

Optical and impedance studies of pure and Ba-doped ZnS quantum dots

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Abstract Chemical precipitation method using a high-boiling solvent is used to synthesize ZnS and Ba-doped ZnS quantum dots. The presence of organic ligands in the prepared nanostructures is verified using Fourier transform infra-red spectroscopic studies. The samples have been analysed using X-ray diffraction analysis confirming nanocrystallinity of the as-prepared quantum dots (QD). The mean crystal size obtained by full width half maxima analysis is 3.2 nm for ZnS and 3.9, 4.2 nm for ZnS:Ba (2, 4 mM). TEM micrographs also reveal nanosized particles of ZnS and Ba-doped ZnS. An optical absorption study conducted in UV–Vis range 150–600 nm reveals the transparency of these quantum dots in entire visible range but not in ultraviolet range. The results based on optical analysis yield band gap values as 4.88 eV for ZnS and 4.69, 4.43 eV for ZnS:Ba (2, 4 mM) quantum dots. Impedance analysis of the samples was carried out to reveal the variation of impedance with frequency at room temperature. These results show the capacitive admittance associated with the quantum dots and hence nanostructure ZnS and Ba-doped ZnS can have potential applications in

electronics as nano-tuned devices in which resonant frequency can be adjusted by controlling the size and shape of the quantum dots.

Keywords CdS Quantum dots · Doping · EDX · TEM FTIR · Optical properties · Impedance properties

Introduction

In recent years, study of nano-materials is becoming the fast growing area of research due to their numerous applications in almost all areas of utilities. This is because it gives an opportunity to understand the physical properties in low dimensions which explore totally different properties than that of bulk materials like blue shift in optical absorption spectrum, increased effective surface area, reactivity, phase–phase transformation, strength etc. (Colvin et al. 1994; Chen et al. 2000). Furthermore, impurity ions doped into these nanostructures can influence the electronic structure and transition probabilities (Soo et al. 1994). Zinc sulfide is an important type of II–VI group semiconductor with its wide band gap energy of 3.67 eV at room temperature. This makes it particularly suitable for use as luminescent host materials for a very large variety of dopants. Doped semiconductor quantum dots have received a considerable effort since the initial research work on the luminescence properties of Mn^{2+} ions doped ZnS quantum dots (Soo et al. 1994; Alivisatos 1996). Doped semiconductor quantum dots have extracted extensive research interests in the recent years due to their unique optical properties and potential applications (Hebalkar et al. 2001; Labert-Robert et al. 2001; Brus 1991). Numerous researchers have investigated the structural and luminescence properties of doped phosphor quantum dots

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(Alivisator 1996). The doping ions act as recombination centers for the excited electron–hole pairs and result in strong and characteristic luminescence. ZnS is a material that has fascinated researchers with its variety of morphologies and range of promising device application (Pool 1990; Qu et al. 2002; Ishizumia et al. 2005; Norris et al. 2001; Yang et al. 2001; Liu et al. 2000; Papakonstantinou et al. 1998; Xu et al. 1998). It has shown promising applications at nano scale. ZnS nano-materials are synthesized using different methods such as hydrothermal, emulsion precipitation sol–gel, citrate-gel, and aero-gels (Trindade and Brien 1996; Trindade and Brien 1996; Artemev et al. 1997; Yang and Holloway 2003). Generally, ZnS becomes good host material, since it is a kind of wide band gap II–VI component semiconductor materials ($E_g \sim 3.6$ eV), and with its energy band characteristics, It is commercially used as a phosphor and thin-film electroluminescence devices (Yang et al. 1997). Luminescence characteristic of impurity-activated ZnS quantum dots differs markedly from those of bulk ZnS (Wang et al. 2006). It is well-known that the properties of pure ZnS quantum dots are obviously different from the bulk materials (Vinotha Boorana Lashmi et al. 2009). The quantum dots of ZnS and Ba modified ZnS were achieved through wet chemical precipitation route and the presence of organic elements of the as-prepared quantum dots was verified by Fourier transform infra-red spectroscopy (FTIR) analysis. In this investigation, emphasis has been given on the impedance study of the ZnS and Ba-doped ZnS nano-materials, which shows the use of these nano-materials in the field of electronics as quantum dot tuned electronic devices. The investigations are also made on structural and optical properties of these quantum dots.

