



## Preparation of Co doped ZnS nanoparticles and their properties

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### Abstract

As nanotechnology is fastly improving branch therefore researcher have concentrated their concentration on the production of novel materials which will more efficient. As the nanoparticles has lot of applications in the different fields. Therefore no one can talk directly by only looking the bulk materials how it will work at nanoscale. Therefore properties of these materials must be checked at nanoscale. In our present work researcher concentrated himself on the production of the Cobalt doped ZnS particle and therefore preparation of Co doped ZnS nanoparticles is one of the aim of the present work. Also research has kept second aim to characterize the prepared sample using suitable characterization technique. Thus researcher want to clear the picture of Co doped ZnS particles.

**Keywords:** Nanoparticles, sol-gel route, synthesis, characterization Co doped ZnS particles and properties

### Introduction

It is well known that initially to place a single computer a compete hall is required but now a day's man make himself ready to place the same computer in his single pen. The credits for this goes to fastly improving science especially goes to nanotechnology

### Defination of nano

Nano means one billionth of the meter i.e. one nanometer is  $1 \times 10^{-9}$  m of meter. To get feel of it one can see that a human hair is 50,000 nanometer across. The smallest thing that can be seen with necked eyes is 10,000 nm across. Ten hundred atoms make one nanometer<sup>[1]</sup>.

### Defination of nanotechnology

Before working in the nanotechnology it is essential to know what actually the term nanotechnology is. The term nanotechnology includes two words.

i.e. nanotechnology=nano + technology Where, Nano=dwarf means below normal size. Technology = science of industrial art.

Thus we can say that nanotechnology is science of industrial art which study at nanoscale.

According to Laura cast low & April Peter nanotechnology in science & Engineering at the scale of atoms and molecules. It is manipulation and use of the material and

device, so tiny that nothing can be built any smaller<sup>[1]</sup>. It means nanotechnology deals with about production and use of materials and devices at nanoscale.

Also an aspect of nanotechnology is vastly increased ratio of surface area to volume present in many nanoscale materials which makes new quantum mechanical effects.

E.g. quantum size effect where the electric properties of solids are altered with great reduction in particle size. This does not come into play by going from macro to micro dimensions.

However it becomes pronounced when nanometer size is reached<sup>[5]</sup>. This means nanotechnology is also study what changes taken place.

Thus in broad view nanotechnology can be defined as "Synthesis and application of ideas from the science and engineering towards understanding and production of novel materials and devices.

### Defination of nanoparticles

We classify the nanoparticles to less than 100 nm in diameter they exhibit new or enhanced size dependant properties compare with longer particle a same material<sup>[1]</sup> means particle is said to be nanoparticles if their particle size is less than 100 nm and its properties may different from its bulk form i.e. on reaching to nanoscale properties of nanomaterials may changes.

Sr. No.	Year	Scientists	Discovery
1	1857	Miecal Faraday	Synthesized gold colloids of nanosized particles.
2	1931	E Ruska & M Knool	Developed the first electron microscope.
3	1951	E. Muller	Developed the field ion microscope.
4	1959	F. Feynman	Developed his now very famous talk, "There is plenty of room at the bottom."
5	1968	A.Y. CHO & J. Arthur	Developed molecular beam epitaxial technique for layer-by-layer growth of materials.
6	1970	L. Esaki	Demonstrated quantum size effect (QSE) in semiconductors.
7	1980	A.I.O. Kimov	Showed QSE in CdS and CdSe particles dispersed in glass, triggering research on nanoparticles.
8	1985	R.F. Curls, H.W. Kroto, A.F. Smalley	Synthesized 60 atoms carbon molecule, later named fullerene.
9	1989	D.M. Eigler	Wrote a letter 'IBM' using Xenon atoms.
10	1991	S. Jijlma	Discovered carbon nanotubes.
11	1999	C.A. Mirkin	Developed "dip pen lithography."
12	2000	D.M. Eigler	Devised "quantum mirage" using Fe atoms on Cu substrate

## Properties of nanomaterials

When particle size of the material is reduced to nanoscale, it is interesting to see what changes are taken in the proper properties. These properties of nanoparticles are as follows.

