

CHAPTER 2

REVIEW OF LITERATURE

2.1. Review of Literature:

Synthesis and characterization of both CdS and ZnS nanoparticles have been carried out by many researchers. So, in order to gather information about the work done, literature survey was done in detail.

This section reviews the earlier works reported on undoped CdS nanoparticles. Qi et. al. (2001) [1] have synthesized monodispersed CdS nanoparticles using double hydrophilic block copolymers consisting of a solvating polyethylene glycol block and a polyethylene imine as a stabilizer in water and methanol. The nanoparticles are found to be cubic in structure with sizes ranging from 2 nm to 4 nm. Prabhu and Khadar (2005) [2] have characterized the synthesized CdS nanoparticles using chemical precipitation method by XRD, UV-visible and photoluminescence. The occurrence of blue shift in the UV spectra have reflected the quantum confinement of the particles and the grain size determined from Brus equation do not agree closely to that obtained from Scherrer equation.. Martinez-Castanon et. al (2005) [3] have reported the synthesis of CdS nanoparticles using aqueous precipitation method. The TEM images showed well dispersed particles and the particle size estimated by Rietveld and optical absorption are in good agreement. They have also shown that the reduction in particle size gave a shift in the optical band gap and luminescence is observed in the red portion of the spectra. R. Devi et. al. (2007) [4] have prepared CdS films by CBD technique in PVA matrix and reported that the crystallite sizes obtained from XRD studies are smaller than those obtained from SEM. Their UV absorption studies on films clearly have shown an increase in band gap which supported the formation of nanocrystallites in the synthesized films. Singh and Chauhan (2009) [5] also have investigated CdS semiconducting quantum dots synthesized by chemical method using thioglycerol as capping agent. XRD, TEM, UV-vis spectrophotometer and PL spectra are employed to characterize the size,

morphology and crystalline structure of the as prepared samples. They have also shown that the synthesized quantum particles are a mixture of cubical and hexagonal crystal symmetry with 12 nm average diameter. Dwivedi et. al. (2010) [6] have synthesized CdS nanoparticles by chemical synthesis method using ethylenediamine as capping agent. Blue shift indicating quantum confinement of charged particles and the transformation of phase of CdS nanoparticle from hexagonal to cubic has been reported. Khan et. al. (2010) [7] have synthesized CdS thin films deposited on Si (1 0 0) substrates by thermal evaporation technique and are found to be polycrystalline in nature with hexagonal structure. Their crystallite sizes obtained by XRD studies are found to be smaller than those obtained from SEM and the lattice parameters in well agreement with the standard values. Sabah et. al. (2010) [8] have prepared five samples of CdS nanoparticles from stoichiometric weights of cadmium sulphate and thioacetamide by using aqueous precipitation techniques with different molar ratios and have treated the samples at different radiations like microwave, ultrasonic and sunlight to control the size, shape and growth of CdS nanoparticles. The formation of CdS nanocrystals with different shape, size and texture are confirmed from SEM analysis and showed that the particle sizes increases with increase in reaction time. Dhanam et. al. (2010) [9] have reported the XRD profiles of nanocrystals synthesized at three different times and have shown that the particles were in uniform shape and size and their surface morphology varied with reaction time. Ramamurthy et. al (2011) [10] have synthesized spherical shaped CdS nanoparticles through chemical method using different capping agent i.e. polyvinyl pyrrolidone (PVP) and sodium polyphosphate (SPP). They have shown that the absorption peak of the capped particles is significantly blue shifted and PL emission are enhanced as compared with uncapped CdS nanoparticles. Both uncapped and capped CdS nanoparticles have revealed cubic structure. Singh et. al. (2011) [11] have reported size tunability of thioglycerol capped CdS nanoparticles by controlling the capping reagent concentration as well as annealing temperature through chemical precipitation method. They have stated that annealing improved the crystallinity and reduced the defect levels. Bansal et. al. (2012) [12] have investigated the chemical colloidal method for synthesis of

CdS nanoparticles by using glucose as capping agent and showed that the method used is eco-friendly for commercial scale production as it does not involve the use of hazardous and toxic capping agents such as thiophenol, thiourea and mercaptoacetate. Further they have also shown the occurrence of blue shift in λ_{max} . Seoudi et. al. (2012) [13] have synthesized CdS nanoparticles with different sizes dispersed in PVA matrices in the form of PVA/CdS nanocomposite and reported the formation of cubic phase in PVA matrix. They have calculated the blue shift and optical band gap as a function of the particle sizes from the UV-visible spectra.

