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Synthesis and characterization of bismuth doped calcium sulfide nanocrystallites

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Abstract

Nanosized bismuth doped calcium sulfide (CaS:Bi) particles have been synthesized by a wet chemical co-precipitation method. The average size of the nanoparticles was found to be about 30 nm. The particles were characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), UV–vis spectroscopy and fluorescence spectroscopy. The effect of particle size on the photoluminescence (PL) of CaS:Bi has been studied. The optimum dopant concentration was found to be 0.025 mol% of bismuth for maximum PL emission intensity. A comparative study between bulk CaS:Bi prepared by a reduction method and nanosized CaS:Bi made by the wet co-precipitation method has been carried out. Increase in band gap with decrease in particle size has been explained on the basis of the quantum size effect. The PL intensity of the nanoparticles was found to increase to almost twice that of the bulk particles. The effect of different dopant concentrations on emission intensity has also been studied.

1. Introduction

Nanoparticles and nanocrystallites are a new class of advanced materials exhibiting different properties from those of bulk materials. A CaS host material doped with rare earth ions, transition ions and even closed shell ions has attracted much attention as a good phosphor that has been studied since 1971 [1, 2], with potential use in cathode ray tubes [3], TV screens, fluorescent screens, fluorescence lamps and thermoluminescence dosimetry [4, 5]. By controlling crystalline size and/or doping with luminescent ionic centres one can tailor the optical properties of the nanocrystallites. The stability, tunability and higher efficiency of the luminescent nanocrystallites may replace all existing bulk phosphors in the future. For

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instance, it has been shown that the smaller the particle size, the higher the screen resolution and the lower the screen loading.

Materials on a micrometre scale mostly exhibit physical properties that are the same as those of bulk form; however, materials on the nanometre scale may exhibit physical properties distinctively different from those of the bulk. For example, a bulk semiconductor becomes an insulator when the characteristic dimension is sufficiently small. There are two reasons for the change of electronic states in nanosized particles—one reason is the quantum size effect [6], which is a consequence of the strong reduction of allowed states in the small particles resulting in an increase in the band gap; the other reason is the much larger surface to volume ratio, which makes surface and interface effects dominant over volume effects. Therefore, from a nanophosphor we can achieve advanced optical properties as a result of quantum size and surface effects originating from enlarging the band gap and widening the surface area with respect to the volume of the bulk particles, respectively.

For the synthesis of CaS nanocrystallites containing different dopants, some methods such as solvothermal [7], sol–gel [8] and wet chemical co-precipitation [9] have been successfully used. Usually, bulk CaS:Bi phosphors are produced by a reduction method or sulfurizing a calcium salt containing a rare earth activator in a carbon atmosphere, which requires a long reaction time and consumes a lot of energy [10, 11]. In a chemical method the crystallinity and size of the particle can easily be controlled. The particle size and the fluorescence characteristics of the bulk phosphors greatly limit their application in life science, disease diagnosis and drug discovery. The ease of control of particle size and crystallinity is important, since performance of the materials depends on the properties of the nanoparticles.

As optoelectronics tend to be used towards the ultraviolet and near-infrared regions, one has to study the optical absorption bands in the ultraviolet and near-infrared regions. Moon-Scog *et al* [12] have studied the optical properties of undoped and doped CaS, CaSe and BaS. Optical absorption on the trapping states of CaS:Eu, Sm and the effect of charge defects and trapping centres on the luminescence properties in CaS:Bi^{3+} and CaS:Eu, Tm have also been studied [13, 14].

We have synthesized 1-thioglycerol capped CaS:Bi nanocrystallites by a wet chemical co-precipitation method. Ethanol was used as the solvent instead of water in order to decrease the hydrolysis of CaS and to enhance the quantum yield of nanoparticles. The absorption spectrum was studied in the range 350–190 nm. Transmission electron microscopy (TEM) and x-ray powder diffraction (XRD) were used to determine the particle size. Optical properties, fluorescence studies and concentration quenching effects were carried out.

