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A Comparative Study on ZnS and CdS Quantum Dots Prepared Through Chemical Method

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Abstract

Both ZnS & CdS are binary semiconducting material formed from II-VI group elements. They are produced by simple chemical reactions where Poly Vinyl Alcohol (PVA), acts as matrix, plays the key role in controlling particle size during synthesis. In this report, we tabled a chart of comparative study in regards synthesis, cluster formation, particle size, blue shift effect and the excitation wavelength for testing the sample as Second Harmonic Generation.
Key words: Blue shift effect, Excitation wavelength.

INTRODUCTION

In recent years , fabrication of quantum dots by various methods has been an emerging area of research for different optical , electronics and non-linear applications[2-6]. This has been possible mainly due to novel physical and chemical properties displayed by these nano meter scale structures. If the semiconductor particles become smaller than the Bhor radius of excitation (2.7 nm) , so called quantum size effects occur. As a result of these quantum size effects, the band gap of the semiconductor increases and the edges of the valance and conduction band discrete energy levels occur. The energy gaps of the listed group IV , III-V, II-VI & I-VII semiconductors shows there is a clear tendency for an increasing energy gap with increasing ionic bonding ie going from gr..IV to III-V to II-VI to I-VII semiconductors. Hence II-VI group compounds are taken for experiment. Synthesis of quantum dots by molecular beam epitaxy technique, sol-gel method as well as simple chemical routes have been found in literature. In our laboratory, we

synthesised both ZnS & CdS through chemical route because methods are simple[8-12]. Economically viable & suitable for large scale production. PVA matix locked the particles in the desired size. The sample has been characterised by different technique to reveal their nano nature. Also both the samples have been subjected to testing for one of the important second order non-linear effect viz Second Harmonic Generation. The second harmonic generation, the phenomenon where by two photons at the fundamental frequency ω are converted into one photon at the harmonic frequency Ω=2ω. Second harmonics can be generated by non-linear optical materials with non – Centro –symmetric molecular organisation[13].

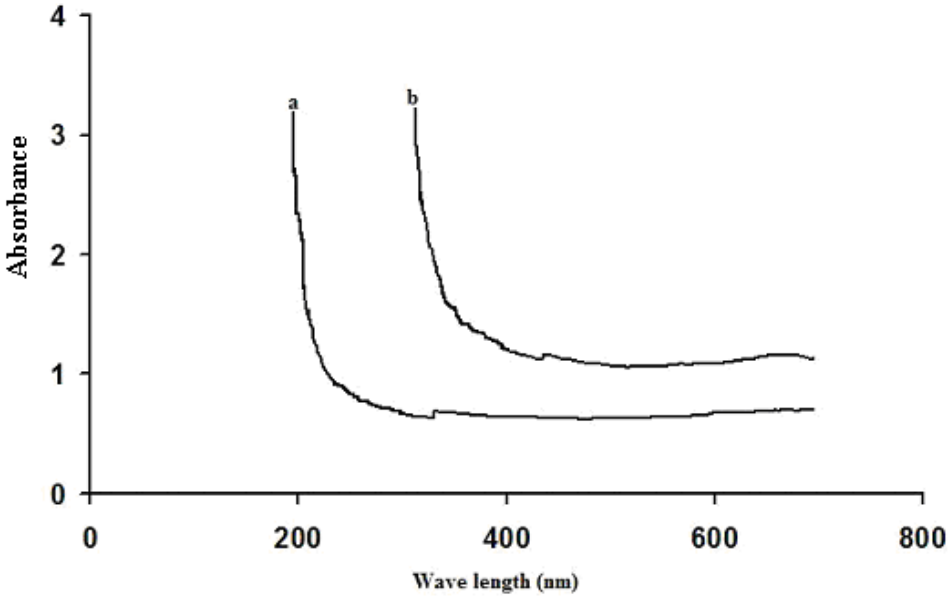
COMPARISON:

Property -	**Compounds**		
	CdS	-	**ZnS**
Intensity -	Relatively high	-	Low
Bandthwidth -	Low	-	\Medium
Phonon Vibration --	High	-	High
Fabrication -	Less time taking	-	Time taking
Stability -	Stable over 9 months	-	Stable over 6 months
Repeatability -	Very good	-	poor
Cost -	Least	-	Least