A variety of dopants are used in the synthesis of CdS nanoparticles. In this section, works for doped CdS that has been reported so far are being reviewed which includes the variety of dopants used for doping with some theoretical considerations and applications oriented work on doped nanoparticles. Levy L. (1996) [14] et. al. have synthesized Mn doped CdS nanoparticles by using reverse micelles with varying Mn concentration from 0 to 0.3 and obtained particle sizes ranging from 1.9 nm to 3.5 nm. They have discussed quantum size effect from optical absorption studies and found fixed size of nonlinear variation of the band gap versus composition. Liu et. al. (2000) [15] have investigated manganese doped CdS nanoparticles in aqueous solution by using mercapto acetate as capping agent. Their optical studies have shown that the emission band is dominated by $\text{Mn}^{2+} {}^4\text{T}_1 - {}^6\text{A}_1$ transition with the photon energy of 2.12 eV and no distinguishable emission from surface defect states of CdS matrix is observed. They have also concluded that there is an efficient energy transfer from shallow surface states to Mn^{2+} centres and minimization of surface defect states to radiative recombination on CdS:Mn nanoparticles. Artemyev et. al. (2001) [16] have reported manganese doped CdS nanocrystals by sol-gel method. They have studied photoluminescence spectra and kinetics of the Mn^{2+} ions emission at room temperature and showed that quantum confinement effect do not modify the emission life time as compared to bulk materials. Nag et. al. (2008) [17] have prepared different sized $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ by merely varying the synthesis temperature using 1-thioglycerol as capping agent and reported that a very

small fraction of Mn^{2+} ions are incorporated into the CdS lattice. They have shown that with increase in temperature, the Mn^{2+} ions shift towards the surface of the nanocrystals and the PL spectra of doped nanocrystals differ from that of undoped nanocrystals with an additional peak due to Mn d - d transitions. Marandi et. al. (2008) [18] have studied the thermo-mechanical growth of Mn doped CdS nanoparticles and found that a prolonged reaction time decreases the intensity of Mn luminescence peak to about 35% of the original value. Rathore et. al. (2009) [19] have synthesized Cu doped CdS nanoparticles by wet chemical method having cubic structure and about 2 nm in size. Photoluminescence spectrum of undoped CdS exhibited a defect related emission peak whereas doped CdS emission peak is due to relaxation of carrier from excitonic state of host CdS to T_2 level of Cu. Bisen et. al. (2009) [20] have reported the synthesis and luminescence of CdS:Mn doped nanoparticles of different sizes by chemical route in the presence of thioglycerol at different temperature and have shown that temperature is an important parameter for the synthesis of CdS:Mn nanoparticles. Verma et. al. (2010) [21] have synthesized Mn^{2+} doped CdS nanoparticles using PVP as capping agent by chemical co-precipitation method and have shown that PVP help in stabilizing the nanoparticles and increases the doping efficiency which leads to enhancement in optoelectronic properties and controlling the size of the particles. Salimian and Farjami (2010) [22] have prepared CdS:Mn nanocrystals by aqueous solution method and discussed the effect of Mn doping on the luminescence properties of CdS nanoparticles which showed that narrow size distribution samples have better luminescence intensity because they have less broadening of wavelength emission due to their broad sizes. Rao et. al. (2011) [23] have investigated nickel doped CdS nanoparticles in aqueous medium through chemical co-precipitation method which exhibited hexagonal phase. SEM images also showed the formation of nanoclusters and EDX results have confirmed that the sample with clear peaks of Cd, S and Ni is around the nominal composition. Again, they (2011) [24] have reported Ni doped CdS nanoparticles by chemical co-precipitation method with varying Ni concentration (2, 4, 6, 8 and 10 at %) and have proved that the onset wavelength is directly related to nanoparticle size. Hasanzadeh and Shayesteh (2011) [25] have

