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Photoluminescence Studies of Cu and Ni co-doped ZnS Nanoparticles

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ABSTRACT: *Copper and Nickel co-doped Zinc Sulfide nanoparticles were prepared by low-cost chemical co-precipitation method at room temperature. The effect of Cu dopant concentration on structural, morphological, compositional and photo luminescence properties of ZnS: Ni, Cu nanoparticles were studied using X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive analysis of X-rays (EDAX) and photo luminescence studies. Broadened XRD studies revealed the cubic structure of as prepared ZnS: Ni, Cu nanoparticles. Nano-size distribution of samples was confirmed by TEM. Surface morphology and effective elemental composition of prepared nanoparticles were studied by SEM and EDAX analysis. The Photo Luminescence intensity of Ni and Cu co-doped ZnS nanoparticles is remarkably enhanced by the incorporation of Cu ions.*

Keywords: *capping agent, co-precipitation, photoluminescence, SEM, XRD*

I. INTRODUCTION

Among the II–VI semiconductors, ZnS is chemically stable semiconductor and due to its unique physical, optical and electrical properties caused by quantum confinement effect, the material exhibits high luminescence efficiency and good host for transition metal ion [1]. Zinc Sulfide (ZnS) exhibits interesting optical and luminescence properties and hence finds potential applications in light–emitting diodes, flat panel displays, ultraviolet injection lasers, catalysts, opto-electronic devices, heterojunction solar cells [2, 8]. Doped ZnS nanoparticles have special interest and preference due to their unique magnetic, optical and electronic properties and hence find potential applications in spintronic and optoelectronic devices. Shift in emission spectrum of ZnS can be achieved by doping with some transition metal elements and a green light source can be created. In this paper, ZnS nanoparticles doped with Ni and Cu ions have been obtained by chemical co-precipitation from homogeneous solutions of zinc, nickel and copper salt compounds with S^{2-} as precipitating anion formed by decomposition of sodium sulfide. And the effect of Cu dopant concentration on structural, surface morphology, composition and photoluminescence properties of ZnS: Ni nanoparticles were studied and presented.

II. EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

All the chemicals used for preparing ZnS: Ni, Cu nanoparticles were of analytical reagent grade and were used without any further purification. The samples were prepared by chemical co-precipitation method using pure zinc acetate, nickel chloride, copper acetate and sodium sulfide. Appropriate amounts of $Zn(ac)_2$, $NiCl_2$. $6H_2O$ and $Cu(CH_3COO)_2$. H_2O were dissolved in 50 ml distilled water. Polyvinylpyrrolidone (PVP) was used as a capping agent. To this solution, 50 ml of sodium sulfide solution is added drop wise under constant stirring until to get fine precipitate of Ni, Cu co-doped ZnS nanoparticles. After the completion of the reaction, products were collected and thoroughly washed for several times with distilled water and ethanol. Ni, Cu co-doped ZnS nanoparticles were subjected to various characterization studies. The X-ray diffraction patterns of the samples were collected on a Seifert 3003 TT X- Ray Diffractometer with the Cu Kα radiation (λ=1.5405A°). Surface morphology and elemental composition for the prepared samples were analyzed through EDAX using Oxford Inca Penta FeTX3 EDS instrument attached to Carl Zeiss EVO MA 15 Scanning Electron Microscope. Transmission electron microscope analysis was carried out by TECHNAI TEM-FEI. Photoluminescence spectra of the prepared nanosamples have been recorded using a Horiba-Fluorolog-3 (Model FL3-22) spectrofluorometer at room temperature (300 K).

III. RESULTS AND DISCUSSION

3.1 Structural analysis:

The XRD patterns of pure ZnS and Ni, Cu co-doped ZnS nanoparticles are represented in Fig. 1. All the XRD peaks of prepared nanosamples exhibited three diffraction peak positions correspond to the lattice planes of (111), (220) and (311) and are very well matched with the cubic zinc blended structure (JCPDS card no. 80-0020). The broad peaks observed in the XRD spectra were due to the nanocrystalline nature of the prepared samples. It is to note that the incorporation of Ni and Cu into ZnS host matrix has not changed its cubic structure. From the XRD spectra it was also observed that no diffraction peaks corresponding to the impurity phases were detected and this rule out precipitation or secondary phases of Ni or Cu. The average particle size of the prepared samples calculated by Debye Scherrer's equation [a] in the range of 4-8 nm as in table (1) and is well supported by the TEM analysis.