Comparison: Characterisation Result:-

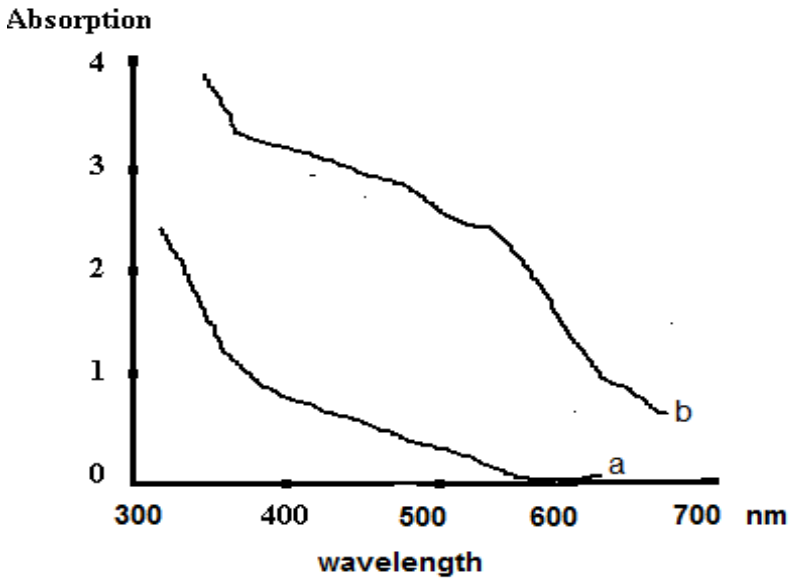
Uv- Visible test / Optical absorption spectroscopy

1) ZnS quantum dots



Blue shift occurs at around 219 nm

2) CdS quantum dots



Blue shift occurs at around 350 nm

Observations: Both the samples are scanned for range 800 nm to 200 nm and has been seen that blue `shift occurs around 219 nm in case of ZnS and around 350 nm in case of CdS **.** Particle size calculated from hyperbolic band model

$$R = \sqrt{\frac{2\pi^2 h^2 E_{gb}}{m^*(E_{gn}{}^2 - E_{gb}{}^2)}} \quad \text{.....(1)}$$

Where, R is the quantum dot radius

E_{gb} is the bulk band gap

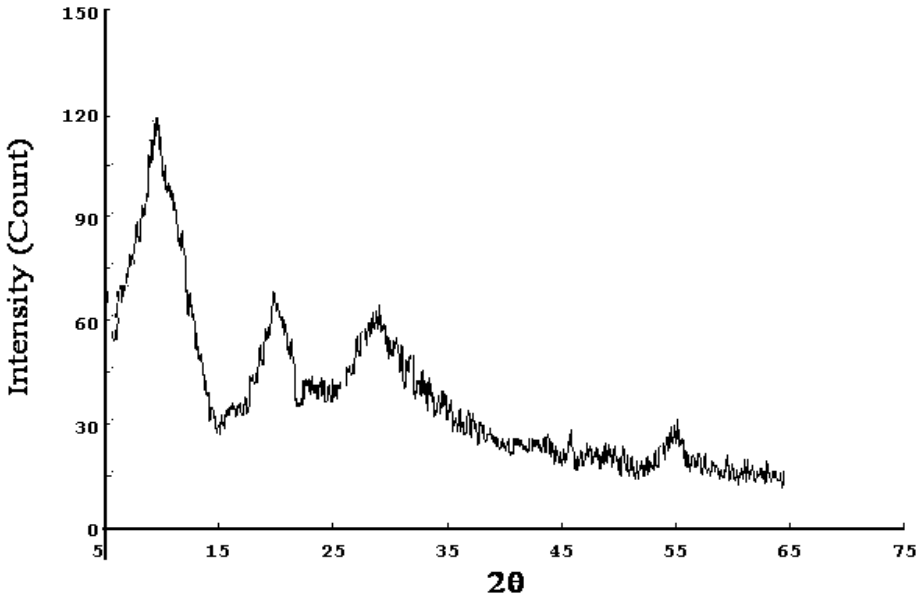
E_{gn} is the quantum dot band gap

Name of the samples	Bulk Band gap	Effective mass (m*)	Value of effective mass	Estimated particle size
ZnS	2.42ev	0.4 me	3.64×10^{-31}kg	9.3nm
CdS	3.54ev	0.2 me	1.82×10^{-31}kg	9.2nm

Bulk band gap and effective masses of II-VI semiconductor.