prepared Cu and Fe doped CdS nanoparticles by chemical method and thioglycerol (TG) as capping agent and showed that PL intensity depends on TG concentration which includes two bands due to emission of traps and surface state. Vishwakarma et. al. (2011) [26] have synthesized CdS nanoparticles doped with various concentration of manganese by wet chemical route using mercaptoethanol as capping agent and reported that the average size obtained from TEM is larger than that of XRD. The absorption spectra have shown absorption edge at 448 nm for the prepared samples. The particle size estimated by using Effective Mass Approximation (EMA) relation is found to be nearly the same as compared to TEM. Thambidurai et. al. (2012) [27] have synthesized CdS and Co-doped CdS quantum dots by chemical precipitation technique and have obtained hexagonal structure for both the samples. The particle sizes of Co-doped CdS nanoparticles are slightly greater than that of CdS which is confirmed from HRTEM images. Saliman and Farjami (2012) [28] have prepared CdS nanocrystals doped with Mn by aqueous method using thioglycerol (TG) as the capping molecule and investigated the effect of Mn concentration on the crystal structure, optical and magnetic properties. They have found that the prepared samples were in hexagonal phase and the EDX result confirmed the presence of doping ions. In that paper, they have also reported that the nanoparticles luminescence quantum efficiency is expected to increase with increase in doping concentration but in case of high doping, quenching effect can occur. Venkatesan et. al. (2012) [29] have discussed the preparation of sodium bis (2-ethylhexyl) sulfosuccinate (AOT) capped uniform CdS nanoparticles and thin films with magnetic impurity Mn. They have noticed red shift at the addition of dopants with excitonic feature greatly suppressed and FTIR revealed the stretching of the functional group present in the system. Gupta and Kripal (2012) [30] have investigated the synthesized Mn:CdS nanoparticles using chemical co-precipitation method and suggested that with increase in concentration of Mn^{2+} ions, the absorption peaks shift towards longer wavelength side and the band gaps of all the samples are found to increase as compared to bulk CdS. Fediv et. al. (2012) [31] have synthesized semiconductor CdS:Mn nanoparticles in PVA matrix by using the absorptive doping method and have shown that doping can be

achieved only during the growth and no diffusion of Mn ions from the surface of nanoparticles. Kumar et. al. (2012) [32] have reported CdS nanoparticles doped with Ni and Cu using chemical method and mercaptoethanol as capping agent. They have investigated the synthesized nanoparticles morphologically and structurally by HRTEM image and XRD gave particle size of the order of 5 nm. The presence of capping agent has been confirmed from FTIR study. Madhu (2013) [33] has reported the synthesis of pure and Pb²⁺ doped CdS by Mahadevan's method using a domestic microwave oven and characterized them structurally and electrically. She has reported that the yield percentage and observed grain size indicates the suitability of the method adopted. Venkatesu and Ravichandran (2013) [34] have prepared CdS:Mn nanocrystalline samples by chemical co-precipitation method using thiophenol as surfactant with varying Mn concentration. They have shown the formation of template groups on the surface of the nanoparticles from FTIR study and XRD studies confirmed wurtzite, hexagonal structure and the particle sizes to be 15 nm - 50 nm from HRTEM studies. The photoluminescence study has indicated the presence of surface states within the band gap region of the nanoparticles. Ramrakhiani (2013) [35] have synthesized undoped and Mn doped CdS nanoparticles by chemical route using PVK and PVA as capping agent and proposed that properly passivated cadmium sulphide nanocrystals can be used in luminescent devices. Chauhan et. al. (2013) [36] have synthesized Cd_{1-x}Mn_xS (where x=0.00 - 0.10) nanoparticles by chemical co-precipitation method. They have shown from XRD and TEM measurement that the size of crystallites are in the range of 10 nm to 40 nm and indicated a red shift in the absorption band edge upon Mn doping. Tiwari et. al. (2013) [37] have reported the synthesis of CdS:Cu nanoparticles by chemical route at room temperature with varying Cu concentration using thiophenol as capping agent having sizes in the range 25 nm - 45 nm and hexagonal in structure. They have also reported that band gap of all the samples increases with the increase in doping concentration of Cu. Venkatesu et. al. (2013) [38] have synthesized CdS nanoparticles with varying Mn doping concentrations using thiophenol as capping agent. They have reported that optical

measurements exhibit a blue shift in the band gap energy of the samples and band bowing which is attributed to particles of varying sizes.

