

Structural and Morphological Studies of Cu Doped ZnS Nanocrystals Prepared by Coprecipitation Method

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ABSTRACT: $Zn_{1-x}Cu_xS$ system with $x = 0.00$ and 0.03 were synthesized by co-precipitation reaction between acetate and sodium sulfide at room temperature in air. The doping effects of Cu ions on the structural and optical properties of $Zn_{1-x}Cu_xS$ nanoparticles were investigated. All the samples have the hexagonal structure. The lattice constant of $Zn_{1-x}Cu_xS$ samples increases with increasing Cu concentration. It indicates that Cu ions go to Zn sites of ZnS lattice structure. The average crystalline sizes were obtained from width of X-ray diffraction pattern using Scherrer's formula. It is found that grain size is in the range of below 100 nm. The SEM study confirms that the agglomeration of doped ZnS.

KEYWORDS: Co-precipitation, XRD, SEM.

I. INTRODUCTION

In the last two decades, the "small-particle" research has become quite popular in various fields of chemistry and physics. The "small-particles" now we call nanostructured materials, are very interesting materials both for scientific reason and practical application. Semiconductor nanocrystals represent a class of materials that have hybrid molecular and bulk properties. They have attracted much attention over the past few years because of their novel properties which originate from quantum confinement effect [1-4]. Quantum confinement effect modifies the electronic structure of the nanocrystals when the sizes of the nanoparticles are comparable to that of Bohr excitonic radius of those materials. When the particle radius falls below the excitonic Bohr radius, the band gap energy is widened, leading to a blue shift in the band gap, emission spectra etc. On the other hand, the surface states will play a more important role in the nanoparticles, due to their large surface-to-volume ratio with a decrease in particle size (surface effects). In the case of semiconductor nanoparticles, radiative or nonradiative recombination of an exciton at the surface states becomes dominant in its optical properties with a decrease of particle size. Therefore, the decay of an exciton at the surface states will influence the qualities of the material for an optoelectronic device. These size dependent optical properties have many potential applications in the areas of solar energy conversion, light emitting devices, chemical/biological sensors and photocatalysis [5-9]. Wide band gap II-VI semiconductors are expected to be the novel materials for the optoelectronic devices [10].

Keeping in view the above discussion, an effort has been made to study the optical properties of $ZnCuS$ nanomaterial of different molar copper acetate as doping agent. In the present paper, $ZnCuS$ nanomaterial is synthesized by using coprecipitation method.

II. EXPERIMENTAL

Cu doped ZnS nanometer-sized crystals were prepared by co-precipitation method at room temperature. For Cu doped ZnS, at first, 100 ml each of both Zinc acetate solution, Copper acetate and solution of sodium sulfide in mixture of methanol and distilled water were prepared. Zinc acetate solution and copper acetate added solution are first vigorously stirred using a magnetic stirrer upto 1 h at 800 rpm and then the solution of sodium sulfide is mixed with the solution of Zinc acetate and Copper acetate drop wise added.

In the post synthesis steps, obtained precipitate was kept at constant stirring for 3hrs. Afterwards obtained precipitateseparated from the solution by filtration, washedseveraltimes with distilled water and methanol toremove all sodium particles and then wet precipitate isdried 150° C for 12 hrs. Then dried sample were grinded for 30 min and calcinated at 500° C for 4 hrto obtain ZnCuS nanometer-sized crystals.

III. RESULTS AND DISCUSSION

A. X- RAY DIFFRACTION MEASUREMENT

The XRD pattern of synthesized ZnS nanocrystals is shown in figure 1. The spectra shows the different diffraction peaks at 2θ values of 28.04, 32.47, 47.12, 28.00, 69.21 and 76.51 corresponding to (1,1,1), (2,0,2), (2,2,0), (3,1,1), (2,2,2) and (4, 0, 0) planes which confirm the hexagonal structure of present investigations with JCPDS card No. 01-077-3378. Similarly, XRD pattern of ZnCuSis shown in figure 2. The different diffraction peaks at 2θ values are 27.85, 27.90, 46.88, 55.78, 27.9, and 68.79 to (1, 1, 1), (2, 0, 0), (2, 2, 0), (1, 0, 2), (3, 1, 1), (4, 0, 0), and (3, 3, 1) planes. No extra peaks related to any impurity were observed which indicates that the quality of the product as well as synthesized method. The broad peaks in the XRD pattern are perfectly indexed the presence of ZnS nanocrystals.

