Room Temperature Synthesis and photoluminescence studies of Eu doped and Cu co-doped ZnS nanoparticles

Murali Ankinapalli[1,a], Harish G S[2,b] , Sowjanya Munga[1,c], Sreedhara Reddy P[1,d,*]

[1]Department of Physics, Sri Venkateswara University, Tirupati, India- 517502

[2]Lecturer in Physics, Government Polytechnic, Pillaripattu, A.P., India-517583

Keywords: Chemical Co-precipitation, EDS, XRD, TEM, photoluminescence.

Abstract. ZnS: Eu, Cu nanoparticles were synthesized by the chemical co-precipitation method. The effect of doping of Eu^{3+} and Cu^{2+} co-doping on the photoluminescence (PL) of the samples were investigated at room temperature. Crystallite sizes of the prepared nano samples were calculated using the X-ray diffraction patterns, and broadened peaks showed the nano regime of the prepared particles. The results showed that all the nanoparticles had a cubic zinc blende structure. The morphological effects were studied using scanning electron microscopy (SEM) evidenced the accumulation of nanoparticles, and a marginal decrease in the particle size was observed with Cu doping. Energy dispersive spectroscopy (EDS) analysis showed the effective doping of Cu into ZnS: Eu and the transmission electron microscopy (TEM) image (ZnS: Eu (4 at. %), Cu (4 at. %)) indicate the formation of nanoparticles of nearly uniform size. Photoluminescence (PL) spectra of the samples showed prominent emission peaks around 450 nm, 507 nm, 518 nm and 591 nm with the incorporation of Eu^{3+} and Cu^{2+} into ZnS host lattice. The PL intensity increased with an increase in Cu concentration. This work suggests that Eu^{3+} doped and Cu^{2+} co-doped ZnS nanoparticles prepared by the chemical co-precipitation method can be used for Light-Emitting Diodes.

Introduction.

Zinc sulfide is one of the best suitable host for tuning the electrical, photocatalytic, photoluminescence, optical and magnetic properties by doping with rare earth and transition metal ions. Because of the abundant availability on the earth, non-toxicity, easy production, good electrical properties, and thermal stability, ZnS nanoparticles find many applications like light-emitting diodes, UV laser emitters, pyroelectric and gas sensors, nano-phosphors, photo-catalysts, optoelectronic devices, bio-medical devices, spintronic devices [1-7]. Furthermore, due to the nano-size distribution, they exhibit enhanced luminescence and exciting properties compared to bulk ZnS. ZnS nanomaterials can be prepared by various top-down and bottom-up techniques. Among those synthesis methods, chemical co-precipitation [8] is used because of its advantages over other techniques as it enables the tune of the dopant concentration and cost-effective facile approach.

Zinc sulfide doped with rare-earth ions and transition metal ions exhibits enhanced photoluminescence electrical and magnetic properties. To lower the accumulation of the prepared

nano particles and reduce the particle size to nano regime, Polyvinylpyrrolidone was used as a capping agent. In this present study, Eu doped ZnS is co-doped with copper and various properties of ZnS: Eu, Cu were investigated in detail.

Experimental and Characterization techniques.

ZnS: Eu, Cu nanoparticles were prepared by the facile chemical co-precipitation technique using pure Zinc acetate, Europium chloride, Copper acetate and Sodium sulfide with PVP as capping agent. In this technique, Appropriate amounts of $Zn(ac)_2$, ($EuCl_3$), $(CH_3COO)_2Cu.H_2O$ and PVP were dissolved in 50 ml of Ethanol. Then, Na_2S is dissolved in 50 ml of Ethanol and is added drop wisely added to the previous solution under constant stirring. Then, the stirring was continued for 3 hours, and fine precipitates of Eu, Cu co-doped ZnS nanoparticles capped with PVP was obtained. Then, the impurities were removed by filtering and washing the solution 3 to 4 times. Finally, this white precipitate is dried at 80^0C using an oven, and a nano sample is obtained.

