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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF METAL DOPED NANOCRYSTALLINECOPPER SULPHIDE

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ABSTRACT

Copper sulphide (CuS) is an excellent material for optoelectronic applications. It is interesting to investigate the optical properties of CuS at nanometer regime where the properties become size dependent. The present paper deals with the synthesis and characterization of undoped and M (M=Mn, Co, Zn, Fe, Ni) doped copper sulphidenanoparticles. The CuS and CuS : M nanoparticles of different sizes were synthesized by organometallic precursor route. The samples were characterized by XRD, UV-Vis absorption, and photoluminescence techniques. It was observed that, the size decreases with increasing capping agent. The crystal size computed using Debye Scherrer formula was found to be in the nano range. The UV-Vis absorption shows blue shift in the absorption edge and in some cases stepwise absorption. It was observed that the doped nanoparticles show better photoluminescence and thus are suitable materials for large area display devices.

INTRODUCTION

Copper sulphide (CuS) is a semiconductor material and has a variable stoichiometric composition. This variability results in many interesting electronic and optic behaviors.

Doping on CuS with transitional metals is an important aspect to yield different nanostructures. However literature survey shows few reports on metal doped CuS. Therefore, it was desirable to dope CuS nanoparticles with metals to study their structural and optical properties. In this paper the chemical synthesis of CuS, CuS: Zn, CuS: Mn and CuS: Co nanoparticles and their structural and optical studies have been discussed.

Experimental

Nanocrystalline copper sulphide was synthesized by chemical route. CuS nanocrystalline powder and M doped CuS nanocrystalline powder were prepared as follows:

CuSnanocrystalline powder

Single source organometallic precursor technique was used to prepare nanocrystalline CuS particles.

The precursor solution A was prepared by dissolving copper chloride ($CuCl_2.2H_2O$) and thiourea [$(NH_2)_2$ CS] in ethanol at 60°C in water bath under magnetic stirring. Another solution B was prepared by dissolving sodium hydroxide (NaOH) in ethanol. Now the solution B was added into solution A. The mixed solution was kept at 60°C under magnetic stirring. In the beginning a white solution was obtained which gradually became transparent and the colour changed from white to creamy yellow.

The solution samples were filtered from the solution, centrifuged and washed with ethanol and then with acetone.

M doped CuSnanocrystalline powder

For synthesis, 1-2 mole aqueous solution of $CuCl_2$, mercaptoethnol (C_2H_5SH) and Na_2S each were taken. For doping of M (M=Mn, Fe, Co, Ni & Zn) MCl_2 solution was simply added to $CuCl_2$ solution.

First mercaptoethnol solution was added drop wise to $CuCl_2$ (MCl_2 for doping) solution at the rate of 1ml per minute, while stirring it continuously so that solutions are properly mixed. Then Na_2S solution was also added in a similar manner. The chemical reaction gives CuS.

$$CuCl_2 + Na_2S \rightarrow CuS + 2NaCl$$

CuS thus precipitated was insoluble in water. The presence of mercaptoethnol does not allow the particles size to grow. The

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precipitate thus obtained was thoroughly washed in double distilled water, centrifuged and then air-dried.

The samples were then characterized by XRD and UV-Vis absorption and their photoluminescence were investigated.

RESULTS AND DISCUSSION

XRD studies

The X-ray powder patterns of CuS and M doped CuS are shown in Figure 1. It is observed that the synthesized compounds are crystalline in nature.The average crystallite size was calculated using Debye schererr's formula[3] for the following compound CuS, CuS-Mn, CuS-Co, CuS-Zn.

$$D = K\lambda/\beta cos\theta \qquad \text{---------- (1)}$$

Where D = average crystal size, K = shape factor, β = full width of half maxima, λ=wavelength.

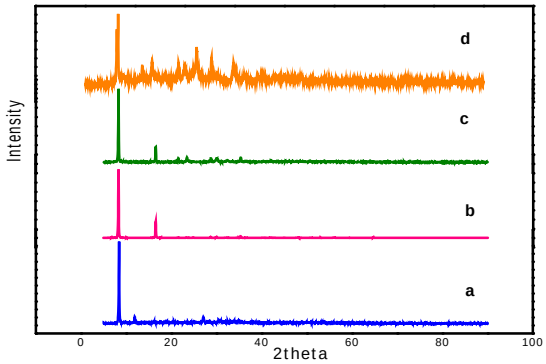

Figure 1 *X-ray diffraction pattern of a) CuS b) Mn doped CuS c) Co doped CuS d) Zn doped CuS*

Table 1.represents the same. The somewhat less sharp peaks in the X-ray diffraction patterns confirm the nano size of particles. It can be observed from the X-ray patterns of all the synthesized compounds that the M doped CuS were different from CuS indicating that the M takes part in the lattice along with Cu and S. The average particle size of M doped CuS from X-ray powder data was found to be ~ 10-15nm. It can be observed that Mn and Co doped CuS are isomorphous.

