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Structural and Optical Properties of $Cd_{0.3}Zn_{0.7}S$ Ternary Semiconducting Alloy

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ABSTRACT:

$Cd_{0.3}Zn_{0.7}S$ semiconducting nanomaterial doped with Cu and Cu,Mn have been synthesized successfully using chemical co-precipitation method. The XRD results have confirmed that as prepared quantum dots have hexagonal structure with only addition of Cu but with the addition of Mn there exists a phase change and structure becomes cubic. Furthermore, FTIR spectra of the prepared samples were observed for identification of COO- and O-H functional groups. The TEM study has also reported the spherical shape of the prepared nanoparticles. Absorption spectra show blue shifts in absorption as comparison to the bulk. The band gap value has also been calculated by Tauc's plot.

Keywords: *Co-precipitation, FTIR, TEM, UV-absorption spectra.*

1. INTRODUCTION

The doping in II-VI semiconducting nanomaterials change the structural and optical properties of the materials. Transition metal ion like Cu,Mn has been widely used as a dopant because of these ions give efficient luminescent properties [1]. Doped II-VI semiconductors are potentially applicable in LED's, cathode ray tube, flat panel displays, sensors, detectors and other optoelectronic devices [2,3].

From many years, the large energy band gap nanocrystalline materials like CdS, ZnS, CdSe, ZnSe were investigated by many scientists [4] but research work on their doped ternary type alloy nanostructures is found still very less. Although, in binary semiconducting materials the gap of energy band is also tuned by varying the particle size while in case of ternary semiconducting materials, it is also tuned with change in the proportion of composition of its elements [5]. In these materials like cadmium sulphide or telluride, the band energy gap value can be changed by mixing of an another host material like Zn (e.g.CdZnS) that opens a different opportunity for tremendous use in diverse areas like solar cells, photo-catalysis, sensors, photonic and other optoelectronic devices [6]. In the present work, we investigate the structural properties with the addition of Cu and Cu,Mn both in the host ternary alloy $Cd_{0.3}Zn_{0.7}S$. However band gap also estimated with the help of Tauc's plot.

2. EXPERIMENTAL DETAILS

2.1 Sample preparation

About 0.5 M cadmium acetate (30%) and zinc acetate (70%) were used according to their molar ratio taken in a beaker and stirred about half an hour at a temperature 60°C. In an another beaker 1M urea, 1M thiourea and 8 ml triethylamine have been taken and dissolved in100 ml of double distilled water under vigorous stirring condition at 60°C for half an hour. In the first beaker 1M % of copper acetate monohydrate as a dopant was added. The solution of first beaker was then added drop wise in the second beaker under vigorous stirring at a

heating temperature of 60°C. As a result the color of the solution changes light yellow to deep yellow during the reaction. After ending of the stirring the precipitates have been kept undisturbed for one day and then washed and filtered. For filtering the precipitates we used Whatman 40 with size 12.5 cm filter paper. After that the precipitates were dried in an air oven at a temperature 90°C for 8 hours. Finally, they were crushed in powder form using a pestle mortar. By following the same procedure we next time add 1M% of Mn and prepare the sample.

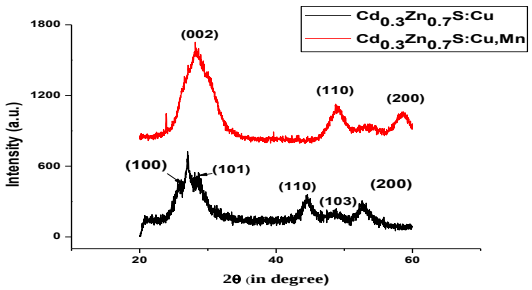
2.2 Characterizations

The XRD patterns of powdered form samples were recorded on Rigoku Powder X-ray diffractometer with CuKα (λ=0.15406 nm) radiation at voltage 40 kV and current at 30 mA with a scanning rate 2 degree min^{-1} from 2θ =20º to 60º. Further, a SHIMADZU IR Affinity-1 FTIR spectrometer was used in the range 400-4000 cm^{-1} to identify of various functional groups present in the precursors. TEM images were measured on a FEI TECNAI G^2 high resolution transmission electron microscope (HRTEM) operated at 200 kV. The optical absorption spectra of the prepared samples were measured by using a UV-VIS-NIR Spectrophotometer (Varian Cary-5000) in the range 200-800 nm.