Synthesis and characterization of undoped ZnS nanoparticles are also reported by many workers. This section deals with undoped ZnS nanoparticles. Kumbhojkar et. al. (2000) [39] have synthesized ZnS quantum dots using wet chemical routes with 1-thioglycerol, thiophenol and mercaptoethanol to passivate the nanoclusters and obtained remarkably narrow size distribution of quantum dots. Sharma et. al. (2008) [40] have worked on the core-shell ZnS nanocrystals and synthesized them using chemical precipitation method. TEM results have shown uncapped agglomerated nanoparticles as well as PVP capped ZnS particles and the formation of core-shell nanostructures. They have stated that the band gap of PVP capped ZnS nanoparticles are found to increase in comparison with uncapped ZnS nanoparticles. Rathorea et. al. (2008) [41] have studied the structural and optical characterization of ZnS nanoparticles using simple chemical method with confirmation of nano size of the particles using XRD and optical band gap data. They have suggested that the particle size is dependent on molar concentration of reactant solution and have also discussed about the nucleation and growth process. Borah et. al. (2008) [42] have reported in their paper that ZnS nanoparticles of different crystallite sizes have been synthesized by chemical route with the sizes controlled by stirring rate, temperature of the solution, pH and time of stirring. XRD have revealed the formation of ZnS nanoparticles having sizes between 5 nm - 7 nm and found the optimum pH value for maximum size to be 1.4 nm and PVA: ZnCl₂ ratio to be 5:1. Bhadra et. al. (2009) [43] have synthesized ZnS nanocrystals by chemical method and the synthesized samples are characterized by XRD, UV-vis spectroscopy, EDX, PL and HRTEM technique. They have shown that the size of the synthesized ZnS nanoparticles is found to be smaller than excitonic Bohr radius which signifies strong confinement. Chandran et. al. (2010) [44] have prepared ZnS nanoparticles by hydrothermal method and have calculated average crystallite size from XRD pattern and found hexagonal wurtzite in structure. TEM analysis also confirmed the formation of spherical

nanoparticles. John and Florence (2010) [45] have reported the synthesis of ZnS nanoparticles by simple chemical method with sizes to be 12 nm. They have used SEM images to study the morphology, FTIR spectra to show the possible stretching and bendings modes of ZnS, UV spectra for blue shifting and PL to determine the crystalline nature. Baishya and Sarkar (2011) [46] have prepared ZnS-PVA nanocomposites by chemical bath deposition method by varying the concentration ratio of sulphur to zinc sources and from PL spectra, they showed that there is a decrease in intensity and blue shift with the increase in the ratio. Tiwari et. al. (2011) [47] have synthesized polyphosphate capped ZnS nanoparticles by simple aqueous method using thiourea as S^{2-} source. XRD studies have revealed the zinc blende structure with 1.38 nm in size and showed the surface to be smooth and spherical. Somayeh et. al. (2012) [48] have synthesized ZnS nanocrystals with chemical method using methacrylic acid as capping agent and have found cubic structure with 1.77 nm - 2.05 nm in size. They have suggested that the position of the UV peaks changed according to the amount of the capping agent. Alexander (2012) [49] have reported the synthesis of ZnS nanoparticles by wet chemical route using two capping agents i.e. polyvinyl alcohol (PVA) and alpha-methacrylic acid (MA). The synthesized ZnS nanoparticles have revealed the influence of the capping agents in the formation of nanosize ZnS semiconductor. The particle size estimated using Scherrer formula is found to be 3.75 nm for ZnS/PVA and 2.60 nm for ZnS/MA respectively. They have reported that the estimated energy band gap showed blue shift. Kaur et. al. (2013) [50] have synthesized PVA capped ZnS nanocrystals by hydrothermal method and using Scherrer formula, they found the particle sizes to be 32.6 nm and 30.6 nm for pure and PVA capped ZnS nanocrystals respectively. The nanoparticles are spherical in shape for both pure and PVA capped ZnS. They have shown the presence of characteristic bands for PVA in the FTIR spectrum which revealed the capping of ZnS nanocrystals and strong absorption at 363 nm - 390 nm wavelength regions along with the strong excitonic peaks at 287 nm and 313 nm respectively for the capped and pure ZnS nanoparticles. Rahdar (2013) [51] have reported in his paper the effect of 2-mercaptoethanol as capping agent on the structural and optical properties of

nanocrystalline ZnS particles by chemical co-precipitation method. The crystallites showed hexagonal structure with 1.80 nm - 2.45 nm in size and have suggested that the optical direct band gap increases with increase in molar concentration of the capping agent.

