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Effect of yttrium doping on structural and optical properties of zinc sulfide nanoparticles

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ABSTRACT

Present work deals with the effect of Yttrium (Y) doping on the structural and optical properties of Zinc Sulfide (ZnS) nanoparticles synthesized by chemical co-precipitation method. The incorporation of Y in ZnS structure and the resulting elemental composition were confirmed using EDAX analysis. The SEM and HR-TEM images depicted the formation of ZnS agglomerates with narrow size distribution. Using XRD spectra it was analyzed that with increase in concentration of Y atoms, the crystallinity of ZnS lattice structure decreases, a significant deviation in the lattice structure was observed at 15 wt% Y doping. Raman analysis showed a monotonic decrease in vibration frequency of ZnS lattice with the incorporation of bulky Y ions. A decrease in the band gap from 3.97 to 3.75 eV was also observed with increase in Y doping upto 15 wt%. The photoluminescence spectra depicted that Y doping has a strong effect on the emission properties of the ZnS nanoparticles. Initially, it enhances the band edge emission by occupying the Zn vacancies in the lattice structure but at higher doping levels their tendency to move into the interstitial sites suppresses back the band edge emission. The blue emission from S vacancies is also observed to increase with Y doping.

1. Introduction

Study of nano-sized semiconductors is gaining popularity for their promising applications in optoelectronics due to their unique optical and physical properties that result from quantum size effects [1–4]. Among various II-VI compound semiconductor nanomaterials, ZnS has been widely explored for its potential device applications in solar cells, LED, anti reflection coating in IR devices, production of hydrogen, electroluminescence and other non linear optical devices [5–7]. This is attributed to its large band gap (of ~3.67 eV), high binding energy, high refractive index, good transmittance properties and non toxicity [8]. In $CuInGeSe_2$ (CIGS) solar cells ZnS has been used to replace the conventional CdS buffer layer as CdS is highly toxic [9]. It is also found to be an excellent phosphor material when doped with a variety of transition elements. On activation with Ag, ZnS shows bright blue color with maximum emission at 450 nm, where as Mn doping yields an orange color emission centered at ~590 nm, and Cu gives familiar greenish color [10–12].

Recently, rare earth ions have gained considerable attention to act as luminescent centers as their intra 4f or 4f-5d transitions produce sharp and intense lines in the optical spectrum [13–15]. Although, the direct photo excitation of these ions is inefficient, but it can be overcome by using energy transfer mechanism from a host material [16,17] and ZnS being a large bandgap material can be used for this purpose. It has been shown by Heo et. al. [18] that Yttrium (Y) doping in ZnO, another high band gap material, resulted in increased optical activity and photo catalytic efficiency. Although the literature in this direction is widely available [19–21] but studies on the effect of rare earth ions doping in ZnS are sparingly available [22–25]. In addition to the choice of material for doping the extent of doping is also a crucial parameter to attain desired optical and electrical properties from a material. For ZnO, Kumar et al. [26] have reported that phase segregation occurs at 5 wt% Y doping, but no such findings are available for Y doping in ZnS and it needs further investigations.

In the present work, we have investigated the effect of Y doping in ZnS nanoparticles. ZnS nanoparticles were synthesized by simple and inexpensive chemical co-precipitation technique. This technique is known to produce size controlled nanoparticles with less impurities and higher yield. The doping concentration of Y is varied from 0 to 15 wt% and the doped nanoparticles were characterized structurally and optically. The results indicated that high doping of Y should be avoided to prevent structural degradation of

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the nanoparticles.

2. Experimental details

To synthesize nanoparticles, zinc acetate dihydrate ($Zn(CH_3COOH)_2 \cdot 2H_2O$), sodium sulfide ($Na_2S$), and Yttrium nitrate hexahydrate ($Y(NO_3)_3 \cdot 6H_2O$) were procured commercially. Initially, two different solutions (100 ml each) of 0.5 M zinc acetate in methanol and 0.5 M sodium sulfide (Na_2S) in water, were prepared by ultrasonication. To zinc acetate solution, 25 ml of polyethylene glycol (PEG-6000) solution was added to act as surfactant. Afterwards, Na_2S solution was added to zinc acetate solution, drop by drop with continuous stirring, till the mixture turned milky white. This mixture was then vigorously stirred for 2–3 h and centrifuged at 5000 rpm for 15 min to obtain ZnS precipitate. The precipitate was then dried at 150 °C for ~2 h and was thinned using mortar and pestle to obtain ZnS nanoparticles [5]. For Y doping, measured quantities of yttrium nitrate hexahydrate was added to zinc acetate solution to obtain Y concentration of 5, 10 and 15 wt%. The structural characterization of the dried powdered sample was done using X-ray Diffraction (XRD) (Model: Bruker D8 X-ray Diffractometer) and the material composition was studied using Energy Dispersive Spectroscopy (EDS) (Model: Jeol 6610LV). The characteristics of doped ZnS nanoparticles were also studied by Raman spectroscopy using Renishaw Laser Raman Spectrophotometer (514 nm Argon ion laser). For optical characterization UV–vis spectrometer (Model: Thermo Scientific 300UV VIS) and UV–vis spectrofluorophotometer (Shimadzu RF 5301PC) were used. To study the morphology of the nanoparticles, Field Emission Scanning Electron Microscope (FESEM) (Model: Tescan Mira 3), and Transmission Electron Micrsoscopy (HRTEM) (Model: Technai G2T30) were employed.

