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Greenish yellow emission from wurtzite structured ZnS:Ce nanophosphor synthesized at low temperature

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ABSTRACT

Cerium doped ZnS nanoparticles were synthesized by aqueous colloidal precipitation method at 70 °C and post sintering at 650 °C. Their structural, morphological, and photoluminescence properties were investigated. Fourier transform infrared and X-ray diffraction were used to determine chemical bonding and crystal structure of the synthesized nanoparticles. A phase transformation from cubic to wurtzite structure was observed due to sintering at 650 °C. Scanning electron microscope revealed that the sintered particles exhibit uneven blocky particles with irregular shape. The band-gap of the nanoparticles was determined from diffuse reflectance spectrum. For the sintered ZnS:Ce nanoparticles when excited at about 350 nm, in addition to host UV emission, transitions from ^2D to both $^2F_{5/2}$ and $^2F_{7/2}$ levels of Ce^{3+} in ZnS lattice were observed resulting in a broad greenish yellow emission band centered at 538 nm.

1. Introduction

Semiconductor nanoparticles have attracted widespread attention due to their unique properties and potential applications arising from quantum confinement effects. Among luminescent II–VI materials as a wide band-gap semiconductor (3.6–3.9 eV), ZnS has various applications other than biomedical labelling, such as displays, sensors and lasers [1–5]. From the fundamental point of view, a wide variety of semiconductors can be expected to generate tunable dopant emission in different spectral window once they get successfully doped with transition metals, rare earth metals, etc. It is well known that lanthanide ions (rare earth metals) are effective luminescent centres because the excitation of rare earth ions can occur by the recombination of carriers in the confined semiconductors and subsequent energy transfer to the rare earth ions. Since the rare earth ions offer the possibility of attaining blue, greenish yellow and red colours, which are necessary for full colour devices, lanthanide doped nanocrystals have drawn growing attention as phosphor materials for the use in optical display devices. Bhargava et al. has discussed the doping of RE ions in ZnS nanoparticles [6] and also reported that they can be used for producing efficient luminescent materials. Among the rare earth metal ions, Ce^{3+} is one of the most interesting dopant due to their wide application for visible light-emitting phosphors in display, high-power laser, and light-emitting diode [7–9]. The electronic structure of rare earth ions differ from the other elements because of incompletely filled 4f and 5d shells. The 4f and 5d energy levels of the Ce^{3+} ions in the host materials determine the excitation and emission properties of Ce doped phosphors. These 4f ground state and 5d excited state of free Ce^{3+} ion are separated by energy difference of around 6.2 eV. In the crystal field of host material this gap is decreased due to crystal field splitting and downward shift of the centroid of the 5d energy level [10]. The spectra related to excitation and emission will be broad for transition between $4f^{n-1}5d^1$ and $4f^n$ levels compared with the very narrow peaks from transitions between $4f^n$ levels. The key issue for good understanding of energy transfer mechanism in Ce is the crystal field splitting of Ce^{3+} ions in the crystalline lattice of ZnS. The 4f shell is located between the 5p and 5d shell so the influence of the crystal field on the 4f energy levels is weak. As a result the 4f energy levels in solids are not very different from those of free ions and further do not change much even when the host lattice is changed. By the influence of crystal field of the host, the 4f energy levels may slightly split and the transition between these energy levels leads to narrow emission peaks. The exact position of split 4f levels is dependent on the crystal field of the host lattice. Excitation of nanocrystals doped with such ions leads to the electric dipole allowed 5d → 4f optical transitions resulting in broad emission of UV, Visible and IR light. In ZnS:Ce^{3+} nanoparticles two PL emission peaks can be observed corresponding to two transition $^2D \rightarrow {}^2F_{5/2}$ and $^2D \rightarrow {}^2F_{7/2}$. But in the present work, broad PL spectrum centered at 538 nm with greenish yellow colour is observed. It is considered that the two PL bands corresponding to two transition $^2D \rightarrow {}^2F_{5/2}$ and $^2D \rightarrow {}^2F_{7/2}$

