CHAPTER - II

2.1 LITERATURE REVIEW

Generally metal oxide semiconductor nanocrystals are potential materials for many applications in the field of electronics, magnetic materials and optical studies viewing it many workers, researchers have done a fantastic job in synthesizing nanocrystals and characterizing them in different areas. In this angle in my project work I have searched for different works by scientists in the same metal oxide area. Here I have compared some of the papers with authors and their works particularly.

G. Machado et al have synthesized Indium doped zinc oxide thin films obtained by co-electrodeposition (precursor and dopant) and the characterization of their sample by XRD analysis showed typical patterns of the hexagonal ZnO structure for both doped and undoped films and the incorporation of In into the ZnO film was verified by both EDS and XPS measurements. The bandgap energy of the films varied from 3.27 eV to 3.42 eV, increasing with the Indium concentration in the solution. The grain sizes estimated from the (002) X-ray diffraction peak width, using Scherrer’s formula were in all cases greater than 50 nm, and in most cases even greater than 100 nm. Thus, grain sizes were larger than the maximum critical values acceptable that can be deduced for these XRD measurements. This confirms the good crystallinity of the samples and is in agreement with previous works that show an increase in the grain sizes with increasing [In] \(^{3,4}\). Even if this FWHM is assigned to micro strain inside the grains, the maximum micro strain is in the order of 0.001. The band gap energy was calculated by the first derivative method described elsewhere \(^{5,6}\). It
depends on [In], at different electro deposition potentials. The energy gap increases with [In] for almost all electro deposition potentials, except for the most cathodic one.

[7] Hua-Wei Zhang et al have synthesized Zn$_{1-x}$Mn$_x$O crystal prepared by hydrothermal method. Crystal Zn$_{1-x}$Mn$_x$O magnetic semiconductors have been obtained by using a hydrothermal method at temperature of 703 K with substituent fraction ranging from x=0 to 0.04. They had characterized their sample by X-ray diffraction and optical absorption measurements. It provides evidence for the location at Zn site of Mn ion in ZnO crystals. Diluted magnetic semiconductors (DMS) have been of great interest in the last years due to the combined properties of the magnetic elements and the carriers of the host. So far most studies concentrated on Mn doped II–VI chalcogenide semiconductors [8] and III–VI semiconductors [9]. Among them, the ZnO–Mn system received much more attention, for excellent properties with Curie temperatures above room temperature that is predicted [10] if it is doped into p-type.

ZnO is a wide band gap (3.3 eV) semiconductor, so a ferromagnetic version could also be used as a material for magneto-optical devices. We observe an initial red shift in the band gap up to x=0.005, followed by a linear increase with the Mn concentration. It is reasonable to expect the band gap energy (Eg) to increase with increasing concentration of Mn, since the band gap of MnO (bulk) 4.2 eV is greater than that of ZnO (bulk) band gap energy 3.3 eV. Typical room temperatures UV–vis for Zn$_{1-x}$Mn$_x$O samples have been performed to continue confirmation that Mn$^{2+}$ is inside the lattice. The UV–vis measurements have found the short ranged interactions between the d electrons of Mn and the s and p electrons of the host bands.

[11] Y. Wang a, Y. Zhang et al have synthesized ZnO and they studied about the Mn effect on wurtzite-to-cubic phase transformation in ZnO. Mn doping effect on a wurtzite-to-cubic
phase transformation in ZnO has been investigated by in situ high pressure X-ray powder diffraction using synchrotron radiation.

Unit cell expansion is clearly observed in Mn-doped ZnO samples. Mn ions sit at Zn site in the wurtzite structure. The onset transition pressure for the wurtzite-to-cubic phase transformation decreases from about 9.5 GPA for pure ZnO to 6 GPA for sintered 2at. % Mn-doped ZnO while the compressibility and volume collapse at transition pressures are not sensitive to the Mn doping in the wurtzite phase. The doping of Mn ions in ZnO increases the onset transition pressure for the cubic-to-wurtzite phase transformation. Mn ions sit at Zn site in the wurtzite structure. It seems that the doping of Mn ions in ZnO increases the onset transition pressure for the cubic-to-wurtzite phase transformation.

[12] Jiaping Han, P.Q. Mantas et al have synthesized undoped and Mn-doped ZnO and they studied the Defect chemistry and electrical characteristics. In the Mn-doped ZnO case, the ionization energy of the Mn defect in ZnO was estimated to be ~ 2.0 eV. Using the experimental conductivities and the calculated electron concentrations, the electron mobilities were calculated between 70 and 300 K. They found that the temperature dependence of the mobility in undoped ZnO is similar to that in ZnO single crystals observed in other works, and heavy Mn doping significantly reduces the electron mobility below room temperature probably due to impurity scattering. They found that the temperature dependence of the ionisation energies of the defects in ZnO significantly affects the defect equilibria at different temperatures and the temperature coefficient of the band gap but also the temperature coefficients of the ionisation energies of the defects must be taken into account for the calculations of the defect equilibria. The role of Mn is to make ZnO highly conductive at high temperature, and resistive at room temperature, with the resistivity depending on the Mn concentration and on the sintering temperature.
[13] Zhigang Yina, Nuofu Chen et al have synthesized Ni-doped ZnO and they have studied about the structure, magnetic properties and also photoemission.

From the magnetization measurements, not ferromagnetic but paramagnetic behavior was found for Zn_{0.86}Ni_{0.14}O. They studied the electronic structure of Zn_{0.86}Ni_{0.14}O by valence-band photoemission spectroscopy. The spectra demonstrate a structure at \sim 2 \text{ eV} below the Fermi energy EF, which is of Ni 3d origin. Zn_{1-x}Co_xO and Zn_{1-x}Mn_xO are the most widely investigated among TM doped ZnO. Valence-band PES spectra for Zn_{0.86}Ni_{0.14}O taken at various photon energies. Continuous Spectral lines are smoothed curves as guide to the eye. No ferromagnetic signals were found down to 5 \text{ K} for Zn_{0.86}Ni_{0.14}O.

[14] Y. Wang a, Y. Zhang a, W.J. Chang et al have synthesized and studied the Mn effect on wurtzite-to-cubic phase transformation in ZnO. They studied the Mn doping effect on a wurtzite-to-cubic phase transformation in ZnO investigated by in situ high pressure X-ray powder diffraction using synchrotron radiation. It seems that the doping of Mn ions in ZnO increases the onset transition pressure for the cubic-to-wurtzite phase transformation. The results could be explained by a reduction of phase transform- ation barriers for both transition paths by Mn doping.

[15] J. Alaria a, P. Turek et al have studied the ferromagnetism in Mn doped ZnO semiconductors. They synthesised Polycrystalline Zn_{1-x}Mn_xO by co-precipitation method.

