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Ceramics International 38 (2012) 5497–5500

CERAMICS INTERNATIONAL

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Blue light emission from barium doped zinc sulfide nanoparticles

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Received 29 February 2012; received in revised form 25 March 2012; accepted 26 March 2012

Available online 10 April 2012

Abstract

ZnS nanoparticles with Ba^{2+}doping have been prepared at room temperature through chemical route, namely the chemical precipitation method. The nanostructures of the prepared nanoparticles have been analyzed using X-ray diffraction (XRD) for phase analysis, Field emission scanning electron microscope (FESEM) for the morphological characterization, UV–Vis–NIR spectrophotometer for determining band gap energy and fluorescence spectroscopy for determining the emission wave length. The sizes of as prepared nanoparticles are found to be in 9–10 nm range. FESEM morphology shows the formation of nanostructure of ZnS samples. The value of optical band gap has been found to be in range 4.10–4.63 eV. Room temperature photoluminescence (PL) spectrum of the undoped sample exhibits emission in the blue region with multiple peaks under UV excitation. On the other hand, the Ba^{2+} doped ZnS samples exhibit visible light emissions under the same UV excitation wavelength of 310 nm.

Keywords: Semiconductors; Optical absorption; Band gap; Photoluminescence

1. Introduction

Undoped and doped semiconductor nanocrystals have been studied extensively during the past few decades. ZnS is an important semiconductor compound of the II–VI group with novel physical properties and wide band-gap energy has attracted great attention in the last few decades. ZnS is a direct-transition semiconductor with the widest energy band gap among the groups II–VI compound semiconductor materials and it is an important material with an extensive range of applications such as optical coating, electro-optic modulator, photoconductors, optical sensors, phosphors, and other light emitting materials [1]. ZnS has been used widely as an important phosphor for photoluminescence (PL), electroluminescence (EL) and cathodoluminescence (CL) devices due to its better chemical stability then other chalcogenides. Luminescent properties of ZnS can be controlled using various dopants such as Ni^{2+}, Fe^{2+}, Mn^{2+}, Ag^{2+} and Cu^{2+}. They not only give luminescence in various regions but also improve the properties of ZnS.

A large variety of methods are employed for synthesizing during last few decades such as chemical method [2,3], mechano-chemical method [4,5], hydrothermal process [6], sol–gel method [7], electro-spinning technique [8], ultrasonic radiation method [9], colloidal chemical treatment method [10], reverse micelle method [11] and solvothermal method [12].

This paper reports the PL emission properties of the undoped and Ba doped ZnS samples at room temperature without any capping agent. The luminescence quantum efficiency is important for the potential use of semiconductor nanomaterials in light emitting devices. The size of the prepared ZnS and ZnS:Ba samples is in the 9–10 nm range as has been confirmed from X-ray diffraction (XRD) peak broadening. The optical absorption properties show a blue shift of the absorption edge due to the quantum confinement effect. The value of optical band gap has been found to be in range 4.10–4.63 eV. PL emission band from undoped ZnS nanoparticles shows multiple peaks in blue region. Peaks are found at 426, 444 and 485 nm. Ba^{2+} doped ZnS nanoparticles shows PL emission at 426, 448, 463 and 486 nm in visible region when excited with 310 nm UV light.

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0272-8842/$36.00
http://dx.doi.org/10.1016/j.ceramint.2012.03.063

2. Experimental

All the chemicals used are of AR grade (Merck), without further purification. We prepare 10 ml each of zinc nitrate and sodium sulfide in distilled water. Zinc nitrate solution is first stirred using a magnetic stirrer up to 30 min, and then the solution of sodium sulfide is mixed with above solution drop wise and stirred up to 1 h. The precipitate is separated by centrifugation (Remi, PR 24) for 4 min at 5000 rpm and is washed with methanol several times to remove all sodium particles. The precipitate is then heat treated at 200 °C for 2 h for further measurements. ZnS with 2% Ba doped was prepared at room temperature by mixing calculated amounts of zinc nitrate solution, barium nitrate in distilled water stirred using a magnetic stirrer up to 30 min and followed by the drop wise addition of 10 ml solution of sodium sulfide. The mixture was vigorously stirred using a magnetic stirrer up to 1 h. The precipitate was separated from the reaction mixture by centrifugation for 4 min at 5000 rpm and was washed with methanol several times to remove all sodium particles. The wet precipitate was then heat treated at 200 °C for 2 h for further measurements.

