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SYNTHESIS AND CHARACTERIZATION OF COPPER (Cu) DOPED ZINC SULFIDE (ZnS) NANOPARTICLES BY CHEMICAL PRECIPITATION METHOD

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ABSTRACT- Nanocrystalline materials have been studied extensively, especially II–IV semiconductor nanoparticles, showing interesting size-dependent electrical and optical properties due to the quantum confinement effect of the carriers. In the present work, the author's report the structural, optical and FT-IR properties of the Cu doped ZnS nanoparticles were synthesized by chemical method. The crystal structure studies show that samples have cubic phase crystal structure. The optical energy bandgap of pure and Cu doped samples were determined by optical study. The presence of functional groups of pure and Cu doped ZnS have been identified by FT-IR study.

Keywords - [ZnS: Cu^{2+} nanoparticles, Band gap, Semiconductor, Optical study, X-ray diffraction.]

1. INTRODUCTION

Zinc sulfide (ZnS) is one of the first discovered II-VI compound semiconductor materials with versatile fundamental properties [1]. Semiconductor nanoparticles are themselves highly unstable and in the absence of capping agent, they agglomerate very rapidly [2]. ZnS-based phosphors activated by transition or rare earth metals are famous materials with diverse luminescence properties, such as photoluminescence (PL) and thermoluminescence (TL) [3-7]. Especially, ZnS is a direct-transition semiconductor with the widest energy band gap among the groups II–VI compound semiconductor materials, and it is an important material with an extensive range of applications from blue/green light-emitting diodes (LEDs) and electroluminescence devices (ELDs) to optoelectric modulators, data storage, data transfer and coatings which are sensitive to UV light.[8]. Zinc Sulfide (ZnS), a typical II-VI compound semiconductor is a promising opto-electronic device material because of its wide direct band gap (3.72 - 3.77eV) [9]. Transitional elements ions (e.g. Mn^{2+}, Ni^{+2} and Cu^{2+} [10-12] and rare earth ions (e.g. Eu^{2+} [13, 14] have been incorporated into ZnS nanostructures by thermal evaporation, sol–

gel processing, co precipitation, micro emulsion, etc. These doped ZnS semi-conductor materials have a wide range of applications in electro-luminescence devices, phosphors, light emitting displays, and optical sensors. In this work we report on a successful synthesis of pure and Cu doped ZnS by chemical precipitation method and characterization such as powder XRD, Optical and FT-IR.

2. EXPERIMENTAL PROCEDURE

2.1(a) Synthesis of ZnS nanoparticles

The samples of undoped ZnS were synthesized by chemical method. In this procedure to prepare pure ZnS, the appropriate amount of Zinc acetate ($C_4H_6O_4Zn.2H_2O$), Sodium sulphide ($Na_2S.H_2O$) were dissolved distilled water, stirred for 3-5 hours using hot plate with a magnetic stirrer. The temperature was maintained at room temperature for complete dissolution. After the stirring process, a predicate was collected then washed 3 times with ethanol. The collected sample centrifuged using 2000 rpm and dried at 60°C to get the powdered sample of pure ZnS.

2.1(b) Synthesis of Cu doped ZnS nanoparticles

Synthesis of copper doped zinc sulphide for preparation of Cu doped ZnS, the appropriate amount of 3 precurors of Zinc actetate ($C_4H_6O_4Zn.2H_2O$), Sodium sulphide ($Na_2S.H_2O$), Copper chloride ($CuCl_2$) was dissolved in distilled water, stirrer for 3-5 hours using hot plate with magnetic stirrer. The temperature was maintained at room temperature for complete dissolution. After the stirring process, a precipate was collected then washed 3 times with ethanol. The collected sample centrifuged using 2000 rpm and dried at 60°C to get the powdered sample of Cu doped ZnS.

3. RESULTS AND DISCUSSION

3.1 XRD analysis of Pure and Cu doped ZnS nanoparticles

The pure and Cu doped ZnS nanoparticles prepared by chemical method and powdered by grinding and X-ray diffraction were recorded on a X-ray powder diffractometer using Cu-k radiation (1.5406) the maximum high intensity of the peaks appeared at the position of 2 values of ZnS and Cu doped ZnS nanoparticles such as 30.527, 47.560, 56.391 exhibits the cubic phase crystal structure. It is good agreement with the reported data [JCPDF No: 000361450]. The X-ray spectrum of pure and doped samples were shown in fig 1 and 2, the average particle size of the nanoparticles have been calculated by using Debye-scherer's formula

$D_{av}= K\lambda/\beta \cos\theta$

The average particle size of pure and Cu doped ZnS nanoparticles values is given in table1.

