# Theoretical approach to substantiate the Generation of Second Harmonic frequency by ZnS Quantum Dots

**[1]Ajoy Roy, [2]S.S. Nath**

[1]Department of Physics, [2] Central Instrumentation Laboratory,
Assam University, Silchar-788011, Assam, India.

***Abstract:*** **Second Harmonic Generation in ZnS nanocrystal quantum dot is observed in laboratory. ZnS quantum dots have been synthesized by simple chemical method. Absorbance UV-visible spectrum, XRD, HRTEM study established its nano characteristics. Approximate sizes are found around 10 nm. Size of quantum dots is restricted by synthesizing them in PVA matrix. Here in this paper we have taken a mathematical approach of origin of generation of S.H. wave and finally to substantiate our result found in practice.**

***Index terms*: SHG, Quantum dots, Synthesis, PVA matrix**

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## I. Introduction

There has been a rapid research activity in the field of non- linear optics where the interaction processes between the exciting electromagnetic waves and the material are no longer linear in the field amplitude but involves higher orders[1,14,]**.** In the pre-laser era, light wave with a low intensity is not able to affect atomic fields to the extent of changing optical parameter. But high degree of coherence of the laser radiation ceases the linear relationship between electric polarization **P** and the field strength **E** & some interesting non-linear effects come to the fore.

Non-linear properties in optical region have been strikingly demonstrated by the harmonic generation of light observed for the first time by Franken co-workers in 1961.

A dielectric medium when placed in an electric field is polarized. Each constituent molecule acts as a dipole, with dipole moment $\mathbf{P_i}$. The dipole moment vector per unit volume $\overline{\mathbf{p}}$ is given by

$$\overline{p} = \sum P_i$$

Where summation is over the dipoles in the unit volume. The orienting effect of the external field on the molecular dipoles depends on the properties of the medium and on the field strength . Thus we can write.

$$\overline{p} = \epsilon_0 \chi E \qquad \text{--------(1)}$$

Where $\chi$ is called the polarizability or dielectric susceptibility of the medium.
This relation is valid for the field strengths of conventional source. The quantity $\chi$ is a constant.

## II. Brief Theory of condition of SHG:

At high values of electric field, many material show non-linear relation of extent polarizabilities. This can be explained by non-linear susceptibilities.

With sufficiently intense laser radiation the relation (1) does not hold good and has to be generalized by Taylor expansion of the polarization reaction to electric field which involves non-linear susceptibilities.

$$p = \epsilon_0\chi E + \epsilon_0) E^2 + \epsilon_0 \chi^{(3)} E^{(3)} + \text{- - - - -}$$

Where $\chi^{(1)}$ is the same as in $eq^n$ (1), the coffients where $\chi^{(2)}$, $\chi^{3)}$, …….define the degree of non-linearity and are known as non-linear susceptabilities. Higher the value of the electric field, more significant become the higher order terms. Optical characteristics of a medium, such as dielectric permittivity , refractive index, which depend upon susceptibility, also become functions of the field strength **E** if it is sufficiently high.

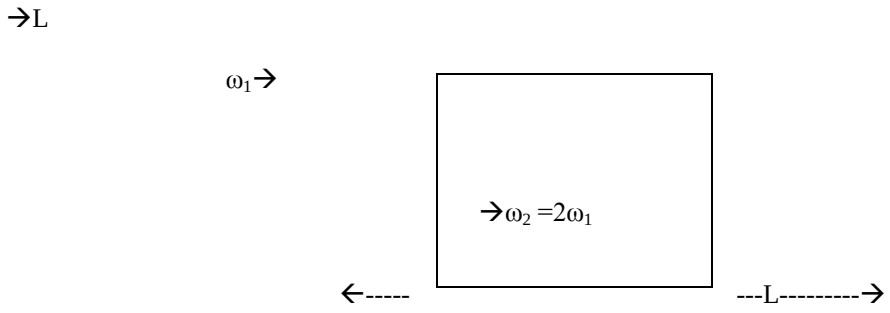



**Figure-1**

Generated S.H wave at frequency $2\omega_1$ radiates an electro-magnetic wave of the same frequency which propagates with same velocity as that of the incident wave. The produced wave has the same characteristics of directionality and monochromocity as the incident wave and is in the same direction.
Non-linear susceptibility $\chi^{(2)}$ depends on the direction of propagation, polarization of the electric field and the orientation of the optic axis of the crystal. Hence $\chi$ must be treated as tensors and $P^{NL}$ therefore may be represented by

$$Pi^{(2)} = \epsilon \sum_{j,k} X^2_{i,j,k} E_j E_k$$

Where i, j, k represents the co-ordinates x, y, z.

