CHAPTER - 8

CONCLUSION AND FUTURE SCOPE OF THE WORK
8.1 Conclusion

The present work deals with the PLA of iron, cobalt, manganese and synthesis of Li doped ZnO diluted magnetic semiconductor and biological application of iron, cobalt and iron sulfate NPs. Pulse laser ablation technique has been employed for the synthesis of magnetic colloidal NPs, which is very easy, green, eco-friendly and rapid, there is no need of any toxic chemicals. This technique can be used to produce ultra pure and different shaped nanostructures for biological and medicinal applications. PLA contains large number of parameters for controlling the structure, shape, size and morphology of nanomaterials. Optical, structural, magnetic and thermal transport properties of as synthesized nanomaterials have been studied using various techniques. Brief of the work done is given below.

(i) PLA of Fe Target in Different Liquid Media

Ablation of iron target in DDW produces FeO NPs but after the oxidation and agglomeration it converts into Fe$_2$O$_3$ phase. Absorption bandgap of as synthesized FeO and agglomerated Fe$_2$O$_3$ NPs have been estimated using tauc plot. Two optical bandgaps are found due to charge transfer and pair excitation process. Nanoparticles have spherical shape with diameter in the range of 1-10 nm. The FeO NPs show antiferromagnetic character with coercivity 47 Oe and remanence 0.009 emu / gm. Field cooled (FC) and zero field cooled (ZFC) measurements confirm that FeO NPs have blocking and Neel temperature 245$^{0}±2$ K and 181$^{0}±2$ K, respectively. Thermal conductivity measurement confirms that iron oxide ferrofluids have larger thermal conductivity than base fluid. Ablation of iron target in CTAB liquid media resulted mix phases of iron oxide / hydroxide such as, β-Fe$_2$O$_3$, ε-Fe$_2$O$_3$ and FeO (OH), with size in the range of 5-20 nm. Magnetic particle size, coercivity, saturation magnetization and remanence are found in the range of
3.00-5.00 nm, 95-193 Oe, 0.038-0.045 emu/gm and 0.0011-0.014 emu/gm respectively as recorded in the temperature range of 80-300 K. This shows that magnetic property of mix phase of iron oxide hydroxide NPs depend on temperature. PLA of iron target in SDS liquid media produces Fe$_3$O$_4$ NPs. Optical bandgaps have been calculated in the range of 2.86-2.27 eV and 2.64-2.27 eV of the as synthesized and agglomerated NPs respectively. It is found that optical bandgap of agglomerated NPs decreases due to ageing effect in liquid environment. Particle size was found in the range of 10-30 nm. The coercivity (Hc) and remanence magnetization (M$_r$) of Fe$_3$O$_4$ NPs are found to be 33.65 Oe and 0.010 emu / gm, respectively.

Fe$_2$O$_3$ bulk powder was ablated by laser ablation technique in DDW, SDS and CTAB liquid media. The optical bandgap energy is found in the range of 1.98-2.03 eV, while 1.92 eV is bandgap of bulk powder. Mix phases of iron oxide are formed in presence of CTAB liquid media. The coercivity has been found in the range of 206-298 Oe, though 239 Oe is bulk sample coercivity.

Thus we have synthesized all possible phases of iron oxide colloidal NPs in aqueous media using PLA technique in different liquid environment. Cationic and anionic surfactants play important role for determining of phase, particle shape and size of iron oxide NPs while laser energy affects optical bandgap. It is clear that as synthesized magnetic colloidal NPs in different liquid media are not stable in corresponding environment for longer time due to ageing and oxidation effect. FeO NPs can be used efficient heat transfer, catalysis and gas-sensor application. Based on optical and magnetic properties of Fe$_2$O$_3$ and Fe$_3$O$_4$ NPs can be used in biosensor, ion exchangers, lubrication and corrosion protective coatings and biomedical applications.
(ii) PLA of Cobalt Target in Different Aqueous Media

PLA of cobalt in DDW gives Co$_3$O$_4$ NPs, but in ethanol, pure cobalt NPs can be obtained. The optical bandgap of as synthesized cobalt oxide NPs have been tuned in the range of 2.18- 2.50 eV and 3.35-3.60 eV these bandgap corresponds to charge transfer from Co$^{+2}$ and Co$^{+3}$ to O$_2^{-2}$ respectively. After agglomeration it takes value 1.35- 1.73 eV and 2.80-3.75 eV, correspondingly. As synthesized cobalt oxide colloidal NPs have been found in the range of 1-5 nm but pure cobalt NPs have diameter 40-60 nm. Thermal conductivity based measurement shows that as synthesized cobalt and cobalt oxide NPs can be used as efficient coolant material and ferrofluids.

