

ENHANCED PHOTOLUMINESCENCE OF ZnS NANOPARTICLES DOPED WITH TRANSITION AND RARE EARTH METALLIC IONS

D. SRIDEVI, K.V.RAJENDRAN

Department of Physics, Presidency College, Chennai-5, India

Pure and doped ZnS nanocrystalline phosphors were prepared at room temperature using a chemical synthesis method. Transmission electron microscopy observation shows that the size of the ZnS crystals is in the 2-3 nm range and SAED pattern confirms the cubic and crystalline nature of the observed samples, which are in agreement with X-Ray analysis. Interesting luminescence characteristics such as strong and stable visible-light emissions were observed from the doped ZnS nanocrystals at room temperature whereas dominant UV emissions were observed for pure ZnS. These results strongly suggest that impurities, especially transition metals and rare-earth metals-activated ZnS nanocrystals are useful in the field of optoelectronics.

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1. Introduction

The synthesis and study of nanostructured materials have become a major interdisciplinary area of research over the past 20 years. II – VI group semiconductor nanomaterials are very important in the field of optics due to their strongly size dependent optical properties[1]. Doped nanoparticles of dimensions below Bohr diameter exhibit interesting optoelectronic properties due to quantum size effect and are potential candidates for variety of applications. ZnS has been used widely as an important phosphor for photoluminescence (PL), electroluminescence (EL) and cathodoluminescence (CL) devices due to its better chemical stability compared to other chalcogenides such as ZnSe. Doping of ZnS nanoparticles by transition metal ions e.g. Mn²⁺ [2,3], Cu²⁺ [4,5] and rare earth ions e.g. Eu²⁺ [6,7] have been successfully done by techniques such as thermal evaporation, sol-gel processing, co-precipitation, microemulsions, etc. These doped ZnS semiconductor materials have a wide range of applications in electroluminescence devices, phosphors, light emitting displays, and optical sensors. Accordingly, study of luminescence properties of ZnS has received special attention. In addition to the blue luminescence of ZnS host, emission in different visible bands related to various dopants has been reported. This includes orange luminescence from ZnS:Mn nanoparticles[8], red emission from ZnS:Eu nanoparticles and green luminescence in ZnS:Cu[9]. Hence the doping ions act as recombination centers for the excited electron- hole pairs and result in strong and characteristic luminescence. However, with the decrease of particle size, extremely high surface to volume ratio causes the surface states to act as luminescent quenching centers[10]. Hence the passivation of surface is of crucial importance for the applications of this type of luminescent semiconductor nanomaterials.

In this article we report the synthesis and characterization of transition metal and rare earth metal doped ZnS nanomaterials. The unique luminescence property such as strong and enhanced visible light emission due to transition metal and rare earth ion doped ZnS nanoparticles is also discussed.

2. Experimental procedure

Doped ZnS nanoparticles were synthesized by using chemical precipitation method. Doped zinc sulfide (ZnS) nanoparticles have been obtained by precipitation from homogeneous solution of zinc, transition metals and rare-earth salt compounds, with S^{2-} as a precipitating anion formed by decomposition of thioacetamide(TAA) under acidic pH conditions. Spherical particles with narrow size distribution can be obtained by controlling the synthesis parameters[11] The precipitation of doped ZnS nanoparticles was performed starting from homogeneous solutions of zinc acetate($Zn(CH_3COO)_2 \cdot 2H_2O$), cobalt acetate, Manganese acetate, Nickel acetate and Lanthanum acetate at 0.5M and TAA at 0.5M for each precipitation reaction. The above solutions were stirred for half an hour after that the solutions were poured into autoclaves and kept at 120 °C for five hours. After getting cooled as precipitated ZnS nanoparticles were then centrifuged and washed several times with acetone to remove impurities. The cleaned powders were dried for about 10h at 80 °C until complete evaporation of solvent was achieved.

The powdered samples were characterized by a powder X-ray diffractometer XPERT PRO with CuK_{α} X ray radiation ($\lambda=0.15496nm$). The composition of elements like Zn, S, and dopants are confirmed by Energy Dispersive X-ray spectra (EDX). The surface morphology of the samples is observed by Scanning Electron Microscopy (SEM, JEOL, JSM-67001). Optical Absorption spectra of the samples are recorded with SHIMDZU UV-310PC, UV scanning spectrophotometer. The room temperature photoluminescence (PL) spectra of ZnS and doped ZnS nanoparticles are recorded with fluorescence spectrometer (FLS920) using a Xe lamp as the excitation source at excitation wavelength of 325nm.