3.RESULTS AND DISCUSSIONS

3.1 XRD Analysis

X-ray diffraction (XRD) spectra of samples Cu (0.01M) and Cu,Mn (0.01M) $Cd_{0.3}Zn_{0.7}S$ nanomaterials have been shown in "Fig. 1". The XRD spectra of Cu doped sample have exhibited main peaks at different values of 2θ ~25.66º, 27.18º, 28.7º, 44.68 º, 48.75 º, 52.83 º with respect to the (100), (002), (101), (110), (103), (200) hkl plane respectively. However with the addition of Mn numbers of planes are reduced and peaks are shifted towards higher angle having 2θ values at 28.51º, 48.92º, 53.6º, 58.6º. This may be due to the phase change with codoping and structure of the samples changes from hexagonal to the cubic. The XRD peaks of codoped samples are found well matched with JCPDS no. 35-1469.



"Fig.1 XRD pattern of Cu and Cu,Mn doped $Cd_{0.3}Zn_{0.7}S$ nanomaterials."

It has been observed that broadening increases with Mn addition. This indicates that there is decrease in size by addition of codopant. The average nanocrystallite size was estimated using Debye-Scherer formula about 5.73 and 2.4 nm for Cu doped and Cu,Mn doped alloy respectively. The lattice constants, lattice plane, d-spacing, unit cell volume, Lorentz factor and dislocation density were also calculated from XRD data. There

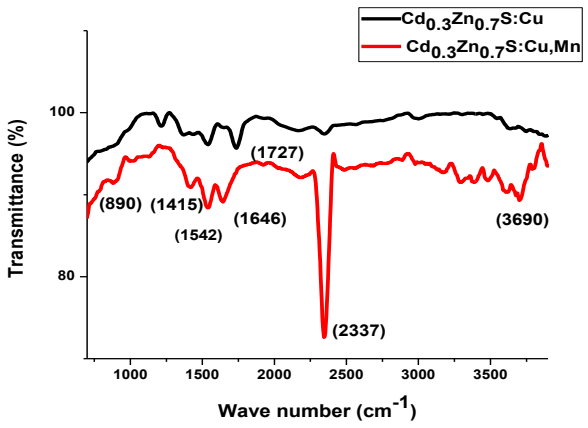
exists negative strain in both the samples. The crystallite size was also estimated from the Williamson-Hall method and its value found to be 4.43 and 1.43 nm. Hence the crystallite size decreased by W-H method in comparison to the Debye-Scherer method. This difference may be due to the smaller ionic radii of Cu (0.72Å) and Mn (0.67Å) ion in comparison to the Cd ion (0.97Å) [7] which induces the negative strain in the prepared samples.

TABLE I Structural parameters of the prepared samples.

Samples	$D_{D\text{-}S}$ (nm)	a(Å)	c(Å)	Volume of unit cell $(Å)^3$	Strain ε	Dislocation density $1/<D>^2$ $(\rho)*10^{-2}$ (cm^{-2})	Lorentz Factor(L)
$Cd_{0.3}Zn_{0.7}S$:Cu,(1M%)	5.73	4.062	6.591	94.17	-0.01007	0.0304	4.727
$Cd_{0.3}Zn_{0.7}S$:Cu,Mn(1M%)	2.04	3.951	6.369	86.14	-0.03829	0.240	4.411

3.2 FTIR Analysis

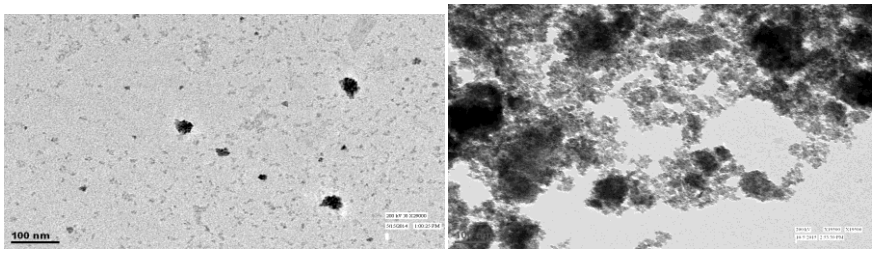
The FTIR spectra of Cu doped and Cu, Mn co doped samples were shown in the "Fig. 2". FTIR shows the presence of acetate, sulphide and water group. Absorption of O-H group was found at 3610-3690 cm^{-1} in higher energy region which corresponds to the stretching vibration of water molecules. However in Mn doped it start at the 3300 cm^{-1} range. The absorption peak around 1727 cm^{-1} corresponds to C-H stretching vibration [8]. However in lower energy region a small peak at wave number 890 cm^{-1} has been assigned to CdS stretching mode. The absorption peak at 1415-1643 cm^{-1} 2337cm^{-1} presents the symmetric and asymmetric stretching of the COO- of acetate group [9].



