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Photoluminescent Polystyrene/ZnS: Mn nanocomposites

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ABSTRACT

In this paper we report the synthesis and characterization of transparent polymer nanocomposites Polystyrene/ ZnS: Mn. ZnS: Mn nanoparticles have been synthesized by chemical co-precipitation method. PS/Zns: Mn nanocomposites are prepared with different concentrations of ZnS: Mn in PS. These are characterized using XRD, SEM,EDAX, UV-Vis Spectroscopy and PL studies.XRD results indicate the cubic crystalline nature of ZnS.An Yellow Orange emission is obtained in the nanocomposites which are characteristic of ZnS: Mn nanoparticles and is preserved in PS/ ZnS: Mn.

Key words: Nanocomposites, Photoluminescence, Polystyrene, ZnS: Mn

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INTRODUCTION

The combination of nanoparticles with polymers hasopened newer and newer pathways of designing materials with new properties and wide range of applications.Polymer nanocomposites have been synthesized with a variety of nanomaterials such as carbon nanotubes, inorganic nanoparticles, and clay minerals, in order to improve mechanical, thermal, transport, and optical properties[1-3].Nanocrystalline semiconductors have been extensively studied in recent years due to their novel physical properties, potential photonic applicationsand the possibility of tuning their properties to suit a specific application by changingtheir size[4].Among the semiconductors of interest is zinc sulphide (ZnS) which is used in the violet and blue regions, owing to its wide band gap[5].ZnS nanoparticles when doped with Mn^{2+} (ZnS:Mn) gives an orange luminescence with high fluorescence quantum efficiencies[6,7]. The optical applications of polymer nanocomposites have become more into the forefront due to the developments in the field of optoelectronic devices, solar cells etc. The nanocomposites of a transparent polymer and nanosized semiconducting particle have attracted a great deal of interest[8, 9].These polymer nanocomposites have potential applications in the field of waveguides[10-12] liquid crystal display coating [13] and non-linear optical materials[14].

In this paper we have reported the optical properties and photoluminescence characteristics of nanocomposites of Polystyrene with ZnS:Mn synthesized via chemical method. XRD result does not show any major shift in the peaks of the doped sample indicating the cubic crystalline nature of ZnS is preserved. In the nanocomposites these particles acts as nucleation centers. FESEM images shows that the synthesized particles were spherical in nature and these are the particles which are used for the synthesis of the composites with Polystyrene. The UV-Visible spectra show a blue shift in the absorption for the nanoparticles as well as for the nanocomposites. The bandgap energy calculations from the UV-Visible spectra also show that there is an increase in the energy gap. The

photoluminescence studies of these nanocompositesindicate that there is yellow orange emission from the nanocomposite samples as is in the case of the nanoparticles.

MATERIALS AND METHODS

Nanoparticles of Mn^{2+} doped ZnS were prepared by chemical co-precipitation method. All the chemicals were of AR grade and were used without further purification. Freshly prepared aqueous solutions of the chemicals were used for the synthesis of nanoparticles. These particles were prepared at room temperature by dropping simultaneously 100ml solution of 0.4M of Zinc Sulphate, 100ml of 0.1M solution of Manganese Sulphate and 100ml of 0.5M solution of Sodium Sulphide into 250ml of distilled water containing 100ml of 0.1M solution of EDTA which was vigorously stirred using magnetic stirrer. The role of EDTA is to stabilize the particles against aggregation. The prepared reaction mixture was kept for stirring for two hours at constant rate of stirring after which the mixture was precipitated. The precipitated mixture was then separated from the reaction mixture, washed twice with distilled water to remove the impurities and the smell. The wet precipitate was dried and thoroughly grinded. The same procedure is used to synthesize ZnS nanoparticles without Manganese doping.

ZnS:Mn in PS matrix was prepared as follows: 5 wt% of PS solution was prepared by dissolving 2gm of PS in 40ml of Toluene. 5 wt% of PS/ZnS:Mnnanocomposite was prepared by adding 0.1gm of the prepared ZnS:Mn nanoparticle into the PS solution. The solution was kept for stirring for 2 days so that the particles are completely dispersed into the PS solution. The final solution was poured into a Petridish and kept for drying. The dried film of the sample was obtained after a week of drying. Nanocomposites of various wt% of ZnS:Mn^{2+} in PS were prepared by a similar procedure.