In doped ZnO the Zn ions located on the tetrahedral sites of the wurtzite structure can be substituted by magnetic transition-metal. Structural and optical measurements have demonstrated the presence of Mn^{2+} in substitution of Zn^{2+}. No indication of ferro magnetism has been evidenced neither in low doped (\leq 6 0.05) nor in highly doped (0.05 6 x 6 0.10) samples, which is very likely due to a lack of free carriers. A pure paramagnetic behavior was observed for the
low doped samples in agreement with the random character of the Mn distribution in the ZnO host matrix.

[16] Guangqing Peia, b, Changtai Xia have synthesized Ni-doped zinc oxide powder and they studied about the magnetic properties of the sample. Polycrystalline Zn\textsubscript{1-x}Ni\textsubscript{x}O diluted magnetic semiconductors have been successfully synthesized by an auto-combustion method.

Diluted magnetic semiconductors are formed by partial substitution of the cations of the host semiconductive with small amount of magnetic transition-metal (TM) ions. With charge and spin degrees of freedom in a single substance, DMSs have attracted a great deal of attention in recent years as enabling materials in the emerging field of “spintronics” [17]. This has stimulated numerous experimental groups to grow room temperature ferromagnetic ZnO semiconductors doped with a transition metal.

Using pulsed laser deposition technique, Ueda et al. [18] Reported a ferromagnetic behavior with TC higher than room temperature, while Jin et al. [19] found no indication of ferromagnetism for films grown by laser molecular beam epitaxy. Therefore, the presence of free carriers and localized d spins is a prerequisite for the appearance of ferromagnetism. These defects like Zn interstitials and O vacancies usually induce n-type characteristics. Radovan Vic and Gamelin attributed the appearance of ferromagnetism in nanocrystalline Ni\textsuperscript{2+}: ZnO upon reaction-limited aggregation to the combined effects of increased domain volumes and the introduction of n-type lattice defects [20].

[21] D. P. Norton, M. E. Overberg, S. J. Pearton, and K. Pruessner et al have synthesized cobalt-implanted ZnO and they had studied the magnetic and structural properties of cobalt-implanted ZnO single crystals. Electron doping of Fe, Co, or Ni-doped ZnO was predicted to stabilize high-Curie-temperature ferromagnetism. [22,23] The x-ray diffraction results demonstrate
the utility of x-ray diffraction in detecting and identifying precipitate phases in transition metal doped semiconductors. In the present case, the Co nanocrystals are epitaxial, thus yielding a unique orientation of both the hard and easy magnetic axes.

For the development of nanomagnetic arrays for high-density memory, controlling the orientation of the magnetic axes is critical to maximizing the density of addressable bits. Unimplanted control samples showed paramagnetic behavior, indicating that the introduction of the Co is the cause of the observed ferromagnetism. Based on the observed magnetization behavior, it is reasonable to assign the magnetic behavior of the implanted samples to the Co nanocrystals detected in x-ray diffraction. For hexagonal Co spheres at room temperature, the critical diameter is; 5 nm. Based on the x-ray diffraction data, the average size of the Co nanocrystals is below the superparamagnetic limit at room temperature, which is consistent with the magnetic properties observed.

[26] Witold Lojkowski et al have synthesized nanocrystalline zinc oxide doped with Mn$^{2+}$, Ni$^{2+}$, Co$^{2+}$ and Cr$^{3+}$ ions by solvothermal method. ZnO nanopowders doped with Mn$^{2+}$, Ni$^{2+}$, Co$^{2+}$ and Cr$^{3+}$ ions have been synthesized using a solvothermal reaction with microwave heating. The Mn$^{2+}$ doped powder displayed a paramagnetic behaviour.

ZnO is a semiconductor of high chemical and thermal stability, with an energy gap of about 3.5 eV. Due to the large band gap, ZnO efficiently absorbs ultraviolet light and emits blue light. Nanosized ZnO has found application in the production of UV sun screens but extensive studies are being carried out for its application in optoelectronics and spintronics.

Hydrothermal microwave reactions are especially advantageous for obtaining doped nanopowders, as high purity conditions can be achieved in a microwave reactor because the reacting fluids have no contact with the heating elements and they have the ability to achieve the
maximum possible degree of powder crystallinity, whilst keeping a small crystallite size, at a lower temperature than is needed for the calcination process. Conducting a microwave reaction under solvothermal conditions makes it possible to obtain single-phase ZnO nanopowders doped to a high level with Mn$^{2+}$, Ni$^{2+}$, Co$^{2+}$ and Cr$^{3+}$ ions, without any clustering of the ions. All these ions are commonly used in diluted magnetic semiconductors. The density of the powders doped with Mn$^{2+}$ and Co$^{2+}$ ions is close to that of pure ZnO.

The powders with low densities are shown to possess a greater surface area. Doped nanopowders acquire new magnetic or optical properties, depending on the doping ion. Furthermore, the nanoparticles can shield the ion from chemical reactions with the environment. ZnO with Mn$^{2+}$ results in powders exhibiting paramagnetic behaviour. The average grain size of the nanopowders was in the 20 nm range, and the dispersion was about 5 nm. Various methods give results for the average grain size that differed by about 5 nm.

ESR and magnetisation investigations have shown that there was no formation of Mn$^{2+}$ or Co$^{2+}$ clusters. The lattice constants increased with the increase of doping level, both for the Mn$^{2+}$ ion, which has larger ionic radii, and for the other ions with smaller ionic radius than that of Zn$^{2+}$. The experiments confirm the high potential offered by solvothermal chemistry in producing oxides with increased dopant concentrations.

[27] L. B. Duan, G. H. Rao et al have synthesized Zn$_{1-x}$Mn$_x$O nanoparticles by a combustion method and they had studied the structural and magnetic properties of nano Zn Mn O particles. The main challenge for practical applications of the DMS materials is the attainment of Curie temperatures $T_C$ around or preferably above room temperature $RT$ to be compatible with junction temperatures. One of the promising materials is the wide-band gap 3.36 eV and wurtzite-phase semiconductor ZnO which is formed by tetrahedral $sp^3$ bonding.
It was shown that the combustion method is an effective way to fabricate homogeneous solid solution Zn$_{1-x}$Mn$_x$O. The $M$-$T$ measurement is very sensitive to magnetic impurity phase embedded in the samples.$^{[28]}$ The smooth and featureless $M$-$T$ curve indicates the absence of any secondary magnetic phase and confirms the single phase nature of the fabricated Mn-doped ZnO samples, in agreement with the XRD and HRTEM studies. Furthermore, the characteristic behavior observed in many other ZnO-based DMS. $^{[29]}$ is a steep decrease of magnetization at low temperature. It shows a clear hysteresis with a coercive field $H_c$ 70±5 Oe. The small coercivity was frequently reported for other FM Mn-doped ZnO DMS$^{[30]}$.

