

## 5.1 Introduction

Addition of magnetic impurity in the semiconductor resulting in dilute magnetic semiconductor (DMS) and by this way magnetic property can be tuned [1]. There are reports where even undoped nanoparticles of diamagnetic materials are found to be ferromagnetic [2]. There are many reports on the origin of ferromagnetic property of the materials. Sundaresan et al. proposed the exchange interaction between localized electron spin moments resulting from oxygen vacancies at the surface of uncapped ZnO nanocrystals as origin of ferromagnetism [3]. Wang et al. reported Zn vacancies to be responsible for the ferromagnetism [4].

In the present study, we have synthesized undoped and doped ZnO nanoparticles using polyethylene glycol (PEG) as a capping agent at room temperature. We have studied the effect of different transition metal ions as dopants ( $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$ ) on the optical properties and magnetic properties of ZnO nanoparticles.

## 5.2 Synthesis

The aqueous solution of zinc nitrate (0.2 M) and manganese acetate (0.118 M) were mixed under continuous stirring followed by addition of aqueous solution of PEG-400 (0.2 M). An aqueous solution of NaOH (0.4 M) was added drop wise. The reaction mixture was continuously stirred for 24 h to get a homogenous stabilized dispersion. The resulting precipitate were separated by centrifugation at 8000 rpm, washed with deionised water several times and then dried at 100 °C to obtain a  $\text{ZnO:Mn}^{2+}$  powder sample. Similarly Co doped and Cu doped nanoparticles were synthesized by mixing zinc precursor with different metal ions solution like 0.110 M of  $\text{CoCl}_2$ , and 0.103 M of  $\text{Cu}(\text{CH}_3\text{COO})_2$  respectively. Undoped ZnO nanoparticles were synthesized by the same method without any dopant ions.