The as-prepared nanopowders were analyzed using structural, compositional, surface morphological and photoluminescence studies. The X-ray diffraction analysis of the prepared nanopowders was carried out using "Rigaku - D X-ray diffractometer using Cu-Kα (λ=1.5406A°) radiation". The surface morphological and elemental analysis of the prepared nano samples were studied by "EDAX using Oxford Inca Penta FeTX3 EDS instrument attached with a Carl Zeiss EVO MA 15 scanning electron microscope". Surface morphology of the sample and particle size were studied using "TECHNAI-TEM FEI Transmission Electron Microscope (TEM)", with an operating acceleration of 100–200 kV Photo-luminescence studies were carried out in the wavelength range of 350–700 nm, using a PTI (Photon Technology International) Fluorimeter with a Xe-arc lamp (power 60 W). The excitation wavelength was 320 nm.

Structural analysis.

Fig.1 shows the XRD peaks of the prepared ZnS: Eu, Cu nanopowder samples. Three broad peaks corresponding to the lattice planes (111), (220) and (311) were observed, and the diffraction pattern of the samples exhibits cubic zinc blende structure, which is confirmed by the JCPDS card no. 80-0020. Broad peaks indicate the nanoparticle nature, and any other peaks due to impurities were observed.

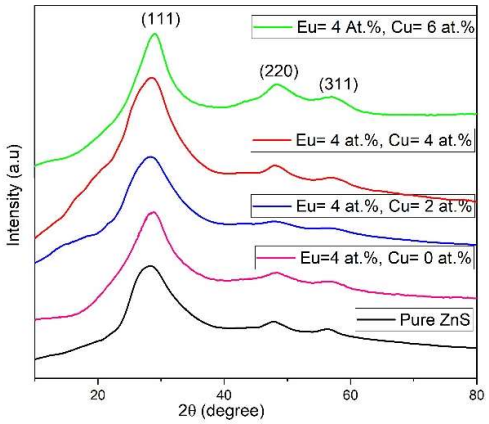

Figure 1. XRD study of Eu and Cu co-doped ZnS nanoparticles

The average particle size is determined using Debye-Scherer's equation [9] shown below:

$$D = 0.94\lambda/\beta\cos\theta$$

Where D is average particle size, λ is wavelength in A0, β is full-width, half-maximum and θ is Bragg's angle. Co-doped ZnS samples were the particle size obtained for the Pure ZnS, Eu (4 at. %) and Cu (0 at. %, 2 at. %, 4 at. % and 6 at. %) 14.2, 10.4, 8.8, 6.2 and 7.6 nm, respectively. In addition, an increase in particle size at higher concentrations was observed, which may be due to Cu-Cu ions interaction in the ZnS host lattice.

Morphological studies.

The surface morphological studies of ZnS: Eu, Cu nanoparticles are shown in Fig.2 confirm the spherical particles with agglomeration, and the accumulation of the particles is slightly decreased for Eu= 4 at. % and Cu= 4 at. % co-doped ZnS nano sample.