2. Experiments

Two different methods were used for the preparation of bulk phosphors and nanophosphors. Bulk phosphors were prepared by a reduction method and a co-precipitation method was used for the preparation of nanocrystallites. To prepare bulk phosphors, calculated amount of $CaSO_4{\cdot}2H_2O$ and anhydrous Na_2SO_4 (flux) were crushed to a fine powder and a dopant (Bi^{3+}) was added in the form of $Bi(NO_3)_3$ solution. After mixing, this whole charge was fired in a muffle furnace at 900 °C for 2 h. Flux was removed by boiling it with distilled water. In order to avoid the formation of CaO, a reducing atmosphere was created by burning a suitable quantity of carbon inside the furnace [3–5]. A wet chemical co-precipitation method was used for preparation of nanocrystallite phosphors. The starting materials for the synthesis of CaS:Bi nanoparticles are $CaCl_2{\cdot}5H_2O$ (99.9%), ethanol (99.9%), $Na_2S{\cdot}9H_2O$, $Bi(NO_3)_3{\cdot}5H_2O$ (99.5%) and 1-thioglycerol (90%) acquired from CDH, New Delhi. A 0.0125 M sulfide solution was prepared by dissolving 0.030 02 g of $Na_2S{\cdot}9H_2O$ and 0.11 ml of 1-thioglycerol in 100 ml of ethanol and leaving it for 30 min. A 0.025 M $CaCl_2{\cdot}5H_2O$ solution was prepared by dissolving 0.367 g in 100 ml of ethanol. A 0.01 M Bi solution was prepared by dissolving 0.097 g $Bi(NO_3)_3{\cdot}5H_2O$ in 20 ml of ethanol. Ethanol was found to be best solvent for dissolving the original reagents $CaCl_2{\cdot}5H_2O$, $Bi(NO_3)_3{\cdot}5H_2O$ and $Na_2S{\cdot}9H_2O$. It has already been reported that 1-thioglycerol is absorbed on the surface of cadmium sulfide host particles, which stabilize nanometre-sized cadmium sulfide in dimethylformamide [15]. This has prompted us to use 1-thioglycerol as a capping agent in CaS:Bi. For the synthesis of CaS:Bi nanoparticles 100 ml of $CaCl_2$ solution and different amount of bismuth solution were placed in a three-necked round-bottomed flask fitted with valves and a stopper. Nitrogen was used to protect the reaction mixture from forming calcium carbonate. The solution was deoxygenated with nitrogen for 15 min, followed by swift injection of 100 ml of sulfide solution under vigorous stirring. The mixture was left undisturbed for 3 h at room temperature. Particle growth occurred at this stage via *Ostwald ripening*. Then the mixture was concentrated down to approximately 50 ml in volume by heating and tetrahydrofuran (THF) was added dropwise until turbidity occurred. The solution was stirred for 2 h. The solid portion was collected by centrifugation and washed with 0.01 M K_2CO_3 (99%) ethanol solution three times and once with ethanol. The mixture was kept for some time at 70 °C under a nitrogen atmosphere to remove residual ethanol. Finally, it was annealed at 700 °C for 4 h in a silica crucible to get the optimal fluorescence. The crucible was then taken out of the furnace and allowed to cool to room temperature. The final product gave the CaS:Bi nanoparticles.

The morphology and sizes of the product were determined by TEM carried out on a H-7500 (Hitachi Ltd Tokyo Japan) operated at 120 kV. Diluted nanoparticles suspended in absolute ethanol were introduced on a carbon coated copper grid, and were allowed to dry in air. The structural characterization of the samples was carried out by XRD using a Bruker Advance D8 x-ray diffractometer using Cu Kα radiation. Photoluminescence (PL) measurements were recorded on a FluoroMax-3 (Jobin-Yvon, Edison, NJ, USA) equipped with photomultiplier tube and a xenon lamp. The optical absorption spectra were recorded on an UV–vis 2500PC spectrophotometer (Shimadzu Corp., Japan).

3. Results and discussion

Figure 1 shows the XRD pattern for CaS:Bi nanocrystallites. The average size of the nanoparticles was estimated from the line broadening of the XRD peaks and Scherrer's equation [16] was used

$$d = \frac{0.89\lambda}{\beta \cos\theta_B}$$

where d is the average diameter of the nanoparticles, λ is the wavelength of Cu Kα (1.543 Å) radiation, β (in radians) is full width at half maximum (FWHM) and θ_B is the Bragg angle. The average particle size was found to be 30 nm. The pattern was compared to a diffraction pattern available in the PDF-2.01 database with PDF no. 77-2011. The structure of the host material is cubic in form (rock salt) with lattice parameter $a = 5.686$ Å. A peak in the diffraction pattern has been assigned to BiNa. The effect of a peak at 51° due to the BiNa phase was discussed by Park *et al* [17]. They assigned the 520 nm emission band to a Bi–Na pair. To see the effect of this phase the emission spectrum is taken over a large wavelength. A small peak appears at 507 nm in nanocrystallites of CaS:Bi. Due to the quantum size effect this peak may shift to a lower wavelength. Figure 2 shows the TEM image of CaS:Bi (0.025 mol%) nanoparticles. The diameters of most of the particles lay in the range 30–35 nm.

