

# Crystallographic and optical studies on Cr doped ZnS nanocrystals

## *(Estudos ópticos e cristalográficos de ZnS dopado com Cr)*

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### Abstract

Chromium doped ZnS nanocrystals with pure and 10% compositions were synthesized by chemical co-precipitation route. Samples were characterized by X-ray diffraction (XRD) technique, Fourier transforms infrared spectroscopy (FTIR) and UV-Visible spectrometer. Lattice parameter 'a' decreases and grain size increases with increasing Cr concentration. XRD study shows that both the samples have cubic structure. Grain size increases due to ionic radius. The functional groups and chemical species of Cr doped ZnO samples were determined using FTIR data. UV-Vis study revealed that red shift is clearly observed in absorption band. Surface morphology of pure and 10% Cr doped samples was investigated by SEM technique and it is confirmed that images exhibit cubic form of the samples. Using EDS, percentage of chemical compositions of material recorded.

**Keywords:** ZnS, grain size, functional group, unit cell volume, red shift.

### Resumo

Foram sintetizados nanocristais de ZnS puros e dopados com 10% cromo pela rota química de co-precipitação. As amostras foram caracterizadas pela técnica de difração de raios X (DRX), espectroscopia de infravermelho com transformada de Fourier (FTIR) e espectrometria UV-Visível. O parâmetro de rede 'a' diminui e o tamanho de grão aumenta com o aumento da concentração de cromo. O estudo de difração de raios X mostra que ambas amostras tem estrutura cúbica. O tamanho de grão aumenta devido ao raio iônico. Os grupos funcionais e as espécies químicas de amostras de ZnS dopadas com cromo foram determinadas com os dados de FTIR. O estudo de UV-Vis revelou que o deslocamento para o vermelho observado na banda de absorção. A morfologia da superfície de amostras puras e dopadas com 10% de cromo foi investigada por microscopia eletrônica de varredura e foi confirmado que as imagens exibem a forma cúbica das amostras. Usando EDS, foi avaliada a composição química.

**Palavras-chave:** ZnS, tamanho de grão, grupo funcional, volume de célula unitária, red shift.

## INTRODUCTION

Among the family of II-VI group inorganic semiconductor nanomaterials like CdS, ZnS, CdSe, ZnSe are proved to be versatile materials because of their applications in optoelectronic devices due to large variation of band gap as a function of particle size. Zinc Sulfide (ZnS) is one of the first semiconductor discovered [1] and it has traditionally shown remarkable fundamental properties versatility and a promise for novel diverse applications, including light-emitting diodes (LEDs), electroluminescence, flat panel displays, infrared windows, sensors, lasers, etc. Efficient doping of rare-earth ions into II-VI semiconductor host is not favorable compared to the transition metals. In view of this, transition metal doped ZnS, like ZnS: Mn [2], ZnS:Cu [3], ZnS:Co [4] and ZnS:Ni [5] have been widely investigated. However, surprisingly, inspite of both applied and academic interest, Cr doped ZnS has been least studied. In fact to the best of our knowledge, there are only a few reports [6-8] on

Cr doped ZnS and all these reports are on ZnS: Cr prepared by physical methods only. Particularly doping of ZnS with Cr is attractive because Cr is an important transition metal and it has ionic radius (0.63 Å) closer to that of Zn<sup>2+</sup> (0.74 Å) which means that Cr can easily substitute Zn<sup>2+</sup> in the host lattice. Based on density- function calculations [9], Cr is theoretically proposed to be a reliable dopant in ZnS.

In view of the above, Cr doped ZnS nanocrystals were synthesized by chemical co-precipitation route. XRD technique was employed to understand crystal structure. Using FTIR, chemical species were detected. E<sub>g</sub> was estimated by UV-Vis spectra.