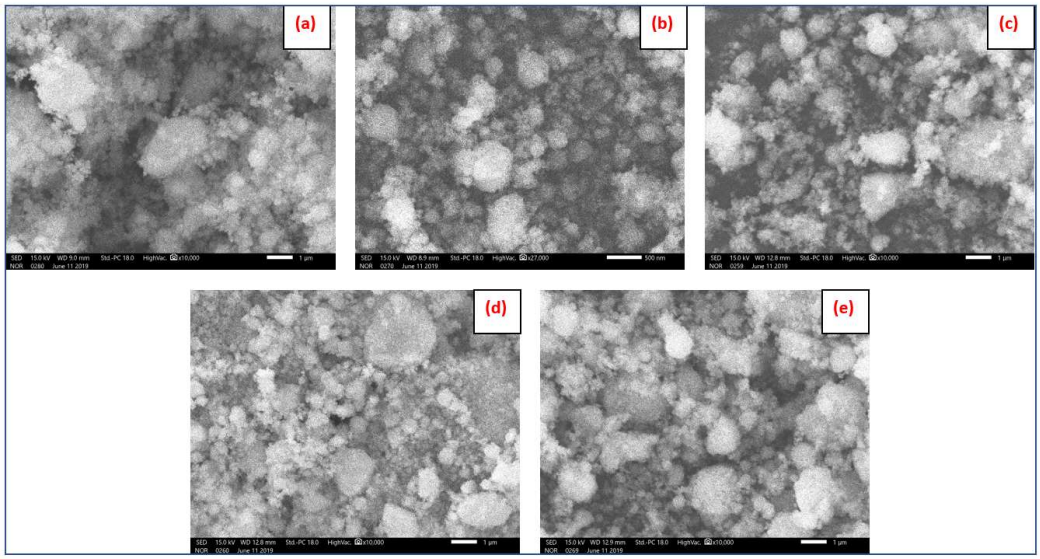

Figure 2. SEM images of ZnS: Eu, Cu nanoparticles. (a) Pure ZnS and (b) Eu= 4 at.% (c) Eu = 4 at. %, Cu= 2 at. % and (d) Eu = 4 at. %, Cu= 4 at. % and (e) Eu = 4at. %, Cu= 6 at. %.

Compositional analysis.

Fig.3 shows EDS spectra of the prepared ZnS nanoparticles co-doped with Eu and Cu. The EDS spectra confirm the existence of Zn, Eu, Cu and S, and hence the incorporation of Eu and Cu ions into the ZnS host lattice.

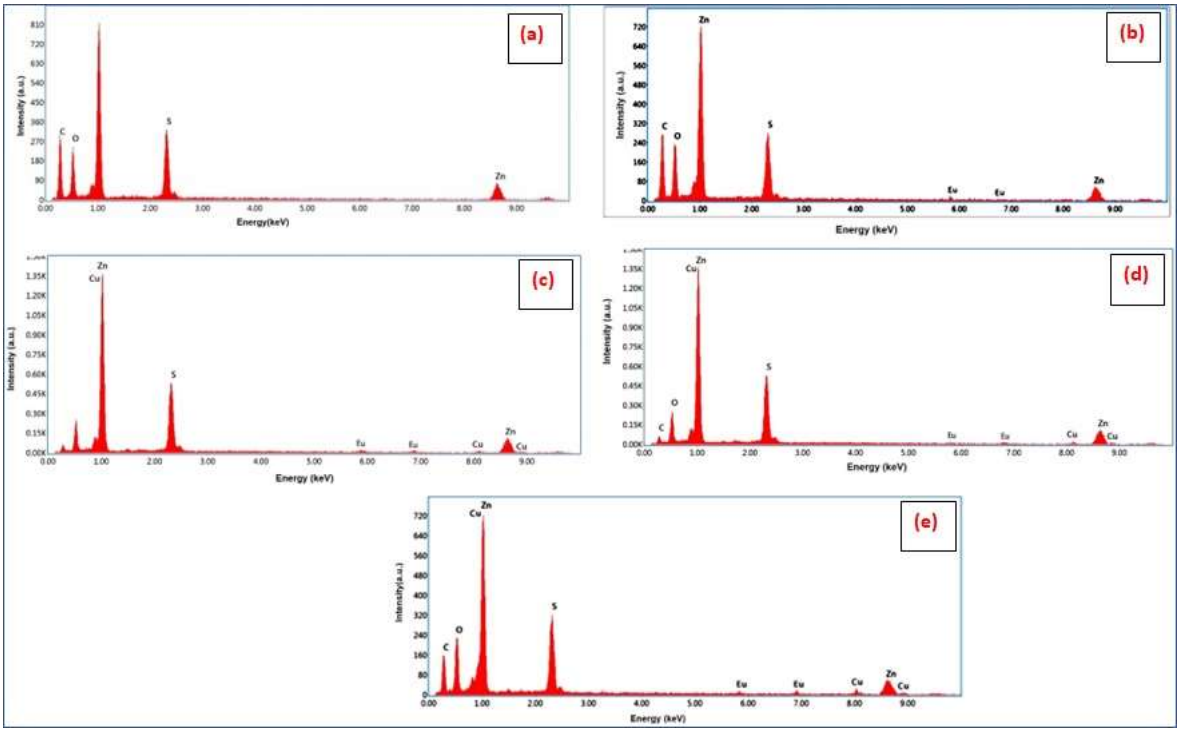

Figure 3. The EDS spectra of ZnS:Eu, Cu co-doped nanoparticles. (a)Pure ZnS, (b)Eu = 4 at. %, Cu= 0 at. %. (c) Eu = 4 at. %, Cu= 2 at. % and (d) Eu = 4 at. %, Cu= 4 at. % and (e) Eu = 4 at. %, Cu= 6 at. %

From the EDS spectra, the Eu peaks intensity is almost the same, but the intensity of the characteristic Cu peak increased with increasing the Cu dopant concentration. It denotes the effective doping of Eu and Cu into the ZnS.