2.1. Characterization techniques

The size of the samples is determined by Bruker AXS D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm). XRD data are collected over the range 20–80° at room temperature. The crystallite size is calculated using the Scherrer formula. The morphology of the nanoparticles is determined using field emission scanning electron microscopy (FEI-QUANTA200F). Energy-dispersive analysis of X-rays (EDAX) coupled with FESEM was used for the semi-quantitative investigation of the microstructure of the samples. Absorption spectra of the samples dispersed in methanol are studied with the help of UV–Vis–NIR (Varian, Carry 5000) Spectrophotometer. The PL spectrum of the ZnS has been measured at room temperature using F-2500 FL Spectrophotometer.

3. Results and discussion

3.1. X-ray diffraction studies

XRD studies are an efficient tool for analyzing the structural properties of the samples. The size of all the samples are determined by Bruker AXS D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm) operating at 40 kV and 30 mA. The XRD patterns of undoped and Ba doped ZnS samples are shown in Fig. 1.The crystallite size can be calculated with the help of Scherrer's equation

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where D is the mean grain size, λ is the X-ray wavelength (for Cu Kα radiation, λ = 0.15406 nm), θ is the diffraction angle and

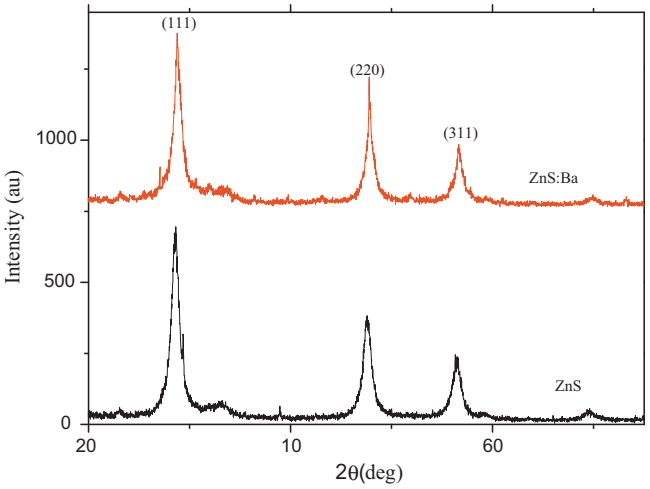

Fig. 1. X-ray diffraction (XRD) pattern of ZnS and ZnS:Ba samples.

$\beta = (\beta^2_M - \beta^2_I)^{1/2}$, β_M is the full width at half maximum (FWHM), β_I is the correction factor for instrument broadening, The crystallite size of the undoped and doped ZnS nanoparticles calculated using Eq. (1) is in range of 9–10 nm. Fig. 1 shows the three diffraction peaks at 2θ values 28.6°, 47.6°, 56.6°. The peaks are appearing due to reflection from the (1 1 1), (2 2 0) and (3 1 1) planes of the cubic phase of the ZnS. The obtained peak positions correspond to zinc blended type patterns for all the samples. The XRD pattern of the nanocrystal is well matched with the Standard cubic ZnS (JCPDS Card No. 5-566). No other phases have been observed.

3.2. FESEM analyses

Fig. 2(a) shows FESEM images of 2% Ba^{2+} doped ZnS nanoparticles and (b) shows EDAX spectrum of ZnS:Ba. The actual size of the nanoparticles cannot be determined from the FESEM images as it is limited by the resolution of the used FESEM instrument. The EDAX spectrums confirmed the composition of ZnS:Ba samples. Strong peaks of Zn and S are found in the EDAX spectrum and also detectable amounts of dopants indicate that impurity has doped into ZnS nanocrystallites.

3.3. Optical absorption and band gap

The optical absorption spectra have been observed using UV–Vis–NIR (Varian, Cary 5000) spectrophotometer and the results are shown in Fig. 3. To measure the absorption characteristics, the synthesized ZnS and ZnS:Ba nanopowders are first dispersed in methanol and then taken in a quartz cuvette. The characteristic absorption peaks due to undoped and ZnS:Ba nanoparticles appear in the wavelength range 240–340 nm. These peak positions reflect the band gap of nanoparticles and the synthesis ZnS nanoparticles have no absorption in the visible region (800–400 nm). The fundamental absorption, which corresponds to electron excitation from the valance band to conduction band, can be used to

