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Fe induced optical limiting properties of $Zn_{1-x}Fe_xS$ nanospheres

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ABSTRACT

$Zn_{1-x}Fe_xS$ (x = 0.00, 0.01, 0.03, 0.05) nanospheres were synthesized by polyethylene glycol assisted hydrothermal method. XRD studies revealed that samples of all concentrations exhibited cubic structure with crystallite grain size 7–9 nm. TEM and SEM show the formation of nanospheres by dense aggregation of smaller particles. Increasing Zn/Fe ratio tune the band gap from 3.4 to 3.2 eV and also quenches the green luminescence. FTIR spectra reveal the presence of capping agent, intensity variation and shifting of LO and TO phonon modes confirm the presence of Fe ions. Nonlinear optical properties were measured using open and closed aperture z-scan techniques, employing frequency doubled 532 nm pumping sources which indicated reverse saturable absorption (RSA) process. The nonlinear optical coefficients are obtained by two photon absorption (2PA). Composition dependent nonlinear optical coefficients "β", nonlinear refractive index, third order susceptibility and optical limiting threshold were estimated. The sample shows good nonlinear absorption and enhancement of optical limiting behavior with increasing Fe volume fraction. Contribution of RSA on optical nonlinearity of $Zn_{1-x}Fe_xS$ nanospheres are also investigated using three different input energies. $Zn_{1-x}Fe_xS$ with comparatively small limiting threshold value is a promising candidate for optical power limiting applications.

1. Introduction

ZnS is a very interesting wide band gap semiconducting material having direct band gap (3.7 eV) with large binding energy (~40 meV) and a small exciton with Bohr radius of 2.5 nm at room temperature [1–3]. When the size of ZnS nanocrystal is reduced below its Bohr excitonic radius, band structure will be modified and all the optoelectronic properties are enhanced. Nanometer scale semiconductor materials with a defined size and shape have attracted much interest due to their unique properties and potential applications in solar cells, light-emitting diodes (LEDs), photocatalysis, sensors and bio-labels and so on [4–7].

Among the variety of semiconductors, II-VI group inorganic nanocrystals such as ZnO, ZnS, ZnSe, ZnTe, CdO, CdS, CdSe and CdTe have attracted great interest of the scientific community because of their excellent electronic, magnetic and optical properties for diverse applications in optoelectronic sensors, displays, electronic devices, laser devices and nonlinear optical devices, etc. Among these semiconducting nanocrystals, ZnS is less toxic with high luminescence efficiency in the ultra violet to blue spectral range, low absorption coefficient, and excellent transparency to infrared. Hence, it is recognized as one of the most promising material for various optoelectronic device applications.

ZnS has been targeted as an efficient semiconductor host to dope different metal impurities which in turn enhances the optical, electrical and magnetic properties. The optoelectronic properties can be engineered by controlling the crystallite size and size distributions or by doping impurities into the nanocrystals. Doped semiconductor nanoparticles have been regarded as a new class of materials which have wide range of applications in sensors, displays, electronic devices, laser devices and nonlinear optical devices, etc. Effective interaction between the dopant ion and the host material determines the novel property of the developed material

To synthesize ZnS nanocrystals with different morphology, various methods have been employed, including the solvothermal and hydrothermal, the single-source molecular precursor, the chemical vapor deposition (CVD), the liquid–crystal template, and the γ-irradiation [8–14]. Among various methods, the hydrothermal method is more promising for the synthesis of crystals due to its low cost, high efficiency and the potential for large scale produc-

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tion. Recently, transition metals doped ZnS host materials have been developed by various organometallic routes with improved optoelectronic properties [15–19].

Introduction of discrete energy levels in the intrinsic quantum energy levels via impurity doping is an effective tool to tune all the optoelectronic properties of the semiconductor material. ZnS is a more desirable functional material with different morphology such as nanorods, nanobelts, nanocages nanocombs, nanorings and nanohelixces. TM-ZnS (TM = Mn, Cu, Ni, Pb, Cd) synthesized by different techniques are extensively studied. Among the different transition metals, doping of Fe^{3+} has much attention because of it reduced the toxicity of prepared samples [20,21].

Recently, high power lasers are extensively used in many scientific, military, medical and commercial applications. Lasers of high power with a low divergence angle can cause immediate damage to human tissues and other optical sensors. The search for new materials which can control the high energy laser and protect optical sensors and tissues from laser induced damage is also increased [22].

In this report, we prepared and studied the properties of zinc blende PEG-$Zn_{1-x}Fe_xS$ (x = 0.00, 0.01, 0.03, 0.05) nanospheres. The characteristic structure of the PEG network can stabilize the growth of quantum dots by capping the large surface area at the same time mediate the agglomeration of PEG capped quantum dots forming larger molecular architecture. The aggregates can be more stable and chemically passive with improved optoelectronic properties. The role of Fe on structural, optical and photoluminescence properties of PEG-$Zn_{1-x}Fe_xS$ nanospheres was investigated. The main objective of this paper is to find out the composition dependent nonlinear transmission properties and optical limiting efficiencies of $Zn_{1-x}Fe_xS$ nanospheres at different Fe-Zn ratio. The nonlinear property and limiting efficiency in transition metals (Cu, Mn, Cd, etc.) doped ZnS nanoparticles are well documented but, to the best of our knowledge, the role of Fe is not yet explored [23–26].