In isotropic crystal $\chi$ is independent of direction, hence is a constant, which means $Pi^{(2)} = 0$ & hence $X^2_{i,j,k} = 0$. Second Harmonic Generation , therefore , cannot occur in an isotropic medium such as liquids or gases, nor in Centro symmetric crystals. It has been found that only crystals that lack inversion symmetry exhibit S.H.G. In case of non-centro symmetric materials ( e.g anisotropic crystals, such as uniaxial crystals ) second order term dominates & other higher order terms may be ignored.

For such material, we can write

$\mathbf{P} = \epsilon_0 \chi^{(1)}\mathbf{E} + \epsilon_0 \chi^{(2)}\mathbf{E}^2$ Scalar form of this equation represents vector equation .If we consider a second order non-linearity, then the polarisation $\overline{p}$ takes the form

$$\mathbf{P}^{NL} = \epsilon_0 \chi^{(2)}\mathbf{E}^2(t)$$

It was observed that the efficiency of the generation of harmonics depends not only on the intensity of excitation radiation but also on its direction of propagation in crystals . To generate $2\omega$ frequency from $\omega$ ,system must satisfy some condition called **Phase matching condition**, otherwise efficiency of generation of new frequency will be very weak.

To find an expression for the intensity of SHG at the end of length L of non-linear material , the amount of Second Harmonic radiation produced within width dz at z is

$$dE_L^2 \propto e^{2i(k_1 z - \omega t)} dz$$

Where $dE_L^2$ is the amount of second harmonic radiation within the slab.

We see that the spatial variation of the second harmonic polarisation is characterised by a wave number $2k_1$

The second harmonic radiation produced at the end of the crystal i.e at Z= L obviously will be

$$dE_L^2 \propto dE_z^2 e^{2i(k_1(L-Z)} dz$$

Where L-Z =distance from the slab to the end of the crystal. $k_2$ = Propagation wave number of S.H radiation

In general $k_1 \neq k_2$ because of dispersion

$$\therefore dE_L^2 \alpha \exp^{2i(K_1 Z - wt)} \exp^{LK_2(L-Z)dz}$$

$$= \exp^{\{i(2k_1 - k_2)\}Z} \exp^{\{i(K_2 L - 2wt)\}dz}$$

Strength of the incident beam is considered constant as the beam propagates through the crystal.

∴ Integrating

$$E_L^2 \propto \int_0^L \exp\{i(2k_1 - k_2)z\} \exp\{i(k_2 L - 2\omega t)\}\, dz$$

$$E_L^2 = \frac{\exp\{i(k_2 L - 2\omega t)\}\,[\exp\{i(2k_1 - k_2)L\} - 1]}{i(2k_1 - k_2)}$$

On simplification and some modification , we get

$$E_L^2 \alpha \frac{\mathrm{Sin}(\frac{2k_1 - k_2}{2})L}{(\frac{2k_1 - k_2}{2})}$$

Where we have taken only real part of the proportionality factor

This will be maximum when $(\frac{2k_1 - k_2}{2})L = \frac{\pi}{2}$ i,e the field of the second harmonic generation will be maximum when L =

$$\frac{\pi}{2k_1 - k_2} = \frac{x}{4(n_w - n_{2w})}$$

Where $n_w, n_{2w}$ are the refractive indices at $w$ & $2w$ respectively

The magnitude of L given by above equation is called the **coherence length** for the second harmonic radiation

The expression for intensity

$$I\alpha \frac{\mathrm{Sin}^2(\frac{2k_1 - k_2}{2})_L}{(\frac{2k_1 - k_2}{2})}$$

is sharply peaked about

$$\frac{2k_1 - k_2}{2} = 0 \quad \text{i.e when} \quad K_2 = 2k_1$$

For efficient frequency doubling this relation must be satisfied This requirement is known as **phase matching criterion** .

