

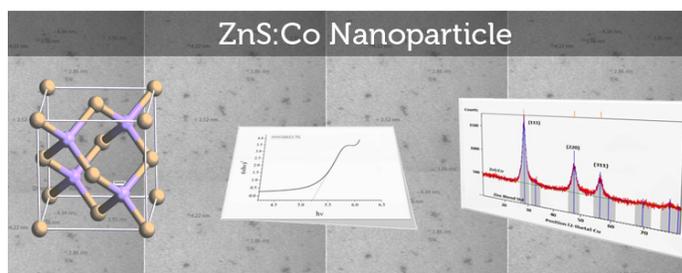
Synthesis and characterization of cobalt doped ZnS nanoparticles

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ABSTRACT



In this study ZnS nano particles were synthesized using chemical method without using any capping agent. The particles were doped with Cobalt from 1% to 8%. The synthesized samples were characterized for structural and optical properties using x-ray Diffraction (XRD), Transmission Electron Microscope(TEM), UV spectrometer, X-ray fluorescence (XRF). The observed XRD patterns revealed that particle size of ZnS:Co particles varied from 3.2 to 3.7 nm and confirmed zinc blend structure. The size of particles was further confirmed by TEM studies. The optical band gap was calculated from data obtained from UV analysis. The band gap variation was observed with doping and it varied from 4.95 to 5.8 eV. Ultraviolet studies showed the blue shift as the particle size decreases starting from bulk ZnS indicating quantum confinement. this material may potentially be used as window layer in solar cells or filter material when used in multiple layers.

Keywords: ZnS, Nanoparticle, Cobalt, Characterization, Band Gap, Semiconductor, crystallite

INTRODUCTION

The low cost versatile semiconductors have always attracted the researcher's attention. With the change in technology the need of higher speed, higher power and temperatures limited the utility of widely used semiconductor material silicon. To address the challenge of growing needs, several compound semiconductors are explored. In this process the group II-IV semiconductors are widely studied¹ due to their functional properties and cost

effectiveness. ZnS is one of the promising candidate having excellent electronic, optoelectric properties and its filter properties when used in layered semiconductor.²⁻⁴ When brought to nano form the properties of these materials change considerably with decreasing size.⁵ These materials respond excellently to luminescence and magnetism when doped with rare earth elements.⁶ It has also been reported that despite of doping with transition metals, the transport properties do not change whereas there is a substantial change in the magnetic properties.

The ZnS nanoparticles may be synthesized in several ways. The chemical method is simpler, cost effective and it is easier to tune the size of the particles. The ZnS nano particles were synthesized using chemical methods.⁷⁻⁸ and these were characterized using TEM and XRD for crystallite size, XRF was used to confirm the doping, whereas UV spectrometry was used to find out cutoff wavelength and optical band gap of synthesized material. Due to decrease in size the cut off wavelength shows considerable blue shift in comparison to bulk material.

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EXPERIMENTAL

The ZnS was synthesized through chemical technique using Zinc acetate, Cobalt acetate and Sodium sulfide as the starting material. No capping agent was used while synthesis process. All the chemicals were procured from Sigma Aldrich and no further purification was carried out. Triple distilled water was used to make the solutions of 1 Molar Concentration of all the compounds. A doped compound $Zn_{1-x}Co_xS$ was synthesized, where $x=1,3,5,7,8$. A solution of 100ml $Zn(O_2CCH_3)_2$ was stirred continuously and drop wise Na_2S was added to it. The precipitate formed was washed five times with distilled water. The remaining water after washing was removed with two washings of ethanol. The precipitate was dried for 12 hours at $80^\circ C$ temperature.

The final product was characterized using Panalytical Xpert pro x-ray diffraction, Hitachi 7500 Transmission Electron Microscope and Perkin Elmer lambda 750 UV-VIS-NIR spectrophotometer

RESULTS AND DISCUSSION

XRD spectrum was observed in the range of $10^\circ (2\theta)$ to $80^\circ (2\theta)$ using $cu\ ka$ radiation. Three main peaks observed in the XRD match with crystal planes (111), (220), (311) of standard Zinc blend (ICDD 03-065-309) (Figure 1). All the doped as well as undoped samples were in cubic form.