A strong interaction between the ZnS and the Polystyrene chains has reduced the requirement for an interfacial material. This also might be the reason for a reduced scattering at the interface between the nanoparticle and the polymer and transparent films were formed.

The X-ray diffraction (XRD) pattern were recorded to characterize the phase and structure of the nanocomposites in a Rigaku model Dmax 2500 X-ray powder diffractometer with a rotating anode and Cu K_α source operated at 150 mA and 40 kV.The size and morphology of the ZnS:Mn^{2+}nanoparticles were observed by FEI Quanta FEG 200-High Resolution Scanning Electron Microscope.Optical absorption was measured in Schimadzu 1800 UV – Vis spectrophotometer.Room temperature photoluminescence (PL) of the samples were measured using JY Fluorolog -3-11 Spectroflurometer between the wavelength of 300 and 700 nm.

Tab.1: Sample codes with its details

SAMPLE CODE	DETAILS
ZM0	ZnSUndoped
ZM2	ZnS Doped with Mn^{2+}
ZM3	PS/ZnS:Mn^{2+} (5%)
ZM4	PS/ZnS:Mn^{2+} (10%)
ZM5	PS/ZnS:Mn^{2+} (15%)
ZM6	PS/ZnS:Mn^{2+} (20%)

RESULTS AND DISCUSSION

XRD Analysis

The structure of the nanocomposites was evaluated by performing wide-angle X-ray Diffraction (WAXD) experiments using a Rigaku model Dmax 2500 X-ray diffractometer.

The following figures illustrate the XRD patterns of the samples. The XRD pattern of the ZnS: $Mn2^+$ sample contains broad peak at $2\theta = 28.8316°$ indicating the formation of nanostructure[15]. XRD pattern (figure 1(a)) shows three prominent peaks at 28.8°,48° and 56.8° corresponding to (110), (220), (331) lattice planes of Zinc blend structure of ZnS (JCPDS NO.05-0566). A similar set of peaks are observed in ZnS: Mn^{2+} samples also. There is an obvious broadening of the XRD pattern which indicates the formation of nano sized ZnS and ZnS:Mn^{2+}.In addition there are two peaks observed at around $10^\circ$and 19° for the PS/ZnS:Mn^{2+} (figure1(c))nanocomposites corresponding to the crystallization of polystyrene. ZnS: $Mn2^+$ particles are acting as

nucleating agents leading to the crystallization in amorphous PS.The polymer chains may be anchoredon the nanoparticles leading to an increase in crystallinity.

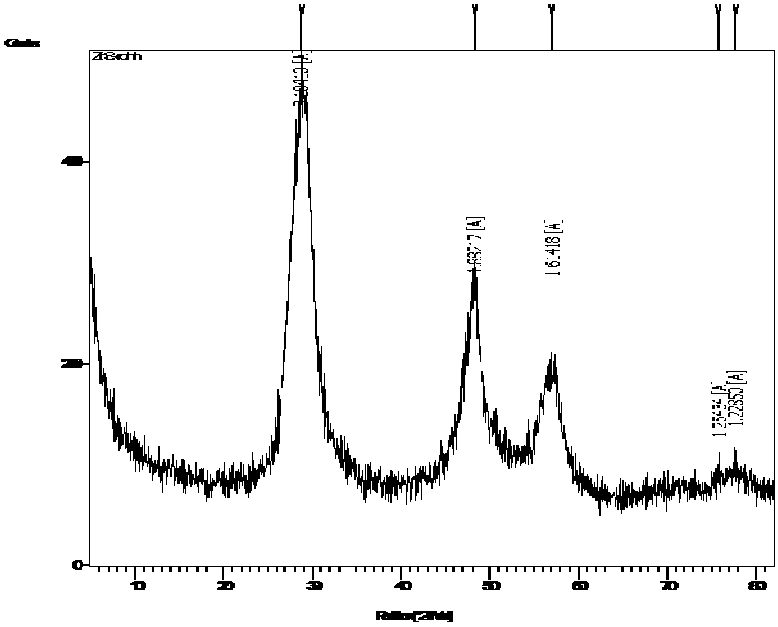
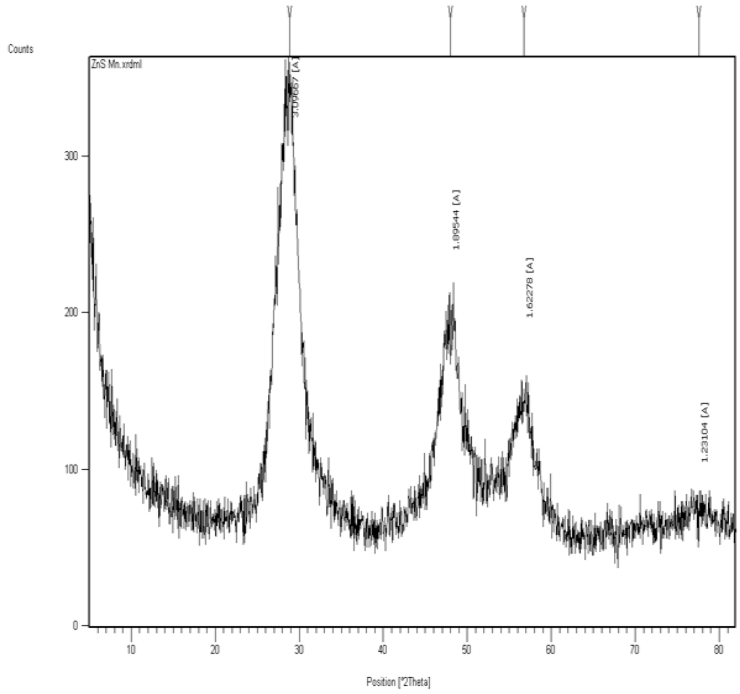


