



## Study of structural and optical properties of ZnS:Cr nanoparticles synthesized by co-precipitation method

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### Abstract

In this paper, we report structural and optical properties of nanocrystalline chromium (Cr) doped ZnS particle, which have been synthesized by co-precipitation method. The structural properties of ZnS:Cr nanoparticles have been characterized by X-ray diffraction (XRD) analysis. The XRD patterns show hexagonal structure in nanoparticles without any additional phase. The mean crystallite size calculated from the XRD patterns has been found in the range 2.45-1.50 nm with the increase in molar concentration of doping agent. Absorption spectra have been obtained using UV-Vis spectrophotometer to find the optical direct band gap. The obtained values have been founded to being range 3.82-4.42 eV. It was also found that optical band gap ( $E_g$ ) increases with the increase in molar concentration of doping agent is attributed to size quantization effect due to the small size of the particles.

**Keywords:** ZnS:Cr, Chemical co-precipitation, 2-Mercaptoethanol, Optical band gap.

### Introduction

During the past 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 originating from quantum confinement effect (Rossetti *et al.*, 1984; Sang *et al.*, 2002; Wageh *et al.*, 2003; Prabhu & Abdul Khadar, 2005). 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 (Alivisatos, 1996; Henshaw *et al.*, 1996; Anderson *et al.*, 1997; Rajeswar *et al.*, 2001; Hirai *et al.*, 2002).

Wide band gap II-VI semiconductors are expected to be the novel materials for the optoelectronic devices (Zhai *et al.*, 2002). ZnS has been used widely as an important candidate for photoluminescence (PL), electroluminescence (EL) and cathodoluminescence (CL) devices due to its better chemical stability compared to other chalcogenides such as ZnSe. In optoelectronics, it finds use as light emitting diode, reflector, dielectric filter and window material (Zhai *et al.*, 2002). Research on nanocrystals of ZnS containing Mn, Fe, Ni and Cu has been in full swing as the solubility limit for these transition metals in II-VI host lattice is high (Yang *et al.*, 2002; Warada *et al.*, 2005; Sambasivam *et al.*, 2008).

Nevertheless the theoretical and experimental researches on Cr doped ZnS are still limited.

Keeping in view the above discussion, In the present paper an effort has been made to study the structural and optical properties of ZnS:Cr nanoparticles of different molar  $\text{CrCl}_2$  as doping agent and 2-Mercaptoethanol as capping agent. The main purpose of the present research is to study the effect of Cr doping on structural and optical properties of ZnS:Cr nanoparticles synthesized by co-precipitation method.

### Experimental procedure

#### Material

Zinc chloride ( $\text{ZnCl}_2$ ), sodium sulfide ( $\text{Na}_2\text{S}$ ) and chromium (II) chloride ( $\text{CrCl}_2$ ) as starting materials, 2-mercaptoethanol ( $\text{HOCH}_2\text{CH}_2\text{SH}$ ) as a capping agent for control particles size and double-distilled water as dispersing solvent were used to prepare ZnS:Cr nanoparticles.

#### Preparation of ZnS:Cr nanoparticles by co-precipitation method

The ZnS:Cr nanoparticles were prepared by the chemical co-precipitation method as follows. First,  $\text{ZnCl}_2$  was dissolved in double-distilled water with 0.1 molar concentrations and then obtained molar solution was stirred for 20 min at room temperature to achieve complete dissolution. Sodium sulfide and chromium chloride was also dissolved in double-distilled water separately as per molar concentration. Afterwards, first sodium sulfide solution was added drop by drop to the zinc chloride solution. Next the chromium chloride solution with desired molar concentration was added to this solution. Then, an appropriate amount of 2-mercaptoethanol (0.1 M) was added to the reaction medium to control the particle size of ZnS:Cr. The resulting solution was stirred continuously for 4 h. In the final step, the white obtained precipitate was filtered and dried at room temperature to remove both water and organic capping and other byproducts formed during the

Fig. 1. The flow chart of preparation ZnS:Cr nanoparticles by chemical co-precipitation method.