## EXPERIMENTAL

Cr doped ZnS with chemical composition Zn<sub>1-x</sub>Cr<sub>x</sub>S (x = 0% and 10%) were synthesized by chemical co-precipitation route. All chemicals were used of analytical grade. Methanol was used as solvent. The starting materials

zinc nitrate, chromium nitrate and sodium sulfide. 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. A high alkaline medium (pH=10) was maintained by adding sodium sulfide solution into mixed solution of zinc nitrate and chromium nitrate drop wise, the light sky-blue coloured precipitate was obtained, the colour of the precipitate becomes dark for 10% Cr concentration. The precipitate was stirred for 2 h again to get homogeneous particle size. The precipitate was collected and washed several times by DI water and methanol. Finally to get Cr doped ZnS nanocrystals, the precipitate was dried in the oven at 50 °C for 4 h. The X-ray diffraction patterns of undoped and 10% Cr doped ZnS nanocrystals were recorded using  $\text{CuK}\alpha$  radiation (Bruker,  $\lambda=1.5406 \text{ \AA}$ ) with  $2\theta$  ranging 20-80°. FTIR (Jasco FTIR, Japan) spectra were recorded at room temperature. The UV-Vis measurements were done with UV-Vis spectrometer (Jasco UV-VIS-NIR spectrophotometer V-670) in the wavelength range of 200 nm to 1000 nm.

## RESULTS AND DISCUSSION

### Diffraction study

XRD patterns of Cr doped ZnS nanocrystals are as shown in Fig 1. The broadening of diffraction confirmed that the crystallites were nanosized. The diffraction peaks corresponds to (111), (220) and (311) planes are in good agreement with the standard diffraction peaks (JCPDS 00-001-0792) of cubic structure and also indicates that the  $\text{Cr}^{2+}$  ions substituted into  $\text{Zn}^{2+}$  site has no effect on the crystal structure. No additional peaks were observed. The lattice parameter, volume cell, X-ray density, grain size and % of crystallinity were determined using XRD data. Grain size of the nanoparticles determined by the Debye-Scherrer's equation  $D=K\lambda/\beta\cos\theta$ , where  $K=0.09$  [12] and their values are depicted in Table I.

Reddy *et al* [10] reported that the diffraction peak of

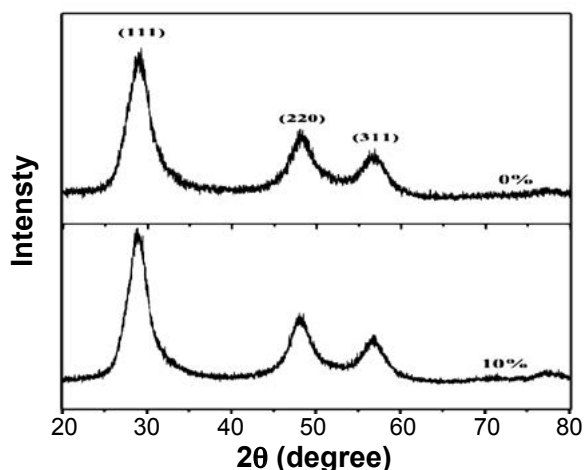


Figure 1: XRD pattern of  $\text{Zn}_{1-x}\text{Cr}_x\text{S}$  nanocrystals.

[Figura 1: Difratoograma de raios X de cristais de  $\text{Zn}_{1-x}\text{Cr}_x\text{S}$ .]

Table I - Lattice parameter, volume cell, X-ray diffraction density, grain size and % of crystallinity of  $\text{Zn}_{1-x}\text{Cr}_x\text{S}$ .

[Tabela I - Parâmetro de rede, volume da célula, densidade por difração de raios X, tamanho de grão e % de cristalinidade de  $\text{Zn}_{1-x}\text{Cr}_x\text{S}$ .]

Conc. x (%)	'a' (Å)	Volume (Å) <sup>3</sup>	X-ray density (gm/cm <sup>3</sup> )	Grain size (nm)	% of crystallinity
0	5.3913	156.151	1.0366	3.853	57.4
10	5.3423	152.475	1.0470	3.886	56.6

(111) is slightly shifted to higher angles as the concentration increases. Rahdar *et al* [11] reported that the Cr doped ZnS nanocrystals synthesized by co-precipitation route was wurtzite (hexagonal) structure. In the present investigation the (111) diffraction peak is also shifted to higher angle for 10% Cr doped ZnS in comparison to pure ZnS samples. It may be due to the small ionic radii of  $\text{Cr}^{3+}$  (0.63 Å) compared to that of  $\text{Zn}^{2+}$  (0.74 Å), which have entered into ZnS. Our XRD data is in good agreement with the diffraction data of cubical structure and the cell parameter 'a' is very close to the reported value in JCPDS 00-001-0792 data. From Table I we attribute that the grain size and the X-ray density are more and lattice parameter 'a', volume of unit cell and % of crystallinity are less for Cr doped ZnS than in undoped nanocrystals.