PLA of cobalt in CTAB liquid media produces cobalt oxalate and cobalt complex nanomaterials. It is seen that 1 mM CTAB provides effective capping or more steadiness of as synthesized cobalt oxalate and complex with respect to time in liquid media. Particle size is found to be in the range of 1-10 nm. Magnetic characterization reveals that as synthesized nanomaterials show ferromagnetic property. Ablation of cobalt target in SDS liquid media gives cobalt sulfate NPs. As synthesized cobalt sulfate NPs have bandgap 4.50 eV while agglomerated cobalt sulfate NPs have 4.50 and 3.20 eV bandgaps. Saturation magnetization and retentivity are found to be 0.40 and 0.017 emu/gm respectively.

Based on magnetic and optical properties of Co$_3$O$_4$ NPs they are useful in lithium ion batteries, heterogeneous catalysts, gas sensing, ceramic pigments, multi-enzyme activities and electrochemical devices and efficient coolant materials for electronic devices. Cobalt oxalate can be used in lithium ion battery, as a catalyst and precursor for cobalt oxide preparation.
(iii) PLA of Manganese in Different Liquid Media

Ablation of manganese target in DDW produces MnO NPs, optical particle size has been found in the range of 4.50-3.31 nm, calculated from UV-visible absorption. TEM/SEM confirms formation of different nanostructures, it agrees with UV-visible absorption. Bandgap of colloidal MnO NPs synthesized by 20, 30, 40 and 50 mJ / pulse energy, were found to be 4.70, 4.80, 4.90 and 5.10 eV respectively. M-H loop shows that MnO NPs are weak antiferromagnetic in nature.

PLA of manganese in CTAB liquid media results Mn$_2$O$_7$ nanocrystals, phase and crystal structure are confirmed by synchrotron XRD. Optical bandgap of as synthesized and agglomerated NPs were found to be in the range of 2.20-2.38 eV and 1.51-2.36 eV. TEM image shows that as synthesized nanocrystals have rod and spherical shape. The length of nano rod is about 100 nm and nano spheres are very small in order of 5-10 nm. Saturation magnetization, retentivity and coercivity are found to be 1.72, 0.015 emu/gm and 10.20 Oe, respectively.

Ablation of manganese in anionic SDS liquid media produces manganese hydroxide MnO(OH) NPs. The formation of branched micro rod is confirmed by TEM/SEM analysis and mechanism has been described. I–V plot shows that manganite thin film on glass substrate has better current efficiency in presence of white light source (CFL) in comparison to dark regime. Manganite thin film can be used as visible light detector. M-H loop confirms diamagnetic nature of MnO(OH) NPs.

Optical bandgap has been studied using UV-visible absorption spectroscopy and tuned using laser energy and concentration of CTAB and SDS surfactant. MnO and Mn$_2$O$_7$ phases of manganese oxide show week antiferromagnetic and near supper paramagnetic character respectively, but MnO(OH) NPs show diamagnetic property. MnO NPs can be
used in MRI contrast agent and Mn$_2$O$_7$ NPs can be used in colossal magneto resistance (CMR).

(iv) Application of These Magnetic NPs

To study the morphological effect of FeO colloidal NPs on plant, growing *Sesbania cannabina* seed has been chosen. Various morphological characters i.e. plant height, stem girth, number of leaves and root length have been studied at 0.025, 0.10 and 0.20 mM concentration of FeO NPs. It is seen that 0.10 mM FeO is more effective towards plant height, stem girth and number of leaves/plant while 0.20 mM shows most toxic character. To estimate the toxicity in growing seed of *Sesbania cannabina* we have used cobalt oxide, pure cobalt and ethanol while DDW was used as control. Thus from AMI% it was clear that cobalt oxide NPs are more toxic than pure cobalt NPs and causes a significant reduction in AMI(active mitotic index). It is found that cobalt oxide NPs are more chromotoxic and mitodepressive than cobalt NPs due to smaller particle size or more ROS production. The reduction in AMI may be due to slower progression of cells from S (DNA synthesis) phase to M(mitosis) phase of the cell cycle as a result of treatment. As synthesized bulk/nano sample of hydrated iron sulfate was used in co-culture of *Rhodobacter sphaeroides* and *E.coli* in hydrogen production. It was seen that 300 mg/l bulk/nano samples are more effective towards hydrogen production while nano sample is dominant over bulk samples in respect of enhancement effects.

