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Abstract. ZnS quantum dots having a narrow size distribution are chemically synthesized and characterized as regards their linear and non-linear optical properties. Quantum-size effects are revealed by the size-dependent blue-shift observed in the optical absorption spectra. The third-order optical non-linearity of a colloidal solution of ZnS quantum dots is studied by a third-harmonic-generation technique at the fundamental wavelength of 1.06 μm. The third-harmonic signal is size dependent and increases with particle size over the range 7 to 21 Å. The third-harmonic signal of ZnS dots is also dependent on the choice of embedding medium (for example, DMF and acetonitrile). The results are qualitatively explained on the basis of the local field effect.

1. Introduction

Three-dimensional quantum confinement in semiconductor nanocrystals occurs when the crystallite size approaches the bulk exciton Bohr radius. Because of this, the linear optical absorption spectrum of quantum dots consists of a series of lines corresponding to transitions between quantum-confined electron–hole states. The origin of the optical non-linearity for quantum dots is mainly the state-filling effect. This may be described as the saturation of the optical absorption due to quantized energy levels which are located at relatively large energy separation in quantum dots [1].

These effects give rise to possible applications of quantum dots in new atomic lasers, switching elements and optical data-storage devices. CuCl nanocrystallites embedded in glass have been paid great attention in this respect [2–6]. Masumoto *et al* [4] have studied the non-linear properties of excitons in CuCl microcrystallites in NaCl host crystals by the absorption saturation method. Hanamura [2] has theoretically analysed the oscillator strength and $\chi^{(3)}$ for semiconducting microcrystallites of CdS. The linear and non-linear optical properties of CdSe quantum dots are widely investigated [7–9].

The resonant $\chi^{(3)}$ non-linearity of semiconductor dots has been studied extensively [10, 11], following earlier work on commercial coloured glasses which contain 100 to 1000 Å CdS–Se particles [10]. Wang *et al* [12–14] have reported a non-resonant $\chi^{(3)}$ for a CdS cluster, in solution, polymer and glass, over the range 7 Å to 120 Å.

In this paper, investigations on linear as well as non-linear properties of cubic ZnS quantum dots synthesized using a wet-chemical route are reported. The energy gap variation in these

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quantum dots as a function of their size is well exhibited by the absorption spectra of these quantum dots. Non-resonant third-order non-linearity of the ZnS cluster in solutions over the range 7 Å to 21 Å is studied by the third-harmonic-generation technique.

2. Experimental procedure

2.1. Synthesis of ZnS quantum dots

The ZnS particles were synthesized by a method reported by Mahamuni *et al* [15]. The method was originally proposed by Herron *et al* [16] for synthesis of CdS quantum dots capped with thiophenol (C_6H_5SH). A very narrow size distribution could be achieved using this route.

The approximate size was estimated from x-ray diffraction patterns using the Scherrer formula. Different-sized quantum dots having diameters ranging from 7 Å to 21 Å are stabilized here. X-ray diffraction patterns were recorded using a PW 1840 powder x-ray diffractometer. Selected-area electron diffraction patterns indicate a highly crystalline nature of the quantum dots and were reported earlier [15]. The optical absorption spectra were recorded by dispersing ZnS quantum dots in acetonitrile and using a HITACHI 330 double-beam spectrophotometer.

2.2. Non-linear optical studies

The second-order non-linear optical effects are studied for ZnS quantum dots by using a TEM_{00}-mode Q-switched Nd-YAG laser with energy 20 mJ for 17 ns at 5 Hz, by adopting the powder method described by Kurtz and Perry [17].

A fine-powder sample of ZnS quantum dots (7–21 Å) is placed in a thin cell made from two microscope cover slips having a separation of 0.5 mm. The laser is incident normally to the cell and the second-harmonic signal is detected in the transmission mode by a combination of a monochromator (McPherson) and a PMT (EMI6255QB) on a storage oscilloscope, Tektronix 466 (least count: 2 mV). The second-harmonic signal from a DCDA crystal (Quantum Technology) is used as a reference.