### Estimation of chemical species

FTIR absorption spectra of Cr doped ZnO nanocrystals are shown in Fig 2.

The FTIR spectra of the pure and 10% Cr doped ZnS nanocrystals samples of present investigations are in good agreement with the reported values [13]. One can observe that broad bands appeared around 3440  $\text{cm}^{-1}$  and 3470  $\text{cm}^{-1}$  typically due to O-H stretching. The additional weak bands and shoulders that are observed at 1631  $\text{cm}^{-1}$  and 1639  $\text{cm}^{-1}$  may be due to microstructural formation of the samples. The C-H bending of methylene in ME is observed at the 1407  $\text{cm}^{-1}$

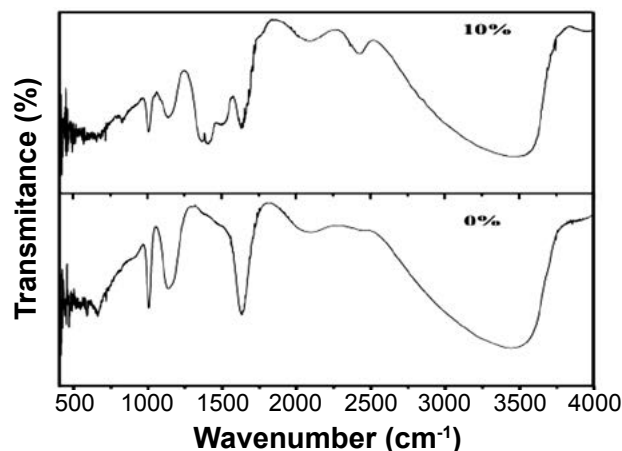


Figure 2: FTIR spectra of  $\text{Zn}_{1-x}\text{Cr}_x\text{S}$  nanocrystals.

[Figura 2: Espectros FTIR de cristais de  $\text{Zn}_{1-x}\text{Cr}_x\text{S}$ .]

band. The spectra at  $1135\text{ cm}^{-1}$  is due to IR characterization size frequency of inorganic ions. The bands at  $1008\text{ cm}^{-1}$  and  $1010\text{ cm}^{-1}$  are due to C-O stretching. The spectra at  $661\text{ cm}^{-1}$  and  $668\text{ cm}^{-1}$  are ZnS bands that correspond to sulfide. Two more bands are observed in the FTIR spectra for 10% Cr doped ZnS nanocrystals sample at  $2103\text{ cm}^{-1}$  and  $2433\text{ cm}^{-1}$  and are assigned to the  $\text{CO}_2$  mode, it may be due to the  $\text{CO}_2$  absorbed from the atmosphere. From this study one can say that the substitutional effect of Cr concentration takes place in the ZnS nanocrystals synthesized by chemical co-precipitation route.

### Optical Properties

The Tauc plot was employed to determine the energy band of the samples. The UV-Vis study of the samples was carried out with a view to explore their optical properties. The UV-Vis spectra of the samples are shown in Fig 3. The

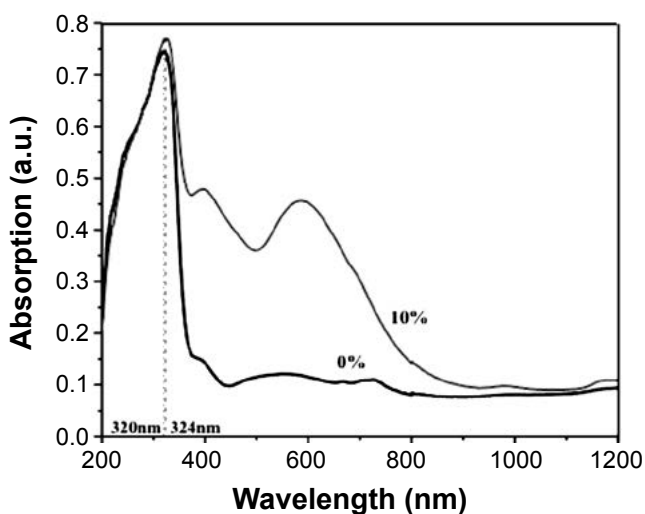


Figure 3: UV-Vis absorption spectra of  $\text{Zn}_{1-x}\text{Cr}_x\text{S}$  nanocrystals.  
[Figure 3: Espectros de absorção óptica UV-Vis de nanocristais de  $\text{Zn}_{1-x}\text{Cr}_x\text{S}$ .]

