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Fabrication and characterization studies of capped Cu^{2+} Ion Doped ZnS nanoparticles

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Abstract
The present study is focused on the synthesis and characterization of optical and structural properties of nanocrystalline copper doped ZnS particles with mercaptoethanol as a capping agent synthesized by co-precipitation method. The prepared nanoparticles were characterized optically by UV –Visible spectra and structurally by X- ray diffraction (XRD), Energy dispersive X-ray analysis (EDAX). The optical band gap energy (E_g) for all Cu doped ZnS and ZnS nanoparticles were evaluated by using UV-Visible optical absorption spectral data. The band gap energy values for all the nanoparticles are in the range of 3.60 to 3.0 eV. The results show that the optical band gap energies decrease with the increase in molar concentration of doping agent which is attributed to size quantization effect due to electron-electron and electron-impurity scattering effect. The XRD pattern show cubic zinc blende structure with the lattice parameter of 5.31-5.34 Å. The average crystallite sizes are in the range of 1.64-2.24 nm and also the crystallite size depends linearly on the molar concentration of doping agent. The calculated values of average strain and dislocation density from the XRD data indicate that the nanoparticles formed were less strained. EDAX analysis confirms that all the nanoparticles contain corresponding elements in the samples.

Keywords: Co-precipitation, nanoparticles, band gap, electron-electron, electron-impurity scattering.

1. Introduction
In recent year, the technological application on the new nano sized materials has stimulated great concern because of their unique physical and chemical properties. Among the semiconductor nanoparticles, ZnS is an important semiconductor compound of the II - VI group with excellent physical properties and wide band gap at room temperature. The materials has been extensively investigated due toits wide potential applications such as window layers for solar cell, production of hydrogen, blue-light diodes, electro-luminescence displays and anti-reflection coating for infrared devices and other non-linear optical devices[1]. In contemporary research, the optical and structural properties of nanomaterials can be controlled by their particle size and therefore attracted much interest for their fundamental and applied aspect. Doped nanoparticles make up an important subgroup of nanomaterials where just a small percentage of an impurity or dopant is introduced to semiconductor nano particles to alter their electronic, magnetic, and optical properties which are different from bulk materials [2].
The nano-sized particle doped semiconductor crystallites change the physical and chemical properties. Currently, the varieties oftransition and rare earth metals such as Cu^{2+}, Mn^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Eu^{2+}, Sm^{2+}, To^{2+}, and Er^{2+} were doped with ZnS nano particles [3]. In addition, it can be predicted that the properties are closely related to the concentration of metal ion doped nanocrystallite and also alter the band gap energy and form luminescence of different energy level [4].
ZnS nanoparticles have been synthesized by many researchers with the support of different capping agents, and those materials exhibited strong confinement effects. The capping agents are used to arrest the growth of nanoparticles and to stabilize them from aggregation. The capping agents also modify the structural, morphological and optical properties of nanoparticles. The present report focuses on the fabrication of ZnS and copper doped ZnSnanoparticles were synthesised with mercaptoethanol as capping agent by co-precipitated

method. The Cu^{2+} ions doped ZnS and ZnS nanoparticles were characterized by different technique likes UV-Visible spectra, powder X-ray diffraction (XRD) and energy dispersive analysis of X-rays (EDAX).

2. Experimental

2.1 Materials

Zinc sulphate ($ZnSO_4$), Copper nitrate ($Cu(NO_3)_2$), sodium sulphide nonahydrate ($Na_2S.9H_2O$), Mercaptoethanol ($HOCH_2CH_2SH$) were purchased from S.D's fine, India and were of high purity (99.99%). All chemicals were of analytical grade and were used as such without further purification. Ultrapure water was used in the entire synthesis.

2.2 Synthesis

ZnS nanoparticles (NPs) with varying content of Cu ($Zn_{1-x}Cu_xS$; (x = 0, 0.01, 0.02, 0.03) were synthesized with mercaptoethanol as capping agent by simple chemical co-precipitation method [5]. The solution of $ZnSO_4$ and $Cu(NO_3)_2$were prepared in 50 ml of ultrapure water and were stirred for 30 min. separately. 2 ml mercaptoethanol is dissolved in 50 ml of ultra pure water and was stirred for 30 min. The solution of Na_2S was also prepared in 50 ml ultrapure water separately and was stirred for 30 min. The stirred solution of $Cu(NO_3)_2$ and $ZnSO_4$, solution of capping agent were poured drop-wise. After 30 min. of stirring, the solution of Na_2S was poured into the above stirred solution. The reaction was allowed to proceed for 3 hr. at 75 °C and overnight ageing was done. The resulting solution was centrifuged to remove the excess chemical reagent and capping agent. The washed precipitates were then dried at 80 °C for 24 hr. and were crushed to obtain fine powder.