Standard 2¯ values [JCPDF NO: 000361450]	**Standard d values A^0**	**Observed 2¯ values of Pure ZnS**	**h,k,l**	**Particle size («m)**
30.527	2.9259	29.51	111	0.113
47.560	1.9103	47.511	220	0.169
56.391	1.6302	56.639	311	0.360
Standard 2¯ values [JCPDF NO: 000361450]	**Standard d values A^0**	**Observed 2¯ values of Cu doped ZnS**	**h,k,l**	**Particle size («m)**
30.527	2.9259	29.631	111	0.435
47.560	1.9103	48.127	220	0.445
56.391	1.6302	56.759	311	0.451

Table1 -The comparison of X-ray powder diffraction data of pure and Cu doped ZnS nanoparticles

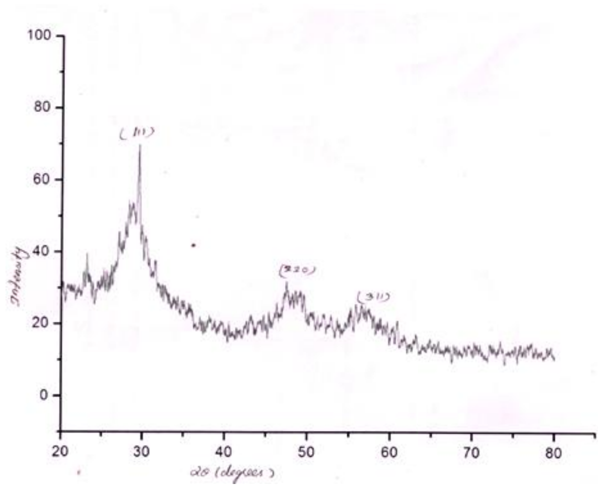

Figure 1- XRD pattern of the Pure ZnS nanoparticles

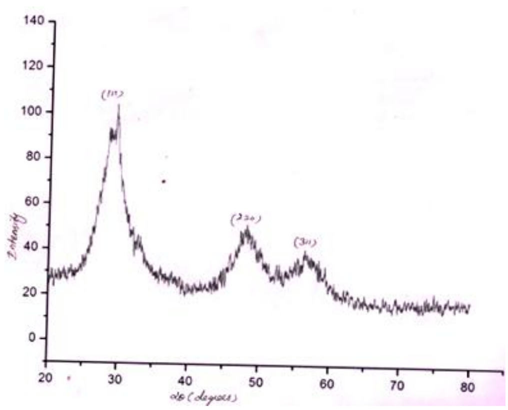

Figure 2- XRD pattern of the Cu doped ZnS nanoparticles

3.2 Optical study of Pure and Cu doped ZnS nanoparticles

The effect of Cu on the energy bandgap of pure ZnS was determined using UV-Visible optical spectroscopy measured in the range of 200-800 nm and shown in fig 3 and 4 by calculating the bandgap of the pure and Cu doped ZnS nanoparticles using the formula $E_g = hc/\lambda$

h- Plank's constant
C- velocity of the light
λ - Absorbance of the sample

From the optical absorption spectrum of pure and Cu doped samples of bandgap found to be 5.43 and 5.51 eV.

