratios (0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) and co-doped with C/Cu (II). The formed nano-powders were investigated using EDX, XRF, XRD and HR-TEM and studying their optical properties using UV spectrum and photoluminescence (PL). The prepared nano-powders were developed by loading them with carbon spheres. Then, they were investigated using all the previous instruments to be found that there is a decrease in the crystal size and optical band gap. From that; it is an evidence there is a great combination between CSs and $\text{Zn}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0 molar ratios). The importance of the present work stems from the success of development of optical properties of modified zinc aluminate semiconductor doped with Cu ion and co-doped with C/Cu and consequently more optical and industrial applications. The co-doping of semi-conductors usually very efficient in changing its energy gap and consequently its optical activity as proved in this research. It is also proved that the presence of glycine as chelating agent help efficiently doping and co-doping process and consequently efficiently changing characters of the studied and newly prepared zinc aluminate semiconductor by sol-gel method.

Keywords: Doped Zinc Aluminate, Sol-gel Preparation, Carbon Spheres, Structure Investigation, EDX, XRD, XRF, HRTEM, Optical Properties.

1 Introduction

Metal aluminates are ternary metal oxides having a general formula MAl_2O_4 , where M is a divalent metal ion. ZnAl_2O_4 shows an excellent photo resistivity, high chemical stability, endurance in storage, shows no emission of radiation and is robust in different environmental conditions which make them widely applicable in a number of fields such as forensics, signage, electronics [1-4]. ZnAl_2O_4 has interesting properties such as high chemical, thermal, and mechanical stabilities and also have interesting electrical, magnetic, and optical properties that make them suitable for applications such as photocatalysis, sensing, optoelectronic devices, displays, and imaging. ZnAl_2O_4 has a combination of desirable properties, such as high stability, high mechanical strength, better diffusion, low surface

acidity and high quantum yields. ZnAl_2O_4 is one of best wide band gap compound semiconductor ($E_g = 3.8$ eV). Thus, ZnAl_2O_4 spinel is a nontoxic, low-cost material and has high thermal stability.

These are used as a catalysts or catalyst support in several industrial and automobile applications [5] as a transparent conductive oxide [6] and are also used for its dielectric properties [7, 8]. Moreover zinc aluminate nanoparticles are used as a catalyst transesterification of waste cooking oil [9]. ZnAl_2O_4 spinels are excellent hosts for doping with rare earth ions (RE (III)) and transition metal ions to tune their photo-physical properties, for applications such as displays, solid state lighting, waveguides, biomarkers [10-13]. Surface modification with carbon spheres (CSs) have been of considerable interest recently. Coating the CSs with metal, alloy, oxide, or semiconductor nanoparticles could improve the functionality, compatibility, and reactivity of

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the surface. Therefore, spheres with specific catalytic, magnetic, electronic, optical, or optoelectronic properties have greatly widened their utility in the fields of electronics, magnetism, optics, catalysis, and bioscience [14–20]. Carbon provides several advantages as a metal nanoparticle support including inertness in acidic and basic conditions, thermal and mechanical stability of the porous structure, and high surface area and defined/modifiable porous structure [21]. For example, [15] fabricated ZnO nanoparticles and nano-rods coated on CS surfaces. The results were observed in all products.

The aim of the present paper, $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ nanoparticles have been synthesized by sol-gel in presence of glycine as a chelating agent where x (0.0, 0.2, 0.4, 0.6, 0.8 and 1.0). Then, it was developed by loading the prepared nanoparticles with CSs. The effect of CSs on $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ nanoparticles were investigated.

2 Experimental

2.1 Materials

The employed aluminum source is aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ 98%, 241.45 g mol⁻¹, Loba. Chemie). Zinc chloride (ZnCl_2 97%, 136.286 g mol⁻¹ Loba Chemie) is the source of zinc. Copper source is copper chloride (CuCl_2 98%, BDH chemical Ltd.). Sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$ 99.5%, 342.30 g mol⁻¹, Sigma-Aldrich) is the source of carbon spheres. Glycine ($\text{C}_2\text{H}_5\text{NO}_2$ 98%, 75.06 g mol⁻¹ Sigma Aldrich) is chelating agent. Hydrochloric acid (HCl) (M.wt = 36.46 g mol⁻¹) with purity 30-34 % were purchased from ADWIC. The distilled water used in all preparations usually collected from all glass equipment.

2.2 Solutions

A solution of 0.1 M Zinc chloride ZnCl_2 (> 97% purity) (M.wt = 136.286 g mol⁻¹), was prepared by dissolving the accurately weighed amount (1.3629 g) in least amount of HCl (~1 ml) the appropriate volume of distilled water and the volume completed with distilled water 100 mL.

A solution of 0.1 M aluminum chloride hexahydrate $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (> 98%) (M.wt = 241.45 g mol⁻¹), was prepared by dissolving the accurately weighed amount (2.4145 g) in the appropriate volume of distilled water and the volume completed to 100 mL volumetric flask.

2.3 Preparation Procedures

2.3.1 Synthesis of Carbon Spheres

Carbon spheres (CSs) were prepared by one step process, where sucrose is the source of carbon then heated at 100°C for 24h.

2.3.2 Synthesis of Zinc Aluminate Doped With Cu(II) Nanoparticles using sol- gel in Presence of Glycine Method Unloaded with Carbon Spheres

$\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ nano-powder ($x = 0.0, 0.2, 0.4, 0.6, 0.8$, and 1.0) has been successfully synthesized using glycine for calcination. Firstly, aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ 98%) solution was added to zinc chloride (ZnCl_2 97%), that were used without any further purification, with Zn: Al molar ratio of 1:2 and a solution of copper chloride (CuCl_2 98%) possess molar ratios 0.0, 0.2, 0.6, 0.8, 1.0. A solution of glycine was added to the solution related to metals ions content. Then, ammonia was added to the solution until pH = 7. Thereafter, the solution was gently stirred for 15 min on hot-plate magnetic stirrer at room temperature. After that, the solution was evaporated at 80 °C with constant stirring until viscous gel was obtained. The gel was dried at 100 °C for 24 h to form pure and doped zinc aluminate. Finally, the dry precursors were thermally treated at a rate 4°C/min in static air in muffle furnace at 1000 °C.

2.3.3. Synthesis of Zinc Aluminate Doped with Cu(II) Nanoparticles Using sol -gel Method Loaded with Carbon Spheres

The prepared zinc aluminate doped with copper nano-powder from 2.3.2 were grinded with carbon spheres in proportions 25% of CSs and 75% of Zinc aluminate substituted by Cu(II) nanoparticles for 20 min.

X-ray fluorescence (XRF) is a powerful quantitative and qualitative analytical tool for *elemental* analysis of materials. Determination of the elements in nano-powders were carried out using X-ray fluorescence spectroscopy (XMDS 2726), with max.45 KV/ 50 µA.

