

SYNTHESIS AND CHARACTERIZATION OF WATER-SOLUBLE ZnS: Mn²⁺ NANOCRYSTALS

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Mn²⁺ - doped ZnS nanoparticles were synthesized by a chemical precipitation method at air atmosphere. The synthesis of water-soluble Mn²⁺ - doped ZnS nanocrystals with EDTA as a stabilizer was described. From the peak broadening of the X-ray diffraction, the particle size is found to be 4.5 nm when EDTA was not used as a stabilizer and size is reduced to 3.6 nm with EDTA. The particle size and properties are studied using SEM and photoluminescence. The emission peak of the sample corresponding to photoluminescence is observed at 591 nm.

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1. Introduction

During the past 20 years, nano materials have been widely studied in everywhere [1-2]. Now-a-days the nanostructure materials are of major significant and their technology of production are used rapidly into a powerful industry. These potential applications are resulting from quantum size confinement. The optical properties of nanocrystalline semiconductors have been studied extensively in recent years. Especially, ZnS is a direct-transition semiconductor with the widest energy band gap among the group II-VI compound materials. The most striking feature of ZnS nanocrystallites is that their chemical and physical properties differ dramatically from those of the bulk solids. It has also attracted much attention owing to its wide applications including UV- light emitting diodes, efficient phosphor in flat-panel displays, photovoltaic devices etc [3]. Warad et al. [4] reported that ZnS doped with Mn²⁺ has potential application in the field emission devices (FED). ZnS: Mn²⁺ nanoparticles have received much attention, since these used are phosphors and also in thin film electroluminescent devices [5-9]. Pure nano-sized ZnS particles show emission at 420-450 nm. In order to obtain different emission in the visible region ZnS nanoparticles can be doped with transition and rare-earth metals such as Cu²⁺, Mn²⁺, Ni²⁺, Cd²⁺, Co²⁺, Eu²⁺, Sm³⁺, Tb³⁺, and Er³⁺. ZnS doped with Mn²⁺ nano materials are having high quantum efficiency and luminescence intensity [10]. The band structure of the semiconductor changes with decreasing in particle size. Hence, the present study is aimed to synthesize nanoparticles of ZnS doped with Mn²⁺ and to characterize by optical studies.

2. Experimental

Mn²⁺ -doped ZnS nanoparticles were prepared by chemical co-precipitation method in air atmosphere. All chemicals used were of AR grade. Freshly prepared aqueous solutions of the

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chemicals were used to synthesized of the nanoparticles using Zn (CH₃COO)₂ .2H₂O, Mn (CH₃COO)₂ .4H₂O, Na₂S.9H₂O as starting materials. 50 ml of 1M Zinc acetate, 10 ml of 0.1M solution of manganese acetate and 50 ml of 1M solution of sodium sulphide were mixed using magnetic stirrer at 80 °C. Then 50 ml of ethanol was also added during stirring. Then 1 gram of 10 ml EDTA was added drop by drop and the process was continued for two hours. The role of EDTA is to stabilize the particles against aggregation, which may lead to decrease the size of particles. After 2 hours, the solution was cooled at room temperature. The precipitate was separated from the mixture at several times using distilled water and alcohol to remove the impurities, including traces of EDTA and the original reactants, if any. Finally the wet precipitate was dried in hot air oven.

X-ray diffraction (XRD) analysis of the samples were carried out on a XPERT-PRO diffractometer system operating at 40 kV and a current of 30 mA with CuK_α radiation ($\lambda=1.54060$ Å). SEM images of the particles were obtained using HITACHI S-3400 electron microscope with 20 Kv and elemental analysis were done using EDX attachment. The Photoluminescence measurements were carried out using a Jobin Yvon-Spex Spectro-fluorometer (Fluorog version-3; Model FL3-11). Xenon arc lamp was used as a excitation source and the detector (PM tube R928P) has a flat response from 240-1000 nm.