2. Materials and methods

Zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$], Ferric chloride [$FeCl_3$], Thiourea [$CH_4N_2S$], polyethylene glycol 400 [PEG] were used as starting materials without further processing. All the chemicals were used as received since they were of analytical regent grade with 99% purity. Double distilled water is used as the solvent for all reactions.

3. Experimental

In a typical synthesis, Aqueous solutions of zinc acetate dihydrate, Zn $(CH_3COO)_2{\cdot}2H_2O$ (0.15 M), Ferric chloride $FeCl_3$ (0.15 M), and Thiourea CH_4N_2S, (0.6 M) were first prepared. Zinc acetate dihydrate and Ferric chloride $FeCl_3$ (0.15 M) were mixed with appropriate amounts in 50 ml water and the mixture was kept stirring. After 20 min, 2 ml of polyethylene glycol 400 (PEG) was added to the solution vigorously under stirring. 25 ml of 0.6 M thiourea was added into the above solution and continue stirring for 1 h. Afterward, the solution was transferred to the 100 ml Teflon-lined stainless steel autoclave and was placed inside an electric hot air oven at 140 °C for 8 h. The autoclave was cooled down to room temperature naturally. The obtained PEG capped $Zn_{1-x}Fe_xS$ was collected by centrifugation at 10,000 rpm for 10 min and then washed with de-ionized water and ethanol to remove the last traces of adhered impurities and dried overnight at 50 °C.

3.1. Characterization

Powder X-ray diffraction (XRD) patterns of the synthesized samples were recorded using a PANalytical, X'Pert PRO with mono-chromatized CuKα radiation. Scanning was performed over the 2θ range 20−65° with a step size of 0.02° and step time of 5 s. Transmission electron microscopy (TEM) images were acquired by a HRTEM JEOL JEM 2100 with an accelerating voltage of 200 keV and scanning electron microscopy (SEM) images were obtained using a Hitachi S-4700. The reflectance spectra have been recorded using UV–visible spectrometer (ShimadzuUV2550) in the wavelength range 300–450 nm. Photoluminescence spectra of the samples were collected on a fluorescence spectrometer (FLUROMAX-4) at an excitation wavelength of 340 nm. The micro-Raman spectra were recorded on Labram HR-800 spectrometer with 340 nm excitation from an argon ion laser. An open aperture Z-scan technique was employed to measure the nonlinear optical transmission, optical power limiting of the synthesized samples and closed aperture method is used to calculate nonlinear refractive index and third order susceptibility. The samples were uniformly suspended in 2-propanol and kept in a quartz cuvette of 1 mm path length so that the transmittance with respect to the focal point was 70%. The samples were excited using Q-switched Nd:YAG laser that emits 5 ns laser pulses at a wavelength of 532 nm with 100 μJ. The sample was mounted on a programmable linear translation stage automated using a LabVIEW program. Plots of T(z) vs z gives the Z-scan curves, from which the nature of the optical nonlinearity can be determined.

4. Results and discussion

4.1. Structural characterization

To investigate the crystallite phase and size of as-prepared PEG capped $Zn_{1-x}Fe_xS$ (x = 0, 0.01, 0.03, 0.05) samples, powder X-ray diffraction technique was carried out. As shown in Fig. 1, the prepared samples show three dominant diffraction peaks located at 28.5°, 48.53° and 57.21° corresponding to the reflections from (1 1 1), (2 2 2) and (3 1 1) planes of the Zinc blende crystal structure. This matches well with standard JCPDS card No. 05-0566. No impurity related peaks are found, showing the high purity of the sample and also confirms that the crystal structure is not affected by Fe substitution. Moreover, the relatively broadened diffraction peaks indicate that the $Zn_{1-x}Fe_xS$ crystals have short range order in nano dimension. It has been observed that the diffraction peaks

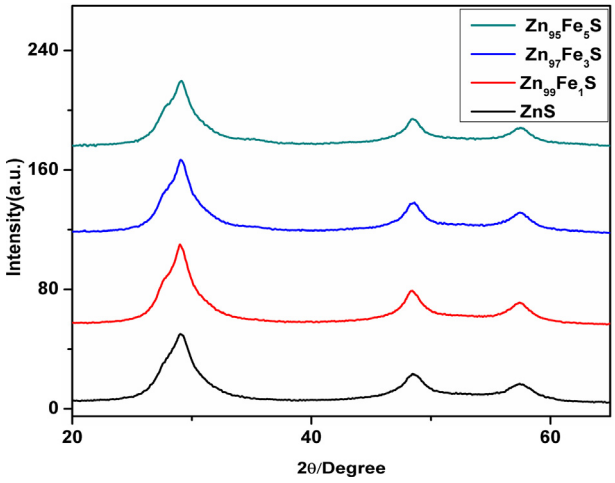

Fig. 1. XRD pattern of cubic $Zn_{1-x}Fe_xS$ (x = 0.0, 0.01, 0.03, 0.05) nanospheres.

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