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# Structural and Optical properties of Cr doped ZnS nanorods

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**Cr doped ZnS nanorods with formula $Zn_{1-x}Cr_xS$ (x = 0.00, 0.08 and 0.10) were synthesized by co-precipitation method. All samples exhibits cubic structure, confirmed from X-ray diffraction data. Using Debye-Scherrer's formula, grain size estimated and indicating that samples define quantum confinement effect (QCE), which means that as prepared samples exhibits quantum dot. Chemical compositions of all samples were confirmed by energy dispersive spectra (EDS). $Cr^{3+}$ ions doping has significant influence on the optical properties of ZnS nanorods. UV-Vis absorption study exhibited the presence of red shift for Cr doped ZnS compare to undoped. TEM study revealed nanorods for 8 at% and 10 at% Cr concentrations.**

**Key words: Semiconductors, Chemical synthesis, Energy dispersive analysis of X-rays (EDS), Crystallography, Optical properties.**

## Introduction

ZnS is a promising candidate for optoelectronic and luminescent device applications on account of its wide energy band gap (3.68 eV) and large exciton binding energy (40 meV) [1-3]. Therefore, doped ZnS materials attracted extraordinary attention especially for their nanoscale forms. Compared to the pure semiconductors, transition metal (TM) and rare earth (RE) doped nanoscale semiconductors are more likely to achieve novel physical properties due to the quantum confinement effects [4, 5] and surface effects [6].

Different ZnS nanostructures including nanowires, nanobelts, nanoribbons, nanosaws and nanocables have been successfully synthesized using a variety of employing methods such as thermal evaporation, intermittent laser-ablation catalytic growth, in-situ formation in liquid-crystal templates, chemical vapour deposition, etc. [7-10]. ZnS nanowires have attracted much research attention because they promise to open huge potential applications at room temperature for optoelectronics and other interdisciplinary utilities such as nano LEDs, nano FETs and nano LASERs [11-15].

As a transition element with various valences and possible high magnetic moment, Cr is a promising dopant for both optical and magnetic purposes. In this study, we synthesized samples by chemical co-precipitation route. Structural, morphological and optical measurements were undertaken. Results of such an investigation are presented in this paper.

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## Experimental

Samples of $Zn_{1-x}Cr_xS$ with compositions (x = 0.00, 0.08 and 0.10) nanoparticles were synthesized by chemical co-precipitation route at room temperature. The starting materials analytical grade Zinc nitrate, Chromium nitrate, Sodium sulphide were used and methanol was used as solvent. The appropriate amounts of zinc nitrate and chromium nitrate were dissolved separately in 100 ml methanol and stirred at room temperature for 2 h. Chromium nitrate solution was added into zinc nitrate and stirred for 20 min. Sodium sulphide solution was added drop wise into mixed solution of zinc nitrate and chromium nitrate with vigorous stirring and pH 10 maintained. The light sky-blue coloured precipitate was obtained, the colour of the precipitate gets darken as Cr concentration increases. The precipitate was continuously stirred for 2 h again to get homogeneous particle size. The precipitate was collected and washed several times by deionised water followed by methanol. The washed precipitate was dried at 50 ºC for 4 h in the oven and ground for 15 min to get Cr doped ZnS nanoparticles and nanorods finally.

The X-ray diffraction patterns were recorded by X-ray diffraction spectrometer (Bruker) using CuKá radiation ($\lambda$ = 1.5406 Å) with 2$\theta$ scanning range from 20 º to 80 º with a scanning speed of 4 degree/min. Chemical composition analysis was carried out using EDS. The TEM images were obtained on a JEOL-2010 transmission electron microscope at an acceleration voltage of 200 kV with magnification 2 nm and 50 nm for undoped and 8%, 10% Cr dopent concentration. The optical measurements were undertaken with UV spectrometer [JASCO, V-670] in the wavelength range of 200 nm to 1000 nm.

## Results and Discussion

The XRD patterns for pure and Cr doped ZnS samples were recorded and are shown in figure 1. The diffraction peaks corresponded to (111), (220) and (311) planes, d-spacing values and relative intensities of the peaks are well matched with the JCPDS data (00-001-0792) of cubic structure. No extra peaks observed in XRD patterns, which confirms that undoped and Cr doped ZnS samples are pure. The lattice parameters, volume cell, X-ray density, grain size were determined using XRD data and are recorded in table 1.

