



## **Influence of Mn<sup>2+</sup> doping on the optical properties of ZnS<sub>x</sub>O<sub>1-x</sub> quantum dots**

**G. Janita Christobel<sup>1\*</sup> and C.K. Mahadevan<sup>2</sup>**

<sup>1</sup>Physics Research Centre, S. T. Hindu College, Nagercoil-629002, Tamil Nadu, India

<sup>2</sup>Center for Scientific and Applied Research, PSN College of Engineering and Technology, Melathediyoor, Tirunelveli-627152, Tamil Nadu, India

**Abstract :** The physical properties of two semiconductor quantum dots like ZnO and ZnS are found to get modified significantly when they are mixed with each other or doped with a transition metal element. With an aim of discovering new useful quantum dots, in the present study, we have prepared Mn<sup>2+</sup> doped ZnS<sub>x</sub>O<sub>1-x</sub> nanocomposite quantum dots (x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0) by a simple solvothermal method using a domestic microwave oven. Powder X-ray diffraction, scanning electron microscopic and energy dispersive X-ray absorption spectroscopic analyses were carried out to characterise the prepared quantum dots chemically and structurally. UV-Vis-NIR absorption, photoluminescence (PL) and photoconductivity measurements have been carried out to understand the influence of Mn<sup>2+</sup> doping on the optical properties of ZnS<sub>x</sub>O<sub>1-x</sub> quantum dots. Results obtained indicate significant changes in the optical properties like absorption edge wavelength, PL yield and photoconductivity. All the nanocrystals (quantum dots) prepared in the present study are found to have their absorption edge wavelengths within the UV region, exhibit five prominent peaks (observed at around 400, 440, 480, 490 and 530 nm) in the PL spectra and possess positive photoconductivity.

**Keywords:** Quantum dots, Doped ZnS<sub>x</sub>O<sub>1-x</sub> nanocrystals, Solvothermal method, Optical properties.

### **Introduction**

Recently a large number of researchers have put their efforts in investigating the properties of transition metal ions (TMIs) doped semiconductor nanoparticles for superior or even new optical, electrical and magnetic properties associated with the reduced size, for a wide range of their potential applications [1-3]. One of the most investigated activating ions is Mn<sup>2+</sup>. Among the wide range of II-VI semiconductor nanoparticles, ZnO (E<sub>g</sub> = 3.37 eV) and ZnS (E<sub>g</sub> = 3.77 eV) have been studied extensively due to their wide band gaps [4-9]. When we dope II-VI nano structured semiconductors with Mn<sup>2+</sup> ions, the fluorescence efficiency and magnetic ordering of the synthesised nanoparticles become very high which could help for creating potential applications in photonic and spintronic devices, respectively [9-12]. A thorough knowledge of localization, concentration and electronic state properties of doping Mn<sup>2+</sup> ions into the material is required to have efficient instrumental fabrication.

Dhara and Giri [13] have reported improvements in photoluminescence (PL) and photoconductivity (PC) for the ZnO/CuPc hetero-structure due to modification of surface defects and interfacial charge transfer process. A 30-fold increase in PL intensity has been observed by Lu *et al* [14] from Mn<sup>2+</sup> doped ZnS nanoparticles after surface passivation by a passivating agent with carboxylic functional groups. Murugadoss *et al* [15] have reported an additional yellow-orange emission due to Mn<sup>2+</sup> addition to water soluble ZnS nanoparticles. Bera and Basak [16] have reported that through surface modification by ZnS, the UV photosensitivity can be enhanced in ZnO nanowires, which is promising for optoelectronic applications. Wang *et al* [17] have found that for ZnS:Mn<sup>2+</sup>/ZnO core-shell nanocrystals, the PL intensity of Mn<sup>2+</sup> is enhanced by the growth of an additional ZnO shell on the ZnS:Mn<sup>2+</sup> due to the elimination of the surface defects.