Since $K_2 = \frac{2\omega n_{2\omega}}{c}$ & $k_1 = \frac{\omega n_\omega}{c}$

Relation reduces to $n_{n_{2\omega}} = n_\omega$ This is also a **Phase matching condition**

Now, in general, the threshold of photon absorption of a semiconductor determined by the energy gap where as refractive index is a measure of transparency to the incident photon. Moreover, electronic properties such as atomic polarizability and dielectric constant depend on the refractive index of the materials which ultimately can be calculated from the knowledge of the energy gap We use the relation between refractive index and energy gap developed by Rabindra as

$$n = 4.084 - 0.62\, E_g$$

## III. Experiment :

### Synthesis of ZnS quantum dots on PVA Matrix :

To prepare ZnS quantum dots , a simple low cost chemical method is adopted.[9-11] To prepare ZnS specimen by this method, 3gms of $Zncl_2$ is dissolved in 100ml of double distilled water, heated for 4hrs at temperature between $70^0$c -$80^0$c. The solution is degassed by boiling $N_2$ for 3hrs. A few drops of $HNO_3$ is added followed by moderate stirring. Then aqueous solution of $Na_2S$ is prepared on dissolving 3gm of $Na_2S$ in 100ml of double distilled water. This aqueous solution is added slowly by means of dropper to the solution of $Zncl_2$ until whole solution turns white. It is kept in a dark chamber at room temperature for 12 hrs for stabilization. Simultaneously, 4 gms of PVA is dissolved in 100ml of double distilled water and stirred by magnetic stirrer for 4 hrs at $80^0$c until transparent and then kept for 2 hrs for stabilization in dark chamber. Finally, 20ml of PVA matrix is mixed with 10ml of ZnS solution. The mixture is heated and stirred for 2hrs , kept in dark chamber for 12 hrs. Thus ZnS quantum dots are prepared `which are embedded in PVA matrix.

## IV. Characterisation: /RESULT AND DISCUSSION :

### A. Optical absorbance spectroscopy

Optical absorption spectroscopy ( using Perkin Elmer Lamda 35) display strong blue shift (figure -1) in the absorption edge at 240 nm which indicates the formation of nanostructures.

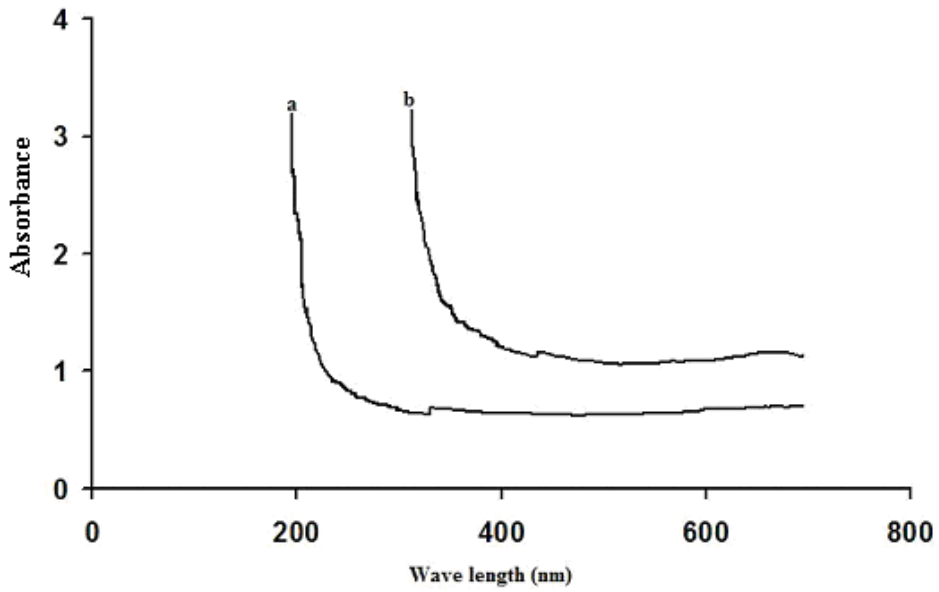



**Figure-2**

The appropriate size can be assessed by using the following hyperbolic band model [10,16]. The model yeilds the average quantum dot size at 9.3 nm. Formula for hyparabolic Band Model is

