Chapter 6

Synthesis of nanoparticles by liquid phase pulsed laser ablation

6.1 Introduction

In the last few decades, research interest in nanostructured materials has arisen due to their unusual properties which are different from their bulk materials, such as their electronic, optical, magnetic and chemical properties. In recent years, great efforts have been made on the synthesis of nanoparticle colloids because of their special properties and their promising application in various fields of research like drug delivery [258], imaging [259, 260], diagnostics [261, 262] and for nanocomposites with special optical, mechanical, or bioactive properties [263, 264].

Pulsed laser ablation (PLA) was first developed in the 1960s, shortly after the invention of the pulsed ruby laser. Since then, laser ablation in
a vacuum or dilute gas has been studied by many researchers. By using different target materials and background gases, and varying parameters such as the laser wavelength, fluence, and pulse duration, it is possible to produce a wide variety of thin films [265]. These include high temperature superconductors [266], metals, semiconductors, oxides, diamond-like carbon [267] and other ceramics [268].

Pulsed laser ablation also has appeared to be the most flexible and promising technique because of its ability to ablate almost all kinds of materials due the ultra-high energy density and control over the growth process by manipulating the process parameters like irradiation time, duration, energy density, wavelength, etc [269].

The introduction of pulsed laser ablation at the solid-liquid interface was first reported by Patil and co-workers in 1987, who used a pulsed laser to ablate a pure iron target in water to form iron oxides with metastable phases [270]. This method is known as liquid phase pulsed laser ablation (LP-PLA), in which a solid target is immersed in a liquid medium and the laser beam is focused through the liquid onto the target surface. This pioneering work opened new routes for materials processing based on the PLA of solids in various liquids. Since then, the LP-PLA method has been used to produce a wide range of novel materials, such as nanodiamond and related nanocrystals, metallic nanocrystals, nanocrystal alloys, and metal oxides. Formation of nanoclusters under laser ablation in liquid environment has been much less studied.

LP-PLA techniques has become a successful material fabrication technique, allowing versatile design through choosing suitable solid targets and confining liquids. Compared to the other conventional physical methods
such as pulsed laser ablation in vacuum, sputtering etc and chemical methods, LP-PLA technique has many advantages. It is a chemically simple and clean process. The final product is usually obtained without any byproducts and therefore no need for further purification. It requires only inexpensive equipment for controlling the ablation atmosphere and easy to control the parameters. It requires minimum amount of chemical species for synthesis compared to the conventional chemical process. The extreme confined conditions and induced high temperature and high pressure region in this techniques favours the formation of metastable phases. Thus nanostructures of metals and semiconductors can be easily grown by this technique.

Commercial colloids are usually derived from sol-gel or salt precipitation processes, for which a precursor, additive and surfactant system need to be designed for each type of nanoparticle. Suitable chemical precursors like metal acetates and carbonates are a requirement for every synthesis process in nano-chemistry. Oxidation of metal or hydroxylation of ceramic nanoparticles is often unavoidable, and unreacted precursors and additives tend to remain in the final colloidal product [271, 272]. Today, huge efforts are being made for an efficient purification of these impurities [272]. Despite advances in the field of wet chemistry, the possibilities of sol-gel processes, especially with regard to product diversity, have not been exploited sufficiently [273]. In addition, the products are often restricted to thermodynamically stable crystal structures, which complicates the generation of hard ceramics like alpha aluminium oxide and tetragonal zirconium dioxide. Nanoparticles from such hard materials cannot be gained by mechanical milling, as the required forces increase exponentially with smaller particle size. In addition, milling may introduce impurities from grinding media [274]. But LP-PLA technique enables the development and supply of
new nanomaterials with comparably little effort. Still, the yield is mostly restricted to about \((0.01-0.1) \, \mu g \, \text{min}^{-1}\) \cite{275}, and there are knowledge deficits on the physical and chemical processes involved.

LP-PLA involves focusing a high power laser beam onto the surface of a solid target, which is submerged beneath a liquid. The interaction of the laser with the target causes the surface to vaporise in the form of an ablation plume, which contains species such as atoms, ions, and clusters, travelling with high kinetic energy. The species in the plume collide and react with molecules of the surrounding liquid, producing new compounds containing atoms from both the original target and the liquid. Due to the intensity of the laser and the nanosecond timescales, the instantaneous temperatures and pressures within the reaction volume can be extreme (many thousands of K at tens of GPa). Such high temperature, high pressure, and high density conditions results in the synthesis of novel materials which are not possible by other conventional techniques.