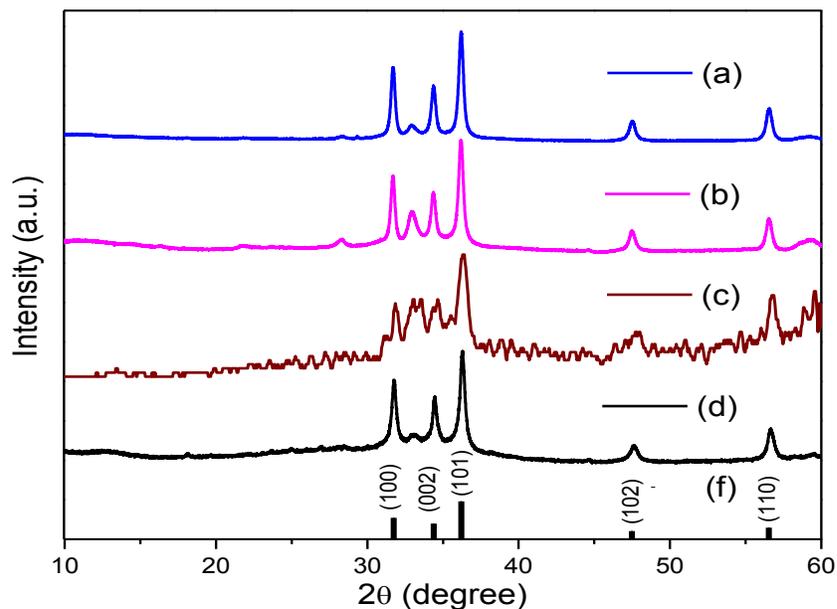
### 5.3 Results and discussion

#### X-Ray Diffraction (XRD)

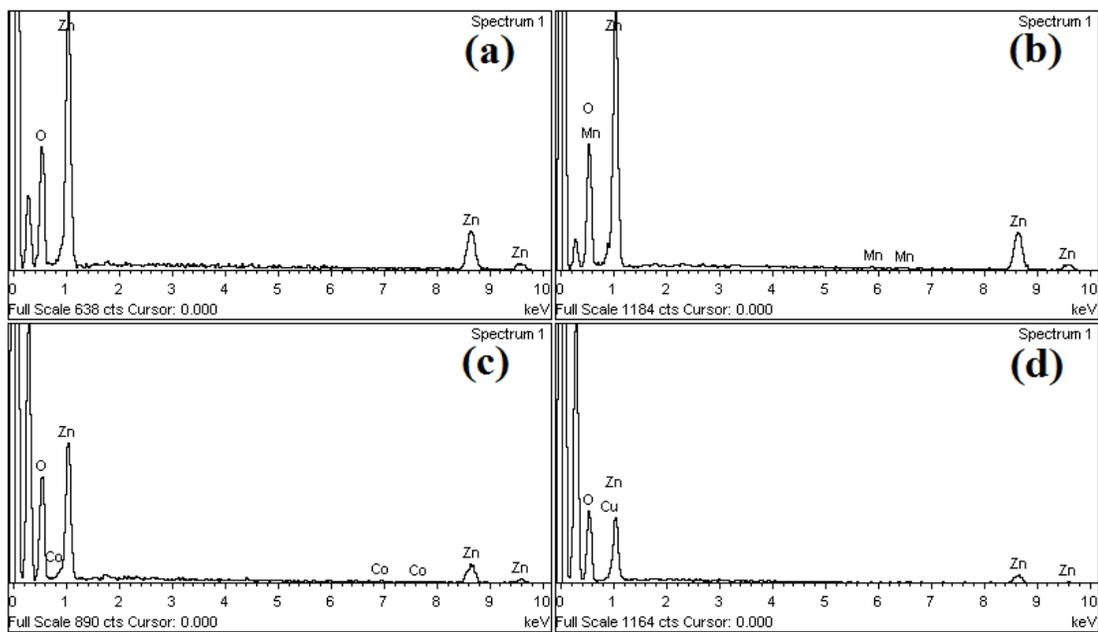
The purity and crystallinity of as-synthesized nanoparticles were studied from XRD pattern as shown in Figure 5.1. The XRD pattern matches with the standard data for ZnO hexagonal structure (JCPDS card no. 89-1397). The XRD patterns matches with the standard ZnO material. The average particle sizes were in the range of 12-20 nm as given in Table. 5.1, calculated using Debye-Scherrer formula [5].

#### Energy Dispersive X-ray (EDX)

Elementary composition of the doped and undoped ZnO nanoparticles were studied by Energy Dispersive X-ray (EDX) analysis. EDX spectra of the as-synthesized nanoparticles are shown in Figure 5.2. From EDX analysis the compositions of the nanoparticles confirmed the presence of dopant ions (Table 5.2). The ZnO:Cu<sup>2+</sup> nanoparticles showed highest zinc deficiency when compared with the other doped and undoped ZnO nanoparticles.



**Figure 5.1** The X-ray diffraction pattern of (a) undoped ZnO (b) ZnO:Mn<sup>2+</sup> (c) ZnO:Co<sup>2+</sup> (d) ZnO:Cu<sup>2+</sup> nanoparticles and (f) bulk ZnO standard (JCPDS card no 89-1397).



**Figure 5.2** EDX spectrum for (a) undoped ZnO nanoparticles (b) ZnO:Mn<sup>2+</sup> (c) ZnO:Co<sup>2+</sup> and ZnO:Cu<sup>2+</sup> nanoparticles.

## Transmission Electron Microscopy (TEM)

The particle size and morphology of the as-synthesized nanoparticles were studied by TEM microscopy as shown in Figure 5.3. TEM image of undoped ZnO nanoparticles show particles of average size about 42 nm, which seems to be formed of smaller thin sheet like nanoparticles. The SAED pattern reveals a crystalline pattern of the material. The TEM image of ZnO:Mn<sup>2+</sup> nanoparticles shows a spherical morphology of size 450 nm, which is composed of small nanorods of length ~ 45.1 nm and breadth of ~ 7.0 nm. The SAED pattern shows a crystalline pattern of the material. The TEM image of ZnO:Co<sup>2+</sup> nanoparticles shows a irregular morphology of size 400 nm, which is composed of small nanorods of length ~ 91.0 nm and breadth of ~ 4.6 nm. The SAED pattern reveals a crystalline pattern of the material.

There are report of use of PEG as a capping agent for the synthesis of ZnO nanostructures different research papers such as Zhou et al. reported ZnO nanorods solid nanocones, or hollow prisms using poly ethylene glycol (PEG) with different molecular weights [6]. Li et al. reorted ZnO nanocolumns, synthesized by a microemulsion-mediated hydrothermal method with the assistance of PEG400 as passivant [7].

## Dynamic light scattering (DLS)

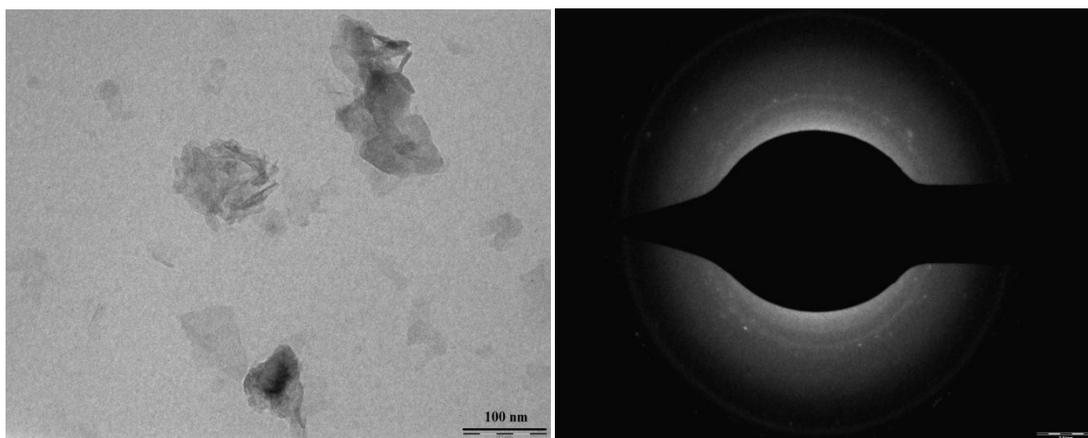
The particle size of the doped and undoped ZnO nanoparticles was studied by DLS study as given in table 3. The particle size distribution is shown in Figure 5.6. The particle diameter of undoped and doped ZnO nanoparticles was in the range of 300-400 nm as given in table 2. The ZnO:Mn<sup>2+</sup> and ZnO:Cu<sup>2+</sup> doped nanoparticles showed monodispersed size distribution. At the same time undoped and ZnO:Co<sup>2+</sup> nanoparticles showed a two type of population.