2.3 Characterization

Optical absorption spectra of the samples were recorded with a double beam UV–Visible spectrophotometer (Hitachi, Model-U-3900H). The prepared samples were characterized by X-ray diffraction (XRD) technique using Panalytical's X'Pert Pro diffractometer with Cu Kα radiation. Elemental analysis of prepared samples was done by using equipment of energy dispersive X-ray spectrometer (EDXS; Oxford INCA).

3. Results and Discussion

3. 1 Optical properties

The absorption spectra Cu $^{2+}$ions doped ZnS samples are given in Fig 1(a). The absorption spectra of Cu^{2+} doped samples are different from that of undoped samples. Due to the effect of doped ions on the band gap structure of the host materials, the absorption shoulder peak and absorption edge of the samples vary with change in the impurity concentration of Cu^{2+} ions. The shift of the absorption peaks indicates a very monodispersed nanoparticle distribution. It has been found that the transitions from defect levels to the conduction band can be associated with the presence of Zn and Cu vacancies. The absorption edges of suspension NPs were much broader. The value of the band gap of Cu^{2+} doped ZnS was found to be lower than the pure ZnS (shown in fig 1(b)). Band gap shrinkage has occurred during the doping process, this happens in doped semiconductors (called band gap renormalization) as a result of mutual exchange and coulomb interactions between the added free electrons in the conduction band and electron-impurity scattering [6].

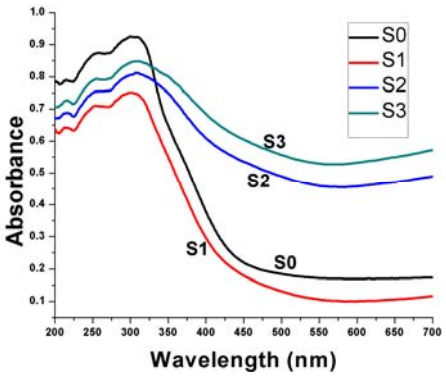

Fig 1(a)

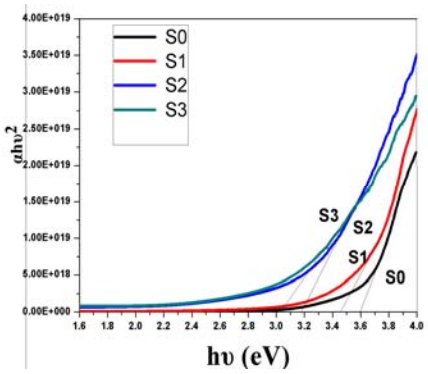

Fig 1(b)

Fig 1: (a) UV Visible spectra of Cu doped ZnS, 1(b) Tauc plot of Cu doppedZnS

3.2 Structural Properties

3.2.1 XRD Pattern

Fig. 2 shows the XRD pattern of $Zn_{1-x}Cu_xS$; (x = 0, 0.01, 0.02, 0.03) nanoparticles. Diffraction peaks from (111), (220) and (311) planes match well with those of the β-ZnS (cubic) reported in JCPDS file No: 05-0566[7]. In all the samples, broadening of diffraction peaks indicate nanosize formation of ZnS. The XRD peaks of doped ZnS NPs became weaker and broader as compared to that of undoped ZnS. This suggests that the crystallinity of $Zn_{1-x}Cu_xS$; x = 0.01, 0.02, and 0.03 NPs is decreased with the increase in Cu content in the source materials. No appreciable peak shift was observed in any sample which may be attributed to the very small difference in ionic radius of Cu^{2+} (0.57) and Zn^{2+} (0.6)[5].