$^{[31]}$ O.D. Jayakumar et al have synthesized Mn doped ZnO nanoparticles by reverse micelle method and they undertook the magnetization and structural studies.

The X-ray photoelectron spectroscopy and electron paramagnetic resonance (EPR) studies indicated that manganese exist as Mn$^{2+}$ in ZnO lattice. DC magnetization measurements as a function of field and temperature, of 2.5 at% Mn doped ZnO nanoparticles annealed at 675 K, showed room temperature ferromagnetism (RTF). The EPR spectrum of the sample shows a distinct ferromagnetic resonance signal, at room temperature. These results indicate that the observed RTF in Mn-doped ZnO may be attributed to the substitutional incorporation of Mn at Zn sites. The substitution of transition metal (TM) dopants into wide band gap oxides and III–V semiconductors has been shown to have carrier-induced ferromagnetism $^{[32,33]}$.

Weak ferromagnetism in Co/Mn-doped ZnO can be made robust by surfactant-assisted synthesis $^{[34-36]}$. The XRD patterns showed broadening of the peaks due to the formation of particles in the nanophase regime. Average crystallite size was determined from the extra broadening of the XRD peaks of the sample using Scherer’s formula applied to the strongest
peak. The average crystallite size of the 675K annealed samples was found to be 10–15 and 6–8nm for ZnO and 2.5 at% Mn doped ZnO, respectively.

In addition, since the particle size is in the nanophase regime, some of the particles could behave superparamagnetically and the above two terms complicate the magnetic behavior at low temperatures. This also explains the observed smaller value of saturation moment at RT. The ferromagnetism in DMS materials and its origin challenges our current understanding of magnetism.

[37] O D Jayakumar1, 4, H G Salunke have synthesized Mn-doped ZnO nanoparticles prepared by a co-precipitation method and studied about the magnetic properties. The introduction of transition metal dopants into wide band gap oxides and III–V semiconductors has been shown to propagate carrier-induced ferromagnetism. Observation of ferromagnetic ordering at room temperature in 2 at. % Mn-doped ZnO nanoparticles annealed at 675 K, which may be caused by the incorporation of Mn$^{2+}$ ions into the ZnO lattice rather than due to the formation of phase segregated metastable impurities.

The low-field hysteresis (0–5000 Oe) shows ferromagnetic behaviour within clusters and high-field paramagnetic behaviour above 20 000 Oe. The paramagnetic behaviour, being linear, has been fitted to a straight line with an intercept (about 0.25 emu g$^{-1}$). The idea of defect-mediated room temperature ferromagnetism has already been applied to the Mn-doped CdGeP$_2$ system. Another possible mechanism could be the disorder effects or the interaction between bound magnetic polarons. Calculations based on LDA suggest that the formation of nanoclusters is energetically favourable for ferromagnetic ordering.

[47] Y. S. Wang, P. John Thomas et al have synthesized ZnO Nanocrystals doped with Cd, Mg, Mn, and Fe ions and they have studied the optical characteristics of nano crystals by X-ray
diffraction, energy-dispersive X-ray analysis, transmission electron microscopy, UV-visible, luminescence, and excitation spectroscopy. They found that the band gap of the nanocrystals can be tuned in the range of 2.9-3.8 eV by the use of the dopants and in most cases; the nanocrystals are sufficiently defect-free to exhibit band edge luminescence. ZnO, a wide band-gap semiconductor, has been extensively studied due to its intrinsic properties and potential for uses in devices, such as field-effect transistors, resonators, gas sensors, and solar cells, and as a catalyst.

X-ray diffraction patterns of pure and doped nanocrystals reveal the presence of a single hexagonal phase with zincite structure (JCPDS no. 80-0075), indicating that phase-pure doped nanocrystals were obtained by this synthetic scheme. Doping with the Cd ions also leads to expansion of the lattice depending on the doping level. Doping with Mn ions produces no appreciable shift in the lattice parameters since both ions possess similar radii. Shifts indicating a small increase in the unit cell dimensions are seen in the case of Fe. The changes to the unit cell dimensions, although discernible in many cases, are not quantified, as the peak widths introduce errors significant enough to obscure the changes.

Transmission electron microscopic images of pure and doped ZnO nanocrystals reveal nearly spherical nanocrystals in most cases, with dimensions in the range of 9-12 nm. The presence of small amounts of Mn and Mg ions (up to 2%) influences the growth process, resulting in elongated nanocrystals. Simply increasing the concentrations of the dopant ions yields spherical nanocrystals.

A linear increase in the band gap from 3.30 to 3.66 eV with an increase in Mg concentration from 0 to 15% is observed. The optical band gap falls nearly linearly from 3.30 to 2.92 eV with the increase of Cd doping levels from 0 to 10%. The indicated band gaps are
similar to that which has been observed on other forms of ZnO doped with Mg and Cd. Doping with Fe also produces a blue shift proportional to the concentration of the ions. The increase in the absorption in the region of 2.9-3.2 eV is due to the d-d transition of Fe ions. [52]

The systematic and linear shifts with doping levels suggest that the introduction of dopant ions, rather than size effects, brings about these changes. Further, a number of previous experimental and theoretical investigations have suggested that size effects have little or no influence on the band structure of ZnO nanocrystals with diameters greater than 7.0 nm. [50,51]

Pavle V, Radovanovic and Daniel R. Gamelin have synthesized Ni doped ZnO and they have studied about high-temperature Ferromagnetism. Ferromagnetism with \( T_c > 350 \) K is observed in the diluted magnetic semiconductor Ni2: ZnO synthesized from solution. Whereas colloidal \( \text{Ni}^2: \) ZnO nanocrystals are paramagnetic, their aggregation gives rise to robust ferromagnetism. The appearance of ferromagnetism is attributed to the increase in domain volumes and the generation of lattice defects upon aggregation.

Preparation of \( \text{Ni}^{2+}: \) ZnO is particularly challenging due to the large driving force for phase segregation into NiO and ZnO. Ferromagnetism has been observed only at 2 K in \( \text{Ni}^2: \) ZnO films fabricated by pulsed laser deposition using ZnO=NiO ceramic targets [54].

An isocrystalline core/shell procedure [55, 56] involving epitaxial growth of ZnO shell layers on the nanocrystal surfaces was applied to internalize any surface-exposed \( \text{Ni}^{2-} \). The ferromagnetism is an intrinsic property of the true DMS \( \text{Ni}^2: \) ZnO. This value suggests that only a small fraction of the \( \text{Ni}^{2-} \) dopants gives rise to all of the observed ferromagnetism. High-\( T_c \) ferromagnetism has been observed in nanocrystalline \( \text{Ni}^2: \) ZnO synthesized from solution. The appearance of ferromagnetism upon aggregation of colloidal paramagnetic \( \text{Ni}^2: \) ZnO
nanocrystals are attributed to the increase in domain volumes and the generation of defects at interfaces between nanocrystals.