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

where Egb = bulk band gap = 1242/λgb,

λgb= bulk transition wavelength,

Egn=QD band gap=1242/λgn, λgn=wavelength corresponding to the strong absorption =5.1nm

edge of the quantum dots and m* ( for ZnS: $3.64\times10^{-31}$ kg) effective mass of the quantum dots and R is the radius of quantum dot .

**Table-1**

| Name of the samples | Bulk Band gap | Effective mass (m*) | Value of effective mass | Estimated particle size |
|---|---|---|---|---|
| **ZnS** | 2.42ev | 0.4 me | $3.64\text{x}10^{-31}$kg | 9.3nm |

**B. XRD :**

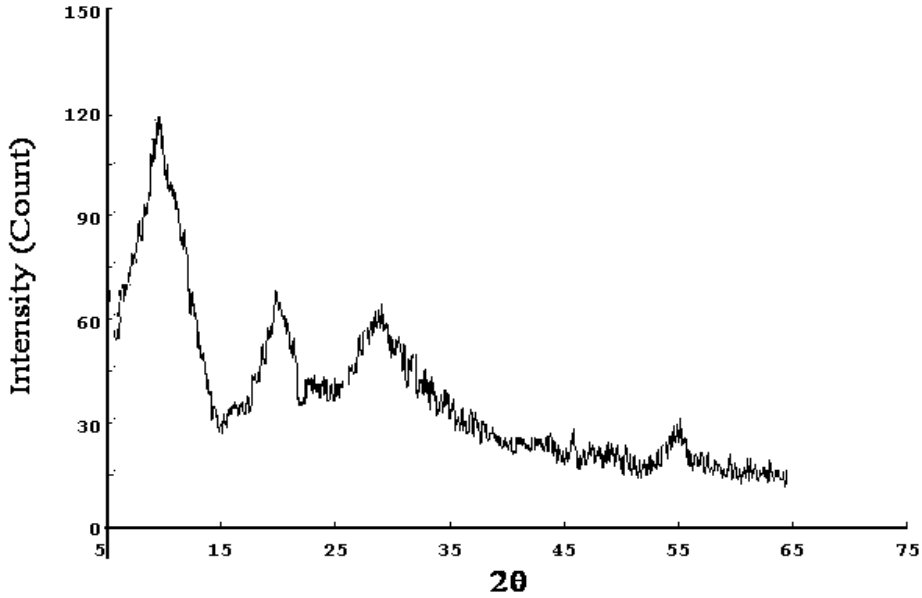



**Figure -3** X-ray diffraction spectrum of ZnS quantum dots in PVA matrix

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

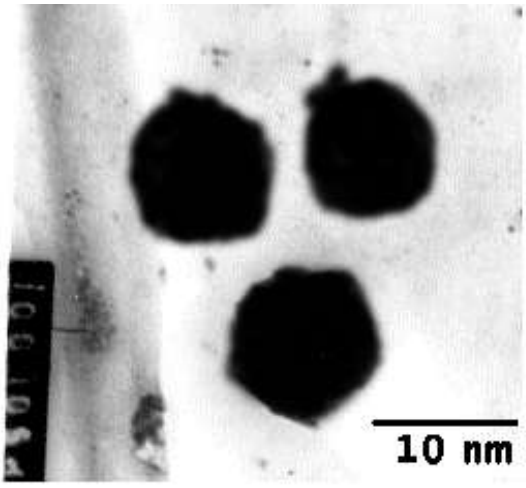
$$D = \frac{0.9\lambda}{W Cos\theta}$$

**Table -2** : 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 | |

**C. HRTEM :**

High resolution Transmission Electron Microscopy (HRTEM) ( using JEOL, 100CXII, 100Kv) shows the particle size of the sample (Figure-2). Average diameter of the particles are found around 10 nm. (fig-4)