Experimental

Pure and doped ZnS:Ba (2, 4 mM) quantum dots were precipitated from a mixture of zinc acetate and barium dichloride with sodium sulfide in aqueous solution. In a typical procedure, aqueous solution of sodium sulfide was added into aqueous solution of zinc acetate and aqueous solution of barium dichloride with the molar ratio of Zn:S being 1:1 to obtain white fluid. Then mercaptoethanol ($\text{HOCH}_2\text{CH}_2\text{SH}$) was added to the above solution, with constant stirring at room temperature. The resulting precipitates were filtered and washed several times with double distilled water and ethanol. Washings were done to remove any organic part or any other impurity from the particles. The characterization of the grown crystals was carried out using X-ray powder diffraction, FTIR analysis. The Powder XRD patterns of the grown crystal were obtained using Bruker D-8 Advanced X-ray diffractometer

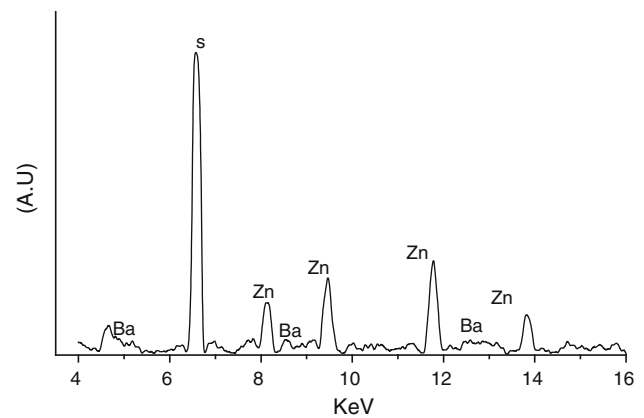


Fig. 1 EDX spectrum of Ba-doped ZnS nanocrystals

with a Cu $K\alpha$ radiation ($\lambda = 1.54060$ Å). The optical absorption spectra of the same particles in de-ionized water were recorded using UV-1231PC SHIMADZU spectrometer. The TEM micrographs are taken using PHILIPS model-CN202 with resolution 2.4 Å. Impedance measurement was done using Agilent Precision Impedance Analyzer-4042 A to study the variation of impedance with frequency at room temperature. For this, powdered samples were molded into pellets of equal thickness by applying the pressure of 4 tons in hydraulic press.

Results and discussion

Structural and FTIR analysis

The elemental analysis EDX of the prepared samples shows the presence of doping element Ba in the parent matrix as shown in Fig. 1. TEM micrographs of synthesized ZnS and Ba-doped ZnS are shown in Figs. 2, 3, respectively, which clearly indicate the formation of nanosize particles with the average particle size around 3.5 nm for pure ZnS, 4.1 and 4.6 nm for Ba-doped ZnS nanoparticles. Figure 4 shows the X-ray powder diffractogram of quantum dots ZnS and Ba-doped ZnS. The peaks originating from planes (111), (220), and (311) are assigned with zinc blend structure (Norris et al. 2001). The broadening of peaks in XRD pattern verifies the nanocrystalline nature of the as-prepared quantum dots. These quantum dots have less lattice planes in comparison to bulk, which contributes to the broadening of the peaks in the diffraction pattern. It is clear from Fig. 4 that there is a small shift in broad peaks of Ba-doped ZnS with respect to the pure ZnS quantum dots, this shift in intensity may be attributed to the presence of dopant (Ba) in modified ZnS quantum dots. This broadening of the peak could also arise due to the micro-straining of the crystal structure arising from defects like dislocation and twinning etc. These