### a. Melting point and lattice constant

As we know that the surface energy increase with the decreasing particle size. Therefore nanoparticles of metal, inert gases semiconductor and molecular crystal all are have low melting point as compared to their bulk form.

### b. Mechanical properties

The mechanical properties of nanoparticles are as follows.

1. Nanoparticles possess the high perfection and no dislocation.
2. Nanostructure metal will have higher or lower strength and hardness to coarse (rough) grained material depending on the method used to vary the grain size.
3. Elastoplasticity of nanomaterial is different from their bulk form.
4. E.g. Twinning is observable in nanosized aluminum grain.

### c. Optical properties

Like bulk material nanomaterial also shows following optical properties.

#### 1. Surface plasma resonance

The continuous excitation of free electron within the conduction band causes an in phase oscillations called surface Plasmon resonance. This effect of surface Plasmon resonance is occurring in nanoparticles when particle size is smaller than wavelength of the incident radiations.

The energy of the surface Plasmon resonance depends on both the free electron density and dielectric medium surrounding the nanoparticles <sup>[2]</sup>.

#### 2. Quantum confinement effect

It is found that nanoparticles of same material having different size emit the light of different colors. The main reason is the quantum confinement effect.

When size of nanoparticles is smaller than the de-Broglie wavelength electrons and holes are spatially confined and forms electric dipoles. This gives rise to formation of discrete energy levels. The energy separation between adjacent level increase with decreasing particle size. The effect is called as quantum confinement effect.

According to this effect it is found that larger the particle size redder (i.e. low energy) will be the fluorescence spectrum. If smaller the size of particle bluer will be the fluorescence spectrum (high energy).

#### 3. Quantum size effect

When we reduce the material at nanoscale there is possibility of alternating their properties. This alternation in properties due to reduction in particle size is called quantum size effect.

When material is reduced. Its properties changes due to increase in quantum efficiency of the material with decreasing particle size and change in energy states of the materials.

E.g. when material is reduced to two dimension and one dimensional material have continuous energy states but one dimensional material have discrete energy level which has maximum quantum efficiency up to 10 nm.

## 4. Conductivity and Resistivity

Due to the decrease in particle size electron get scattered at grain boundaries resulting into the increase in the resistance. <sup>[3]</sup> Therefore resistivity of nanoparticles is larger as compared to their bulk form. It means electrical conductivity decrease with decreasing particle size.

### Aim and objective of present work

As nanotechnology is fastly improving branch therefore researcher have concentrated their concentration on the production of novel materials which will more efficient. As the nanoparticles has lot of applications in the different fields. Therefore no one can talk directly by only looking the bulk materials how it will work at nanoscale. Therefore properties of these materials must be checked at nanoscale.

In our present work researcher concentrated himself on the production of the Cobalt doped ZnS particle and therefore preparation of Co doped ZnS nanoparticles is one of the aim of the present work. Also research has kept second aim to characterize the prepared sample using suitable characterization technique. Thus researcher want to clear the picture of Co doped ZnS particles.

### Preparation of material

In this preparation regarding actual experimental details and characterization to prepare cobalt doped Zinc-sulphids, we have selected sol-gel technique. Reason for selecting the sol-gel technique is that it is one of the simplest wet-chemical methods, also sol-gel method is very inexpensive and requires less instrumentation and simple to handle. A Sol-gel technique operates at low temperature and it maintains desired purity of material.

For characterization of the prepared material we have selected XRD technique. Using this technique we want to calculate lattice parameter and to know the structure of prepared material also using this technique we want to determine particle size, x-density of obtained material.