Table 1 crystallite size as obtained from X-ray powder diffraction data

Synthesised compounds	Crystallite size nm
CuS	21.26
Mn doped CuS	15.05
Co doped CuS	16.19
Zn doped CuS	12.11

Solid state uv

The uv absorption of CuSnano crystalline powder were determined in the range between 200-900nm. Fig.2 shows the absorption of CuS and CuS-M doped nanocrystalline powder. CuS is a direct band gap material, which has the band gap energy ~ 2.3 eV with absorption edge at about 550nm. Fig. 3 (350nm-600nm) shows the absorption spectra of CuS and M doped CuS. From the figure it is clear that the absorption edge for all the M doped CuS were blue shifted as compared to CuS. The blue shift in the absorption edge indicates increase in effective bands of the doped CuS samples.

The increase in effective band gap in nanoparticles due to quantum confinement has the quantitative form,

$$\Delta E_g = E_{g(nano)} - E_{g(bulk)} = \frac{h^2}{8MR^2} \qquad \text{----------(2)}$$

Where, h is Planck's constant, R is the radius of the particle and M is the effective mass of the system. Equation (2) can be used to estimate size of the particle taking proper value of M and increase in band gap obtained from blue shift in absorption edge.

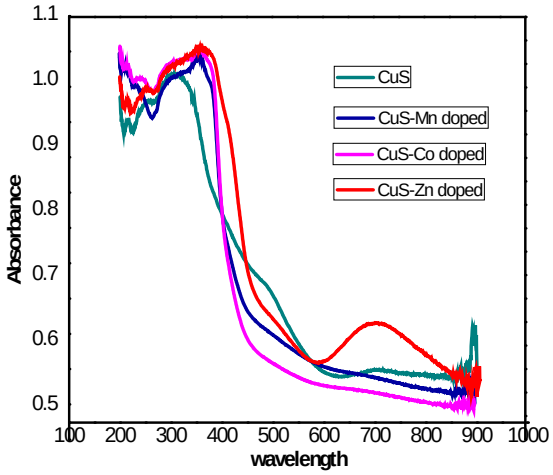

Figure 2 shows the absorption of CuS and CuS-M doped nanocrystalline powder

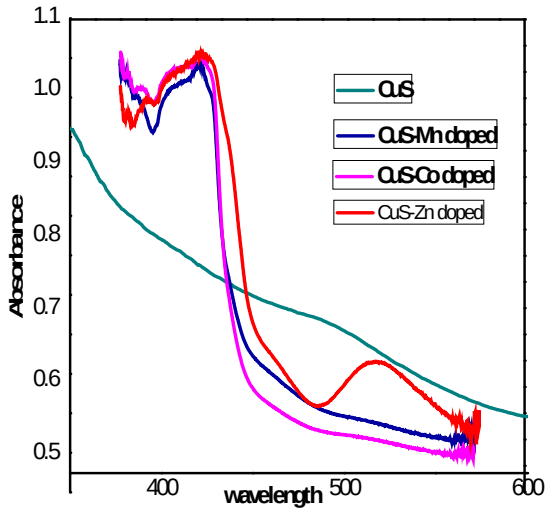

Figure 3 shows the absorption spectra ofCuS and M doped CuS in 350-600nm.

Absorption co-efficient α associated with strong absorption region of CuS & CuS-M doped nanoparticle was calculated from absorbance (A) and thickness (t) using the relation(3),

$$\alpha = \frac{2.303A}{t} \qquad \text{-------- (3)}$$

The absorption co-efficient α was analysed using the following expression.

$(\alpha h\upsilon) = k\,(h\upsilon - E_g)^{n/2}$ ------- (4)

Where k is Boltzmann's constant, E_g is separation between valence and conduction and n is constant which is equal to 1 for direct band gap semiconductor. The ban gap have been determined from the interest of straight line portion of $(\alpha h\upsilon)^2$verses hυ which is shown in Fig 4.

There are some differences between the band gap values obtained from $(\alpha h\upsilon)^n$ versus hυ graph and the values reported in the literature. The band gap value of a semiconductor can be affected by several factors and therefore it might not be definitive.