The experimental set-up used for THG measurements is described in detail elsewhere, by Kajzar and Messier [18]. The fundamental laser beam is obtained from a TEM_{00} Q-switched Nd-YAG laser having a wavelength of 1.06 μm with an energy of 10 mJ for 17 ns at 5 Hz. The laser beam, after parasitic light filtering, was focused using a lens (focal length: 10 cm) on the first liquid–glass interface of the cell [19]. The ratio of the THG from one compartment of the cell to that from the other is measured using benzene as a standard liquid in the second compartment.

Non-phase-matched third-harmonic-generation measurements were performed to observe Maker's fringes using a thin cell of size 1 cm × 1 cm × 1.5 mm [20]. The detection system consists of a 1.06 μm stop filter (Schott KG3), a 0.354 μm line filter (10 nm Melles Griot), a monochromator (McPherson) and a PMT (EMI 6255QB). The signal is fed to a boxcar averager (PAR 162 and 164 from EG&G), with an aperture duration of 5 ns. The integrated signal was fed to a chart recorder.

To study the size-dependent non-resonant third-order effects and also the effect of embedding the cluster in various media, a set of four solutions with graded concentrations were prepared for ZnS quantum dots ranging in size from 7 Å to 21 Å in acetonitrile and DMF. The Maker's fringe experiments were carried out for cluster sizes varying from 7 to 21 Å in acetonitrile at a fixed concentration (0.1 g cm^{-3}).
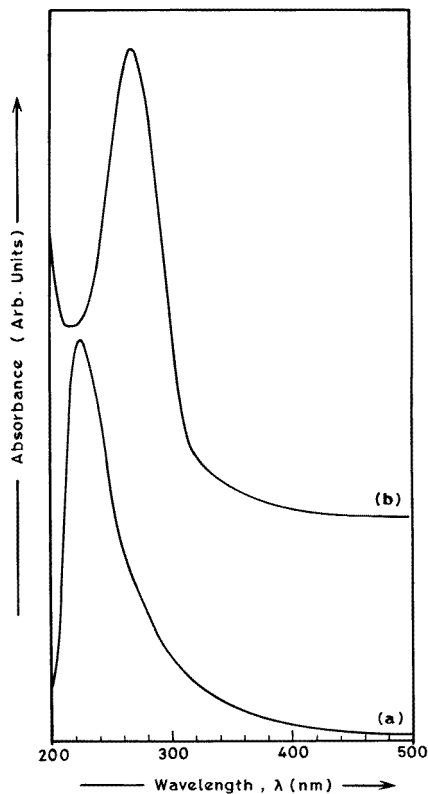
Figure 1. Optical absorption spectra for ZnS nanocrystallites having average sizes (a) 7 Å and (b) 15 Å. ZnS quantum dots are dispersed in acetonitrile.

## 3. Results and discussion

3.1. Optical absorption

The quantum-size effects in semiconductor materials are studied using optical spectra. The optical absorption wavelength is blue-shifted in these materials as a consequence of the decrease in size. Two different-sized ZnS quantum dots showing excitonic features at 5.3 ± 0.24 eV (230 nm) and 4.7 ± 0.19 eV (260 nm) were used for studying the non-linear optical effects. The optical absorption spectra are shown in figure 1. The size is estimated to be 7 Å for those quantum dots which exhibit excitonic absorption features at 5.3 eV while it is 15 Å (± 3 Å) for the quantum dots which exhibit absorption features at 4.6 eV. The presence of such a sharp absorption peak is a signature of monodispersity of the particles.

3.2. Studies on non-linear effects

The second-harmonic signal generated by DCDA crystal is 60 mV. However, no second-harmonic generation was detected in ZnS quantum dots using the above experimental set-up.

The absence of second-harmonic generation in ZnS quantum dots can be attributed to the fact that the confining potential is symmetric, and hence the second-order susceptibility is zero [21].