**Table 5.1.** UV absorption edge, band gap energy of doped and undoped ZnO nanoparticles.

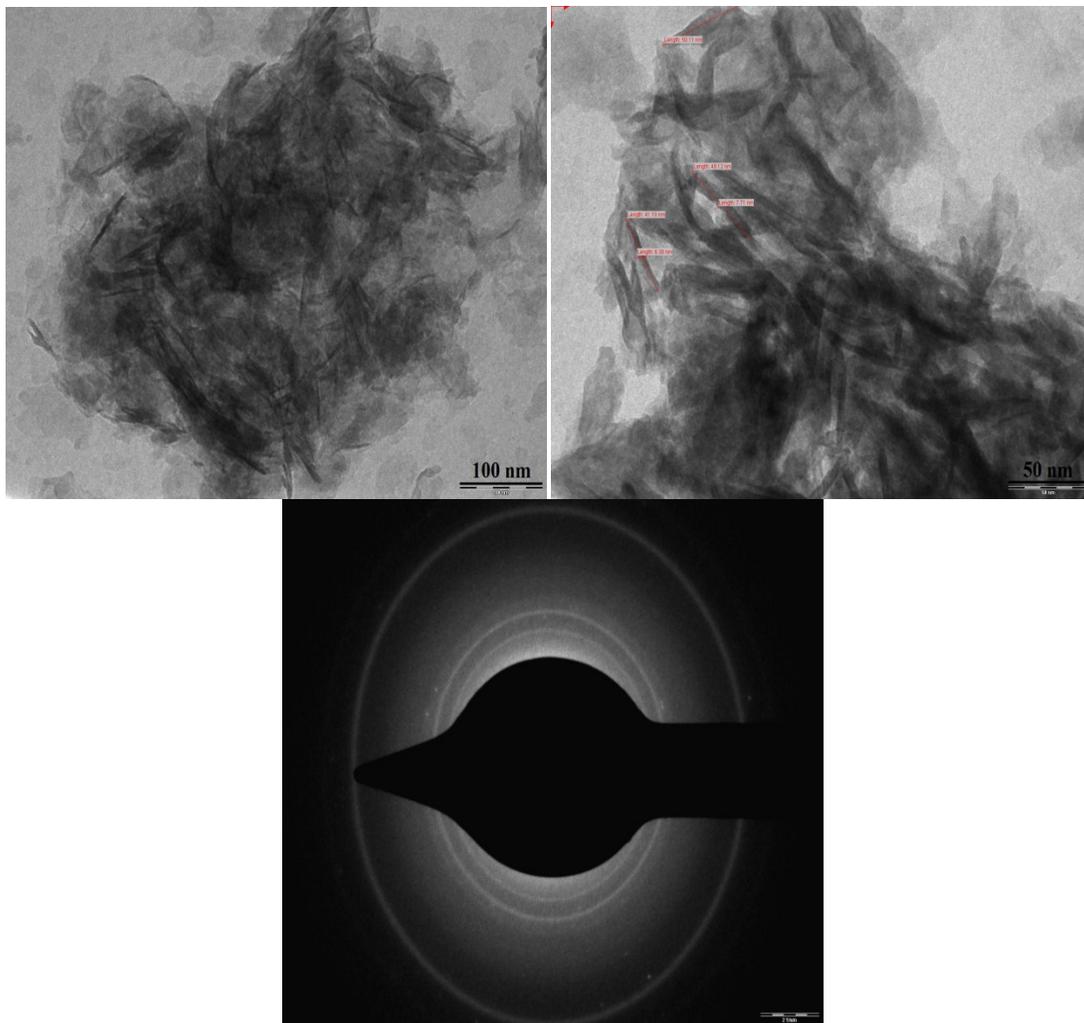
Sample	Absorption shoulder (nm)	$E_g$ (eV)	Particle size (calculated from XRD) (nm)
ZnO (Bulk)	370	3.36	-
undoped ZnO	360	3.45	20.3
ZnO: Mn <sup>2+</sup>	352	3.53	17.8
ZnO: Co <sup>2+</sup>	356	3.49	12.3
ZnO: Cu <sup>2+</sup>	361	3.44	19.3