3. Results and discussion

The XRD patterns of the Mn²⁺ doped ZnS particles are shown in Figure.1 (with and without EDTA). The obtained results are very well matched with the standard cubic ZnS [11]. The peak broadening in the XRD pattern clearly indicates that small nanocrystals are present in the samples.

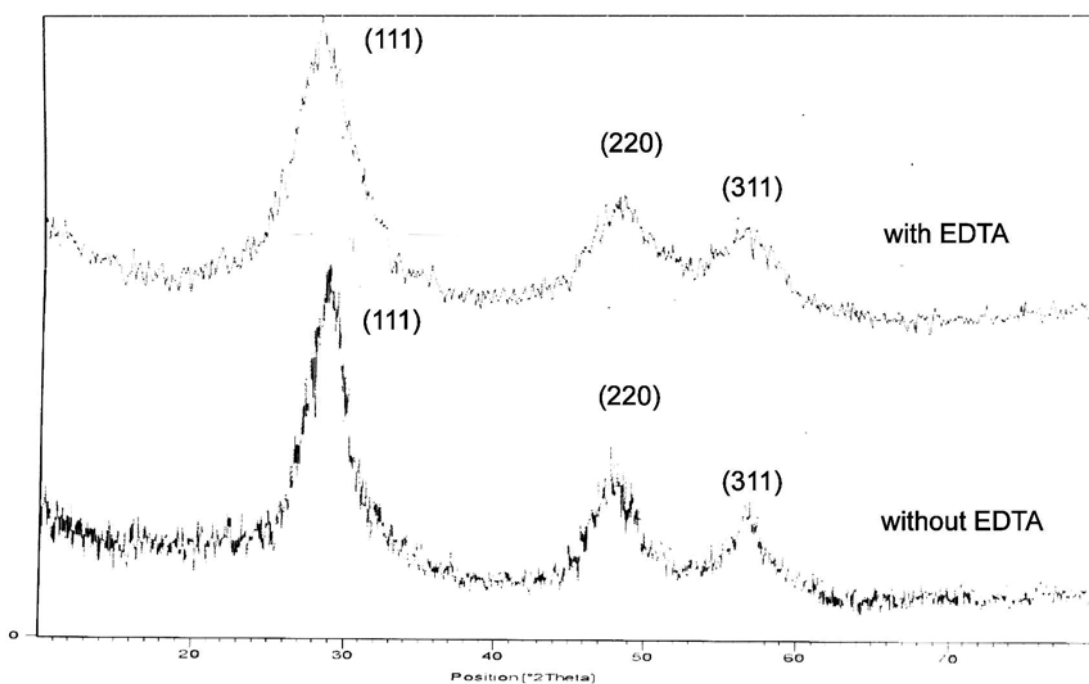


Fig..1.XRD Pattern of Mn²⁺ -doped ZnS nanoparticles.

From the value of FWHM, the mean crystalline sizes were calculated using Scherer's equation $D = 9\lambda/\beta \cos\theta$, where λ is the X-ray wavelength (for Cu k_α radiation, $\lambda=1.54060$ Å) and θ is the diffraction angle. The calculated mean crystal size is 4.5 nm for the material without EDTA and 3.6 nm with EDTA. To confirm these sizes, SEM microphotographs were taken and shown in figures 2a, 2b, 2c and 2d. The obtained results show the size of particles. The addition of EDTA

shows well dispersed images. The results are almost coincides with values obtained through XRD. Figure 3 shows the elemental concentration of sample.

