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The Experimental Investigation on the Structural, Morphological and Optical properties ofUndoped and Ag doped ZnSNano Crystallites

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Abstract :- *In the present article wereport the investigation on the structural and optical properties of Undoped Zinc Sulfide (ZnS) Nano crystallites and Silver Nitrate (AgNO3) doped Nano crystallites prepared by wet chemical co precipitation method using Zinc acetate and Sodium sulfide as sulfur sources. The pure and Ag doped ZnSNano crystallites were characterized by X-ray Diffraction, Scanning Electron Microscopy (SEM), Ultraviolet-Visible absorption spectrum. The size and structure of the as preparedNanocrystallites were studied using X-Ray Diffraction pattern. The crystallite size ofpure and silver nitrate ($AgNO_3$) doped ZnSNano crystallites were calculated by Debye–Scherer formula. Morphology of the as prepared Nano crystallites were observed and investigated using the Scanning Electron Microscopy.. The optical properties of Nano crystallites were studied with Ultraviolet-Visible Spectroscopy. Elemental analysis from the Energy Dispersive X-ray analysis (EDAX) confirms the stoichiometry of the final product*

Keywords: *Nano Crystallites, Wet Chemical Co precipitation, Zinc Sulfide, Silver Nitrate, Polyvinyl Pyrrolidone, EDAX,SEM*

I. INTRODUCTION

During the recent decades, the "small-particle" research has gained great deal of attention in various fields of science. The ''small-particles'' known as Nano crystallites [1] are very interesting materials both for scientific reason and practical application. Semiconductor Nano crystallites represent a class of materials with hybrid molecular and bulk properties. These size dependent properties have many potential applications in the areas of solar energy conversion, light emitting devices, chemical/biological sensors [2]and photo catalysis .Wide band gap II–VI semiconductors are expected to be the novel materials for major % of optoelectronic devices. Zinc Sulfide (ZnS), an important member of this family, has been extensively investigated as it has numerous applications [3] to its credit. ZnS has been used widely as an important phosphor for photoluminescence (PL), electroluminescence (EL) and cathode luminescence (CL) devices due to its good chemical stability compared to other chalcogenides such as ZnSe. In optoelectronics, it finds numerous applications such as Light Emitting Diode, Reflector, Flat panel Displays[4] Dielectric Filter and Infra-red window material [5]. Keeping in view the above features, an effort has been made to study the structural and optical properties of Undoped and Ag doped ZnS Nano crystallites. The synthesis of ZnS remains a topic of interest for researchers, as new synthetic routes [6] are being explored to get a single phase material via an economically and technically viable method. In this article, wet chemical co precipitation method has been used to synthesize the Undoped and Ag doped ZnS Nano crystallites. Till now, many studies on Nanoparticles have focused on the synthesis of different Nanoparticle assemblies with different capping agents [7–10]. In the present article Undoped and Ag doped ZnS Nano crystallites were synthesized by using Polyvinyl Pyrrolidone (PVP) asa capping agent.

II. EXPERIMENTAL DETAILS

A. Materials

Nanocrystallites of Pure and Silver Nitrate doped ZnS were obtained by using a novel wet chemical co precipitation reaction as reported by Iqbal.Aet al.[11] using analytical reagent grade chemicals such as Zinc Acetate Dehydrate ($Zn(CH_3COO)2{\cdot}2H_2O$), Sodium Sulfide ($Na_2S.H_2O$), Polyvinyl Pyrrolidone (PVP (C_2H_9NO)n) Silver Nitrate ($AgNO_3$) as source materials. Deionized water is used throughout the entire experimental process.

B.Synthesis

For the synthesis of UndopedZinc Sulfide Nano crystallites,0.3 mol of zinc acetate and 0.032gms of PVP (capping ligand)[11].were dissolved in 50 ml of de ionized water under continuous stirring .After that 0.6 mol of sodium sulfide is dissolved in 50 ml of de ionized water. The Na_2S solution was then poured drop by drop in to the zinc acetateand PVP solution[12]. under continuous stirring. After the reaction was completed, a milky white precipitate was formed. The white mixture was centrifuged at 300 rpm for 30 minutes and dried at 120 ° C for about 1 hour in a hot air oven.