### Powder preparation

For the preparation of cobalt doped ZnS nanoparticles, powder we have selected the Zn<sub>1-x</sub>Co<sub>x</sub>S system. The sample is synthesized by taking the Zinc nitrate, Cobalt nitrate and Sodium sulphids.

While preparing the material first we have taken appropriate weights of the Zinc nitrate, cobalt nitrate and Sodium sulphids depending on the concentration. Then all these three compounds are dissolved in 100 ml distilled water in separate beaker, then we have stirred for 10 minutes at room temperature. Then we have mixed zinc nitrate and cobalt nitrate solution to maintain the pH of solution at 10.3 we have add in it NaOH. After this we have added sodium sulphids in it and stir for 15 minutes after this sol will obtain. This obtained sol is then evaporated in furnace at 150°C for 6 hours. Finally results in powder were sintered at 450°C for 12 hour followed by furnace cooling.

### X-Ray Diffraction

In XRD, a collimated beam of X-rays, with a wavelength typically ranging from 0.7 to 2 Å is incident on a specimen and is diffracted by crystalline phases in the specimen according to Bragg's law:

$$n\lambda = 2d \sin\theta$$

Diffraction peak position are accurately measured with XRD, from the shift in peak position, one can calculate the change in d-spacing, which is the result of the change of lattice constant under a strain. Peak broadening is also caused by the finite size of crystallites, but here the broadening is independent of  $\sin \theta$ . The crystallite size,  $D$ , can be estimated from the peak width with the Scherer's formula11:

$$D = 0.9\lambda / \beta \cdot \cos\theta$$

Where the  $\lambda$  is the X-ray wavelength,  $B$  is the full width of height maximum (FWHM)of a diffraction peak,  $\theta$  is the diffraction angle, and is the Scherer's constant of the order of unity for usual crystal. It should be noted that since the estimation would work only for small particles, this technique is very useful in characterizing nanoparticles.

**UV-vis spectroscopy**

This technique involves the absorption of near-UV or visible light.

Determine the analyze concentration from absorbance at one

wavelength and using the Beer-Lambert law:

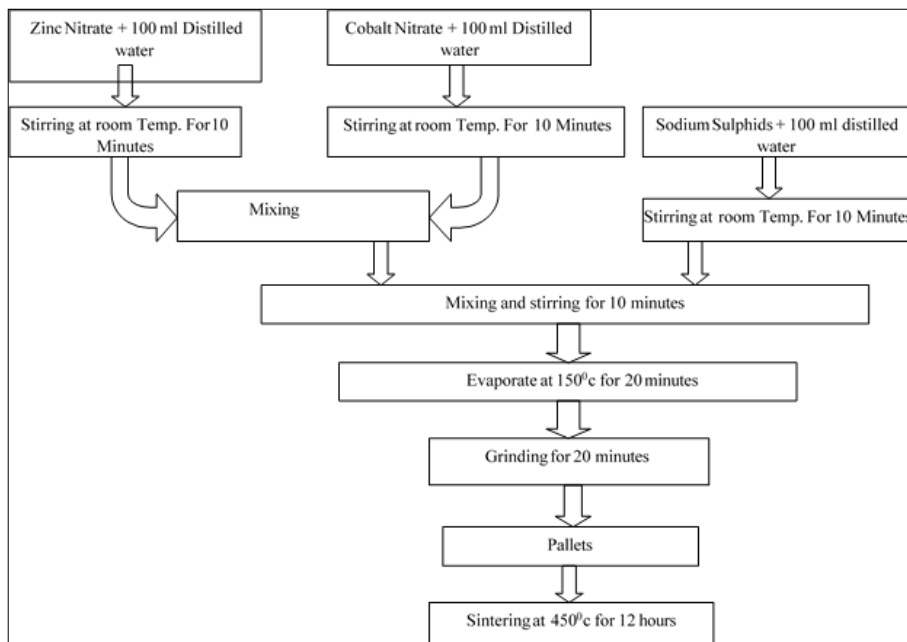
$$A = -\log (I/I_0) = a \times b \times c,$$