Melting of the solid is a necessary condition for the formation of nanoparticles under ablation in liquid environment. This is gained under sufficiently high laser fluence depending on the absorptivity of the material at the laser wavelength.

Formation of nanoparticles (NPs) using laser ablation of solids, either in gas or in vacuum, has been extensively explored during the last decade. Understanding the mechanisms of cluster formations is needed to control the process of pulsed laser ablation now widely used for the deposition of a large variety of compounds. LP-PLA can be seen as the extension of this concept. Therefore, the process of laser interaction with the target is similar for both laser ablation in a vacuum and ablation at the solid-liquid interface. Both produce plasma and create a strong confinement of
the emission species, resulting in an efficient electron-ion recombination. The difference is that the expansion of plasma occurs freely in vacuum in normal PLA, where as it is confined by a liquid layer in LP-PLA. The liquid delays the expansion of the plasma, leading to a high plasma pressure and temperature, which allows the formation of novel materials. Another advantage of LP-PLA is that both the solid target and the liquid are vaporized, so the product can contain atoms from the target material and the liquid. The generation of various NPs by LP-PLA is an alternative to the well-known chemical vapour deposition (CVD) method. Moreover, NPs produced by laser ablation of solid targets in a liquid environment are free of any counter-ions or surface-active substances [276]. This method combines the advantages of pulsed laser deposition (PLD) and those of chemical routes. As with the soft chemical routes, the product obtained is a stable colloidal dispersion of nanoparticles in a liquid medium but the ablation process allows the growth of materials with complex stoichiometries. Moreover, using pulsed laser ablation in a liquid medium gives access to materials which can only be synthesized at high pressure. Briefly, when a target is irradiated with fluences over 0.1 GWcm$^{-2}$, material is ejected and evaporated. According to Fabbro et al [277], a laser power density of several GWcm$^{-2}$ ensures a maximum pressure of several GPa generated by shock waves.

The mechanisms involved in the nucleation and phase transition of nanocrystals upon LP-PLA are not well understood. A recent review by Yang [278] gives an understanding of some of the nucleation thermodynamics, the phase transition, and the growth kinetics of nanocrystals by laser ablation of liquids.
LP-PLA is very fast and far-from-equilibrium process, so that all metastable and stable phases forming at the initial, intermediate and final stages of the conversion could be reserved in the final products, especially, for any metastable intermediate phases [278]. In other words, the quenching times in LP-PLA are so short that the metastable phases which form during the intermediate stage of the conversion can be frozen in, and form the synthesized final products.

According to Barther and co-workers [279], at the very initial stage of interaction of the high energy laser with the interface between the solid and the liquid, species ejected from the solid target surface have a large initial kinetic energy. Due to the covering effect of the liquid, these ejected species form a dense region in the vicinity of the solid-liquid interface. This stage is similar to that which occurs in vacuum or low pressure gas, where the laser generates a plasma plume. In LP-PLA, since the plasma is confined in the liquid, it expands adiabatically at supersonic velocity creating a shock-wave in front of it. This shock-wave will induce an extra, instantaneous pressure as it passes through the liquid. This laser-induced pressure will result in the increase of temperature in the plasma [280, 281]. Therefore, compared with a PLA plasma formed in gas or vacuum, the plasma formed in LP-PLA is at higher pressure and higher density. Another effect of the localized high temperature is that a small amount of the surrounding liquid is vaporized to form bubbles within the liquid. As more material is vaporized, the bubbles expand, until, at a certain critical combination of temperature and pressure, they collapse [282]. It is believed that when the bubbles collapse, the nearby species are subjected to temperatures of thousands of Kelvin (K) and pressures of several gigapascals (GPa), and that these extreme conditions allow novel materials to be created [283].
LP-PLA has been used to produce nanoparticles of many different metal elements including titanium [284], silicon [285], cobalt [286], zinc [287], copper [288], silver [289] and gold [290]. This technique can also be used to prepare NPs of compound materials such as TiO$_2$ [291], TiC [292] and CoO [286] in water, and ZnSe and CdS in various solvents, including water [293]. The use of this method opens up the possibility of studying new materials at the nanoscale range and therefore to envision new applications.