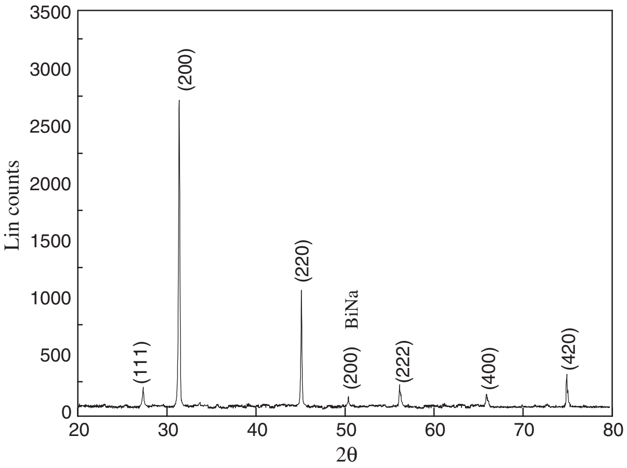

Figure 1. XRD pattern for CaS:Bi(0.025 mol%) nanocrystallites.

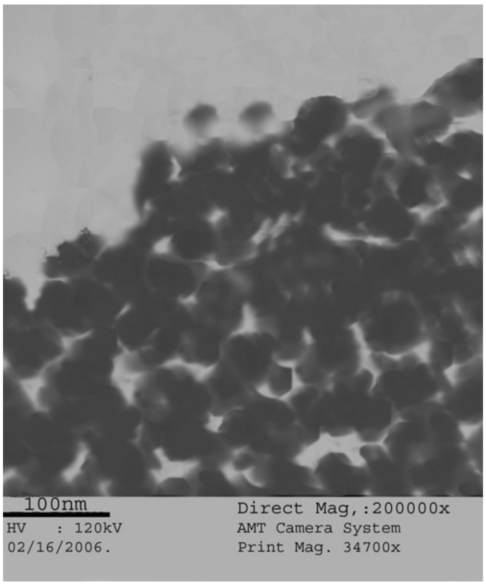

Figure 2. TEM image of CaS:Bi(0.025 mol%) nanoparticles.

Figure 3 shows the optical absorption spectra of the nanosized and bulk CaS:Bi phosphors near the fundamental absorption edge. CaS is a wide indirect energy band gap (E_g) semiconductor [12], and the optical energy gap E_g of the nanophosphors as well bulk phosphors was calculated by the following relation [18, 19]:

$$\alpha\,(h\nu) \sim \left(h\nu - E_g\right)^2$$

where $h\nu$ is the photon energy and α is the optical absorption coefficient near the fundamental absorption edge. The absorption coefficients α were calculated from these optical absorption spectra. Figure 4 shows the values of $(\alpha h\nu)^{1/2}$ for nanosized and bulk CaS:Bi crystallites plotted as a function of incident photon energy. The indirect energy band gap was obtained

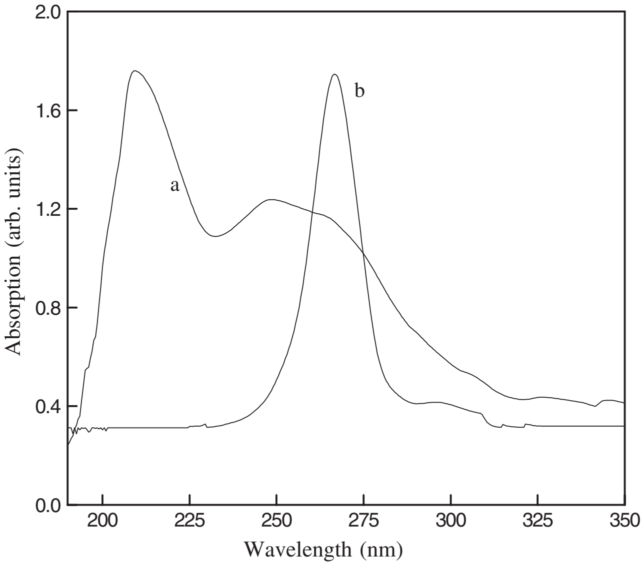

Figure 3. UV–vis absorption spectrum for the CaS:Bi(0.025 mol%) (a) nanosized and (b) bulk crystallites.