----------[a]

$$D = \frac{0.94\lambda}{\beta_{hkl}\cos\theta}$$

Where, D is the average particle size and βhkl is full width at half maximum of XRD peak expressed in radians and θ is the position of the diffraction peak.

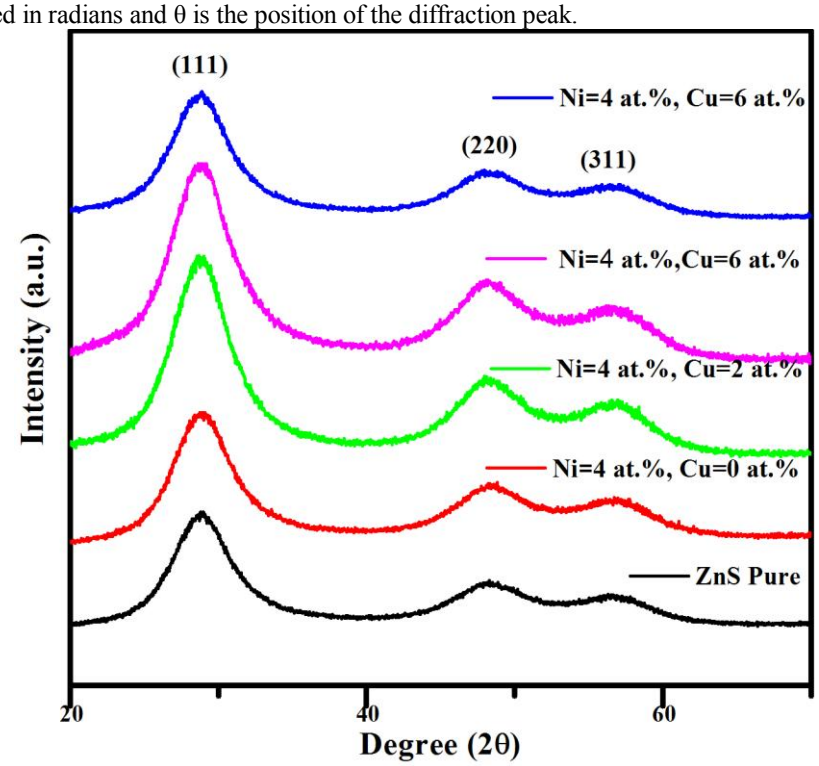

Fig. 1. XRD patterns of Pure ZnS, $Zn_{1-x-y}Ni_xCu_yS$ (x=0.04, y=0.00, 0.02, 0.04, 0.06) nanosamples

Table 1. Average Particle size of Ni, Cu co-doped ZnS nanoparticles

S.No	Doping concentration (at. %)	Particle size (nm)
1	Pure ZnS	7.4
2	Ni=4%, Cu=0%	6.8
3	Ni=4%, Cu=2%	6.1
4	Ni=4%, Cu=4%	4.2
5	Ni=4%, Cu=6%	5.8

3.2 TEM analysis:

Fig.2 shows the TEM image of 4 at.% Ni and 4 at.% Cu co-doped ZnS nanosamples. It is clearly observed that the particle size is around 6 nm and is well in agreement with the XRD studies. Hence this confirms the nano-size distribution of the prepared sample.