Only very recently has LP-PLA gained intensive attention for its ability to form more complex, higher dimensional nanostructures, and instigated the study of the dynamical process among laser-solid-liquid interactions.

6.2 Synthesis of ZnO nanoparticles by liquid phase pulsed laser ablation

Zinc oxide (ZnO) is a wide band gap (3.37 eV) promising semiconductor having large exciton binding energy (60 meV) at room temperature and has important applications in electroluminescent displays [294], optoelectronics [295, 296], sensors [297], lasers [122] etc. Because zinc is an important trace element for humans [206], ZnO is environment friendly and is suitable for in vivo bioimaging and cancer detection.

There have been reports on synthesis of ZnO nanoparticles by LP-PLA techniques from metal target [287, 298]. This chapter discusses the synthesis of highly luminescent, transparent, chemically pure and crystalline ZnO nanoparticles by LP-PLA technique from sintered ZnO mosaic target and Zn metal target without using any surfactant. The dependence of oxygen and nitrogen bubbling during ablation and pH of the medium on the properties of the ZnO nanoparticles were also investigated. The surfactant free
nanoparticles were grown by LP-PLA in acidic and basic medium. The surface charge of the nanoparticles provided the repulsive force between nanoparticles which suppressed the growth through coagulation.

6.2.1 Experimental

A ZnO (99.99%) mosaic target sintered at 1000°C for 5 h was used for the synthesis of ZnO nanoparticles. The ZnO target immersed in 15 mL of the liquid media having different pH was ablated at room temperature by third harmonic of Nd: YAG laser (355 nm, repetition frequency of 10 Hz, pulse duration of 9 ns). The experimental arrangement is shown in figure 6.1. The laser beam was focused using a lens and the ablation was done at a laser fluence of 15 mJ/pulse. The spot size of the laser beam is about 1 mm. The duration of ablation was 1 h in all the media. This simple room temperature method produced a highly transparent ZnO nanoparticles well dispersed in the liquid media.

Zinc nanoparticles were produced by pulsed laser ablation of a piece of zinc granules in water. Zn granules in 15 mL water was ablated at room temperature using third harmonic of Nd: YAG laser (355 nm, repetition frequency of 10 Hz, pulse duration of 9 ns). During the ablation, oxygen was bubbled in the water media and the ablation was carried out at different laser fluence and different time duration. This results in the formation of highly transparent colloidal solution of Zn nanoparticles well dispersed in water.

The formation of ZnO and Zn nanoparticles was confirmed by transmission electron microscopy (JEOL, TEM) operating at an accelerating voltage of 200 kV. The sample for TEM was prepared by placing a drop of nanoparticle colloidal solution onto a standard carbon coated copper grid.
The grids were dried before recording the micrographs. Photoluminescence (PL) spectra were recorded using Jobin Yvon Fluoromax-3 spectrofluorimeter equipped with 150 W xenon lamp.

Figure 6.1: Experimental setup for the LP-PLA technique

6.2.2 Results and discussion

Transmission electron microscopic (TEM) studies confirm the resulting product after laser ablation in different media consisted of particles in the nanoregime. The selective area electron diffraction (SAED) pattern shows concentric rings corresponding to the hexagonal ZnO. This clearly shows the growth of crystalline ZnO nanoparticles. From these studies, the formation of other species like Zn(OH)$_2$ or ZnO/Zn core shell structure is not found. Because the ejected molten material from the target normally reacts with medium only at the outer surface [299], the ejected plasma readily cools, thereby forming ZnO itself. Because there are many surface oxygen
deficiencies, these nanoparticles will be charged. The ZnO nanoparticles
grown by LP-PLA in pure water is usually charged because the isoelec-
tronic points of ZnO (\(\sim 9.3\)) is well above the pH 7.0 of pure water [300].
This surface charge provides a shield, preventing further agglomeration and
forming self stabilized particles even in the absence of surfactant.