TEM analysis.

Eu (4 at. %), Cu (4 at. %) co-doped ZnS nano sample with spherically shaped nanoparticles are visible in fig 4. The nano-sized distribution was obtained due to the adding of PVP. The nanoparticle distribution observed in this Characterization is in good agreement with the XRD studies.

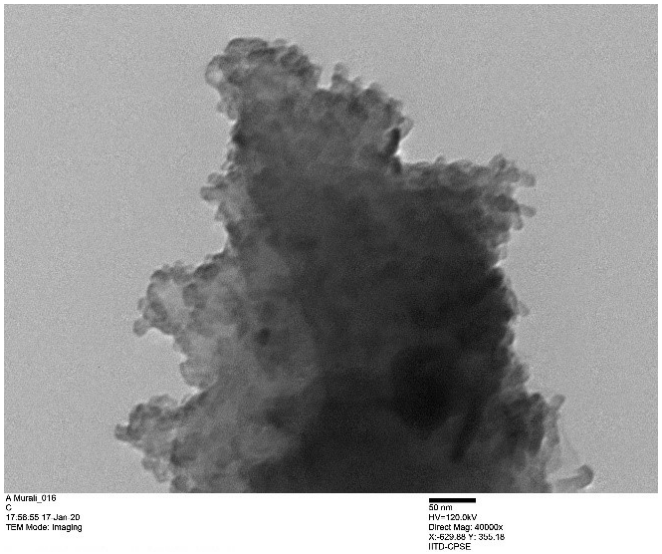

Figure 4. TEM image of Eu = 4 at. % and Cu= 4 at. % co-doped ZnS nanoparticles

Photoluminescence Studies.

The photoluminescence (PL) spectra of Eu, Cu co-doped ZnS nanoparticles prepared at room temperature are shown in fig.5. All the samples were excited at a wavelength of 320 nm, and the photoluminescence spectra showed broad and intense peaks around 450 nm, 507 nm, 518 nm and 591 nm. The broad peak observed around 450 nm is due to the recombination of sulfur vacancies with the holes in Zn. The green emission peak at 507 nm arises due to the recombination of the sulfur vacancy with the t_2 level Cu^{+2}[11].

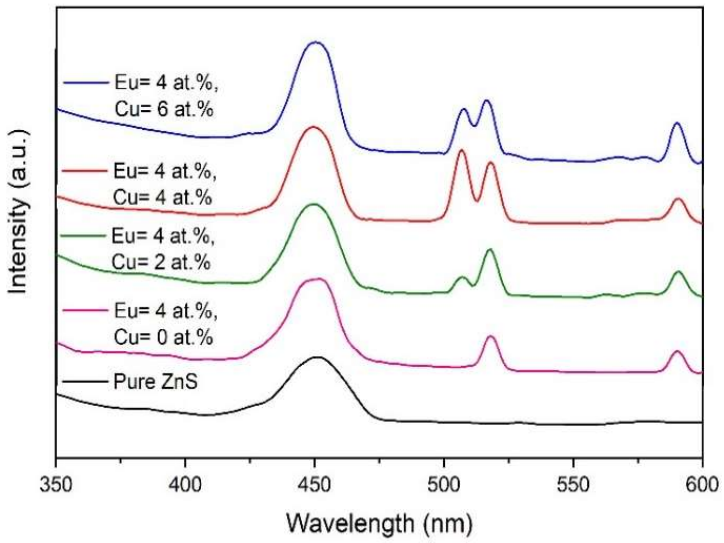

Figure 5. Room temperature photoluminescence spectra of Eu, Cu co-doped ZnS nanoparticles

The intensity of this peak is increased with cu dopant concentration. The emission peaks observed at 518 nm and 590 nm were attributed to the incorporation of Eu into ZnS and were well

supported by the reports of C.K. Krishna Sagar et al. [12] and Sabit Horoz et al.[13]. Eu^{3+} ions doped ZnS shows a luminescence peak at 591 nm due to the $^5D_0$ to $^7F_2$ energy level. An increase in luminescence intensity leads to scope in light-emitting diode applications.