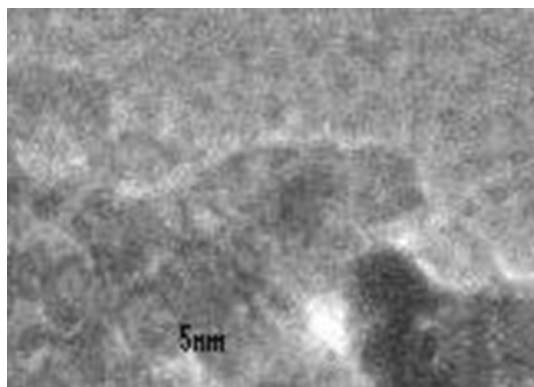


Fig. 2 TEM image of pure ZnS nanocrystals

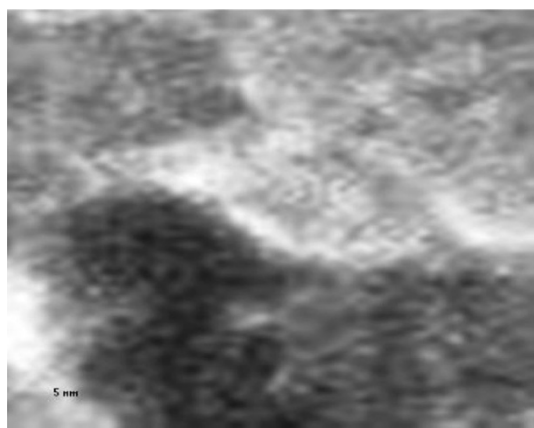


Fig. 3 TEM image Ba-doped ZnS nanocrystals

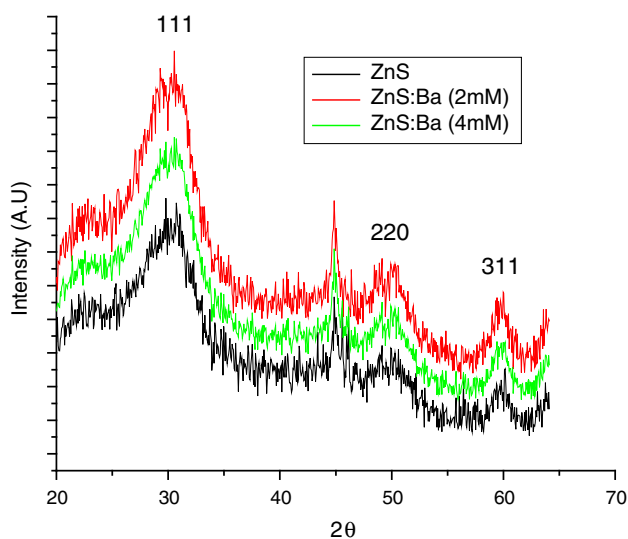


Fig. 4 XRD pattern of ZnS and ZnS:Ba (2, 4 mM) quantum dots

defects are believed to be associated with the chemically synthesized quantum dots as they grow spontaneously during chemical reaction. As a result, the chemical ligands get negligible time to diffuse to an energetically favorable

site. It could also arise due to lack of sufficient energy needed by an atom to move to a proper site in forming the crystal. From the value of full width half maxima (FWHM), the mean crystalline sizes were calculated using Scherer's equation.

$$(D = 0.9\lambda/(\beta\cos\theta)) \quad (1)$$

where λ is the X-ray wavelength, θ is the diffraction angle, and β is the full with half maximum of the particles. The calculated mean crystal size is 3.2 nm for ZnS and 3.9, 4.2 nm for ZnS:Ba (2, 4 mM).