D. P. Norton et al have synthesized cobalt-implanted ZnO and they have studied about the magnetic properties. For Co-doped ZnO, there is some evidence that the observed ferromagnetism may be due to Co precipitates instead of carrier-mediated exchange in the ZnO matrix. \(^{58}\)

While the presence of Co nanocrystals can account for magnetism in these implanted samples, it does not prevent the possibility that magnetism originating from Co substitution on the Zn sites also contributes. Total energy calculations suggest that Co doping of \(n\)-type ZnO would produce ferromagnetism. \(^{59}\) The magnetic properties are consistent with the presence of Co nanocrystals, but do not preclude the possibility that a component of the magnetism is due to Co substitution on the Zn site in the ZnO matrix. For hexagonal Co spheres at room temperature, the critical diameter is; 5 nm. \(^{60,61}\) Based on the x-ray diffraction data, the average size of the Co nanocrystals is below the superparamagnetic limit at room temperature, which is consistent with the magnetic properties observed.

C. N. R. Rao and F. L. Deepak have synthesized Mn and Co doped ZnO and they have studied about the magnetic properties. A report of ferromagnetism in Co-doped TiO\(^2\) \(^{63}\) gave the hope that Co- and Mn-doped oxides may indeed be useful for spintronics. Theoretical calculations of Sato and Katayama-Yoshida \(^{64}\) showed that ZnO doped with several 3d transition metal ions such as V, Cr, Fe, Co and Ni may exhibit ferromagnetic ordering. The present investigations on Mn and Co doped ZnO establish them not to be ferromagnetic and throw considerable doubt about the ferromagnetic nature of these materials reported in the literature. It seems unlikely that these materials would be candidates for spintronics. This
conclusion finds support from the recent work of Spaldin [65] who finds that robust ferromagnetism cannot occur in Mn- and Co-doped ZnO. If at all, it may occur if additional charge carriers are present. In order to obtain robust ferromagnetism, it may be worthwhile to investigate the effect of codoping of Mn or Codoped ZnO samples with other cations to induce additional charge carriers.

[66] Dana A. Schwartz, Nick S. Norberg have synthesized Co$^{2+}$ and Ni$^{2+}$ Doped ZnO Nanocrystals and they have studied about the magnetic and optical properties by the preparation of colloidal ZnO-diluted magnetic semiconductor quantum dots (DMS-QDs) by alkaline-activated hydrolysis and condensation of zinc acetate solutions in dimethyl sulfoxide (DMSO). Operational spin-dependent light-emitting diodes (spin LEDs) have been demonstrated that use II-VI and III-V DMSs as the key spin-polarization materials. [67] Low temperature electronic absorption, magnetic circular dichroism (MCD), Zeeman, and magnetic susceptibility techniques have been applied to study the electronic structural properties of these DMS-QDs. The intrinsic optical electronic transitions of DMSs fall into three broad classifications: ligand-field, charge-transfer (CT), and semiconductor band-to-band transitions. Each type of transition provides complementary information about the electronic structure of the DMS as a whole that we then relate to the spintronics-relevant functional properties of these materials. These narrow bandwidths demonstrate a high degree of Ni$^{2+}$ homogeneity in these DMS-QDs.

Emission spectra measured for pure ZnO QDs synthesized by alkaline-activated hydrolysis are dominated by surface trap luminescence occurring in the visible spectral range and are very similar to those reported previously. [68] No discrete charge-transfer transition can be identified in the absorption spectrum of Co$^{2+}$:ZnO, even at low temperatures. [69] This synthetic procedure allows the relatively rapid preparation of gram quantities of doped quantum
dots in open containers with no need for special precursors, precautions to avoid atmospheric contamination, or temperature stabilization.

[70] V. A. L. Roy and A. B. Djuris’ic’ et al have prepared Mn doped ZnO tetrapod structures by diffusion doping at temperatures 600 and 800 °C, and they have studied about the magnetic characteristics. Theoretical calculations predict that Mn doped p-type ZnO should be ferromagnetic at room temperature. [71, 72] In the absence of p-type doping, theoretical calculations predict that Mn doped ZnO would exhibit antiferromagnetic properties. There have been several experimental works on transition metal doping of ZnO thin films. [73-77] The obtained results have been contradictory. Paramagnetic properties were reported for Zn$^{0.93}$Mn$^{0.07}$O films prepared by magnetron sputtering. [74] Antiferromagnetic behavior was observed in Z$^{0.64}$Mn$^{0.36}$O films prepared by pulsed laser deposition [77] and polycrystalline ZnO: Mn powder samples. Most likely the differences in the reported results are due to different preparation methods, since the properties of ZnO are sensitive to the preparation conditions. Here synthesis of ZnO tetrapod nanorods and nanowires were under different gas flow. [78] The fabrication of ZnO nanostructures was performed in humid argon flow as reported previously. The obtained samples have shown clear magnetic hysteresis at 5 K. Curie temperature was determined to be ±50 K. The sample diffused at 600 °C exhibited higher Mn concentration and higher remnant magnetization at 5 K, as well as higher coercive field. Both samples exhibited very high coercive field, which is about one order of magnitude higher compared to values reported for ZnO: Mn thin films.

[79] Jung H. Park, Min G. Kim et al had synthesized Co-doped ZnO thin films and they had studied about the Co-metal clustering as the origin of ferromagnetism. The origin of ferromagnetism in ZnO-based systems was investigated using Co-doped ZnO thinfilms as prototypical examples of II–VI-based diluted magnetic semiconductors. In spite of the atomic-
scale dissolution of Co ions in wurtzite ZnO, both the magnetization-temperature curve and the magnetization-field curve demonstrated that Zn$_{1-x}$Co$_x$O thin films were paramagnetic for $x<0.12$. On the other hand, Zn$_{1-x}$Co$_x$O films with $x$ greater than 0.12 were characterized by the Co-metal clustering and apparently showed room-temperature ferromagnetism. The discrepancy between the zero-field cooling and the field cooling curves further indicates that Co-doped ZnO films (For $x>0.12$) are superparamagnetic and the observed ferromagnetism originates from the nanometer-sized Co clusters. The recent success in the synthesis of Mn-doped III–V type diluted magnetic semiconductors DMS such as InMnAs1 and GaMnAs2 has made them possible to fabricate a spin injecting structure as well as structures for electrical or optical control of ferromagnetism. They found that the structure-magnetic property correlation and the ferromagnetic origin deduced from the sol-gel processed films were also valid for the rf sputtered Co-doped ZnO films (300 nm-thick).