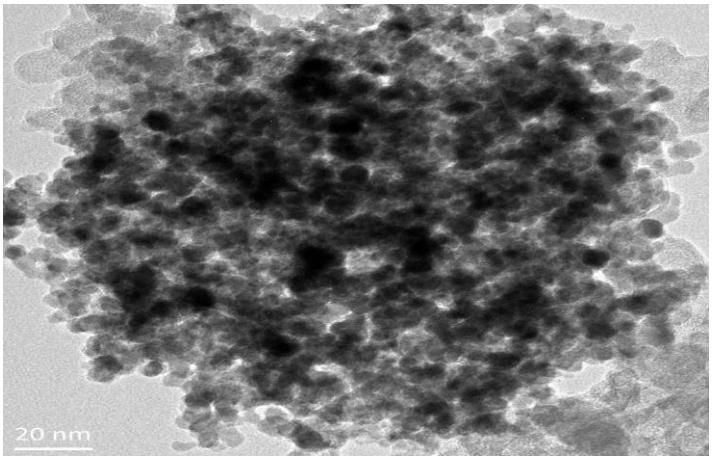

Fig. 2. TEM image of $Zn_{1-x-y}Ni_xCu_yS$ (x=0.04, y=0.04) nanoparticles

3.3 Elemental analysis:

Compositional analysis of all samples was done by EDS technique. In order to analyze the amount of Ni content and distribution in doped ZnS this technique is much useful. Fig.3 (a), (b), (c) and (d) shows EDS spectra of Pure ZnS, $Zn_{1-x-y}Ni_xCu_yS$ (x=0.04, y=0.00, 0.02,0.04,0.06) nanoparticles respectively. EDS spectra of the samples confirmed that the amount of Zn, S and Ni and Cu were close to the nominal(target) values.

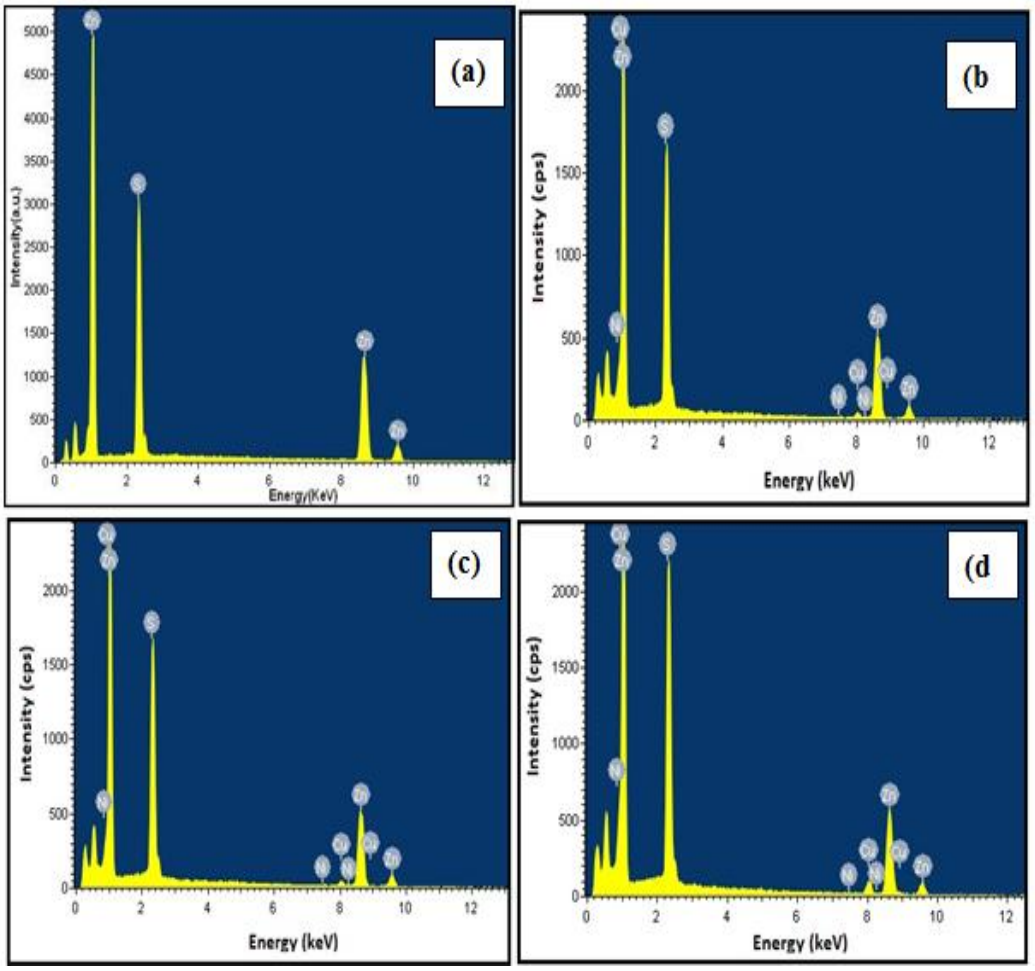

Fig.3. EDS spectra of (a) Pure ZnS nanoparticles, (b) $Zn_{1-x-y}Ni_xCu_yS$ (x=0.04, y=0.00), (c) $Zn_{1-x-y}Ni_xCu_yS$ (x=0.04, y=0.02), (d) $Zn_{1-x-y}Ni_xCu_yS$ (x=0.04, y=0.04) and (e) $Zn_{1-x-y}Ni_xCu_yS$ (x=0.04, y=0.06) nanoparticles

