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Influence of Fe doping on the structural, optical and magnetic properties of ZnS diluted magnetic semiconductor

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HIGHLIGHTS

- Microwave assisted co-precipitation method is used to synthesize the nanoparticles.
- Yellow–orange emission peak in PL spectra exhibits $^4T_2$ (4G)–$^6A_1$ transition of Fe^{3+} ion.
- Isolated Fe^{3+} are present in higher Fe doped ZnS nanoparticles.
- Antiferromagnetism is observed in higher Fe doped ZnS nanoparticles.

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ABSTRACT

Fe doped ZnS nanoparticles with different concentrations of Fe, synthesized by microwave assisted co-precipitation method have been reported. The incorporation of Fe^{2+} and Fe^{3+} ions into ZnS lattice are confirmed by X-ray diffraction (XRD) and Electron Paramagnetic resonance (EPR) study. XRD and High Resolution Transmission electron Microscope (HRTEM) results confirm the phase purity of the samples and indicate a reduction of the particle size with increase in Fe concentration. EDAX analysis confirms the presence of Zn, S and Fe in the samples. A yellow–orange emission peak is observed in Photo-luminescence (PL) spectra which exhibits the Characteristic $^4T_2$ (4G)–$^6A_1$ (6S) transition of Fe^{3+} ion. The room temperature magnetic studies as analyzed from *M–H* curves were investigated from vibrating samples magnetometer (VSM) which shows a weak ferro and superparamagnetic like behavior in 1% and 3% Fe-doped ZnS nanocrystals, whereas; at 10% Fe-doping concentrations, antiferromagnetism behavior is achieved. The ZFC-FC measurement reveals that the blocking temperature of the nanoparticle is above the room temperature.

1. Introduction

Magnetic semiconducting materials have attracted wide-ranging research attention for their potential applications in nano-spintronic devices [1,2]. To date, Semiconducting quantum dot-based magnetic semiconductor have been mostly studied due to their high physical properties, good chemical stability, interesting optical properties, low cost and therefore their molecular conjugates are becoming important in broad range of applications within physics, environmental science, chemistry, biotechnology and medicine [3,4]. Therefore, it is essential to develop diluted magnetic semiconductor material with high efficiency under room temperature. Recently the research of transition metal ions (Ni, Co, Cu, Fe, Cr etc) doped II–VI semiconductors (ZnS, ZnO, CdS, ZnSe etc.) has attracted much attention [3,5–7]. The transition metal ions are the most interesting impurities as they produce deep levels in the gap region which can influence in the optical, electrical and magnetic properties of the semiconductor. The Semiconducting materials doped with transition metal ions alter their optical, electronic and magnetic properties for various desired applications [4,8]. Numerous researchers have investigated the magnetic phase transition and their relation with PL emission spectrum by tuning doping concentration in magnetic semiconductor nanoparticles. Murali et al. [5] studied the feasibility and tailoring of the type of magnetism in CdS nanoparticles as a function of Fe doping concentration. They observed the iron-iron super exchange interaction at higher Fe concentration which causes ferromagnetic to paramagnetic transition. Devaraja et al. [9] studied the yellow–orange photoluminescence of MgO nanoparticles doped with Fe^{3+} in which they observed the enhancement of PL intensity with increasing Fe content and then

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quenching of PL intensity at higher concentration of Fe. The authors explained that when dopant concentration continues to increase, the interaction between the dopant ions increases, leads to self-quenching and hence PL intensity decreases. Kumar et al. [10] studied the room temperature ferromagnetism of Ni doped ZnS nanoparticles. They observed non-saturated hysteresis loop which is the result of reduced Ni-Ni distance and may strengthen antiferromagnetic interaction. The photoluminescence intensity is enhanced and quenched by the doping concentration of Ni ion. Poornaprakash [8] explained the defect induced ferromagnetic to paramagnetic transition of Fe doped ZnS nanoparticles.

In view of these, in this work, an attempt has been made to synthesize Fe doped ZnS nanoparticles with different Fe concentrations. In this study we will mainly focus on doping induced structural, magnetic and optical transition of magnetic semiconductor nanoparticles.

2. Experimental

Fe doped ZnS nanoparticles with varying Fe concentration are synthesized by microwave assisted co-precipitation [1] method. All the chemicals are of AR grade and are used without further purification. For the preparation of 1% Fe doped ZnS (sample a) nanoparticles, 0.2 M Zinc acetate [$Zn(CH_3COO)_3 \cdot 2H_2O$] prepared in 50 ml de-ionized water is mixed with 0.002 M Iron chloride [$FeCl_3$] prepared in 50 ml de-ionized water. The resulting solution is stirred continuously for 1 h at 70 °C using magnetic stirrer. This is followed by drop wise addition of 0.2 M Sodium sulfide [Na_2S] solution prepared in 50 ml de-ionized water. The solution is then stirred continuously for 2 h at 70 °C until the formation of precipitates. The solution is then centrifuged and washed several times with de-ionized water and finally the product is dried for 8 h at 80 °C to obtain powder sample. For the preparation of 3% (sample b) and 10% (sample c) Fe doped ZnS nanoparticles, same procedure is adopted as 1% Fe doped ZnS nanoparticles except the molar concentrations of $FeCl_3$ are taken as 0.006 M and 0.04 M for 3% and 10% Fe doped ZnS nanoparticles respectively.