Figures 2(a) and 2(b) show the concentration dependence of the third-harmonic signal for different sizes of ZnS quantum dots in DMF and acetonitrile. It is clear from figures 2(a) and 2(b) that the third-harmonic signal increases with the increase in cluster size from 7 to
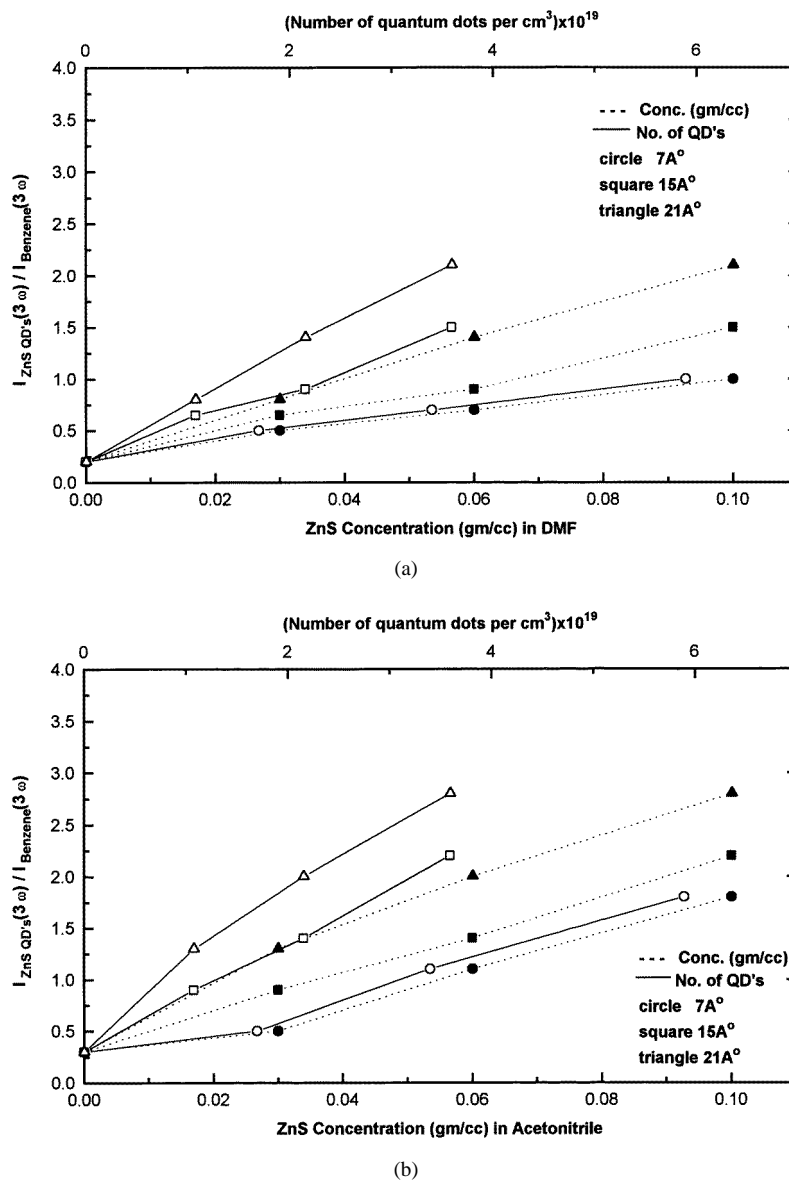
Figure 2. The ratio of the third-harmonic signal from ZnS quantum dots to that from benzene in (a) DMF solutions and (b) acetonitrile solution, plotted as functions of the ZnS concentration and number of quantum dots.

21 Å. Moreover, the third-harmonic intensity of the ZnS cluster in the acetonitrile solution is observed to be greater than that in the DMF solution for each individual size. The typical Maker's fringe pattern observed for a ZnS cluster (15 Å in size) in acetonitrile is shown in figure 3.

