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Synthesis and photoluminescent and nonlinear optical properties of manganese doped ZnS nanoparticles

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ABSTRACT

In this work we synthesized ZnS:Mn^{2+} nanoparticles by chemical method using PVP (polyvinylpyrrolidone) as a capping agent in aqueous solution. The structure and optical properties of the resultant product were characterized using UV–vis optical spectroscopy, X-ray diffraction (XRD), photoluminescence (PL) and *z*-scan techniques. UV–vis spectra for all samples showed an excitonic peak at around 292 nm, indicating that concentration of Mn^{2+} ions does not alter the band gap of nanoparticles. XRD patterns showed that the ZnS:Mn^{2+} nanoparticles have zinc blende structure with the average crystalline sizes of about 2 nm. The room temperature photoluminescence (PL) spectrum of ZnS:Mn^{2+} exhibited an orange-red emission at 594 nm due to the $^4T_1$–$^6A_1$ transition in Mn^{2+}. The PL intensity increased with increase in the Mn^{2+} ion concentration. The second-order nonlinear optical properties of nanoparticles were studied using a continuous-wave (CW) He–Ne laser by *z*-scan technique. The nonlinear refractive indices of nanoparticles were in the order of 10^{-8} cm^2/W with negative sign and the nonlinear absorption indices of these nanoparticles were obtained to be about 10^{-3} cm/W with positive sign.

1. Introduction

In recent years, semiconductor nanoparticles have attracted much attention because of their novel optical and electrical properties, which are different from those of bulk materials, arising from the quantum confinement effects [1–3]. The size dependence of the band gap is the most identified aspect of quantum confinement in semiconductors; the band gap increases as the size of the particles decreases [4]. Zinc sulfide is a II–VI compound semiconductor with direct and wide band gap of 3.68 eV. These properties have made it a good candidate for application in optical sensors and electroluminescence devices [5,6]. Zinc sulfide nanoparticles doped with manganese triggered a great interest due to the luminescence enhancement compared to the bulk material [7]. The Mn^{2+} ion, used as a dopant in many luminescent materials such as ZnS, has a d^5 configuration. The Mn^{2+} ion exhibits a broad emission peak that the emission color can vary from green to deep red, corresponding to the transition of Mn^{2+} from the excited state of $^4T_1$ to the ground state of $^6A_1$ [1,2,8]. Various methods have been developed for the synthesis of Mn^{2+}-doped ZnS nanoparticles, including precipitation, micro-emulsion, sol–gel, chemical method, chemical vapour deposition and molecular beam epitaxy and spray pyrolysis [9]. Chemical synthesis involving colloids is the most energy efficient 'bottom-up' technique for the synthesis of nanoparticles. Chemical method has several advantages like producing size-controlled, un-agglomerated nanoparticles, easy handling and large-scale-production potential.

In this work, a simple chemical method has been reported for the synthesis and characterization of ZnS:Mn^{2+} nanoparticles, polyvinylpyrrolidone (PVP) was used as the capping agent and concentration of Mn^{2+} ions was 1%, 5% and 10%. XRD analysis indicated that all samples are in zinc blende structure. The band gap of all samples was obtained to be about 4.25 eV from absorption spectra. Synthesized nanoparticles exhibited an emission peak centered at around 594 nm in the PL spectrum.

The *z*-scan technique, which is a proper method to define the sign and magnitude of nonlinear refraction and nonlinear absorption of species [10–12], has been employed to study the nonlinear responses of ZnS:Mn^{2+} nanoparticles. In this work, the nonlinear refractive indices and the nonlinear absorption coefficients of synthesized nanoparticles were in the order of 10^{-8} cm^2/W and 10^{-3} cm/W, respectively.

2. Experimental

2.1. Preparation of ZnS:Mn^{2+} nanoparticles

Synthesis of ZnS:Mn^{2+} nanoparticles was carried out in aqueous medium and at room temperature. The method is very similar to what has been described earlier [2,13,14]. At first, solutions of 1 M zinc acetate, 0.1 M manganese acetate and 0.8 M sodium sulfide

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were prepared in deionized water. Zn^{2+} and Mn^{2+} solutions were mixed (mole ratios of Mn^{2+} to Zn^{2+} were 1%, 5% and 10%) and an appropriate amount (0.025 g) of PVP as a capping agent was added into the mixture under stirring to control the growth of the nanoparticles during the reaction. In the next step, a known volume of 0.8 M Na_2S solution was added dropwise under vigorously stirring. A white precipitate was formed immediately. The precipitate was separated from the reaction mixture by centrifugation for 10 min at 4000 rpm and was washed with deionized water. This procedure was repeated two times. The wet precipitate was dried at room temperature.

2.2. Characterization

The ZnS:Mn^{2+} nanoparticles were characterized by X-ray diffraction (XRD) (Model: Philips, X′pert) with Ni-filter CuK_α radiation to determine the nanocrystalline phase and structure.

The optical absorption spectra of ZnS:Mn^{2+} nanoparticles were recorded with an UV–vis spectrophotometer (Model: T80+spectrophotometer, PG instrument Ltd) in the range of 200–500 nm. The room temperature PL spectra were measured using an Avantes spectrometer (AvaSpec-2048 TEC).

To consider the nonlinear optical properties of these samples, nanopowder of ZnS:Mn^{2+} was dispersed in water, and then the solution of sample was placed in a 1 mm quartz cell.