XRD patterns of the resulting products were characterized by a Bruker D8-advance X-ray powder diffractometer Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The crystallite sizes of the produced $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ (where $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) spinels were calculated from the most intense peak using Debye Scherrer formula:

$$d_{RX} = \frac{k\lambda}{\beta} \cos 2\theta \quad (1)$$

Where d_{RX} is the crystallite size, $k = 0.9$ is a correction factor to account for particle shapes, β is full width at half maximum (FWHM) of the most intense diffraction peak (3 1 1) plane, λ is the wavelength of Cu target = $1.5406 \text{ \AA}$, and θ is the Bragg angle at $2\theta = 35.42^\circ$ which is strongest peak was used to calculate the average size of the nanoparticles. The micrographs of produced $\text{Cu}_{(x)}\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ spinel samples were inspected by direct observation via high resolution transmission electron microscope (HR TEM; JEM-2100, Japan). HR-TEM samples were prepared by dispersing the powders in acetone. Ultrasonic oscillation for 1 h was introduced to decrease the aggregation followed by placing a drop of the suspension on holey carbon film supported on copper grids. The UV-VIS absorption and diffuse reflectance spectrum were recorded at room temperature using UV-VIS-NIR spectrophotometer (Jasco-V-570 spectrophotometer, Japan) fitted with integrating sphere reflectance unit (ISN) in the wavelength range 200-2000 nm. Photoluminescence (PL) spectra were obtained at room temperature using fluorescence spectrophotometer (SHIMADZU RF-5301PC Japan) with xenon discharge lamp (150 W) as excitation source, at room temperature using an excitation wavelength equal to 200 nm. All of the above measurements were made at Central Metallurgical Research and Development Institute and Institute of Petroleum technology, Cairo Egypt.

The EDX had been performed in Faculty of high education Bani Suif University, Giza Egypt. It was measured for the prepared nanomaterial samples using the instrument JEOL 6510(LA), under conditions Acc. Voltage: 30.0 kV, Probe Current: 1.00000 nA, PHA mode : T2 Real Time : 176.69 sec.

3 Results and Discussion

3.1 EDX Study of Zn Aluminate $\text{Cu}_{(x)}\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ of $x = 0.0$ to 1% Prepared by sol-gel Method Unloaded with Carbon Sphere using Glycine Catalyst

The prepared pure Zn aluminate nano-material obtained by sol-gel procedure before doping with Cu is actually tested by EDX and to test elements ratios present in its proposed general formula $\text{Cu}_{(x)}\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ of $x = 0.0$ to 1% . The results of EDX analyses of pure Zn aluminate are given in Fig (1).

These results confirm the successful preparation of pure Zn aluminate of the formula $\text{Cu}_{(x)}\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ of $x = 0$, by sol-gel method in presence of glycine without carbon sphere loading. This success encourage us to start doping of pure zinc aluminate with different ratios of Cu to change its morphology and consequently its electrical and optical properties, with aim to use them in various industrial applications as semiconductors.

The first trial starts with doping with 0.2 % Cu and results obtained are shown in Fig (2).

These results refer to success of doping of Cu into the moiety of pure Zinc aluminate on the expense of Zn ion. To confirm these results the second trial starts with doping Zinc aluminate with 0.6 % Cu to get $\text{Cu}_{(x)}\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ of $x = 0.6$ and the results obtained are shown in Fig (3).

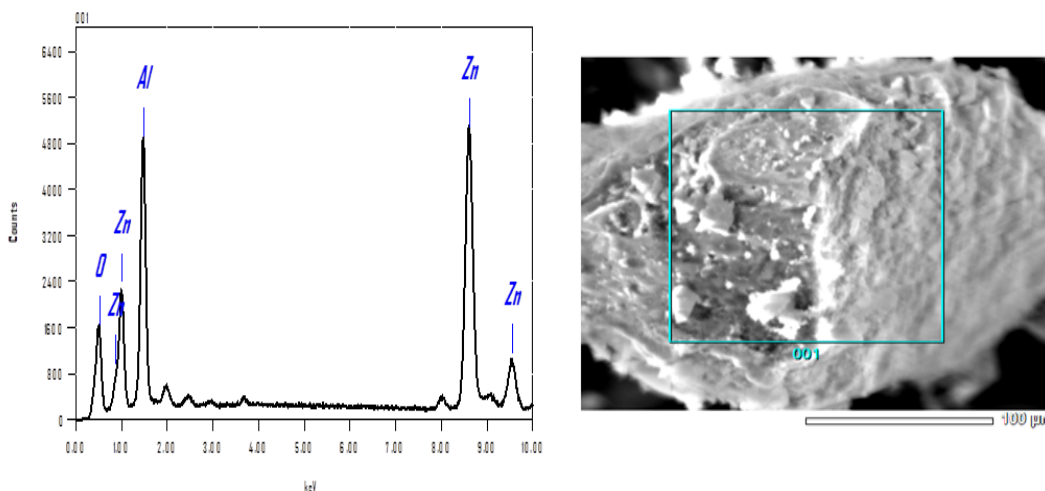


Fig.1: EDX of non-doped zinc aluminate with Cu ions, $\text{Cu}_{(x)}\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ of $x = 0$, nano-material, prepared by sol-gel non-loaded by carbon sphere.

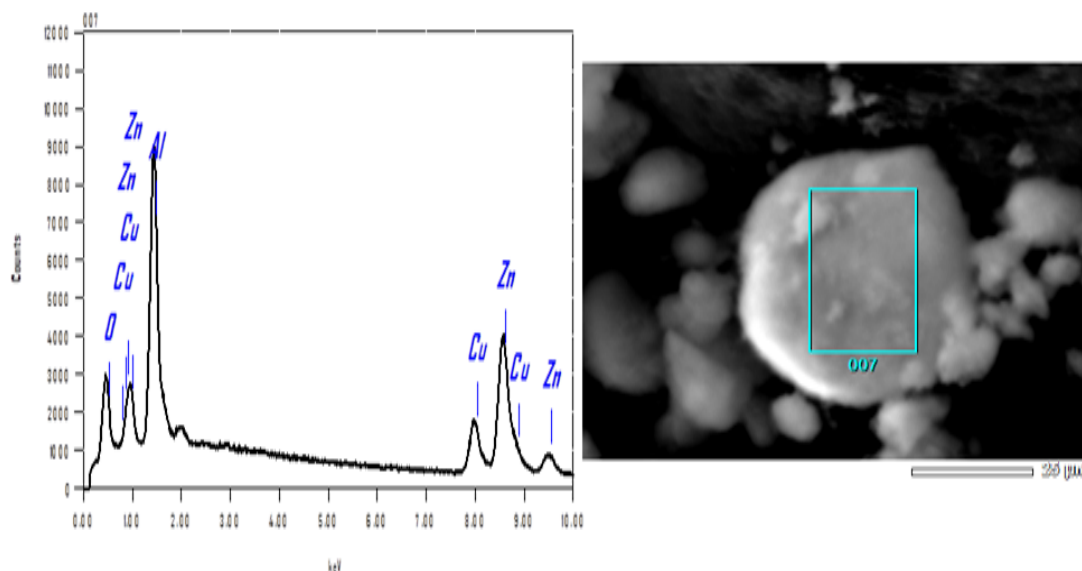


Fig.2: EDX graph of Zn aluminate doped with 0.2 % Cu, $\text{Cu}(x) \text{Zn}(1-x)\text{Al}_2\text{O}_4$ of $x = 0.2$, nano-material, prepared by sol-gel non-loaded by carbon sphere.