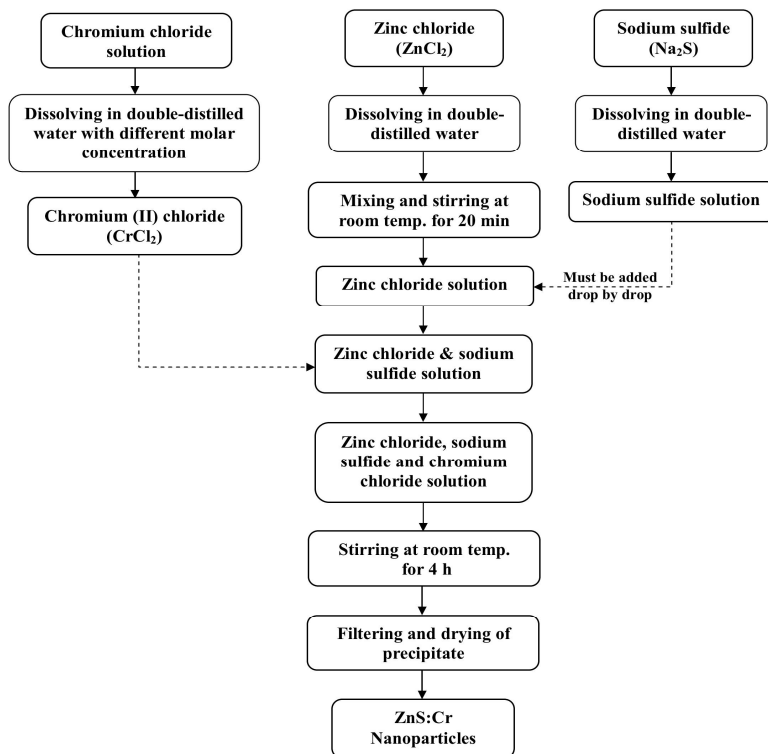
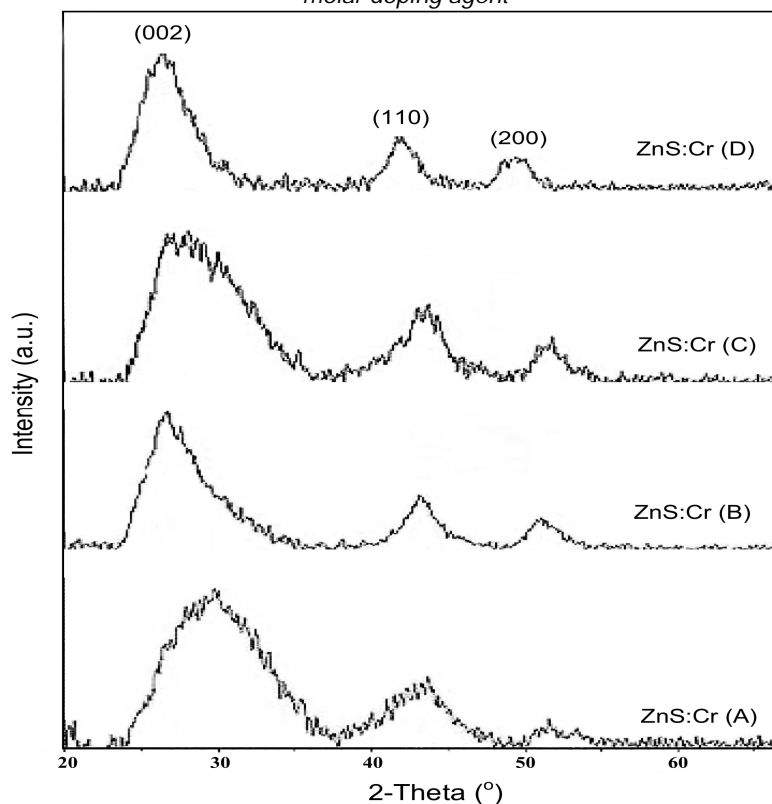


Fig. 2. XRD patterns of ZnS:Cr nanoparticles with different of molar doping agent



reaction process. After sufficient drying, the precipitate was crushed to fine powder with the help of mortar and pestle.

It is necessary to mention that different sample of nanoparticles has been obtained by changing the molar concentration of doping agent namely ZnS:Cr (A) , ZnS:Cr (B), ZnS:Cr (C) and ZnS:Cr (D) as the amount of molar concentration of doping agent used in the preparation is 0 M, 0.5 M, 1 M and 1.5 M respectively. The synthesis process of ZnS:Cr nanoparticles by the co-precipitation method is summarized in a flow chart shown in Fig. 1.

#### Powders characterization

The X-ray diffraction (XRD) patterns of ZnS:Cr nanoparticles were recorded by Bruker system using Cu  $K_{\alpha}$  radiation ( $\lambda=0.154056$  nm) with  $2\theta$  ranging  $20-70^{\circ}$ . The optical absorption spectra of nanoparticles were measured using a USB-2000 UV-Vis spectrophotometer. Therefore, obtained nanopowders have been suspended in glycerol using magnetic stirrer and their optical absorption spectra has been recorded at room temperature over the range 200 to 800 nm for determining the energy band gap values.