Summary

Eu, Cu co-doped ZnS are successfully prepared by the facile, chemical co-precipitation method and PVP was used as a capping agent. The crystalline size decreases with increasing Cu dopant concentration up to 4 at. %. SEM images exhibit spherically shaped particles with agglomeration. EDS data shows the effective doping of Eu and Cu into the ZnS host lattice. The HRTEM image shows nanoparticle distribution, which is well supported by the XRD studies. PL spectra show green emission corresponding to Cu2+, which finds optoelectronic device applications.

References

[1] Wood, V., Halpert, J. E., Panzer, M. J., Bawendi, M. G., & Bulovic, V. Alternating current driven electroluminescence from ZnSe/ZnS: Mn/ZnS nanocrystals. Nano letters, (2009): 9(6), 2367-2371.

[2] Horoz, S., Dai, Q., Maloney, F. S., Yakami, B., Pikal, J. M., Zhang, X., Tang, J. Absorption induced by Mn doping of ZnS for improved sensitized quantum-dot solar cells. *Physical Review Applied*, (2015): *3*(2), 024011.

[3] Fang, X., Zhai, T., Gautam, U. K., Li, L., Wu, L., Bando, Y., & Golberg, D. ZnS nanostructures: from synthesis to applications. *Progress in Materials Science*, (2011): *56*(2), 175-287.

[4] Mehta, S. K., & Umar, A. Highly sensitive hydrazine chemical sensor based on mono-dispersed rapidly synthesized PEG-coated ZnS nanoparticles. *Talanta*, (2011): *85*(5), 2411-2416.

[5] Lei, Y., Chen, F., Li, R., & Xu, J. A facile solvothermal method to produce graphene-ZnS composites for superior photoelectric applications. *Applied surface science*, (2014): *308*, 206-210.

[6] Yin, J., Wang, J., Li, H., Ma, H., Li, W., & Shao, X. Unique ZnS nanobuns decorated with reduced graphene oxide as an efficient and low-cost counter electrode for dye-sensitized solar cells. *Journal of energy chemistry*, (2014):*23*(5), 559-563.

[7] Chu, B., Zhang, N., Zhai, X., Chen, X., & Cheng, Y. Improved catalytic performance of Ni catalysts for steam methane reforming in a micro-channel reactor. *Journal of energy chemistry*, (2014): *23*(5), 593-600.

[8] Harish, G. S., Reddy, P. S. Synthesis and characterization of Ce, Cu co-doped ZnS nanoparticles. *Physica B: Condensed Matter*, (2015): *473*, 48-53.

[9] Patterson, A. L. The Scherrer formula for X-ray particle size determination. *Physical review*, (1939): *56*(10), 978.

[10] Chen, Z., Li, X. X., Chen, N., Du, G., Li, Y., Liu, G., & Suen, A. Y. Study on the optical properties of $Zn_{1-x}Mg_xS$ ($0 \leq x \leq 0.55$) quantum dots prepared by precipitation method. *Materials Science and Engineering: B*, (2012):*177*(3), 337-340.

[11] Peng, W. Q., Cong, G. W., Qu, S. C., & Wang, Z. G. Synthesis and photoluminescence of ZnS: Cu nanoparticles. *Optical Materials*, (2006): *29*(2-3), 313-317.

[12] Sagar, C. K., Sajan, P., & Bushiri, M. J. Eu^{3+} and Cu^{2+} ions doped ZnS microspheres emission in the yellow–orange region. *Journal of Materials Science: Materials in Electronics*, (2019): *30*(19), 18220-18226.

[13] Horoz, S., Yakami, B., Poudyal, U., Pikal, J. M., Wang, W., & Tang, J. Controlled synthesis of Eu^{2+} and Eu^{3+} doped ZnS quantum dots and their photovoltaic and magnetic properties. *AIP Advances*, (2016): *6*(4), 045119.