3. Results and discussion

In the XRD pattern there were three diffraction peaks corresponds to (111), (220) and (311) planes of the cubic crystalline ZnS. Due to size effect, the XRD peaks were broadened and their widths become larger as the particles become smaller. No characteristic peaks due to impurities like Co, Mn, La and Ni were observed. The average particles size doped with different dopants, estimating from the Debye-Scherrer formula ($d=0.9\lambda / \beta\cos\theta$) are 2-3 nm. as given in table.1

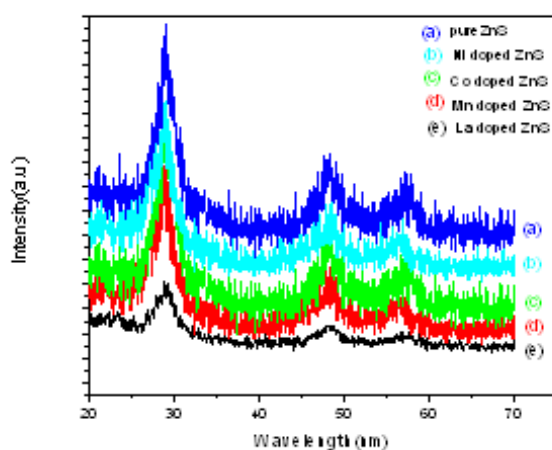


Fig. 1 XRD pattern of ZnS nanocrystallites with different dopants.

Table.1. Size of the particle determined from XRD

Nanoparticle	FWHM (deg)	Particle Size (XRD) nm
Pure ZnS	2.7	3.08
Co doped	2.8	2.97
Ni doped	3.5	2.37
Mn doped	3.38	2.45
La doped	3.6	2.14

From the FESEM images, the formation of nanoparticles with sizes much below 10nm is clearly observed. But actual size of the nanoparticles cannot be determined from the FESEM images as it is limited by the resolution of the FESEM instrument. The inset of fig.2 shows the EDAX the very strong peak of Zn and S are found in the spectrum and also detectable amounts of dopants indicate that impurity has doped into ZnS nanocrystallites.