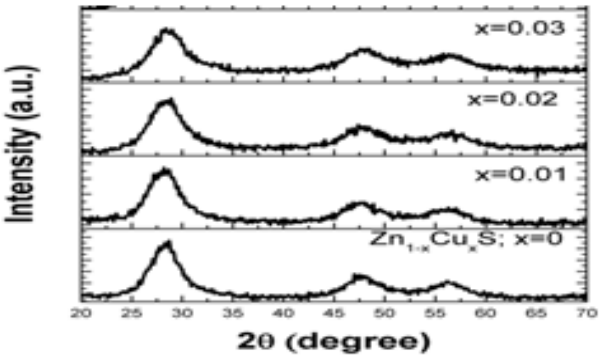

Fig 2: XRD Pattern for Cu doped ZnS and ZnS NPs

Crystallite size of NPs ($Zn_{1-x}Cu_xS$; x = 0, 0.01, 0.02, 0.03) was calculated by following Scherrer's equation.

$$D = k \lambda / \beta \cos\theta$$

where k = 0.9, D is the crystallite size, λ is the wavelength of Cu K_α radiation and β is full width at half maximum (FWHM) after correcting the instrument peak broadening (β expressed in radians). All samples exhibit crystallite size 1.64-2.24 nm.Decreased crystallinity of Cu doped samples as compared to that of undoped ZnS indicate the increase in disorder due to incorporation of impurity ions. XRD broadening could be due to other contributions like strain (ε). The average strain of the ZnS nanoparticles were estimated by using Stokes-Wilson equation:

$$\text{Strain} = \beta/4 \tan\theta$$

The Dislocation density (δ) was also calculated from the following relation [8]:

$$\text{Dislocation Density} = 15\ \varepsilon / aD$$

Where, ε is average strain, $'a'$ is the lattice parameter and D is average crystal size. The average strain and the dislocation densities values are given in Table 1. The increase in lattice strain and dislocation density of Cu^{2+} ion doped ZnS NPs is associated with the incorporation of small quantity of Cu^{2+} ion in the crystal lattice of ZnS.

Table 1: Structural Parameters of undoped and Cu doped ZnS NPs

Sample	Lattice constant (a) (Å)	Particle Size (D) (nm)	Strain (ε)	Dislocation density (δ)(lines/Å)
$Zn_{1-x}Cu_xS$; x = 0	5.33	2.24	0.063	0.078
$Zn_{1-x}Cu_xS$; x = 0.01	5.34	2.17	0.065	0.083
$Zn_{1-x}Cu_xS$; x = 0.02	5.31	1.83	0.077	0.117
$Zn_{1-x}Cu_xS$; x = 0.03	5.32	1.64	0.084	0.142

3.2.2 EDAX Study

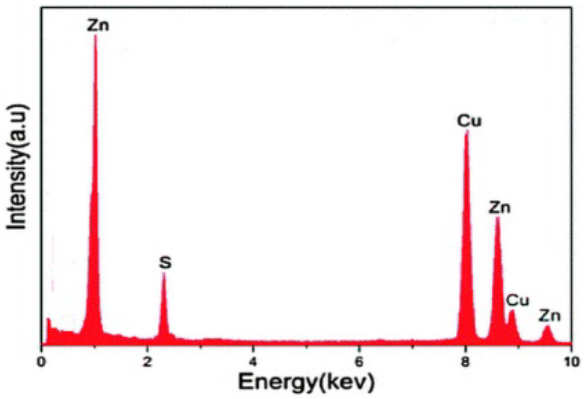

Fig 3: EDAX analysis of copper doped ZnS nanoparticle

The compositions of the samples were examined using an Energy Dispersive X-ray analysis (EDAX). The EDAX analysis (Fig. 3) demonstrated that Zn, Cu and S elements are present in the sample which further confirmed the successful doping of Cu^{2+} ions in the ZnS host structure.

4. Conclusion

The Cu^{2+} ions doped ZnS NPs were successfully synthesized by co-precipitation method with mercaptoethanol as capping agent from homogenous solution of zinc, copper salt compounds with S^{2-} as precipitating agent. This method is simple and low cost chemical for industrial large scale product. The Cu^{2+} ions doped ZnS NPs were characterized by UV-Visible spectra, XRD, EDAX and HRTEM. Optical absorption spectra show red shift in the absorption edge indicating decrease in effective band gap due to size quantization effect due to electron-electron and electron-impurity scattering effect. The XRD results show that copper doped ZnS NPs exhibit a zinc blende (cubic) structure with uniform size distribution of approximately 1.64 to 2.24 nm calculated from XRD using Scherrer's equation. Hence it is observed that copper incorporated into ZnS NPs results in changing its structural and optical properties.

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