In the study of efficient tailoring of  $\text{Mn}^{2+}$  with ZnO-ZnS nanoparticles, we noticed the quantum confinement effect [18]. It is found that large concentrations of  $\text{Mn}^{2+}$  ions incorporated at substitutional sites can modify the lattice parameters as well as the band gap of semiconducting nanomaterials. These changes in the structural characterization of  $\text{Mn}^{2+}$  doped ZnO-ZnS have aroused an interest in studying the optical properties too [15, 19, 20]. In the optical studies it is fascinating to know that substituting the  $\text{Zn}^{2+}$  site with  $\text{Mn}^{2+}$  in ZnO and ZnS could produce blue and yellow–orange emissions respectively in the visible region [21].

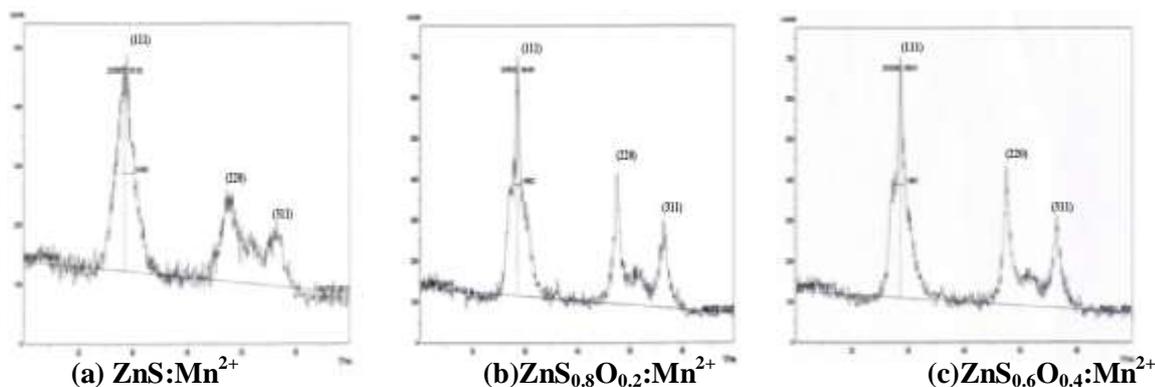
Vimalan and Mahadevan [18] have reported the preparation and electrical (both DC and AC) characterization of a set of seven nanocomposite quantum dots ( $\text{ZnS}_x\text{O}_{1-x}:\text{Mn}^{2+}$  ( $x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8$  and  $1.0$ )). In order to understand the effect of simultaneous mixing (ZnO and ZnS) and doping (with 5 wt%  $\text{Mn}^{2+}$ ) on the optical properties, in the present study, we have prepared in the same way those seven nanocomposite quantum dots and optically characterized them by carrying out UV-Vis-NIR absorption, PL and PC measurements. The details are presented here.

## Material and Method

The proposed  $\text{ZnS}_x\text{O}_{1-x}:\text{Mn}^{2+}$  ( $x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8$  and  $1.0$ ) nanocomposites (a total of seven samples) were prepared by a simple solvothermal process using Mahadevan's method [22-27] and characterized chemically and structurally by carrying out powder X-ray diffraction (PXRD), scanning electron microscopic (SEM) and energy dispersive X-ray absorption (EDAX) analyses as reported earlier by Vimalan and Mahadevan [18]. So, the details of these are not presented here. A Shimadzu UV-2400 PC spectrometer with medium scan speed was used for recording the UV-Vis-NIR absorption spectra in the wavelength range 200-800 nm. The PL spectra were recorded using a PerkinElmer LS55 model luminescence spectrometer. The visible photo-response was measured using a commercial bulb of 200 W as a photo-excitation source. A stabilized DC field (in the range 50 - 500 V/cm) was applied across the cell to which a digital DC nanoammeter, NM-121 (Scientific Equipment, Roorkee) for the measurement of current and RISH Multi 15S with adapter RISH Multi SI 232 were connected in series. The light intensity over the cell surface was changed by varying the distance between slit and light source. Before measuring photoconductivity of the sample, the cell was first kept in dark till it attained equilibrium. With all these the photoconductivity studies were also carried out in the darkness and illuminating the light source.