Synthesis and characterization of Li doped ZnO is based on diluted magnetic semiconductor. The optical band gap of Undoped ZnO NPs has been found to be 3.26 eV and in ZnO:Li it varies from 3.00 to 3.34 eV. Undoped ZnO shows diamagnetic behavior and Li doped ZnO NPs show ferromagnetic behavior. It can be used in die synthesized solar cell and in magneto electronics.
(v) **Summary of the Work Done**

Ablation of Fe, Co and Mn targets in DDW give oxides of corresponding metals. Ablation of Fe target in DDW gives FeO NPs while ablation of Co and Mn target give Co$_3$O$_4$ and MnO NPs. FeO phase is unstable and it converts in stable Fe$_2$O$_3$ but Co$_3$O$_4$ and MnO remain same phase in DDW but ageing effect take place. Due to ageing effect optical band gap of these NPs changes. FeO and MnO NPs show antiferromagnetic character while Co$_3$O$_4$ NPs show ferromagnetic. Ablation of Fe, Co and Mn target in cationic CTAB liquid media give mix phases of Fe$_2$O$_3$ and FeO (OH), (C$_2$O$_4$Co) and Mn$_2$O$_7$ respectively. In Anionic SDS liquid media ablation of Fe, Co and Mn target give Fe$_3$O$_4$, CoSO$_4$ and Mn(OOH) NPs. Li doped ZnO synthesized by co-precipitation method.

### 8.2 Future Scope of the Work Done

Magnetic NPs offer various beautiful possibilities in biomedicine and biological applications. First, they have controllable size ranging from a few nanometers up to tens of nanometers, which places them at dimensions, that are smaller than or comparable to those of a cell (10–100$\mu$m), a virus (20–450 nm), a protein (5–50 nm) or a gene (2 nm wide and 10–100 nm long). Second, NPs are magnetic, which means that they obey Coulomb’s law, and can be manipulated by an external magnetic field gradient.

A few applications of magnetic NPs in biomedicine can be described as following.

The concept of magnetic targeting is to inject magnetic NPs to which drug molecules are attached and to guide these particles to a chosen site under the localized magnetic field gradients, hold them there until the therapy is completed, and then to remove them. Another interesting application of magnetic NPs is in hyperthermia treatment which is considered as a supplementary treatment to chemotherapy, radiotherapy, and surgery in cancer therapy. The idea of using magnetic induction
hyperthermia is based on the fact that when magnetic NPs are exposed to a varying magnetic field heat is generated by magnetic hysteresis loss, Neel-relaxation and Brown-relaxation.

The basic principle of MRI is based on nuclear magnetic resonance (NMR) together with the relaxation of proton spins in a magnetic field. When the nuclei of protons are exposed to a strong magnetic field, their spins align either parallel or antiparrallel to the magnetic field. During their alignment, the spins precess under a specified frequency, known as the Larmor frequency. When a ‘resonance’ frequency in the radio-frequency (RF) range is introduced to the nuclei, the protons absorb energy are excited to the antiparrallel state. After disappearance of the RF pulse, excited nuclei relax to their initial and lower-energy state. Magnetic NPs offer to contribute in relaxation time by introducing external magnetic field to enhance MRI contrast.

In microelectronics ferrofluids can be used as efficient coolant for cooling electronic devices. Magnetic thin films can be used for data recording and storage. As synthesized iron, cobalt and manganese NPs are ultra pure due to absence of any chemicals, based on above description the NPs can be used in numerous fields such as Drug delivery, Magnetic hyperthermia, MRI contrast enhancement agent, Spintronic application, Ferrofluids and efficient coolant. A controlled dose (concentration) of magnetic NPs on biological system can stimulate enzymatic and mutagenesis activity. Magnetic NPs are also effective towards hydrogen production from Rhodobacter sphaeroides and E. coli bacteria.