Also observed from figure 1 that the (111) diffraction peaks were shifted to higher 2θ values with increasing Cr concentration in ZnS than undoped sample. It may be due to the small ionic radii of $Cr^{3+}$ (0.63 Å) compared to that of $Zn^{2+}$ (0.74 Å), which was substituted into ZnS lattice structure. Rahdar *et al.* [16] reported that the Cr doped ZnS nanoparticles synthesized by co-precipitation route exhibits wurtzite (hexagonal) structure. However, in our study, XRD peaks were matched well with JCPDS data. Our report shows as prepared samples are having cubic structure.

Average crystalline size of all the samples were determined by the Debye-Scherrer's formula. The lattice constant 'a' and volume of unit cell decrease with Cr concentration in ZnS nanostructures. X-ray density and crystalline size decrease from undoped to 8% Cr doped then increases for 10% Cr concentration as shown in figure 2.

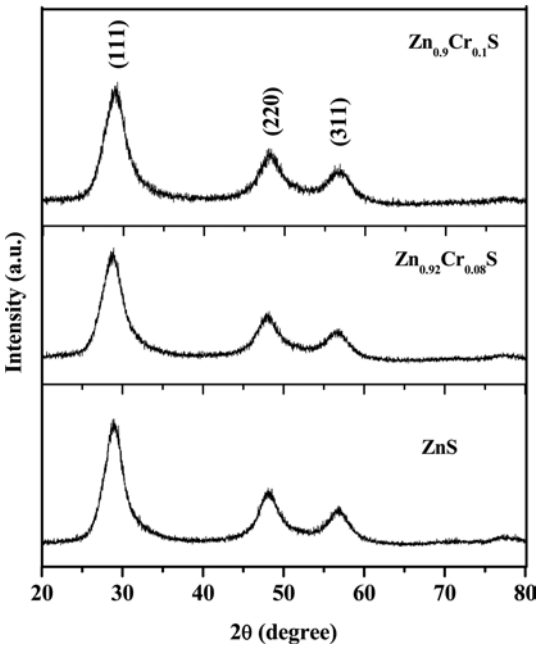


**Fig. 1.** XRD patterns of pure and Cr doped ZnS nanostructures.

**Table 1.** Structural parameters of pure and Cr doped ZnS samples.

| Conc. 'x' | 'a' (Å) | Volume $(Å)^3$ | X-ray density $(g/cm^3)$ | Grain size (nm) |
|---|---|---|---|---|
| 0.00 | 5.3913 | 156.151 | 1.0366 | 3.853 |
| 0.08 | 5.3777 | 155.466 | 1.0101 | 3.653 |
| 0.10 | 5.3423 | 152.475 | 1.0470 | 3.886 |