## Results and Discussion

The annealed (at  $200^\circ\text{C}$  for 1 hour) samples prepared in the present study are white in colour and stable at atmospheric conditions. The PXRD patterns shown in Figure 1 indicate that the samples prepared in the present study are  $\text{ZnS}_x\text{O}_{1-x}:\text{Mn}^{2+}$  nanocrystals and the crystallite sizes are within 1.4-6.6 nm except for  $\text{ZnO}:\text{Mn}^{2+}$  (15.3 nm). The PXRD analysis indicate that the  $\text{ZnS}:\text{Mn}^{2+}$  and  $\text{ZnO}:\text{Mn}^{2+}$  nanocrystals possess respectively the cubic (sphalerite) and hexagonal (wurtzite) structures. The mixed nanocrystals have both cubic and hexagonal phases and they can be considered as multi phased nanocomposites.





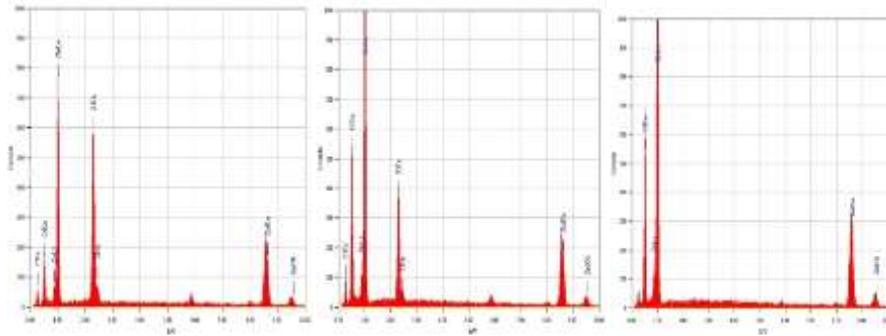
(e)  $\text{ZnS}_{0.4}\text{O}_{0.6}:\text{Mn}^{2+}$ (f)  $\text{ZnS}_{0.2}\text{O}_{0.8}:\text{Mn}^{2+}$ (g)  $\text{ZnO}:\text{Mn}^{2+}$ 

Figure 2: The EDAX spectra obtained in the present study

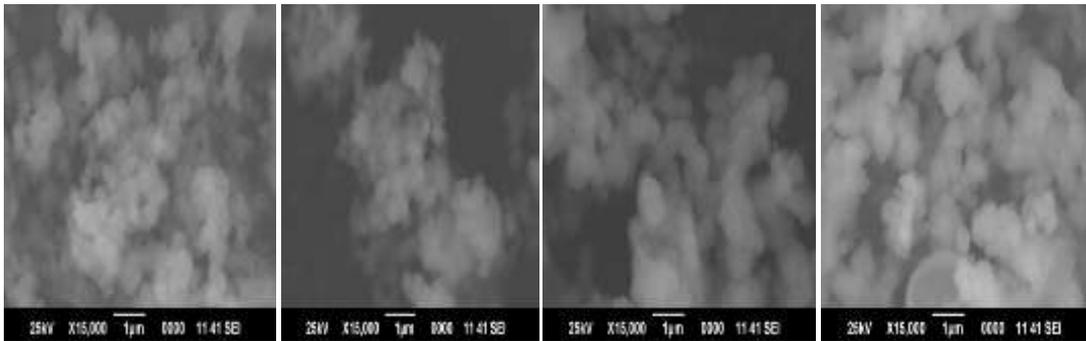
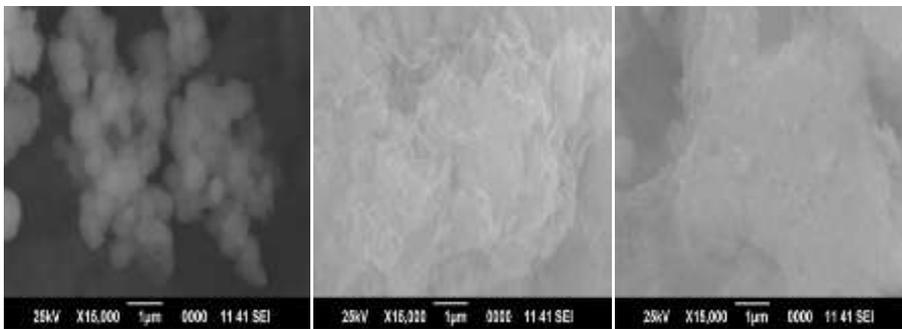
(a)  $\text{ZnS}:\text{Mn}^{2+}$ (b)  $\text{ZnS}_{0.8}\text{O}_{0.2}:\text{Mn}^{2+}$ (c)  $\text{ZnS}_{0.6}\text{O}_{0.4}:\text{Mn}^{2+}$ (d)  $\text{ZnS}_{0.5}\text{O}_{0.5}:\text{Mn}^{2+}$ (e)  $\text{ZnS}_{0.4}\text{O}_{0.6}:\text{Mn}^{2+}$ (f)  $\text{ZnS}_{0.2}\text{O}_{0.8}:\text{Mn}^{2+}$ (g)  $\text{ZnO}:\text{Mn}^{2+}$ 

