

Chapter – 7

Summary and Conclusions

A summary of the results obtained in the present investigations and conclusions are outlined in this chapter. Based on the results, the scope for further studies in this direction is presented.

7.1. Summary

Pure ZnO nanoparticles have been synthesized by cost effective low temperature solution combustion method in a short time using ODH fuel. It is significant that our synthesis method involved a lower temperature of 300 °C, very short processing time and produced powder samples without post calcinations. PXRD profiles confirmed that the prepared ZnO products have Wurtzite structure without any secondary phases. The average particle size of the synthesized powder determined by Debye–Scherrer’s formula is found to be in the range 14–51 nm which was confirmed by W–H plots and TEM results. The crystallinity increases when calcined to high temperatures. SEM profiles show that the product is porous with voids, spongy and agglomerated. Raman studies indicate first and second order active modes of ZnO phase. Optical energy band gap of prepared ZnO nanocrystals is slightly lower than that of bulk ZnO.

The PL spectrum of ZnO nanopowders gives the near band edge UV emission and defect related blue and green emissions. EPR studies also confirmed the Presence of defects in ZnO nanopowders. TL glow curves of gamma irradiated ZnO nanoparticles show a broad peak at 343 °C, which is attributed to the recombination of charge carriers released from the surface states associated with oxygen defects, mainly interstitial oxygen ion centers, for a γ -dose range of 10–50 Gy. It is observed that the glow peak intensity increases with increase of gamma dose without changing glow curve shape. These two characteristic properties such as TL intensity increases with gamma dose and simple glow curve structure are

indications that the combustion synthesized ZnO nanopowder might be used as a good TL dosimeter for high temperature applications.

In section 3.3 we have reported the synthesis of nanocrystalline ZnO by organic-free hydrothermal process at different temperatures. The molarity and pH of the raw material was kept constant in order to study the effect of experimental temperature (60–260 °C for 16h) in the hydrothermal reaction on the resultant product and in turn the morphology and structural properties. The PXRD patterns indicate that the sample is composed of wurtzite structural ZnO, consistent with the standard PDF database (JCPDS file No. 36-1451). SEM images of the samples prepared at lower temperatures (60–140 °C) reveal the presence of a large quantity of quasi-hexagonal shaped nanoparticles, nanowires and nanostructures with varying sizes in the range 50–100 nm. SEM images of ZnO prepared at 180 °C show the presence of hexagonal shaped nanorods and nanoparticles dual structure. The hexagonal shaped rods were found to have smooth, uniform surfaces with an acute tip and varying diameters in the 100–200 nm range and few micrometers in length.

During the hydrothermal growth process, $\text{Zn}(\text{OH})_2$ dissolves with increasing temperature. When the concentrations of Zn^{2+} and OH^- reach the critical value of the supersaturation of ZnO, fine ZnO nuclei form spontaneously in the aqueous complex solution. When the solution is supersaturated, the nucleation begins. Afterwards, ZnO nanoparticles combine together to form hexagonal shaped nanorods in order to reduce the interfacial free energy. This is because the molecules at the surface are energetically less stable than the ones already well orderly formed and packed in the interior. In our experiments, the concentrations of Zn^{2+} and OH^- have attained critical values at 180 °C and incorporation of growth units into crystal lattice of the hexagonal nanorods by dehydration took place at this temperature. When the temperature was less than 180 °C, OH^- concentration could not attain the critical value to form nanorods and hence resulted in tiny hexagonal particles. With further increase in hydrothermal

temperature to 260 °C, it is interesting to observe that the morphology consists of flake-like interconnected discrete nanocrystallites forming a loose porous structure which is fluffy in nature with nanopores in it. The defects associated with surface states in hydrothermally prepared ZnO nanostructures are analyzed from the EPR and thermoluminescence studies.

Cu and Mn dopants have been successfully incorporated into ZnO lattice by solution combustion method at lower initial temperature of 300 °C. The characterization of the samples presented in section 4.2 confirmed that Cu dopant substitute for Zn cation sites homogeneously. For undoped ZnO, the particles are connected to each other to make large network systems with irregular pore sizes and shapes whereas, in Cu doped ZnO, the powder shows honeycomb structure with broken type of hollow shells formed by the escaping gases during combustion. A red shift and narrowing of band gap in Cu doped ZnO is due principally to the strong p–d mixing of O and Cu and it confirms the incorporation of Cu into ZnO lattice. In PL study, the slight decrease in green emission and enhancement of UV emission in Cu doped ZnO might be due to the decrease in defects. The EPR spectrum exhibits a broad resonance signal at $g \sim 2.049$ and two narrow resonances one at $g \sim 1.990$ and other at $g \sim 1.950$. The broad resonance signal at $g \sim 2.049$ is a characteristic of Cu^{2+} ion whereas the signal at $g \sim 1.990$ and $g \sim 1.950$ can be attributed to ionized oxygen vacancies and shallow donors respectively. The number of spins participating in resonance and its paramagnetic susceptibility is found to be 1.55×10^{22} and 3.96×10^{-3} emu/mol respectively. We chose to determine the spin susceptibility from EPR, because this technique has several advantages over a static measurement, where a diamagnetic contribution must be subtracted.