The preliminary studies carried out in this laboratory [35] shows that
higher laser fluence results in bigger size and wide size distribution. The
larger duration of LP-PLA at lower fluence does not increase the size of the
nanoparticles but increase the particle density.

The size of the particle is found to increase when the experiment is
done with oxygen bubbling into the water during laser ablation of ZnO
targets while size remains the same as that grown in pure water when ZnO
nanoparticles were grown in nitrogen atmosphere. Figure 6.2(a) and (b)
shows the TEM images of the ZnO nanoparticles prepared in oxygen atmo-
sphere and nitrogen atmosphere. The TEM image of nanoparticles grown
in nitrogen atmosphere keeping the other parameters of the experiment
the same has same size as those grown in neutral demonized water (figure
6.2(b) and 6.2(c)). The oxygen bubbling during the ablation increases the
amount of dissolved oxygen and promotes the growth of ZnO. This leads to
bigger ZnO nanoparticles, where as nitrogen bubbling through the solution
does not provide any extra oxygen other than the oxygen in the plasma
produced by the laser interaction with the ZnO target. Thus the size of
the particle is same as those obtained by LP-PLA in pure water.
Results and discussion

The growth of ZnO nanoparticles by LP-PLA can be modeled as follows. The plasma consisting of ionic and neutral species of Zn and oxygen \([301]\) along with water vapor is produced at the solid-liquid interface on interaction between the laser beam and the ZnO target. Due to the high intensity of the laser beam in the nano second scales, high temperature \((10^4-10^5K)\) and pressure of few GPa \([302]\) in the volume is produced. The adiabatic expansion of the plasma leads to formation of ZnO. The ZnO thus formed interact with the solvent water forming a thin layer of Zn(OH)\(_2\) since ZnO is extremely sensitive to H\(_2\)O environment \([303]\). Thus the ZnO nanoparticles prepared by LP-PLA may have a thin passivation layer of Zn(OH)\(_2\). The oxygen bubbling during the ablation increases the amount of dissolved oxygen and promotes the growth of ZnO. This leads to bigger ZnO nanoparticles, where as nitrogen bubbling through the solution does not provide any extra oxygen other than the oxygen in the plasma produced by the laser interaction with the ZnO target. Thus the size of the particle is same as those obtained by LP-PLA in pure water. The ZnO nanoparticles grown by LP-PLA in the acidic medium pH=5 shows relatively bigger size in comparison with those grown in pure water under identical experimental
conditions. The very thin passivation layer of Zn(OH)$_2$ during the cooling of laser plasma interacting with the liquid medium may be slower owing to higher dissolution of hydroxide in acidic medium. Hence this favours the growth of bigger ZnO nanoparticles. Whereas the ablation in alkali medium favours growth of Zn(OH)$_2$ by providing hydroxyl group and hence result in smaller nanoparticles.

Figure 6.3: (a) TEM image and (b) HR TEM image of ZnO NPs synthesized in acid media by LP-PLA method. Inset of (a) shows the corresponding SAED pattern

Figure 6.3(a) shows TEM and figure 6.3(b) is the high resolution transmission electron microscopic (HRTEM) image. The SAED pattern of the ZnO NPs prepared in acid media (pH~5) keeping all other experimental parameters the same shows the ring pattern corresponding to the (002) plane of ZnO. The particles have an elliptical shape with 15 nm size along the elongated region (semi major axis) and 11 nm along the compressed region (semi minor axis) is observed from the HRTEM image. From the
diffraction rings in the SAED pattern, (002) plane of the wurtzite ZnO was identified.

![Figure 6.4](image)

**Figure 6.4:** (a) TEM image and (b) HR TEM image of ZnO NPs synthesized in basic media by LP-PLA method. Inset of (a) shows the corresponding SAED pattern

Figure 6.4(a) shows the TEM and the SAED pattern (inset) of ZnO nanoparticles prepared by pulsed laser ablation in basic media (pH~9). Spherical particles were observed in the HRTEM image (Figure 6.4(b)) having a size about 4 nm. The (002) plane of wurtzite ZnO is observed in the SAED pattern. This confirms the formation of crystalline ZnO nanoparticles by pulsed laser ablation in liquid.

