Mn-doped ZnS (Mn$_x$Zn$_{1-x}$S) nanorods were synthesized by a simple solvothermal process. Synthesized nanorods were single crystalline. Mn incorporation in the ZnS lattice induces a phase transformation from hexagonal wurtzite to cubic zincblende structure. Intense orange luminescence at $\lambda = 585$ nm was observed for the doped ZnS nanorods. Six-hyperfine splitting was observed in the EPR spectra for lower Mn concentrations and broad Lorentzian-shaped EPR spectra were obtained for higher Mn concentrations.

**Keywords** Mn-doped ZnS, nanorod, solvothermal, photoluminescence, EPR

**INTRODUCTION**

Applications, such as luminescent materials on flat panel displays, lasers etc.,[1–4] have depended to a great extent on the types of materials available for the use as the active components in these devices. One of the most studied materials for this purpose has been Mn-doped ZnS. ZnS is particularly suitable for use as host material for a large variety of dopants because of its wide band gap (3.75 eV).[5] Manganese usually occupies substitutionally the Zn lattice sites as a divalent ion and the excitation and decay of this ion produces an orange luminescence at approximately 590 nm.[6] Keeping in mind, the recent interest of one-dimensional nanostructures,[7–10] we have synthesized Mn-doped ZnS nanorods in powder form via solvothermal process. Photoluminescence and EPR properties of these Mn$_x$Zn$_{1-x}$S nanorods were also studied.

**RESULTS AND DISCUSSIONS**

Mn$_x$Zn$_{1-x}$S nanorods were prepared through the solvothermal process in the form of white powder. Crystal structure and phase of the products were studied through the XRD. Figure 1 shows the XRD spectra of the Mn$_x$Zn$_{1-x}$S nanoforms. Undoped ZnS nanorods had phase pure hexagonal wurtzite structure. Hexagonal to cubic phase transformation was observed by Mn incorporation in the ZnS nanorods. Cubic phase of the Mn$_x$Zn$_{1-x}$S nanorods were evident from the XRD spectra shown in Figure 1. At sufficiently high Mn concentration ($\sim$20% Mn) two small peaks at 34.3° and 49.2° due to (200) and (220) planes of stable $\alpha$-MnS with rocksalt structure appeared in the XRD spectra. As the ionic radius of Mn$^{2+}$ is about 10% larger than that of Zn$^{2+}$ ion, the substitution has forced a small change in the site symmetry and that might be the reason behind the phase transformation of ZnS by Mn incorporation. The growth and morphology of the crystals in solvothermal process were controlled by the solubility of the precursors in the particular solvent at the synthesis temperature. Also the growth of the crystals with some preferred structure or planes were governed by the surface energy of the planes in that particular condition and the planes with lower surface energy tends to dominate over the others, which is called “shape-selective surface absorption.”[11] So the presence of the Mn$^{2+}$ ion in the solvent might have an effect on the solubility and absorption of Zn$^{2+}$ ion in the ZnS crystals, which caused the phase transformation of the Mn$_x$Zn$_{1-x}$S nanorods. Also it was reported that wurtzite ZnS nanocrystals can be transformed to the sphalerite (cubic) phase in presence of some organic molecules.[12] So the presence of the organic Mn-salt (manganese acetate [(CH$_3$COO)$_2$Mn · 4H$_2$O]) could be another reason for the phase transformation of the Mn$_x$Zn$_{1-x}$S nanorods.

The compositional analysis of the Mn$_x$Zn$_{1-x}$S nanocrystals was performed by XRF analysis. Three representative XRF spectra of the Mn$_x$Zn$_{1-x}$S nanorods were shown in Figure 2. Elemental Zn and S were found in near stoichiometric ratio with little sulfur deficiency. On the other hand the amount of Mn detected by the XRF analysis was much less than those actually added during synthesis. As for example only 0.24, 2.49, and 5.58 atomic percent Mn was detected for 1, 6 and 20% doped ZnS nanorods.
The microstructures of the $\text{Mn}_x\text{Zn}_{1-x}\text{S}$ nanostructures were studied through TEM images. Figures 3a–d shows the TEM images of the ZnS, $\text{Mn}_{0.01}\text{Zn}_{0.99}\text{S}$, $\text{Mn}_{0.06}\text{Zn}_{0.94}\text{S}$ and $\text{Mn}_{0.2}\text{Zn}_{0.8}\text{S}$ nanorods respectively. The diameters and lengths of the undoped ZnS nanorods varied within 12–15 nm and 100–200 nm, respectively. With the incorporation of the Mn in the ZnS the width of these nanorods increased gradually and became $\sim 100$ nm for 20% Mn-doped ZnS nanorod.

The crystal structures of these $\text{Mn}_x\text{Zn}_{1-x}\text{S}$ nanorods were further studied through HRTEM and SAED patterns. Figure 4a shows the HRTEM image of a single nanorod with lattice spacing 3.13 Å corresponding to the (002) lattice plane of wurtzite ZnS and also the growth direction of the undoped ZnS nanorods. The FFT pattern (inset of Figure 4a) taken from the above image also confirms the growth direction to be (002). Figure 4b shows the HRTEM image of 20% Mn-doped ZnS nanorods, which clearly indicates the cubic ZnS structure with lattice spacing 3.12 Å corresponding to the (111) plane. This (111) plane was the growth direction of the Mn incorporated cubic ZnS nanorods, which is also confirmed from the SAED pattern shown in the inset of Figure 4b.
Room temperature photoluminescence spectra measured for the \( \text{Mn}_x\text{Zn}_{1-x}\text{S} \) nanorods with 335 nm excitation wavelengths were shown in Figure 5. Photoluminescence spectrum recorded for the undoped \( \text{ZnS} \) nanorods showed two emission peaks, one blue emission band at \( \sim 400 \text{ nm} \) and another green band \( \sim 497 \text{ nm} \). The blue emission band was associated with the recombination of free charge carriers at defect sites, possibly at surface of the nanostructures. The green band at \( \sim 497 \text{ nm} \) was most likely due to the self-activated defect centers formed by the zinc vacancy inside the lattice. A strong orange emission at 585 nm along with a weak blue emission at \( \sim 400 \text{ nm} \) was observed for all the doped \( \text{ZnS} \) nanorods.