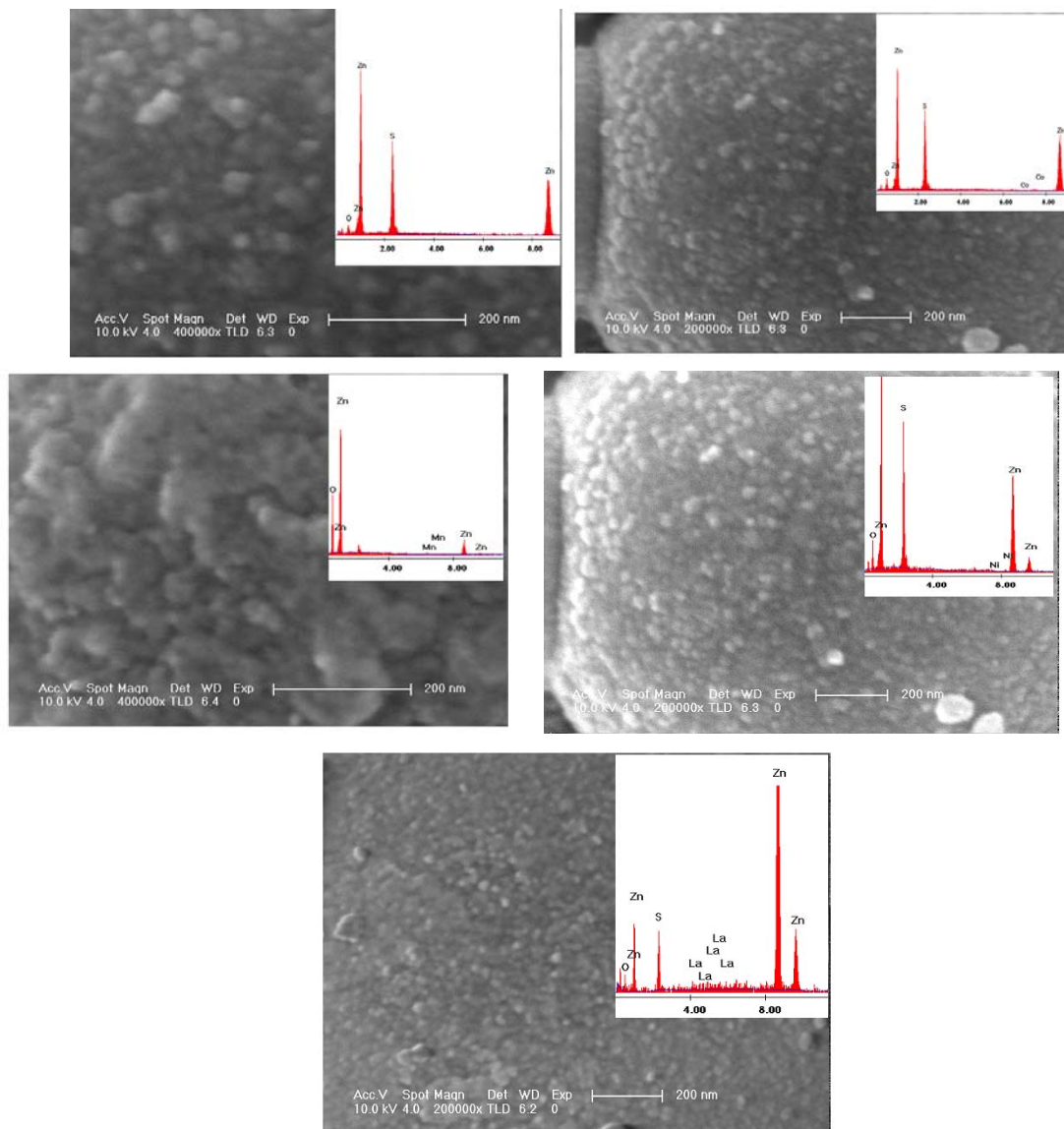


Fig.2. SEM images of pure and transition metal ion doped ZnS nanocrystals

The size and morphology of ZnS nanoparticles were determined by TEM as fig.3. From the TEM images it is clear that the particles are almost spherical and the size decrease from pure to doped samples and the size of the particle lies in the range of 3-2 nm, which is in good agreement with XRD results. The inset of fig.3 depicts the SAED pattern of the corresponding product. Three concentric rings are shown, which indicates that the products are crystalline and can be indexed as the cubic ZnS.

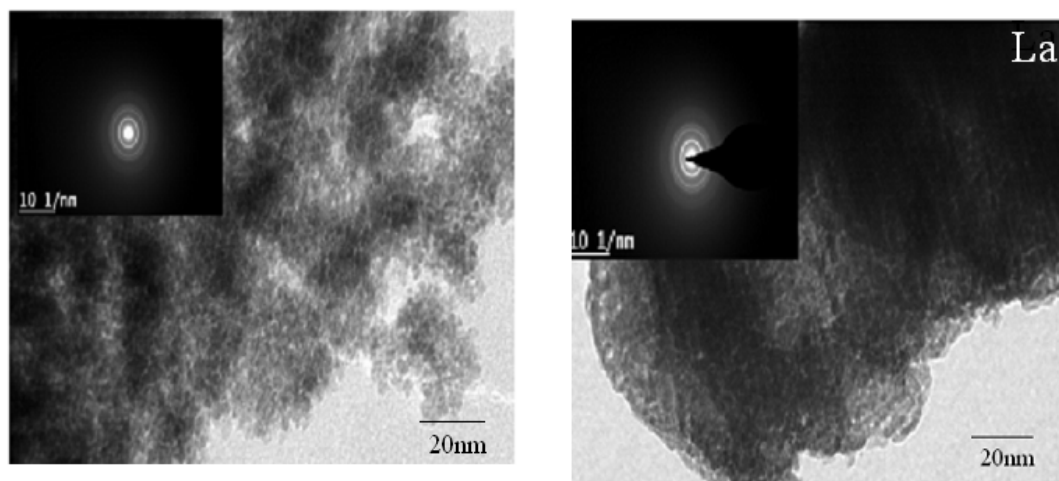


Fig.3 TEM images of pure and La doped ZnS nanocrystals.