[80] Kevin R. Kittilstved and Daniel R. Gamelin have synthesized Mn$^{2+}$ Doped ZnO using amines and they have studied about the activation of High-TC Ferromagnetism. Here, they report that high-TC ferromagnetism in Mn$^{2+}$: ZnO can be activated reliably by amine binding and calcination, a process interpreted as incorporating nitrogen into the ZnO lattice as a p-type dopant. Aerobic synthesis and calcinations aid suppression of native donor defects, such as OV, Zni, or H.21 Amine capping passivates surface defects that could otherwise be trapped during sintering. We note that addition and calcinations of amines after spin coating also enhances the ferromagnetism of the Mn$^{2+}$: ZnO films. The experimental observations are consistent with a microscopic mechanism involving formation of bound magnetic polarons upon introduction of p-type dopants, analogous to that proposed recently for n-type DMOs. [81] Calcination of amines activates high-TC ferromagnetism in Mn$^{2+}$: ZnO. Perhaps the most important aspect of this result
is the clear demonstration that the magnetism of Mn$^{2+}$: ZnO is critically dependent upon factors other than the transition metal dopants themselves. Such factors are likely responsible for the broad range of magnetic properties previously reported.

[82] Dana A. Schwartz, Kevin R. Kittilstved et al have synthesized Ni$^{2+}$ doped ZnO thin films prepared from colloidal diluted magnetic semiconductor quantum dots and they have studied about the ferromagnetic property above room temperature. They reported the preparation of spin-coated nickel-doped zinc oxide nanocrystalline thin films using high-quality colloidal diluted magnetic semiconductor quantum dots as solution precursors. They have initiated a systematic study of nanocrystalline oxide DMSs synthesized by solution chemical routes, and have recently reported direct chemical methods for the synthesis and purification of high-quality internally doped colloidal ZnO DMS quantum dots (QDs). [83, 84, 85] Doping also introduces sub-bandgap optical transitions that can be used to selectively probe the geometric and electronic structures of the dopant ions themselves. They therefore conclude that the observed ferromagnetism is an intrinsic property of Ni$^{2+}$: ZnO. These solution synthetic methods allow the speciation of magnetic dopant ions to be controlled chemically, and thereby provide an avenue for avoiding the formation of undesired magnetic phases. In this letter, we report the use of colloidal Ni$^{2+}$ doped ZnO s Ni$^{2+}$: ZnO d DMS nanocrystals as solution precursors for the preparation of nanostructured ZnO thin films.

[86] Petra Lommensa, Philippe F.Smet b, performed luminescence experiments on strongly confined Co$^{2+}$ doped ZnO nanocrystals (Co:ZnO) to probe the electronic structure of Co$^{2+}$ in the ZnO host, the assumed formation of a Co$^{2+}$ related d-band within the band gap of the ZnO. Several authors reported room temperature magnetic hysteresis loops for ZnO doped with Mn, Co or Ni, although others did not find any evidence of ferromagnetism [87-90]. Co$^{2+}$ doped
ZnO nanocrystals were synthesized at room temperature using a wet chemical route as described by Schwartz et al.\textsuperscript{87} The spectra were taken respectively 5 and 370 min after initiation of particle growth. In this time interval, the mean particle diameter increases from 2.5 to 3.5 nm. As reported in the literature, both the exciton and the trap emission shift to lower energy with increasing particle size.

\textsuperscript{91} Y. Q. Chang, D. B. Wang have synthesized Zn_{1-x}\text{Mn}_xO nanowires via vapour phase growth and they have studied the optical and magnetic characteristics. Detailed SEM analysis revealed that the as-doped ZnO nanowires have a length of a few micrometers and diameter between 20 and 100 nm. Most nanowires are straight in morphology and smooth in surface, in consistence with the SEM observation. The photoluminescence of the Zn_{1-x}\text{Mn}_xO nanowires excited by a 325 nm wavelength laser at room temperature, and a ultraviolet emission at about 367 nm and an intensive green emission band, broadened at 521 nm were observed. The blueshift emission is related to the change of band gap (E_g) structure of Zn_{1-x}\text{Mn}_xO, which increases with the increase of the Mn content.\textsuperscript{93,94} The broad and very intensive green emission around 521 nm is ascribed as arising from defects in the nanowires.\textsuperscript{92} The Zn_{0.87}\text{Mn}_{0.13}O nanowires exhibit obvious ferromagnetic ordering which was ascribed to be originated from the change of the band gap structure of the ZnO crystal caused by the Mn substitution for Zn sites at the ZnO crystal.

\textsuperscript{95} O.D. Jayakumar et al prepared Mn doped ZnO with and without Li co-doping by standard solid state reaction route and studied the room temperature ferromagnetism of Mn doped ZnO. The lattice parameters of ZnO are a = 3.2403(5) Å and c = 5.1901(6) Å. DC magnetization loops indicate their ferromagnetic nature. Kittilstved et al\textsuperscript{96} found injecting
n-type carriers into Mn doped ZnO is detrimental to ferromagnetism. These works clearly shows reservation about intrinsic nature of ferromagnetism in transition metal doped diluted magnetic semiconductor oxides and also unambiguously shows that the incorporation of Mn into ZnO in the presence of p-type carriers induces room temperature ferromagnetism which is intrinsic in nature.\textsuperscript{[97]}

\textsuperscript{[98]} O.D. Jayakumar et al synthesized Zn$_{1-x}$Mn$_x$O nanopowders and studied their properties. XRD data of Zn$_{1-x}$Mn$_x$O showed that they are single phase with the wurtzite structure. TEM images of the Mn doped ZnO samples show that they are free from secondary phases. The bright field images of the particles of Mn doped ZnO show narrow distribution in shape and size, with particles exhibiting predominantly rod like microstructure developing into platelets and sizes in the range of 50–200 nm. Sharma et al.\textsuperscript{[99]} observed a saturation moment of 0.007 emu g$^{-1}$ for bulk Mn doped ZnO prepared by solid state reaction between ZnO and MnO$_2$ where they observed less than 4% manganese was responsible for ferromagnetism at room temperature.