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overlap, resulting in broad emission spectrum with a single peak. Okamoto et al. observed one broad peak in ZnS:Ce^{3+} nanoparticles giving green emission [11]. In our work a phase change from cubic to hexagonal takes place for sintered sample. Stachowicz et al. discussed crystal field splitting of energy levels of rare earth ions in cubic and hexagonal GaN based on PL emission [12]. Tang et al. found that the phase transition from cubic to hexagonal phase of ZnS:Sm will boost the overall photoluminescence emission intensity only [13]. Similarly in our work same intensified host emission and dopant related emission is obtained for the sintered sample with a phase change from cubic to hexagonal phase. Larger ionic radius of Ce^{3+}(1.03 Å) than that of Zn (0.74 Å),the valence mismatch of Ce ion (trivalent) and Zn ion (divalent) and higher coordination number of rare earth ions in comparison with Zn ions, make it difficult for the substitution of Ce into a Zn site in ZnS compound [14]. Hence, only on sintering ZnS:Ce^{3+} nanoparticles synthesized at 70 °C produces greenish yellow colour spectrum corresponding to Ce $^{3+}$ ions.

Many approaches have been used for the controlled synthesis of pure ZnS and transition metal doped ZnS nanocrystals in the form of nanoparticles, nanosheets, and various hierarchical nanostructures [15–23]. At room temperature for ZnS, cubic phase is the most stable phase. From the literature survey, it is known that usually rare earth doped ZnS nanoparticles in wurtzite phase were synthesized at high temperature (above 750 °C) [11,12,24–26]. But in the present work Ce doped ZnS nanoparticles with wurtzite phase is obtained at 650 °C. A limited number of reports is available which has focused on optical properties, especially emission properties of ZnS nanoparticles doped with rare earth ions. However no reports are available which deals with the synthesis and optical characterization of hexagonal ZnS:Ce^{3+}nanocrystals from which the two characteristic emissions corresponding to two transition $^2D \rightarrow {}^2F_{5/2}$ and $^2D \rightarrow {}^2F_{72/}$are obtained. In this article, synthesis of ZnS nanocrysallites doped with cerium, changes in optical and structural properties on sintering and the origin of greenish yellow luminescence have been reported.

2. Experimental details

2.1. Materials

Analytically pure zinc acetate [$Zn(CH_3COO)_2$], sodium sulphide [Na_2S] and cerium nitrate [$Ce(NO_3)_3$] were used as received without further purification. All solutions were prepared using ultra-pure deionized water as solvent.

2.2. Synthesis

Pure ZnS nanoparticles synthesized by wet chemical method were reported by the authors previously [27]. We followed the same procedure in the synthesis of cerium doped ZnS nanoparticles. Twenty five ml each of zinc acetate Zn ($CH_3COO)_2$, $Ce(NO_3)_3$ and Na_2S solutions in water were used for the preparation of Ce^{3+} doped ZnS nanoparticles. 0.02 M solution of $Ce(NO_3)_3$ was added drop wise to 1 M zinc acetate $Zn(CH_3COO)_2$ solution to reduce agglomeration and to disperse cerium equally, later it was heated to 70 °C. One molar Na_2S solution was added drop wise with continuous stirring using magnetic stirrer. The solution was stirred for 20 min keeping temperature constant. The resulting white colloidal suspension was filtered, and the filtrate was washed with de-ionized water and dried by keeping in an oven at 70 °C for 1 day. A part of this sample was then sintered at 650 °C for six hours in furnace with the passage of hydrogen sulphide to prevent the formation of ZnO.