Where,  $a$  = absorbance,  
 $b$  = path length, and  
 $c$  = concentration

**Optical Spectroscopy**

Optical spectroscopy uses the interaction of light with matter as a function of wavelength or energy in order to obtain information about the material. For example, absorption or Emission (photoluminescence or PL) experiments with visible and UV light tends to reveal the electronic structure. Vibrational properties of the lattice (i.e., phonons) are usually in The IR and studied either using IR absorption or Raman spectroscopy. Raman is an example of an inelastic process whereby the energy of the incoming light is changed. The others are elastic processes where the intensity is changed. Typical penetration depth is of the order of 50 nm. Optical spectroscopy is attractive for materials characterization because it is fast, non-destructive and of high resolution.

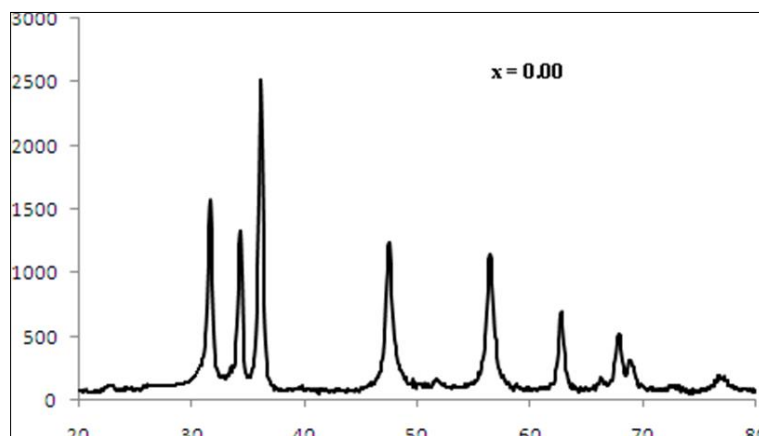
**Flow-Chart**

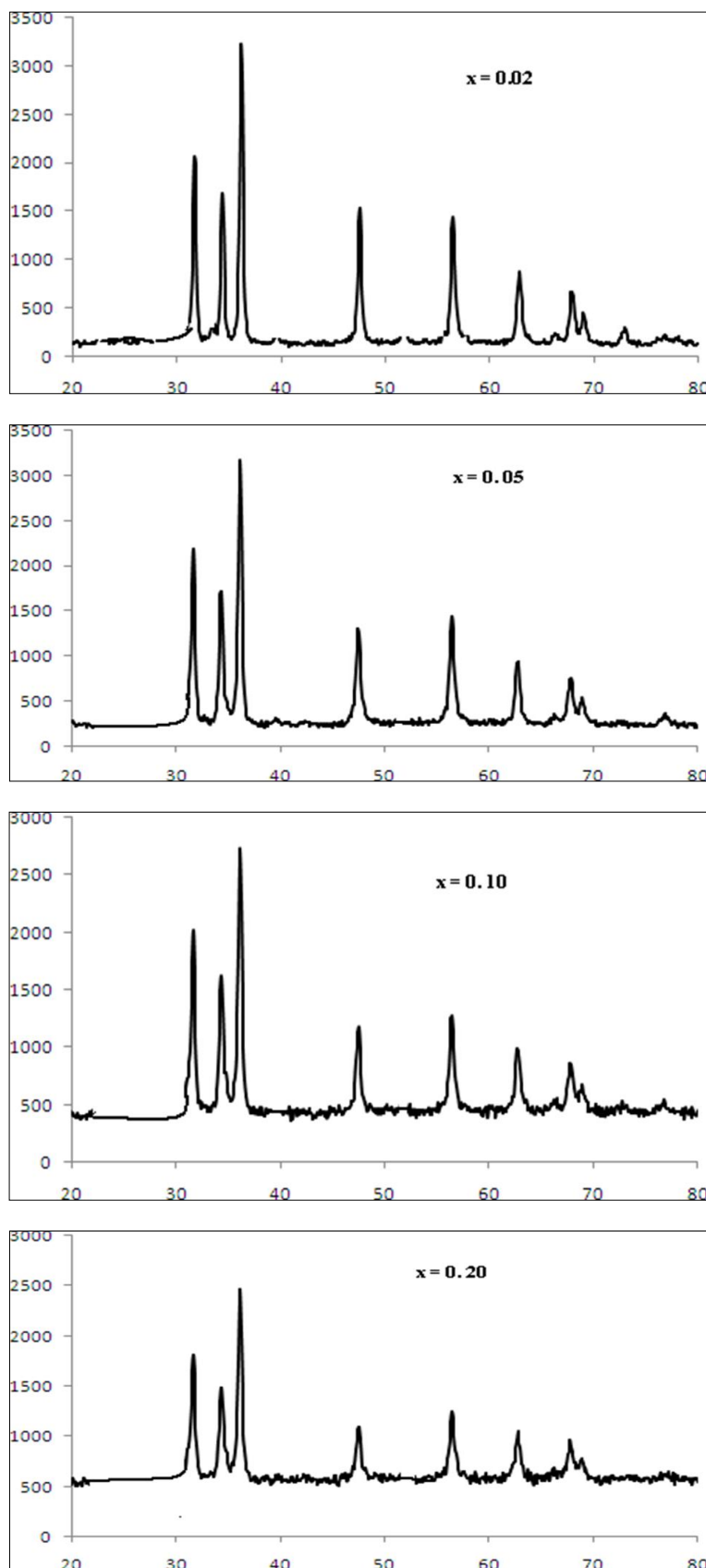


**Results and discussion**

The X-ray diffraction patterns for all the grown samples  $Zn_{1-x}Co_xS$  with compositions ( $x = 0.0, 0.02, 0.05, 0.10,$