Chemical precipitation of silver nitrate (AgNO3)doped ZnS Nanocrystallites has been carried out at room temperature using the reactants Zinc Acetate Dehydrate ($Zn(CH_3COO)2{\cdot}2H_2O$), and Silver Nitrate (AgNO3) Sodium Sulfide

(Na2S) with PVP as capping agent. 0.003 mol of zinc acetate and 0.032gms of PVP (capping ligand) were dissolved in 50 ml of de ionized water. Now 10 units of silver nitrate (AgNO3) solution using BD needle was injected into the solution and continuously stirred. The Na_2S solution was then poured drop by drop in tothe zinc acetate, PVP and silver nitrate solution under continuous stirring.[13]. After the reaction was completed a white precipitate was formed. The mixture was centrifuged at 300 rpm for 30 minutes and dried at 120 ° C for about 1 hour in hot air oven. After grinding, Ag doped ZnS Nano crystallites were obtained.

III. CHARACTERIZATION

The phase purity and crystal structure of as prepared Undoped ZnS and Ag doped ZnS Nano crystallites were carried out by analyzing the X-Ray Diffraction (XRD) patterns using monochromatic Cu- Kα radiation in 2θ range of 10º to 80 º with a X' Pert PRO Diffractometer (PANalytical, Netherlands) running under the continuous scanning mode in steps of 0.050[14-17]. A JEOL-Scanning Electron Microscopy (SEM) (Model JSM – 6390, Made in JAPAN) was used to record the micrograph for the samples of Undoped ZnS and Ag doped ZnS Nano crystallites.. Optical absorption studies were carried out using a UV-Visible Spectrometer (JASCO V- 570, CANADA Make) in the range of 200 - 1200 nm[18]. The elemental compositions of UndopedZnS and Ag doped ZnS Nano crystalliteswere analyzed and the characteristic elements were identified by using EDAX.

IV.RESULTS & DISCUSSION

A.XRD Analysis

XRD analysiswasperformed to determine the crystalline structure and phase formation of Zinc sulphideNano crystallites. . Figure 1.a represents the XRD profile of theUndoped sample (1:2 molar ratio of Zn and sulfur source). From the XRD results it is revealed that theUndoped ZnS material has a Rhombohedral structure. The XRD pattern of UndopedZnS Nano crystallites shows 3 distinct peaks at 2θ = 18.80º, 33.64 º, and 36.65 º which corresponds to the (1025), (1058) and (0171)planes [19].The peaks are well matched with the Joint Committee on Powder Diffraction Standard (JCPDS) Card No. 89-2176. XRD confirms the phase singularity of the synthesized Nano crystallites,i.e no other peak is observed corresponding to their binary system, which confirms the formation ofNano crystallites