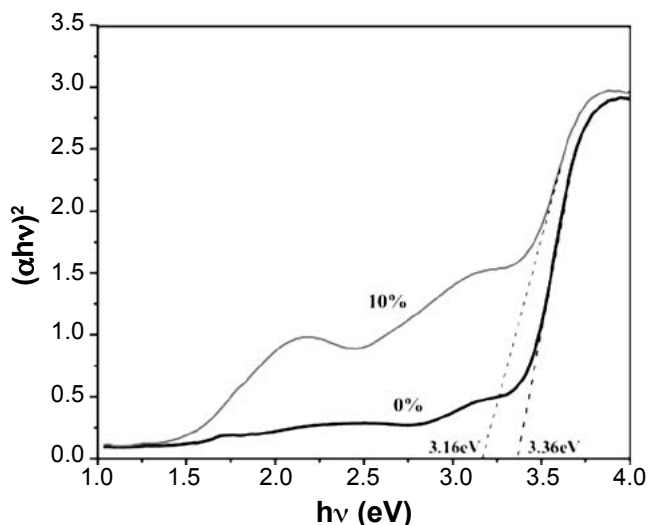


Figure 4: Tauc plots of photon energy for  $\text{Zn}_{1-x}\text{Cr}_x\text{S}$  nanocrystals.  
[Figure 4: Gráficos de Tauc da energia de fótons de nanocristais de  $\text{Zn}_{1-x}\text{Cr}_x\text{S}$ .]

absorption bands were 320 nm and 324 nm for pure and Cr doped ZnS respectively. The band-edge emissions show blue shift for pure to Cr doped ZnS nanocrystals. The energy band gap was calculated from the Tauc plots of photon energy ( $E = hv$ ) versus  $(\alpha hv)^2$ . It was reported that the band gap increase with increasing Cr concentration and is attributed to size quantization effect due to the smaller size of the particles [10]. In the present work, the band gap from Tauc plots of pure ZnS and 10% Cr doped ZnS samples were 3.36 eV and 3.16 eV respectively. It is confirmed that the band gap of pure ZnS is higher than that of 10% Cr doped ZnS nanocrystal and is attributed to the s-d and p interactions and the quantum confinement effect. Fig. 4 shows the red shift of the band gap, which confirms the uniform substitution of Cr ions into the ZnS lattice.

### Surface morphology

SEM images of pure and 10% Cr doped ZnS were recorded and are shown in Fig. 5a and 5b, respectively. It is confirmed that pure and 10% Cr doped ZnS samples exhibit cubic shape but the pure ZnS sample has more agglomeration than Cr doped ZnS sample. It means that Cr doping effect is clearly observed.

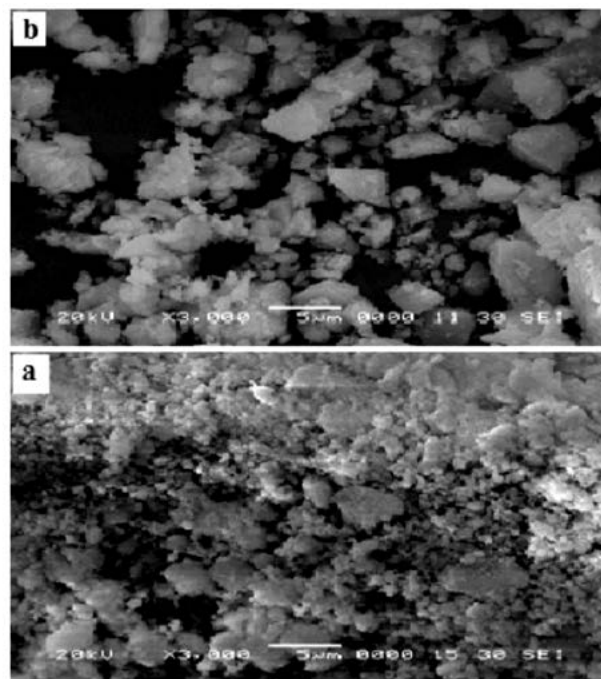


Figure 5: SEM images of (a) pure ZnS nanoparticles and (b) 10% Cr doped ZnS nanocrystals.