Figure 3: The SEM images obtained in the present study

Figures 4 and 5 respectively show the UV-Vis-NIR absorption and PL spectra obtained in the present study. Five prominent emission bands are observed at around 400, 440, 480, 490 and 530 nm in the PL spectra. The Near Band Edge (NBE) emission may be because of the interstitial zinc and the ionized oxygen vacancies [28,29]. The intense blue band around 400 and 440 nm are due to the formation of dense interstitial zinc states. The formation of zinc ion ( $\text{Zn}^{2+}$ ) from the starting material may be faster than forming the oxide ( $\text{O}^{2-}$ ) and sulfide ( $\text{S}^{2-}$ ) ions.

In order to understand the exact phenomenon of PL, we need to understand the mechanism of optical absorption at 330nm. The peaks observed at around 330nm (Figure 4) are known as the B band. The B band originates from the orbital transition[30]. In our study, the absorption edges of all quantum dots except for  $\text{ZnO}:\text{Mn}^{2+}$  fall within 330 to 350 nm whereas the absorption (band) edge for  $\text{ZnO}:\text{Mn}^{2+}$  is around 370 nm.

When the synthesized nanoparticles are excited with 320 nm laser, both the zinc oxide or sulfide layers get excited and excitons are created. These higher occupied molecular orbital electrons are injected into the conduction band of ZnO-ZnS. The process continues and the charge carriers are formed in the conduction

band. This will simultaneously boost the electron-hole recombination possibility. This results in the blue-green emission[31]. Also it is known that substituting the  $Zn^{2+}$  site with  $Mn^{2+}$  in ZnO and ZnS could produce blue and yellow–orange emissions respectively in the visible region.