Figure 1(a)



Figue 1(b)

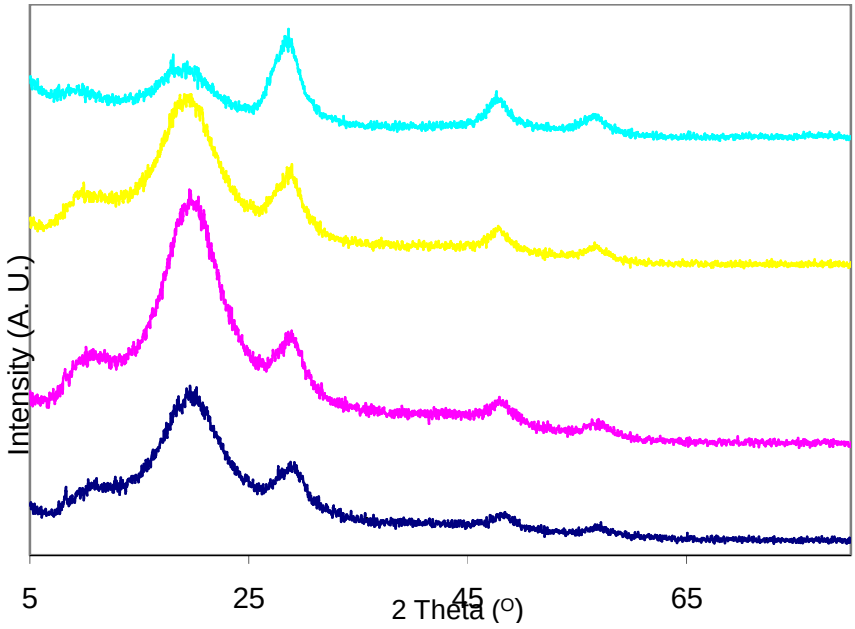


Figure 1(c)

Figure 1: XRD patterns of ZM0(a), ZM2(b), the composites(c)

The average particle size of the crystallites of each sample were determined from the full-width at half maxima (FWHM) of the XRD peaks by using the Scherrerformula, taking the average of the results from the most prominent (111),(222) and (311) peaks. The average particle size of the ZnS and ZnS: $Mn2^{+}$was found to be 6.31nm and 5.47nm respectively.In the case of nanocomposites with various concentrations of ZnS:Mn^{2+} , the average grain size was found to be 4.006, 4.438, 4.976 and 5.469 which implies that there is no increase in the particle dimensions or aggregation after it is dispersed in the polymer matrix. The polymer chains that are anchored on the nanoparticle will hinder the growth of nanoparticles and can form uniform particle sizes[16].