## Results and discussion

### Structural Characterization

The XRD patterns of prepared ZnS:Cr nanoparticles with different amounts of doping agent ( $CrCl_2$ ) are shown in Fig. 2. All of the crystalline Bragg peaks in the XRD pattern ((002), (110) and (200) planes) are in a good agreement with the diffraction data of hexagonal structure with cell parameters  $a=3.600$  Å and  $c=6.130$  Å from JCPDS card. Furthermore, The peak broadening in the XRD patterns clearly indicates the formation of ZnS:Cr nanocrystals with very small size.

The peak broadening at lower angle is more meaningful for the calculation of particle size, the mean crystallite size (D) of nanoparticles was also estimated using the Scherrer formula (Scherrer, 1918) using (002) reflection from the XRD pattern as follows:

$$D = \frac{0.9\lambda}{B \cos \theta}, \quad (1)$$

Where  $\lambda$ , B, and  $\theta$  are the X-ray wavelength of the radiation used ( $K_{\alpha}(Cu) = 0.154056$  nm), the full width at half maximum (FWHM) of the diffraction peak and the Bragg diffraction angle, respectively.

The values of mean crystallite size obtained from XRD for different molar doping agent are listed in Table 1. It is clear that the crystallite size increases (1.5-2.45 nm) with decrease the molar of doping agent.



Table 1. Mean crystallite size and optical band gap variation of ZnS:Cr nanoparticles with different concentration of doping agent.

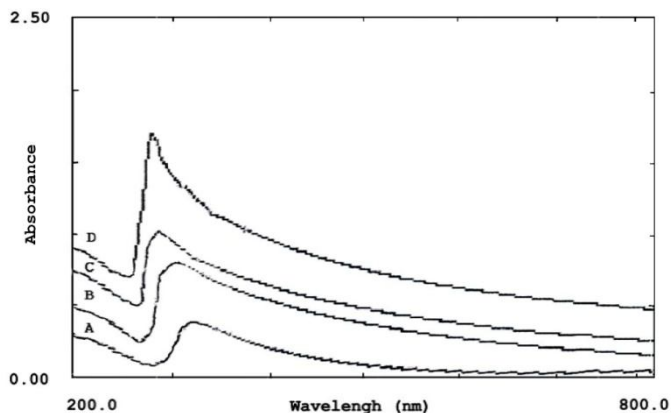
Sample	Molar concentration of Capping agent	Molar concentration of doping agent	Mean crystallite size (nm)	Optical band gap $E_g$ (eV)
ZnS:Cr (A)	0.1	0.0	2.45	3.82
ZnS:Cr (B)		0.5	2.28	4.15
ZnS:Cr (C)		1.0	2.12	4.27
ZnS:Cr (D)		1.5	1.50	4.42

#### Optical characterization

The absorption spectra of the different samples are shown in Fig. 3. The absorption edge is observed in the range of 325-280 nm, which is blue shifted compared to bulk ZnS. As the Cr concentration increases, the absorption edge shifts to lower wavelength side and intensity also increases with increasing Cr concentration compared to undoped ZnS.

This blue shift of the absorption edges for different

Fig. 3. Absorption spectra of different samples of ZnS:Cr nanoparticles.



sized nanocrystals is related to the size decrease of particles and is attributed to the quantum confinement limit reaching of nanoparticles. The quantum confinement effect is expected for semiconducting nanoparticles, and the absorption edge will be shifted to a higher energy when the particle size decreases (Zhu *et al.*, 2006; Sarhaddi *et al.*, 2010).

The obtained optical band gap values for different samples are shown in Table 1. It is necessary to mention that the optical band gap values of the ZnS:Cr nanoparticles were determined by Tauc's relation (Tauc, 1966; Liu *et al.*, 2006):

$$\alpha h\nu = \alpha_0 (h\nu - E_g)^{1/2} \quad (2)$$

Where  $h\nu$ ,  $\alpha_0$  and  $E_g$  are photon energy, a constant and optical band gap of the nanoparticles, respectively. Absorption coefficient ( $\alpha$ ) of the powders at different wavelengths can be calculated from the absorption spectra. Finally, the values of  $E_g$  were determined by extrapolations of the linear regions of the plot of  $(\alpha h\nu)^2$  versus  $h\nu$ . As seen in Table 1, the values of optical band gap ' $E_g$ ' increases with the increase in molar concentration doping agent and therefore decrease

