PREFACE

ZnO, II-VI compound semiconductor is thought to be the most promising candidate for application in spintronics and optoelectronics devices. It is being frequently used in solar cells, transparent thin film transistors, UV photodetectors, light emitting diodes, piezoelectric devices.[1] Due to its high band gap of 3.37 eV at room temperature (RT) and high exciton binding energy of ~60 meV which is much higher than in GaN, its demand increases remarkably for RT UV lasing devices.[2] Recently, Tang et al. have shown optical UV lasing at room temperature in ZnO thin film.[3] ZnO nanostructures have been synthesized in various shapes, such as nanodots,[4] nanowires (NWs),[5] nanorods (NRs),[6] nanobelts,[7] nanorings,[8] nanotubes (NTs),[9] nanocages[10] and hierarchical patterns[11] using synthesis techniques like electrochemical, hydrothermal, microemulsion, vapour transport and condensation process etc. Although these nanostructures have promising advantages for the fabrication of nanodevoices,[12] limited success has been achieved so far. The proper investigation shows that the limited success is due to, in part, to a lack of understanding of the role of various defects in the ZnO material. The consequences of the defects in ZnO show n-type conduction,[13, 14] difficulties in realizing p-type ZnO,[15] ferromagnetism in pure ZnO nanostructure[16] and green light emission.[17, 18] These are basically few unresolved issues till date. Though modern techniques

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1.H. Morkoc and U. Ozgur, Zinc Oxide, Fundamentals, Materials and Device Technology (WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2009);2. Pearton et al., Superlattices and Microstructures 34, 3 (2003);3. Tang et al., Applied Physics Letters 72, 3270 (1998);4. Xu et al., Chem. Phys. Lett. 411, 37 (2005);5. Huang et al., Adv. Mater. 13, 113 (2001);6. Guo et al., J. Am. Chem. Soc. 124, 14864 (2002);7. Pan et al., Science 291, 1947 (2001);8. Kong et al., Science 303, 1348 (2004);9. Zhang et al., Chem. Commun. 3, 262 (2002);10. Fan et al., Solid State Commun. 130, 517 (2004);11.Lao et al., Nano Letters 2 (11), 1287 (2002);12. Park et al., Adv. Mater. 16, 87 (2004);13. Look et al., Phys. Rev. Lett.82, 2552 (1999), and references therein;14. C. G. Van de Walle, Phys. Rev. Lett. 85, 1012 (2000); 15. Zhang et al., J. Appl. Phys. 83, No. 6, 3192 (1998);16. Sundaresan et al., Phys. Rev. B 74, 161306 (R) (2006);17. Ke et al., J. Appl. Phys. 108, 084502 (2010);18.Ohashi et al., J. Appl. Phys. 93, No. 10 (2003).

have been developed for the growth of high quality ZnO crystals without any defects, interestingly, poly-crystalline and nano-crystalline ZnO offers more flexibility in tuning the properties for device applications. The production of such materials is not only easy but also cost effective. However, one needs to understand the defects in ZnO which are always present in polycrystalline ones and are expected to be more in nano size ZnO.

In addition to ZnO, doped/codoped ZnO have great potential to be used as a highly multifunctional material with coexisting magnetic, semiconducting, electromechanical, and optical properties.[19] The elements are doped either in the Zn or O site with higher concentrations show higher solubility limit. Higher is the limit, higher is the tunability in the properties. For example, Mg and Cd dopant are frequently used for tuning the band gap of ZnO,[20, 21] Li, Na, K, N, P, As and Sb dopant used to realize p-type ZnO.[22] Other transition metals such as Ni, Co, Fe, Mn and Cr are doped to fulfill the purpose of room temperature ferromagnetism (RTFM) in ZnO and are exploited for spintronics applications.[19] In addition, some rare earth dopants like Er^{3+}, Tb^{3+} are used to enhance the luminescent properties of ZnO.[23] However, the properties in doped ZnO strongly depend on the conditions and methods of preparation. In addition to defects in doped ZnO, the secondary phases like cluster of dopants or oxides, another form of extrinsic defects responsible for the physical properties. These cluster of dopants or oxides are extremely difficult to detect through even with high resolution x-ray diffractometer.[24] Therefore in doped/codoped ZnO the confirmation of successful doping and their consequences on the microstructure and physical properties of ZnO through different advanced characterisation techniques are indispensible.

