



Enhanced luminescence of triethanolamine capped calcium sulfide nanoparticles synthesized using wet chemical method



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ABSTRACT

Semiconductor nanophosphors have smart technological applications in optoelectronic devices and in nanomedicine. Here we report the synthesis of Calcium sulfide nanophosphors by wet chemical method using Triethanolamine (TEOA) as capping agent. The structural characterization of the prepared nanoparticles was done using X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM). The XRD pattern confirmed the cubic CaS phase with an average grain size of 21 nm of the formed samples. From TEM images, the TEOA capped nanoparticles were found to have a spherical morphology with diameter in the range 5–15 nm. The optical studies of the capped nanoparticles were carried out using Photoluminescence spectroscopy and UV–vis absorption spectroscopy. We obtained a highly intense blue emission on exciting the TEOA capped nanoparticles at 318 nm which was found to be greater than the luminescence intensity of uncapped CaS nanoparticles. The optical band gap of the capped nanoparticles was estimated from the Diffuse Reflectance Spectra and an increase in bandgap was observed which can be explained on the basis of quantum size effect. Thermogravimetric analysis and Fourier Transform Infrared Spectra analysis confirmed the presence of capping agent in the synthesized CaS nanoparticles.

1. Introduction

Luminescence in phosphors of alkaline earth sulfide family has been a subject of great interest for researchers over the past decades. Calcium sulfide (CaS) is one of the most investigated alkaline earth sulfide and it is widely considered to be a competent and excellent phosphor host material because of its interesting properties such as long afterglow, high accumulation capability and high sensitivity to infrared radiations [1]. Also known as Lenard phosphor, CaS is a wide bandgap semiconductor (4.5 eV) which can accommodate a large variety of dopants such as rare earth ions and transition metal ions making it the most versatile material for various applications like cathode ray tubes, TV screens, fluorescent lamps and thermoluminescent dosimeters [2–9].

Nanocrystalline forms of phosphors are presently of great interest since their properties are entirely different from their bulk counterparts on account of quantum confinement effect. A bulk semiconductor becomes an insulator when the characteristic dimension is sufficiently small. There are two reasons for the change in electronic states in nanosized particles - one reason is the quantum size effect and the other reason is the much larger surface to volume ratio [10].

CaS nanophosphors without dopants have been less investigated. Wang et al. [11] prepared undoped CaS and SrS nanophosphors using solvothermal process. CaS nanoparticles without dopants were synthesized using wet chemical co-precipitation method by Wu et al. [12]. Luminescence of CaS nanocrystallites co-activated sol-gel derived silica xerogel prepared by sol-gel processing has been studied by Yang et al. [13].

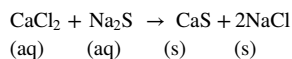
In the present study, we report the synthesis of Triethanolamine (TEOA) capped undoped CaS nanoparticles using wet chemical co-precipitation method. TEOA which is a water soluble aminoalcohol have been used as capping agent for the synthesis of CdS and CdSe nanoparticles by several investigators [14,15]. Depending on the synthesis conditions each particle on nucleation grow in all directions and the use of capping agent will restrict the growth of particle thereby reducing the particle size. The prepared samples were characterized using X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), room temperature Photoluminescence (PL), UV–Vis Spectroscopy, Thermo-gravimetric analysis (TGA) and Fourier Transform Infrared (FTIR) spectroscopy.

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2. Experimental

CaS nanoposphors were prepared by wet chemical co-precipitation method [8,10,12]. The chemicals used were calcium chloride [CaCl₂·2H₂O, 97% Merck] and sodium sulfide [Na₂S·xH₂O, 55% Nice chemicals]. 2-propanol was used as the solvent instead of water and TEOA was used as the capping agent. A 0.5 M CaCl₂ solution was prepared by dissolving suitable amount of CaCl₂·2H₂O in 50 mL of 2-propanol. A 50-mL solution of 0.25 M Na₂S was prepared in 2-propanol and to this solution 1 mL of TEOA was added. The sodium sulfide solution was then added drop wise to CaCl₂ solution for sudden nucleation and the solution mixture was vigorously stirred for 2 h for particle growth. The chemical reaction involved is as follows:



After 2 h the solution was evaporated till the volume of the initial solution reduced to approximately 40 mL. Tetrahydrofuran was added drop wise till the solution became turbid. The remaining solution was then stirred and filtered to collect the nanoparticles formed. It was then washed with water to remove the NaCl formed during the reaction process. The nanoparticles formed were further washed with 2-propanol 2–3 times, dried at 70 °C for 6–8 h and made into a fine powder using an agate mortar and pestle. Uncapped CaS nanoparticles were also prepared using the same method without adding TEOA.

The XRD measurements were performed using a Bruker AXS D8 Advance X-ray diffractometer by using Cu-K α lines ($\lambda = 1.5406 \text{ \AA}$). The morphology was studied using a Jeol/Jem 2100 model Transmission Electron Microscope and the chemical composition analysis was done using a JEOL Model JSM-6390LV Scanning Electron Microscope equipped with an Electron Dispersive X-ray (EDX) spectrometer. The PL emission and excitation spectra of the samples were analyzed with spectrofluorometer (Fluoromax4C, Horiba instruments). The Diffuse Reflectance Spectrum (DRS) was recorded using a UV–vis–NIR spectrophotometer (Varian, Cary5000). The TGA was carried out using a Perkin Elmer, STA 6000 instrument under 100 mL/min nitrogen flow with a heating rate of 10 °C/min. The FTIR spectrum of the prepared nanoparticles were recorded using Thermo Nicolet, Avatar 370, FTIR spectrometer.