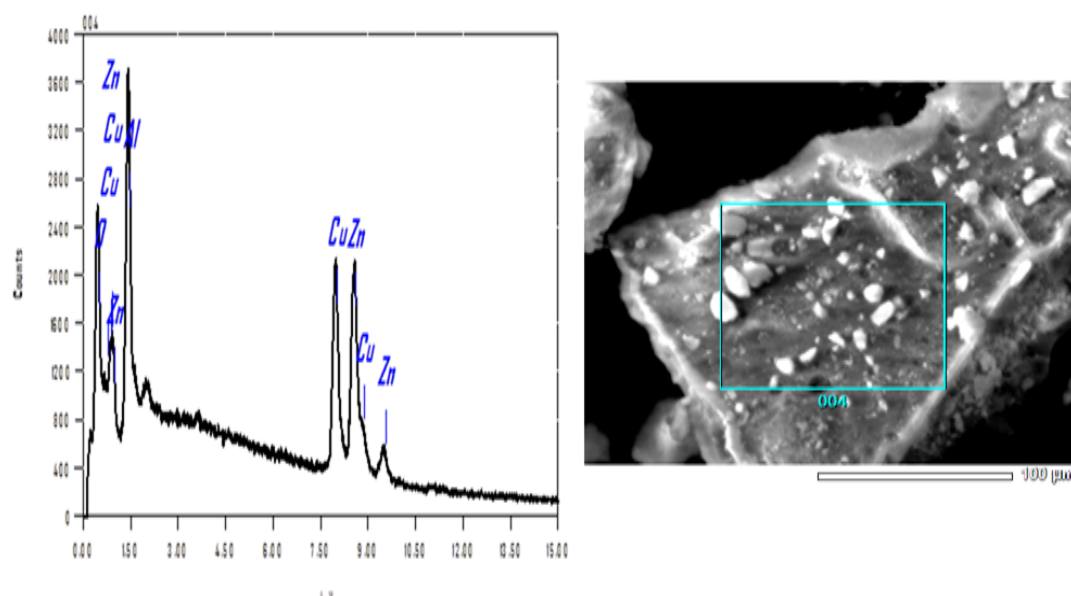


Fig.3: EDX graph of Zn aluminate doped with 0.6 % Cu, $\text{Cu}(x) \text{Zn}(1-x)\text{Al}_2\text{O}_4$ of $x = 0.6$, nano-material, prepared by sol-gel non-loaded by carbon sphere.

These results refer to the increase of Cu doping into the moiety of pure Zinc aluminate on the expense of Zn ions and particles sizes are varied with the variation of doped copper percent due the increasing of Cu concentration.

These results are also confirmed by preparation of pure copper aluminate nanomaterial $\text{Cu}(x) \text{Zn}(1-x)\text{Al}_2\text{O}_4$ in which $x = 1$, and Zn % = 0.0. The EDX results of pure

copper aluminate nanomaterial prepared by sol-gel method using glycine chelating agent without carbon sphere loading are given in Fig (4).

These results (Figs 5-7) confirm the variation of morphology of the prepared nanomaterials by the variation of elements percent under the given conditions. The practical determination of the elements as constituents of the given nanomaterial is

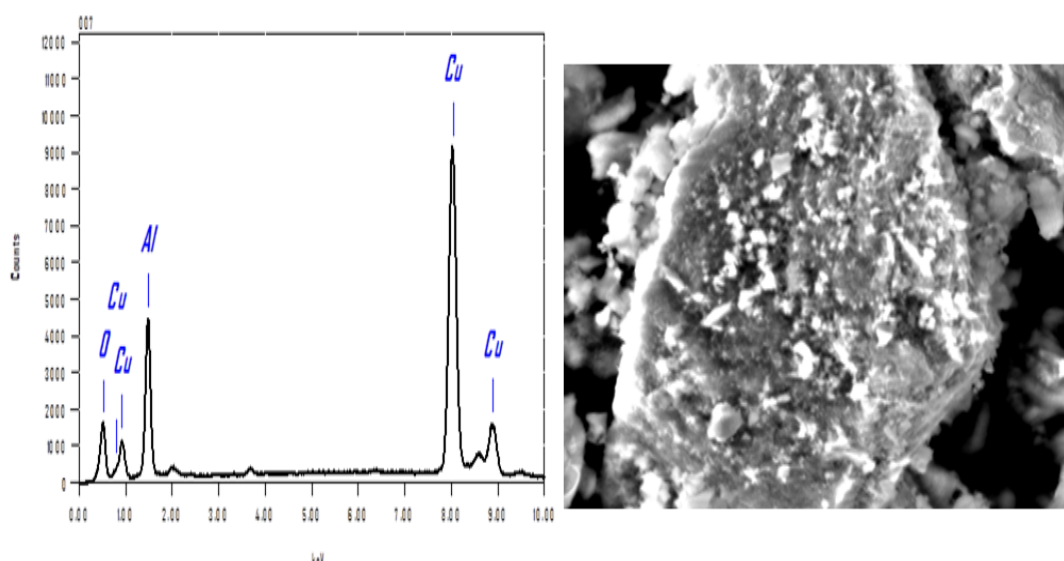


Fig.4: EDX graph of pure copper aluminate, $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ of $x = 1$, nano-material, prepared by sol-gel non-loaded by carbon sphere.

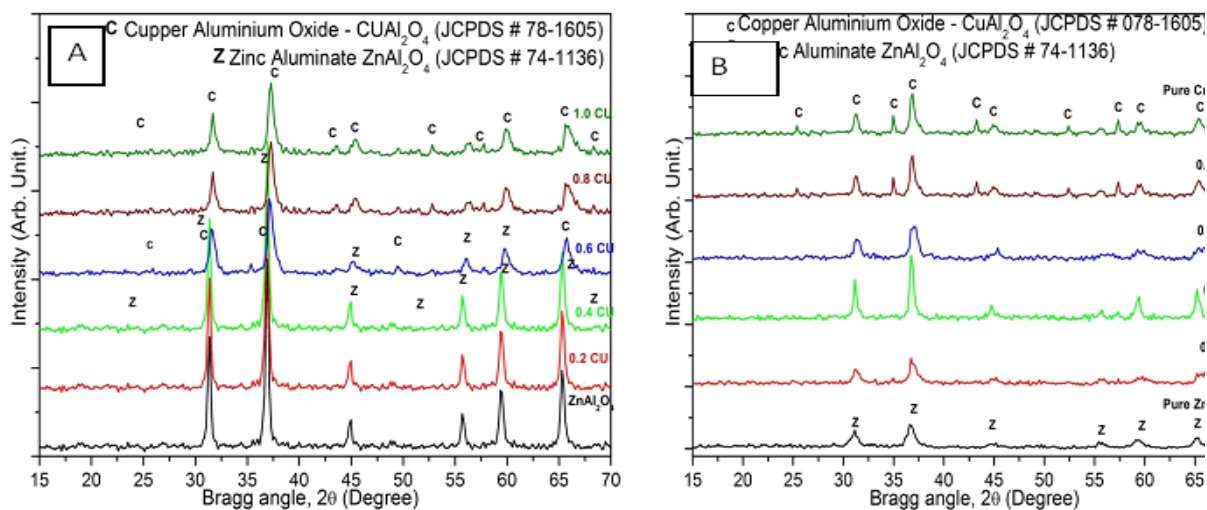


Fig.5: XRD patterns of $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ (x from 0.0 to 1.0 molar ratios) annealed at 1000 °C for 2 h using sol-gel method in presence of glycine A) Unloaded with CSs, B) Loaded with CSs