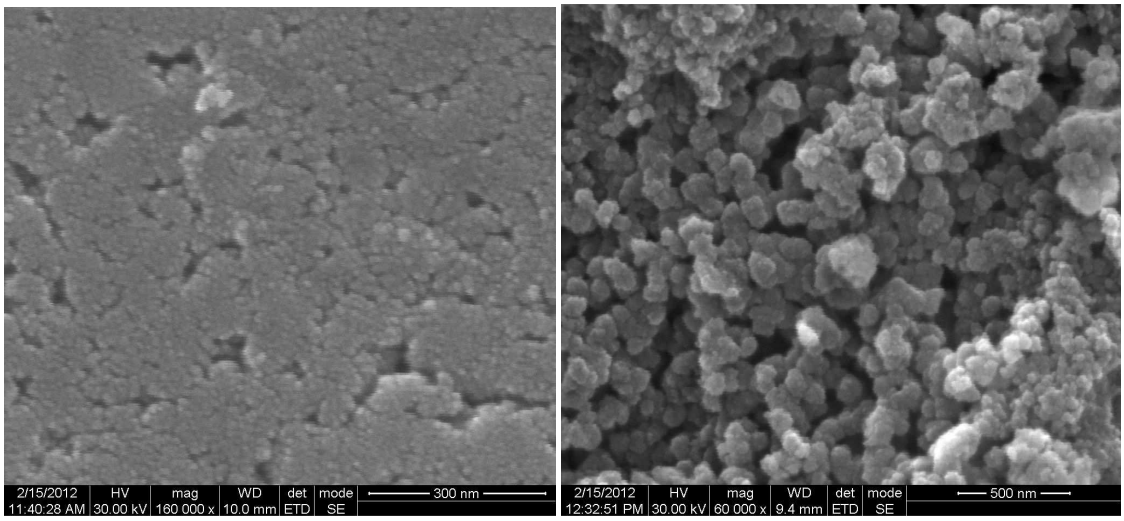


Figure 2: SEM images of ZM0 and ZM2 samples

SEM Images

SEM images of ZM0 and ZM2 samples were recorded using F E I Quanta FEG 200 - High Resolution Scanning Electron Microscope and the images are shown below. The morphology of the nanoparticles is identified by SEM analysis and is found to be spherical. The SEM images of the ZM0 show that there are large no of particles in the nanometer dimensions. Even ZnS: Mn^{2+} nanoparticles are having a similar behavior as can be seen.

EDAX Spectra

The elemental composition of the nanoparticles formed were given by energy dispersive X-ray (EDAX) spectra. Figure 3 shows the EDAX spectra of ZM0 and ZM2 samples.

OK	04.91	13.72
SK	29.87	41.65
MnK	00.16	00.13
ZnK	65.06	44.50
Matrix	Correction	ZAF

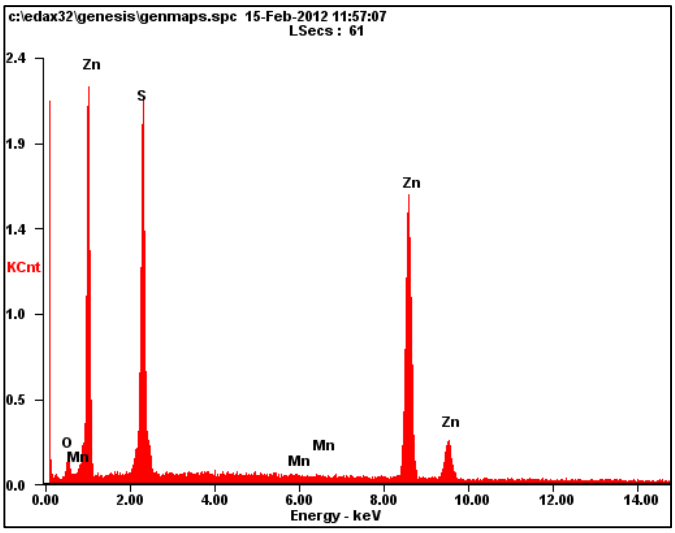


Figure 3(a): EDAX Spectra for ZnS sample

OK	06.20	17.10
SK	27.90	38.41
MnK	3.17	3.01
ZnK	62.73	41.48
Matrix	Correction	ZAF