The organic composition of the samples and the presence of various bonds have been studied through FTIR. As shown in Fig. 4, the FTIR spectra of ZnS and Ba-doped ZnS quantum dots show the presence of OH group, with a broad band centered at around 2523 cm^{-1} . The weak band appearing at $1,923\text{ cm}^{-1}$ may be attributed to O–H bending in carboxylic acids. It might be due to O–H in-plane bending vibrations in alcohols. The weak peaks appearing in both ZnS and Ba-doped ZnS samples, at $1,895$ and at $1,890\text{ cm}^{-1}$, respectively, might be due to C–O stretching. It may be due to bending vibrations of C–H due to absorption of hydrocarbons and presence of C–S linkage. This shows the presence of mercaptoethanol ($\text{HOCH}_2\text{CH}_2\text{SH}$), which has been used as the surfactant/capping agent in the synthesis of the ZnS:Ba (2, 4 mM) quantum dots.

Optical and impedance studies

Figure 6 exhibits the UV–Visible absorption spectra of the pure ZnS and ZnS:Ba (2, 4 mM) quantum dots. An absorption shoulder at about 316 nm (3.92 eV) was observed in ZnS and its position shows small change in Ba-doped ZnS quantum dots. This is because of Ba ions incorporated into the quantum dots are small and do not change the particle size under similar synthesis conditions. The band gap energy is increased compared to that (3.6 eV) of bulk ZnS (Zou et al. 1999); the enlargement of the band gap can be attributed to the quantum confinement effect of the ZnS:Ba (2, 4 mM) nanostructures. As it is clear from Fig. 5, the absorption edge of ZnS is at around 302 nm and that of Ba-doped ZnS is (325 nm), which is fairly blue shifted from the absorption edge at 345 nm of the bulk ZnS. Optical absorption studies show that the shifting of absorption edge towards blue region with respect to bulk samples of ZnS indicates increase in effective band gap energy with decreasing particle size. The observed blue shift in the excitation wavelength is attributed to quantum confinement effect with respect to bulk materials of these compositions (Ghosh et al. 2007). Since the particle size as calculated by Deby–Scherer formula for both ZnS (=3.22 nm) and Ba modified ZnS

