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UV Visible Spectroscopy and Photoluminescent Characteristics of Li^{+1} and Cs^{+1} co-doped ZnS nanoparticles

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Abstract: **ZnS nanoparticles is synthesized by the chemical co-precipitation method using L-arginine as a capping agent and co-doped with different concentrations of Li+1 and Cs+1. The UV visible absorption spectra showed a blue shift in the absorption peaks of the co-doped sample as the doping concentration was increased. The photoluminescence spectra of ZnS nanoparticles showed a blue shift when doped with Li+1 and Cs+1. On increasing the concentration of dopants, the relative intensity of the emission peaks showed a considerable enhancement.**

Index Terms: **Blue shift, Doped ZnS NPs, Photoluminescence, quantum confinement, UV Visible spectroscopy**

I. INTRODUCTION

Zinc Sulphide is the most investigated II–VI compound semiconducting material with direct and wide band gap of 3.6 eV (Fang X. et al., 2011). It has traditionally shown remarkable versatility, novel fundamental properties and diverse applications such as field emitters, field effect transistors (FETs), p-type conductors, catalysators, UV-light sensors, chemical sensors (including gas sensors), biosensors, nonlinear optic devices and nano generators (Bhargava R. N et al.,1994;Yang P et al., 2003). The quantum confinement effect in ZnS nanoparticles with large S/V ratios has resulted in high density of surface states and a spectral blue-shift of absorption (Talwalkar S. et al., 2018). The optical and electrical properties of Zn Scan are tailored easily by adding suitable dopants. The intentional addition of impurities to ZnS matrix during the growth process induces dramatic changes in the corresponding morphological and optical properties. The efficiency of the dopant element depends on its electronegativity and ionic radius. Various researchers have reported the enhancement of optical properties of ZnS doped with rare earth elements e.g., ZnS-Mn, ZnS-Ag, ZnS-Ni, ZnS-Ce, etc. (Bhargava R. N et al.,1994; Diaz &Torres, et al., 1998; Khosaravi A et al., 1995; Murase N. et al., 1999; Papakonstantnou D. et al. 1998; Xu S. J et al. 1998; Yang P. et al., 2001; Yu I. et al., 1995; Yu J et al. 1998). Yang et.al (2003) reported luminescent characteristics of Cu^{2+} and Co^{2+} co-doped ZnS nanoparticles and found the luminescent intensity to be dramatically higher than undoped samples.

An attempt has been made to synthesis of Li^{+1} and Cs^{+1} co-doped ZnS nanoparticles using L-Arginine as capping agent by chemical reduction method. The chemical reduction method is generally used for the synthesis of II–VI semiconductor nanostructures and this method has a number of advantages including easy process ability at ambient conditions, possibility of doping different kinds of impurities with high doping concentrations even at room temperature, good control over the chemistry of doping and easiness of surface capping with a variety of different steps involved in the synthetic process of nanoparticles (Firdous et al., 2012). The synthesized nanoparticles are characterized by UV-visible (UV-visible) spectroscopy and photoluminescence (PL).

II. MATERIALS AND METHODS

Zinc chloride ($ZnCl_2$, 99 % purity), sodium sulphide (Na_2S), lithium chloride (LiCl), Cesium chloride (CsCl), L-Arginine purchased from Sigma-Aldrich (Germany) were analytical grade purity and used without further purification. Double distilled water was used in the synthesis process.

ZnS NPs were synthesized by using chemical co-precipitation method. L-Arginine was used as a capping agent and Na_2S was used as reducing agent in the process. The precipitates were centrifuged for 25 min at 4800 rpm. Final product washed several times with methanol followed by water and dried optically at a temperature 40^{o}C for 20 hrs to remove water and other volatile organic by-products formed during synthesis process. The samples in powder form were used for further characterizations.

III. RESULTS AND DISCUSSION

A. *UV Visible Spectroscopy*

Figure 1 shows UV absorption spectra and Figure 2 shows UV transmission spectra of L-Arginine capped ZnS nanoparticles co doped with Li^{+1} and Cs^{+1}. From the absorption spectra we see that absorption edge is observed at 347 nm for 1wt% doping concentration, 326 for 2wt% doping concentration and 320 for 5wt% co-dopant concentration. A shift in the absorption edge is observed towards the lower wavelength side as doping concentration is increased, i.e., blue shifted. The blue shift in the absorption spectra of doped ZnS nanoparticles in comparison with the undopedZnS (3.65 eV) is related to quantum confinement effect.