3. Results and discussion

Fig. 1 shows the XRD pattern of capped and uncapped CaS nanoparticles which shows major reflections from (200), (220), (222), (400) and (420) planes as per JCPDS data file No: 77-2011. The average size of the nanoparticles was estimated from the line broadening of the XRD peaks using Debye–Scherrer's equation [16],

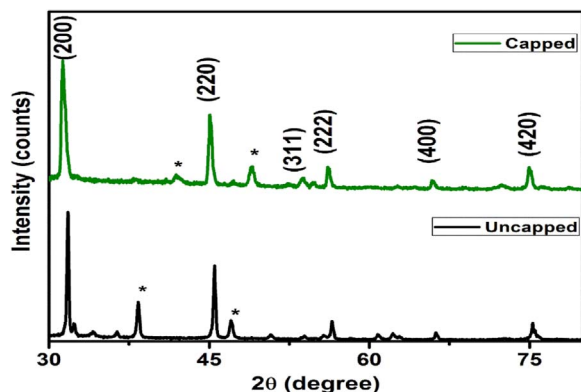


Fig. 1. XRD pattern of TEOA capped and uncapped CaS nanoparticles (*corresponds to small amount of CaO phase present in the sample).

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

where D is the average diameter of the nanoparticles, λ is the wavelength of the Cu-K α (1.5405 Å) radiation, β (in radian) is the full width at half maximum (FWHM) and θ is the Bragg angle. The average particle size of TEOA capped CaS nanoparticles was found to be 21 nm whereas for uncapped CaS nanoparticles the average particle size was found to be 34 nm. Capping agents increases stability of nanoparticles and decreases their agglomeration. Here, amino group of triethanolamine prevents agglomeration of CaS nanoparticles by interacting with Ca atom thereby reducing the particle size. The starred peaks in the XRD pattern of uncapped and capped samples are due to the presence of minute amount of CaO present in the samples (as per JCPDS File No: 28-0775). Additional impurity peaks are observed in the diffraction pattern of uncapped CaS nanoparticles due to calcium hydroxide phase (JCPDS File no:44-1481). Capping reduced the impurity phases in the sample as observed in the XRD spectrum.

The structure of CaS was found to be cubic and the lattice parameter was calculated using the equation,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2)$$

where d_{hkl} is the interplanar distance, a is the lattice parameter and h, k, l represents the Miller indices. The value of lattice parameter for TEOA capped CaS nanoparticles was found to be $a = 5.677 \text{ \AA}$ which is slightly less than the literature value 5.686 \AA (JCPDS File No:77-2011).

The diffraction line broadening caused by the strain and small grain size were analyzed using Williamson-Hall (WH) method. The W-H plot for capped CaS nanoparticles is shown in Fig. 2. The lattice strain and crystallite size were calculated using the formula,

$$\beta \cos \theta = \frac{0.9\lambda}{D} + 2\xi \sin \theta \quad (3)$$

where ξ represents the lattice strain, β (in radian) is the full width at half maximum (FWHM), θ is the Bragg angle and D is the diameter of the nanoparticles [17,18]. The slope of the curve represents the average internal strain and the grain size is obtained from the intercept value. The average grain size of the capped CaS nanoparticles is found to be 20 nm which is close to the value obtained from XRD studies (21 nm). The average internal strain of the particles is obtained as -0.305 . Negative slope of W-H plot indicates compressive strain experienced by particles during formation and this is confirmed by the reduced lattice parameter of the nanoparticles formed.

The EDS spectrum of capped CaS nanoparticles is depicted in Fig. 3 which confirms the presence of major elements calcium and sulfur. Trace impurities of sodium and chlorine is also present which is due to the occurrence of NaCl even after washing. Minute amounts of oxygen and carbon are also present in the EDS spectrum. Carbon tape used as

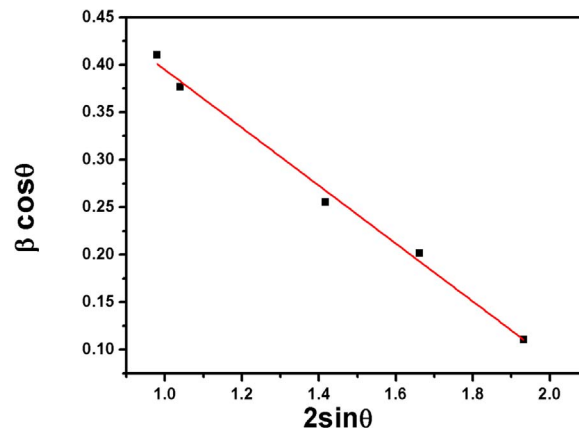


Fig. 2. W-H plot of TEOA capped CaS nanoparticles.

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