Enhancement of photoluminescent and magnetic properties of surface modified zinc sulphide nanoparticles by manganese doping

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Abstract: In the current paper we have reported the structural, optical and magnetic properties of manganese doped (1% to 10%) zinc sulphide nanoparticles synthesised by simple chemical co-precipitation method at room temperature. The crystal structure of the synthesised nanoparticles has been confirmed by X-ray diffraction and the average crystallite size calculated by Scherrer formula was about 3.0 nm. A slight quenching in the crystallite size with the doping was also observed. The FESEM images showed spherical shape particles with uniform size distribution. The elemental composition of pure and manganese doped zinc sulphide was confirmed by EDAX attached to FESEM. The UV-Vis spectra has an absorption edge at 321 nm with sharp fall in the absorption confirming the particles of uniform size distribution with no shift in the absorption edge with the doping. The band gap widening was observed (4.4 eV) and the particle size (3.4 nm) calculated was by effective mass approximation. The photoluminescence spectra has wide emission spectra with the peaks at 397 nm, 414 nm and 487 nm with increase in the intensity with the doping concentration giving a peak at 1% of doping and decrease in emission intensity after that. The hysteresis curve shows the ferromagnetism and the saturation magnetisation increases with the doping concentration.

1. Introduction

Semiconductors are one of the most appreciated materials in the field science and technology owing to their use in the field of electronics, chemical and biomedical. In general the traditional semiconductors have band gap less than 2 eV, which put several restriction in their applications in the field power electronics. On other hand, the wide band gap semiconductors with higher band gap allow the development of smaller, faster, reliable and efficient devices when compared to normal semiconductors [1]. Amongst all the wide band semiconductors, zinc sulphide (ZnS) is a nontoxic and chemically [2] stable group II-VI material having found applications in the field of UV-light emitting diode, solar cells, dye degradation, bioimaging and sensors [3-4]. The bulk zinc sulphite shows the zinc-blende and wurzite crystalline form with direct band gap of 3.68 eV and 3.77 eV respectively. It has been observed that the properties of zinc sulphide nanoparticles are dramatically different from its bulk counterpart due to quantum confinement effect [5]. As the size of the nanoparticles is reduced to exciton Bohr radius it exhibits the quantum confinement effect resulting in broadening of the band gap with decrease in the size of the nanoparticles.

Doping of the zinc sulphide nanoparticles with transition metals are easy and introduce deep levels of the band gap and thereby influencing the physical properties – optical, electrical and magnetic. In 1994 Bhargava et al reported the high luminescent efficiency and lifetime shortening of the manganese doped zinc sulphide nanoparticles which further encouraged the research in the field. The
doping of the group II-VI semiconductors with rare earth elements is not preferred as their chemical properties are totally different than the host metals, like cadmium and zinc. But their chemical properties are similar to transition metals such as manganese, cobalt, copper etc. and therefore can be easily doped in zinc sulphide nanoparticles.

Emission in the zinc sulphide contributed by the sulphur ion interstitial and vacancies is in the blue region (around 450 nm). Whereas, the zinc ion interstitials and vacancies give emission around 490 nm [6]. Upon doping with the manganese impurity orange (around 600 nm) luminescence has been also documented by many groups [7]. Thus, one is compelled to conclude that the overall spectra of manganese doped zinc sulphide nanoparticles have minimum three peak contributed by each element present in the composite.

The pure zinc sulphide exhibit diamagnetism at room temperature but the introduction of transition metal impurity induces superparamagnetism showing weak ferromagnetism [8]. But at nano size the surface defects resulting due to higher surface to volume ratio may show some room temperature ferromagnetism [9]. The doping induced magnetism depends on the type impurity introduced and the saturation magnetisation increases with the increase in the concentration of the impurity.

Upon doping the zinc sulphide nanoparticles having particle size in the range of 2.2-2.7 nm with manganese with the doping concentration from 1.5 to 5%, three photoluminescence peaks were observed at 445 nm, 476 nm and 520 nm in with slight red shift in all the samples. Also the intensity of orange peak increased with the increase in the manganese concentration [10]. But some reports show the drastic changes in the properties of particle size of 20 nm to 50 nm and photoluminescence showing orange peak (587 nm) along with blue peak (463 nm) with shift to 449 nm when doped with the manganese [11]. The single orange peak (602 nm) has been reported in some work with either missing blue peak or negligible intensity [12] and showing a shift in the emission peak with the surface modification [13,14]. Induction of ferromagnetism in zinc sulphide nanoparticles when doped with transition metals has been reported. The doping (1, 3 and 10%) with the zinc sulphide nanoparticles with iron in the size range of 2-5 nm have shown the weak ferromagnetism and increase in the saturation magnetisation with doping percentage. Similarly, doping with the copper (1 to 10%) has shown the origin of ferromagnetism [15].