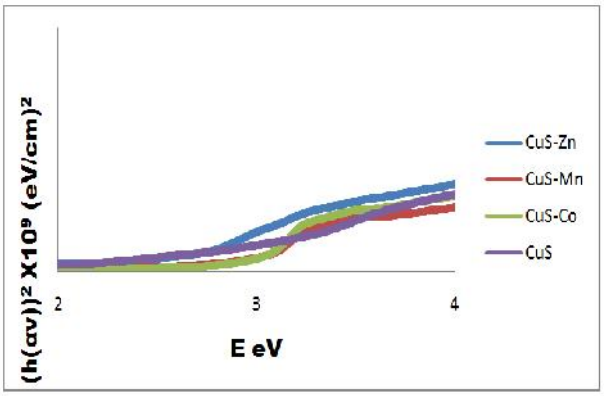

Figure 4 uv absorption pattern of $(h(\alpha\upsilon))^2$ verses E for CuS and M doped CuS nanoparticle.

These factors include: (i) size quantization effect that results to a shift in the absorption band position of semiconductors (Burstien–Moss shift)[4-5] ; (ii) improved crystallinity apart from other factors. Conduction band energy requires the amount of energy required to excite the the conduction electrons from the lowest to higher energy states by uv visible electromagnetic radiation.

$E = hc / \lambda_{max}$ ---------- (5)

Table no. 2 shows the conduction energy as obtained from figure 3 using the equation 5 and the band gap *Eg* as obtained from Figure 4.

Table 2 E and E_g as obtained from uv data

Synthesised compound	E *eV*	E_g *eV*
CuS	2.26	1.315
Mn doped CuS	2.64	1.375
Co doped CuS	2.69	1.373
Zn doped CuS	2.76	1.379

As the size of the synthesised compounds increases the average semiconductor band gap is seen to decrease.

Photoluminescence

PL properties of semiconductor nanocrystals depend on their surface states, surface passivation capped effect and size distributions [6]. Figure.5 represents PL spectrum of CuS and M-doped CuS nanocrystalline powder. The synthesized CuS nanocrystals exhibit strong emission peak at ~310 nm due to recombination of electrons and holes in the surface states [7], and broad shoulder peaks at 404 nm and 466 nm. The position of the emission peaks of CuS nanocrystals synthesized using different metals remains unaltered, whereas the relative intensities of the peaks seems to be closely related to the crystalline quality of the nanocrystals. Although, the emission peaks differs from the earlier reports of CuS[8, 9], results in this project were still consistent with the PL result reported by[10,11]. Besides, Jiang *et al.*[12] observed no emission peak for CuS between 400 nm and 800 nm. The different PL emission peaks of CuSnanocrystals observed in the present work as well as in the earlier reports may be attributed to the various size and shape of the CuS. Hence, these results indicate that luminescence properties of CuS strongly depend on the crystallinity and morphology of the nanocrystals.

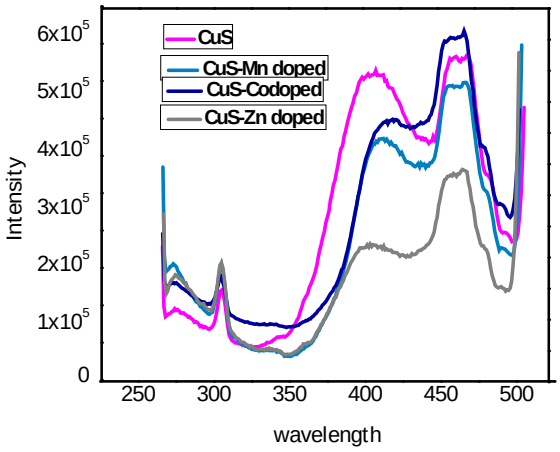

Figure 5 Photoluminescence of synthesised CuS and M doped CuSnanocrystals.

CONCLUSION

Copper sulphide and metal doped copper sulphidenanocrystalline particles were synthesized using mercaptoethanol as a stablising agent to control the size.

The synthesized nanoparticles were characterized using X-ray diffraction spectrometer (XRD), Photoluminesence (PL) and solid state uv-visible spectroscopy. It was observed that the average particle size of metal doped CuS was less than that of CuS nanoparticles.

The $E_g$and *E* were also determined for all the synthesized compounds from solid state uv-visible data. As the size of the synthesised compounds increases the average semiconductor band gap is seen to decrease. The synthesized CuS nanocrystals exhibit strong emission peak at ~310 nm broad shoulder peaks at 404 nm and 466 nm. The position of the emission peaks of CuS nanocrystals synthesized using different metals remains unaltered, whereas the relative intensities of the peaks seems to be closely related to the crystalline quality of the nanocrystals. As the size of Metal doped CuS nanoparticles synthesised using mercaptoethanol were relatively small, all the application involving nano-scale dimensions can be studied further. (Solar cells, optoelectronic devices, sensors).

Acknowledgements

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