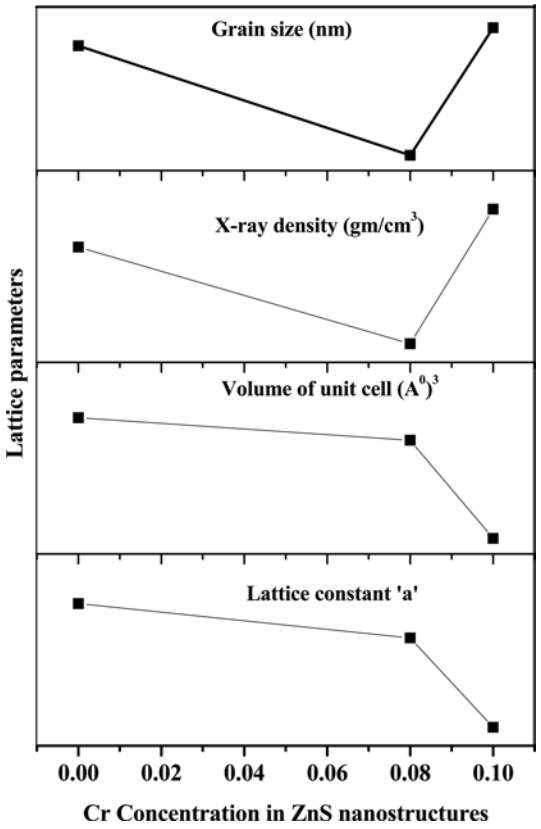


**Fig. 2.** Variation of lattice parameters with Cr concentration in ZnS nanostructures.

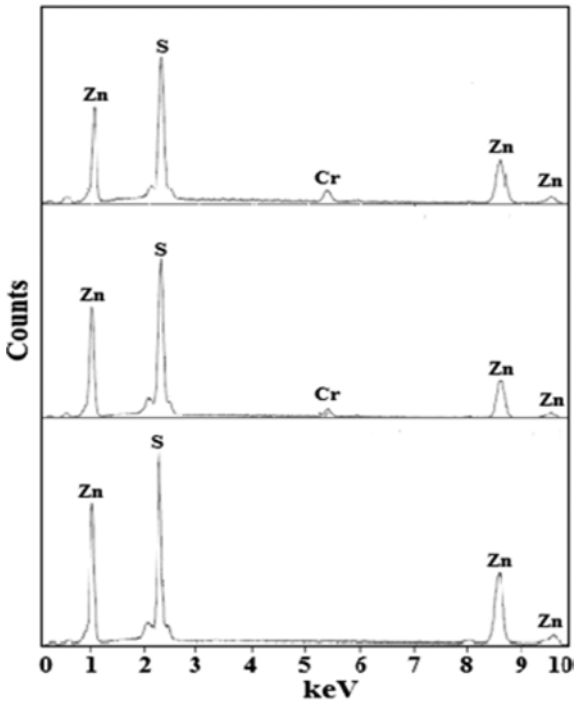


**Fig. 3.** EDS analysis of pure and Cr doped ZnS nanostructures.

**Table 2** Chemical analysis of pure and Cr doped ZnS nanostructure samples.

| Element | Pure | 8% Cr | 10% Cr |
|---|---|---|---|
| | (Wt%) | | |
| Zn | 60.32 | 51.24 | 52.97 |
| Cr | 0.00 | 3.42 | 4.94 |
| S | 39.68 | 45.04 | 42.09 |