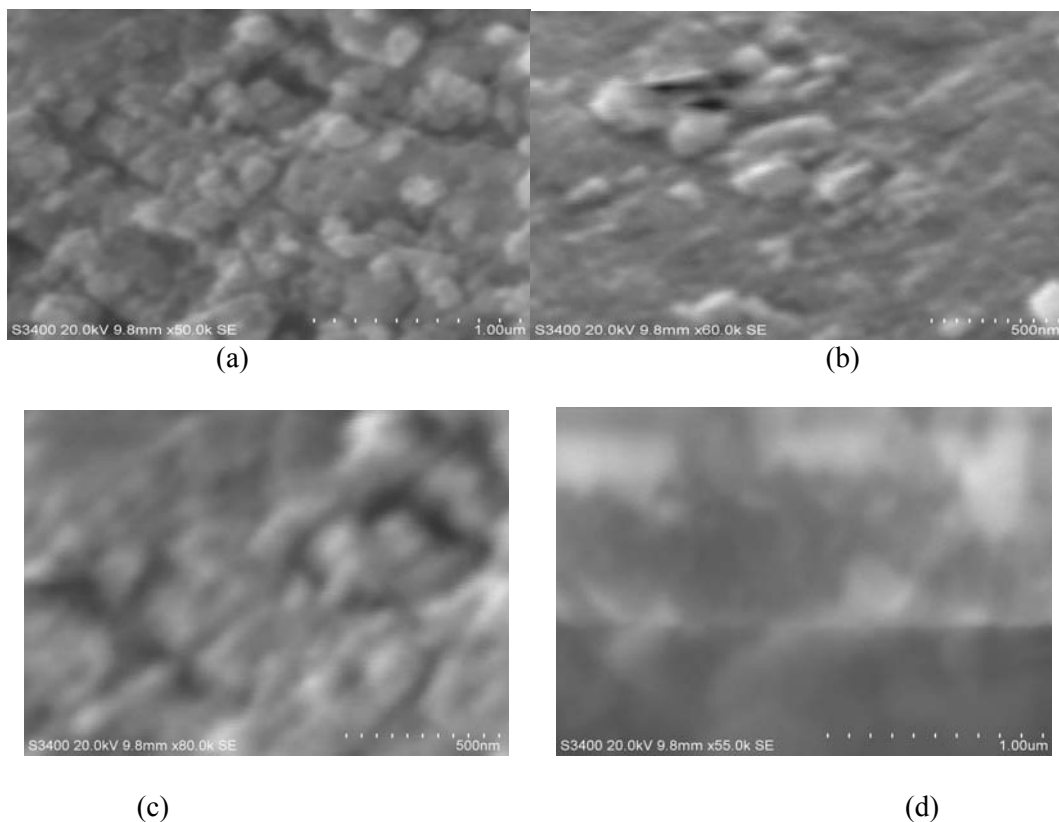


Fig. 2 (a,b)&(c,d) Show SEM image of with and without EDTA of Mn^{2+} doped ZnS nano particles.

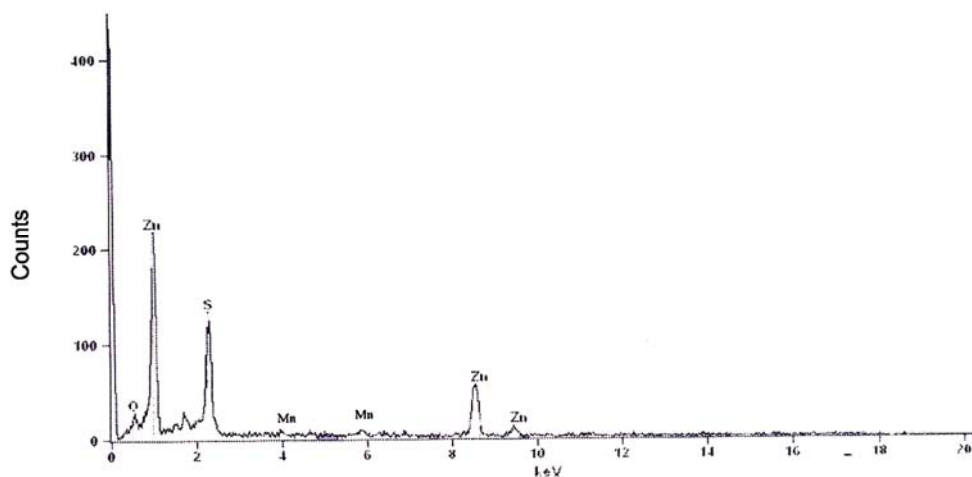


Fig. 3 Shows EDX spectrum of Mn^{2+} doped ZnS nanocrystals.