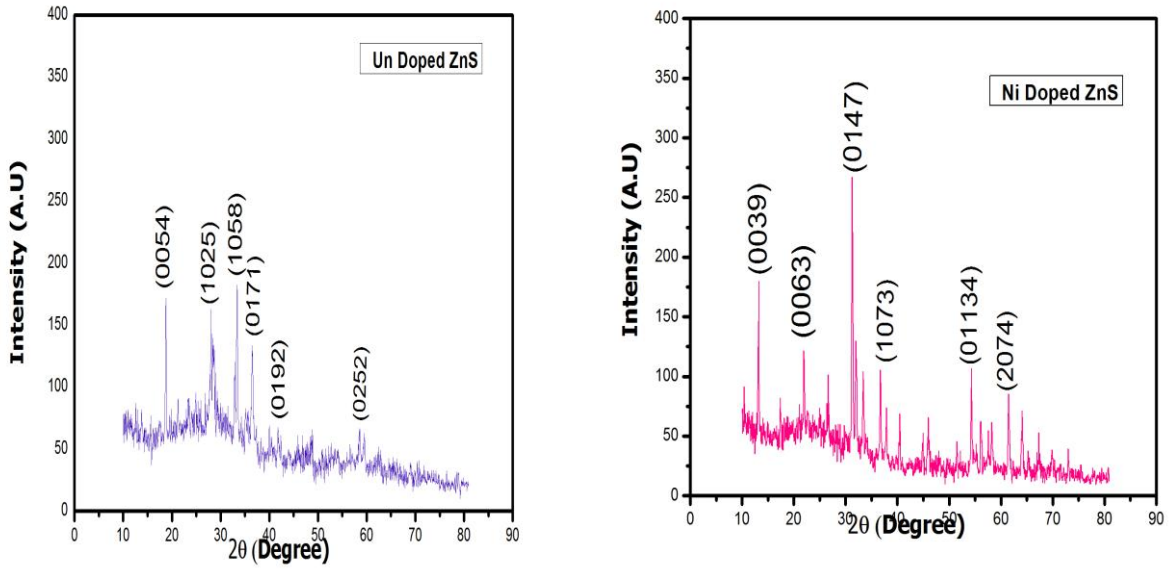

Figure1.a XRD Patterns of Undoped ZnS Crystallites 1.b Ag doped ZnS Crystallites

Figure 1.b represents the XRD profile of the Ag doped sample (1:2 molar ratio of Zn and sulfur source). From the XRD results it is revealed that the Ag doped ZnS material has a Rhombohedral structure. The XRD pattern of Ag doped ZnS Nano crystallites shows 3 distinct peaks at 2θ = 21.91º, 31.30 º, and 36.66 º which corresponds to the (0063), (0147) and (1073) planes [19].The peaks are well matched with the Joint Committee on Powder Diffraction Standard (JCPDS) Card No. 89-2176. Average crystallite size of UndopedZnS and Ag dopedNanocrystallites werecalculated using the Debye-Scherer's equation

$$D = K \lambda / \beta \cos \theta \qquad (1)$$

where, D is the mean grain size, K is constant, λ is the X-ray's wavelength (1.5406 Å), β is the full width at half maximum and θ is the Bragg's diffraction angle.The crystallinesize of Undoped ZnSNano crystallites was found as36Nanometers and the size found to be increased from 36 Nanometers to 40Nanometers with the $AgNO_3$ doping

B.SEM Analysis

The SEM has been used to characterize the size, shape and morphologies of formed Nano crystallites .The morphologies are noticeably dependent on the preparation procedure and crystal composition. SEM images of Undoped ZnSNano crystallites were shown in Fig. 3. Microscopic images resemble the rose flower petals like ZnS Nanoparticles.

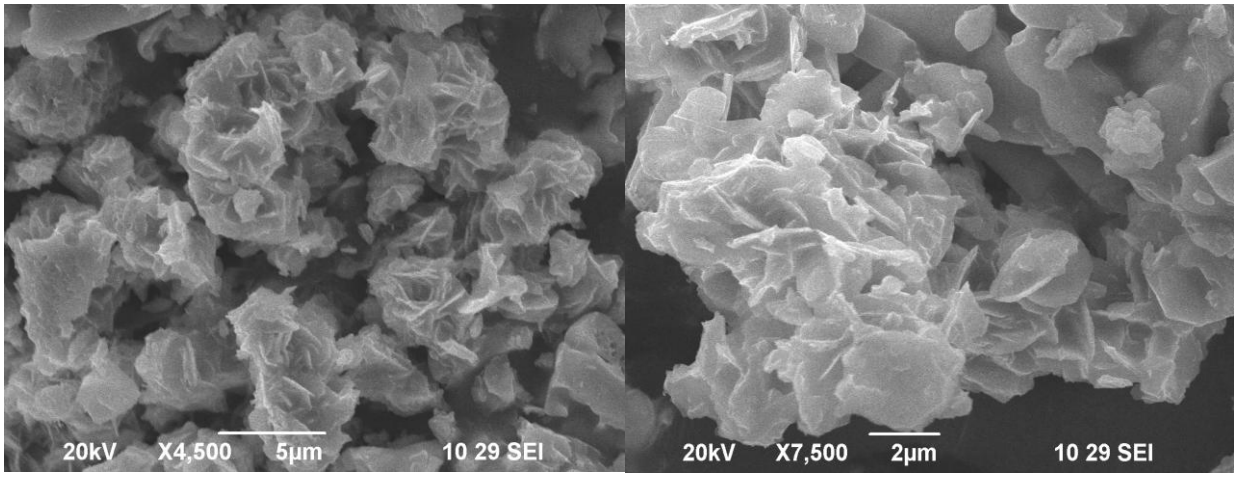

Figure3. SEM Images of Undoped ZnS Crystallites

SEM images of AgNO3 doped ZnS Nanocrystallites were shown in Fig. 4.It clearly shows the surface morphology ofZnS-Ag Nano crystallites which were arranged inform of cluster [20]. It reveals that there is large homogeneity at the surface.

