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ZnS Quantum Dots for Second Harmonic Generation

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Abstract

We report the preparation, characterization and second harmonic generation in ZnS quantum dots. For preparation of ZnS quantum dots the simple, cost effective chemical method has been adopted. After synthesis, the samples have been characterized by UV/VIS absorption spectroscopy and Transmission Electron Microscopy. These study infer the ZnS particle size to be within 10 nm. Further, ZnS specimen has been tested for second harmonic generation. For that, ZnS samples have been illuminated with Nd:YAG laser beam of 700 nm of wavelength and the optical output is detected at a wavelength of 350 nm. This shows that ZnS quantum dots can be used for the purpose of second harmonic generation.

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-, 15] New features are observed and eventually leads to new applications. Literature reports the generation of second harmonic by metal quantum dots which acts as non-linear optical material.[4] The optical properties of quantum confined semiconductor structures such as quantum dots have also attracted recent attention as potential non-linear material for many non-linear optical devices.[5, 6, 12] Size Dependence of Second Harmonic Generation in CdSe nanocrystal quantum dots has been studied by Michal Jacobsonh and Uri Banin.[7] However, many aspects of the effect of confinement on the linear and non-linear optical properties of compound semiconductor are yet to be studied extensively. Here in this paper, it is attempted to synthesize ZnS quantum dots (a II-VI group binary semiconductor compound) by chemical route to characterize, and finally to test its application for second harmonic Generation by illuminating the specimen with an intense monochromatic laser source in the UV-Visible range and thereafter detecting its optical output with the help of a photo multiplier tube (PMT)

Experimental :

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 70^0c-80^0c. 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 80^0c 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.

Result and discussion :

Optical absorption spectroscopy (using Perkin Elmer Lamda 35) display strong blue shift (figure-1) in the absorption edge at 210 nm which indicates the formation of nanostructures.

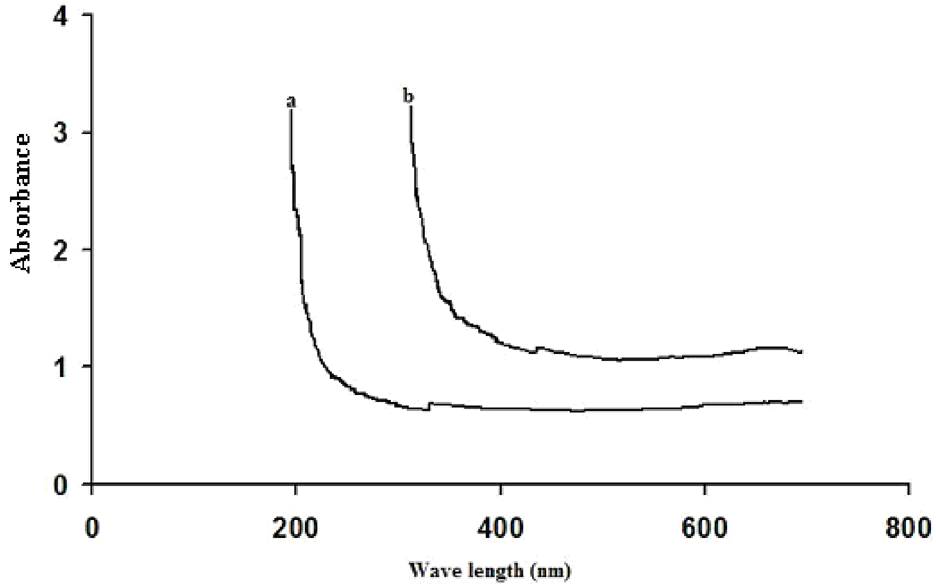

Figure-1

The appropriate size can be assessed by using the following hyperbolic band model [10, 16]. The model yeilds the average quantum dot size at 13nm. 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 edge of the quantum dots and m* (for ZnS: 3.64×10^{-31} kg) effective mass of the quantum dots and R is the radius of quantum dot,

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.