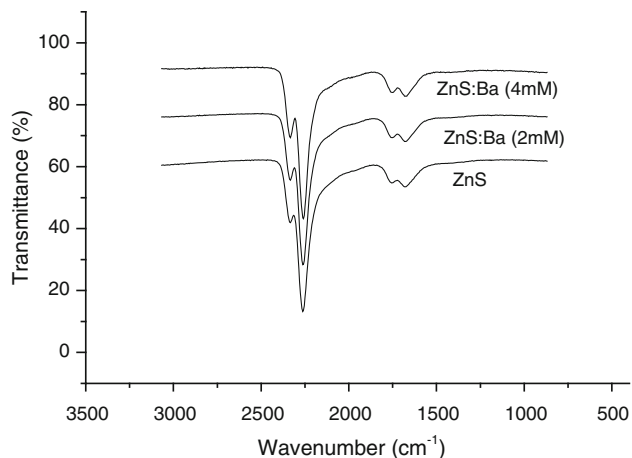


Fig. 5 FTIR spectrum of pure and Ba-doped ZnS quantum dots

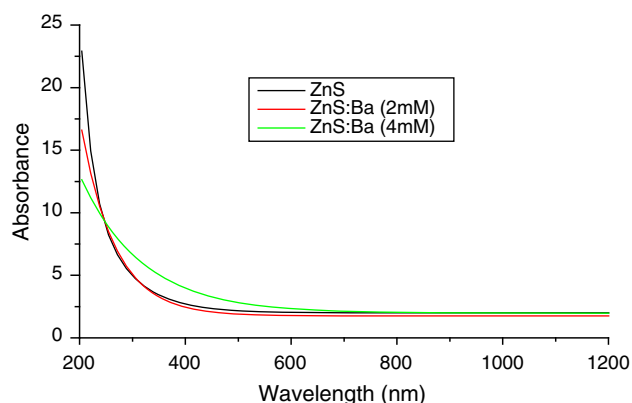


Fig. 6 Absorption spectra of Ba (2, 4 mM) doped ZnS quantum dots

(=4.22 nm) is less than Bohr radius (10.4 nm). Therefore, both ZnS and Ba modified ZnS as-prepared nano-materials fall within the strong confinement. Generally, semiconductor crystallites in the diameter range of few nanometers show a quantum size effect in their electronic structure. These quantum size effects on the band gap absorption energy can be measured by UV–Vis absorption spectroscopy. From this study, one can calculate the energy band gap. The fundamental absorption, corresponds to the transmission from valence band to conduction band, is employed to determine the band gap of the material. From Fig. 6, the absorption coefficients (α) were calculated. The relation between absorption coefficient (α) and incident photon energy ($h\nu$) can be written as.

$$\alpha = A (h\nu - E_g)^n / h\nu \quad (2)$$

where A is a constant and E_g is the band gap of the material. Exponent “ n ” depends upon the type of the transition; n may have values 1/2, 2, 3/2, and 3 corresponding to the allowed direct, allowed indirect, forbidden

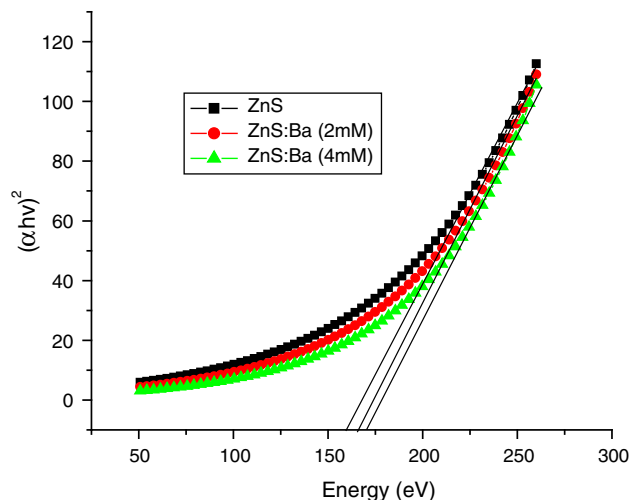


Fig. 7 $h\nu$ versus $(\alpha h\nu)^2$ of the samples

Table 1 Calculations based on structural and optical analysis

Samples	Optical band gap (eV)	Particle size XRD (nm)	Particle size TEM (nm)	Average particle size (nm)
ZnS	4.88	3.2	3.5	3.35
ZnS:Ba (2 mM)	4.69	3.9	4.1	4.00
ZnS:Ba (4 mM)	4.43	4.2	4.6	4.40

direct and forbidden indirect, respectively (Wang et al. 2006). In the nanocrystalline sample, the transition is same as in the case of bulk. However, there may be some deviation from the bulk. From the above equation, it is clear that, plot of $(\alpha h\nu)^2$ versus $h\nu$ will indicate a divergence of an energy value, E_g where the transition takes place. The exact value of the band gap is determined by extrapolating the straight line portion (Fig. 7) of $(\alpha h\nu)^2$ versus $h\nu$. The calculated band gap values are 4.88 eV for ZnS and 4.69, 4.43 eV for ZnS:Ba (2, 4 mM) quantum dots. It is noticed that the band gap value decreases with the substitution of barium. These can be ascribed to $sp-d$ exchange interaction. The d -orbitals in Ba^{+2} , which are close in energy to Ba^{+2} s -orbitals, are energetically close to the conduction band of the semiconductor (ZnS). This band is primarily composed of metal (Zn) s -orbitals with energy comparable to that of the Ba s -orbitals. For large bandgap like ZnS, the d -orbitals should stay below the conduction band. Now the mixing of d -levels with the conduction band will increase the energy of the host conduction band. Consequently, the bandgap will decrease on introduction of Ba in the ZnS matrix (Ghosh et al. 2007). The existence of the exciton has a strong influence on the electronic properties of the semiconductor and its optical absorption (Cho et al. 1999). The values of optical band gap and particle size of pure and Ba-doped ZnS quantum dots are given in Table 1.