\textsuperscript{[100]} J.W. Zhao et al synthesized and characterized the flower-shaped ZnO nanostructures by the oxidation of metallic Zn powder mixed with some Sn powder. The synthesized products were characterized by scanning electron microscopy, X-ray diffraction, high-resolution transmission electron microscopy and photoluminescence (PL) spectra were obtained at room-temperature. The high-magnification SEM image, show that the thickness of the nano saw is about 70 nm. The energy-dispersive X-ray spectrocope (EDS) revealed that the flowers are composed of elements Zn and O. The TEM image showed the presence of some short nanorods with length of 300–400 nm.
Jin Li et al synthesized Mn-doped ZnO single-crystalline nanorods by solvothermal method and studied the structural and photoluminescence characterization of them. They used zinc acetate and manganese acetate for their preparation of Mn-doped ZnO nanorods. Undoped ZnO nanorods were also synthesized using the identical procedure for comparison. X-ray diffraction (XRD) data of the samples showed the presence of hexagonal wurtzite ZnO crystal structure (space group P63mc; JCPDS card No.36-1451). From the TEM images of the prepared ZnO and Mn$_{0.046}$Zn$_{0.954}$O nanorods it was found that the diameter of these nanorods ranges from ~20 to 80 nm; the nanorods, thus, have aspect ratios that range from ~6 to 20. It indicated that our low-temperature synthetic method yields small quantity nanoparticles. The doping of Mn does not change the morphology of the final product. Energy-disperse X-ray analysis (EDX) showed that these doped nanorods are composed of Zn, O and Mn elements only. This confirmed that the nanorods contain Mn. Photoluminescence studies of the undoped ZnO nanorods show a UV emission at 370.8 nm (3.3441 eV). The doping of Mn into ZnO will lead to the shift of the absorption edge of ZnO to shorter wavelength because of the larger band gap (Eg) of MnO relative to that of ZnO (4.2 eV vs 3.37 eV) [102,103].

Samanta Cimitan et al synthesized ZnO nanoparticles doped with Indium and gallium by solvothermal route and discussed the effects of indium and gallium doping on structural, electrical and optical properties of ZnO nanoparticles prepared by hydrothermal reaction in ethanol and methoxyethanol. The XRD patterns of the ZnO based samples synthesised in methoxyethanol and ethanol at increasing loadings show a stable wurtzite structure with all reflections assigned to hexagonal P6$_3$mc structure of ZnO indexed on the basis of JCPDS card No. 36-1451. TEM images of the ZnO and In/ZnO nanoparticles exhibit nearly spherical morphology with an average diameter of about 20 nm, agreeing well with the XRD data. The
presence of in profoundly influences the formation of ZnO and the shape of particles varies from rounded to rod-like. The optical properties of doped ZnO nanopowders show absorption bands at about 360–380 nm. Indium introduction causes the appearance of absorbance in the near IR range; the influence of n-doping due to indium presence is seen by the strong absorption occurring in the range from 900 nm < \( \lambda \) <2000 nm, due to the presence of free carrier in the materials\textsuperscript{[105]}.

\textsuperscript{[106]} C. Satienpattanakoon et al synthesized Zinc Oxide Nanocrystals by Solid-State and Solvothermal Techniques for a solvothermal procedure. The SEM image of the nanostructures of ZnO synthesized via solid-state method with two types of stabilizer: SDS and b-CD was added into the solid-state reaction to investigate the effect of molecular structure on the ZnO morphology. The FTIR spectrum of ZnO in KBr matrix show that there is a broad band with very low intensity at 3493 cm\(^{-1}\) corresponding to the vibrational mode of water OH group indicating the presence of small amount of water adsorbed onto the ZnO nanocrystal surface. Those at 2920cm\(^{-1}\) are found to be due to the C-H stretching of methyl and methylene. The spectra revealed the attachment of SDS molecules on the ZnO surface\textsuperscript{[107]}. The band at 1400-1628 cm\(^{-1}\) are due to the vibration mode present in C=O. A strong band at 500 cm\(^{-1}\) is attributed to the Zn-O stretching band that reported in the literature\textsuperscript{[108]}. From the XRD pattern of ZnO nanocrystals synthesized via solid-state route we see that the diffraction pattern indicates the nanocrystalline nature (JCPDS card no. 05-0664).

\textsuperscript{[109]} Dewei Chu et al synthesized Room-Temperature Ferromagnetic Co-Doped ZnO nanocrystals under a High Magnetic Field which would allow spintronic devices to operate at room temperature\textsuperscript{[110,111]}. Samples are in good rod shape but the average length of the 12 T sample is significantly decreased The high-resolution transmission electron microscopy
(HRTEM) images show that both of the samples are single crystalline and the preferred growth directions of the two samples are parallel to the [001] direction (c-axis). Well-resolved lattices with a measured interplanar spacing of 0.52 nm is shown in 12 T sample, consistent with the distance between (002) crystal planes. The jiggling of nanoparticles by the Brownian motion allows adjacent particle to collide and rotate to find a low-energy configuration, resulting in a coherent grain-grain boundary. The cobalt concentration in the nanorods is determined by energy-dispersive X-ray spectroscopy. The appearance of ferromagnetism on Co\(^{2+}\) doped ZnO is usually attributed to the oxygen vacancy, fusion of defects at the interfaces, and the randomization of the dopant ions.\(^{[112]}\). There was no association between this vibrational mode and the appearance of ferromagnetism in Co\(^{2+}\) doped ZnO.

\(^{[113]}\) Yonghong Ni et al synthesize and characterized flowerlike ZnO nanocrystals built up by nanoflakes by hydrothermal method. SAED pattern of these nano flakes shows some regular light dots, which implies the single crystal nature of the ZnO product. A high resolution SEM image shows that the flowerlike structures are comprised of a great amount of nanoflakes with a mean thickness of~ 50 nm. The oxidation and reduction peak potentials were 583 mV and 49 mV, respectively. The photoluminescence (PL) studies show that the as-prepared ZnO nanocrystals owned well photo-catalytic property for degradation of safranine T. The as-obtained flowerlike ZnO nanocrystals had stronger photo-catalytic property for degradation of safranine than the spherical ZnO nanoparticles.

\(^{[114]}\) Hanmei Hu et al prepared skin-colored N-doped ZnO nanocrystals and characterized them. The sharp diffraction peaks indicate the good crystallinity of the as-prepared crystal. The morphology of N-doped ZnO show that the average diameter of the products is 20 nm. The X-ray photoelectron spectroscopies (XPS) spectra of the as-synthesized products show that there
were no impurities. The binding energy peak centered at 399eV was assigned to the N1s, which is almost consistent with the reported value of N-doped ZnO\textsuperscript{[115]}. The composition and quality of the product was analyzed by the FTIR spectroscopy\textsuperscript{[116]}. IR spectrum of ZnO showing characteristic bands in the region from 680 up to 300 cm\textsuperscript{-1} confirms the shape of the ZnO particles. The optical properties show a strong and sharp peak located at 384 nm in ultraviolet region\textsuperscript{[117]}.\[118\]