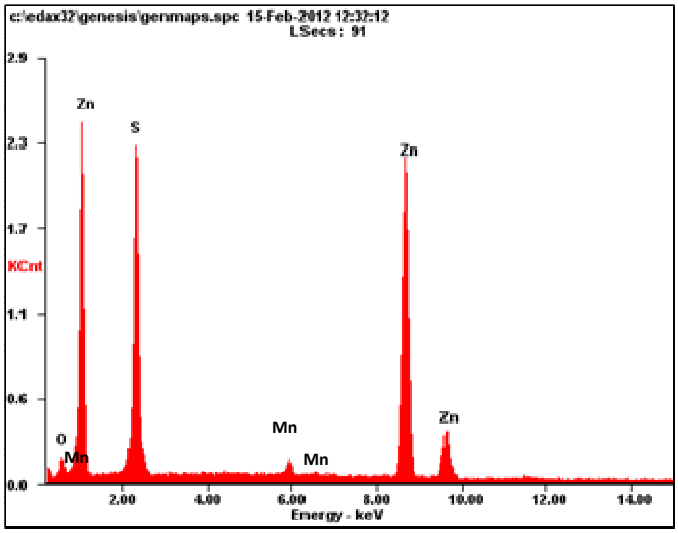


Figure 3(b): EDAX Spectra for ZnS: $Mn2^{+}$ sample

EDAX spectra of the samples show that in the sample about 62% of Zn^{2+} ion and about 3% Mn^{2+} ion by atomic mass are present. The Mn^{2+} ions may be incorporated in the Zn^{2+} lattice sites[17]. EDAX spectrum also shows some presence of Oxygen in the samples which could indicate the formation of a ZnO phase.

UV-VIS Analysis

The UV-Vis spectra of ZnS nanoparticle consists of a peak at around 325 nm which corresponds to a band gap of 3.4 eV.The UV-Vis spectra of the sample doped with Mn^{2+} shows a shift in the absorption peak, which indicates that the ZnS nanoparticle band gaps are modified by the presence of the Mn^{2+}.No further change is observed in the nanocomposites of ZnS:Mn with Polystyrene indicating that the band gap structure of the nanoparticles is preserved in the composites.Polystyrene essentially acts as capping for the ZnS:Mn particles and also as the matrix for the filler.

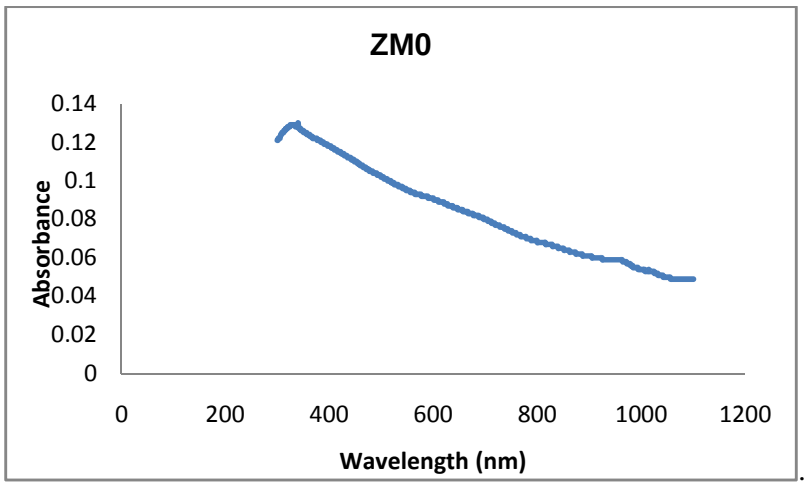


Figure 4(a)

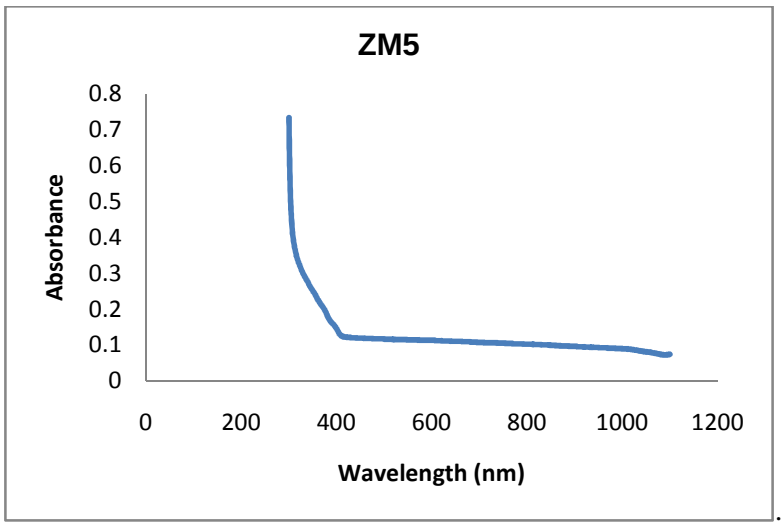


Figure 4(b)

Figure 4: UV-VIS Spectra for ZM0 (a) and ZM5(b))samples.