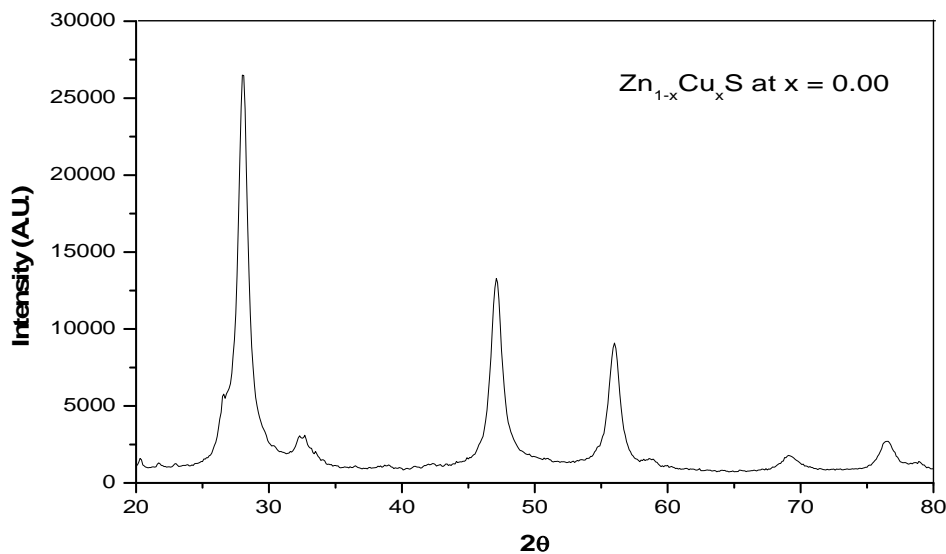


Figure 1. XRD Pattern of Zn_{1-x}Cu_xS at x=0.00

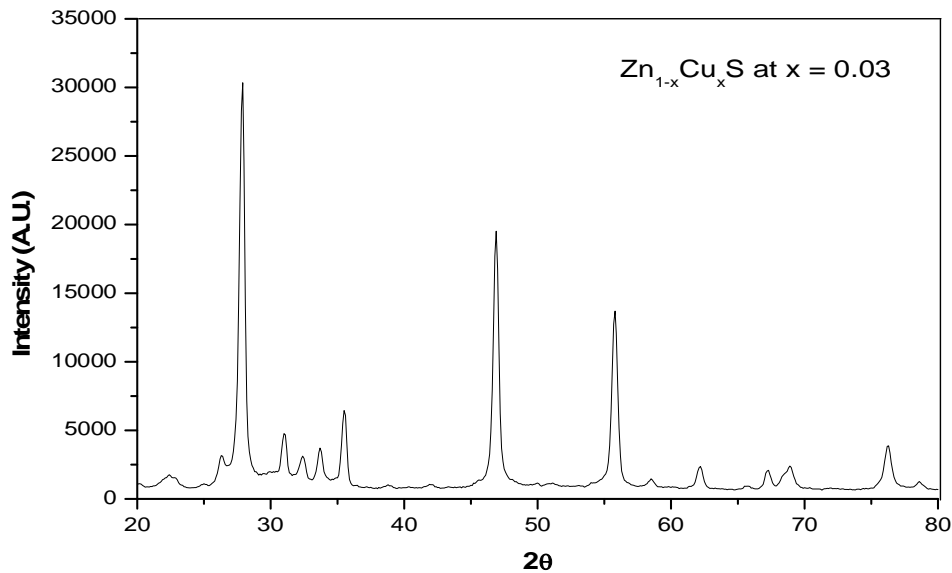


Figure 2. XRD Pattern of Zn_{1-x}Cu_xS at x=0.03

The broadening of XRD peaks attributed nano-sized formation of prepared ZnCuS samples. The average crystallite size was estimated from Debye-Scherrer's formula [11],

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where, D is the crystalline size, β (in radian) is full width at half maxima (FWHM) of diffraction peak, K is the geometric constant factor (0.89), λ is the wavelength in nanometer, θ is known as Bragg's diffraction angle measured in radian also. It is observed that the average grain size of Zn_{1-x}Cu_xS at x=0.00 nanocrystal 9.137nm while Zn_{1-x}Cu_xS at x=0.03 is 21.109nm. It is observed that the grain size and X-ray density increases while Volume of unit cell decreases with increase in doping concentration of Cu in ZnS. It indicates the doping play an important role in the structural properties of ZnS nanocrystals.

Table 1. The lattice parameters, volume, x-ray density and grain size of Zn_{1-x}Cu_xS samples.

Samples	Lattice parameters in (Å ⁰)		Volume of unit cell in (Å ⁰) ³	X- ray density dx (g/cm ³)	Average Grain Size (D) in nm
	a	c			
X=0.00	3.8209	6.2573	79.1142	3.4181	9.137
X=0.03	3.8210	75.1200	949.7800	0.2847	21.109

B. SCANNING ELECTRON MICROSCOPY

SEM images of Zn_{1.00}Cu_{0.00}S and Zn_{0.97}Cu_{0.03}S nanocrystals are shown in figure 2 (a, b). These images reveal a systematic evaluation of morphology of the prepared sample. It is observed that the preparation technique plays the important role for the formation of nanocrystals. It is observed that at same calcinations temperature i.e. 500°C, the formation of Zn_{1.00}Cu_{0.00}S and Zn_{0.97}Cu_{0.03}S nanocrystals is different in shape and size.