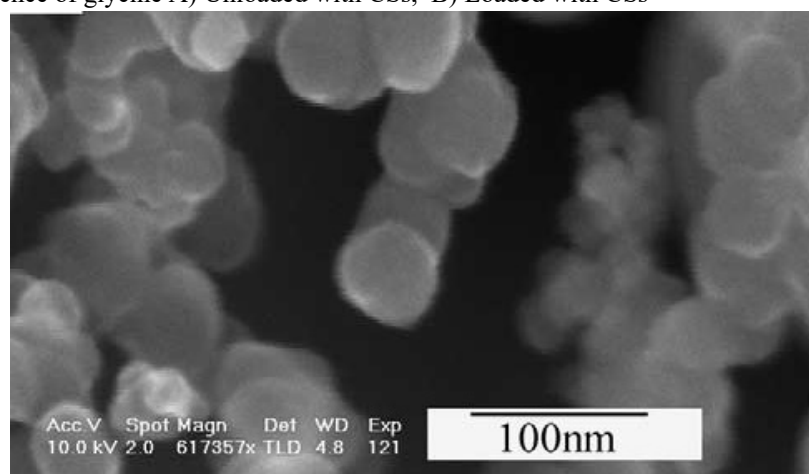


Fig.6: FESEM micrographs of carbon sphere.

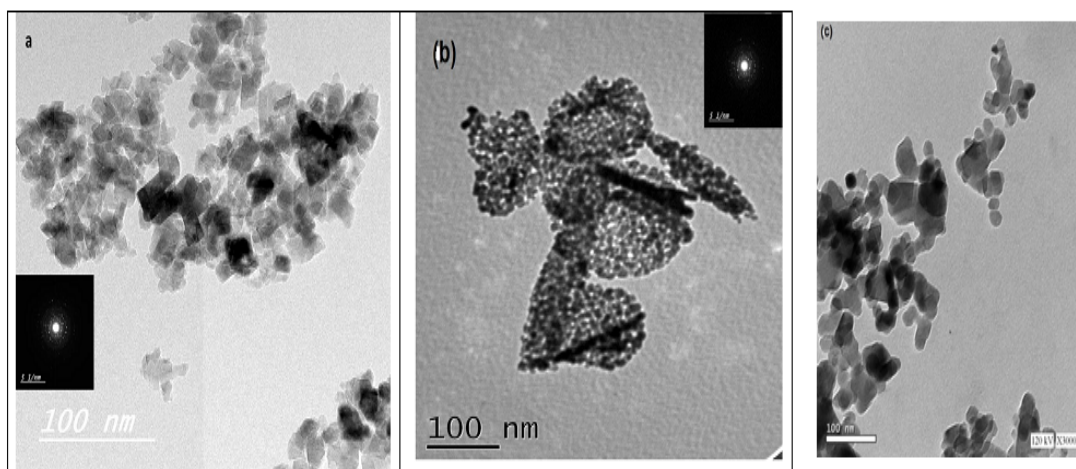


Fig.7. HR-TEM micrographs for $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ where **a)** x is 0.0, **b)** x is 0.6 molar ratios and **c)** x is 1.0 molar ratios annealed at 1000°C for 2 h using sol-gel method in presence of glycine unloaded with carbon spheres.

required to confirm its general formula $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$. This is well be done by the XRF as a more accurate analytical tool to confirm results that obtained by EDX tool.

3.2 X-Ray Fluorescence Study of zinc Aluminate Nanoparticles Doped with Cu(II) Synthesized by sol-gel using Glycine Method Unloaded with Carbon Sphere.

The XRF as a more accurate analytical tool is used for elemental analysis of the prepared zinc aluminate nanomaterial, $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ doped with Cu(II) synthesized by sol-gel of unloaded with carbon sphere using glycine as catalyst, and the results are shown in Table (1).

From the data presented in Table1, it can be seen that; the formed nanoparticles have similar proportions without any contaminations; that confirms the formation of a pure zinc aluminate doped with Cu(II) nanoparticles. Moreover, the listed results show that the practical and theoretical weight percentage of each element is much closed to each other. So zinc aluminates doped with copper is formed in correct proportions. These results are more / or less correlated with EDX; which confirms purity of the prepared nanomaterials without contamination with extraneous ions.

3.3 XRF of Carbon Spheres Loaded with Zinc Aluminate Doped with Cu(II) Nanoparticles Synthesized by sol- gel Method in Presence of Glycine

XRF data in Table 2 give an indication that; the proportions of carbon spheres in $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ ($x=0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0 molar ratios) are closely to 25% and 75% of other constituents.

It also confirms the successful doping of the prepared nano-materials with carbon sphere of different ratios aiming to change its electrical conductivity and its optical properties to be used as more efficient nano-materials and semi-conductors in different industrial applications. The study of the crystallographic structure and fine morphology of the prepared and doped zinc aluminate with copper and carbon sphere is very important in evaluation of their future uses. This study on both nano-materials doped and/ or non-doped with carbon sphere, shall be done by XRD and high resolution tem (HRTEM).

3.4 Structure Identification of Zinc Aluminate Doped with Cu(II) Nanoparticles Unloaded and Loaded with Carbon Spheres

3.4.1 X-ray diffraction (XRD) Study of the Prepared Nanomaterials:

XRD diffraction patterns of zinc aluminate doped by Cu(II) ions with different molar ratios (0.0, 0.2, 0.4, 0.6, 0.8, 1.0) synthesized by sol-gel method using glycine catalyst that unloaded and loaded with carbon spheres (CSs) are shown in Fig.5.

Table1: The practical and theoretical weight percentage of $\text{Cu}_{(x)}\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ nanopowder $x= 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$ using sol-gel in presence of glycine method unloaded with carbon sphere using XRF

	<i>Cu(II) ions molar ratio</i>	<i>Practical Weight percentage (%)</i>	<i>Theoretical Weight percentage (%)</i>
Zn(II)	0.0	34.00	36.00
	0.2	30.00	28.85
	0.4	22.00	21.48
	0.6	16.00	14.35
	0.8	5.00	7.19
	1.0	0.01	0.00
Al(III)	0.0	27.80	29.43
	0.2	26.99	29.48
	0.4	27.10	29.54
	0.6	28.24	29.60
	0.8	30.00	29.66
	1.0	28.90	29.72
Cu(II)	0.0	0.00	0.00
	0.2	9.00	6.90
	0.4	12.19	13.90
	0.6	19.00	21.00
	0.8	29.00	27.95
	1.0	36.57	35.01
O(II)	0.0	38.20	34.91
	0.2	34.01	34.77
	0.4	38.71	35.08
	0.6	36.76	35.08
	0.8	36.00	35.20
	1.0	34.52	35.27

Table 2: Weight taken and weight found percentage of carbon spheres used for loading with zinc aluminate substituted by Cu(II) nanoparticles synthesised by sol- gel method in presence of glycine using XRF

<i>Cu(II) ions molar ratio</i>	<i>Weight taken percentage (%)CSs</i>	<i>Weight found percentage (%) of CSs</i>
0.0	25.00	23.88
0.2	25.00	23.64
0.4	25.00	24.50
0.6	25.00	24.80
0.8	25.00	24.26
1.0	25.00	24.56

Table 3 : Variation of crystallite size, Bragg angle, lattice parameter, unite cell volume and X-ray theoretical density of $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ unloaded with carbon spheres; where x 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 molar ratios annealed at 1000°C for 2 h using sol- gel method in presence of glycine.