XRD patterns of all the samples were taken in Seifert XRD (3003TT) operating at 40 KV and 30 mA using CuKα ($\lambda = 1.542$ Å) radiation. Photoluminescence (PL) spectra of the samples were recorded by fluorescence spectrometer (Thermospectronic AMINCO BOWMAN (Series2)). High resolution transmission electron microscope (HRTEM) (JEOL, Model: JEM 2100) was used to examine the particle size and morphology. Magnetic properties were recorded by Vibrating Sample Magnetometer (VSM) (Model: 7410 series) and the Electron Paramagnetic Resonance analysis of the samples were recorded by Electron Spin Resonance (ESR) Spectrometer (Model: JES: FA200). The elemental analyses (EDAX) were carried out using LEO 1430 VP attached with scanning electron microscope (SEM).

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the typical XRD spectra of 1% (sample a), 3% (sample b) and 10% (sample c) Fe doped ZnS nanoparticles. The diffraction peaks of all the samples are matching with JCPDS Card no. 65-0309 indicating the formation of cubic Zinc blend structure corresponding to the lattice planes (111), (220) and (311). There is no observable sign of other magnetic phase existing [11]. The zinc blende structure is not affected by the addition of iron into the ZnS lattice. Doping of Fe into ZnS crystal causes the broadening and variation in intensity of XRD patterns. It is observed from the XRD

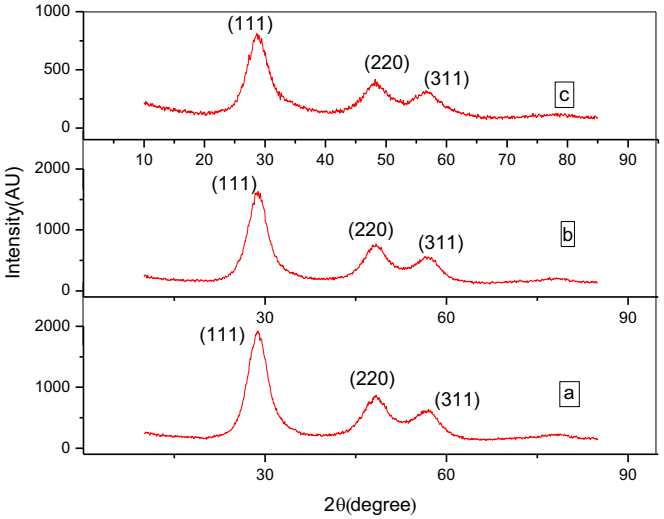

Fig. 1. XRD spectra of (a) 1% (b) 3% and (c) 10% Fe doped ZnS nanoparticles.

patterns that the width of the peaks increases with increase in iron content, it is well known that broadening of peaks is related to iron substitution in ZnS lattice that creates lattice defects which suppresses the particle growth [12]. This is mainly because of decrease in nucleation and subsequent growth rate due to increase of Fe doping percentage [13]. XRD patterns also show the decrease of peak intensity with increasing Fe concentrations, which is an indication of reduction of the crystalline quality of ZnS nanoparticles [14]. The average crystalline size of the prepared samples are calculated by Debye scherrer formula [3]

$$D = k\lambda/\beta \cos\theta \quad (1)$$

where k is constant (about 0.9), λ is the wavelength of X-ray, β is the full width of half-maxima (FWHM) of the diffraction line and θ is the Bragg's angle. To calculate the accurate values of crystalline size and micro strain of Fe doped ZnS nanoparticles, Williamson–Hall (W–H) plot is used, which is given by the equation [15]

$$\frac{\beta\cos\theta}{\lambda} = \frac{1}{\varepsilon} + \frac{\eta \sin\theta}{\lambda} \quad (2)$$

where β is the FWHM in radians, ε is the effective particle size, and η is the effective strain. Fig. 2 shows the Williamson–Hall plot of the samples a, b and c. The y-intercept and the slope of the graph give the average crystalline size and strain of the nanoparticles

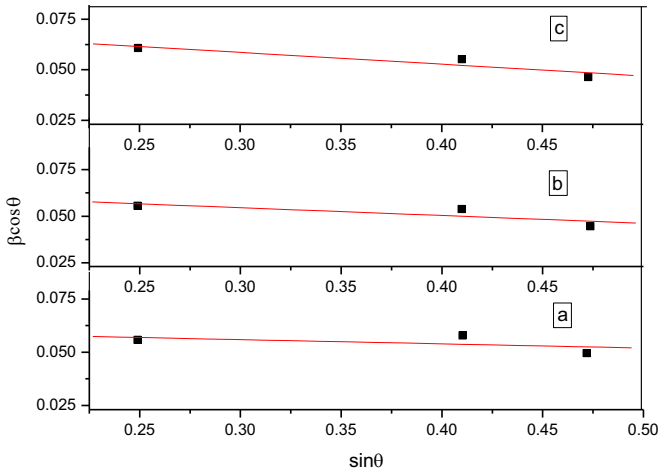

Fig. 2. Williamson–Hall plot of (a) 1% (b) 3% and (c) 10% of Fe doped ZnS nanoparticles.