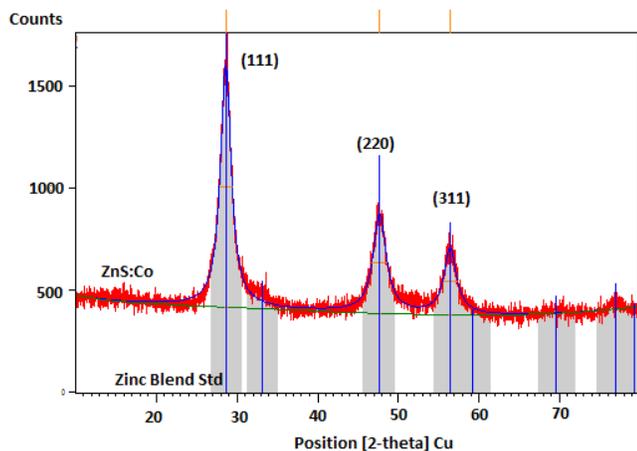


Figure 1 : XRD Spectrum

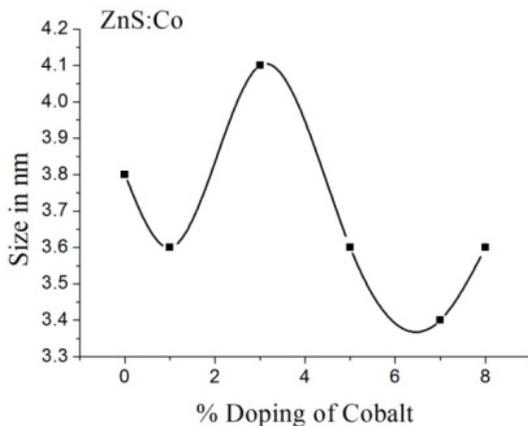


Figure 2: Variation of size with Cobalt doping

Thereafter the size of all the samples was calculated using Scherrer equation

$$D = K\lambda / (\beta \cos \theta)$$

Where K is a constant, λ is $Cu\ K\alpha$ wavelength and β is FWHM of the peak at angle θ . The calculated crystallite size varies from 3.4 nm to 4.1 nm as shown in figure 2.

The size was confirmed with TEM which also revealed the spherical structure of particles.