It is evident from the above figures that the samples exhibit an absorption maximum. This is fairly blue shifted with respect to the bulk ZnS arising from quantum confinement effect in the nanoparticles [15].

Energy Gap

From the UV study we can calculate the energy band gap[17].Manifacier model is used to determine the absorption coeffcient α from the transmittance data. The fundamental absorption, which corresponds to the transmission from

valence band to the conduction band, is employed to determine the band gap of the material.The relation between absorption coefficient (α) and incident photon energy (hν) can be written as:

$$\alpha = A(h\nu - E_g)^n / h\nu \quad (1)$$

where A is a constant and Eg is the band gap of the material. Exponent 'n' depends on the type of the transition, n may have values 1/2, 2, 3/2 and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. But in the nanocrystalline sample, there may be some deviation from the bulk like transition. From the above equation, it is clear that, plot of $(\alpha h\nu)^2$ vs hν will indicate a divergence at an energy value E_g where the transition takes place. Taking the values at discontinuities as the band gap, the nature of the transition (i.e., the n value) is determined. The exact value of the band gap is determined by extrapolating the straight line portion of $(\alpha h\nu)^2$ vs hνgraph to thehνaxis.

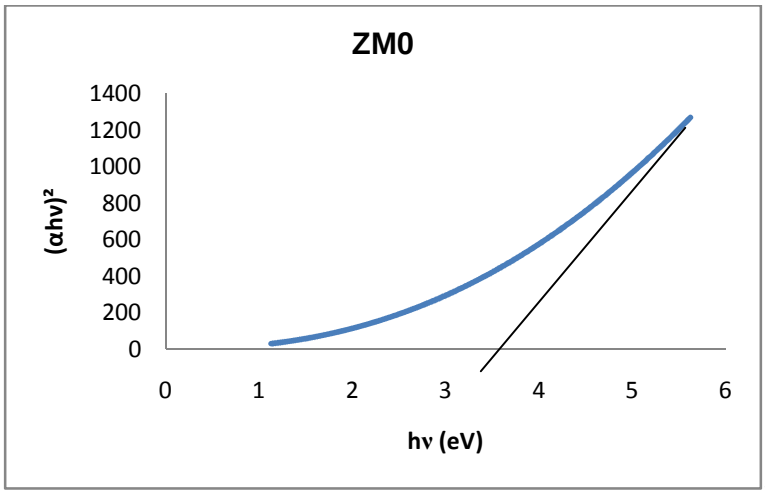


Figure5(a)

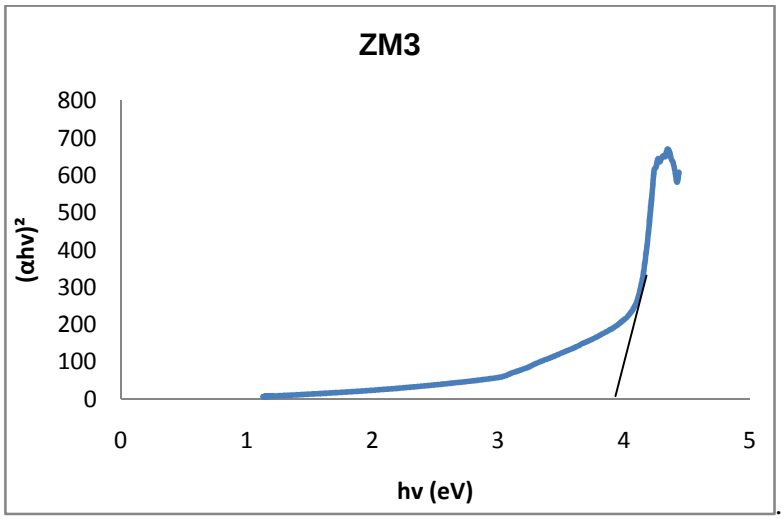


Figure5(b)

Figure 5: Plot of $(\alpha h\nu)^2$ vs hνfor ZM0(a), and ZM3(c) samples to determine optical band gap

The calculated bang gapfor pure ZnS is 3.4eV.The band gaps for the composites are 3.45,3.9, 4 , 3.92 , 3.95 eV for ZM2, ZM3, ZM4, ZM5 and ZM6 respectively.