For the lower Mn value another peak at 497 nm was observed as was observed for the undoped one. Intensity of the first peak was almost constant for all the \( \text{Mn}_x\text{Zn}_{1-x}\text{S} \) nanorods. With the incorporation of Mn, the intensity of 497 nm peak first increased and with further increase in the Mn concentration the peak gradually quenched. On the other hand the peak at 585 nm first increased with the increase of Mn concentration and became maximum for 1% Mn-doped nanorods. The intensity decreased gradually with further increase in the Mn value and almost vanishes with 20% Mn incorporation. These observations confirmed our assumption that the blue emission was due to surface defect states and remained unaffected with Mn incorporation.

The initial increase and then gradual decrease in the intensity of the 497 nm peak with Mn incorporation confirms its origin to be zinc vacancy related defect states. As ionic radius of \( \text{Mn}^{2+} \) is 10% larger than \( \text{Zn}^{2+} \) ion, the initial incorporation of minute quantity of Mn in to the \( \text{ZnS} \) lattice might have aggravated the defect sites resulting the increased intensity of the peak. But further incorporation of the \( \text{Mn}^{2+} \) ion, which had substituted the Zn vacancy sites, caused the reduction of this peak. The origin of the orange emission can be attributed to the \( ^4\text{T}_1 \rightarrow ^6\text{A}_1 \) transition of the \( \text{Mn}^{2+} \). The quenching of the orange luminescence with increasing Mn concentration might be due to the interaction of the neighbouring \( \text{Mn}^{2+} \) ions.

Embedding of Mn inside the matrix is also inferred from EPR measurements. Because the hyperfine splitting constants depend on the environment of Mn atoms, the bonding characteristics between Mn atoms and host lattice can be explained by EPR analysis. Figure 6 shows the EPR spectra of \( \text{Mn}_x\text{Zn}_{1-x}\text{S} \) nanorods with various compositions of Mn atoms. Typical six line hyperfine structure of the fine structure transition \( |1/2| \rightarrow |−1/2| \) for the \( \text{Mn}^{2+} \) ion in the \( \text{ZnS} \) lattice for lower Mn concentrations were shown in Figure 6. This hyperfine structure originates from the interactions between the \( \text{Mn}^{2+} \) electron cloud and the \( ^{55}\text{Mn} \) nucleus (100% natural abundance) of spin \( I = 5/2 \). With increasing Mn concentrations a Lorentzian curve shape starts appearing and became gradually broader due to the increased Mn-Mn interaction. For more than 3% Mn incorporation in \( \text{ZnS} \) nanorods a single Lorentzian-shaped spectrum was obtained. So these broad single line spectra could be attributed to the Mn-centers or small Mn clusters formed within the \( \text{ZnS} \) lattice due to the incorporation of excess Mn.

**EXPERIMENTAL**

For the synthesis of Mn-doped \( \text{ZnS} \) (\( \text{Mn}_x\text{Zn}_{1-x}\text{S} \)) nanorods a teflon-lined stainless steel cylindrical closed chamber with
110 ml capacity was used. All the chemicals were of analytical grade and were used without any further purification. The x value was varied within 0 to 0.2. Appropriate amount of zinc nitrate (Zn(NO3)2·6H2O), manganese acetate [(CH3COO)2·Mn·4H2O] and thiourea (NH2CSNH2) were taken in the Teflon-lined chamber, which was then filled with ethylenediamine–water mixture (in 1 : 1 volume ratio) up to 80% of its volume. Thiourea was used three times of the stoichiometric ratio. After 30 minutes of stirring, the closed chamber was placed inside a box furnace at a preset temperature 200 °C. After 12 hrs, the steel chamber was cooled down to room temperature. The resulting white precipitates were filtered off and washed several times in water and ethanol. The final products were dried in vacuum at 60 °C for 6 hrs to get white powder.

The products were analyzed using Seifert 3000P X-ray diffractometer (XRD) with Cu Kα radiation and the compositional analysis was done by X-ray fluorescence spectroscopy (JSX-3202M Element analyzer). Microstructures and crystal structure of the nanorods were obtained using transmission electron microscopic (TEM) and high-resolution TEM (HRTEM, JEOL 2010) studies. Photoluminescence (PL) measurements were carried out at room temperature using 335 nm as the excitation wavelength with a luminescence spectrometer (Perkin-Elmer, LS50B). Electron paramagnetic resonance study of the powder sample was done with Varian E-109C X-band spectrometer.

CONCLUSION

In summary, we have synthesized single crystalline Mn-doped ZnS nanorods via simple solvothermal process. Highly intense orange emission at ~585 nm was obtained from the Mn0.1Zn0.9S nanorods. Maximum intensity was obtained for 1 atomic% Mn-doped ZnS nanorods. Six hyperfine line EPR spectra was obtained for the lower Mn content ZnS nanorods, whereas a single line spectra were observed for higher Mn contents, indicating the Mn cluster formation at higher Mn concentrations.

REFERENCES