The room temperature UV spectra of the pure and doped ZnS nanoparticles are reported in fig.4 (a). For semiconductor materials, the quantum confinement effect is expected if the semiconductor dimension becomes smaller than the Bohr radius of the exciton, and absorption edge will be shifted to a higher energy[12]. From the spectrum the band edge is shifted to the shorter wavelength side of the doped ZnS samples as compared to the pure ZnS sample due to quantum confinement effect. The blue shift in the absorption spectrum edge is a clear indication for the incorporation of dopant inside the ZnS lattice.

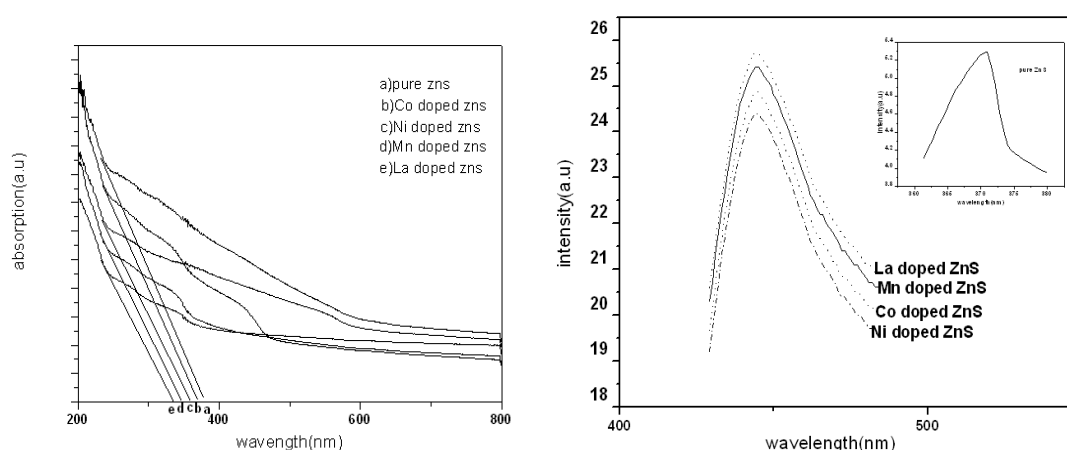


Fig.4 (b) Shows the photoluminescence (PL) for pure and doped ZnS nanocrystals.

The luminescence of pure ZnS nanoparticles possess the UV emission peak at 372 nm. Such dominant emission at 372 nm has been attributed to the radiative annihilation of excitons. The peaks due to the doped ZnS nanocrystallites shifted towards visible region centred at 450 nm. For pure ZnS nanoparticles, both excitons and trapped carrier at surface states are confined by quantum size effect, so the excitonic and trapped luminescent bands are size dependent, shifting to the blue as the particle size decreases. However, as the impurity ions doped in ZnS nanocrystalline, lead to the photo-luminescent emission spectrum red shifted. Hu et al [13]

explained that the red-shift may come from the quantum confinement effect in nanoparticles, which leads to the change of the field surrounding the dopant ions. From the figure it is clear that fluorescence intensity of doped ZnS are 5-6 times that of pure ZnS. The enhancement of luminescence intensity is one of the ascribed to quantum size effect that luminescence intensity increases with decrease of particle size[14]. The luminescence quantum efficiency is important for the potential use of semiconductor nanomaterials in light emitting devices where a high luminescence quantum efficiency is required. In doped nanoparticles large number of dopant centers are situated near the surface regions than interiors, it is expected to give better emission efficiencies compared that of pure ZnS.

4. Conclusion

TM and rare earth ion doped zinc sulfide nanoparticles have been obtained by precipitation from homogenous solution of zinc, transition metals and rare earth salt compound, with S²⁻ anion formed by decomposition of thioacetamide(TAA). ZnS nanoparticles of size about 2-3 nm with cubic structure has been observed by TEM and XRD. PL experiments show a strong visible light emitting from these doped nanocrystals having peak at 450nm at room temperature. The luminescence efficiency of the doped nanocrystals is remarkably enhanced by 5-6 times than that of pure ZnS. In conclusion TM and rare earth metal-doped ZnS nanoparticles form a unique luminescent materials with strong and stable visible emission.

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