Siqingaowa et al synthesized nanocrystalline ZnO by direct precipitation method and characterized them. The morphologies and grain size of ZnO samples were measured using transmission electron microscopy. The Infrared (IR) spectrum of the precursor and ZnO samples calcined at 300°C for 1, 2 and 3 hours, show that, the absorption peak in 3380–3600 cm\textsuperscript{-1}, which is due to stretching vibration of hydrogen bond, indicating the plentiful existence of hydroxyl group\textsuperscript{[119]}. The XRD patterns of precursor and ZnO samples show that the three characteristic peaks of zinc hydroxy carbonate are at 20 13.2°, 32.9° and 59.2°. According to well coincidence with PDF 19-1458, it can be revealing that the precursor is zinc hydroxycarbonate. The ZnO samples calcined at 300°C can be identified as a perfect cube structure in crystallography in response to PDF 36–1451 data. The TEM images of ZnO samples calcined at 300°C for 2h. The single particle size of ZnO samples are approximately 8–15 nm, it is due to the adsorption of Cl\textsuperscript{−} to terminate the growth of precursor, which was called capping mechanism of colloid\textsuperscript{[120]}.

\[121\] Hanmei Hu et al synthesized ZnO nanowires and nanobelts on large scale by hydrothermal method. The typical XRD pattern of the as-prepared ZnO products show that all the reflections can be indexed to wurtzite structure of ZnO with lattice parameters \( a = 3.247 \) Å and \( c = 5.20 \) Å, in good agreement with the reported data for ZnO \((a = 3.249 \) Å, \( c = 5.205 \) Å, JCPDS File, 5-664. The diameters of ZnO nanowires are about 20–100 nm and the widths
of ZnO nanobelts are in the range of 80–250 nm. Further structural characterizations of the ZnO nanowires/belts were performed by TEM and HRTEM. With increase in the TEM magnification, belt-like ZnO nanostructures are apparently observed. The TEM image of a well-developed single crystal ZnO nanobelt with width of 220 nm is also shown. The SAED pattern of the nanobelt indicates its single crystal nature and its growth direction along c-axis.

[122] Amish G. Joshi, Sonal Sahai, et al synthesized highly luminescent ZnO:Na nanocrystals of size ~2 nm using a improved sol-lyophilization process. The surface analysis were studied using x-ray photoelectron spectroscopy (XPS) to establish the presence of Na\(^+\) ions. The observed increase in bandgap from 3.30 eV (bulk) to 4.16 eV (nano), is due to the quantum confinement of the motion of electron and holes in all three directions. The x-ray diffraction (XRD) pattern of the ZnO: Na NC powder shows that the particles are ultra-fine and have wurtzite phase. From the broadening of XRD lines and TEM image, the average sizes of NCs were estimated to be ~1.5 and ~1.7 nm, respectively, after duly subtracting the XRD profile broadening due to lattice strain. Incorporation of Na\(^+\) in ZnO samples were initially confirmed by atomic absorption spectroscopy Using x-ray photoelectron spectroscopy (XPS) and corelevel spectra the surface of ZnO:Na samples is analysed.

[123] B. Martinez, F. Sandiumenge et al prepared Co-doped ZnO nanophase particles by the vaporization-condensation method in a evaporation chamber. From the XRD spectra for samples of 2%, 5%, and 10% Co it is evident that only the peaks corresponding to the ZnO wurtzite SG \textit{P63mc}, \(a=0.32\) nm, \(c=0.52\) nm structure are detected. Electron microscopy techniques TEM have been used to characterize particles. No traces of impurities or secondary phases have been detected. The growth rate of particles is controlled by changing the pressure
inside the evaporation chamber and it also has a very strong effect on the microstructure of the samples.

[124] Jin Li, Huiqing Fan et al prepared Co-doped ZnO nanocrystals by a solvothermal route and studied the enhanced blue-green emission and ethanol sensing properties of Co-doped ZnO nanocrystals. The SEM image of the Co-doped ZnO nanocrystals showed that the average diameter of Co-doped ZnO is about 30 nm. From the XRD pattern of the Co-doped ZnO nanocrystals it was shown that it has hexagonal wurtzite ZnO crystal structure alone. The absence of the diffraction peaks of cobalt oxides in the XRD pattern implies that the Co got incorporated in the ZnO matrix by means of substitution for Zn. The ICP-AES studies confirmed that 2.1% of Co is present in the matrix of ZnO. From the XRD pattern, the average size of the particle is calculated using the scherrer’s formula and it agreed well with the SEM image. The optical absorption spectra at room temperature of the Co-doped ZnO showed that Co-doped ZnO nanocrystals exhibit a typical exciton absorption around 3.4 eV. Apart from that it additionally has three weak absorption peaks at 1.9 eV, 2.02 eV and 2.19 eV in it. These peaks correspond to the electronic transition of a Co 3d orbital in the oxygentetrahedron: 4A2(F)→2E(G), 4A2(F)→4T1(P), and 4A2(F)→2A1(G), respectively. From the absorption spectrum, the band-gap values Co-doped ZnO is calculated to be about 3.24 eV. Comparison of this with the Eg value of undoped ZnO nanocrystals (3.27 eV), show that the Co doping causes a band-gap narrowing about 30 meV. The Photoluminescence (PL) measurements showed the intrinsic and extrinsic defects in semiconductors, which was helpful for understanding structural defects in semiconductors. The room temperature PL spectra of the Co-doped ZnO showed that it exhibits UV emission near 382 nm corresponding to the near band edge (NBE) transition from direct exciton dissociation. This showed that the incorporation of Co into the ZnO host leads to
the evident weakening and broadening of the NBE peak due to the doping effect and its modifications on the lattice.

[128] F. Golmar, M. Villafuerte et al synthesized Cobalt-doped ZnO films were grown on SiO2/Si and sapphire substrates in N2 or O2 atmospheres by pulsed laser deposition (PLD). The magnetic and electrical properties of these samples were investigated by measuring the in-plane Magnetization versus magnetic field and also the electrical and electromagnetic transport as a function of temperature between 5 K and room temperature and how it varies with the micro or nano-structural inhomogeneity is studied. These results were correlated with structural and compositional studies and it showed that the samples doped with Co showed a paramagnetic behaviour. The pure samples were diamagnetic, independently of the growth atmosphere. A giant positive magnetoresistance was estimated using I–V curves taken at constant temperatures in zero magnetic field and in 10 T. Structural and magnetic characterizations showed that the system ZnO:Co has a hybrid nanostructure.