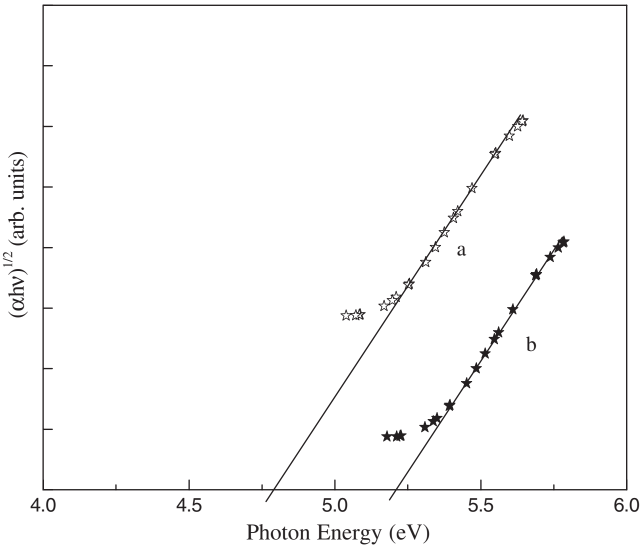

Figure 4. Plot for $(\alpha h\nu)^{1/2}$ as a function of the incident photon energy $(h\nu)$ for the CaS:Bi(0.025 mol%) (a) bulk and (b) nanosized crystallites.

by extrapolating the linear portion of the graph and making $(\alpha h\nu)^{1/2} = 0$. The optical energy band gap for the CaS single crystal [12], Bi doped bulk and nanosized CaS are given in table 1. The maximum absorption was found at 208 nm instead of 267 nm obtained in case of the bulk phosphor (CaS:Bi). This indicated that there was a blue shift in the absorption wavelength. This is also in agreement with the quantum size effect. Compared with bulk materials, more bismuth ions lie at the surface of the solid. The smaller the particle, the more ions surround

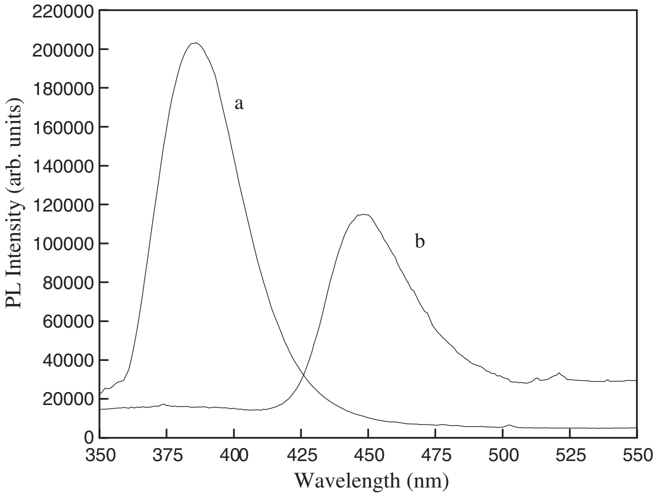

Figure 5. PL emission spectrum for (a) nanosized and (b) bulk crystallite CaS:Bi(0.025 mol%) excited with 267 nm.

Table 1. Optical energy band gap for CaS, CaS:Bi (bulk) and CaS:Bi (nano).

Material	Structure	Indirect energy gap (eV)
CaS (single crystal) [12]	Cubic	4.52
CaS:Bi (bulk)	Cubic	4.80
CaS:Bi (nano)	Cubic	5.20

the particles. The different absorption characters observed with different particle sizes can be related to the different contributions of the bismuth ions to the character of the absorption in interior and exterior ions. The same behaviour in the same material with different dopant ions has also been reported [20] in the literature.

When the samples were excited with a wavelength of 267 nm, the PL intensity peak of CaS:Bi(0.025 mol%) in the nanophosphors was found at 385 nm (figure 5) and in bulk phosphors it was at 447 nm i.e. the sample is showing a blue shift.