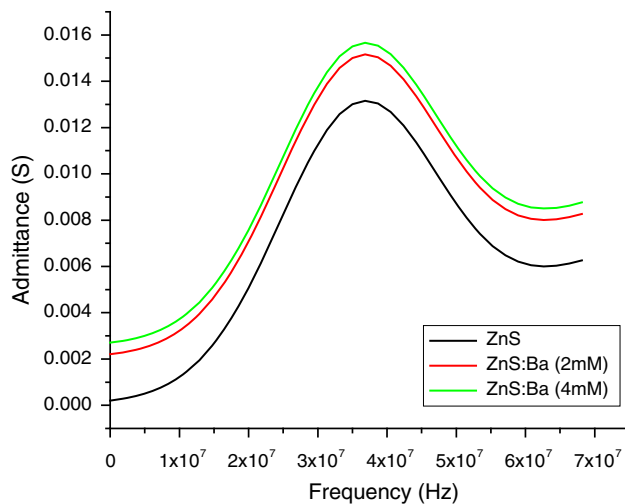


Fig. 8 Plot of frequency versus admittance of pure and Ba-doped ZnS nanocrystals

Table 2 Maximum admittance, minimum impedance corresponding to resonant frequency

Samples	Resonant frequency (MHz)	Max admittance (S)	Min impedance (Ω)
ZnS	35.5	0.0130	76.92
ZnS:Ba (2mM)	36.80	0.0150	66.67
ZnS:Ba (4mM)	36.82	0.0157	63.69

Impedance study of ZnS and Ba-doped nano-materials was carried out to analyze the variation of impedance (Z) in terms of admittance (Y) with frequency shown in Fig. 8. It is observed that initially admittance increases slowly for lower frequencies and then rapidly up to certain frequency called resonant frequency and then decreases at higher frequency. The values of critical frequency and corresponding minimum impedance and maximum admittance are listed in Table 2. Such variation of impedance with applied frequency shows the capacitive impedance associated with the nano-materials. Quantum dots are associated with capacitance and quantum dot impedance (or admittance) is basically due to capacitance in the specimen (Cho et al. 1999; Ghosh et al. 2007). Due to variation in size as well as shape, capacitive impedance and critical frequencies for the samples are different. Impedance analysis indicates that materials under investigation display steep rise and fall of admittance at a particular frequency. This is the property of electronic tuned circuit and the frequency at which maximum admittance is attained may be compared to the resonant frequency of a conventional tuned circuit and this frequency may be called ‘equivalent resonant frequency’. In a conventional tuned circuit, resonance frequency is adjusted by tuning passive

components (R & C), whereas in a quantum dot tuned devices, the ‘equivalent resonant frequency’ can be adjusted by controlling the size and shape of the quantum dots. Bulk materials of ZnS do not show any variation in admittance. Therefore, ZnS and Ba-doped ZnS nano-materials can be used in nano-tuned devices.

Conclusions

In summary, the pure and Ba-doped ZnS quantum dots prepared through chemical route are found to have cubic crystal structure with the diffraction peaks coming from (111), (220), and (311) planes. Due to the quantum confinement effect, the band gap of the quantum dots is increased compared with bulk material. The broad peaks in XRD confirm the nanocrystallinity of the prepared samples. On modifying pure ZnS by Ba, optical band gap decreases. The optical absorption studies show that the absorption edge shifts towards blue region for both ZnS and Ba modified ZnS of the as-prepared nano-materials with respect to bulk (ZnS) indicating that effective band gap energy increases with decreasing particle size. The observed blue shift in the excitation wavelength is reflection of the band gap increase owing to quantum confinement. Impedance analysis shows that synthesized materials have minimum impedance at a particular frequency which is 35.5 MHz for ZnS and 36.80, 36.82 MHz for Ba (2, 4 mM) doped ZnS quantum dots. The variation of impedance with frequency indicates the capacitive impedance associated with these nano-materials. Such materials can be used in electronic nano-tuned devices.

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