Many earlier workers have reported a variety of dopants to enhance the properties of ZnS. This section illustrates the variety of dopants used in the synthesis of ZnS nanoparticles and their characterization. Beckar et. al. (1983) [52] have synthesized quantum dots of manganese doped ZnS by a simple precipitation reaction using aqueous route resulting particle sizes of 60 nm - 80 nm with the nanoparticles sterically stabilized using polyphosphate of sodium triopolyphosphate (STTP) and sodium hexametaphosphate (SHMP). They have shown that SHMP is a superior capping agent than STTP and concluded that the particle sizes are dependent on the amount of stabilizing agents. Bhargava et. al. (1994) [53] have synthesized nanophosphor of ZnS:Mn²⁺ in methanol by using sodium polyphosphate as the capping agent and have stated that the luminescence efficiency increases with decreasing particle size. Lu et. al. (2001) [54] have synthesized Mn²⁺ doped ZnS nanoparticles by chemical precipitation method at room temperature in the presence of 3- methacryloxypropyl trimethoxysilane (MPTS) as surface passivating agent and observed a 30-fold enhancement after the surface passivation with carboxylin groups. Kubo et. al. (2002) [55] have found modification of ZnS:Mn nanocrystals suspension by a surfactant with a phosphate or carboxyl group. They have found increase in photoluminescence and its quantum efficiency through two routes of energy transfer ZnS-Mn²⁺ and ZnS-phosphate or carboxyl groups-Mn²⁺. Karar et. al. (2004) [56] have prepared ZnS:Mn in nanocrystalline form by chemical method using polyvinyl pyroledone as capping agent with varying Mn concentration i.e. 0% to 40% and showed that there is no crystalline phase change with Mn concentration variation. They have stated that the photoluminescence intensity in Zn:Mn have shown significant enhancement upon Mn incorporation and presence of extra PL peaks after Mn incorporation in the nanocrystalline ZnS:Mn. Manzoor et. al.

(2004) [57] have studied multi-colour emitting doped ZnS nanocrystals capped with pyridine (P- ZnS) or polyvinyl pyrrolidone (PVP- ZnS) and synthesized by wet chemical methods. They have reported that the photoluminescence studies showed dopant related emission from P - ZnS nanocrystals and in case of PVP capped ZnS, there is considerable enhancement in the emission intensity. Peng et. al. (2006) [58] have reported ZnS:Cu nanoparticles synthesized by wet chemical method with copper concentration varying from 0 to 2 mol % and showed that the nanoparticles exhibit cubic zinc blende structure. The decreased in PL intensity at Cu^{2+} concentration of 2% and occurrence of concentration quenching are also reported. Sarkar et. al. (2008) [59] have prepared ZnS nanoparticles doped with Mn^{2+} varying from 1 to 2.5% concentration using chemical precipitation method and reported the crystallite sizes to be in the range of 2 nm - 3 nm. The room temperature PL spectrum of the undoped sample exhibited a blue-light emission whereas for Mn^{2+} doped samples exhibited a yellow-orange emission along with blue emission. They have also shown that 2.5% Mn^{2+} doped sample showed efficient emission of yellow-orange light with blue emission suppressed. Verma et. al. (2009) [60] have prepared luminescent nanoparticles of ZnS:Mn by co-precipitation method with the nanoparticles sterically stabilized using PVP and CA and suggested that PVP was a superior capping agent to CA with the particle size dependent on the amount and type of the stabilizing agent. Rastogi et. al. (2009) [61] have prepared undoped and Mn^{2+} doped ZnS nanoparticles by chemical precipitation method. XRD results showed that the crystallite sizes to be in the range 1 nm - 3 nm and the UV-vis spectra confirmed the blue shift as compared to that of bulk ZnS. They have reported that the photoluminescence spectra of all the samples have been recorded at room temperature and yellow emission is observed from the doped ZnS samples. Murgadoss et. al. (2010) [62] have synthesized PVA capped ZnS: Mn^{2+} nanoparticles by chemical precipitation method. XRD and TEM studies revealed the formation of cubic structures with average size of ~ 3 nm and the capped synthesized nanoparticles showed enhanced luminescence property compared with that of uncapped ZnS: Mn^{2+} particles. Krishna et. al. (2010) [63] have reported the synthesis, structural and optical studies of zero-dimension nanoparticles