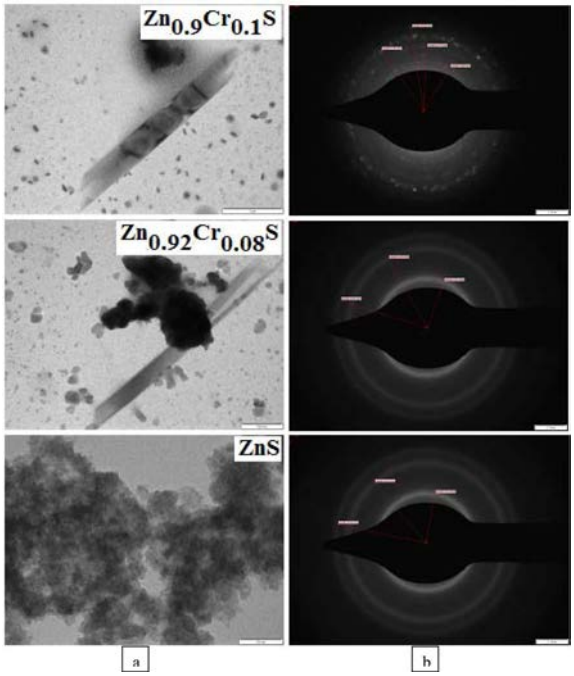


**Fig. 4.** (a) TEM images and (b) SAED pattern of undoped and Cr doped ZnS nanostructures.

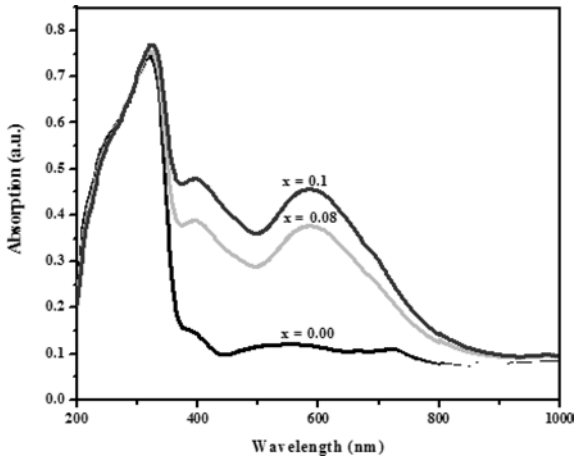


**Fig. 5.** Absorption spectra of pure and Cr doped ZnS nanostructures.

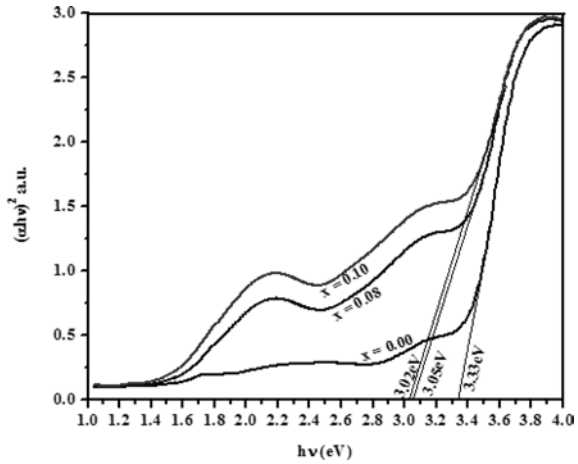


**Fig. 6.** Tauc's plots for pure and Cr doped ZnS nanostructures.

The chemical composition analysis was carried out using energy-dispersive spectra (EDS), details are shown in figure 3 and table 2. Figure 3 shows the typical EDS of undoped and Cr doped ZnS nanocrystals and nanorods. EDS shows only sharp peaks of Zn, Cr and S. It clearly shows that the intensity of Cr increases with increasing Cr content in ZnS system. No extra peaks observed in EDS spectra. From table 2, it is confirmed that the prepared samples are pure.

The morphological study was carried out using transmission electron microscope. The TEM images are shown in figure 4. The selected area electron diffraction (SAED) pattern consists of three concentric sharp rings, which corresponded to (111), (220) and (311) the diffraction peaks for undpoed and 8% Cr doped ZnS nanostructures and fourth concentric ring was observed, which corresponds to the diffraction peak (331) for 10% Cr doped ZnS nanorods. Therefore, it is further confirmed that the nanocrystals and nanorods are cubic in structure.

The absorption spectra and optical energy band gap study of undoped and Cr doped ZnS samples were carried out by UV visible spectrometer and is shown in figure 5. Zeng *et al*. [17] reported that, two main absorption bands in the visible light region were observed in Cr-doped ZnS nanostructures as compared to undoped sample. In our study, three absorption bands were observed and are located at 320 nm for pure ZnS sample, bands observed at 395 nm and 588 nm for 8% and 10% of Cr doped ZnS nanostructure samples.

The energy band gap values were evaluated from Tauc's plots as shown in figure 6. Rahdar *et al.* [16] reported that the band gap values enhanced with increasing Cr concentration and is attributed to size quantization effect due to the smaller size of the particles. In our study, even though the particles are quantum dots the band gaps were 3.33 eV, 3.05 eV and 3.02 eV for pure ZnS, 8% and 10% Cr doped ZnS samples respectively and are decreasing with increasing Cr contents into ZnS lattice. The red shift in the optical energy band gap confirms the uniform substitution of Cr ions in the ZnS lattice.

## Conclusions

Samples of $Zn_{1-x}Cr_xS$ with nominal compositions (x = 0.00, 0.08, 0.1) were synthesized by chemical co-precipitation route. From XRD data it is confirmed that

the prepared samples have cubic structure and grain size is in the range of 3 nm to 4 nm which means that samples exhibit quantum dots. EDS study revealed that the prepared nanostructures are intrinsic and confirms Cr substitution in to ZnS cite. From TEM images, it is revealed that two types of nanostructures like nanocrystals for pure ZnS and nanorods for 8% and 10% Cr doped ZnS samples were observed. From SAED patterns, it is evidenced that the samples are having cube structure. Red shift in the band gap observed in optical study. Three absorption bands are recorded in the absorption spectra and energy band gap decreases as Cr content increases.

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