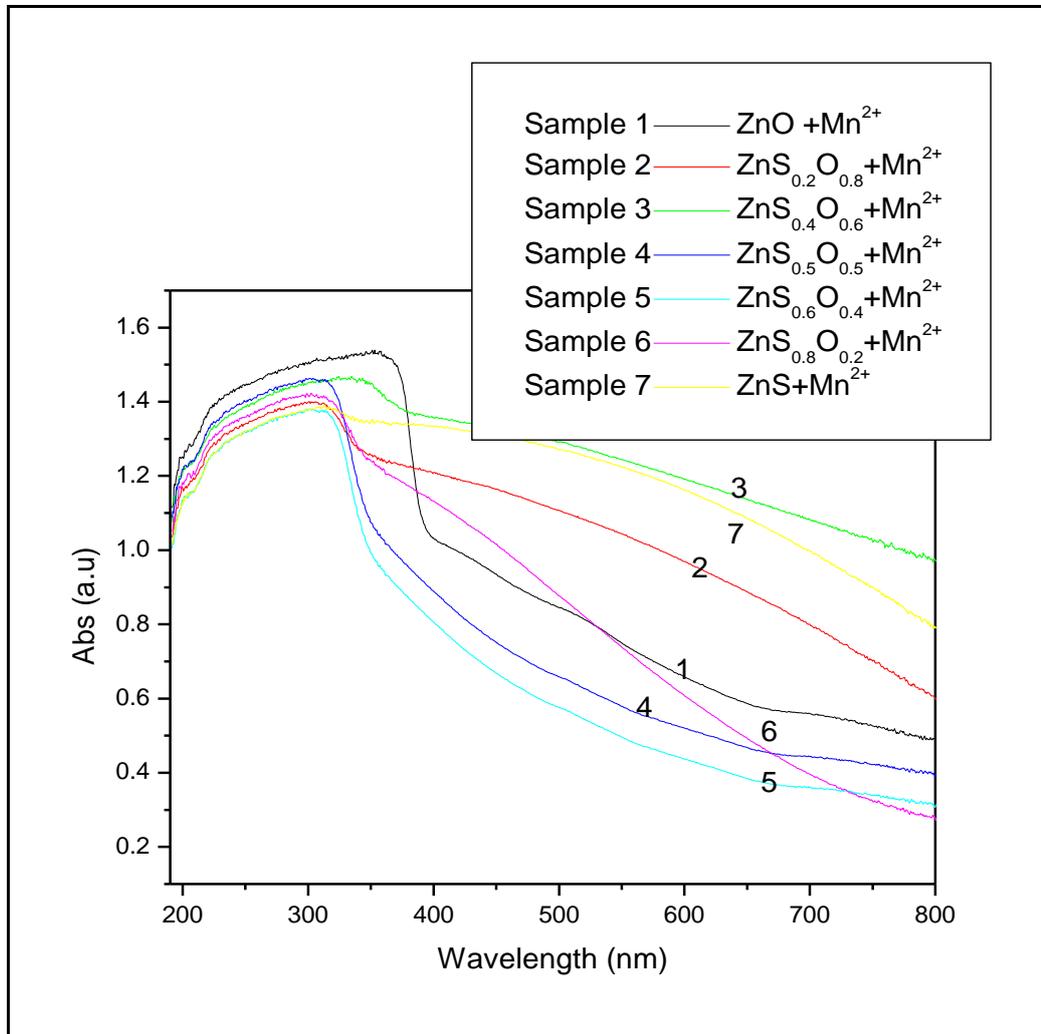


Figure 4: The UV-Vis-NIR absorption spectra obtained in the present study

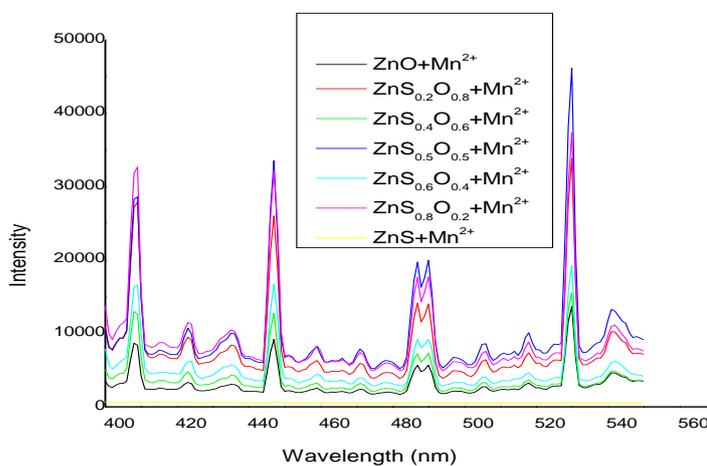
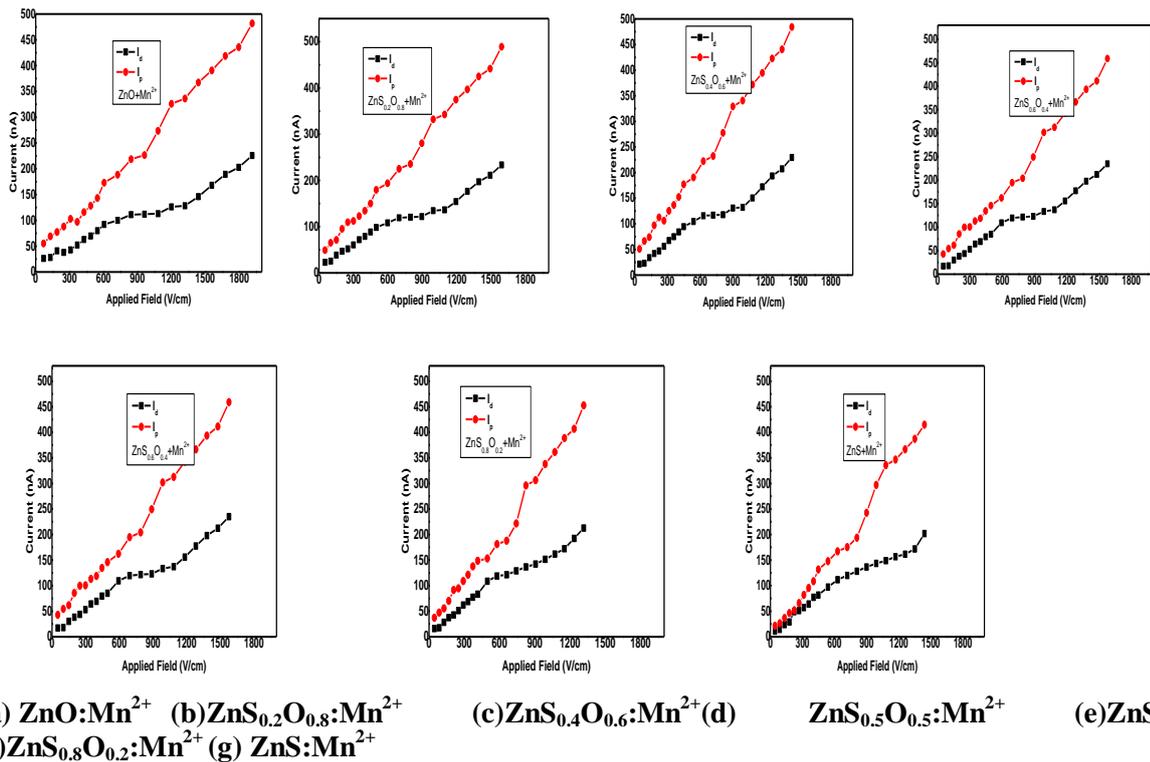