3.4 Morphological studies:

The surface morphology of the prepared samples was studied using a powerful tool called Scanning Electron Microscope, especially by observing the top and cross-sectional views of the sample.

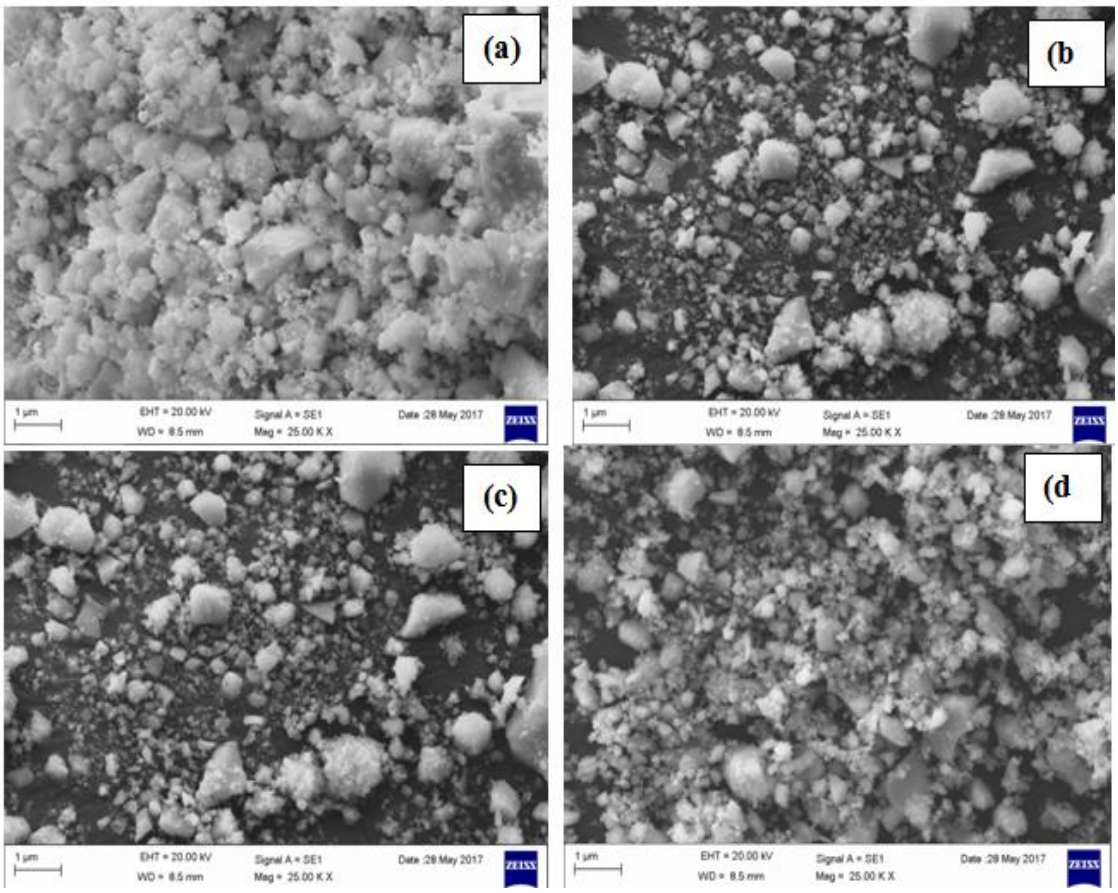

Fig.4. SEM image of (a) Pure ZnS nanoparticles, (b) $Zn_{1-x-y}Ni_xCu_yS$ (x=0.04, y=0.00), (c) $Zn_{1-x-y}Ni_xCu_yS$ (x=0.04, y=0.02), (d) $Zn_{1-x-y}Ni_xCu_yS$ (x=0.04, y=0.04) and (e) $Zn_{1-x-y}Ni_xCu_yS$ (x=0.04, y=0.06) nanoparticles

The surface morphologies of the Pure ZnS, $Zn_{1-x-y}Ni_xCu_yS$ (x=0.04, y=0.00, 0.02,0.04,0.06) nanoparticles were shown in fig.4(a), (b), (c), (d) and (e) respectively. It is noticed that in the doped samples the agglomerated particles appear to be nearly spherical with the distribution becoming nearly homogeneous.