Cu(II) ions molar ratio	Cry. Size (nm)	Bragg angle (2θ)	Lattice parameter (Å)	Unite Cell volume (Å³)	X-ray theoretical density ρ (g/cm³)	Optical band gap energy (eV)
0.0	11.9	36.998	8.076	526.747	4.624	3.23
0.2	35.7	36.915	8.070	525.463	4.626	2.04
0.4	15.4	36.747	8.105	532.439	4.556	2.13
0.6	23.7	36.939	8.064	524.453	4.616	2.06
0.8	16.2	36.937	8.065	524.550	4.606	2.03
1	20.4	36.947	8.063	524.116	4.601	1.98

Fig 5.(1.A) shows formation of single phases of $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ (x =0, 0.2, 0.4, 0.6, 0.8 and 1.0); which confirms single phase results previously obtained by EDX. The peaks are belonging to cubic structure with space group $Fd\bar{3}m$ (JCPDS card # 74-1136) for ZnAl_2O_4 phase and (JCPDS card # 78-1605) for CuAl_2O_4 . The figure shows that a right shift after increasing copper percentage that attributed to the change in microstructure (the lattice strain and crystal size). This effect is mainly due to the difference in ionic radii between zinc and copper. Also it is found, that when Cu(II) have been incorporated into the lattice it changed the lattice constant of the host **Table 3**. This is an evidence that Cu(II) incorporated successfully; which

confirm results previously obtained by EDX . After loaded CSs there is a decreasing in the peaks intensity and become more broader due to the decrease in the crystal size as indicated by Fig 5.(1.B) and Table 3.

3.4.2. Microstructure and Morphology Study of the Prepared Carbon Sphere

The morphology of the synthesized carbon spheres was investigated by the field emission scanning electron microscopy (FESEM) and the results are shown in **Fig.6**.

The results in **Fig.6** certify that; the carbon spheres have a spherical morphology; which deals with the previously

published data [22] with good dispersed structure and highly homogeneous in size. The figure shows that the sizes of the carbon spheres ~ 60 nm; so when carbon spheres added to the nanoparticle (zinc aluminate substituted with copper ion) will form a composite.

3.4.3 Microstructure and Morphology Study of the Prepared Nanomaterials High Resolution Transmission Electron Microscopy (HRTEM)

The microstructure and morphology study of the prepared zinc aluminate doped with Cu (II) nanoparticles synthesized by sol-gel method in presences of glycine unloaded with carbon spheres were studied by High Resolution Transmission Electron Microscopy (HRTEM). The HRTEM micrographs of zinc aluminate substituted by Cu(II) with molar ratios $x=0.0, 0.6, 1.0$ are shown in Fig.(7.a, b, c).

The morphology is homogeneous and spinel particles with cubic structure consist of uniform spherical crystallites of an average size ~ 11 nm in Fig.(7.a) for pure zinc aluminate and for pure copper aluminate ~ 19 nm. After doping with copper ions Fig.(7.b), Cu(II) form a high aggregation between the components due to the dispersion between components due to the calcination during preparation using sol-gel.

3.4.4 HRTEM of Pure Zinc Aluminate and Pure Copper Aluminate Nanoparticles Loaded with Carbon Spheres Synthesized by sol-gel Method Using Glycine Catalyst.

The results of HRTEM used to study the effect of carbon sphere on the morphology of both pure zinc and copper aluminates are shown in Fig 8.

3.4.5. HRTEM of Zinc Aluminate Doped with Copper in Different Ratios Nanoparticles $Cu_{(x)}Zn_{(1-x)}Al_2O_4$ ($x = 0.2, 0.4, 0.6$ and 0.8) Loaded with Carbon Spheres Synthesized by sol-gel Method using Glycine Catalyst.

The results of effects of CSs on the morphology of zinc aluminate doped with copper in different ratios $Cu_{(x)}Zn_{(1-x)}Al_2O_4$ ($x = 0.2, 0.4, 0.6$ and 0.8) loaded with carbon spheres synthesized by sol-gel method using glycine catalyst studied by HRTEM are shown in the following Fig. (9):

This figure shows that, there is a pronounce variation in the crystal size in presence of carbon sphere and with the variation of doped Cu (II) % $x = 0.2$ of crystal size in the range 51.2-30.4 nm, at $x = 0.4$ the size in the range 22.7 to 13.7 nm, at $x = 0.6$ the crystal size is in the range 13.9 to 10.2 nm and at $x = 0.8$ the size is in the range of 12.5 to 10.2 nm. This refer to the good combination between CSs and moiety of nano-materials of $Zn_{(1-x)}Al_2O_4$ ($x = 0.2, 0.4, 0.6$ and 0.8) and the crystal size decreases with the increase of doped Cu (II) ratio. This means also the good doping and insertion of both carbon spheres and copper ions in the entity of the zinc aluminate. The decrease in crystal size of particles of the prepared zinc aluminate at different ratios of CSs and copper ions change effectively the electrical conductivities and optical properties of these materials. The promoted and changed properties shall be proved by measurement of their optical properties applying different spectrophotometric techniques like reflectance and photoluminescence (PL).

3.5 Optical Properties of Prepared nano-Materials

3.5.1 UV-VIS-NIR Spectra of zinc aluminate Doped with Cu(II) Nanoparticles Synthesized by sol Gel Method in Presence of Glycine Unloaded with Carbon Spheres (CSs)

The results of absorbance and reflectance curves of UV-VIS-NIR spectra of zinc aluminate doped with Cu(II) nanoparticles synthesized by sol gel method in presence of glycine unloaded with carbon spheres are shown in Figs.(10 and 11). These measurements were taken over the wavelength range 200–1200 nm.

From the presented results it is clear that, the absorbance is increasing from 0.4 (pure zinc aluminate) unloaded with CSs and during doping of Cu different ratios up to $x = 1$, i.e. reaching 0.85 in case of obtaining pure copper aluminate nanomaterial. The calculated optical band gap energy values are calculated from the above results and are shown in Table 4.

The data in first part of Table 4 reprinting unloded samples with CSs; show 3.23 eV for pure $ZnAl_2O_4$; which is close to the previously published [23] gave 3.89 eV of the band gap for $ZnAl_2O_4$: Eu and the small difference between them may be attributed to the presence of Eu(II) in the lattice of zinc aluminate. So $ZnAl_2O_4$ is one of best wide band gap (3.23 eV) compound semiconductor permit devices to