The powder X-ray diffraction of as-formed ZnO:Mn sample shows completely crystalline, hexagonal wurtzite phase with a particle size of about ~40 nm. SEM micrographs show that the primary particles are uniform, circular in shape and weakly agglomerated. TEM results also confirm that the phosphor

particles are of nano size. The PL spectrum shows a strong green emission peak at 526nm and a weak red emission at 636nm corresponding to $4T_1 \rightarrow 6A_1$ transition of Mn^{2+} ions. EPR spectra of ZnO:Mn exhibit hyperfine structure due to interaction of electron spin ($S = 5/2$) with its nuclear spin ($I = 5/2$) and the each fine structure transition which will be split into six hyperfine components due to ^{55}Mn hyperfine coupling and giving rise to all 30 allowed transitions. The sextets belong to the transitions $5/2 \leftrightarrow 3/2$, $3/2 \leftrightarrow 1/2$, $1/2 \leftrightarrow -1/2$, $-1/2 \leftrightarrow -3/2$, $-3/2 \leftrightarrow -5/2$. In the present study the occurrence of not more than 30 lines suggest that Mn^{2+} ions in this lattice occupy the metal site (Zn). The observed hyperfine splitting constant A, indicates that the bonding between Mn^{2+} ions and surrounding ligands is moderately covalent in nature.

Low-temperature solution combustion method has been successfully used to synthesize Fe doped ZnO nanoparticles and are well characterized as presented in section 5.3. From PXRD results, single phase pure hexagonal wurtzite structure is observed. SEM and TEM images reveal quasi-hexagonal morphology of the nanoparticles. In samples with higher Fe doping concentration, the porous nature is dominated. This is due to large amount of gases escaping during combustion process. The optical band gap E_g is found to decrease with increase of Fe dopant concentration. This is due to exchange interaction between d electrons of the transition metal ions (Fe) and the host s and p electrons.

In Raman studies, the active modes observed at 100, 438, 332, 580 cm^{-1} correspond to pure ZnO. In Fe doped samples, two nonpolar optical phonon (E₂) modes at low and high frequencies at 100 and 435 cm^{-1} are observed. These modes broaden and disappear with increase of Fe dopant concentration. The EPR spectrum suggests that in addition to Fe dopant a small amount of Mn impurity is also present in the sample. A single well resolved thermoluminescent glow peak at ~ 368 °C was observed in all the Fe doped samples. The TL intensity is found to increase with increase of gamma dose which is one of the desired properties of TL dosimeter.

In section 6.2 we have presented the synthesis and luminescent properties of ZnO:Eu (0.1mol %) nanopowders through low-temperature solution combustion method. Hexagonal wurtzite structure without secondary phase was observed from PXRD results. SEM and TEM studies reveal that the particles are agglomerated with quasi-hexagonal morphology. Photoluminescence (PL) emission under 254 nm excitation shows peaks in blue (420-484 nm), green (528 nm) and red (600 nm) regions which correspond to both Eu^{2+} and Eu^{3+} ions. Further, with the increase of excitation wavelength to 488 nm, the emission peaks at 586 and 652 nm are observed which are due to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ transitions of Eu^{3+} ions respectively. The EPR spectrum exhibits a broad resonance signal at $g = 4.195$ the most intense one which is attributed to Eu^{2+} ions. The resonance sharp signals at $g = 1.994$ and $g \sim 2.007$ are attributed to an unpaired electron trapped in an oxygen vacancy site. The resonance signals at $g = 2.145$ have been attributed to Zn vacancy. TL studies on ZnO: Eu nanocrystalline phosphor was studied with γ - irradiation for a dose range 1-10kGy at a linear heating rate $20\text{ }^\circ\text{Cs}^{-1}$. A broad glow curve with peak at $\sim 355\text{ }^\circ\text{C}$ was recorded in the entire range of irradiated samples. The kinetic analysis of the experimental TL glow curve was carried out using Chen's peak shape method and the average activation energy was found to be in the range 0.21-1.26 eV.

In section 6.3 we have presented the synthesis and luminescent properties of Gd doped ZnO nanostructures by combustion method. All the XRD peaks are well matched with the standard hexagonal wurtzite structure of ZnO. The microstructure analysed by SEM and TEM images revealed that the particles have narrow size distribution with diameters in the range $\sim 60\text{--}70\text{nm}$, in agreement with XRD data. In PL spectrum, in addition to the emission bands from undoped ZnO, there is an extra blue emission at 441 nm ($\sim 2.81\text{ eV}$) in Gd doped ZnO sample which is attributed to the doped Gd^{3+} ions that introduce an impurity level into the energy band gap of ZnO.

7.2. Scope for further work

This research work is mainly concentrated on the luminescence properties of pure and doped ZnO nanostructures. The luminescence properties of transition metal ion and rare earth element doped ZnO nanostructures have been reported in the present investigation. However, we believe that there is scope for further investigation such as effect of co-doping, effect of heat treatment and effect of synthesis temperature etc.. on luminescence properties of nano ZnO. It has been observed in other systems that co-doping is more effective in increasing room temperature PL intensity which hints that these approaches lead to improving PL emission intensity over a broader wavelength range.

ZnO is a promising phosphor for UV detection and thermoluminescence dosimeter (TLD). In the present work, although ZnO samples have been irradiated with gamma rays for thermoluminescence studies, the dosimetric properties such as dose response, linearity, fading effect, luminescence efficiency etc... can be studied using different ionizing radiations and the results can be compared with those of commercially available TLD's.

Low cost production is a main attraction of any product and it is believed that ZnO has much potential to introduce low cost LEDs in the market. Investigation of the luminescence from ZnO is very crucial for the future possible application of ZnO nanostructures in the development of white LEDs to replace conventional light sources. Finally, we conclude with the hope of ZnO nanostructure commercialisation in near future.