The PL measurements were carried out for the same samples. Fig. 4 shows emission and excitation spectrum of the doped nanocrystal. The excitation exhibits a dramatic blue shift with respect to the size of the particles which enlarges the energy gap and enhances the excitation energy. The same blue shift was reported by many authors [12-17]. According to Rossetti et al. [18], the blue shifting is due to the increasing in the energy band gap. This may be attributed to

quantum confinement effect. The emission was observed at 591 nm. This is consistent with the emission of Mn^{2+} in ZnS nanoparticles reported in literature [13, 19]. As suggested by Bargava et al. [13], this emission is attributed to the ${}^4\text{T}_1 - {}^6\text{A}_1$ transition of Mn^{2+} . According to Sookal et al. [20], the Mn^{2+} ions are distributed outside the ZnS nanocrystals. The PL is totally different from that of Mn^{2+} which is incorporated within the nanocrystals. Ge et al. [21] studied the same material doped with different concentrations of Mn^{2+} . They observed the optimum concentration level of Mn^{2+} , to get the maximum intensity. With reference to this, the present study is focused on this material.

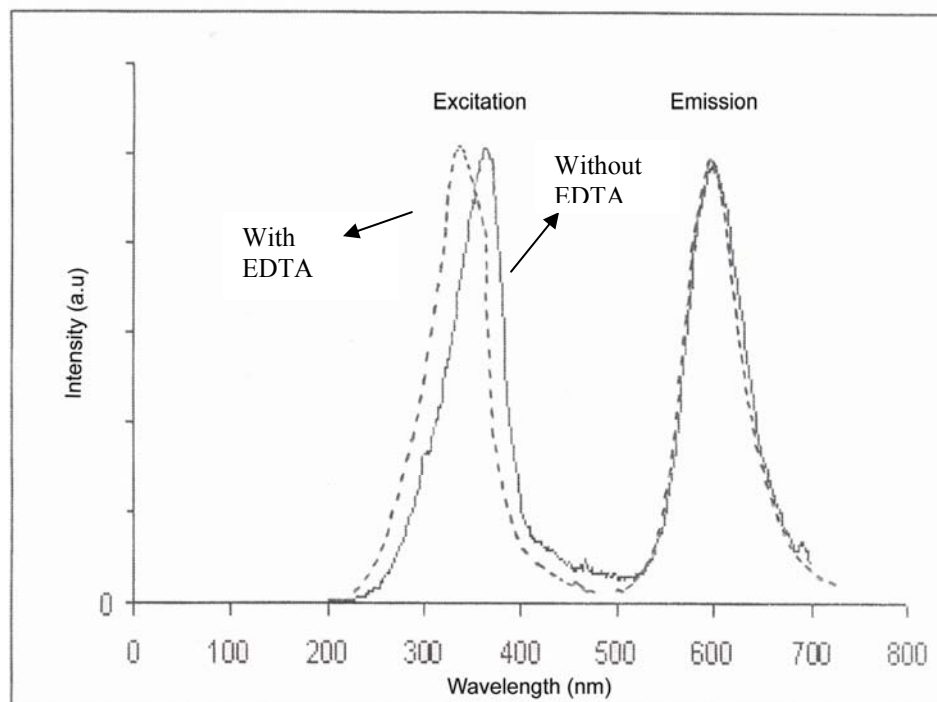


Fig. 4. PL excitation and emission spectra of with EDTA (dashed curve), without EDTA (solid curve) of ZnS: Mn^{2+} nanoparticles.

Su et al. [22] observed the excitation of 342 nm for ZnS: Mn^{2+} as a bulk material and at 310 nm for nanoparticles (3.5 nm) by chemical method. This indicated 32 nm of blue shift. The similar results were arrived for the present study. However, the addition of EDTA shows the blue shift around 25 nm (from 340 to 316) indicating the reduction of particle size from 4.5 nm to 3.6 nm.

