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STRUCTURAL, LUMINESCENCE AND MAGNETIC PROPERTIES OF Cr^{3+} AND Gd^{3+} DOPED ZnS NANOPOWDERS

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Nanocrystalline Cr^{3+} and Gd^{3+} doped ZnS have been synthesized by a co-precipitation method. The structure of the synthesized samples is cubic as demonstrated by X-ray diffraction (XRD) studies. The typical high resolution transmission electron microscopy (HRTEM) images of the Cr and Gd doped ZnS samples, displays the well-resolved lattice fringes, indicating the high crystallinity of the samples. The photoluminescence (PL) spectra of all the samples, displays similar broad emission peak around 475 nm. Both Cr and Gd doped ZnS samples exhibited the weak ferromagnetic feature at room temperature. The electron paramagnetic resonance (EPR) studies confirmed the valence state of the Cr and Gd is +3.

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1. Introduction

Nanocrystalline dilute magnetic semiconductors have recently attracted abundant attention because of their excellent magnetic and luminescence properties [1-4]. Till date, considerable attempts have been devoted to the investigation of these materials. Among the family of II–VI semiconductor compounds, ZnS has been realized to be the potential material for extensive research, possible applications in magneto-optical devices and the potential generalization of results to other candidates because of its wide band gap (3.68 eV), large exciton binding energy (40 meV), and high index of refraction (2.27 at 1 μm). There are several studies of this material in various applications in thin-film electroluminescent and photonic devices [5, 6]. Moreover, it can be also used as DMSs when a fraction of component ions is replaced by transition metal (TM) or rare earth (RE) ion impurities. These studies reveal how the doping can tune the structural, optical and magnetic properties of the semiconductor materials. In spite of both academic and applied interests, Cr and Gd-doped ZnS DMS has been least studied compared other dopants. In addition, these dopants possesses high magnetic moment per atom. It is believed that the miscibility of the dopant and their structure, optical and magnetic properties of the doped semiconductors are strongly depends on the preparation parameters including duration process, temperature and dopant concentrations. The goal of this study is to investigate the structural, luminescence and magnetic properties of Cr^{3+} and Gd^{3+} doped ZnS nanopowders prepared via chemical co-precipitation technique.

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2. Experimental procedure

2.1. Synthesis of Cr and Gd doped ZnS nanopowders

In a typical procedure, 20 ml of zinc chloride solution (0.2 M) and 3 at.% of chromium chloride/Gadolinium acetate solution were mixed in a glass beaker and then stirred for 5 hours. Next, 20 ml of sodium sulfide solution (0.2 M) was added to the above mixture under vigorious stirring. The eventual solution was stirred for 24 hours. The obtained precipitate was repeatedly rinsed with absolute ethanol.

2.2. Characterization

Powder X-ray diffraction measurements were investigated by using a Seifert 3003 TT X-ray diffractometer. High resolution transmission electron microscopy was conducted using a Tecnai G2 F20 S-Twin, electron microscope. Photoluminescence measurements were carried out using a JOBIN YVON Fluorolog-3 spectrometer with a 450W Xenon arc lamp (excitation source). M-H studies were recorded using a Lakeshore 7410 vibrating sample magnetometer. Electron paramagnetic resonance spectra were recorded using a JEOL-FE1X EPR spectrometer.

3. Results and discussion

3.1. Structural studies

Fig.1 depicts the XRD patterns of Cr and Gd doped ZnS nanopowders and shows three diffraction peaks at (111), (220) and (311) planes corresponding to cubic zinc sulfide (JCPDS Card No. 65-9585). The diffraction peaks broadening of these samples imply that the size of the ZnS powder is very small. No extra peaks corresponding impurity phases were recognized in the doped ZnS nanopowders, indicating the dopants have been incorporated into the host matrix. Particle size can be evaluated by using Scherer's equation. The estimated average size of the NPs is of the order of 3-6 nm. The lattice constants of these samples are assessed using the formula $1/d^2 = 1/a^2 (h^2+ k^2+ l^2)$, where'd' is the interplanar separation rendered by the miller indices, viz. the h, k and l values and 'a' is the lattice constant. The evaluated lattice parameters are 5.39, 5.34 and 5.43 for undoped, Cr doped and Gd doped ZnS nanopowders.

