

Synthesis and Characterization of ZnS: Mn Nanoparticles

Bhaskarjyoti Bodo, Divya Prakash, and P. K. Kalita

Abstract—In this work Mn²⁺-doped ZnS nanoparticles were prepared by chemical co-precipitation method at room temperature. The structural and optical properties of the ZnS:Mn nanoparticles were determined by XRD, SEM, UV-Visible and FL analyses. XRD analysis showed the sample prepared were in cubic phase with particle size in the ranges 12nm-25 nm. The SEM analysis reveals the growth of nanoparticles agglomerated in different shapes and orientations. In UV-Visible study the band gap energy corresponding to the absorption edge estimated are found to be 4.4~ 4.3eV which shows the large blue shifting from the bulk band gap 3.6eV of ZnS. The FL peak analysis reveals the strongest absorption at around 329nm which is fairly blue shifted from the absorption edge of the bulk (345nm). Thus Mn incorporated into ZnS nanoparticles results in changing its morphological, structural and optical properties.

Index Terms—ZnS: Mn, nanoparticles, SEM.

I. INTRODUCTION

Zinc Sulfide (ZnS), a typical II-VI compound semiconductor is a promising opto-electronic device material because of its wide direct band gap (3.72 - 3.77eV). Doping on ZnS with transitional metal ions like Mn²⁺ and Cu²⁺ is an important aspect to yield different nanostructures [1]-[9]. Noble luminescence characteristic such as stable light emission with different colors were observed from doped ZnS nanocrystals at room temperature [1]-[4]. It has been reported that the Mn doped ZnS has been one of the best efficient electroluminescent (EL) phosphor material in use and its synthesis and properties have widely been investigated [1]-[3], [6]-[9]. In this work we report on a successful synthesis of Mn doped ZnS with enhanced luminescence characteristics.

II. MATERIALS AND METHODS

A. Synthesis

A simple chemical co-precipitation method was employed to synthesis Mn doped ZnS nanoparticles in colloidal solution [5]. The synthesis was carried out in a matrix solution and thiourea in which MnCl₂ solution was added as doping agent. Zinc Sulphate solution of 0.5M (molarity) was used to get matrix solution and equal volume of thiourea solution of same molarity was prepared. Equal volume of

the matrix solution and thiourea were mixed together to form ZnS and simultaneously MnCl₂ Solution of 0.005 molarity were added to it as doping agent to get the Mn doped ZnS colloidal solution. The mixture of two salts was mixed with 3% solution of poly-Vinyl Alcohol (PVA) and stirred. Finally ammonia solution was added slowly to metal salt solution to form the metal complex and pH was adjusted between 10 and 12.

B. Reaction Mechanism

The zinc sulphate dissociate into zinc ions in aqueous solution and thiourea dissociate into S²⁻ ions. Similarly, manganese chloride dissociates into their respective cations and anions. Particles of ZnS nucleate due to the reaction between Zn²⁺ and S²⁻ which subsequently grow by consuming more ions from the solution. Upon nucleation the surface energy of the particle is very high and consequently the surface is passivated by adsorption of anions in the solution (Cl⁻ and S²⁻). The accumulation of anions in turn attracts cations (Zn²⁺ and Mn²⁺) on the surface of the particle. Zn²⁺ and Mn²⁺ react with S²⁻ and get incorporated into the crystal lattice of the nucleus.

III. CHARACTERIZATION

The structural properties of the Mn doped ZnS was investigated using X-ray powder diffractometer (Model: Seifert XRD 3003 T/T) with CuK_α radiation (λ = 0.15406nm) scanning 2θ in the range 20^o-80^o. Morphological studies of the as-prepared samples were carried out with Scanning Electron Microscope (SEM) [Model: LEO 1430VP] operated with an acceleration potential of 15kV to 20 kV. The UV-Vis absorption of the samples was recorded using an automated spectrometer (Model: HITACI 113210) in the wavelength range 200nm -800nm. FL emission spectra were measured with excitation wavelength 325nm using AMINC BOWMAN series-2 luminescence spectrometer.

IV. RESULTS AND DISCUSSION

A. XRD Study

The Fig.1 represents the XRD of as-prepared Mn doped ZnS nanoparticles. The XRD measurement reveals that the nanocrystalline of ZnS has Zinc Blende structure having plane {111}, {200}, {220} and {222}. The cubic phase of the crystals was identified from the agreement of peak position with standard JCPDS data. It is observed that cubic phase is quite dominant with phases {111}, {200}, {220} and {222}. However no peaks from manganese impurities were detected. It may indicate that the Mn²⁺ ions are dispersed into the ZnS matrix [3]. The particle sizes and particle size distributions as determined from XRD by using Debye

Manuscript received March 9, 2011; revised April 20, 2012.

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Scherrer were in the range 12nm -25nm[10]. The lattice constant of as-prepared ZnS nanoparticles are found to be within 5.38—5.41 Å which is deviated from Bulk value 5.41Å.

The diffraction peaks are considerably broadened that is attributed to the small crystallite sizes [5]. Small crystallites have relatively few lattice planes that contribute to the broadening of the diffraction lines. Broadening the peak may also occur due to the micro-straining of the crystal structure arising from defects like dislocation and twinning etc. These defects are considered to be associated with the chemically synthesized nanocrystals because they grow spontaneously during chemical reaction. In some occasions it could arise due to insufficient energy that is needed for an atom to move a proper site in forming the crystallite.