**Table 5.2.** Elementary composition of the undoped and doped ZnO nanoparticles as studied by EDX.

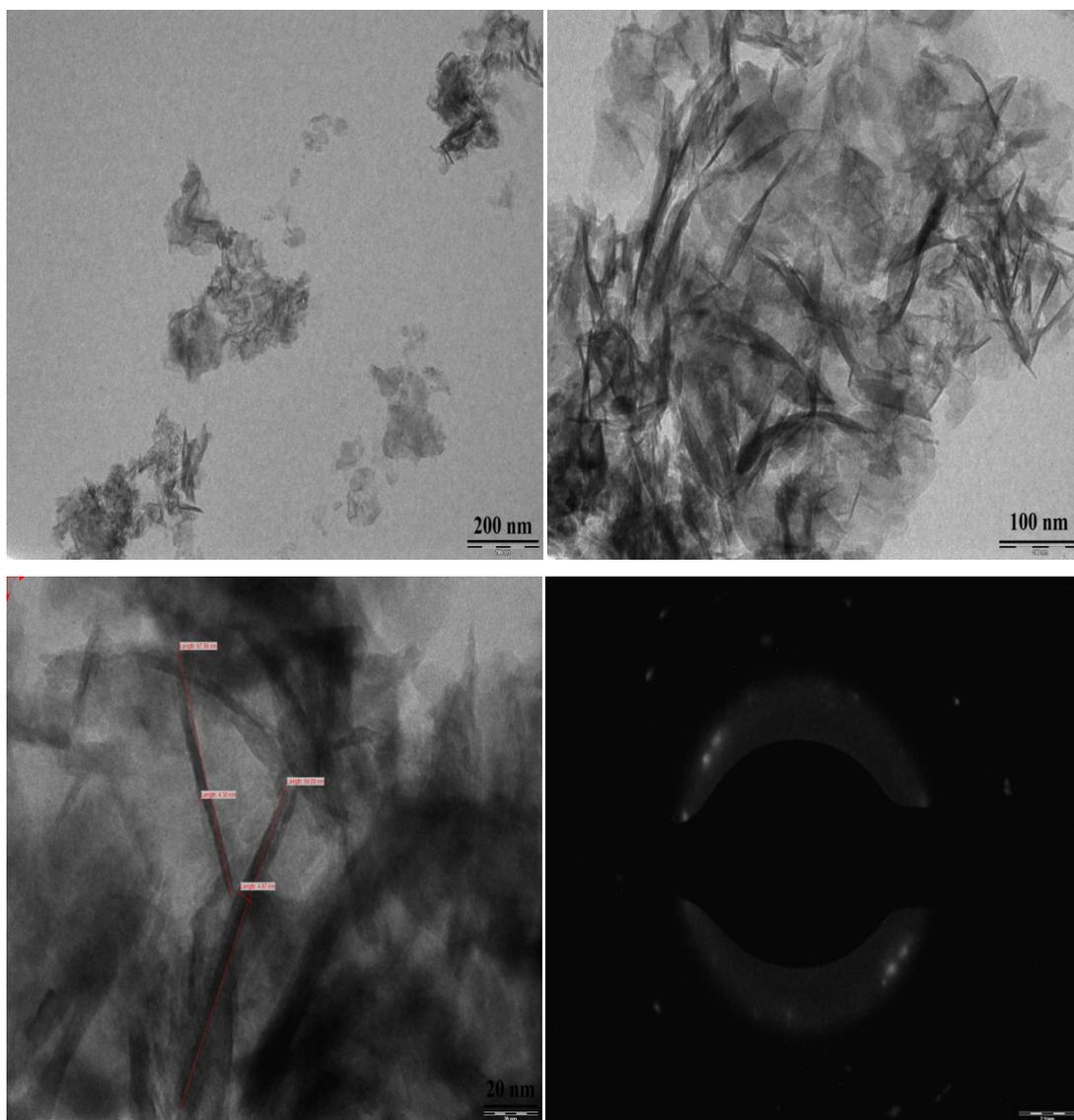
Sample	at. % of element(Zn)	at. % of element(O)	at. % dopant
ZnO	31.69	68.31	-
ZnO:Mn <sup>2+</sup>	31.43	68.33	0.24
ZnO:Co <sup>2+</sup>	23.24	76.56	0.21
ZnO:Cu <sup>2+</sup>	18.70	80.90	0.40