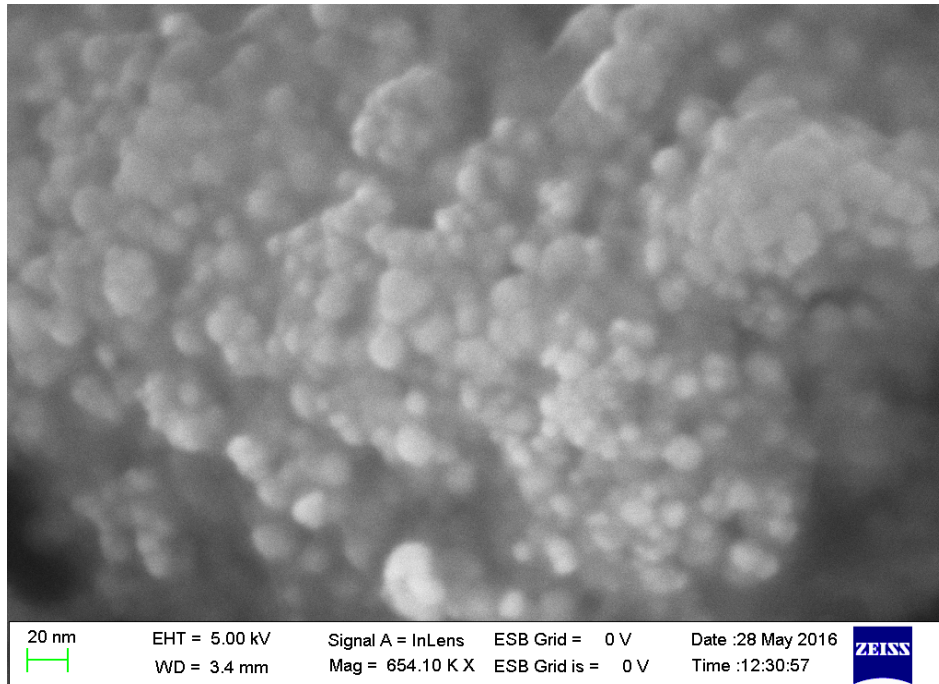


Figure 2 a. SEM images of $Zn_{1.00}Cu_{0.00}S$

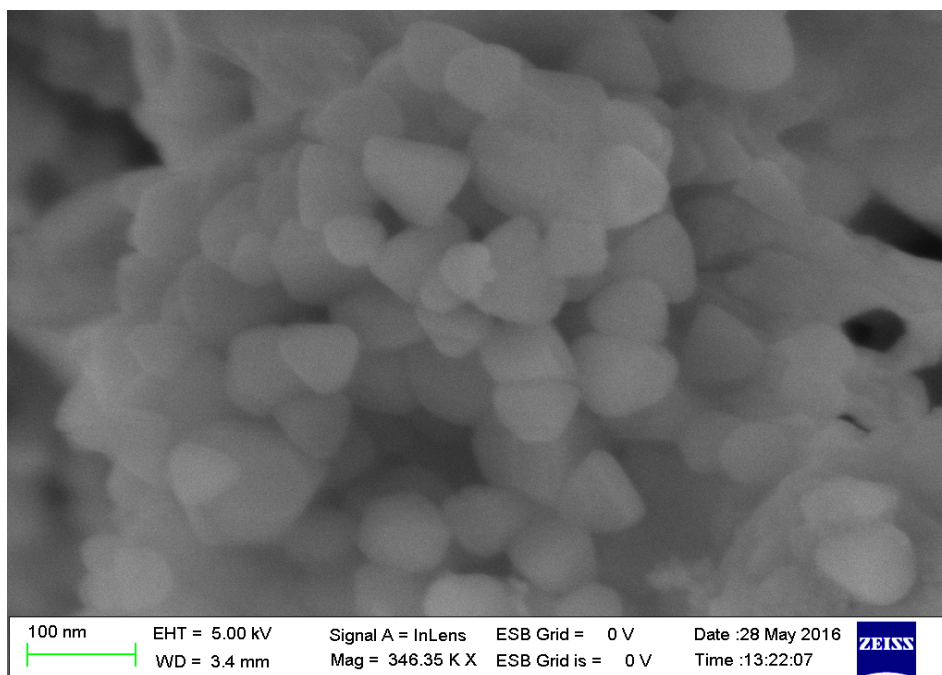


Figure 2 b. SEM images of $Zn_{0.97}Cu_{0.03}S$

IV. CONCLUSION

The effect of doping on structural, morphological, ZnS nanocrystals prepared by Coprecipitation method was studied. From XRD studies it is confirmed that samples having wurtzite hexagonal structural with different symmetry. It is observed that from SEM images that the agglomeration. It is also found that grain size increases with increasing doping concentration plays an important role in structural, morphological of ZnS nanocrystals.

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