Chapter 7

Conclusions and Future Scope

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7.1 Conclusions

In this thesis, we examined the types of defects present in pure ZnO of various morphologies when synthesised in nanorange, doped/codoped ZnO and ZnO in $SrAl_2O_4$ composite. The microstructure, optical and magnetic properties were discussed on the basis of defects. ZnO, doped/codoped ZnO and ZnO-$SrAl_2O_4$ composites were synthesised through various chemical routes including coprecipitation, sol-gel and combustion after varying the synthesis parameters. X-ray diffraction (XRD) technique was used to verify the structure and phase formation of the samples. Using non-destructive Raman technique, we not only checked the phase, but also studied the lattice disorder in the samples after doping/codoping. FTIR was used to study the vibrational bands. Morphology of powder samples were investigated through scanning electron microscope (SEM) and transmission electron microscope (TEM). Although, photoluminescence spectroscopy (PL) indicated the evidence of defects, positron annihilation spectroscopy (PAS), x-ray photoelectron spectroscopy (XPS) and thermoluminescence spectroscopy (TL) were used to compliment them. The main findings of the present thesis work are listed below:

1. ZnO nanoparticles were synthesized through coprecipitation, combustion and sol-gel technique by varying synthesis parameters like pH of precipitation and calcination temperature. We varied the shape of ZnO from 2D plates to triangular and hexagonal rods, needles and finally to hierarchical structure by varying the pH of precipitation from 5.5 to 13 with size mostly in nanorange. XRD and more precisely the Raman techniques revealed the $Zn_5(OH)_8(NO_3)_2(H_2O)_2$ and $Zn(OH)_2$ impurity phases in addition to ZnO at lowest and highest pH, respectively. The pH in-between 9.0 to 10.0, found suitable for the synthesis of pure wurtzite ZnO. Intermediate phases of $Zn_5(OH)_8(NO_3)_2(H_2O)_2$ and $Zn(OH)_2$ were found responsible for the growth of triangular/hexagonal rods and needles of ZnO. Assembly of large number of

nanosheets and small needles gave rise to flowers, a hierarchical structure. Looking at the morphologies a growth mechanism was proposed. The PL study revealed two different emissions, known as near band edge (NBE) and deep band emission (DBE). The DBE emission was found to be increased with increase in pH of precipitation which is responsible for native defects. Therefore, the native defects were increased in ZnO samples with increasing pH which is further confirmed through PAS study. Drying these samples at 250 ^{o}C, the intermediate phases of $Zn_5(OH)_8(NO_3)_2(H_2O)_2$ and $Zn(OH)_2$ decomposed into ZnO showing pure wurtzite structure without any impurities. The defects were reduced in dried samples and confirmed from PL and PAS studies.

ZnO prepared through sol-gel technique was calcined at 250 ^{o}C, 600 ^{o}C, 800 ^{o}C and 1000 ^{o}C for 5 h. In all samples, from XRD and Raman, pure phase of ZnO was confirmed. Williamson-Hall (W-H) plot analysis from XRD peak broadening revealed positive slope that represented tensile strain in ZnO lattice. The magnitude of the slope decreased with increasing calcination and become almost zero in the sample calcined at 1000 ^{o}C. This strain in ZnO lattice could be due to the native defects. In Raman spectrum, the E_1 (LO) mode represented the polar modes with longitudinal vibration, showed anomalously high intensity which could be due to the presence of native defects, most probably due to zinc interstitials (Zn_i). With increase in calcination temperature, the intensity of the E_1 (LO) mode was decreased indicating reduction of defects which was further supported by the absence of DBE peak in PL spectra. Further, the positron annihilation life time showed the presence of cluster of (Zn+O) divacancies which decreased with calcination temperature.

ZnO sample synthesised through combustion method, calcined at 600 ^{o}C, 800 ^{o}C, 1000 ^{o}C and 1200 ^{o}C show pure wurtzite structure. In contrast to sol-gel derived samples, these samples demonstrated negative slope in W-H plot, which indicated the compressive strain in the samples. Raman analysis showed the same anomaly in E_1 (LO) mode which was reduced with increasing calcination temperature. In contrast, DBE band in PL spectrum found to be

increased with increasing calcination temperature. After deconvolution of DBE band into 504/2.46, 548/2.26 and 603/2.1 nm/eV which are responsible for V_{Zn}, V_O and O_i respectively, the latter band at 603/2.1 nm/eV was found responsible for increasing DBE emission with increasing calcination temperature. It is expected that oxygen interstitial (O_i) could be generated with calcination temperature in oxygen rich environments. PAS studies confirmed the cluster of (Zn+O) divacancies in all the samples.

It is interesting to mention that although we synthesised ZnO nanomaterials through sol-gel and combustion techniques, while tensile strain obtained in sol-gel synthesis, combustion technique produced a compressive strain in the lattice. The significance of strain induced defects was further visualised by Raman, PAS and PL measurements.