and 0.20) recorded at room temperature are shown in figure 1.





**Fig 1:** X – Ray diffraction patterns for Zn<sub>1-x</sub>Co<sub>x</sub>S (x = 0.00, 0.02, 0.05, 0.10 & 0.20) system

The analysis of the diffraction peaks revealed the presence of wurtzite (hexagonal) structure phase in all the compositions. No extra peaks of impurity phase were observed in the patterns which indicate that the powders obtained in the present work are in single-phase hexagonal ZnS nanoparticles though some extra peaks are shown in the reported literature [8]. The intensity of this peak goes on

decreasing as doping percentage of Co content increases. The wurtzite lattice parameters *a* & *c* calculated from the XRD spectra for the Co doped ZnS nanoparticles given in table 1. The parameters *a* & *c* are found to Decreases linearly with increasing Co concentration as shown in figure 2.

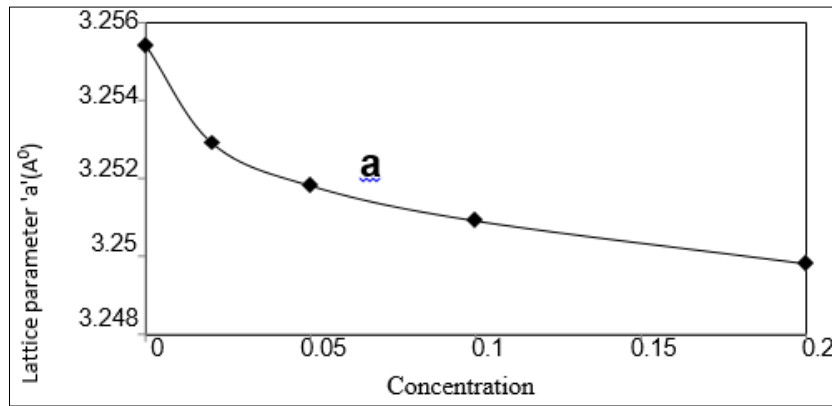


Figure 2 (a): Concentration Vs lattice parameter 'a'