3.5 Photoluminescence Studies:

The room temperature photoluminescence spectra of pure ZnS, $Zn_{1-x-y}Ni_xCu_yS$ (x=0.04, y=0.00,0.02,0.04,0.06) nanoparticles are shown in fig.5. All the samples are excited at a wavelength of 320 nm. For pure ZnS nanoparticles a broad emission peak is observed at around 450nm [9]. Ni doped ZnS nanoparticles showed broad emission ranging from 440-520nm. P.Yang, et.al observed emission peaks of ZnS: Ni nanocrystals at 520nm [10]. Ni doped ZnS nanoparticles showed broad emission peak at around 440 nm, which may be due radiative recombination of sulfur vacancies and ZnS host lattice [11]. In this study with incorporation of copper ions a broad emission ranging from blue region to green region is observed. The Photo Luminescence intensity of ZnS: Ni, Cu Nanoparticles is remarkably enhanced as in fig 5. Here, the peak observed at around ~610nm, may be due to the presence of defects like sulfur vacancies at the surface and the OH ions act as defect centers and affect the green emission ~520-560 nm [12]. The increase in the PL intensity of these peaks may be due to the sulfur vacancies and doping of Cu in ZnS: Ni lattice. As the particle size is decreased with increasing cu co-dopant concentration (upto 4 at.%), PL intensity increased. Increasing the Cu co-dopant concentration generates new radiation centers as the number of defect sites get increased and hence luminescence intensity increased. Futher increasing the Cu concentration, particle size increased due to Cu-Cu interactions and hence the PL intensity is decreased.

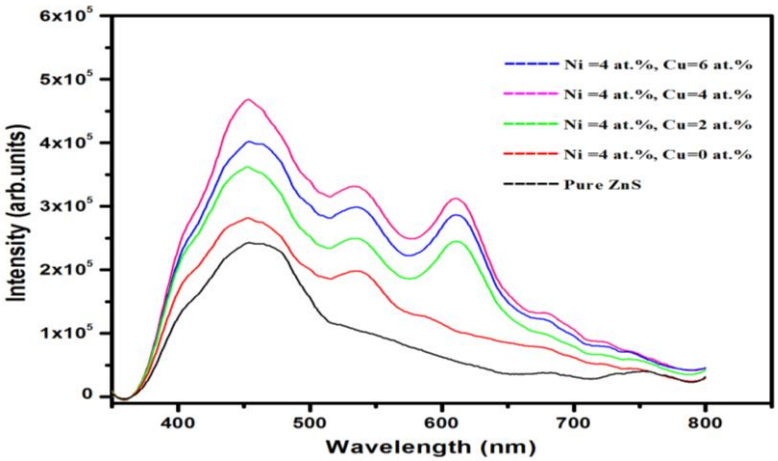

Fig. 5. PL spectra of Pure ZnS, $Zn_{1-x-y}Ni_xCu_yS$ (x=0.04, y=0.00, 0.02, 0.04, 0.06)

IV. CONCLUSION

Pure and Ni, Cu co-doped ZnS nanoparticles were successfully synthesized by cost-effective chemical co-precipitation method. PVP was used as the capping agent. XRD studies showed the cubic zincblende crystal structure of the samples and the calculated particle size lies in the range of 4- 6 nm and this is supported by the TEM studies. The Prepared nanosamples were subjected to chemical analysis (EDAX) and the estimated compositions were compliance with that of the starting compositions. SEM analysis shows decreased agglomeration of the particles. Photoluminescence studies revealed that Ni, Cu co-doped ZnS nanoparticles showed the enhanced emission intensity with increasing Cu dopant concentration up to 4 at.% Cu and thereafter it decreased and shift in green emission is observed.

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