The thermodynamic conditions created by the laser ablation plume in the liquid are localized to a nano meter scale which is not much influenced by the pH of the solution. The increase of laser energy for the ablation results in increase of size of the nanoparticles due to ablation of more material. The hydroxide passivation layer formation is much influenced by the
pH of the aqueous solution which may affect the growth and size of the particles. All the particles grown in acidic, alkali and neutral medium are well dispersed and no agglomeration of the particles are observed as in the case of ablation of zinc metal targets in aqueous solution [304]. In the present study the particles grown with oxygen bubbling during LP-PLA leads to the formation of bigger particles and there by causing agglomeration. This suggests that surface charge of ZnO nanoparticles arise mainly from oxygen deficiency and pH of the medium has less pronounced effect.

Figure 6.5: TEM image of Zn nanoparticles synthesized by LP-PLA method

TEM image of the Zn nanoparticles synthesized by liquid phase pulsed laser ablation of Zn target with oxygen bubbling is shown in the figure
Results and discussion

6.5. These nanoparticles have an average size about 8 nm. The inductively coupled atomic emission spectroscopic (ICP-AES) studies confirms the presence of Zn in the colloidal solution and the Zn content increases as the laser fluence and time of ablation increases. This may be due to the increased particle size and number density. The Zn content in the colloidal solution increases as the pH of the medium changes from basic to acidic.

![Figure 6.6: Room temperature PL emission of ZnO nanoparticles synthesized by LP-PLA technique in basic, neutral and acidic medium](image)

The room temperature photoluminescence measurements of these nanoparticles were carried out at an excitation wavelength of 325 nm. PL studies of ZnO nanoparticles synthesized in basic, neutral and acidic medium shows a emission at 379 nm which corresponds to the band to band transition of ZnO (Figure 6.6). In addition to the peak corresponding to band edge,
Raman peak of water and broad peak centered at 540 nm were observed in the PL spectra of ZnO nanoparticles synthesized by LP-PLA technique. This luminescence emission at 540 nm originates from the native oxygen defects of the prepared ZnO nanoparticles [35]. This emission at 540 nm corresponds to the transition between the photo excited holes and singly ionized oxygen vacancy.

![Figure 6.7: Room temperature PL emission spectra of ZnO and Zn nanoparticles synthesized by LP-PLA technique](image)

Room temperature PL emission of water, ZnO and Zn nanoparticles synthesized by LP-PLA of ZnO and Zn targets at 15mJ/pulse for 1 h were shown in the figure 6.7. It shows that only ZnO nanoparticles have PL emission at 379 nm and 540 nm in addition to the Raman peak of water. The PL spectra of Zn nanoparticles in water contains only the Raman peak of water.
6.2.3 Conclusion

Highly transparent, luminescent, bio-compatible ZnO nanoparticles were prepared in basic, neutral and acidic medium using LP-PLA technique without using any surfactant. Transmission electron microscopic study confirms the formation of crystalline ZnO and Zn nanoparticles. The size of the ZnO nanoparticles increases when oxygen is bubbled, whereas it remains same when nitrogen is bubbled during the LP-PLA. The size of the ZnO nanoparticles is found to be smaller when prepared in basic medium and larger when prepared in acidic medium compared to those synthesized in pure water. The room temperature PL emission studies of ZnO nanoparticles shows peaks corresponding to band edge at 379 nm and yellow emission due to oxygen native defects at 540 nm in addition to the Raman peak of water. PL spectra of Zn nanoparticles shows only the Raman peak of water.