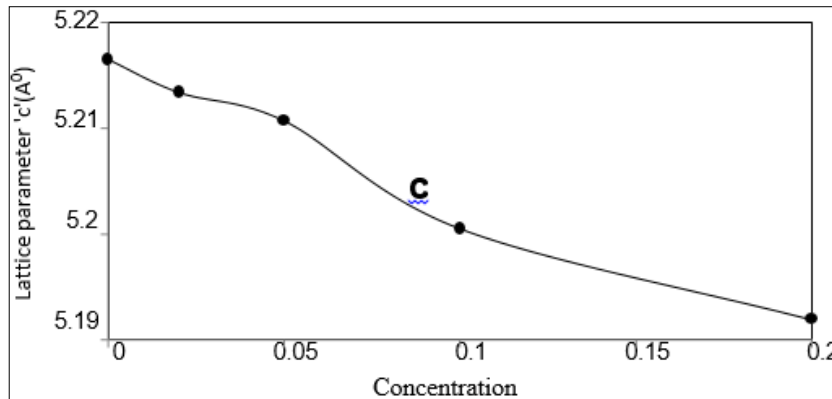


Figure 2 (b): Concentration Vs lattice parameter 'c'

Since the ionic radius of Zn<sup>2+</sup> (0.74 Å) is larger than that of Co<sup>2+</sup> (0.54 Å), [6], the linear dependence lattice constants on Co concentration indicates that the samples with x = 0.00, 0.02, 0.05, 0.10 and 0.20 are homogenous solid solution. This means that the Co<sup>2+</sup> replaces the Zn<sup>2+</sup>

to occupy the 2b crystallographic site. The decrease in the unit cell volume with increasing Co concentrations (see the inset of figure 3), shown for samples annealed at 423 K, indicates the incorporation of Mn at Zn sites.

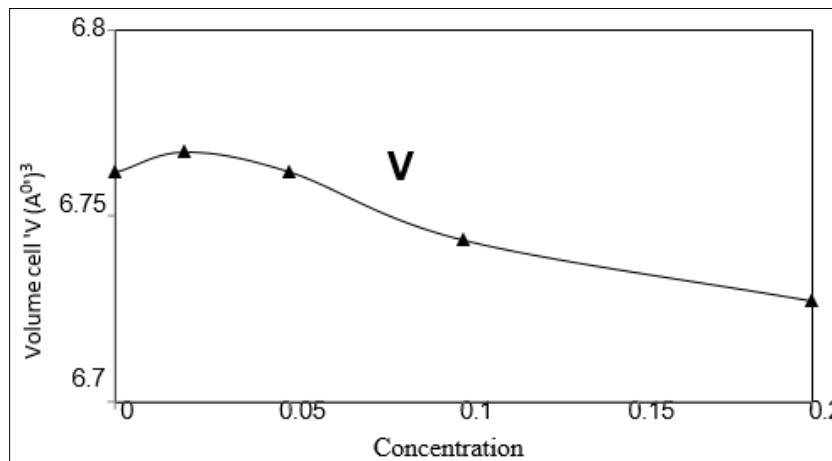
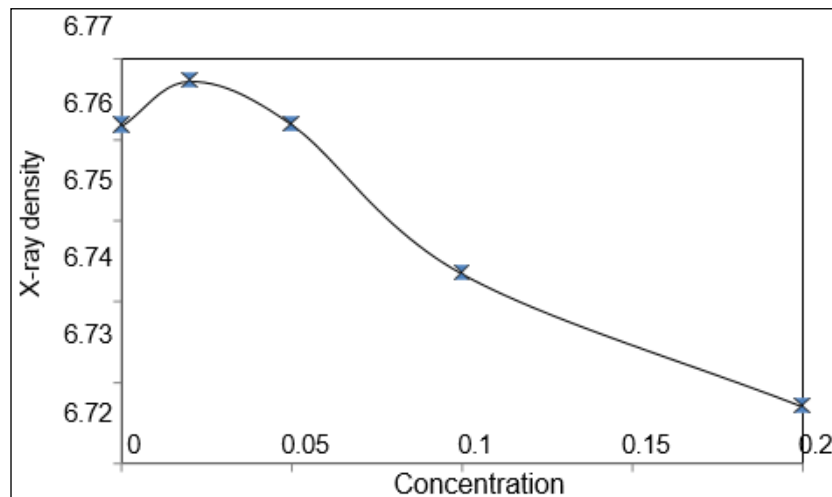