XRD pattern corresponded to the wurtzite structure for all films showing only the (002) and (004) wurtzite reflection. The double peak occurs at 2θ= 34.08°. This result corresponds to a (002) reflection from a composition modulated alloy of two wurtzite systems with different lattice parameter. The XRD patterns of thinner films don’t have double peaks in it, but the XRD revealed the segregation of Co particles in some films. It was already reported about the coincidence of the (002) ZnO and w–CoO reflection [129]. The coexistence of two wurtzite systems in thicker and doped sample, reveals the c-lattice constants as (5.19 ± 0.01) Å and (5.26 ± 0.01) Å. The c-lattice constant for pure ZnO growth in identical conditions was estimated as (5.24 ± 0.01) Å, it shows that the lower c-parameter correspond to a probable secondary phase
of wurtzite CoO. The mean sizes of each system were estimated using a best fitting of Gaussian curves and the Scherrer formula, \( D = 0.94k/W\cos\theta \). Scanning electron microscopy with EDS mapping shows that the Zn and Co distribution in \( \text{Zn}_{0.85}\text{OCo}_{0.15} \) film grown over sapphire substrates in \( \text{N}_2 \) atmosphere. The room temperature SQUID measurements of Co-doped thinner samples show that the values of the coercivity are similar for all samples. The negative values of the Curie–Weiss temperature obtained from the extrapolation of the high temperature range of the inverse moment versus temperature, -280K for a thicker film and -166.6 K for a thinner film indicate the existence of antiferromagnetic interactions.

\[130\] n. volbers h. Zhou et al prepared ZnO: Co\textsuperscript{2+} DMS-QDs by a wet chemical method, and investigate the electronic structure and magnetic properties by optical absorption, photoluminescence (PL), and electronic paramagnetic resonance (EPR) measurements. The diffraction peaks are broad due to the small size of the particles. From the scherrer formula they calculated the size of the ZnO: Co\textsuperscript{2+} nanoparticle to be in the range of 3–8 nm. \[131\] The absorption spectrum of unwashed doped colloid has three peaks at positions corresponding to energies 1.89 eV, 2.02 eV and 2.22 eV. \[132\]

\[133\] Hamid Reza Pouretedal et al, show that nanoparticles of zinc sulfide as undoped and doped with manganese, nickel and copper were used as photocatalyst in the photodegradation of methylene blue and safranin as colour pollutants. Photoreactivity of doped zinc sulfide was varied with dopant, mole fraction of dopant to zinc ion, pH of solution, dosage of photocatalyst and concentration of dye. The characterization of nanoparticles was studied using X-ray powder diffraction (XRD) patterns and UV–vis spectra. The maximum degradation efficiency was obtained in the presence of \( \text{Zn}_{0.98}\text{Mn}_{0.02}\text{S} \), \( \text{Zn}_{0.94}\text{Ni}_{0.06}\text{S} \) and \( \text{Zn}_{0.96}\text{Cu}_{0.10}\text{S} \) as nanophotocatalyst. The effect of dosage of photocatalyst was studied in the range of 20–250 mg/L. It was seen that
150.0 mg/L of photocatalyst is an optimum value for the dosage of photocatalyst. The most degradation efficiency was obtained in alkaline pH of 11.0 with study of photodegradation in pH amplitude of 2–12. The degradation efficiency was decreased in dye concentrations above 5.0 mg/L for methylene blue and safranin dyes. In the best conditions, the degradation efficiency was obtained 87.3–95.6 and 85.4–93.2 for methylene blue and safranin, respectively.

[\textsuperscript{134}] Jianfeng Chen et al prepared zinc sulfide nanoparticles under high-gravity environment and characterised them. Nanosized ZnS particles were prepared under high-gravity environment generated by the rotating packed bed reactor (RPBR) using zinc nitrate solution and hydrogen sulfide gas as raw materials. The effects of experimental conditions such as reactant concentration, reaction temperature, rotating speed of the RPBR and aging time, on the preparation of nanosized ZnS particles were investigated. Under these optimum conditions, a well-dispersed ZnS nanoparticle was obtained. The crystal structure, optical properties, size and morphology of the product were also characterized by XRD, UV-Vis spectrophotometer, and TEM, respectively. Results indicate that the prepared ZnS has a good absorption for light in the wavelength range of 200–330 nm. XRD analysis also shows the prepared ZnS is in a sphalerite crystal phase. The process has great potential for commercialization.

[\textsuperscript{135}] Daixun Jiang et al prepared Mn-doped ZnS nanocrystals by solvothermal method with different thicknesses of Zn\textsuperscript{(OH)}\textsubscript{2} shells through precipitation reaction. The impact of Zn\textsuperscript{(OH)}\textsubscript{2} shells on luminescent properties of the ZnS:Mn nanocrystals was investigated. X-ray diffraction (XRD) measurements showed that the ZnS: Mn nanocrystals have cubic zinc blende structure. The morphology of nanocrystals is spherical shape measured by transmission electron microscopy (TEM). ZnS:Mn/Zn\textsuperscript{(OH)}\textsubscript{2} core/shell nanocrystals exhibited much improved luminescent properties than those of unpassivated ZnS:Mn nanocrystals. The luminescence
enhancement was observed with the Zn\(^{(OH)}_2\) shell thickening by photoluminescence (PL) spectra at room temperature and the luminescence lifetime of transition from 4T1 to 6A1 of Mn\(^{2+}\) ions was also prolonged. This result was led by the effective, robust passivation of ZnS surface states by the Zn\(^{(OH)}_2\) shells, which consequently suppressed nonradiative recombination transitions.

\[^{136}\] M.L. Hassan et al synthesized nanostructured cadmium and zinc sulfides in aqueous solutions of hyperbranched polyethyleneimine. A new simple route for preparing nanocrystals of cadmium and zinc sulfides and their respective core/shell nanostructures in aqueous solution has been developed by precipitation from metal chloride solutions with sodium sulfide in the presence of polyethyleneimine (PEI) hyperbranched polymer. The as-prepared PEI-stabilized nanoparticles were characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), UV–visible spectroscopy, and flurospectroscopy. TEM showed homogeneous nanoparticle size. The sizes of cadmium sulfide (CdS) and zinc sulfide (ZnS) nanoparticles were about 7–53 and 4–17 nm, respectively, on using different proportions of PEI. The sizes of the core/shell and multilayered nanoparticles of both compounds were 19–24, 23–35, 108–185, and 100–130 nm for CdS/ZnS, ZnS/CdS, CdS/ZnS/CdS, and ZnS/CdS/ZnS compositions, respectively.

\[^{137}\] Ram Seshadri discussed the situation on the occurrence or absence of ferromagnetism in diluted magnetic semiconductors based on wurtzite zinc oxide hosts, focusing mainly on the many recent experiments which have been performed on bulk systems. Numerous reports have suggested that partial (typically less than 10 at.%) substitution of Zn\(^{2+}\) in ZnO by magnetic transition metal (tM) ions, particularly Mn\(^{2+}\) and Co\(^{2+}\), can result in samples with ferromagnetic Curie temperatures above the room temperature. Reports which cast doubt on the very existence of any kind of long range magnetic order in clean samples of Zn\(_{(1-x)}\)Mn\(_x\)O at
low transition metal concentrations are also appearing with increasing frequency. The confusing situation clearly calls for a critical, even subjective position to be taken on this topic. The experimental situation on bulk samples strongly favors the view that in cases when ferromagnetism is found, it is not intrinsic to Zn_{1-x}Mn_xO.
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