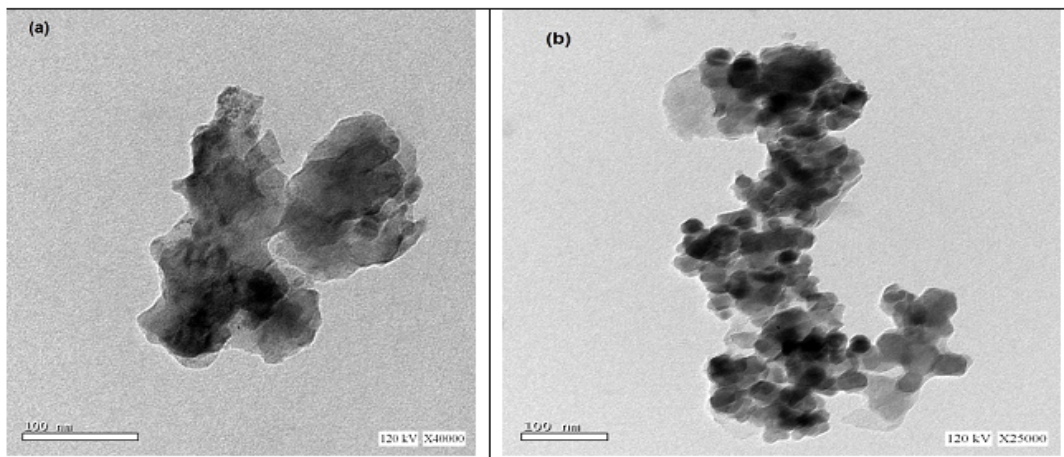


Fig.8: HRTEM micrographs for $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ where **a)** x is 0.0, **b)** x is 1.0 molar ratios annealed at 1000°C for 2 h using sol-gel method in presence of glycine Al_2O_3 loaded with carbon spheres. This figure shows that there is a high decrease in the crystal size to reach $\sim 10\text{nm}$ for ZnAl_2O_4 and $\sim 18\text{nm}$ for CuAl_2O_4 and that related to the good combination between CSs and moiety of nano-materials of $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ ($x=0.0, 1.0$) as shown in Fig. 8(a, b).

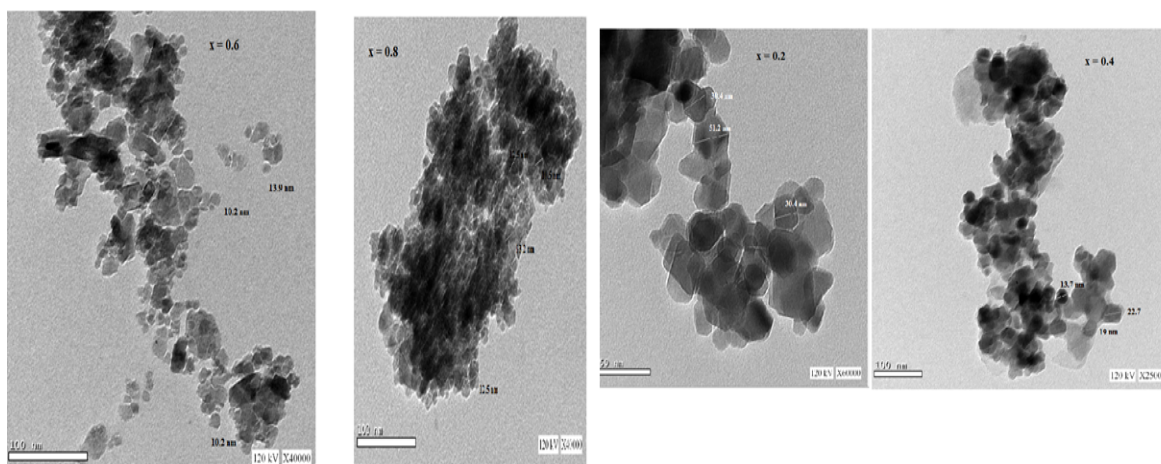


Fig.9: HRTEM of zinc aluminate doped with copper in different ratios nanoparticles $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ ($x = 0.2, 0.4, 0.6$ and 0.8) loaded with carbon spheres synthesized by sol-gel method using glycine catalyst.

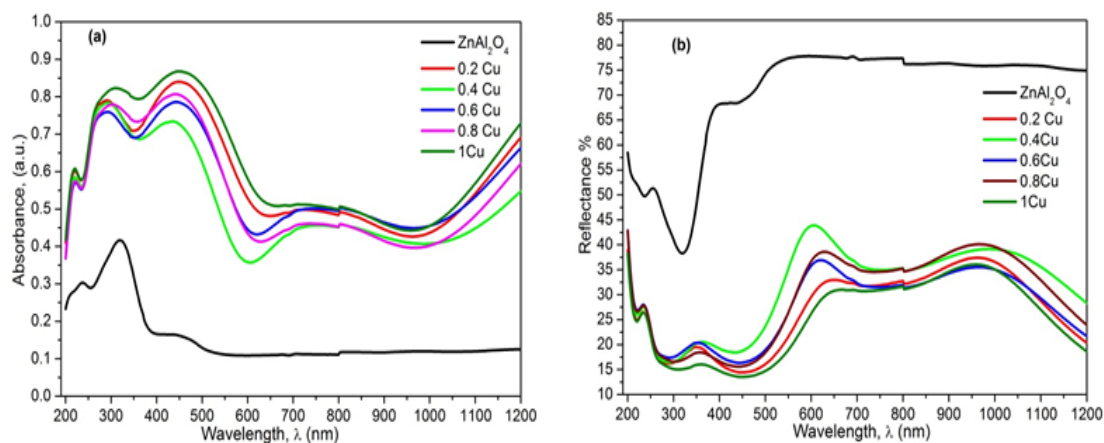


Fig.10 : Absorbance (b) Reflectance of $\text{Zn}_{(1-x)}\text{Cu}_x\text{Al}_2\text{O}_4$ nanopowders (where $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$), using sol-gel method unloaded with CSs.

operate at much higher voltages, frequencies and temperatures than conventional semiconductor material enabling them to be used in several lighting and sensing applications [24], UV-photo-electronic devices [25], electroluminescent displays or optomechanical stress sensors and stress imaging devices [26, 27]. It is found, there is a reduction in the band gap with increasing of Cu(II) ion to reach 1.98 eV for pure CuAl_2O_4 . This decrease in the band gap attributed to quantum limiting effect. Moreover, the crystallite size increases in presence of more atoms and more atomic orbitals for overlap. Therefore, the number of molecular orbitals, both bonding and antibonding, are increased and band gap between

HOMO and UMO (Band gap) will be decrease. Hence, the photocatalytic activity increases by increasing Cu(II) molar ratios.

3.5.2 UV-VIS-NIR Spectra of Zinc Aluminate Doped with Cu(II) Nanoparticles Synthesized by Sol Gel Method in Presence of Glycine Loaded with Carbon Spheres

The UV-VIS-NIR spectral data of zinc aluminate doped with Cu(II) nanoparticles synthesized by sol gel method in presence of glycine loaded with carbon spheres (CSs) are presented in **Figs .12 and 13**.

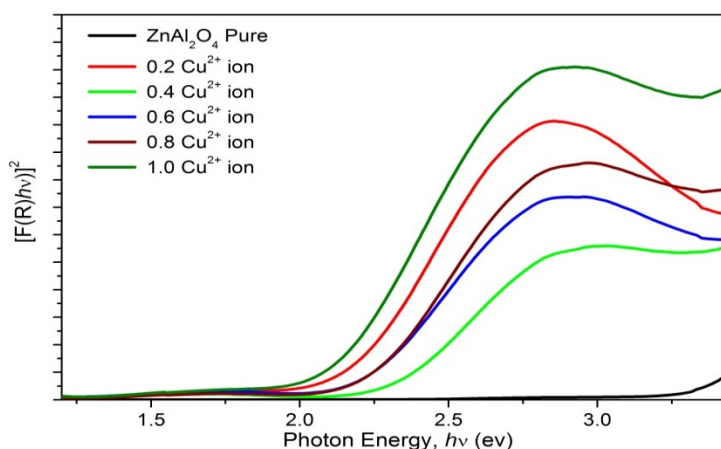


Fig.11: Optical energy gap of $\text{Zn}_{(1-x)}\text{Cu}_x\text{Al}_2\text{O}_4$, nanopowders (where $x = 0.0$ to 1.0) by using sol- gel method in presence of glycine unloaded with CSs.