6.3 Liquid phase pulsed laser ablation of ZnS and ZnS:Mn nanoparticles

Synthesis of nanoparticles has been the focus of an ever increasing number of researchers worldwide, mainly due to their unique optical and electronic properties [122, 305], which make them ideal for a wide spectrum of applications ranging from displays and lasers [306, 307] to in vivo biological imaging. A variety of preparation methods to produce nanoparticles, such as magnetic liquids [308], metals [309, 310], metal-polymer nanocomposites [311], semiconductors [312] and colloidal systems [313] have been reported. Over the past decade liquid-phase pulsed laser ablation (LP-PLA) technique has aroused immense interest [314, 315]. LP-PLA involves the firing
of laser pulses on to the target surface through the liquids transparent to incident laser wavelength. The ablation plume interacts with the surrounding liquid media, creating cavitation bubbles that, upon their collapse, give rise to extremely high pressure and temperature. These conditions are, however, localized and exist across the nanometer scale. LP-PLA has proven to be an effective method for preparation of many nanostructured materials, including nanocrystalline diamond, cubic boron nitride, and nanometer-sized particles of Ti, Ag, Au and TiC. Zinc sulfide is a wide band gap (\(E_g = 3.6\) eV at 300 K) semiconductor, which is considered important for applications such as ultraviolet-light-emitting diodes, electroluminescent devices, flat-panel displays, sensors and injection lasers [316, 317]. Under ambient conditions, ZnS has two types of polymorphs: zinc blende (cubic) and wurtzite (hexagonal). The cubic ZnS is stable at room temperature, whereas the hexagonal ZnS is stable at temperatures higher than 1020°C. When doped with some metal cations (including transition metal ions and rare-earth elements), ZnS is an excellent luminescent phosphor exhibiting photoluminescence (PL), electroluminescence (EL), thermoluminescence and triboluminescence [318–320].

Among these elements, Mn doping in ZnS attracts a great deal of interest since Mn doping can not only enhance its optical transition efficiency, but can also induce the material to exhibit interesting optical properties [321, 322] which is obviously an effective way to enhance the luminescent properties of ZnS for practical application.

Efficient phosphors for lighting applications, flat panel displays, target identification etc have always been a goal for researchers. The particle size of conventional phosphors are in micrometer scale, hence light scattering at grain boundaries is strong and it decreases the light output. Nanophosphors
can be prepared from tens to hundreds of nanometers that are smaller than the visible light wavelength and it will reduce the scattering, thereby enhancing the luminescence efficiency. Manzoor et al [104] reported the growth of Cu$^+$.Al$^{3+}$ and Cu$^+$.Al$^{3+}$.Mn$^{2+}$ doped ZnS nanoparticles by wet chemical method for electroluminescent applications. The high fluorescent efficiency and dispersion in water makes ZnS:Mn nanoparticles an ideal candidate for biological labelling. Since ZnS is an environment friendly material; it will eliminate potential toxicology problems. The growth of doped systems of II- VI semiconductor by LP-PLA is not yet reported to our knowledge. In the present study the growth, structural and luminescent characteristics of undoped and Mn doped ZnS nanoparticles were discussed.

6.3.1 Experimental

Target Preparation

ZnS target was prepared from commercially available ZnS (99.99%, Alfa Aesar) powder, weighed to an accuracy of 0.001 mg, hand mixed thoroughly in methanol medium using an agate mortar and pestle and allowed to dry in an oven. The dried mixture was then pressed into a 4 mm thick disk of diameter 13 mm by using a press applying a force of 3 tons. The pellet is placed in an alumina boat and introduced into the hot temperature zone of a horizontal tube furnace equipped with a proportional integral differential (PID) controller. The sintering was performed at $550^\circ$C for 6 h in H$_2$S atmosphere. The temperature was raised slowly to completely remove moisture from the target. Moisture, if trapped inside the target, leads to cracking during firing. Normally, the outer part of a target heats up faster than the inner part. If the temperature were increased too quickly from
room temperature to the high processing temperature, the outer part of the target would become dense before the moisture in the inner part escapes.

A ZnS:Mn target with 2% Mn was synthesized in the laboratory by high temperature solid state reaction between ZnS (99.99%, Alfa Aesar) and MnO (99.99%, Alfa Aesar). ZnS:Mn target of 4 mm thick and diameter 13 mm were obtained after sintering the pressed ZnS:Mn pellet at 550°C for 6 h in H₂S atmosphere.

**Liquid phase pulsed laser ablation (LP-PLA)**

The sintered ZnS and ZnS:Mn targets were used for the preparation of nanoparticles by liquid phase ablation. These targets, immersed in 15 mL of distilled water, was ablated at room temperature by the fourth harmonics (266nm) of Nd:YAG laser with repetition frequency of 10 Hz and pulse duration of 7 ns. The experimental arrangement is shown in the figure 6.1. The spot size of the laser beam was 2 mm after focusing by a lens of focal length 20 cm which is placed above the target, and the ablation was done at laser fluences of 20 and 25 mJ/pulse. The duration of laser ablation was 1, 2 and 3 h. This simple technique produced doped and undoped ZnS nanoparticles at room-temperature, well dispersed in liquid media.