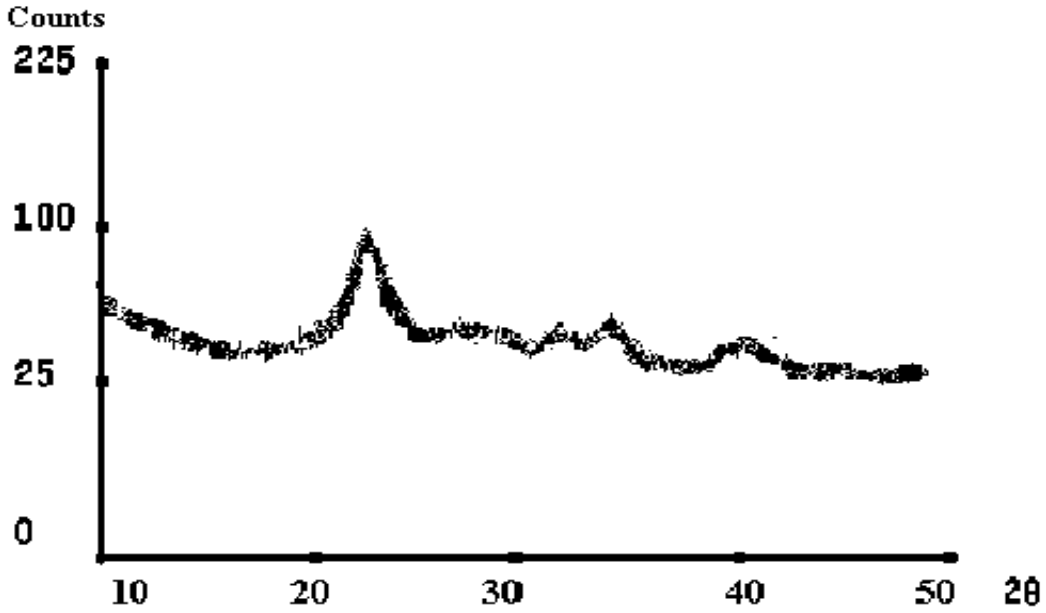
X-ray diffraction study (XRD) Test :

1) ZnS quantum dots



X-ray diffraction spectrum of ZnS quantum dots in PVA matrix

2) CdS quantum dot



X-ray diffraction spectrum of CdS quantum dots in PVA matrix

Observations: X-ray diffract gram is extensively used to calculate particle size using Debye–Scherer equation which gives reasonably particle diameter (size) 'D' The equation is written as

$$D = \frac{0.9\lambda}{W Cos\theta} \quad \ldots$$

Table : Experimental and standard diffraction angles of ZnS specimen

Experimental peak position (2θ in degrees)	Standard peak position (2θ in degrees)
20	21
30	29
50	50

Table : Experimental and standard diffraction angles of CdS specimen

Experimental diffraction angle (2θ in degrees)	Standard diffraction angle (2θ in degrees)
25	24.8
30.66	29
31.40	30.8

Table : Various XRD data of ZnS quantum dot

Peak position (degree)	FWHM (Radians)	d spacing (nm)	Diffraction planes	Size nm	Average size (nm)
20	0.019	0.44	100	7.4	7.5
30	0.020	0.29	010	5.2	
50	0.016	0.18	011	9.7	

Table : Various XRD data of CdS quantum dot

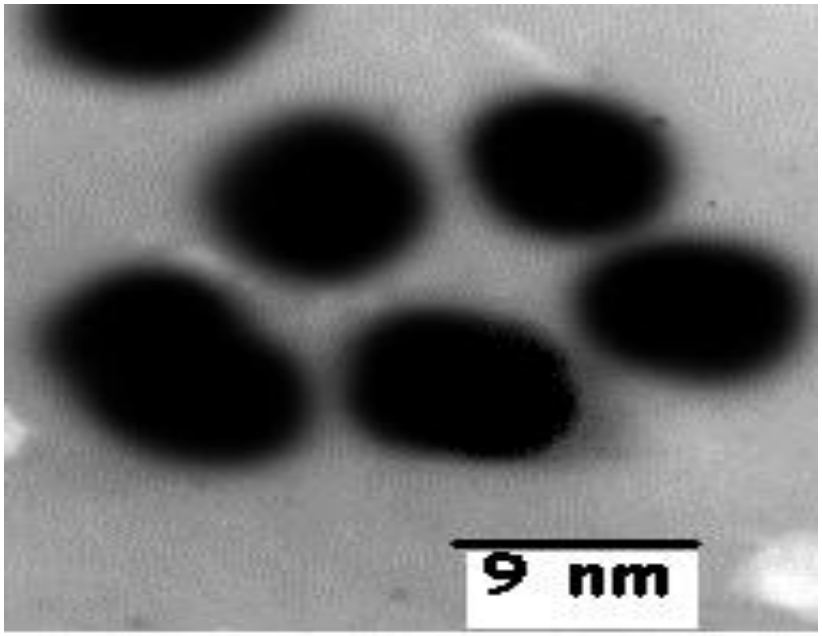
Diffraction angle (degrees)	FWHM (radians)	d spacing (nm)	Diffraction planes	Size (in nm)	Average size (nm)
25	0.020	0.36	100	6.8	8.41
30.66	0.016	0.29	010	8.9	
31.40	0.014	0.28	001	10.1	