Further, ZnO has also been explored for ceramic composites, which can be used in different photonic devices. ZnO as a filler has been mixed with

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19. Liu et al., J. Mater. Sci.: Mater. Electro. 16, 555 (2005);20. Ohtomo et al., Appl. Phys. Lett. 72, 2466 (1998);21. Vigil et al., Thin Solid Films 53, 361(2000);22. A. Janotti and C. G. Van de Walle, Rep. Prog. Phys. 72, 126501(2009);23. Ji et al., Phys. Chem. C 113, 16439 (2009);24.Ney et al., Phys. Rev. B82, 041202 (R) (2010).

ZnS,[25] CdS,[26] $CdSe$,[27] PbS,[28] SnO_2,[29] TiO_2,[30] SiO_2,[31] YbF_3,[32] Y_2O_3[33] and spinels like $ZnGa_2O_4$,[34] $ZnAl_2O_4$[35]and $CaAl_2O_4$[36] to improve luminescent and/or photocatalytic properties. Among the above ceramic materials, spinels are found to be most promising. Because they possess high concentration of cationic vacancies and a large proportion of intrinsic disorders, which are found responsible for trapping of electrons and holes after irradiation. Therefore, spinel composites are expected to exhibit better emission. Among other spinels, $SrAl_2O_4$ is one of the most efficient host materials for photo luminescence, cathode luminescence and plasma display panel phosphors in visible region. The ceramic composite made up of ZnO and $SrAl_2O_4$ is proposed for the improved persistent luminescence property. Due to large lattice mismatch between ZnO and $SrAl_2O_4$, it is expected that the presence of nano ZnO would induce internal lattice defects that act as electrons trap, may further improve the luminescence.

In view of the applications of ZnO or doped/codoped ZnO or composites of ZnO, native defects either intrinsic/extrinsic, play a significant role in deciding the microstructural and physical properties of material. Therefore, it is important to detect the defects through various techniques in ZnO, doped/codoped ZnO and composites in order to examine the physical properties. In the present work, we have examined the role of defects through various spectroscopic techniques on microstructure, optical and magnetic properties.

The objectives of the present thesis work are outlined below:-

1. To examine the growth of various morphologies of ZnO synthesised by varying *p*H of precipitation and study the defects and the consequences

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25. Gao et al., J. Phys. Chem. C 117, 14247 (2013);26. Ling et al., J. Mater. Chem. 21, 2883 (2011);27. Lu et al., J. Phys. Chem. C 116, 2656 (2012);28. Vogel et al., J. Phys. Chem. 98, 3183 (1994);29.Huu et al., Appl. Mater. Interfaces 5, 1038 (2013);30. Bahadur et al., Mater. Res. Bull. 45, 1383 (2010);31. Chen et al., Phys. Chem. Chem. 6, 4473 (2004);32. Zhang et al., Funct. Mater.Lett. 06, 1350002 (2013);33. Yadav et al., Spectrochim. Acta, Part A 103, 216 (2013);34. Zhong et al., Nanoscale 4, 1509 (2012);35. Song et al., Semicond. Sci. Technol. 25, 095014 (2010);36. Verma et al., J. Lumin. 131, 988 (2011).

of defects in ZnO synthesized by various chemical routes like coprecipitation, sol-gel and combustion.

2. To study the effect of doping like Mg or Co and codoping like Mg and Co with varying the concentrations on optical and magnetic properties.

3. To see the structural modification and evolution of luminescent properties when ZnO is incorporated as filler in $SrAl_2O_4$ matrix, which is an efficient host material for photoluminescence, cathodoluminescence in visible region.

The above objectives have led to the following publications:

(1) **V. P. Singh**, P. Mohanty, S. P. Lochab and Chandana Rath, "Anomalous Luminescent Properties in ZnO and $SrAl_2O_4$ Composites" RSC Advances **4,** 36765 (2014)**.**

(2) **V.P. Singh**, S.B. Rai, H. Mishra and Chandana Rath, "Stabilization of high temperature hexagonal phase of $SrAl_2O_4$ at room temperature: role of ZnO" Dalton Transactions **43**, 5309 **(**2014).