The synthesized targets were characterized for their structure by x-ray diffraction (Rigaku D max-C) with Cu Kα radiation. The particle size, distribution, and crystallinity of ZnS nanoparticles were investigated by transmission electron microcopy (JEOL, TEM) operating at an accelerating voltage of 200 kV. The sample for TEM was prepared by placing a drop of the ZnS nanoparticle colloidal solution onto a standard carbon coated copper grid. The grids were dried before recording the micrographs. The absorption spectra of the nanoparticle colloidal solution were measured by
JASCO V-570 spectrophotometer. Photoluminescence (PL) spectra were recorded using Jobin Yvon Fluoromax-3 spectrofluorimeter equipped with 150 W Xenon lamp.

### 6.3.2 Results and discussion

The crystalline structure of the target was analyzed by x-ray diffraction (XRD) with Cu K$_\alpha$ radiation (wavelength = 1.5418 Å). The XRD pattern of undoped and doped ZnS pellet is shown in figure 6.8.

![XRD pattern of ZnS:Mn target](image)

**Figure 6.8:** The XRD pattern of ZnS:Mn target synthesized by solid state reaction

The XRD pattern shows the cubic structure of ZnS:Mn (0 and 2%) targets. It can be seen that the Mn incorporation has not changed the structure of ZnS. The lattice constant of pure ZnS is 5.345 and that of ZnS:Mn is 5.438. The Mn$^{2+}$ ions may have replaced the Zn$^{2+}$ considering...
the similar ionic radii of Zn (74pm) and Mn (67pm) in the ZnS:Mn lattice without any structural change.

The formation of nanoparticles of undoped ZnS was confirmed by transmission electron microscopy (TEM). TEM analysis revealed that the resulting product after laser ablation for 1 h with energy of 25 mJ/pulse in water is spherical in shape and particles are in the nano regime, as shown in figure 6.9. From TEM analysis, the formation of other molecules or core shell structure was not observed.

Figure 6.9: The TEM image of ZnS nanoparticles in liquid medium
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Figure 6.10: The particle size distribution of ZnS nanoparticles at laser fluence 25mJ/pulse ablated for 1 h

Statistical size analysis (figure 6.10) shows almost uniform particle-size distribution with a particle size of 7 nm for ZnS nanoparticles grown at laser fluence 25mJ/pulse ablated for 1 h.

Figure 6.11 shows the high-resolution TEM (HRTEM) images of ZnS nanoparticles showing parellel lines of atoms. The interplanar spacing of ZnS as seen from the figure is 0.26 nm which corresponds to (200) plane.
Figure 6.11: The high-resolution TEM (HRTEM) images of ZnS nanoparticles

Figure 6.12: UV-visible spectra of ZnS nanoparticles in aqueous medium ablated at 20mJ/pulse laser fluence for a duration of 2 h
Results and discussion

UV-Vis-NIR absorption spectra of the ZnS nanoparticles in water were measured over the wavelength range of 200-800 nm. Figure 6.12 shows the absorption spectra of ZnS nanoparticles in aqueous medium ablated at 20 mJ/pulse laser fluence for a duration of 2 h. The absorption edge is around 300 nm which correspondence to band gap energy of about 4 eV. This increase in the band gap compared with that of the bulk value (3.7 eV) is due to quantum confinement effects.

Figure 6.13: Room temperature PL emission spectra ($\lambda_{ex} = 342$ nm) of ZnS and ZnS:Mn nanoparticles ablated at 20mJ/pulse for 3 h

Room temperature photoluminescence emission (PL) and excitation spectra (PLE) of ZnS and Mn doped ZnS nanoparticles were studied for its luminescent applications. Figure 6.13 shows the PL emission spectra ($\lambda_{ex} = 342$ nm) of ZnS and Mn doped ZnS nanoparticles ablated at 20mJ/pulse
for 3 h. The emission spectra of ZnS nanoparticles show a peak at 436 nm. The emission at 436 nm can be attributed to the sulfur vacancy. This agrees well with the peak values reported by Becker and Bard [323].