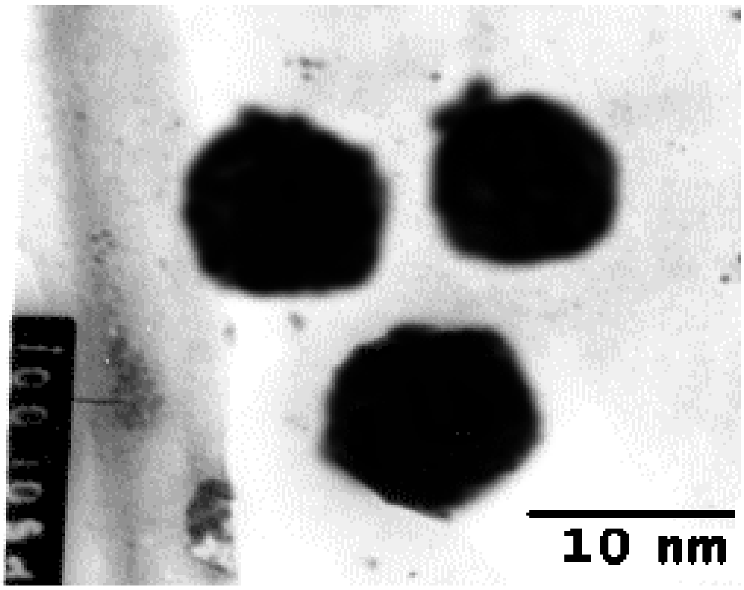

Figure-2

Second Harmonic generation (SHG) :

SHG is a second order non-linear optical phenomena. The non-linear polarization response of a molecule can be expanded as power series of the inducing optical field strength E as

$$P = \alpha.E + \beta.EE + \gamma.EEE + \ldots\ldots\ldots\ldots \quad (1)$$

Where α is the linear polarisability and β is the first hyperpolarisability which determines the second order optical non-linearity [7, 13]. β, which is a material dependent parameter, plays the key role in generation of SHG. Higher the value of β higher is the SHG efficiency and hence more in the SHG intensity.

To test the SHG in our prepared ZnS quantum dots, the sample is illuminated with monochromatic optical pump wave (Nd:YAG laser) and the optical output is detected with a photomultiplier tube (PMT) having maximum sensitivity in the optical range from 300 nm to 400 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 350 nm. The output spectrum is shown in figure-3.

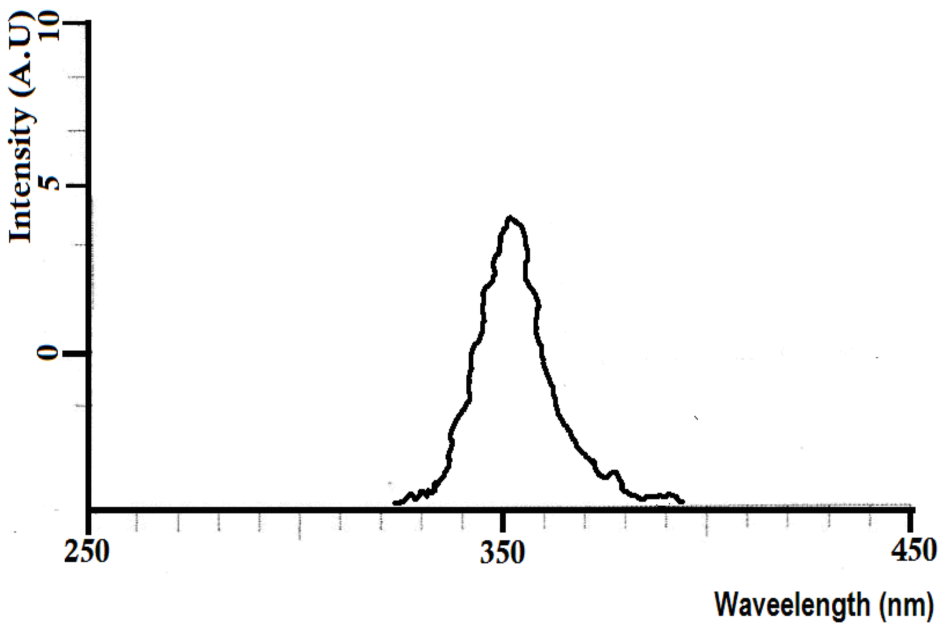

Figure-3

We believe this to be second harmonic generation because of the following facts:

[1] The asymmetry of the molecular structure is the primary source of the second order optical nonlinearity and second harmonic can be generated by non-linear optical material with non-centro symmetric molecular organization.[7, 1].

[2] The efficiency of nano objects to convert fundamental frequency photons (pump wave) into second harmonic photons is determined by the quadratic hyperpolasability (β) [1] as clear in the equation (1)

ZnS is a non centrosymmetrical material even in bulk from and hence is a right candidate to generate second harmonic. Normally the hyperpolasability (β) of ZnS lies between 10^{-25} to 10^{-26} esu. When the size is reduced specially within 10 nm the value of β increases remarkably and goes as high as 1000 $X10^{-30}$ esu. This is because the surface properties of the particles confined within 10 nm are observed through the surface contribution of β[1]

Conclusion:

ZnS quantum dots fabricated by chemical method is within 10 nm of particle size range show high second order hyperpolasability resulting in generation of Second Harmonic wave.

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