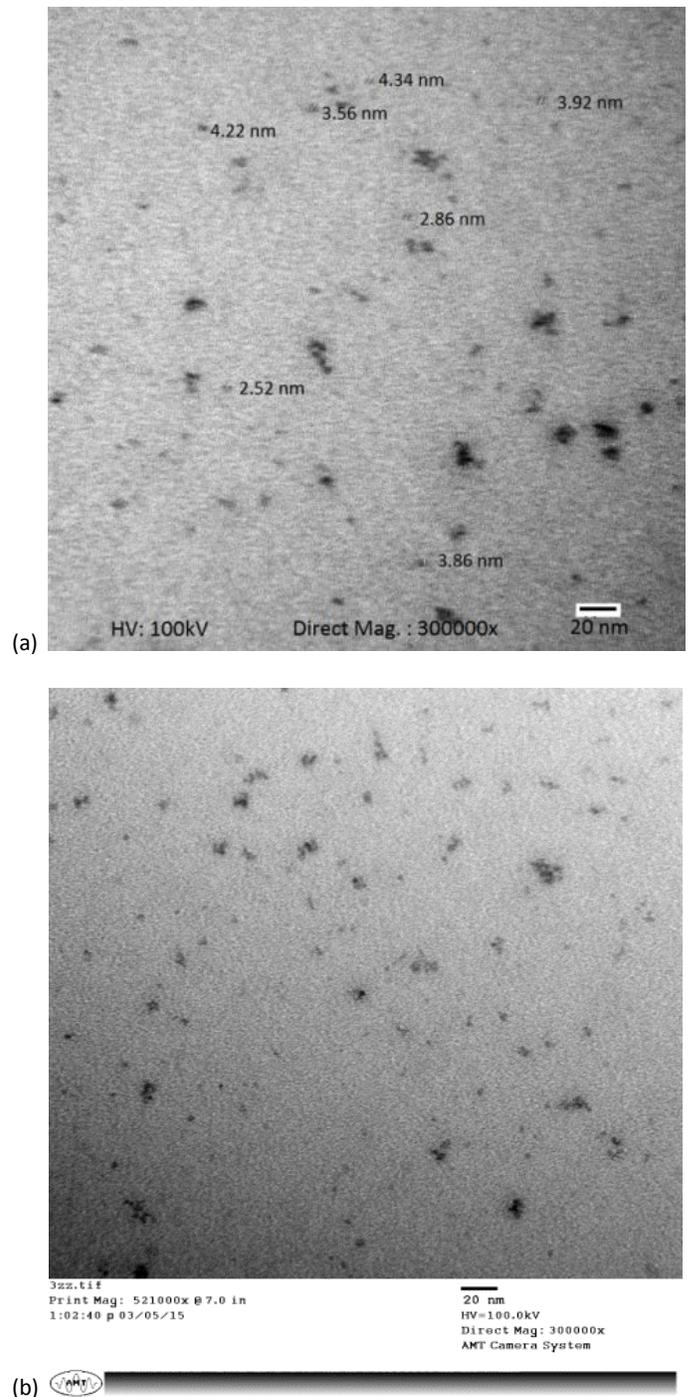


Figure 3: TEM Micrograph of (a) pure ZnS and (b) ZnS:Co 5%

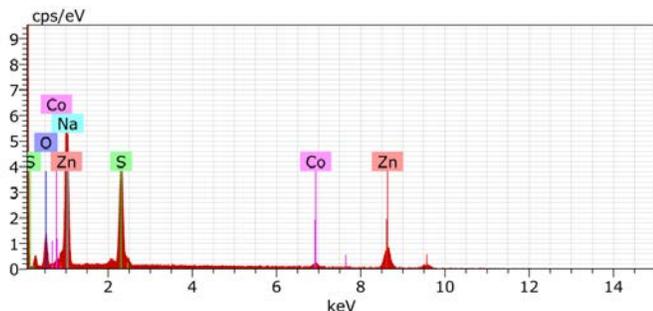


Figure 4: XRF spectrum of 5% Co in ZnS

The doping of Cobalt was confirmed using ED-XRF technique as shown in figure 4 and table 1. The sample consisting of 5% cobalt doping shows 4.86% in XRF results, which is well within error limits and it conforms the doping of ZnS with Cobalt.

Table 1

S No	Element	At. No.	Series	Conc. %
1	Zn	30	K-series	65.35
2	S	16	K-series	14.79
3	O	8	K-series	9.81
4	Na	11	K-series	5.88
5	Co	27	K-series	4.86

The UV absorption spectrum of ZnS:Co was observed as shown in Figure 5. The ZnS characteristic peak corresponding to 3.66eV band gap is shifted to shorter wavelengths as the size of particle has decreased.⁸

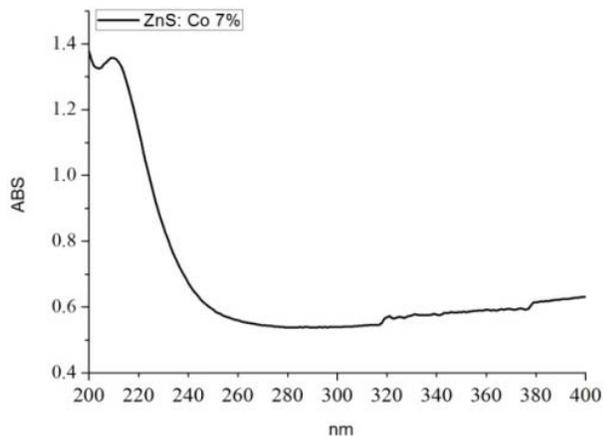


Figure 5: UV absorption spectrum

This blue shift is attributed to the quantum confinement effect at nano scale. The UV absorption spectrum the band gap was also calculated using Tauc plot by plotting $h\nu$ against $(\alpha h\nu)^2$

Extrapolating the straight portion of curve to x-axis gives the value of optical band gap Figure 6. The observed band gap of pure ZnS is 4.95 eV whereas it increased to maximum value of 5.8 eV at 5% doping level of Cobalt. The band gap at 1%, 3%, 7% and 8% doping levels are lower than the band gap at 5% level. It is further observed that the crystallite size is almost constant within error limits.