In view of these, in the current work, a comprehensive study of manganese doped zinc sulphide nanoparticles has been carried out for the different concentration of the impurity. In the current work doping induced changes in the structural, optical and magnetic properties have been investigated.

2. Experimental

2.1 Synthesis

The manganese doped zinc sulphide nanoparticles with different manganese concentration were synthesised by facile chemical co-precipitation method. The chemicals used for synthesis were of analytical grade, locally sourced and used without further purification [16]. For the synthesis of pure zinc sulphide nanoparticles, 0.1 M of Zinc sulphate (ZnSO₄·H₂O) solution was prepared in 50 ml deionised water was mixed with 1 gm of polyvinylpyrrolidone (PVP) and stirred for proper mixing. Then 0.1 M sodium sulphide (Na₂S) solution prepared in 50 ml deionised water was added drop wise with continuous stirring. The addition of sodium sulphide results in white precipitate, the stirring at ambient condition was continued for 2 hours for the proper dispersion. The solution was collected, centrifuged, washed several times using the deionised water as the medium and the finally the centrifuged precipitate was dried overnight in a hot air oven to obtain the powder. For doping with manganese, manganese sulphate (MnSO₄) in calculated proportion was added along with the zinc sulphate in the beginning of the reaction keeping the rest of the procedure same.

2.2 Characterisation

The X-ray diffractometry (XRD) of all the samples was performed on Rikagu Ultima IV operating at 40 kV-40 mA (λ = 1.5406 Å) in the range of 20° to 80°. The scanning electron microscopy (FESEM- FEI Nova NanoSEM 450) was used to study the morphology and determine the particle size. The elemental analysis was performed by Bruker XFlash 6130 attached to FESEM. The optical absorption spectra were recorded by LABINDIA: UV-3000 in the range of 200 nm to 800 nm. The photo luminescence (PL) of the samples was recorded by spectrofluorometer, Fluoromax-4. The
magnetisation was measured by M-H hysteresis curve for the samples at room temperature using physical property measurement system (PPMS) Quantum Design (USA).

2.3 Results and discussion

The fig. 1 shows the X-ray diffractogram of pure and manganese doped zinc sulphide nanoparticles. The diffraction pattern has broadened peaks at $2\theta$ values of 28.66°, 47.98° and 56.51° corresponding to the diffraction planes (111), (220) and (311) respectively [17]. The observed data matches with the JCPDS Card No. 05-0566 confirming the formation of zinc sulphide wurtzite crystals. Other than this no other peak is observed confirming the formation of no other crystalline state upon the doping of manganese.

Figure 1. XRD of pure and manganese doped zinc sulphide nanoparticles

To calculate the diameter of the nanoparticles Scherrer formula [18] used is,

$$D = \frac{0.94\lambda}{\beta\cos\theta} \quad (1)$$

Where $D$ is the average particle size, $\lambda$ is wavelength of X-ray and value is 1.5406Å, $\beta$ is the full width at half maxima and $\theta$ is the Bragg’s angle. The particle size calculated by the above formula is in range of 2.7 nm to 2.9 nm and shows decrease in the particle size with the increase in the doping.

The other crystal parameters are calculated by the formulae,

Interplanar distance,

$$d = \frac{\lambda}{2\sin\theta} \quad (2)$$

Lattice parameter or constant,

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}} \quad (3)$$

where $h, k$ and $l$ are Miller’s indices.

Microstrain,

$$\varepsilon = \frac{\beta\cos\theta}{4} \quad (4)$$

Dislocation density,

$$\delta = \frac{1}{D^2} \quad (5)$$

Stacking fault.

$$SF = \left[ \frac{2a^2}{45(3\tan\theta)^2} \right] \beta \quad (6)$$
The values calculated by above formulae have been tabulated in Table 1. The lattice defect have decreasing values with the increase in the doping percentages, confirms the better crystallisation.

Table 1. Structural properties of the pure and doped zinc sulphide nanoparticles

| Doping (%) | 2θo (°) | FWHM (βo) | Crystallite size (D) (nm) | Dislocation density (δ) × 10^8 nm^-2 | Micro strain (ε) × 10^-2 | Interplanar distance d(111) (Å) | Lattice Constant (Å) | Stacking fault (SF) × 10^-2 |
|------------|---------|------------|--------------------------|-------------------------------------|--------------------------|-------------------------------|----------------------|--------------------------|
| 0          | 28.6587 | 2.7935     | 2.9350                   | 1.1608                              | 1.1810                   | 3.1123                        | 5.3906               | 2.4403                   |
| 1          | 28.7567 | 2.8817     | 2.8460                   | 1.2346                              | 1.2177                   | 3.1020                        | 5.3728               | 2.5129                   |
| 2          | 28.7558 | 2.8943     | 2.8430                   | 1.2372                              | 1.2230                   | 3.1020                        | 5.3728               | 2.5239                   |
| 5          | 28.7949 | 2.8153     | 2.9130                   | 1.1784                              | 1.1895                   | 3.0979                        | 5.3657               | 2.4532                   |
| 10         | 28.7448 | 3.0143     | 2.7210                   | 1.3506                              | 1.2738                   | 3.1032                        | 5.3749               | 2.6294                   |