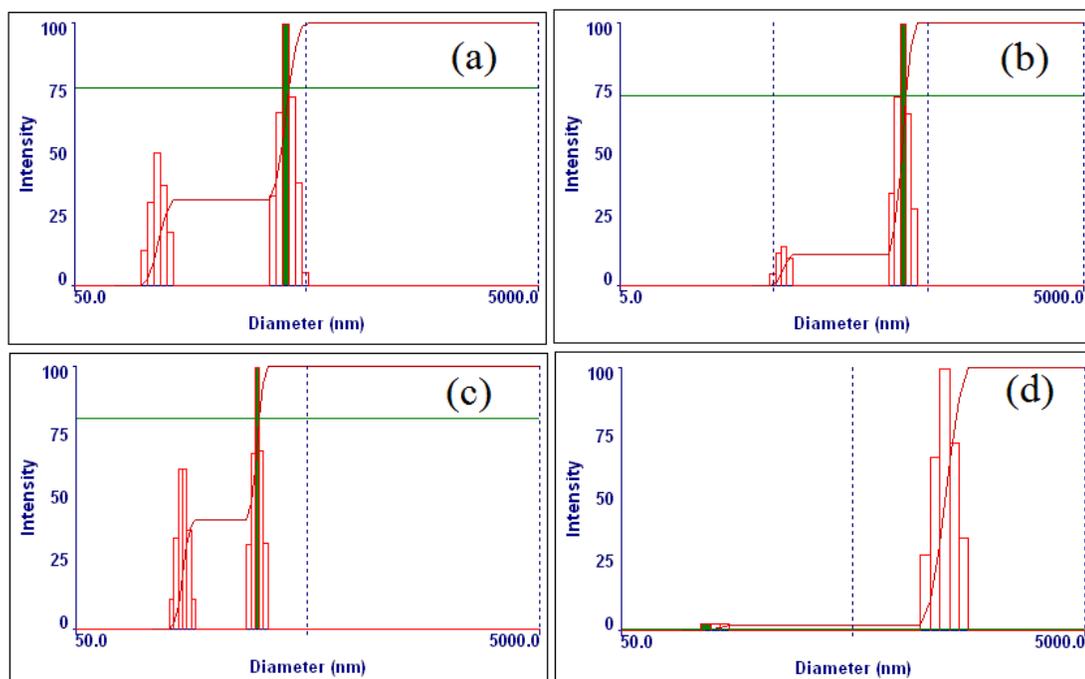
**Figure 5.3** TEM image and selected area electron diffraction (SAED) pattern of undoped ZnO nanoparticles.



**Figure 5.4** TEM image and selected area electron diffraction (SAED) pattern of  $\text{Mn}^{2+}$  doped ZnO nanoparticles.



**Figure 5.5** TEM image and selected area electron diffraction (SAED) pattern of  $\text{Co}^{2+}$  doped ZnO nanoparticles at different magnification.



**Figure 5.6** DLS of ZnO/PEG nanoparticles (a) undoped ZnO (b) ZnO:Mn<sup>2+</sup> (c) ZnO:Co<sup>2+</sup> and (d) ZnO:Cu<sup>2+</sup> nanoparticles.

**Table 5.3** Particle size as studied by Dynamic light scattering of doped and undoped ZnO nanoparticles.

Sample	Particle size (nm)
Undoped ZnO	406.4
ZnO:Mn <sup>2+</sup>	337.0
ZnO:Co <sup>2+</sup>	302.4
ZnO:Cu <sup>2+</sup>	373.7

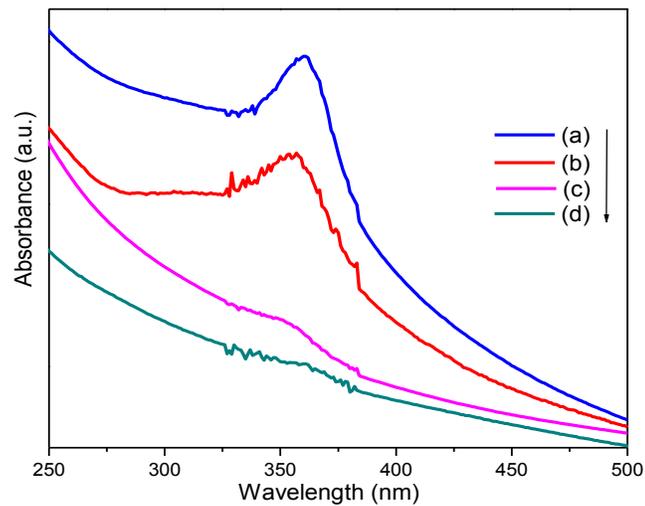
### Optical properties

The UV-visible absorption spectra of the as-synthesized nanoparticles have been shown in the Figure 5.7. The bulk ZnO shows absorption at 380 nm. The as-synthesized nanoparticles show blue shift in comparison to the bulk material. The blue shift of absorption peaks indicate particle in the nanometer dimension.