of ZnS:Mn²⁺ capped with various organic stabilizers such as polyvinyl pyrelidone (PVP), thiophenol and thiourea. They have shown that both the nanoparticles synthesized with and without capping agent showed cubic zinc blende structure. The grain size, lattice strain, dislocation density and the band gaps of the nanoparticles are calculated from XRD and absorbance spectra. They have studied the photoluminescence properties and emission peak is observed at 554 nm for all the nanoparticles irrespective of capping agents. Gogoi et. al. (2010) [64] have prepared ZnS:Mn nanoparticles and showed that significant blue shift is ascribed due to the reduction of nanoparticle size. The PL spectra showed orange - yellow emission band that confirmed the incorporation of Mn in the ZnS host lattice. The average size of the nanoparticles estimated from TEM and XRD studies is found to be almost identical. They have indicated from UV-vis, TEM and AFM study that there is a tendency of decreasing particle size with decrease in Mn concentration. Mahagheghpour et. al. (2010) [65] have reported the synthesis of ZnS nanocrystals with sizes ranging from 1 nm - 10 nm in diameter with varying manganese concentration. They have shown that by adding Mn to ZnS nanoparticles, the emission intensity changed and from PL study that by band to band excitation upon ZnS:Mn resulting to two emission peaks which corresponds to surface states and Mn²⁺ emission. Hao et. al. (2011) [66] have prepared undoped and Mn doped ZnS nanoclusters by hydrothermal method with varying doping concentration of Mn and having cubic structure. The occurrence of blue defect related emission and orange Mn²⁺ emission are also detected from PL spectra. Pathak et. al. (2011) [67] have reported Mn²⁺ doped nanoparticles by chemical precipitation method at room temperature using acrylic acid as surface passivation. They have also observed that with increase in acrylic acid concentration, the absorption peak of ZnS:Mn shift towards shorter wavelength and band gap is in the range of 3.89 eV - 4.51 eV. The room temperature PL spectra of the undoped sample exhibit a blue emission whereas Mn²⁺ doped sample exhibit a yellow emission peak. Chauhan et. al. (2012) [68] have synthesized Zn_{1-x}Mn_xS (where x=0.00, 0.03, 0.05 and 0.10) nanoparticles by chemical precipitation method using polyethylene glycol as capping agent and discussed the structural and optical properties of the prepared nanoparticles. The XRD pattern of

Mn doped ZnS nanoparticles showed a cubic phase with 3 nm - 4 nm in size. They have found the band gap values of ZnS:Mn samples to decrease as compared to undoped ZnS. Rahdar et. al. (2012) [69] have prepared chromium doped ZnS by co-precipitation method using 2- mercaptoethanol as capping agent. The XRD patterns have revealed the hexagonal structure without any additional phase and crystallites size to be in the range of 2.45 nm - 1.50 nm and reported that the optical band gap (E_g) increases with increase in molar doping concentration. Sana et. al. (2012) [70] have reported synthesis of undoped and manganese doped ZnS nanostructures at controlled temperature using thio glycolic acid (TGA) as surface stabilizing agent to prevent surface dangling bonds. They have shown that the prepared samples are highly transparent in the visible region and XRD study revealed the formation of face-centred cubic ZnS quantum dots with grain size approximately 2.5 nm for both undoped and Mn doped ZnS which is confirmed by TEM. They have also shown that the prepared samples showed strong emission. Kole and Kumbhakar (2012) [71] have reported the synthesis of water soluble Mn^{2+} doped ZnS nanoparticles with varying concentration between 1.5 and 5% (wt %) by chemical co-precipitation method at room temperature. The synthesized particles are zinc blende in structure and their sizes varies between 2.2 nm and 2.7 nm with the increase in Mn^{2+} concentration. They have revealed the presence of yellow - orange emission band in all the Mn^{2+} doped samples and the presence of four PL peaks from the Gaussian fittings of the measured PL spectra of all the samples. Ramasamy et. al. (2012) [72] have synthesized ZnS nanoparticles doped with transition metals using chemical precipitation method. They have also shown that the prepared particles are cubic in structure with crystallite sizes of the range 4 nm - 6.1 nm. They have revealed from EDX spectra, the presence of doping ions and from SEM and TEM studies that the particles are spherical in shape. The occurrence of blue shift from bulk and enhanced PL properties from absorption spectra has been reported for all the samples. Harish et. al. (2013) [73] have synthesized PVA capped ZnS:Ce, ZnS:Cu nanoparticles using chemical co-precipitation method at different PVA concentrations and revealed cubic zinc blende structure with average size of about 2 nm - 4 nm. From the UV-vis spectra, the occurrence of blue shift

in the absorption edge with increasing capping concentration is also noted. The photoluminescence study showed that the emission becomes more intensive as the size of the particle is reduced with increase in capping agent. Murugadoss et. al. (2013) [74] have prepared ZnS:Mn²⁺ nanostructures by simple chemical method using 1- thioglycolic acid (TGA) as a stabilizing agent and demonstrated from experimental results that as prepared ZnS:Mn²⁺/TGA nanostructures have an excellent optical property.

2.2. References:

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