Figure 5: The PL spectra obtained in the present study



**Figure 6: Results of PC measurements made in the present study**

The results of photoconductivity (PC) measurements made in the present study are shown in Figure 6. Both the dark and photo currents ( $I_d$  and  $I_p$ ) increase with the applied field; and  $I_p$  is found to be greater than that of  $I_d$ . This indicates the positive photoconductive nature of all the seven systems considered in the present study. As explained earlier, because of the external source, the electron-hole pairs are created in the conduction band. Under external bias, these electrons along with the photo generated electrons from the synthesised nanoparticles contribute to the current conduction process, resulting in an enhanced conductivity when the applied field is increased.

The PL and PC observed for all the seven systems considered in the present study can be due to the changes in the surface defects and interfacial charge transfer process. Also, significant change in PL yield and PC due to  $\text{Mn}^{2+}$  doping could be observed when compared to pure  $\text{ZnS}_x\text{O}_{1-x}$  nanocomposites [32, 33]. The results of optical measurements made in the present study indicate that the nanostructured materials considered in the present study will find their application in optoelectronic devices.

## Conclusion

$\text{ZnS}_x\text{O}_{1-x}:\text{Mn}^{2+}$  (5 wt%) ( $x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8$  and  $1.0$ ) nanocomposite (with simultaneous mixing and doping) quantum dots were prepared by a facile solvothermal (Mahadevan's) method and characterized by PXRD, SEM, EDAX spectral, UV-Vis-NIR spectral, PL spectral and PC measurements. Results of PXRD, SEM and EDAX spectral analyses indicate the proper formation of simultaneously mixed and doped nanocrystals as expected. Results of UV-Vis-NIR spectral, PL spectral and PC measurements indicate significant changes in the optical properties like absorption edge wavelength, PL yield and photoconductivity due to mixing ZnO with ZnS and  $\text{Mn}^{2+}$  doping. Further, the present study indicates that all the seven nanostructured materials considered in the present study are expected to be useful in optoelectronic devices.

## Acknowledgment

One of the authors G. Janita Christobel thanks the UGC, New Delhi for the Postdoctoral Fellowship (Women) [F-15-149/12 (SA-II)].