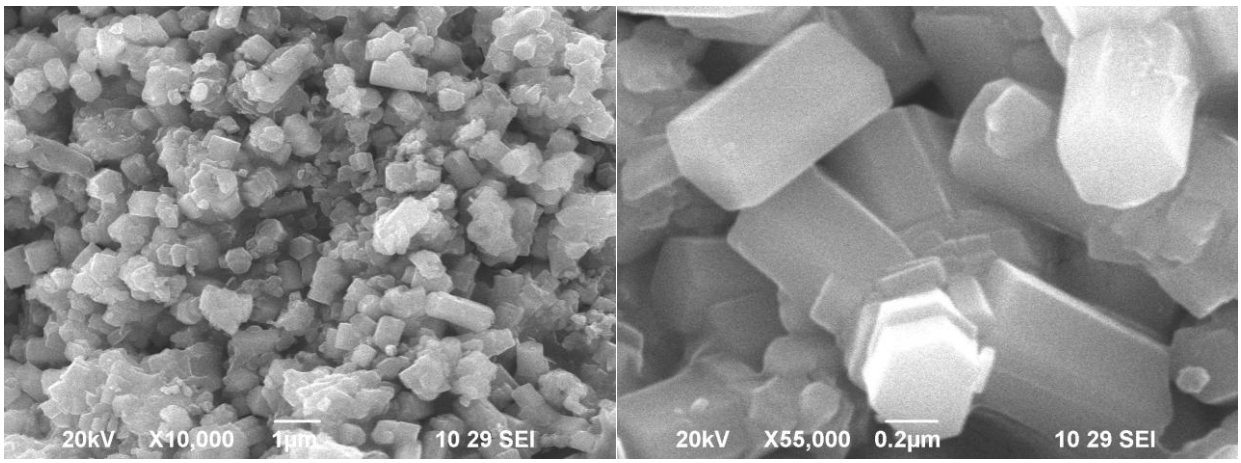

Figure4. SEM Images of Ag doped ZnSNanoCrystallites

C.EDAX Analysis

Chemical composition analysis of all samples were done by EDAX technique .The Energy Dispersive X-ray (EDAX) analysis was used to determine the percentage of zinc and sulfur present in the ZnS sample.Energy dispersive X-ray analysis gives both qualitative and quantitative information about the elemental composition of the materials. From the EDAX spectra, we can conclude that there are other materials, such as impurities or adducts, present in the samples[21]. These impurities occur either accidently with the reagent molecules or are added for modification of the basic materials. Fig.5.a shows EDAX spectra ofUndoped ZnSNano crystallites. From the EDAX spectra of the samples it is confirmed that the amount of Zn, S were close to the nominal (target) values and it is intervened that the as prepared ZnS Nanocrystallites are highly pure.

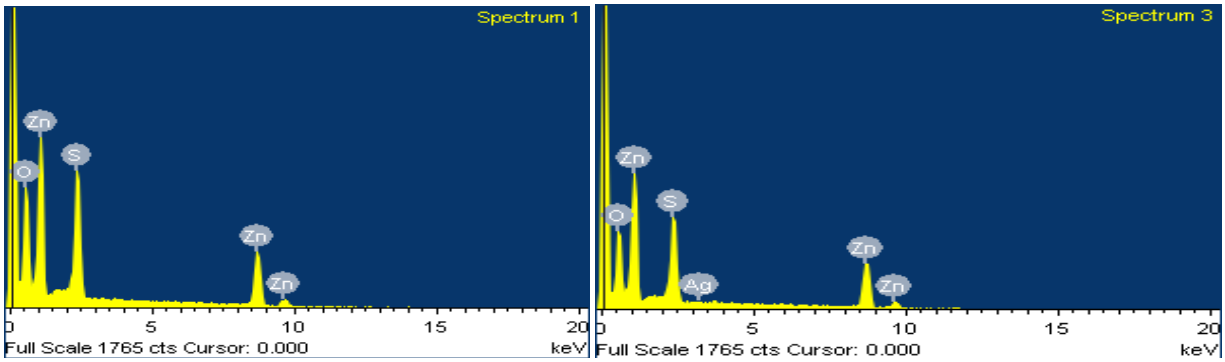

Figure5.a EDAX ofUndoped ZnSNanoCrystallites 5.b EDAX ofAgNO3 doped ZnS NanoCrystallites