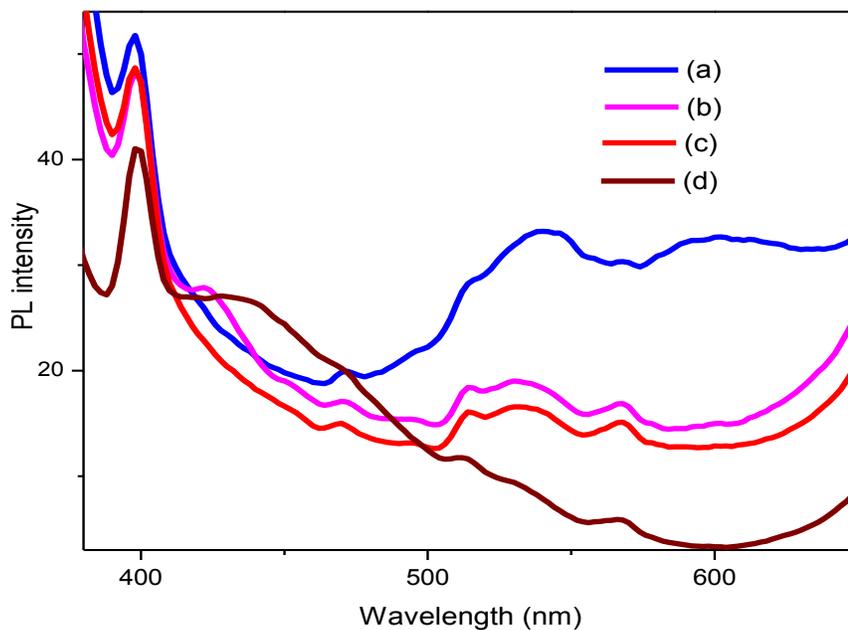
The photoluminescence emission spectra of undoped and doped (Mn, Co and Cu) ZnO nanoparticles are shown in Figure 5.8. The excitation wavelength was set to 350 nm. A sharp emission band at 398 nm was obtained in undoped and doped nanoparticles. This band can be assigned to near-band-edge (violet) emission, which is associated with zinc vacancy related defects [8]. The ZnO:Cu<sup>2+</sup> nanoparticles showed a broad band at 440 nm which can be assigned to the oxygen vacancies of ZnO structures [9]. Another broad emission band around 540 nm was observed. The intensity of emission band around 540 nm varied in presence of different dopant ions in the host matrix. The intensity of this band enhanced in Mn doped nanoparticles while Cu doped nanoparticles showed quenched emission of this band. This band can be attributed to the transition of a photogenerated electron close to the conduction band to a deeply trapped hole in the single ionized oxygen vacancy (V<sup>·</sup>o) [10].

A weak emission band was observed at 570 nm in undoped and doped ZnO nanoparticles, which can be ascribed to singly ionized oxygen vacancies in ZnO, and it arises from the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy [11].

Undoped ZnO nanoparticles showed a broad emission band at 600 nm. This emission is less commonly reported and its origin is considered to be associated with interstitial oxygen ions (O<sub>i</sub><sup>-</sup>) [12]. The intensity of band at emission band at 600 nm is very less in case Mn<sup>2+</sup> and Co<sup>2+</sup> doped ZnO nanoparticles when compared with the undoped ZnO nanoparticles. In case of ZnO:Cu<sup>2+</sup> quenched emission band was observed.



**Figure 5.7** Absorption spectra of (a) undoped (b) ZnO:Co<sup>2+</sup> (c) ZnO:Mn<sup>2+</sup> and (d) ZnO:Cu<sup>2+</sup> nanoparticles.