4. Conclusion

Mn^{2+} doped ZnS nanoparticles have been synthesized by chemical method in air atmosphere with EDTA as a stabilizer and the emission was obtained at 591 nm through PL study. The particles size was controlled by the EDTA. The obtained nanoparticles are in the cubic zinc blended structure and the average sizes were determined using Debye Scherer formula. The results observed through SEM agree with those from XRD measurements.

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References

- [1] S. V.Gaponenko, Optical Properties of Semiconductor Nanocrystals, Cambridge University, Cambridge, 1998.
- [2] F. Himpfel, J. E. Ortega, G. J. Mankey, R. F. Willis, Adv. Phys. **47** 511 (1998).
- [3] Ye Changhui, Fang Xiaosheng, Li Guanghai, Zhang Lide, Appl. Phys. Lett. **85**(15) 3035 (2004).
- [4] H. C Warad, S. C. Ghosh, B. Hemtanan, C. Thaachayanont, J. Dutta, Science Technol. Adv. Mater. **6**, 296 (2005).
- [5] O.A Korotchenkov, A Cantarero, A.P Shpak, Yu A. Kunitskii, A. I. Senkevich, M.O.Borovoy A.B.Nadtochii, Nanotechnology **16** 2033 (2005).
- [6] G. F. J. Grlick, A. F. Gibson, J. Opt. Sos. Am. **39** 935 (1949).
- [7] I. Yu, M.K. Lu, D.R. Yuan, C.F. Song, S.W. Liu, X.F. Chag, J. Opt. Mater. **24** 497 (2003).
- [8] R.N.Bharagava, D.Gallager, T.Welker, J. Lumin.**60** 275 (1994).
- [9] N.Murase, R.Jagannathan, Y.Kanamatsu, M.Watanabe, A.Kurita, K.Hirata,T.Yazawa,T.Kushida, J. Phys. Chem. B **103** 714 (1999)
- [10] H. Hu, W. Zhang, Opt. Mater. **28** 536 (2006).
- [11] Song Wei Lu, Burtrand I. Lee, Zhong Lin Wang, Wusheng Tong, Brent K.Wanger, Wounjhang Park, Christopher J.Lumi **92** 73 (2001).
- [12] Y. Wang, N. Herron, K. Moller, and T.Bein, Solid Sate Commun. **77** 33 (1991).
- [13] R. N. Bhargava, D. Gallagher, X.Hong, and A. Nurmikko. Phys. Rev. Lett. **72** 416 (1994).
- [14] C. Jin, J. Yu, L. Sun, K. Dou, S. Hou, J. Zhao, Y. Chen, and S. Huang, J. Lumin. **66** 315 (1994).
- [15] J. P. Yang, H. Gray, D. Hsu, S. B. Qadri, G. Rubin, B. R. Ratna, W. L. Warren, and C. H. Seager, J. Soc. Inf. Disp. **6** 139 (1998).
- [16] J. Yu, H. Liu, Y. Wang, and W. Jia, J. Lumin. **79** 191(1998).
- [17] A. A. Bol and A. Meijerink. Phy. Rev. B **58** R15997 (1998).
- [18] R. Rossetti, R.Hull, J. M. Gibson, and L. E. Brus, J. Chem.Phy. **82** 552 (1985).
- [19] N. Murase, R. Jagannathan, Y. Kanematsu, M. Watanabe, A. K. Hirata, T. Yazawa, T.Kushida, J. Phys. Chem. B. **103** 754 (1999).
- [20] K. Sookal, B.S. Cullum, S.M. Angel, C. J. Murphy, J. Phys. Chem. **100** 4551 (1996).
- [21] J. Ge, J. Wang, H. Zhang, X. Wang, Q. Peng, Ya Li, Adv. Funct. Mater. **15** 303 (2005).
- [22] F.H. Su, Z. L. Fang, B. S. Ma, K. Ding, G. H. Li, W. Chen, J. Phys. Chem. B **107** 6991