"Fig.2 FTIR spectra of Cu and Cu,Mn doped $Cd_{0.3}Zn_{0.7}S$ nanomaterials."

3.3 TEM Analysis

Transmission electron microscopy has been used to investigate morphology of our prepared samples which gives the size, shape and nano crystalline nature. "Fig. 3(a) and (b)" shows the TEM micrograph of Cu doped $Cd_{0.3}Zn_{0.7}S$ sample. It has been observed that particles are almost in spherical shape. Agglomeration was found in the co-doped samples more. This may be due to the small size of the prepared samples.



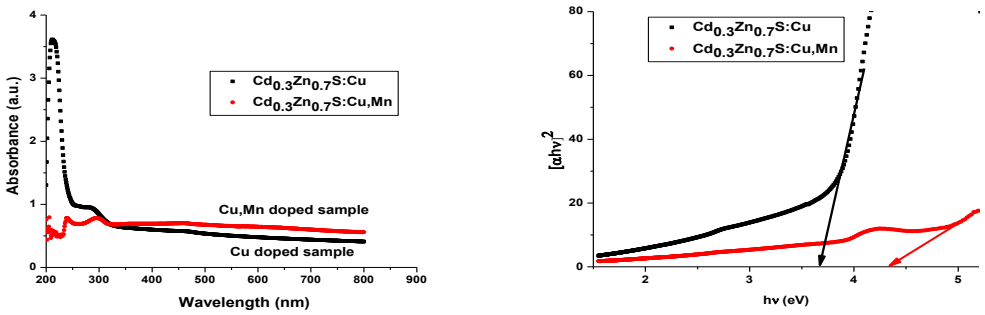
"Fig. 3 (a) TEM micrographs of Cu and (b) Cu,Mn doped $Cd_{0.3}Zn_{0.7}S$ nanomaterials."

3.4 UV-visible Analysis

The optical absorption spectra of Cu (0.01M) and Cu, Mn (0.01M) doped $Cd_{0.3}Zn_{0.7}S$ nanomaterials samples have been shown in the "Fig.4(a)". The UV-Visible spectroscopic observations were carried out at room temperature to investigate the effects of doped concentration (Cu, Mn) in the wavelength range 200-800 nm. In Cu doped sample strongest absorption maxima has been appeared at wavelength 215 nm and 239 nm for codoped sample which is blue shifted in comparison of bulk value of CdS and ZnS [10]. Further shoulder absorption appeared at 288nm and 298 nm for Cu doped and codoped samples. This may be explained that there is more than one population of crystallites of different sizes, indicating a defocused growth process. Blue shifting in absorption peak is attributed to the quantum size effect [11]. Here we are studying the $Cd_{0.3}Zn_{0.7}S$ which is a direct band gap material; hence the absorption coefficient near the band edge is obtained by the Tauc's relation of equation (1)[12].

$$\alpha h\nu = A(h\nu - E_g)^n \quad (1)$$

Where A is a constant and E_g is band gap energy of the materials.



"Fig. 4 (a) UV-visible absorption spectra and (b) band gap energy of Cu and Cu,Mn doped $Cd_{0.3}Zn_{0.7}S$ nanomaterials."

The band gap value for Cu doped has been obtained by the extrapolating the linear region at energy axis. Band energy was found to be 3.68eV and 4.35eV for Cu and Cu,Mn doped samples respectively as shown in "Fig. 4(b)". It has been observed that with the addition of Mn band gap increases due to decrease in size according to quantum confinement effect.

4. CONCLUSIONS

Cu doped and Cu,Mn doped $Cd_{0.3}Zn_{0.7}S$ nanomaterials has been synthesized successfully by using Co-precipitation method. There exists a phase change with the addition of Mn and structure changes hexagonal to the cubic. Crystallite size also decreases with Mn and broadening increases which confirms the formation of quantum dot. Further, FTIR gives the presence of sulphide acetate and water group. Band gap value also increases in codoped samples. Hence codoped samples of $Cd_{0.3}Zn_{0.7}S$ nanomaterials have more potential use in optoelectronic devices.

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