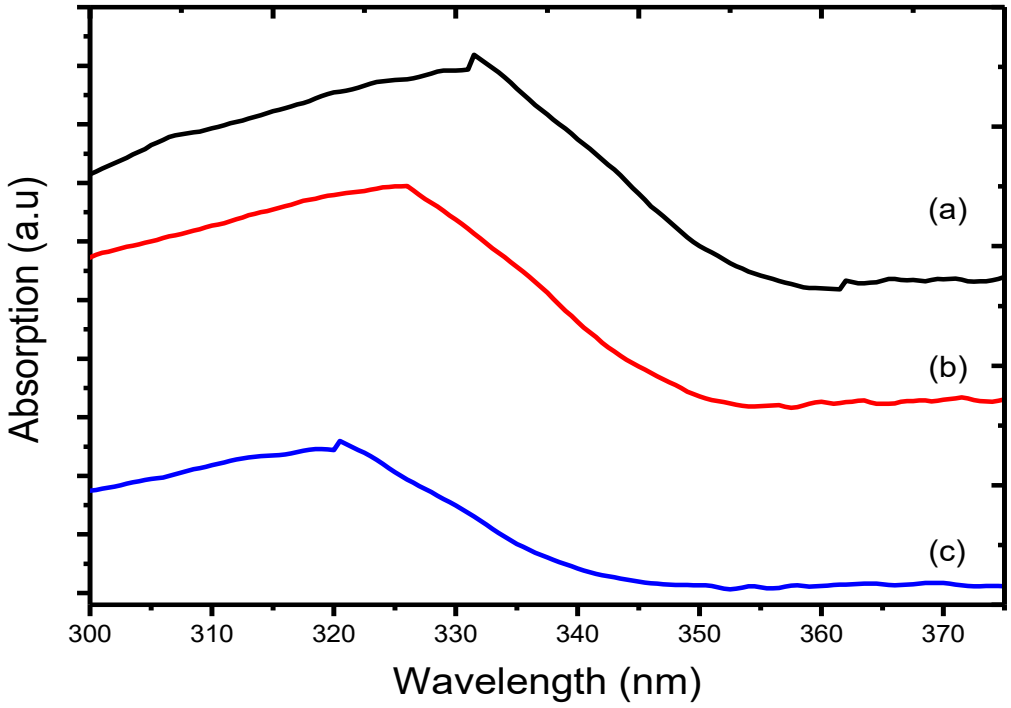

Fig.1 UV visible absorption spectra of L-Arginine capped ZnS nanoparticles co-doped with Li^{+1} - Cs^{+1} with (a)1 (b) 2 and (c)5 wt % concentrations.

The band gap energy is calculated by extrapolating the linear part of the (αhν)2vs (hν) graph on the (hν) axis as shown in the Figure 2. The band gaps estimated for 1, 2 and 5 wt % of co-doped ZnS nanoparticles are 4.2, 4.8 and 5.4 eV respectively. It is found that on increasing the percentage of dopants the band gap value increases which confirms the decrease in the particle size.

B. *Photoluminescence*

Figure 3 show PL spectra of ZnS nanoparticle capped with L-arginine co-doped with Lithium and Cesium with doping concentrations of 1, 2 and 5 wt %. The PL spectra reveals increase in the relative intensity as the doping concentration is increased from 1 to 5wt%. Such dramatic increase in intensity of doped samples is reported earlier (Talwatkar S. et al., 2015). The relative intensity of co-doped nanoparticles is considerably increased as compared to pure form of the sample. From the spectra of ZnS doped with 1 wt% a peak is observed at wavelength 498 nm, for 2wt% the peak is centred at 480 nm and for 5wt% it is centred at 450 nm. i.e., the relative intensity peak of different doping concentrations is blue shifted with increase in the dopant concentration.

For the nanometre luminescent materials, we cannot ignore the existence of the electron- or hole-trapped surface levels on the nanoparticles. The PL mechanism of the doped ZnS nanoparticles is very complex. First, the smaller particles have higher surface/volume ratio and more surface states. Therefore, they contain more accessible carriers for PL (Sunatkari A. et al., 2011). This indicates that the surface states are very important for the physical properties especially the optical properties of nanoparticles. In nanoparticles, most ions at the surface are non-saturated in coordination. Electrons and holes may be excited easily and escape from the ions. Many carriers trapped at the surface states or defect sites may be released by photo excitation. So, PL intensities of nanoparticles are higher than those of bulk material. In the ZnS nanoparticles co-doped with Li^{+1} and Cs^{+1}ion, Li^{+1} and Cs^{+1} ion is assumed to substitute for Zn atoms or to be interstitial ions (Socrates G., 2004; Talwalkar S. et al., 2017; Zhang J., 2007).