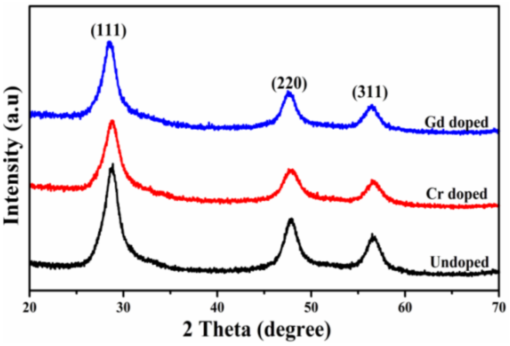
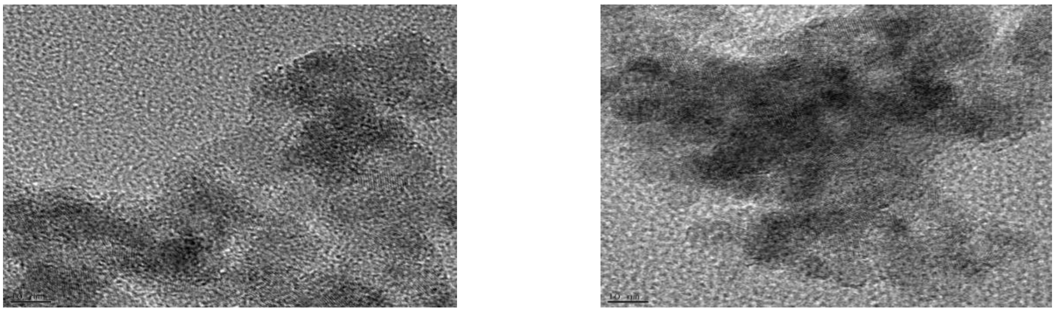


Fig. 1 XRD patterns of undoped, Cr^{3+} and Gd^{3+} doped ZnS nanopowders

3.2. Morphology studies

The representative HRTEM images of the Cr and Gd doped ZnS are shown in Fig. 2 (a) and (b). It is noticed that the well determined lattice fringes, indicating the high crystallinity of the samples. In addition, these samples are having nearly spherical shape with slight agglomeration. The agglomeration is the most normal obstacle in the nanoparticles. The average size of the Cr and Gd doped nanoparticles are approximately 4 and 6 nm.



a) *b)*

Fig. 2. HRTEM images of a) Cr^{3+} and b) Gd^{3+} doped ZnS nanopowders

3.3. Photoluminescence studies

Fig. 3 shows the PL spectra of Cr and Gd doped ZnS nanopowders recorded with an excitation wavelength of 385 nm. The emission spectra of all the samples, displays similar broad emission peak around 475 nm. Both blue shift and red shift were noticed in the Cr and Gd doped ZnS samples. In addition, a notable PL quenching is noticed in the doped samples compared to the undoped ZnS. The blue emission of these samples may be due to the surface defect states of ZnS [2, 7-9]. The shift of the doped samples is clearly confirmed the successful incorporation of the dopants into the ZnS matrix. The decreasing PL intensity of the doped samples may be attributed to the dopant ions, since, they act as quenching centers of fluorescence. More recently, Chandrasekhar et al. [10] noticed blue emission in ZnS:Cr NPs synthesized via co-precipitation. Zeng et al. [11] also observed several emission peaks in ZnS:Cr nanocrystallites. Divya et al. [12] observed the enhanced fluorescence efficiency with an increasing Gd concentration in ZnS NPs.

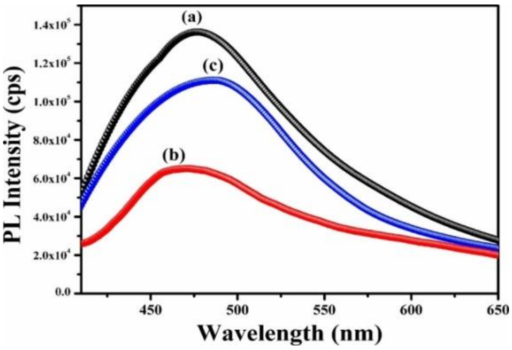


Fig. 3 PL spectra of (a) undoped, (b) Cr^{3+} doped and (c) Gd^{3+} doped ZnS nanopowders