Transmission Electron Microscopy:

1) HRTEM of ZnS

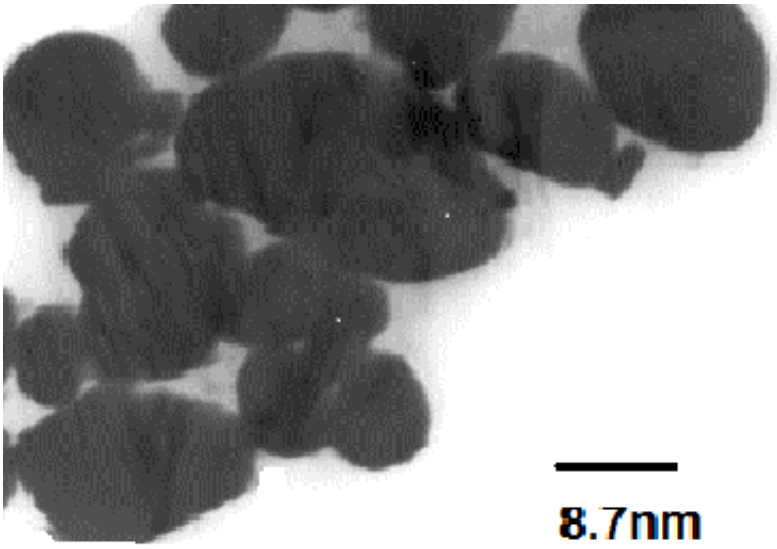
High resolution Transmission Electron Microscopy (HRTEM) (using JEOL, 100CXII, 100Kv) shows the particle size of the sample (Figure-below). Average

diameter of the particles are found around 9 nm.



2) HRTEM of CdS

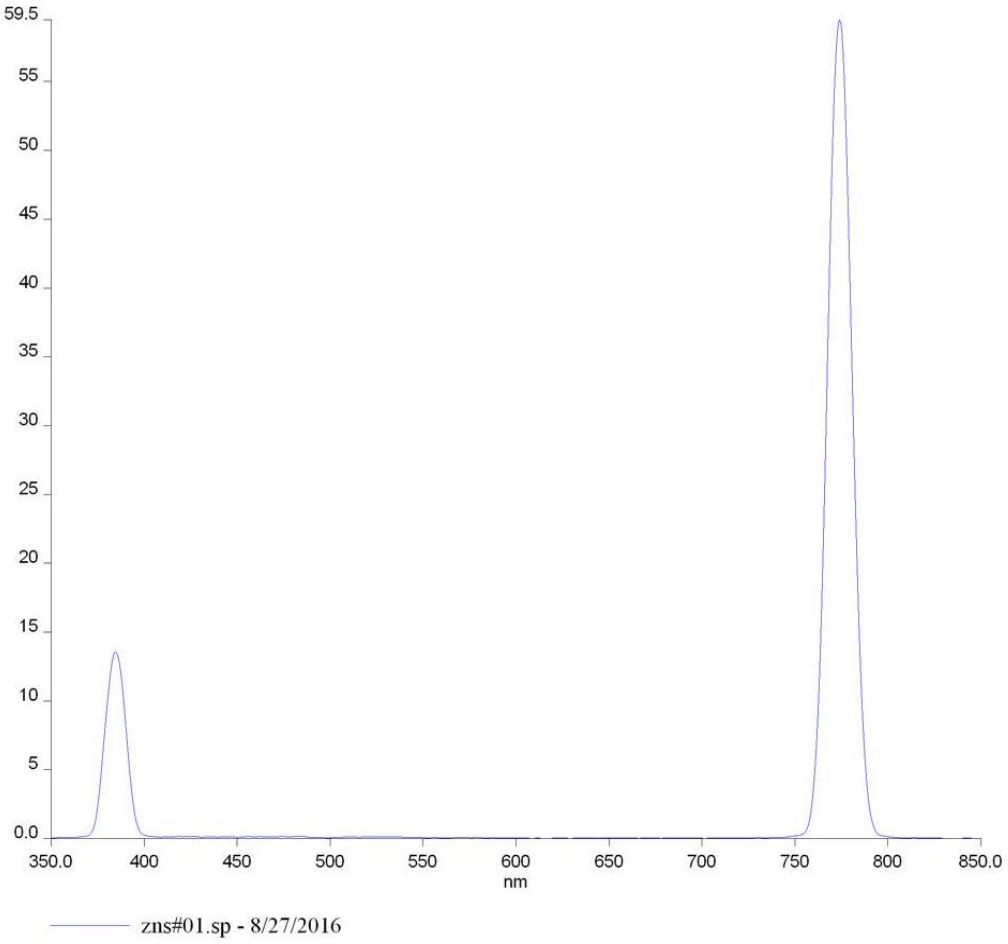
High resolution Transmission Electron Microscopy (HRTEM) (using JEOL, 100CXII, 100Kv) shows the particle size of the sample (Figure-below). Average diameter of the particles are found around 9 nm