2.3. Z-scan theory

The experimental setup for z-scan is shown schematically in Fig. 1. A CW He–Ne laser (Melles Griot 75 mW USA) with Gaussian beam and $\lambda=632.8$ nm was used as a source light. The beam waists were measured to be about $\omega_0=25$ μm and the input power of laser, p_0, is 50 mW. In this method, the laser beam was focused using a lens (which has the focal length of 8 cm in the present case), and the sample was translated along the beam axis (z-axis) in the step of 1 mm through the focal region. The light intensities, transmitted across the samples, were measured as a function of sample position in the z-direction with respect to the focal plane either through a small aperture (closed aperture) or without an aperture (open aperture) in order to resolve the nonlinear refraction and absorption coefficients [15].

The z-scan measurement with an aperture (close aperture) was also performed for the investigation of nonlinear refraction of ZnS:Mn^{2+} nanoparticles. A typical peak–valley (valley–peak) transmittance curve is obtained when the nonlinear refractive index, n_2, of the medium is negative (positive) [16]. The phase shift $|\Delta\phi_0|$ on the optical axis can be obtained as

$$\Delta T_{pv} = f|\Delta\phi_0| \quad \text{for} \quad |\Delta\phi_0| \le \pi \tag{1}$$

In this equation ΔT_{pv} is the difference between the normalized peak transmittance and valley transmittance and $f=0.406(1-S)^{0.25}$ is an experimental constant, where S is the aperture's linear transmittance. $|\Delta\phi_0|$ relates to n_2 through the following expression:

$$\Delta\phi_0 = -(2\pi/\lambda)\Delta n L_{eff} = -(2\pi/\lambda)n_2 I_0 L_{eff} \tag{2}$$

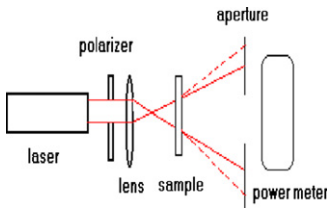

Fig. 1. Close aperture z-scan technique setup [10].

In this equation L_{eff} is the effective thickness of the sample, $I_0=2P_{in}/\pi\omega_0^2$ the incident illumination intensity at focal point and P_{in} the laser power.

From the 'open-aperture' z-scan the variation in the normalized transmission $T(z)$ of a sample as a function of its distance z from the focal plane of the laser beam was obtained. For the nonlinear absorption effect, space integration and simplification of the electric field give a numerically applicable formula for the transmittance when no aperture is used ($S=1$):

$$T_{norm}(z) = \frac{Ln(1+q_0(z,t))}{q_0(z,t)} \tag{3}$$

In this equation $q_0(z,t)=\beta I_0 L_{eff}/(1+z^2/z_0^2)$, $z_0=kw_0^2/2$ is the diffraction length of the beam and $k=2\pi/\lambda$ the wave vector [17,18].

3. Results and discussion

3.1. XRD analysis

Fig. 2 shows the XRD patterns of the prepared Mn^{2+}-doped ZnS samples. All samples show three diffraction peaks at 2θ values 28/5°, 48/4° and 56/5° corresponding to the (1 1 1), (2 2 0) and (3 1 1) planes of cubic zinc blende structure, which is well matched with the standard card (JCPDS no. 5-0566). The broadening of the XRD peaks indicates the nanocrystalline nature of the samples. In addition, no diffraction peaks from manganese impurities were detected. The nanoparticle size is estimated according to the Debey–Scherer Eq. [19]:

$$D = \frac{K\lambda}{\beta\cos\theta} \tag{4}$$

In this equation D is the mean grain size, K the constant (shape factor, about 1), λ the X-ray wavelength (1.54056 Å), β the full width at half maximum (FWHM) of diffraction peak and θ the diffraction angle. Based on the full width at half maximum of the most intense peak (1 1 1), the average crystalline sizes of ZnS:Mn^{2+} with different Mn^{2+} concentrations (1%, 5% and 10%) were estimated to be 2.35, 2.24 and 2.30 nm, respectively. Close average crystalline size indicates that the doping concentration does not affect the particle size.

3.2. UV–vis measurement

Fig. 3 shows the UV–vis absorption spectra for all samples of ZnS:Mn^{2+} nanoparticles. The samples exhibit an excitonic peak at around 292 nm, indicating that the concentration of doping ion did not have any effect in the band gap of ZnS:Mn^{2+} nanoparticles.

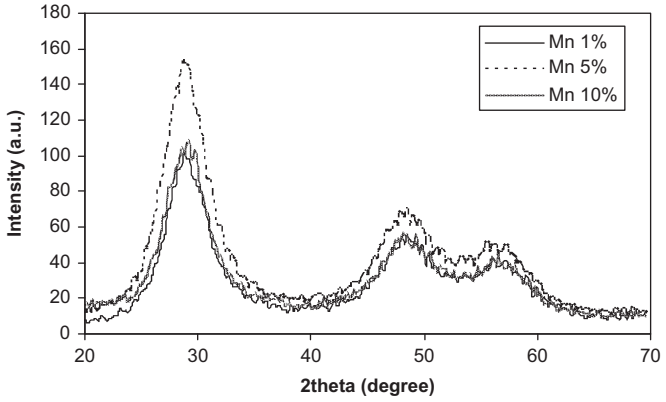

Fig. 2. X-ray diffraction patterns for the ZnS:Mn^{2+} nanoparticles with the Mn^{2+} concentration of 1%, 5% and 10%.