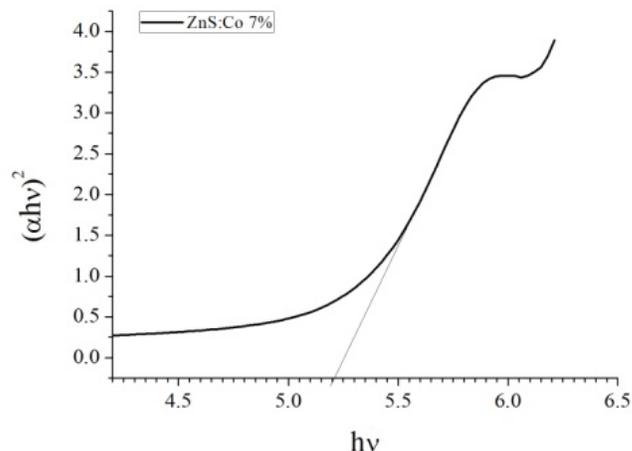


Figure 6 : Tauc Plot

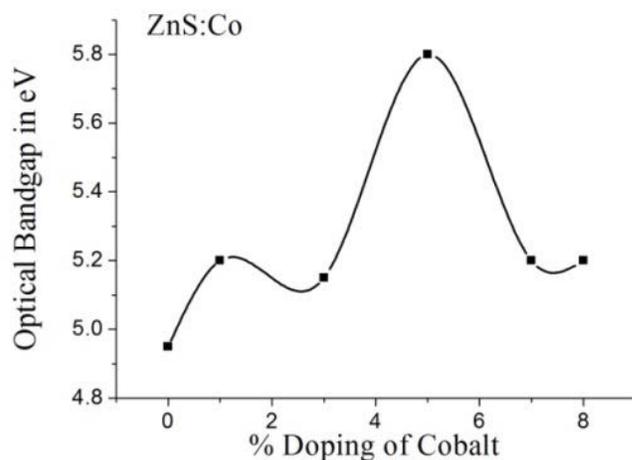


Figure 7: Variation of band gap with size

The calculated optical band gap values are shown in Table 2. The variation in band gap with doping concentration is shown in figure 7.

Table 2

S. No	Sample	Size (nm)	Band gap (eV)
1	ZnS Pure	3.8	4.95
2	ZnS:Co 1%	3.6	5.2
3	ZnS:Co 3%	3.8	5.15
4	ZnS:Co 5%	3.6	5.8
5	ZnS:Co 7%	3.4	5.2
6	ZnS:Co 8%	3.6	5.2

It may be noted that band gap of synthesized alloy $Zn_{0.95}Co_{0.05}S$ is 5.8 eV which is maximum whereas the crystallite size is same as that of $Zn_{0.99}Co_{0.01}S$ that is 3.6 nm in both the cases. This fact indicates that the increase in band gap is only due to the cobalt doping.

CONCLUSION

The synthesized cobalt doped ZnS is having zinc blend structure and its crystallite size varies from 3.4 nm to 4.1nm at

various doping levels this is supported by TEM which also shows that crystallite have spherical structure . The crystallite size for 1% and 5% Cobalt doping is same but band gap has significant difference as it has changed from 5.2 nm (ZnS:Co 1%) to 5.8 nm (ZnS:Co 5%), whereas band gap of pure ZnS is observed to be 4.95 eV at 3.8 nm crystallite size. This blue shift due to doping has brought down the cutoff wavelength to ultraviolet range. Due to this property this material can potentially be used as window layer in solar cells or filter material when used in multiple layers.

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REFERENCES

1. R. N. Bhargava, D. Gallagher, X. Hong and A. Nurmikko, *Phys. Rev. Lett.*, **1994**, 72, 416–419.
2. X. Fang, T. Zhai, U. K. Gautam, L. Li, L. Wu, Y. Bando and D. Golberg *Progress in Materials Science*, **2011**, 56, 175 – 287.
3. X. Liu, X. Cai, J. Mao and C. Jin, *Appl. Surf. Sc.* , **2001**, 183, 103 – 110. 2 N. Fathy and M. Ichimura, *Solar Energy Materials and Solar Cells*, **2005**, 87, 747 – 756.
4. X. Fang, T. Zhai, U. K. Gautam, L. Li, L. Wu, Y. Bando and D. Golberg, *Progress in Materials Science*, **2011**, 56, 175 – 287.
5. W. Chen, J.-O. Malm, V. Zwiller, Y. Huang, S. Liu, R. Wallenberg, J.-O. Bovin and L. Samuelson, *Phys. Rev. B*, **2000**, 61, 11021–11024.
6. H. Yang, P. H. Holloway and B. B. Ratna, *J. Appl. Phys.*, **2003**, 93, 586– 592.
7. H. G. Manyar, P. Iliade, L. Bertinetti, S. Coluccia and G. Berlier, *J. Colloid Inter. Sc.*, **2011**, 354, 511 – 516.
8. G. Murugadoss and M. Rajesh Kumar, *Applied Nanoscience*, **2014**, 4, 67–75.