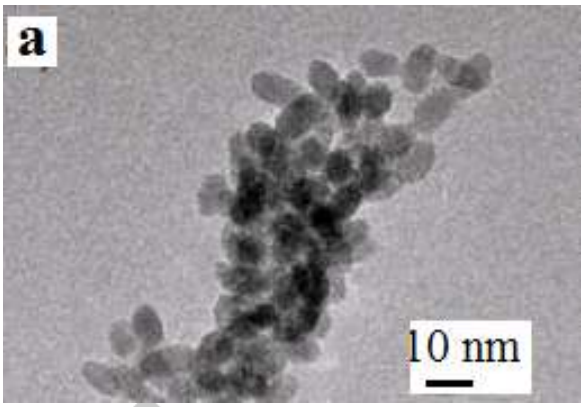




**Figure-4**

## V. Application:

To test the second harmonic wave in our prepared ZnS quantum dots, the sample is illuminated with monochromatic optical pump wave and the optical output is detected with a photomultiplier tube (PMT) having maximum sensitivity in the optical range from 300 nm to 500 nm. In the present study ZnS quantum dots are illuminated with an optical signal ( pump wave) of 750 nm and the optical output is detected at an wave length of around 380 nm. The output spectrum is shown in figure-5 below.

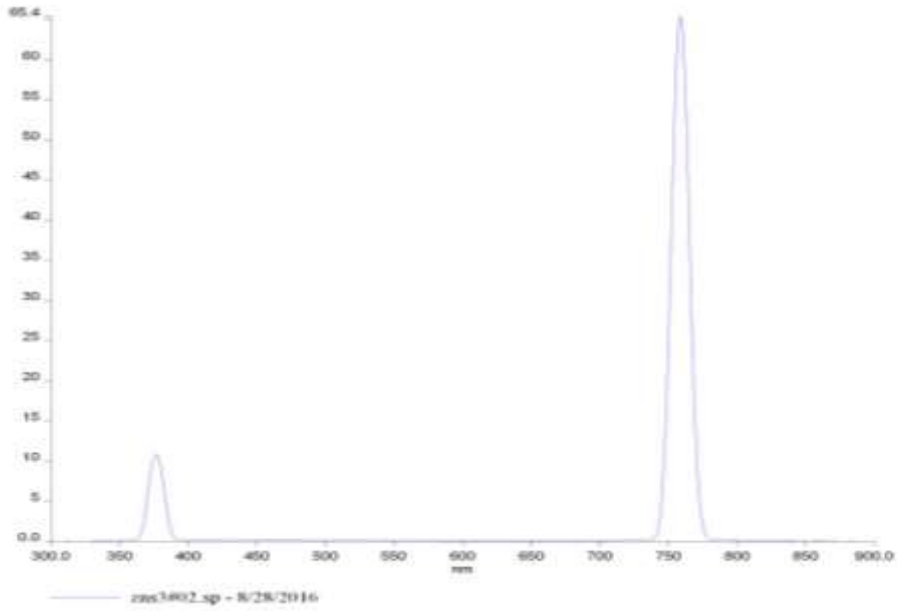



**Figure-5**

Calculation from the relation $n = 4.084-0.62\ Eg$

$= 4.084-0.62x5.1 = 0.922$

Now for air $n_{\omega} = 1$ and $n_{2\omega} = 0.922$ , both the values are nearly equal which follows phase matching condition as desired by theory. Discrepancy in value of refractive index of non-linear material $n_{2\omega}$ is because of dispersion.

## VI. Conclusion:

ZnS quantum dots are prepared though chemical route. Different characterization tools suggest that the prepared quantum dots are of uniform size and are within 10 nm . The as-prepared ZnS quantum dots show Second Harmonic when excited with a pump wave at around 780 nm which has been established through Phase matching Condition of Refractive index relation.

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