Table 4: Variation of crystallite size and optical band gap energy of $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ where $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$ molar ratios annealed at 1000°C for 2 h using sol-gel in presence of glycine unloaded and loaded with CSs.

	<i>Cu(II) ions molar ratio</i>	<i>Cry. Size (nm)</i>	<i>Optical band gap energy (eV)</i>
$\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ Unloaded with CSs	0	11.90	3.23
	0.2	35.70	2.04
	0.4	15.40	2.13
	0.6	23.70	2.06
	0.8	16.20	2.03
	1	20.40	1.98
$\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ Loaded with CSs	0	8.19	3.16
	0.2	28.69	1.56
	0.4	13.95	2.16
	0.6	21.18	1.97
	0.8	14.89	1.94
	1	19.65	1.55

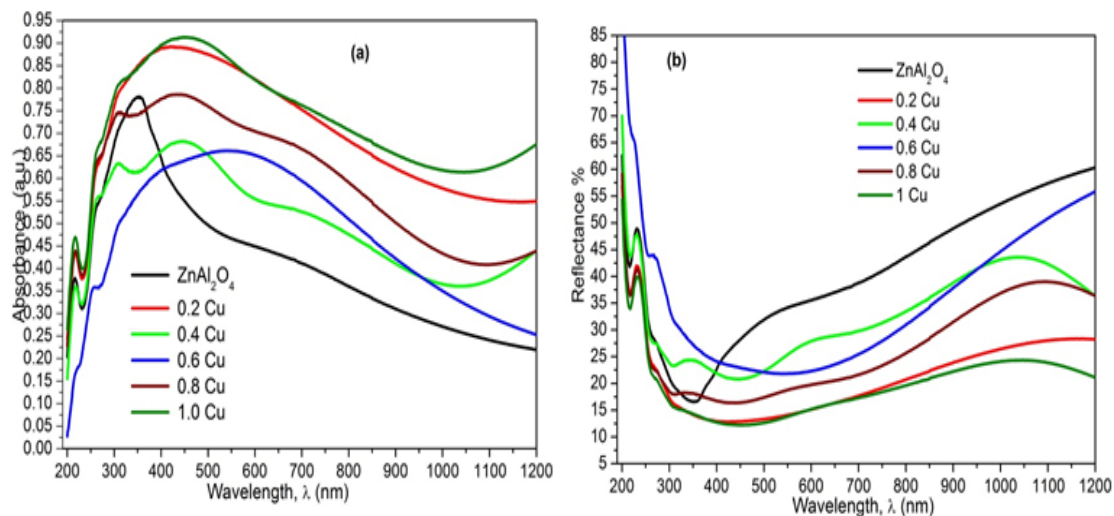


Fig.12: (a) Absorbance **(b)** Reflectance of $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ nanopowders (where $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) using sol gel method in presence of glycine and loaded with carbon spheres.

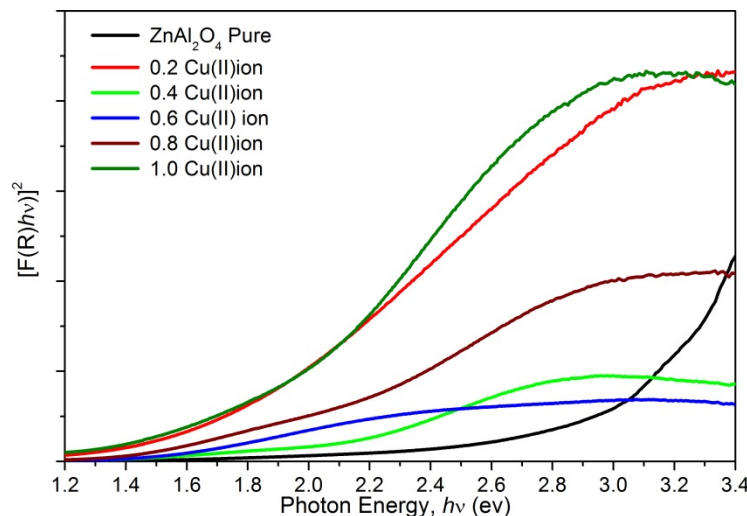


Fig.13: Optical energy gap of $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ nanopowders (where $x = 0.0$ to 1.0) using sol gel method in presence of glycine loaded with carbon spheres.

These data refer to increasing in the absorbance of ZnAl_2O_4 and CuAl_2O_4 to reach 0.80 and 0.93 respectively after combination with carbon spheres. So, the band gap decreases from 3.23 eV to 3.16 eV for pure zinc aluminate and from 1.98 eV to 1.55 eV for pure copper aluminate **Fig.13** and **Table 4**, that attributed to presence of carbon spheres. Therefore the presence of carbon spheres in the entity of the prepared nano-samples and increases of doped Cu% decrease the energy gap of these material and consequently facilitating the electronic transitions and promote their optical properties as semiconductors. Also the decrease in energy gap of these samples as a result of insertion of both CSs and Cu (II) ions enhance the photocatalytic activity of the prepared nanomaterials.

3.6 Photoluminescence Spectroscopy (PL) of the Prepared Nanomaterials

The study of PL spectra of newly prepared nano-materials at different conditions can give additional information about photocatalytic activity of these prepared compounds. It can find the wavelength which has the maximum emission for the sample (the material which has high emission then have high absorbance at this wavelength) **equation (3)**. So; it is possible to obtain the information of sub-band gap defect states (Kurbanov S.S. 2010) [28] in materials which can be influenced by the synthesis conditions (Anand GT. 2013) [29]

$$(\text{Energy}) E = \frac{hc}{\lambda} \dots\dots\dots (3)$$

Where h is Plank's Constant, C is Speed of light and λ is wavelength

PL can study the emission spectrum and provide information about the crystal defects of semiconductor which might be due to the oxygen vacancies.

3.6.1 PL of zinc Aluminate Doped with Cu(II) Nanoparticles Synthesized by sol Gel Method in Presence of Glycine Unloaded with Carbon Spheres

The results of PL of zinc aluminate doped with Cu(II) nanoparticles synthesized by sol gel method in presence of glycine unloaded with carbon spheres are shown in Fig 14. These PL spectra of zinc aluminate doped with Cu(II) nano powders was measured at room temperature and recorded at 200 nm excitation wavelength. It is found that, a sharp decrease in the intensity after addition of Cu(II) to zinc aluminate as shown in Fig.14.

