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Study of optical and thermal properties in nickel doped ZnS nanoparticles using surfactants

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ABSTRACT

The presence of surfactants polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP), sodium hexameta polyphosphate (SHMP) and tri-octyl phosphine oxide (TOPO) on the surface of Ni^{2+} doped ZnS ($ZnS:Ni^{2+}$) nanoparticles resulted variation in their optical properties. The optical properties of each surfactant-capped $ZnS:Ni^{2+}$ nanoparticles were investigated using UV–visible (UV–Vis) absorption and photoluminescence (PL) techniques. The absorption spectra and fluorescent emission spectra showed a significant blue shift compared to that of the bulk zinc sulfide. The effect of the optical properties in colloidal form (wet) and dry samples were investigated. Enhanced PL emission was observed for the dry samples at 80 °C. Thermal properties of the $ZnS:Ni^{2+}$ was also studied using thermo gravimetric-differential thermal analysis (TG-DTA), Fourier transform infra-red spectrometer (FT-IR) and X-ray diffraction (XRD). The results are presented and discussed.

1. Introduction

Semiconductor materials have attracted a great deal of attention in the last few years for their unique characteristics that cannot be obtained from conventional macroscopic materials. Owing to quantum size effects and surface effects, nanoparticles can display novel optical, electronic, magnetic, chemical and structural properties that might find many important technological applications [1]. An extremely active and profilic field in nanomaterials is finding ways to control size and morphology of the nanoparticles since the properties and applications of the nanoparticles are largely dependent on their size and morphology. Such properties make semiconducting nanostructures suitable for several

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kinds of application from antireflecting coatings to bio-electronics [2,3] and light-emitting devices [4]. Among all such materials ZnS is an important material for its application as a phosphor for photoluminescence (PL), electroluminescence (EL) and cathodoluminescence (CL) devices.

Doped materials show different types of luminescent properties which are strongly depended on the type of dopant ions. The transition metallic ion doped ZnS nanomaterials form a new class of luminescent materials [5–12]. These dopant impurities play an important role in changing the electronic structure and transition probabilities of the host material. There are several reports on the photoluminescence properties of ZnS nanostructures doped by various types of impurities like Cu^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, rare earth and transition elements etc. [13–17]. However, there has not much more work on luminescence studies in ZnS:Ni^{2+} semiconductor nanoparticles at air (dry samples) and liquid medium (wet samples). The theoretical studies on the optical spectra and their pressure dependence for ZnS:Ni^{2+} crystal have been completed by Zhang et al. [18]. Yang et al. [19] observed a strong green luminescence in Ni^{2+} doped ZnS nanoparticles. Zhou et al. observed IR emission for Ni^{2+} doped gallium nanoparticles embedded in ceramics and transparent hybrid materials [20,21]. In doped ZnS nanocrystals, impurity ion occupies the Zn lattice site and behaves as a trap site for electron and holes. The electrons are excited from the ZnS valence band to conduction band by absorbing the energy equal or greater than their band gap energy. Subsequent relaxation of these photoexcited electrons to some surface states or levels is followed by radiative decay enabling the luminescence in visible region.

In this paper work, first time we have investigated the effect of PL properties in colloidal (wet) and dry ZnS:Ni^{2+} powder samples capped with surfactants.

2. Experimental

2.1. Materials

To synthesize of Ni^{2+} doped ZnS, the following materials were used. All the glasswares used in this experimental work were acid washed. The chemical reagents used were analytical reagent grade without further purification. Ultrapure water was used for all dilution and sample preparation. Zinc acetate dehydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$], nickel acetate ($Ni(CH_3COO)_2{\cdot}4H_2O$), polyethylene glycol (PEG) and polyvinyl pyrrolidone (PVP) obtained from s–d Fine Chem. Ltd., and sodium sulfide ($Na_2S{\cdot}xH_2O$), sodium hexameta polyphosphate (SHMP) and tri-octyl phosphine oxide (TOPO) obtained from Nice Chemical Company were used as precursors. All the chemicals are above 98% purity.

2.2. Synthesis of doped and undoped nanoparticles

The ZnS nanoparticles doped with Ni^{2+}(2%) was synthesized in deionized water at an air atmosphere. In a typical experiment, 5.48 g (0.5 M) of $Zn(CH_3COO)_2{\cdot}2H_2O$ in 50 ml aqueous and $Ni(CH_3COO)_2{\cdot}2H_2O$ in 25 ml aqueous with different concentrations (1–5%) were mixed drop by drop. The mixture was stirred magnetically at 80 °C until a homogeneous solution was obtained. Then, 2.75 g of 50 ml Na_2S was added drop by drop to the above mixture. After Na_2S injection, a white voluminous precipitate appeared. The obtained dispersions are transparent and are purified by dialysis against de-ionized water and ethanol several times to remove impurities. The products were dried in an hot air oven at 120 °C for 2 h. The undoped ZnS nanoparticles were also synthesized by following the same procedure without doping material.

2.3. Synthesis of surfactants capped ZnS:Ni^{2+} nanoparticles

In a typical experiment, the desired amount of zinc acetate and nickel acetate were mixed drop by drop. Then, different amount of surfactants (PEG, PVP, SHMP and TOPO) were added to the above solution. The mixture was stirred magnetically at 80 °C until a homogeneous solution was obtained. Then, Na_2S was added drop by drop to the above mixture and stirred magnetically for 1 h, a white precipitate was obtained. The precipitate was washed as discussed above and dried in an hot air oven.