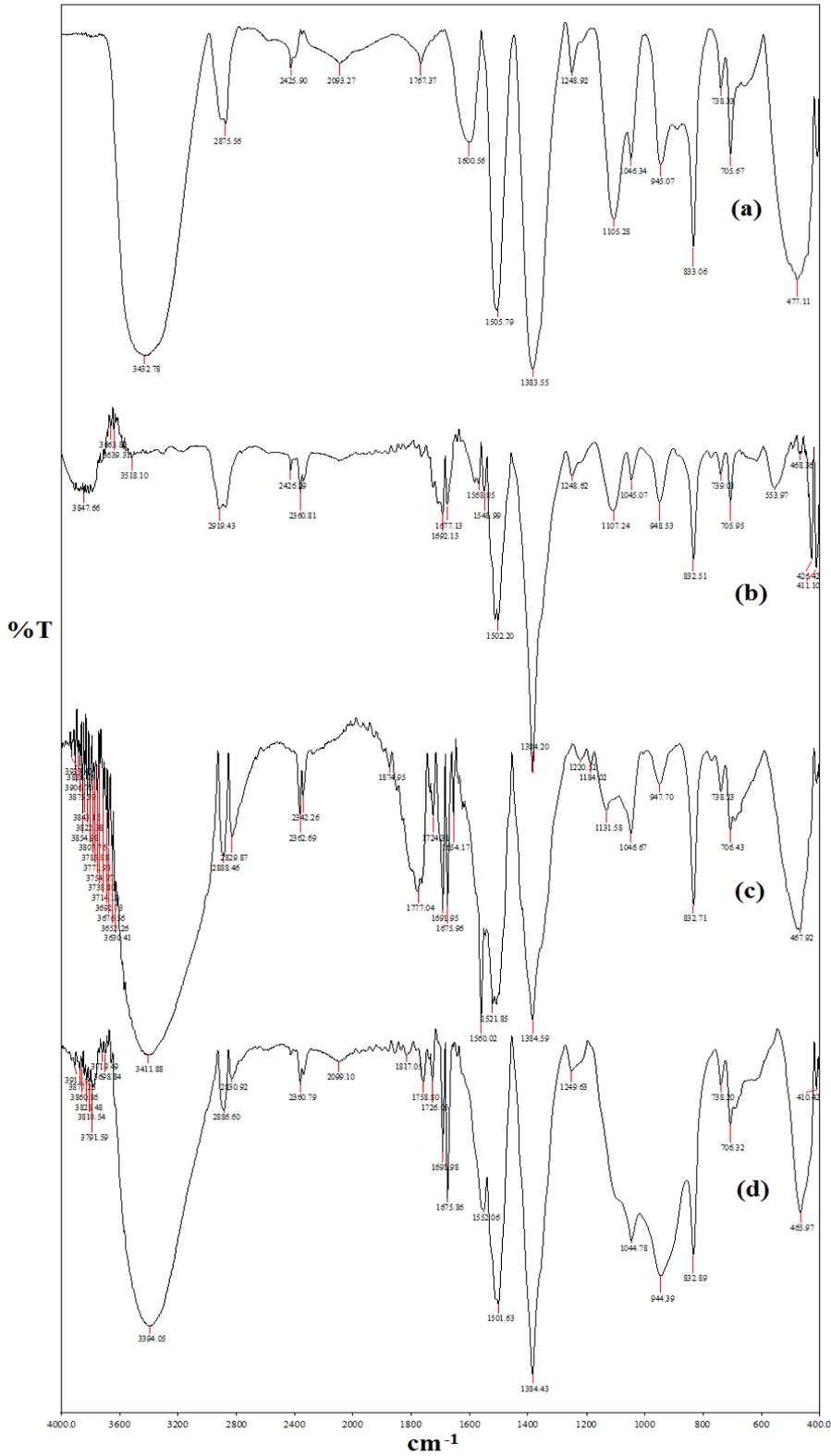
**Figure 5.8** Photoluminescence emission spectra of ZnO nanoparticles (a) undoped ZnO (b) ZnO: Mn<sup>2+</sup> (c) ZnO:Co<sup>2+</sup> and (d) ZnO:Cu<sup>2+</sup>.

## Fourier Transform Infrared Spectroscopy (FT-IR)

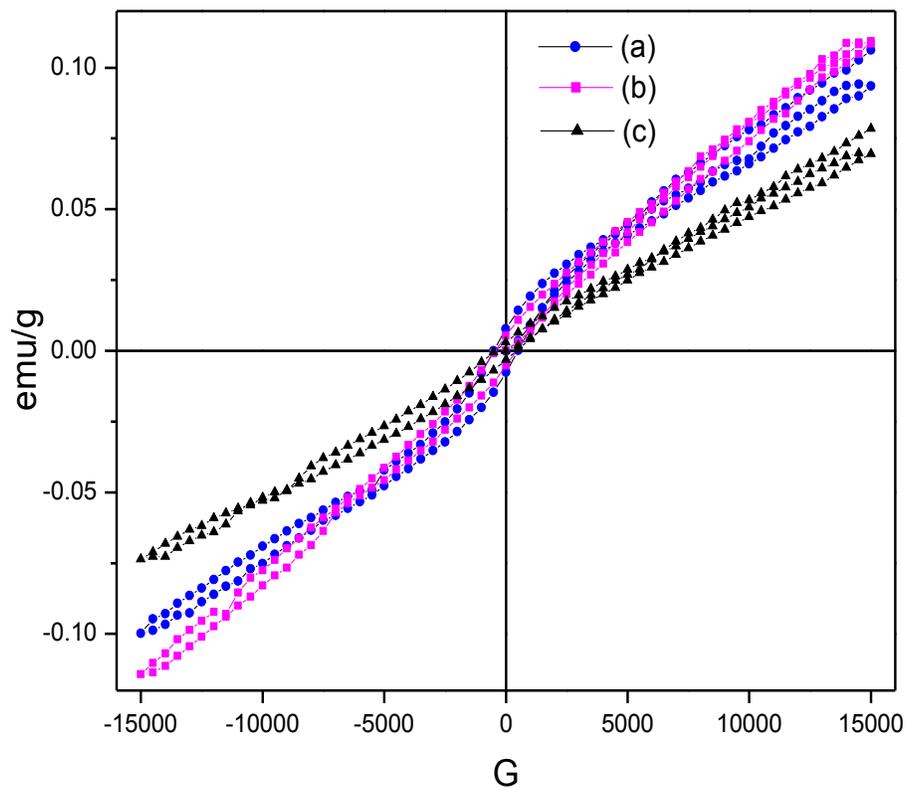
The presence of PEG as a capping agent was confirmed by FTIR spectroscopy as shown in Figure 5.9. A peak at  $477\text{ cm}^{-1}$  can be assigned to Zn-O bonds [13], confirming formation of ZnO. A peak at  $705\text{ cm}^{-1}$  can be assigned to methylene rocking. A peak at  $945\text{ cm}^{-1}$  and  $1505\text{ cm}^{-1}$  can be assigned to O-H out of plane bending and O-H stretching. A peak at  $1383\text{ cm}^{-1}$  can be assigned to the bending vibration of methylene ( $-\text{CH}_2$ ), and the result suggests that some PEG molecules adsorb on the surface of ZnO particles. A peak at  $2875\text{ cm}^{-1}$  indicates methylene symmetric C-H stretching. A broad peak at  $3432\text{ cm}^{-1}$  can be due to adsorbed moisture. From the above observation we can confirm the presence of PEG as a capping agent.