[Figura 5: Micrografias obtidas por microscopia eletrônica de varredura de (a) nanopartículas de ZnZ puro e (b) de nanocristais de ZnS dopado com 10% Cr.]

### EDS Study

Energy dispersive spectra (EDS) were recorded at room temperature in the range of 0-20 keV with the count rate of 7277 cps for the chemical composition analysis. Energy

dispersive spectra of the samples are shown in Figs. 6a and 6b. It is confirmed that there are no extra traces. It is intervened that the as prepared samples are highly pure. From our EDS study it is acknowledged that exact percentage of chemical compositions are highly matchable with standard results. This study reveals accurate information about the

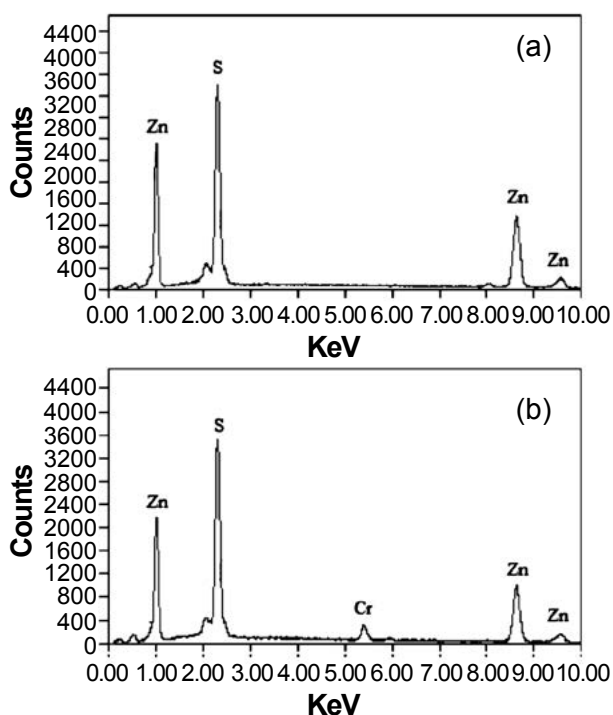


Figure 6: EDS spectra of (a) pure ZnS nanoparticles and (b) 10% Cr doped ZnS nanocrystals.

[Figura 6: Espectros EDS de (a) nanopartículas de ZnS puro e (b) nanocristais de ZnS dopados com 10% Cr.]

Table II - Chemical species present in the pure ZnS and 10% Cr doped ZnS samples.

[Tabela II - Espécies químicas presentes em ZnS puro e em ZnS dopado com 10% Cr.]

Elements	Atomic percentage	
	Pure ZnS	Cr doped ZnS
Zn	60.27	52.94
Cr	0.08	4.94
S	39.65	42.09

chemical compositions and their percentage are summarized in Table II.

## CONCLUSIONS

Pure and 10% Cr doped ZnS nanocrystals were synthesized by the co-precipitation route. Lattice parameters were determined using X-ray diffraction data and it is found that the samples show cubic structure. The average grain size is in the range of 3.85 and 3.89 nm. The chemical groups and the chemical bonding for pure and Cr-doped ZnS samples were confirmed by FTIR spectra. Reduction in  $E_g$  with enhancing Cr concentration may be owing to quantum confinement effect and the ionic radius of Cr, which is smaller than that of Zn. The surface morphology of pure and 10% Cr-doped samples was investigated and it is found that samples are cubic. Compositional percentage was detected using EDS and did not confirm the presence of any other impurity phases. It means that the as-synthesized samples are highly pure.

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- (Rec. 03/04/2014, Ac. 15/05/2014)