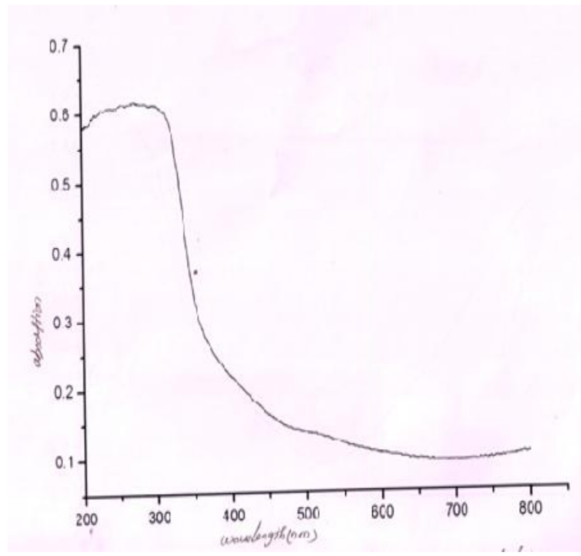

Figure 3- UV-Vis absorption spectrum of Pure ZnS nanoparticles

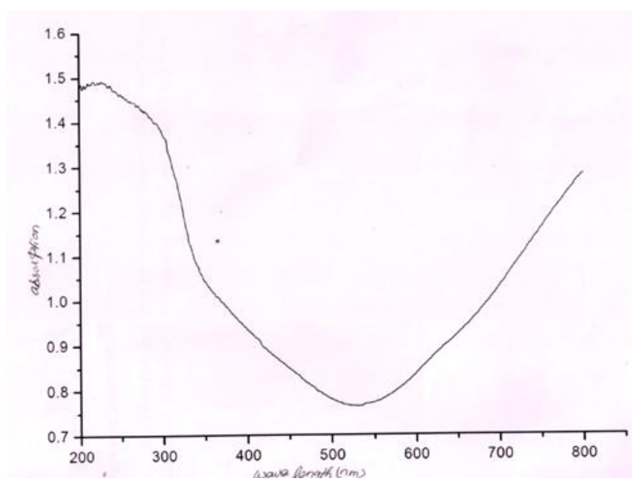

Figure 4- UV-Vis absorption spectrum of Cu doped ZnS nanoparticles

3.3 FT-IR study of Pure and Cu doped ZnS nanoparticles

The infrared absorption **s**pectrum of pure and Cu doped samples were recorded by using a 3436.08 and 3743.06 cm^{-1} in the range 4000-500 cm^{-1} were shown in fig 5 and

6. The peaks appearing at 1116, 750 and 489cm^{-1} are due to Zn–S vibration. The obtained peak values are in good agreement with the reported values [15]. One can observe that broad bands appeared around 3750 cm^{-1} due to O-H stretching. The additional weak bands and shoulders that are observed at 1634 cm^{-1} may be due to microstructural formation of the samples. [16]. For the Cu doped ZnS nanoparticles, the absorption peaks at 2350,1848, 1798,1643,1259 cm-1 are attributed to C-H bonding and other peaks observed at 3650 and 658 cm^{-1} are due to O-H stretching and Zn-S stretching vibrations. The band around 948 due to oxygen stretching and bending frequency. The transmittance peaks of the ZnS: $Cu^{2+}$are slightly shifted towards lower wave number side from pure ZnS, which may be due to the presence of the doping ions.

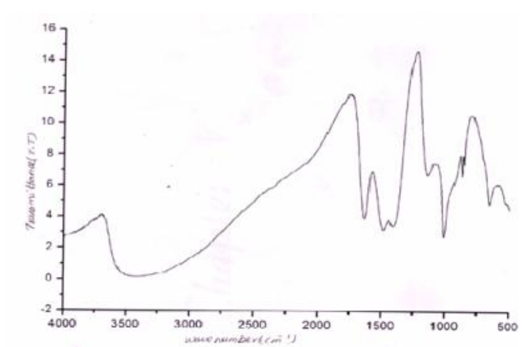

Figure 5- FT-IR spectrum of Pure ZnS nanoparticles

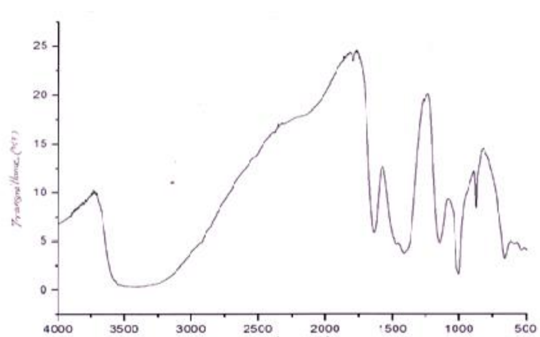

Figure 6- FT-IR spectrum of Cu doped ZnS nanoparticles

CONCLUSIONS

The pure ZnS and Cu doped ZnS nanoparticles were successfully synthesized by the chemical precipitation method. XRD pattern shows that the nanoparticles are in cubic phase crystal structure. The band gap of the Cu doped ZnS has increased when compared to the pure ZnS. The functional group of pure and Cu doped ZnS nanoparticles are determined by FT-IR study.

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