Luminescence spectra of bulk CaS:Bi [21, 22] show a peak at 447 nm. The excitation spectrum gives two peaks at 414 and 316 nm. The corresponding value of emission wavelength in nanosized CaS:Bi is 385 nm and excitation wavelengths are at 391 and 289 nm (figure 6). The blue emission band of CaS:Bi^{3+} at 447 nm is from the transition of $^3P_1$(6s6p) excited states to the ground state $^1S_0$($6s^2$) of the Bi^{3+} [14]. We have already reported the excitation mechanism of the Bi^{3+} luminescence centre in CaS phosphors [23]. The 414 nm band in the excitation corresponds to the transition of $^1S_0$ to $^3P_1$. The 316 nm broad band is assigned to the transition $^1S_0 \rightarrow {}^1P_1$, which might be overlapped with the transition $^1S_0 \rightarrow {}^3P_2$ [24, 25]. The transition $^1S_0 \rightarrow {}^3P_0$ of Bi^{3+} is strictly forbidden. The blue shifting of emission and excitation wavelengths is due to the quantum size effects in the nanocrystallites. Wang *et al* [7] has obtained a blue shift of 30 nm in CaS:Bi nanocrystallites. In our results, this blue shift was found to be 23 and 27 nm for respective peaks compared with the bulk crystallites of CaS:Bi.

Figure 7 shows the dependence of emission intensity of the CaS:Bi nanoparticles with different concentrations of bismuth. It was found that with increase in dopant concentration first the intensity increases and reaches its maximum and then it decreases. This is in accordance

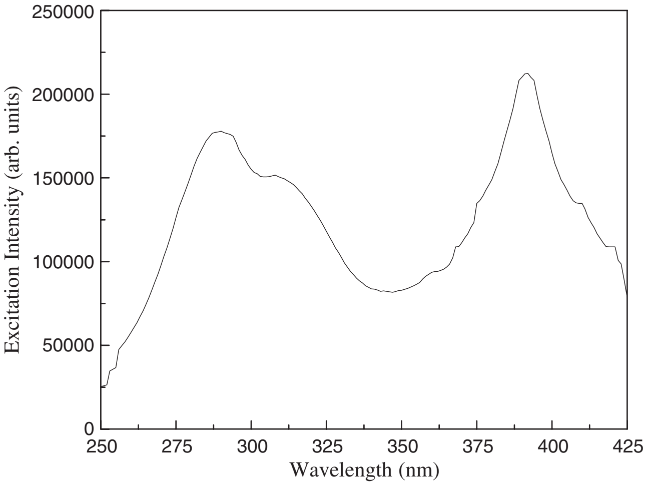

Figure 6. PL excitation spectra for the CaS:Bi(0.025 mol%) nanocrystallites with $\lambda_{em} = 385$ nm.

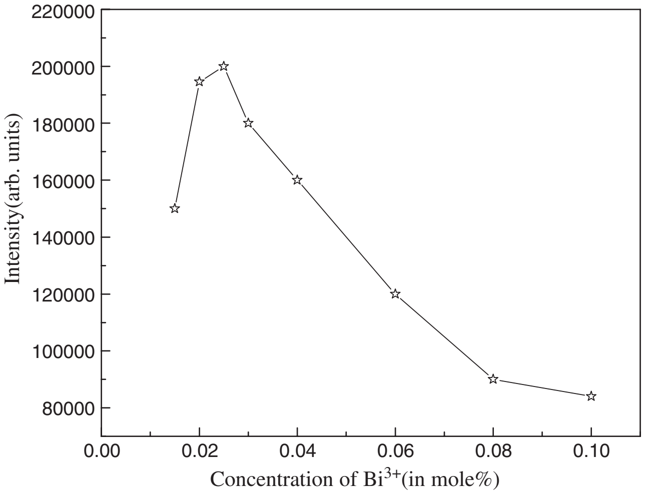

Figure 7. Dependence of PL emission intensity of the CaS:Bi nanocrystallites on the concentration of bismuth.

with the well-known quenching effect of dopant concentration. The emission intensity was found to be maximum for a bismuth concentration of 0.025 mol%.

4. Conclusion

A wet chemical co-precipitation method was used to synthesize CaS:Bi nanoparticles. Nanoparticles having an average diameter of 30–35 nm were obtained. The optical absorption indirect energy band gap was found to increase from 4.8 to 5.2 eV and the PL intensity was found to increase by almost double with the decrease in particle size. The emission intensity was maximum at a dopant concentration of 0.025 mol%. Quenching of the emission intensity with increasing dopant concentration has also been observed and is in line with the earlier reports.

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