From figure 5.b, it is cleared that the stoichiometric of theZn,Ag constituent is maintained in the finally prepared dopedNano crystallites.From the EDAX line traces, the presence of Ag in to the crystal structure of ZnS can also be concluded

D.UV–Visible Optical absorbance and Band gap

The UV–Visible optical absorption spectrum of the samples recorded in room temperature.Tauc plot was used to calculate the more accurate band gap energy by plotting $(\alpha hv)^2$ vs. hv. Here α is absorption co efficient and hv is photon energy.The optical band gap Egcan be estimated from the Tauc plot [22]. For crystalline semiconductors, n can take values l/2, 3/2, 2 or 3 depending onwhether the transitions are direct allowed, direct forbidden, indirect allowed and indirect forbidden transitionsrespectively [23].Optical absorption spectra of samples using UV Vis are indicated in Fig.6.a.The optical band gapof Undoped ZnSNanoparticle is found to be 1.72 eV [24]. With reference to the figure 6.b, the Ag doped ZnS Nano crystallites shows a remarkable increase in the band gap energy of 3.58 eV. This increase in the band gap of 1.86 eV can be explained by its quantum confinement effect of the Nano crystallite. Rise in band gap occurs due to the increase in size of Nano crystallite synthesized.

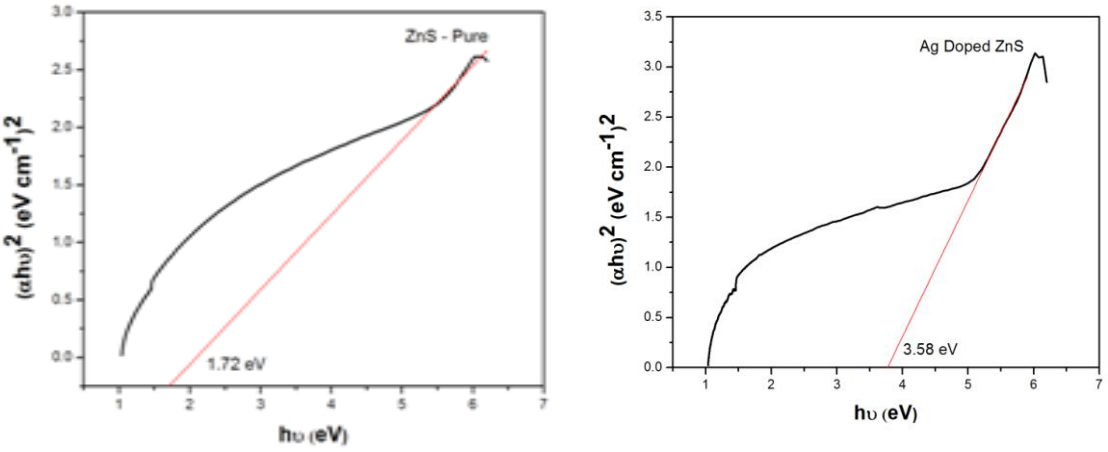

Figure 6.a.Tauc Plot of UV Vis absorption spectra &Figure 6.b.Tauc Plot of UV Vis absorption spectra & Optical Band gap of Undoped ZnS Nano CrystallitesOptical Band gap of AgNO3 doped Nano Crystallites

V. CONCLUSION

In this research study, UndopedZnS Nano crystallites and Ag doped ZnS Nano crystallites were successfully synthesized via the wet chemical co-precipitation method using zinc acetate. The structural properties ofUndopedZnS and Ag doped Nanocrystallites were characterized by X-ray diffraction (XRD)to identify their crystal structure. Crystallographic and morphological studies reveal that theUndopedzinc blende Nano crystallites arehaving average crystallite size of approximately 36 nm and Ag doped Nano crystallites possess an average size of 40 nm.The SEM image reveals that both the Undoped and Ag doped ZnS Nano crystallites have regular shapes. EDAX analysis confirms the presence of Zinc, Sulphur and Silver. From the UV–Visible absorbance spectrum the optical band gap of UndopedZnSNano crystallites is found to be 1.72 eV and the Ag doped ZnS Nano crystallites shows an increased band gap energy of3.58 eV

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