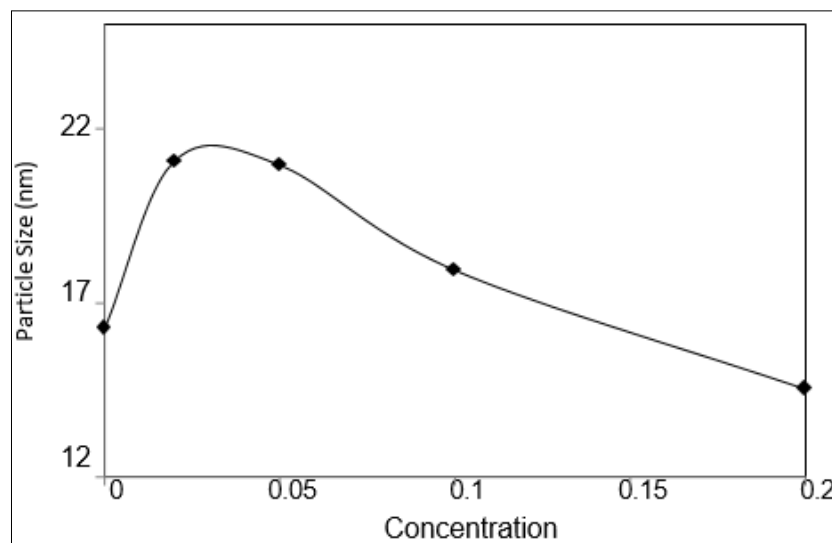
Fig 3: Concentration Vs Volume of the unit cell 'V'

The atomic packing fraction for all the concentration is found to be constant i.e. 0.754%. This shows close relation to Hexagonal Structure. The X-ray density goes on decreasing with increasing concentration as shown in figure 4. It is due to the increased surface to volume ratio which decreases the penetration depth of X-rays. The average Co doped ZnS crystallite size determined from the width of the X-ray diffraction lines using Debye

Scherer's equation (i.e.  $D = 0.9\lambda / \beta \cdot \cos\Theta$ ), where  $\lambda$ - is the wave length of the X-ray diffraction,  $\Theta$ - is the diffraction angle and  $\beta$ - is full width at half maximum (FWHM), is found to decrease with increasing concentration as shown in figure 5. It is evident that the Co doped ZnS grain size is fairly dependent on concentration. This might be due the increase surface to volume ratio.



**Fig 4:** Concentration Vs X-ray density



**Fig 5:** Concentration Vs Grain Size (nm)

### Conclusion

1. Co doped ZnS nanoparticles are successfully synthesized by sol-gel route.
2. Both doped and undoped Zn<sub>1-x</sub>Co<sub>x</sub>S samples crystalline in the wurtzite (hexagonal) ZnS structure.
3. The lattice parameters 'a' and 'c' of Zn<sub>1-x</sub>Co<sub>x</sub>S with x = 0.00-0.20 decrease linearly with the increase of Co content, indicating that Co<sup>2+</sup> ions substitute for Zn<sup>2+</sup> ions.
4. The volume of unit cell decreases and X-ray density decreases as Co concentration increases. It indicates the incorporation of Co at Zn sites.
5. The size of the crystalline has been computed by Debye Scherer's equation the average crystallite size is decreasing with Co content.
6. Packing fraction for all concentrations found to be constant i. e. 0.754% which supports the hcp structure of novel material.

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