## Vibrating Sample Magnetometer measurements (VSM)

The magnetic property of the ZnO nanoparticles was studied by Vibrating Sample Magnetometer measurements (VSM) at 300 K are shown in Figure 5.10. The undoped, Mn doped and Co doped ZnO nanoparticles showed weakly ferromagnetic behavior. The magnetic property was highest in case Mn doped ZnO nanoparticles with  $M_s=0.122\text{ emu/g}$ . The Co doped ZnO nanoparticles showed lowest magnetic property  $M_s=0.076\text{ emu/g}$ . Wang et al. reported ferromagnetic behavior of  $\text{Zn}_{0.96}\text{Mn}_{0.04}/\text{ZnO}$  coaxial nanocables, with a Curie temperature higher than 350 K [14]. Deka et al. reported ferromagnetism in nanocrystalline material of  $\text{Zn}_{1-x}\text{Co}_x\text{O}$ , when Co ( $x < 0.1$ ) are substituted in ZnO [15]. Qiu et al. reported ferromagnetism in hierarchically assembled  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  nanodisk hollow spheres at 300 K [16]. Kittilstved et al. reported high-Curie temperature ( $T_C$ ) ferromagnetism in  $\text{Mn}^{2+}:\text{ZnO}$  colloids, activated by amine binding and calcination [17]. The undoped ZnO nanoparticles showed intermediate magnetic property. The different magnetic parameters observed from VSM are given in Table. 5.4. The magnetic study shows a ferromagnetic behavior of undoped and doped ZnO nanoparticles which may find application as DMS.



**Figure 5.9.** FTIR spectra of TA capped (a) undoped ZnO (b) ZnO: Mn<sup>2+</sup> (c) ZnO:Co<sup>2+</sup> and (d) ZnO:Cu<sup>2+</sup> nanoparticles.



**Figure 5.10** VSM of (a) undoped ZnO (b) ZnO:Mn<sup>2+</sup> and (c) ZnO:Co<sup>2+</sup> nanoparticles.

**Table. 5.4** Magnetisation parameters of VSM of doped and undoped ZnO nanoparticles.

Temperature (K)	ZnO	ZnO:Mn <sup>2+</sup>	ZnO:Co <sup>2+</sup>
Susceptibility ( $\chi$ )	$3.9 \times 10^{-6}$	$4.3 \times 10^{-6}$	$3.7 \times 10^{-6}$
Retentivity(emu/g)	0.008	0.005	0.003
Ms (emu/g)	0.103	0.122	0.076
Coercivity (G)	492.87	423.93	426.48

## Conclusion

We have successfully synthesized undoped and doped ( $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$ ) ZnO nanoparticles using simple wet chemical method at room temperature. PEG is used as a capping agent. TEM showed undoped ZnO nanoparticles of size about 40 nm,  $\text{Mn}^{2+}$  doped ZnO and  $\text{Co}^{2+}$  nanoparticles showed nanostructures composed of nanorods. The optical properties of undoped ZnO nanoparticles showed higher PL emission intensity in comparison to the doped ZnO nanoparticles. The  $\text{Cu}^{2+}$  doped ZnO nanoparticles showed quenched PL emission. The magnetic study showed ferromagnetic behavior of doped and undoped ZnO nanoparticles. The magnetic properties show that these materials may find application in DMS devices.

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