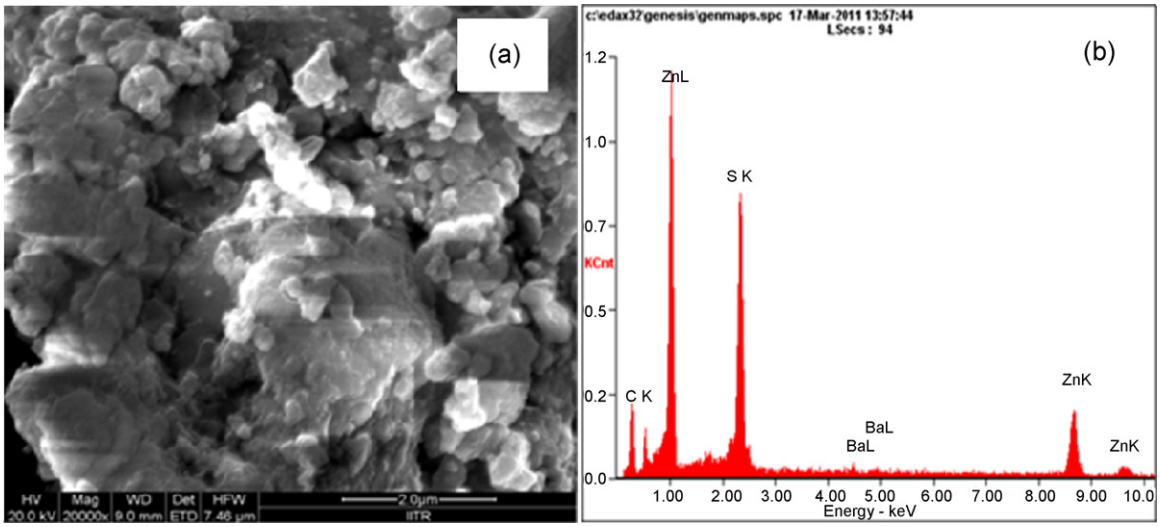

Fig. 2. (a) FESEM image of ZnS:Ba sample and (b) corresponding EDAX spectrum.

determine the value of the optical band gap of the synthesized ZnS nanoparticles.

The relation between the incident photon energy ($h\nu$) and the absorption coefficient (α) is given by the following relation:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (2)$$

where A is constant and E_g is the band gap energy of the material and the exponent n depends on the type of transition. For direct allowed transition $n = 1/2$, for indirect allowed transition $n = 2$, for direct forbidden $n = 3/2$ and for indirect forbidden $n = 3$. Direct band gap of the samples are calculated by plotting $(\alpha h\nu)^2$ verses $h\nu$ and then extrapolating the straight portion of the curve on $h\nu$ axis at $\alpha = 0$ as shown in Fig. 4. The value of optical band gaps are 4.63 eV and 4.10 eV, respectively, for undoped ZnS and 2% Ba doped ZnS. The obtained values of the band gap of ZnS and Ba doped ZnS nanoparticles are higher than that of the bulk value of ZnS (3.68 eV). This blue shift of the band gap takes place because of the quantum confinement effect.

3.4. Photoluminescence study of ZnS and ZnS:Ba nanoparticles

Photoluminescence (PL) of ZnS and ZnS:Ba samples are measured at room temperature using F-2500FL Spectrophotometer. It is observed that PL emission band from undoped ZnS nanoparticles with multiple peaks and Ba^{2+} doped ZnS sample shows emission at visible region, emission band with multiple peak maxima indicate the involvement of different luminescence centers in the radiative process. PL spectra of ZnS and Ba^{2+} doped ZnS nanoparticles are shown in Fig. 5. It is observed that PL emission band from undoped ZnS nanoparticles are broaden with multiple peaks in blue region. The luminescence quantum efficiency is important for the potential use of semiconductor nanomaterials in light emitting

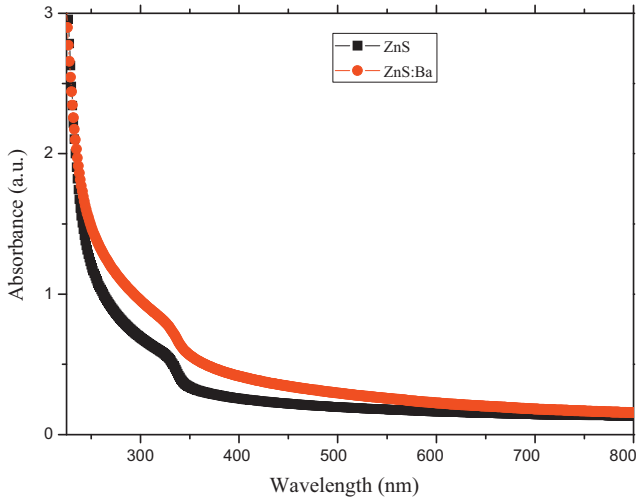

Fig. 3. UV–Vis–NIR absorption characteristics of the ZnS and ZnS:Ba nanoparticles.