## References

1. Y. Yang, S. Xue, S. Li, J. Huang, J. Shen, Appl. Phys. Lett. 69 (1996) 377
2. P.K. Sharma, R. Nass, H. Schmidt, Opt. Mater. 10 (1998) 161
3. E.T. Goldburt, B. Kulkarni, R.N. Bhargava, J. Taylor, M. Libera, J. Luminesc. 72-74 (1997) 190
4. Z. L. Wang, J. Song, Science312 (2006) 242
5. X. Fang, T. Zhai, U.K. Gautam, L. Li, L. Wu, Y. Bando, D. Golberg, Prog. Mater. Sci. 56 (2011) 175
6. Q. Sun, Y.A. Wang, L.S. Li, D. Wang, T. Zhu, J. Xu, C. Yang, Y. Li, Nat. Photonics 1(2007) 717
7. Z. Quan, D. Yang, C. Li, D. Kong, P. Yang, Z. Cheng, J. Lin, Langmuir 25 (2009) 10259
8. U. Ozgur, Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Dogan, V. Avrutin, S.J. Cho, H. Morkoc, J. Appl. Phys. 98(2005) 041301
9. X. Fang, Y. Bando, U.K. Gautam, T. Zhai, H. Zeng, X. Xu, M. Liao, D. Golberg, Crit. Rev. Solid State Mater. Sci. 34(2009) 190
10. R. Beaulac, S.T. Ochsenein, D.R. Gamelin, Colloidal Transition-Metal Doped Quantum Dots, ed. by V.I. Klimov, Nanocrystals Quantum Dots, 2nd edn. (CRC Press, New York, 2010)
11. H. Hu, W. Zhang, Opt. Mater. 28 (2006) 536
12. X.S. Fang, T.Y. Zhai, U.K. Gautam, L.A. Li, L.M. Wu, B. Yoshio, D. Golberg, Prog. Mater. Sci. 56, (2011) 175
13. S. Dhara, P.K. Giri, Functional Mater. Lett. 5 (2012) 1250021
14. S.W. Lu, B.I. Lee, Z.L. Wang, W. Tong, B.K. Wagner, W. Park, C.J. Summers, J. Luminesc. 92 (2001) 73
15. G. Murugadoss, B.Rajamannan, V. Ramasamy, J. Luminesc. 130 (2010) 2032
16. A. Bera, D. Basak, Appl. Mater. Interfaces 2 (2010) 408
17. Y. Wang, C. Li, L. Peng, J. Nanosci. Nanotech. 10 (2010) 2228
18. M. Vimalan, C.K. Mahadevan, Arch. Appl. Sci. Res. 2(2) (2010) 337
19. H. Weller, Angew. Chem. Int. Ed. Engl. 32 (1993) 41
20. A.P. Alivisatos, J. Phys. Chem. 100 (1996) 13226
21. Y. Cheng, R. Chen, H. Feng, W. Hao, H. Xu, Y. Wang, J. Li, Phys.Chem.Chem. Phys.16 (2014) 4544
22. S.M. Sundar, C.K. Mahadevan, P. Ramanathan, Mater. Manuf. Processes 22 (2007) 400
23. R.S.S. Saravanan, D. Pukazhselvan and C.K. Mahadevan, J. Alloys Compd. 509 (2011) 4065
24. S.I.S. Ramya, C.K. Mahadevan, Mater. Lett. 89 (2012) 111
25. G. Janita Christobel, C.K. Mahadevan, Int. J. Adv. Mater. Sci. 4(1) (2013) 67
26. S.Nagaveena, C.K. Mahadevan, J. Alloys Compd. 582 (2014) 447
27. S.I.S. Ramya, C.K. Mahadevan, J. Solid State Chem. 211 (2014) 37
28. B. Lin et al., Appl. Phys. Lett. 79 (2001) 943
29. K. Vanheusden et al., J. Appl. Phys. 79 (1996) 7983
30. J. Mack et al., J. Inorg. Chem. 40(2001) 812
31. S. Dhara et al., Nanoscale Res. Lett. 6 (2011) 504
32. G. Janita Christobel, Ph.D. Thesis (2010), Manonmaniam Sundaranar University, Tirunelveli
33. G.Janita Christobel and C.K.Mahadevan Proceedings of the "International Conference on Advanced Nanomaterials & Emerging Engineering Technologies" 978-1-4799-1379-4/13/ ©2013 IEEE

\*\*\*\*\*