These results may be attributed to the inhibition of recombination of charge carriers, geometrical distortions and creating oxygen vacancy. All samples show violet emission centered at about 400 nm (~ 3.10 eV) and exhibit weak broad luminescence bands with blue emission peak at 475 nm (~ 2.61 eV) and orange emission peak at 590-600 nm (~ 2.10 - 2.07 eV). The emission peaks that occurred in the PL spectra of each metal aluminate samples are attributed to the recombination of electrons and photogenerated holes involving various structural defects, such as the ionized charge states of intrinsic defects, oxygen vacancies, metal (Zn, Cu) vacancy, metal interstitials, and oxygen intensities [30-33]. An electron in the valence band (VB) can be excited to higher energy levels in the conduction band (CB) then falls to the conduction band maximum (CBM) through internal conversion (IC) and vibrational relaxation (VR). The electron at CBM can then radiatively recombine with a hole

in the valence band or defect states in the band gap resulting in the violet, blue and orange light emissions. Therefore, the photoluminescence analysis of nanoparticles doped Cu (II) ions, $\text{Cu}_{(x)}\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ with different molar ratios exhibit interesting abilities for applications in violet, blue and orange light-emitting devices. Moreover, the intensity decreases after doping with Cu (II) due to the inhibition of recombination of charge carriers and inducing geometrical distortion and creation of oxygen vacancy. So during doping the energy levels increase and reducing the band gap Table 4. It also simultaneously decrease in the recombination rate of electron-hole due to which intensity decreases and peak are boarded that means low recombination of electron and holes give better photocatalytic activity [34].

3.6.2 PL of Zinc Aluminate Doped with Cu (II) Nanoparticles Loaded with Carbon Spheres Synthesized by Sol- Gel Method in Presence of Glycine

The PL spectra of zinc aluminate doped with Cu(II) nanoparticles loaded with carbon spheres synthesized by sol- gel method in presence of glycine are given in Fig 15. These data show that, zinc aluminate doped with Cu(II) nanoparticles loaded with carbon spheres give a violet emission at about 400 nm and weak broad luminescence bands with blue emission peak at 475 nm (~ 2.61 eV) and orange emission peak at 590-600 nm (~ 2.10 - 2.07 eV). After addition of carbon spheres the intensity of PL bands of $\text{Cu}_{(x)}\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$, nanopowders decreases so; the photocatalytic activity increases Fig.15. Hence, carbon spheres enhance the photocatalytic activity of the prepared nanomaterials.

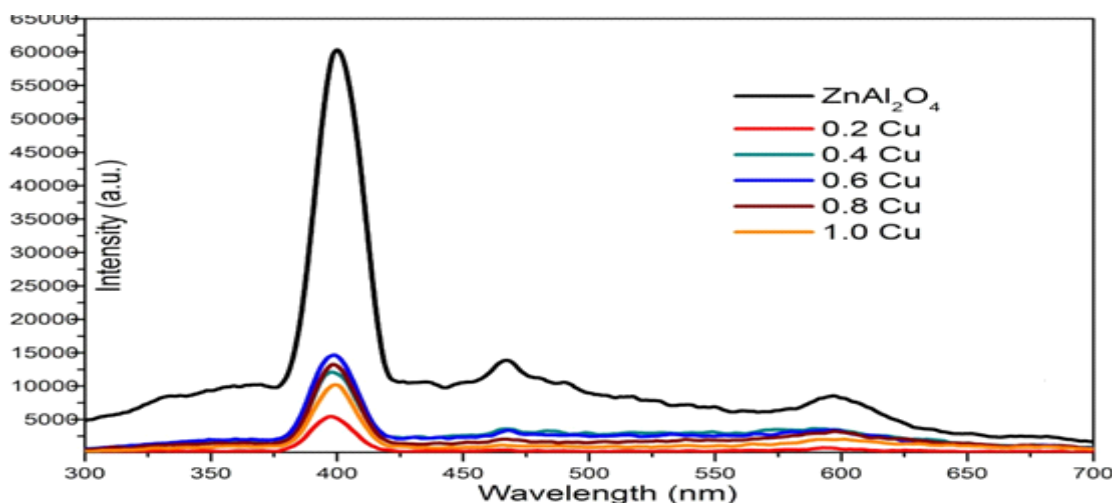


Fig. 14 : PL of $\text{Cu}_{(x)}\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$, nanopowders (where $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) using sol-gel method in presence of glycine unloaded with CSs

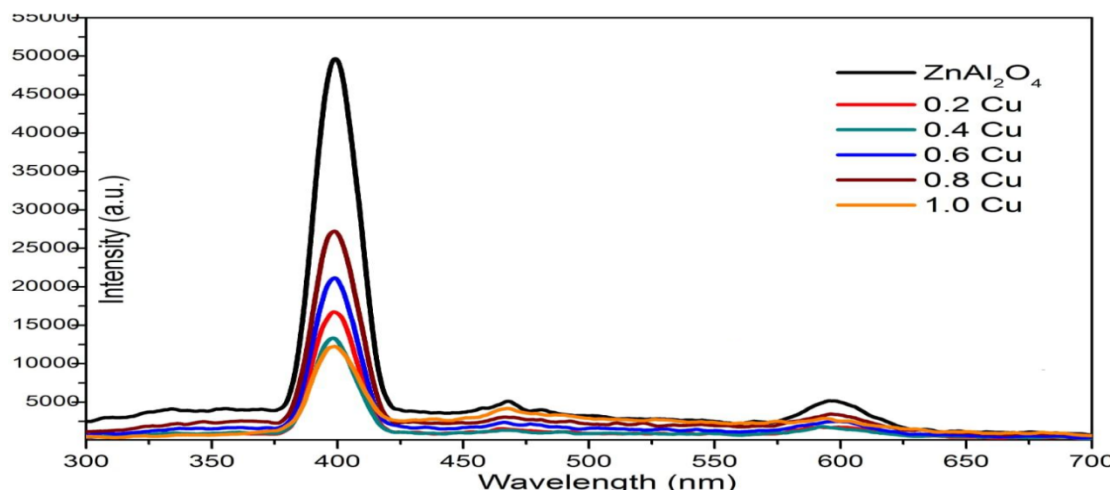


Fig.15: PL of $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ nanopowders (where $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) using sol gel method in presence of glycine loaded with carbon spheres.

4 Conclusions

Zinc aluminate doped with different molar ratios of copper is prepared by sol-gel in presence of glycine. The use of EDX indicates the successful doping of zinc aluminate with Cu (II) ions under different conditions. Using XRF measurements as an effective tool of microanalyses of nanomaterials; the data obtained confirm that zinc aluminate doped with copper nanoparticles is well formed. The prepared nanoparticles have a cubic structure with $Fd3m$ with a homogenous and uniform structure which confirmed by XRD and HR-TEM. By studying the optical properties (band gap) of $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ nanoparticles, it is found that, the prepared nanomaterials can be used as efficient semiconductors that permit devices to operate at much higher voltages, frequencies and temperatures than conventional semiconductor material. This is enabling them to be used in several lighting and sensing applications, UV-photoelectronic devices, electroluminescent displays or optomechanical stress sensors and stress imaging devices. PL curves $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ nanoparticles ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) show a decreasing in the intensity after addition of copper ions, that mean copper ions increase the photocatalytic activity. CSs are prepared by simple one step which confirmed by FE-SEM. Then $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ nanoparticles are loaded with CSs. The size of $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ nano-powders (where $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) is decreasing after loading with CSs; which confirmed by XRD and HR-TEM but, the structure is still a cubic. Moreover, band gap is decreasing after addition of CSs. PL curves show that $\text{Cu}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ where $x = 0.0, 0.2, 0.4, 0.6, 0.8$, and 1.0 can be used in violet, blue and orange

applications in both cases. However, carbon spheres enhance the photocatalytic activity of the prepared nanomaterials. It is also concluded that doping of zinc aluminate with Cu ions and co-doping with C/Cu is actually supported by glycine chelating agent to get photo-catalytically active novel semi-conductors.

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