2. Pure phase of ZnO was successfully obtained by doping Mg upto 20% through coprecipitation technique. In addition, a prominent band at 908 cm^{-1} in ZnO and Mg doped ZnO samples corresponding to the bending vibration of V_{Zn}-H$_{ABO\parallel}$, a few additional modes at 856, 1512 and 3690 cm^{-1} were also observed in Mg doped ZnO. The mode at 856 and 1512 cm^{-1} became more pronounced with increase in concentration of Mg. These modes were assigned to local hydrogen modes of Mg-H and Mg-OH bonds. Further, positron life time spectrum confirmed that the V_{Zn} is attached to a hydrogen and form defect complex V_{Zn}-H$_{ABO\parallel}$ in ZnO. Thus excess hydrogen was observed in Mg doped ZnO present in the form of Mg-H and Mg-OH. Finally, it was concluded from XRD, Raman, PL and PAS analysis that the excess hydrogen present in Mg doped ZnO passivate the native defects observed in ZnO and reduced the strain in the lattice, hence can be one of the promising material for hydrogen storage.

Earlier in our group, Co doping in ZnO was studied by Rath *et al.* (2009). In this thesis, we extended the study after doping Mg, Co and Mg, Co together in ZnO to examine the magnetic behaviour for spintronics application point of view. However, we observed absence of FM ordering in Mg and Co codoped ZnO sample at room temperature, but positive Curie–Weiss

temperature was obtained from Curie–Weiss plot, suggesting ferromagnetic correlation at low temperatures. The incorporation of Mg with Co in ZnO, reduced the segregation of Co_3O_4 impurity phase compared to Co doped ZnO which was confirmed from the Raman measurement. Raman study also revealed few additional modes in Mg, Co doped as well as Mg and Co codoped samples, which were exactly reported as silent modes of ZnO. These modes were attributed to intrinsic host-lattice defects related to doping. PAS study confirmed the presence of cluster of (Zn+O) divacancies in all the samples.

3. When we used ZnO as filler in $SrAl_2O_4$ matrix, we observed a transformation from monoclinic phase of $SrAl_2O_4$ to a high temperature hexagonal phase by increasing ZnO concentration from 2.5 to 20 wt% in $ZnO(\%)$-$SrAl_2O_4$ composite. Again, hexagonal phase of $SrAl_2O_4$ transformed to monoclinic phase, which is a stable phase at room temperature, after increasing the calcination temperature of $ZnO(20\%)$-$SrAl_2O_4$ composite from 700 to 1200 ^oC. XPS study confirmed that the oxygen vacancies were responsible for this phase transformation. With gradual increase in ZnO content in SAO, more and more oxygen vacancies were produced and both monoclinic and hexagonal phases coexist upto 15 % of ZnO. At 20 % of ZnO composite, the oxygen vacancies were sufficient enough to stabilize the hexagonal phase. Further calcining $ZnO(20\%)$-$SrAl_2O_4$ composite at higher temperature in oxygen atmosphere, the oxygen vacancies got filled up and hence hexagonal phase transformed to monoclinic phase again. Ultimately, the V_O played a crucial role in transformation of phase from hexagonal to monoclinic and vice versa. In addition, we observed anomalous luminescent properties in these composites. In photoluminescence spectra, we observed NBE and DBE corresponding to ZnO without any signature of emission corresponding to $SrAl_2O_4$ in both the composites. The DBE peak was found to be stronger in monoclinic phase than that observed in hexagonal phase of $SrAl_2O_4$, indicates more defects in the former composite. Combining the excitation and emission properties, we proposed a tentative model to illustrate the mechanism of excitation and emission processes involved in these composites. Thermoluminescence studies

showed a common glow peak at ~323 ^{o}C in both composites and an additional glow peak at ~158 ^{o}C in composite with monoclinic phase. Additional glow peak further confirmed more defects in monoclinic phase than that of hexagonal phase corroborating the PL and XRD results. With increasing γ-irradiation dose, the additional glow peak showed a linear dosimetric response. The composite with monoclinic phase seems to be suitable for dosimetric application which will be confirmed after doing more measurements in future.

7.2 Future Scope

Our investigations on the defects in ZnO, doped/codoped ZnO and ZnO based ceramic composite systems have revealed several interesting features linked with the native defects/impurities present in ZnO and their effect on structure, optical and magnetic properties. Though, there are several open questions that need to be answered in future investigations, few important suggestions may be taken up in future:

1. A hydrothermal technique may be adopted to synthesise ZnO using various solvents varying pH as well as reaction temperature and time. One may try to make ZnO of different morphologies through hydrothermal technique and study the defects as done by us in this thesis.

2. In present work of Co doped and Mg, Co codoped ZnO, the segregation of impurity phases are observed. Hence, one may pursue the same by making thin films of the aforementioned compositions using pulse laser deposition (PLD) or sputtering techniques.

3. As $SrAl_2O_4$ matrix shows a monoclinic to hexagonal phase transformation with high luminescent properties by introducing ZnO into it, one may the same check by introducing ZnO into other spinels like $CaAl_2O_4$, $NiAl_2O_4$ or other fillers like TiO_2/SnO_2 into $SrAl_2O_4$ host.