(3) **V. P. Singh** and Chandana Rath, "Synthesis of $SrAl_2O_4$ and ZnO Composites: Structure and Optical Properties" Adv. Sci. Lett. **20**, 748 (2014).

(4) **V.P. Singh**, R.K. Singh, D. Das and Chandana Rath, "Defects in $Zn_{1-x-y}Co_xMg_yO$ nanoparticles: Probed by XRD, RAMAN and PAS techniques" Materials Science in Semiconductor Processing **16,** 659 (2013).

(5) **V.P. Singh**, D. Das and Chandana Rath, "Studies on intrinsic defects related to Zn vacancy in ZnO nanoparticles" Materials Research Bulletin **48**, 682 (2013).

(6) **V. P. Singh**, S.B. Rai, H. Misra and Chandana Rath, "Stabilisation of SrAl2O4 hexagonal phase at RT in ZnO-$SrAl_2O_4$" AIP conference Proceeding **1512**, 56 (2013).

(7) **V. P. Singh**, R. K. Singh, D. Das, and ChandanaRath, "Detection of Defects in ZnO Nanoparticles by Spectroscopic Measurements" AIP conference Proceeding **1461**, 205 (2012).

This thesis is organised into VII chapters:

Chapter I presents a brief introduction on structure and physical properties like piezoelectric, electrical, optical, sensing and magnetic of ZnO and their applications.

Chapter II describes the synthesis techniques which are used to get different morphologies of ZnO. As defects in ceramics are omnipresent, the role of native defects in showing green light emission, n-type conductivity and magnetic ordering in ZnO are discussed. The optical and magnetic properties of ZnO modified after doping/codoping with various elements like Mg, Cd, Li, Na, K, Ag, Al, N, P, Ni, Co, Fe, Mn, Cr etc. are compiled. Finally, we review the ceramic composites particularly ZnO based spinel composite.

Chapter III gives an overview of the experimental techniques that has been followed for the present thesis. Coprecipitation, sol-gel and combustion techniques used to synthesize ZnO, doped-/co-doped ZnO and ZnO-$SrAl_2O_4$ composites are discussed in detail. The various characterisation techniques which are used to explain phase, structure, morphology, defects, optical and magnetic properties are incorporated in this chapter.

Chapter IV explains the microstuructural changes observed in ZnO samples synthesised by coprecipitation technique with varying *p*H of precipitation. Different morphology starting from 2D plates to triangular and hexagonal rods, needles and finally to hierarchical structures are obtained after varying the *p*H of precipitation from 5.5 to 13. A growth mechanism is proposed. The emission property which depends on the defects as well as bandgap, are studied not only in ZnO synthesised by coprecipitation but also in ZnO synthesised by sol-gel and combustion techniques. Ultimately, we have shown the signature of native defects as a consequence of the strain in the lattice from XRD. The presence of defects is further supported from the observation of additional modes in Raman spectra as well as large positron life time obtained from positron annihilation spectroscopy (PAS).

Chapter V demonstrates the effect of doping of Mg and Co as well as codoping of Mg and Co both in ZnO on microstructure and physical properties with varying their concentrations. Mg is successfully doped upto 20% at Zn site without showing any impurity phase. While Mg doping shows reduction or passivation of defects in ZnO observed from FTIR and further confirmed by Raman, PL and PAS, Mg doping in codoped sample reduces the impurity phase. The microstructure dependent optical and magnetic properties in doped as well as codoped ZnO are discussed.

Chapter VI elucidates the structural modifications of SAO matrix when ZnO is used as filler in $SrAl_2O_4$-ZnO composites. With increase in ZnO concentration, monoclinic phase of $SrAl_2O_4$ transforms to high temperature hexagonal phase at room temperature. With increasing the calcination from 700 to 1200 ^oC, the transformation is reversed. The luminescent properties of these composites are discussed in comparison with the matrix, $SrAl_2O_4$ as well as filler, ZnO. Thermoluminescent properties of the composite with monoclinic phase seem to be suitable for dosimetric application.

Chapter VII summarises the main findings of the present work. Here we establish that ZnO or doped ZnO or ZnO based composite can display various unusual properties due to the presence of various defects. Finally, we present the future work to be done in the area of ZnO based spinel composites which may open up advance technological applications.