Photoluminescence

PL spectra for the samples were recorded using (JY Fluorolog-3-11) spectroflurometer. The following figure shows the room temperature normalized photoluminescence studies of ZM0, ZM2, ZM3, ZM4, ZM5 and ZM6.

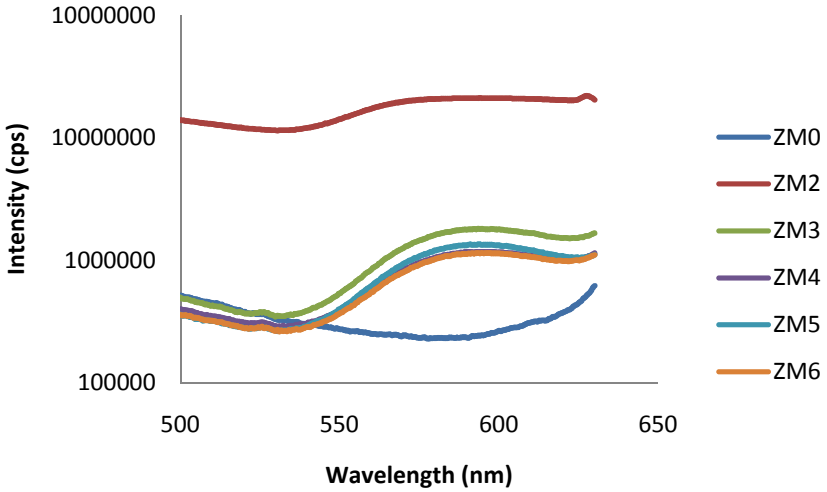


Figure 6: PL spectra of ZM0, ZM2, ZM3, ZM4, ZM5 and ZM6

The PL properties givethe fundamental properties of the nanoparticles embedded in Polystyrene matrix. The PL emission of ZnS, ZnS:Mn and the composites in powder form is as shown in figure. The particles were excited with photons of wavelength 320 nm. Subsequent transfer of electron and hole into the electronic level of the Mn ion leads to the characteristic emission of Mn^{2+} in ZnS[18]. PL spectrum of ZM0 contains peak at around ~342nm which is the band gap of ZnS, PL spectrum of ZM2 contains peak at around ~461nm which is the defect related emission of ZnS host and aYellow Orange emission lying between 590nm-600nm. A similar peak is observed in all the nanocomposites as in the case of pure ZnS:Mnnanoparticles[19] with slightly reduced intensity indicating that nanocomposites still retain the properties of the ZnS:Mn nanoparticles. This indicated that the nanocomposites of ZnS: Mn with Polystyrene can be equally used as a photoluminescent material even though with a lesser emission as compared to pure ZnS: MnThe yellow –orange emission with a peak wavelength of 590 nm is due to the transition involving the d electrons of the Mn^{2+} ions[6],[20].In ZnS:Mnnanoparticles, an Orange luminescence is attributed to the $^4T_1$-$^6A_1$ transition of Mn^{2+} ions excited or an energy transfer from host ZnS[21].

CONCLUSION

PS/ZnS:Mnnanocomposites are prepared using chemical co-precipitation of ZnS:Mn and solution dispersion of the synthesized samples in a solution containing the Polystyrene. The samples are dried by slow evaporation. These samples are studied for the dispersion using XRD and SEM. The ZnS:Mn samples show a spherical agglomerated structure. The observation of blue shift in absorption spectra indicates quantum confinement effect.When excited with 320 nm wavelength there is an yellow-orange emission (590-600nm) from the ZnS:Mn samples which is preserved in the nanocomposites with varying concentration of ZnS:Mn. This implies that the polystyrene polymer is well anchored on the surface of the ZnS:Mn nanoparticle and is acting as a good capping and dispersing agent for the nanoparticles. Polystyrene matrix effectively transmits the light without quenching the luminescence. Such nanocomposites have a wide range of applications including luminescent paintings and coatings.

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