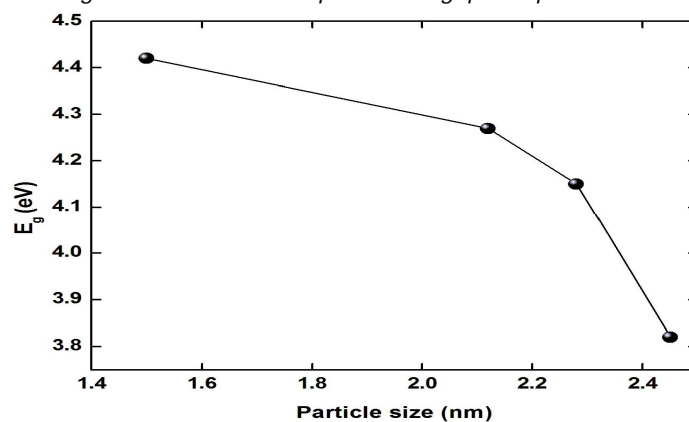
particles size that as mentioned earlier is due to quantum confinement effect. Also, the variation of optical band gap with particle size is shown in Fig. 4. As illustrated in Fig. 4, the optical band gap values of nanoparticles have changed from 3.82 to 4.42 eV by decreasing the particle sizes. The increase in band gap with increase in Cr concentration is attributed to size quantization effect due to the small size of the particles

(Amaranatha Reddy *et al.*, 2011).

Chemical reaction rate directly affects the time evolution of the number of nuclei, which determines both nucleation and growth process. First, the influence on nucleation is obvious: nucleation is faster when the chemical reaction is faster. Second, growth will be strongly influenced by the nuclei number already formed at a given time. A great number of nucleation favours a fast autocatalytic growth, giving rise to a large number of small particles. Chemical reaction controls this kind of growth, being the autocatalytic growth faster as chemical reaction is faster. But in nanoparticle formation, there is another contribution to the growth molecules on the surface of small particle will tend to diffuse through solution and add to the surface of larger particle (growth by ripening). A slow chemical reaction favours continuous nuclei, keeping always a certain number of nuclei in the system. As a result, growth by ripening can take place during the whole process. This fact explains the bigger particle size obtained from a slow reaction. One can conclude that a slow chemical reaction rate is associated with a more important ripening contribution to the growth. A high number of nuclei are still forming at this stage when the reaction is slow at the same time; some particles have already grown to the final value of size. This means that in this case (slow reaction rate), nucleation and growth takes place simultaneously. This overlapping of nucleation and growth processes, which is more pronounced as the chemical reaction is slower, leads to larger nanoparticle sizes (Dios *et al.*, 2005).

Rate of reaction depends on the molar concentration of reactants solution and increases with the increase in molar concentration of reactants solution. In the present

Fig. 4. The variation of optical band gap with particle size.



study, the molar concentration of reactants solution varies from 0 M to 1.5 M, the reaction rate is highest for 1.5 M solution and hence the particle size obtained is smallest for 1.5 M solution as compared to other materials in the series, which is in consistent with the above made argument.

### Conclusions

It is possible to produce different size ZnS:Cr nanoparticles using a simple chemical method with using different molar concentration of doping agent. XRD and Optical band gap data have been obtained to confirm nano size of these materials. It is also observed that the particle size depends on molar concentration of doping agent. A decrease in formation rate of nanoparticles gives rise to a larger final particle size for all the studied synthesis conditions. Chemical reaction rate affects both nucleation and growth process. Nucleation and growth take place simultaneously when the chemical reaction is slow. Besides, a slow chemical reaction rate is associated with a more important ripening contribution to the growth. As the particle size depends upon the molar concentration of doping agent, a decrease in the size of particle is observed with the increase of molar concentration of doping agent. The mean crystallite size range of particles was between 1.5 and 2.45 nm, depending on molar concentration of doping agent. The optical band gap values of ZnS:Cr nanoparticles have changed from 3.82 to 4.42 eV by increasing the molar concentration of doping agent. These values exhibit a blue shift in  $E_g$  which is related to the size decrease of the particles and to the quantum confinement limit reaching of nanoparticles. Considering these results, the chemical co-precipitation method using 2-mercaptoethanol as a capping agent is efficient for the preparation of ZnS:Cr nanoparticles suitable for modern optoelectronic technology and other industrial applications.

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