The ZnS:Mn nanoparticles showed yellow emission at 585 nm. The emission at 585 nm can be attributed to the radiative transition between $^4T_1$ and $^6A_1$ levels within the 3d⁵ orbital of Mn²⁺, indicating the doping effect of Mn²⁺ in the ZnS nanostructures [324]. The emission corresponding to sulfur vacancy is absent in the Mn doped ZnS nanoparticles.

Mn²⁺ ions occupy Zn²⁺ lattice sites in the ZnS host lattice. In the PL process, an electron from the ZnS valence band is excited across the band gap and the photoexcited electron subsequently decays by a normal recombination process to some surface defects or defect states. Now on Mn doping, it occupies the tetrahedral cationic site with $T_d$ symmetry and the electron may be captured by the Mn²⁺ ion in the $^4T_1$ level, from which it decays radiatively to the $^6A_1$ level. Mn doping actually reduces the nonradiative recombination and radiative transition takes place between Mn $^4T_1$ and $^6A_1$ levels [320].

The room temperature PLE spectra of ZnS:Mn monitored at 585 nm is shown in figure 6.14. The figure clearly shows the excitation wavelength at 342 nm. Inset of figure 6.14 shows the schematic representation of the main energy levels identified in the studied samples.
Results and discussion

Figure 6.14: Room temperature PLE spectra of ZnS:Mn nanoparticles. Inset shows simplified energy diagram of ZnS and Mn doped ZnS nanoparticles. The energies of absorption and emission lines are also shown.

Color characterization of a spectral distribution is carried out to gauge the quality of its chromaticity. This is accomplished using color coordinates [171]. In 1931, the Commission Internationale de l’Eclairage (CIE) established an international standard for quantifying color known as CIE color coordinates. The chromaticity coordinates map all the visible colors with respect to hue and saturation on a two-dimensional chromaticity diagram. The CIE coordinates are obtained from the three CIE tristimulus values, X, Y and Z. These tristimulus values are computed by integrating the product of the spectrum of the light source, P(\(\lambda\)), and standard observer functions called the CIE color matching functions, \(x_\lambda(\lambda)\), \(y_\lambda(\lambda)\) and \(z_\lambda(\lambda)\) over the
entire visible spectrum.

The CIE color coordinates measured from the photoluminescent emission of ZnS and Mn doped sample was calculated by above-mentioned method and it was (0.17, 0.12) and (0.54, 0.45) respectively. These coordinates can be represented inside a gamut drawn from the standard x, y values (Figure 6.15). This clearly indicates the purity of the yellow color of the Mn doped ZnS while the undoped sample shows blue emission.

![Figure 6.15: CIE coordinates of PL emission spectra of pure and Mn doped ZnS nanoparticles](image)

### 6.3.3 Conclusion

ZnS and ZnS:Mn nanoparticles were prepared by LP-PLA. The targets for LP-PLA were synthesized by the solid-state reaction. The cubic structure of ZnS:Mn (0, 2%) targets were confirmed by XRD. Mn has been successfully
incorporated into the ZnS host lattice as evident from the increase in lattice constant. The structural characterization of laser ablated nanoparticles is obtained from the TEM measurements. The TEM analysis confirms the average particle size of the ZnS samples to be 7 nm. The absorption spectra show band edge around 300 nm. The blue shift in the band edge is due to the quantum confinement effects. The PL spectrum of the pure sample shows an emission in the blue region at 436 nm corresponding to the sulfur vacancy for an excitation wavelength of 342 nm. The PL spectra of ZnS:Mn shows a yellow emission at 585 nm under same excitation. This can be attributed to the radiative transition between $^4T_1$ and $^6A_1$ levels within the 3d$^5$ orbital of Mn$^{2+}$. The CIE color coordinates calculated from the PL spectrum confirms the yellow emission of ZnS:Mn nanoparticles.

LP-PLA is a suitable method to grow nanoparticles of semiconductors, doped semiconductors and metals without any capping agents. The particle properties can easily tuned by varying the laser fluence, time of ablation, pH of the medium, etc. These surfactant free nanoparticles synthesized in water can be used in biological application by utilizing the luminescence emission from these nanoparticles.
LP-PLA of ZnS and ZnS:Mn nanoparticles