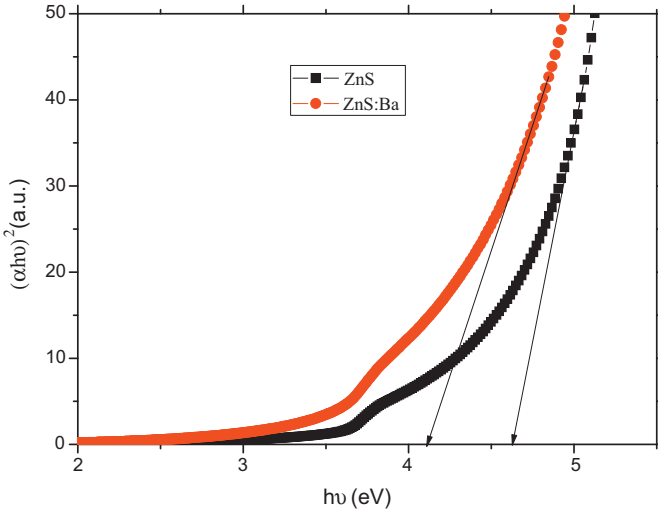

Fig. 4. Calculation of optical band gap from UV–Vis–NIR absorption spectra.

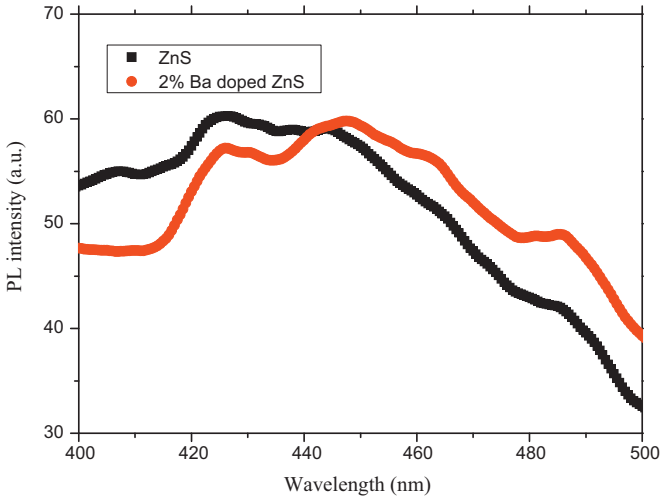

Fig. 5. PL emission from the ZnS and ZnS:Ba nanoparticles dispersed in methanol under UV light excitations.

devices. In the PL process, an electron from the ZnS valence band is excited across the band gap and photo-excited electron subsequently decays by a normal recombination process to some surface or defect states. Peaks are found at 426, 444 and 485 nm. Ba^{2+} doped ZnS nanoparticles shows PL emission at 426, 448, 463 and 486 nm in visible region with excitation wavelength of 310 nm. The UV region peak was due to the near-band-edge transition. Karar et al. [1] reported PL peak at 460 nm was attributed to native acceptor levels. Warad et al. [13] reported the emission at around 424 nm is typical luminescence of undoped ZnS resulting from the transition of electrons from shallow states near the conduction band to sulfur vacancies present near the valence band. Gosh et al. [14] reported the emission peak at 450 nm is due to the presence of sulfur vacancies in the lattice. Chen et al. [15] also reported a PL emission peak at 445 nm from donor–acceptor pairs in undoped ZnS sample.

4. Conclusion

Barium (Ba^{2+}) doped ZnS nanoparticles are synthesized at room temperature using the chemical precipitation method without using any capping agent. This method is simpler and with low cost chemical compounds, it is suitable for industrial large scale production. The sizes of as prepared nanoparticles are found to be in 9–10 nm range. The band gap energy of the samples is found in the range 4.10–4.63 eV. It is found that the undoped sample exhibits PL emission in the blue region with multiple peaks under UV excitation whereas Ba^{2+} doped ZnS sample exhibits PL emission in visible region.

Acknowledgments

One of the authors (CSP) acknowledges to MHRD, Govt. of India for the partial financial support and Indian Institute of Technology, Roorkee for providing FESEM facility.

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