Observations: It has been observed that particle sizes are uniform and more or less spherical in case of ZnS nano quantum dots size diameter ranges around 9nm. Where as in case of CdS quantum dots there are dense formation of particles but their sizes are not uniform through out. And because of dense formation intensity is found more in case of CdS cluster. Sizes varies around 9nm.

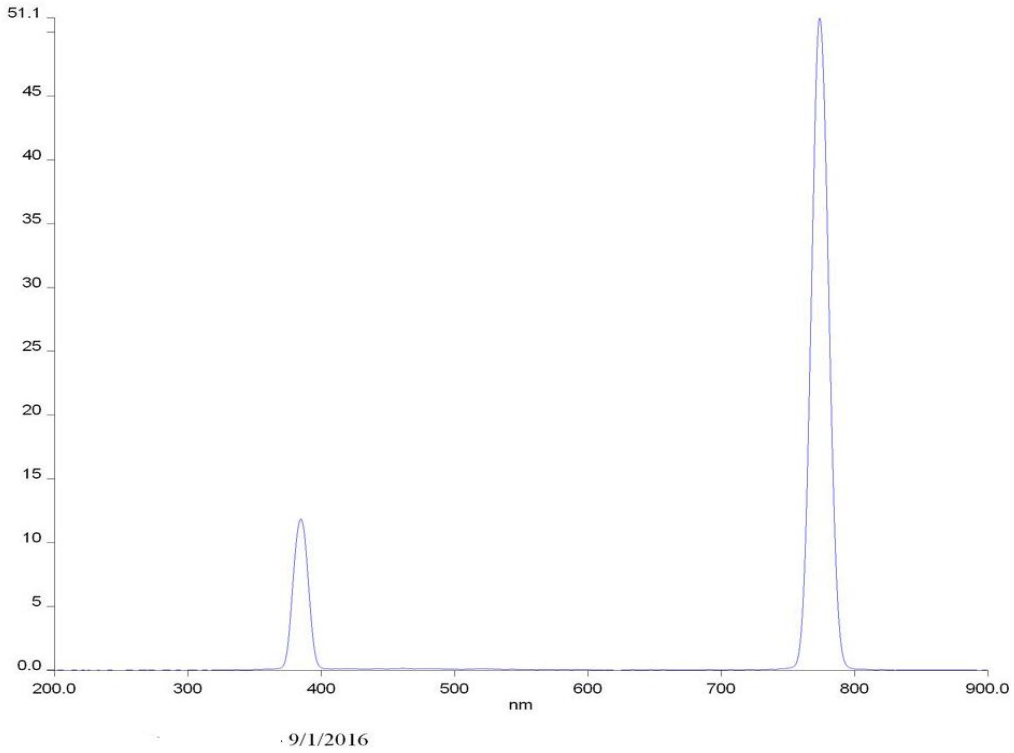
Study of Second Harmonic Generation (Application):

1) **Sample ZnS excited with 780 nm**



SHG at 350n

2) Sample CdS excited with 780 nm



SHG at 390nm

Observation: Both the samples showing SHG with intensity response strong in case of CdS in comparison to ZnS sample . This is because of concentrated cluster of quantum dots particles of CdS .

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