The FESEM images of pure and manganese doped zinc sulphide nanoparticles are shown in the fig. 2. The images show highly aggregated particles due to high surface energy. The nanoparticles are spherical in nature with narrow size distribution. The crystallinity of the nanoparticles shows improvement upon doping with the manganese [19].

Figure 2. FESEM images of (i) Pure and (ii) doped (10%) zinc sulphide nanoparticles

The EDAX spectra (fig. 3) of the samples reveal the presence of all individual elements with suitable composition [20] confirming the purity and the doping of the samples.

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The fig. 4 shows the UV-Vis absorption spectra of pure and manganese doped zinc sulphide nanoparticles. The absorption edge of pure as well as doped nanoparticles is at 321 nm and there is no noticeable shift in the absorption edge upon doping or the doping concentration [21]. Tauc’s plot is employed to estimate the band gap of the synthesised nanoparticles. The widening of band gap (4.4 eV) is observed which is result of quantum confinement effect.
The particle size of synthesised nanoparticles were also calculated by effective mass approximation,

$$E(R) = E_{\text{bulk}} + \frac{\hbar^2}{8R} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1}{8R^2} \frac{\partial^2 E}{\partial R^2}$$ (7)

Where $E(R)$ and $E_{\text{bulk}}$ are the energy band gap of nanoparticles and bulk semiconductor, $m_e^*$ and $m_h^*$ are the effective mass of electron and hole respectively and the third term which is due to Coulomb’s attraction and is negligible. The particle size calculated by above formula comes out to be 3.4 nm which is in good agreement with value obtained by the XRD data.

The photoluminescence emission spectra for 265 nm excitation of pure and manganese doped zinc sulphide nanoparticles are shown in fig. 5. The photoluminescence spectra are highly asymmetric with multiple peaks at 397 nm, 414 nm and 487 nm [22]. The 414 nm peak has the maximum intensity while the 487 nm peak has the least intensity. The multiple peaks are due to involvement of different transition involving the energy levels of interstitial sulphur, zinc interstitials [23]. In the spectra the orange emission was not observed and it can be concluded the manganese impurity is just acting as the sensitising agent, improving the overall emission intensity rather than giving additional emission peak. The intensity of the luminescence reaches a peak value for 1% of the impurity and decreases thereafter confirming the quenching [24, 25].

The fig. 6 shows well defined magnetic hysteresis curve for manganese doped zinc sulphide nanoparticles at room temperature. The pure zinc sulphide nanoparticles do not show the ferromagnetism at room temperature owing to the absence of unpaired electrons in the ‘d’ orbital [26, 27] and is not shown in the figure. But the doped nanoparticles show the ferromagnetism which increases with manganese concentration. At relatively low doping concentrations the manganese atoms replace the host lattice cations and can be considered as an isolated atom, but at the higher concentrations clusters of manganese atoms are formed and the antiferromagnetic behaviour starts dominating [28]. The overall observation is that the saturation magnetisation increases with the doping concentration giving maximum at 10% of the doping.
Conclusion
The manganese doped zinc sulphide nanoparticles have been synthesised by simple one step chemical co-precipitation method. The synthesised nanoparticles have wurtzite crystal structure with average particle size of about 3 nm which was calculated by using X-Ray diffraction spectra and Tauc’s plot. Upon doping with the manganese no extra peak was observed confirming formation of no other crystalline phase. With increase in the doping concentration slight quenching in the particle size was observed. The UV-Vis spectra showed no shift in the absorption edge and band gap with the doping and its amount. Widening in the band gap (4.4 eV) due to quantum confinement effect was also observed. The photoluminescence showed peaks at 397 nm, 414 nm and 487 nm and the intensity changed considerably with doping with no additional peaks. Initially, the intensity increased and decreased thereafter with the doping giving a maximum at 1% of doping. The magnetic hysteresis curve exhibited weak ferromagnetism and the saturation magnetisation increased with the doping concentration. The present study showed that the photoluminescence and ferromagnetism may be tuned by balancing the doping concentration indicating the possible applications in photoluminescent and spintronic devices.

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