3. Results and discussion

3.1. XRD analysis

The XRD analysis of pure and Y doped ZnS nanoparticles is shown in Fig. 1(a). The pattern exhibits three prominent peaks at 28.46°, 48.14°and 56.64°, which are identified to be originated from (111), (220), and (311) planes of cubic (zinc blend) structure of ZnS (JCPDS card No. 5-0566). The broadening of peaks indicate nanocrystalline regime of the synthesized particles. The diffraction pattern of both undoped and doped ZnS samples is observed to maintain the same phases, which indicates that the ZnS cubic structure is not tailored significantly. However, the intensity of diffraction peaks (hence crystallinity) is observed to decrease with an increase in the doping concentration. Also, the size of nanoparticles, as calculated by Scherrer's formula [5], is found to increase with Y doping (Table 1). Both these effects can be attributed to the large ionic radii of Y^{3+} (0.89 Å) ions that replace Zn^{2+} (0.74 Å) ions or add in the ZnS structure. At 15 wt% doping, two additional small peaks at 22° and 25° are observed in the XRD spectrum, which are accompanied by a dip in the average grain size. This indicates change in the crystal structure. It may be possible that incorporated Y ions being larger in size, build obstructions for the movement of grain boundaries and limit the grain growth, thereby, disrupting the crystal structure. This also indicates that additional Y doping would further rupture the cubic crystal structure leading to formation of new phases. The 15 wt% doping concentration, hence defines the upper limit for extent of Y doping in ZnS nanoparticles.

To determine the elemental composition of Y in the ZnS structure EDAX analysis was done (Fig. 1(b)). The evaluated elemental atomic composition of Y is shown in Table 1. For a typical sample of 15 wt% doped ZnS, the elemental atomic percentage of Zn, S and Y are found to be 41.74%, 46.86% and 11.4% respectively.

3.2. Raman spectra analysis

Room temperature Raman measurement was performed to further investigate crystallinity and defects in ZnS:Y nanoparticles (Fig. 2). The Raman peaks at 269 and 344 cm^{-1} are the basic signature peaks of longitudinal optical (LO) and transverse optical (TO) phonon modes in ZnS structure. The peaks are found to be broadened and blue shifted from their bulk counterparts (at 274 and 356 cm^{-1} respectively), which can be attributed to the phonon confinement effect in nano sized particles . With increase in doping content, the LO peak is observed to be shifted towards lower wave-numbers with decrease in intensity. This can be attributed to the larger size of Y ions, when heavy ions are incorporated in the lattice structure it leads to reduction in the

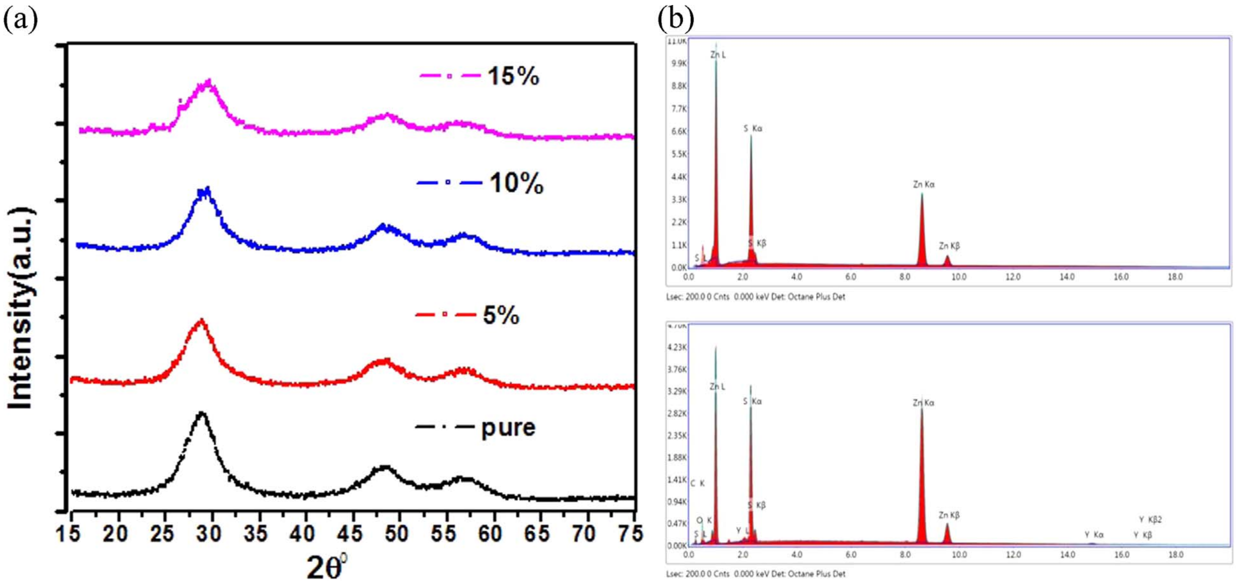

Fig. 1. (a) XRD pattern of pure and Y doped ZnS nanoparticles (b) EDAX Spectra of pure and 5 wt% Y doped ZnS nanoparticles.