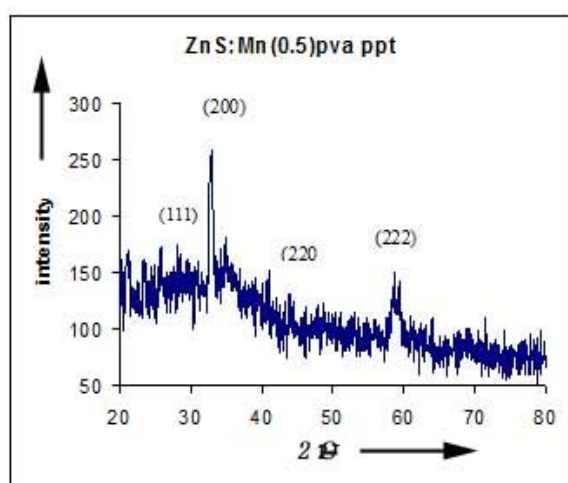


Fig. 1. XRD of ZnS: Mn.

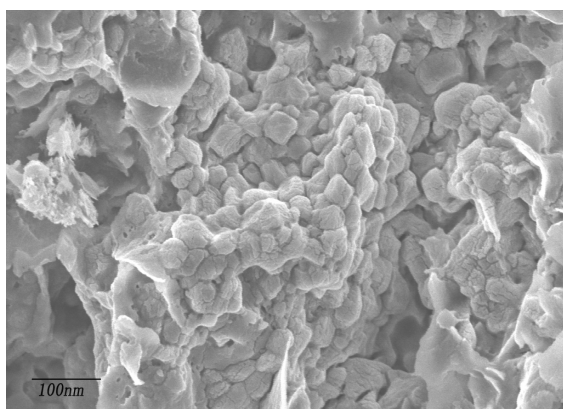


Fig. 2. SEM image of ZnS: Mn.

B. SEM Study

A first sight of the produced structures was obtained with the help of SEM which allowed the synthesis of ZnS:Mn nanoparticles with different sizes. The Fig. 2 shows the SEM image of as-prepared Mn doped ZnS deposited on the thin film and it is observed that the particles size varied from 10nm to 35nm or more. This growth of nanoparticles agglomerated in different shape and orientation may be attributed due to the uncontrolled nucleation growth during the deposition of nanoparticles on the silica glass substrates.

C. UV-Visible Study

The UV-Visible absorption spectra of three Mn doped

ZnS with (0.5M molarity in PVA) are shown in the Fig. 3. It is observed that absorption edge of the samples are between the wavelength range 280 ~ 285nm. However the spectra show a clear additional spectrum. The band gap energy corresponding to the absorption edge as estimated are found to be 4.4 ~4.3 eV which showed the large shifting from the bulk band-gap 3.6eV of ZnS. The absorption spectra also shows a clear additional absorption at 345~388nm. Generally the additional absorption near the band gap is considered as exciton energy. Here this absorption is shifted to longer wavelength side compared to the first absorption edge. Therefore this absorption may be attributed to some defects preferably surface.

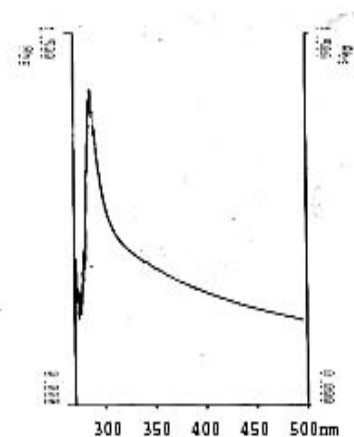


Fig. 3. UV-Vis spectra of ZnS: Mn.

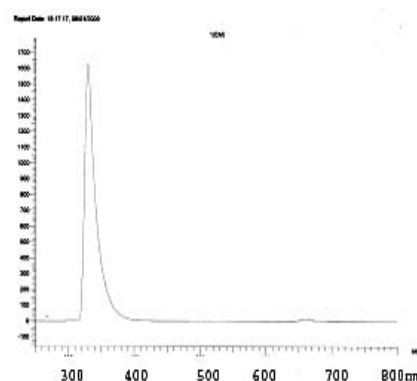


Fig. 4. FL spectra of ZnS: Mn.

D. FL Study

Room temperature fluorescence spectra of the ZnS:Mn nanoparticles measured with a 335 nm excitation are shown in the Fig. 4. The fluorescence spectra recorded for the Mn^{2+} doped ZnS showed two absorption edges, one at effective band gap energy of 326 nm ~329nm with direct band gap 3.7 eV ~3.9 eV and other at effective band gap energy of 655nm~660nm with direct band gap energy of 1.8 eV ~2 eV [2].The first absorption edge is attributed for the ZnS host while the latter one is due to the Mn^{2+} . On doping zinc sulfide with manganese, the Mn^{2+} ions substitute the Zn^{2+} ions in the ZnS crystal acting as trap sites, where the electron and holes can be trapped. An electron can undergo photo-excitation process in the host ZnS lattice of nanoparticles and subsequently decay via a non-radiative transition. The emission could be attributed to the radiative

decay between these localized states of manganese inside the ZnS band gap. For doped ZnS nanoparticles an additional emission spectra due to Mn^{2+} at energy band bag of ~ 658 nm is observed.

V. CONCLUSION

Mn^{2+} -doped ZnS nanoparticles in the colloidal solution form were successfully prepared and their respective size was in the range of 12nm - 25nm. The UV-Visible and F L studies reveal the large blue shifting from the bulk band-gap, (3.6eV) of ZnS attributing enhanced novel properties. Hence it is observed that Mn incorporated into ZnS nanoparticles results in changing its morphological, structural and optical properties.

ACKNOWLEDGEMENTS

Authors sincerely thank CIF and Dept of Physics, IIT Guwahati-39, Dept of Chemistry, Guwahti University, Guwahti-781013 and SAIF, NEHU, Shillong-793022 for providing the facilities for characterizations.

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