All of the media in the path of the laser beam generate third harmonics [22]. In the present case, the contribution from air is minimized by using a long liquid chamber and front window (as compared with the laser beam focal parameters), so that the non-linearity at the front surface
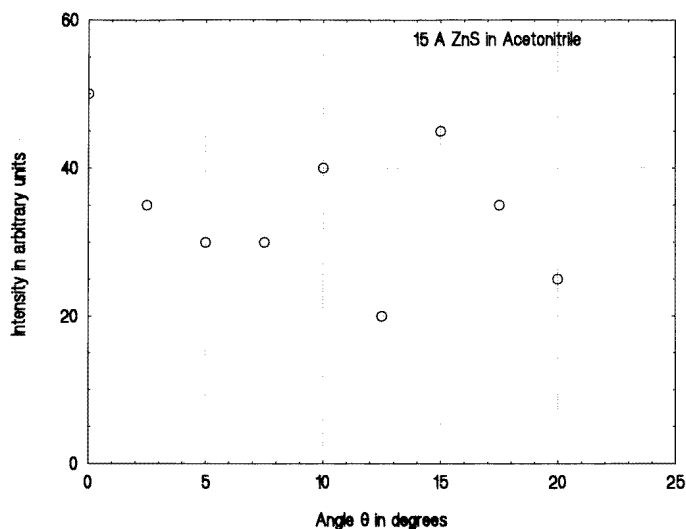
Figure 3. The variation in the third-harmonic signal with rotation of the sample cell for 15 Å quantum dots of ZnS in acetonitrile.

and at the back window are inconsequential [19].

If the laser photon energy ($h\nu$) is far less than that from any electronic transition, $E_s \gg 2h\nu \gg 3h\nu$, the effects of excitation and multiple photon resonances can be ignored. For semiconductor clusters embedded in a dielectric medium, the major factor to be considered is the local field effect. The local field experienced by a cluster in a medium can be described on the basis of the Lorenz–Mie theory of scattering properties of dielectric spheres. Messinger *et al* [23] have measured the near field of a sphere, Q_{nf}, which gives a measure of the local field intensity at the surface. Wang and Herron [14] have used these results from the Lorenz–Mie calculation and the reaction field due to the dipole–dipole interaction to find the total internal field experienced by the clusters.

The Maker's fringe experimental results are presented in figure 3. With the present experimental set-up, it was difficult to determine the coherence length from the fringe pattern, as least-squares curve fitting could not be carried out [20]. The amplitudes of the third-harmonic measurements were analysed using a long sample cell. Figures 2(a) and 2(b) indicate an increase in the THG signal with increase in the cluster size in the quantum-confinement regime (<21 Å). This is in agreement with earlier-reported work on CdS clusters [13, 14, 24]. In the absence of quantum confinement, the third-harmonic signal should be independent of the cluster size in the size regime studied here. As can be seen from the absorption spectra for the ZnS cluster (figure 1), the quantum-confinement effect shifts the absorption edge to higher energies and thus reduces the refractive indices, resulting in a lower local field enhancement factor and therefore a lower third-harmonic signal. The present results on the non-resonant third-order non-linearity provide an interesting contrast with the resonant third-order non-linearity of semiconducting quantum dots, where the non-linearity is predicted to increase with decrease in the cluster size due to an enhanced volume-normalized oscillator strength. Moreover, the third-harmonic intensity of each ZnS cluster size in acetonitrile solution is observed to be greater than that in DMF solution. This can be explained on the basis of the local field model: the local field intensity at the cluster surface is enhanced due to the difference in the refractive indices, which establishes a boundary. The reaction field arising from the

dipole–dipole interaction between the molecule and the surrounding medium is reduced in going from DMF solution to acetonitrile, and this enhances the local field enhancement factor.

4. Conclusions

Monodispersed ZnS quantum dots were synthesized chemically. The linear and non-linear optical properties were studied. No second-harmonic generation was observed. The third-harmonic signal is found to be size dependent and increases with particle size over the range 7 to 21 Å. The observed third-harmonic signal for the ZnS cluster is found to vary according to the choice of dielectric medium (here, DMF or acetonitrile). These effects are explained on the basis of the local field model. Further studies are required for sizes greater than 21 Å, as well as synthesis of ZnS clusters in polymer or glass for any suitable application.

Acknowledgments

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