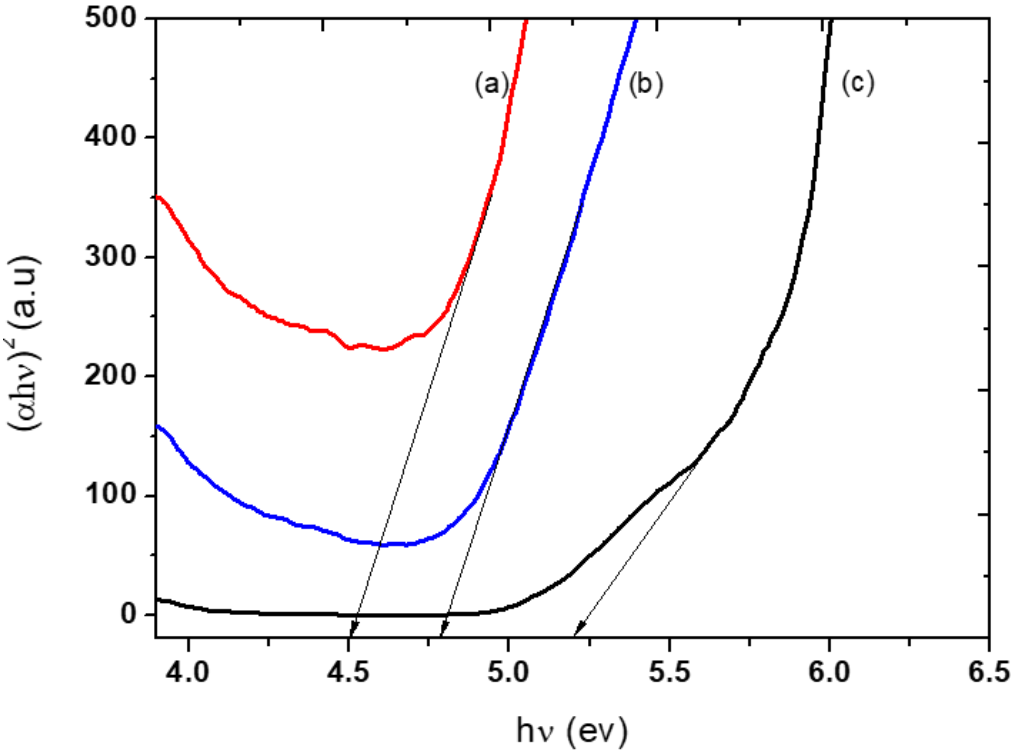

Fig.2 Graph of hυ vs. (αhυ)2 for (a) 1, (b) 2 and (c) 5 wt% of (Li^{1+}+Cs^{1+}) co-doped ZnS.

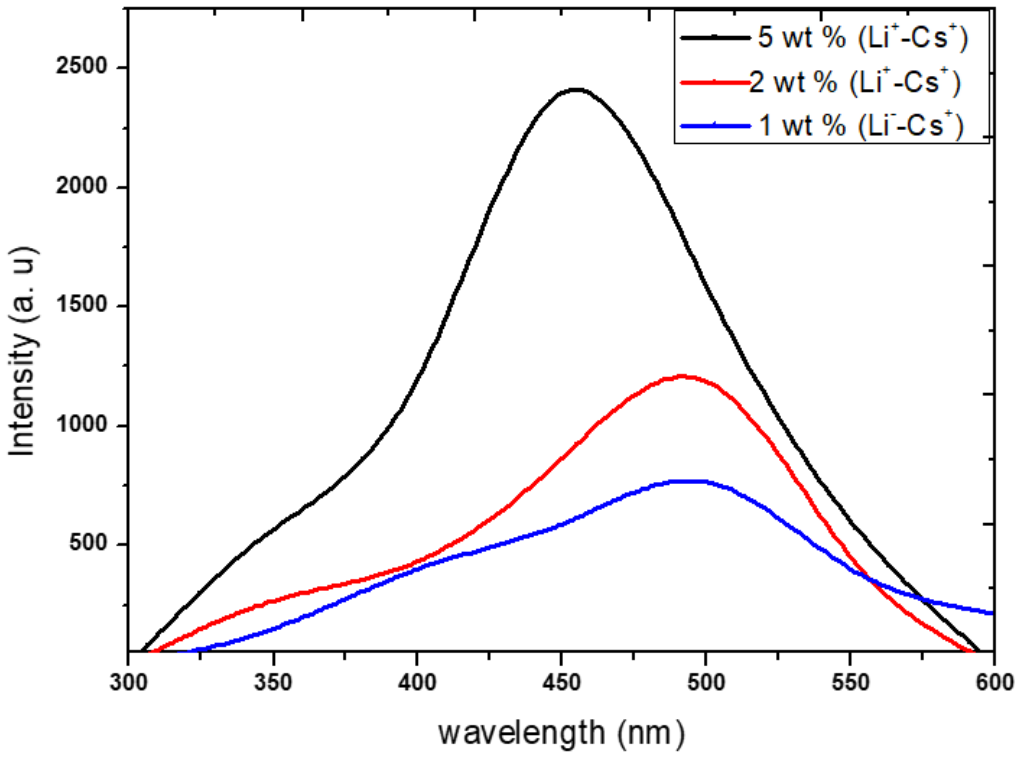

Fig.3 PL spectra of ZnS NPs with 1, 2 and 5 wt% (Li^{1+}+Cs^{1+}) co-dopant.

CONCLUSION

Li^+ and Cs^+ co-doped ZnS nanoparticles were synthesized by chemical co-precipitation method using L-Arginine as a capping agent. Li^+-Cs^+ co-doped ZnS nanoparticles have a broad emission at 347 nm which blue shifted with increase in the concentration of the dopants. The PL spectra shows enhancement in relative intensity for highest doping concentration.

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