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Effect of Gd doping on the structural, luminescence and magnetic properties of ZnS nanoparticles synthesized by the hydrothermal method

B. Poornaprakash [a], U. Chalapathi [a], Maddaka Reddeppa [b], Si-Hyun Park [a, *]

[a] Department of Electronic Engineering, Yeungnam University, Gyeongsan 38541, South Korea
[b] Department of Physics, Chungnam National University, 220, Gung-dong, Yuseong-Gu 30576, South Korea

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This paper reports the synthesis and characterization of ZnS:Gd nanoparticles prepared by a hydrothermal process using different doping concentrations. The chemical, structural, luminescence and magnetic properties of these nanoparticles were investigated by X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL) spectroscopy, and vibrating sample magnetometer (VSM) measurements. XRD confirmed that all the samples had a cubic structure with good crystallinity. HRTEM showed that the particles were polycrystalline with a mean size of 4–6 nm. XPS revealed the oxidation state of Gd in the ZnS lattice to be +3. The PL spectra of all the nanoparticles exhibited broad emission peaks in the visible region. All the Gd doped nanoparticles exhibited well-defined ferromagnetic behavior at room temperature. The saturation magnetization increased significantly with increasing Gd concentration, reaching a maximum for 3 at.% Gd and decreasing for the 5 at.% Gd doped ZnS nanoparticles.

1. Introduction

Among the various important categories of functional materials, dilute magnetic semiconductor nanostructures [DMSs] have attracted considerable attention in recent years [1,2]. These materials have a wide range of promising applications in spintronic as well as optoelectronic devices [3,4]. DMSs are obtained by adding a fraction of a magnetic transition metal or rare earth metal ions into the non-magnetic semiconductor host. Over the past few years, considerable efforts have been made to evolve the diluted magnetic semiconductors with transition metal doping; nevertheless, more study of rare earth ion doping is still needed. Transition metal-doped semiconductor nanoparticles exhibit the radiative recombination of excited electron-hole pairs at the doping ion sites rather than at the surfaces, which shifts the emission wavelength and increases the quantum efficiency. Hence, rare earth ion-doped semiconductor nanoparticles have many potential applications as materials in LEDs and display devices. Moreover, rare-earth metal ions possess high magnetic moments and magneto-crystalline anisotropy compared to 3*d* transition metals [5–7]. Therefore, rare earth ion (RE)-based diluted magnetic semiconductors are the most potential candidates for spintronic and optoelectronic device applications. ZnS is a typical direct wide band gap

* Corresponding author.
E-mail address: sihyun_park@ynu.ac.kr (S.-H. Park).

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II–VI semiconductor and a promising material for luminescent devices that also supports room temperature ferromagnetism (RTFM) [8–10]. Among the various rare earth metal ions, Gd^{3+} is the most well-known magnetic ion, having a high magnetic moment (7 μB) as well as good optical behavior. Recently, Gd-doped II–VI semiconductor nanostructures successfully exhibited the dopant-induced ferromagnetism above room temperature [11–13]. This encouraged the present researchers to examine Gd doping in ZnS for spintronic device applications. According to the literature, there is only one report on the optical properties [14] but there are no reports on the magnetic properties of Gd-doped ZnS in any form. In the present study, ZnS:Gd (0, 1, 3 and 5 at.%) nanoparticles were synthesized by a hydrothermal method and their chemical, structural, luminescence, magnetic properties were studied.

2. Experimental

ZnS:Gd (0, 1, 3 and 5 at.%) nanoparticles were prepared by a hydrothermal method using polyethylene glycol (PEG) as a capping agent. Zinc nitrate hexahydrate, sodium sulfide, gadolinium nitrate hexahydrate, and polyethylene glycol were purchased from Sigma Aldrich, USA and used without further purification. Initially, 0.1 M of the mixed reactants of zinc nitrate with different amounts of gadolinium nitrate were dissolved in 40 ml of ethanol. The mixture was stirred for 10 min. Subsequently, the required amount of sodium sulfide solution was added to the above mixture and stirred for another 10 min and 1 ml of PEG was added to the final mixture. The mixture was sealed in an autoclave with a 100 ml capacity and kept at 80 °C for 17 h, after which it was cooled to room temperature. A yellow colored ZnS:Gd precipitate was filtered and washed many times with deionized water. Eventually, the precipitates were dried in air at 80 °C for 17 h.

The elemental analysis of the ZnS:Gd nanoparticles was carried out using an EDAX attached to the field emission scanning electron microscope (HITACHI, S-4200). Crystal structure of the prepared nanoparticles was determined by X-ray diffractometer (XRD, PANalytical X'Pert[3] PRO, USA) equipped with Cu-Kα radiation (λ = 1.54 Å) and the system was operated at 40 KV and 30 mA. The particle size confirmation was done by high resolution transmission electron microscope (Tecnai G2 F20 S-Twin, USA). The oxidation state and composition of the elements present in the prepared nanoparticles were identified by X-ray photoelectron spectroscopy (Thermo Scientific K-Alpha) using a Al Kα X-ray source (1486.6 eV). Magnetic properties (M-H) of the ZnS:Gd nanoparticles were studied through vibrating sample magnetometer (Lakeshore 7410).

3. Results and discussion

3.1. EDAX analysis

The presence of gadolinium in the doped samples was examined by energy dispersive X-ray spectroscopy (EDAX). Fig. 1 presents the EDAX spectrum of ZnS:Gd (3 at.%) nanoparticles, showing only gadolinium, zinc and sulfur signals. The elemental composition of ZnS:Gd (3 at.%) was found to be Zn: S: Gd = 47.84: 49.35: 2.84, which is close to the targeted stoichiometry. In addition, no traces of any other elements were observed, indicating the purity of the prepared nanoparticles.

3.2. XRD analysis

Fig. 2 shows a typical X-ray diffraction (XRD) pattern of the ZnS:Gd nanoparticles prepared with different Gd concentrations. The XRD patterns of all the samples exhibited peaks due to cubic-structured ZnS (JCPDS No. 05–0566). No XRD peaks due to any other impurities were observed. The broadened XRD peaks of the prepared samples indicated the nanocrystalline nature of the samples. The spectra showed a small shift in the XRD peaks towards a lower diffraction angle with increasing Gd

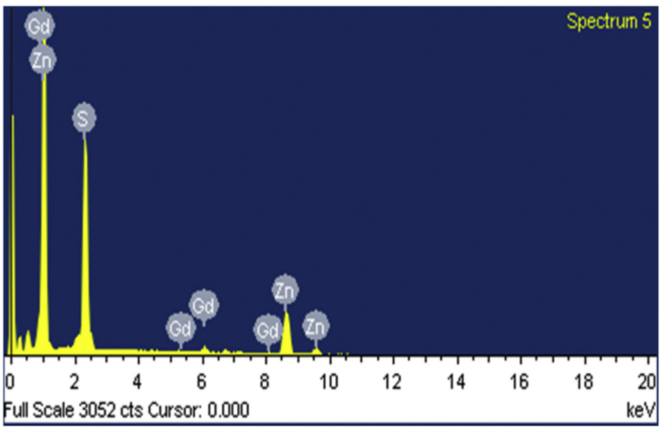

Fig. 1. EDAX spectrum of ZnS:Gd (3 at.%) nanoparticles.