2.3. Instruments and measurements

X-ray diffraction (XRD) patterns of pure ZnS, as synthesized ZnS:Ce and sintered ZnS:Ce powder samples were measured by using Bruker AXS D8 Advance X-ray diffractometer with Cu Kα (λ = 1.5405 Å) as X-ray source at 40 kV and 35 mA in the scan range 200–800. Diffuse reflectance (DRS) measurements of the samples were performed using Varian Cary 5000 UV–VIS–NIR spectrophotometer with a spectral bandwidth of 2 nm for energy gap determination. Fourier transform infrared (FTIR)spectra were obtained on a FTIR (Shimadzu) spectrophotometer. Inductively coupled plasma (ICP) (ICP-1000IV, Shimadzu) analysis was conducted to determine the chemical composition of the samples. Photoluminescence (PL) spectra were recorded at room temperature using Horiba- Fluromax 4C research spectro fluorometer with a 150 W ozone free Xenon lamp as an excitation source of range 200–900 nm. The observation was done keeping the slit width at 3 nm and integration time 0.1 s. Morphological study was carried out using scanning electron microscopy (SEM) with Jeol - JSM 6390.

3. Results and discussion

3.1. Structural characterization and morphology

In order to investigate the crystalline structure and purity of nanoparticles, X-ray diffractometery was performed on the samples of ZnS and the ZnS:Ce^{3+} nanoparticles. The XRD patterns for the three samples are presented in Fig. 1A. The XRD patterns of the pure ZnS and as synthesized doped samples exhibited broad peaks typical of nanosized materials. Broadening of XRD lines is also associated with the non-uniform distribution of local strains arising from defects like dislocation, twinning etc. The crystal structure of the undoped ZnS nanoparticles correspond to the pattern of cubic zinc blend with peaks

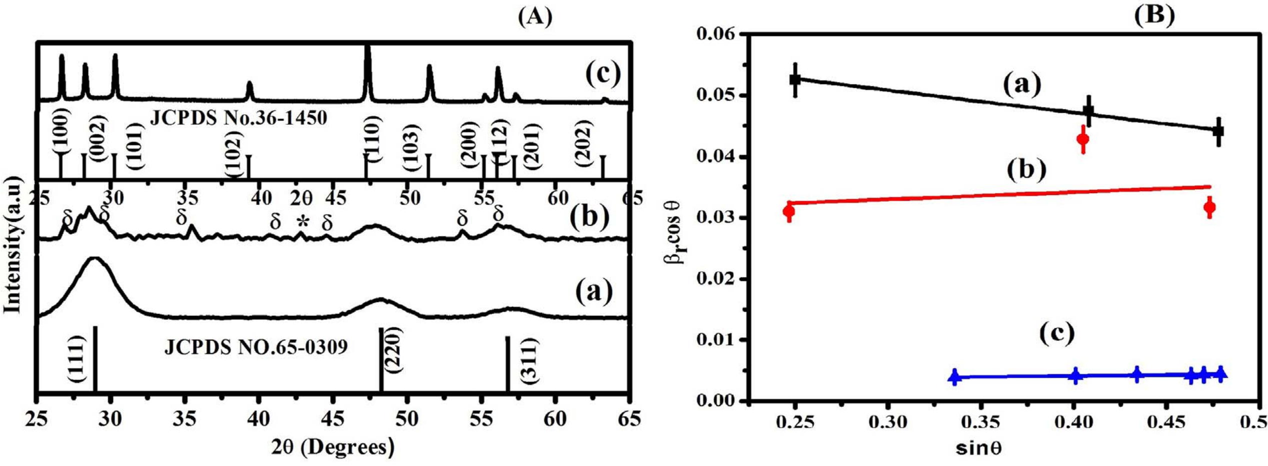

Fig. 1. XRD Pattern (A) and WH Plot (B) of a) ZnS b) As synthesized ZnS:Ce $^{3+}$ and c) sintered ZnS:Ce^{3+} nanoparticles (δ corresponds to peaks of $Zn(OH)_2$. * denotes undefined peak).