3.4. Magnetic studies

To probe the RT magnetic behavior of the Cr and Gd doped ZnS nanopowder, M-H measurements were carried out using a vibrating sample magnetrometry. Fig. 4 shows the *M-H* curves of the Cr and Gd doped ZnS nanopowders and displayed weak ferromagnetic (FM) feature. As is well known, the RTFM in the DMS based nanostructures is a concept of debate. Several groups have asserted to observe FM feature arising only from impurity phases. However, in the present study, the observed FM in these samples may consequence of the substitution of Gd^{3+}/Cr^{3+} in place of Zn^{2+} in the host matrix without changing their internal structure. Since, we do not recognize any dopant related impurities in the XRD studies within the detection limit of the instrument. The observed magnetization values of the Cr and Gd doped ZnS is 0.004 and 0.006 emu/g. Recently, Palvinder et al. [13] observed the enhanced FM in ZnS:Cr NPs by nitrogen co-doping. Amaranatha et al. [14] reported the well-defined RTFM in EDTA capped ZnS:Cr NPs.

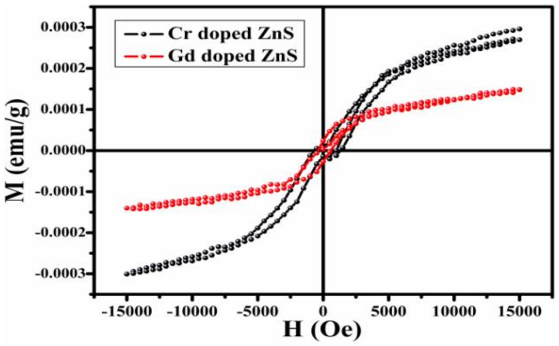


Fig. 4 M-H curves for Cr^{3+} and Gd^{3+} doped ZnS nanopowders

3.5. EPR studies

Fig. 5 illustrates the *RT* EPR spectra of Cr and Gd doped ZnS nanopowders. The Cr doped sample display a sharp single resonance peak at 3097. The assessed g value is found to be 2.159 indicating that the trivalent state of the Cr. The Gd doped sample display two resonance signals with an effective g value of $g \approx 2.02$ and 2.4, respectively, and are attributed to the trivalent Gd ions located at lattice sites with weak and intermediate crystal field [15]. Recently, Amaranatha et al. [14] reported a value of $g \approx 1.989$ for Cr in the ZnS:Cr nanoparticles.

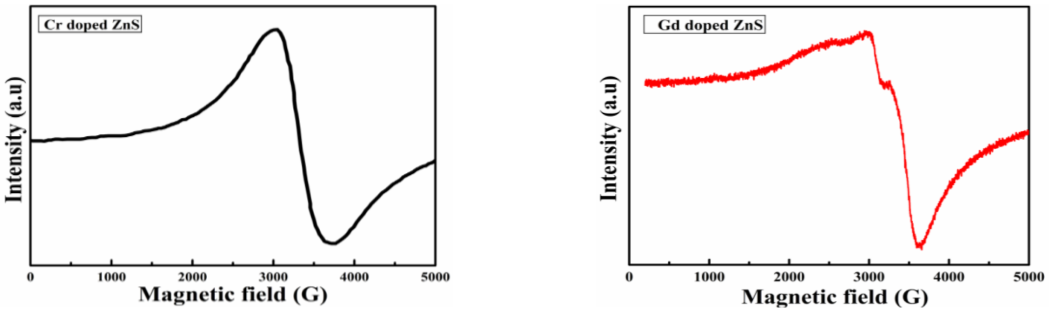


Fig. 5 EPR spectra of Cr^{3+} and Gd^{3+} doped ZnS nanopowders

4. Conclusions

In summary, Cr^{3+} and Gd^{3+} doped ZnS nanopwders were prepared via co-precipitation method without any capping agent. X-ray diffraction studies confrm the successful entry of dopants as a subsitute in the host matrix. The average size of the Cr and Gd doped nanoparticles are approximately 4 and 6 nm.

The PL spectra of all the samples displays broad emission band around 475 nm. Moreover, both blue shift and red shift were noticed in the Cr and Gd doped ZnS samples. Cr and Gd doped ZnS nanopowders displayed the weak ferromagnetic (FM) feature at 300 K. EPR studies confirmed the chemical state of the Cr and Gd is +3.

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